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ÉVALUATION DES TECHNOLOGIES DE PRÉ-TRAITEMENT DES BOUES POUR AMÉLIORER L'EFFICACITÉ DE LA DIGESTION ANAÉROBIE: BILANS MASSIQUE ET ÉNERGÉTIQUE ET ÉMISSIONS DE GAZ À EFFET DE SERRE

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DÉDICACE

This dissertation is lovingly dedicated to my professor, madam Nirmala Tyagi, my parents and my wife Sravanthi and our daughter Samiksha who have lend me a moral support

I also dedicate this to my lord

Hare Kṛṣṇa Hare Kṛṣṇa
Kṛṣṇa Kṛṣṇa Hare Hare
Hare Rāma Hare Rāma
Rāma Rāma Hare Hare

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RÉSUMÉ

La quantité considérable de boues produites chaque année à travers le monde est un problème environnemental croissant pour les usines de traitement des eaux usées (STEPs). Le coût de la gestion des boues représente environ 50 à 60% du montant total d’exploitation des usines de traitement des eaux usées. De plus, au cours du traitement des boues (élimination et/ou réutilisation), la matière organique est convertie en dioxyde de carbone (CO_2), en méthane (CH_4) et en oxyde nitreux (N_2O), en fonction des conditions environnementales. Le CO_2, le CH_4 et le N_2O sont les principaux gaz à effet de serre (GES). Le niveau critique du réchauffement planétaire et les changements climatiques obligent les industries et les municipalités à quantifier les émissions de GES provenant de toutes les sources. Par conséquent, le traitement des boues est devenu un défi important dans l’élimination des déchets. La digestion anaérobie (DA) est la technologie la plus rentable et la plus durable pour la gestion des boues. Afin d’accroître la matière organique biodégradable présente dans les boues et d'augmenter l'efficacité de la DA, un prétraitement de ces rejets est nécessaire. Des chercheurs ayant évalué différentes technologies de prétraitement (l’ultrasonication, l’oxydation Fenton et le prétraitement thermique) ont conclu que la production de biogaz issue de ces prétraitements est améliorée comparativement à ce qui est obtenu avec des boues non traitées. Cependant, il n'est pas encore certain que l’augmentation de la production de biogaz équivaut à l’énergie d’entrée (requise) lors du prétraitement des boues avant la DA. Ainsi, l’originalité et le but principal des travaux de cette thèse sont d'évaluer l’efficacité des technologies de prétraitement (ultrasonication, thermique, prétraitement Fenton), tout en tenant compte de l'énergie consommée et des émissions de GES produites.

L’effet de l’augmentation de la température durant l’ultrasonication de la boue sur l'énergie nette (énergie de sortie-énergie d’entrée) ainsi que sur les émissions de GES a été déterminé. De plus, l’ultrasonication des boues primaires, secondaires et mixtes à différentes concentrations de solides totaux (ST) et une DA ont été effectuées à l’échelle du laboratoire afin d’évaluer la dégradation des matières solides et la production de méthane. L'accroissement de la température des boues a eu un effet positif sur l'énergie nette et sur les émissions de GES. La dégradation des matières a été beaucoup plus rapide pour les boues traitées par ultrasons pendant les cinq premiers jours de la DA. La production cumulative de méthane a été plus élevée pour la boue secondaire par rapport aux boues primaires et mixtes. Une production de méthane cumulative maximale a été observée avec une concentration initiale de 31,45 g ST/L

pour les boues secondaires traitées aux ultrasons. Le bilan énergétique a révélé que l'énergie nette maximale était de l'ordre de 7,89 kWh/Mg de solides secs totaux (SST), et le ratio d'énergie était de 1,0 à 31,45 g ST/L pour les boues secondaires traitées aux ultrasons.

Le bilan de l'énergie employée pour le prétraitement thermique a été effectué à différentes concentrations de ST (1, 2, 3 et 4% (p/v)) et a permis de remarquer que l'énergie nette était positive pour les boues prétraitées par voie thermique lorsque la concentration en solides totaux était supérieure à 1,5% (p/v). Les émissions de GES ont également été réduites due à l'effet du prétraitement thermique. L'énergie nette était positive et le ratio énergétique était supérieur à 1 pour les boues secondaires et mixtes soumises au prétraitement thermique et ce, pour des concentrations en ST de 2, 3 et 4%. Pour les boues secondaires à 30 g ST/L, les émissions de GES pour les échantillons prétraités thermiquement et ceux du contrôle ont été estimées à 73,8 kg de CO_2 équivalent/Mg de SST et à 350,2 kg CO_2 équivalent/Mg de SST, respectivement.

Le bilan masse-énergie a révélé que le procédé d'oxydation Fenton suivi d'une digestion mésophile a produit une énergie nette et un rapport d'énergie plus élevé comparativement à la digestion thermophile. Les émissions de GES ont été diminuées dans ce contexte, et la réduction la plus élevée a été observée pour un temps de rétention (TR) de 20 jours au cours de la DA en condition mésophile. Le bilan énergétique a démontré que l'énergie nette a augmenté avec ce procédé (procédé 2, prétraitement par le procédé Fenton suivi d'une DA). Pour le procédé 3 (procédé 2 suivi d'un prétraitement par le procédé Fenton du digestat produit au cours du procédé 2 accompagné d'une DA) et le procédé 4 (procédé 1 (la DA des boues) avec un prétraitement par le procédé Fenton du digestat produit au cours du traitement 1 suivi d'une DA) une augmentation nette de l'énergie par rapport au processus témoin a été mise en évidence. Les émissions minimales de GES observées étaient de 128 kg CO_2 équivalent/Mg de SST au niveau du procédé 2.

Le prétraitement thermique a été le plus bénéfique en termes de consommation énergétique nette et d'émissions de GES comparativement aux ultrasons et au prétraitement Fenton.L'ordre d'efficacité du prétraitement basé sur les bilans énergétiques et les émissions de GES était le suivant : prétraitement thermique > prétraitement par le procédé Fenton > ultrasonication. Il a été démontré que l'épandage des boues d'épuration pourrait s'avérer une pratique bénéfique pour la réduction des émissions de GES. La méthodologie proposée dans cette étude a été plus efficace/fiable pour l'estimation des émissions de GES, correspondant à l'épandage des boues d'épuration comparativement aux méthodes existantes. Le point fort de cette thèse est qu'elle permet d'obtenir un regard nouveau sur les paramètres importants à considérer lors du choix des différentes technologies de traitement des eaux et de valorisation des boues, en termes énergétiques. Ainsi, l'évaluation de la technologie de prétraitement basée sur l'énergie et les émissions de GES comme critères de gestion sont susceptibles d’influencer, d’une part la prise de décision dans la sélection de la technologie de prétraitement pour la gestion des boues et, d’autre part, l’opinion publique.

ABSTRACT

The unmanageable quantity of sludge generation is a growing environmental problem, affecting the wastewater treatment plants (WWTPs) worldwide. The expenditure associated with sludge management is estimated at around 50-60% of the total wastewater treatment plant operating costs. Moreover, during sludge management (treatment, disposal and/or reuse), the organic matter is converted into carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), corresponding to the environmental conditions. The CO_2, CH_4 and N_2O are the principal greenhouse gases (GHG). Alarming levels of global warming and climate change have made it necessary to quantify GHG emissions from every source. Therefore, sludge treatment has become the most significant challenge in waste management. Anaerobic digestion (AD) is considered the most cost-effective and sustainable technology for sludge treatment. In order to enhance the biodegradable organic matter in sludge and to increase the AD efficiency, pre-treatment of sludge is required. Researchers have evaluated various pre-treatment technologies (such as ultrasonication, thermal, and Fenton pre-treatment) and have concluded that, compared to the untreated sludge, the biogas production is enhanced. However, it was not clear if the increased biogas could correspond to the energy input during pre-treatment and anaerobic digestion. ***Thus, the aim of the study was to evaluate pre-treatment technologies (ultrasonication, thermal, Fenton pre-treatment) by considering energy and GHG emissions as criteria, which is also its novel contribution to this research field.***

Increase in temperature during ultrasonication of sludge and its effect on the net energy (energy output − energy input) and GHG emissions were evaluated. Further, ultrasonication of sludge (primary, secondary, and mixed sludge) at different solids concentrations and lab scale AD was carried out to evaluate the solids degradation and methane production rates. Increase in the sludge temperature resulted in a positive impact on the net energy and GHG emissions. The solids degradation was much faster for the ultrasonicated sludge during the first five days of AD. The cumulative methane production was higher for the secondary sludge compared to the primary and the mixed sludge (with and without pre-treatment). The maximum cumulative methane was observed at 31.45 g TS/L for the ultrasonicated secondary sludge. Energy balance revealed that the maximum net energy was 7.89 kWh/Mg of total dry solids (TDS) and the energy ratio of 1.0 at 31.45 g TS/L for ultrasonicated secondary sludge.

Mass-energy balance for thermal pre-treatment was assessed at different solids concentrations (1%, 2%, 3% and 4%, w/v) and it was observed that the net energy was positive for the thermally pre-treated sludge, when the total solids concentration was greater than 1.5% (w/v). GHG emissions were also reduced with thermal pre-treatment. The net energy was positive and the energy ratio was greater than one for the thermally pre-treated secondary and the mixed sludge, at solids concentrations of 2%, 3% and 4%. At 30 g TS/L, for the secondary sludge, GHG emissions for the thermally pre-treated and the control samples were 73.8 kg CO_2 equivalent/Mg of TDS and 350.2 kg CO_2 equivalent/Mg of TDS, respectively.

Mass-energy balance revealed that Fenton pre-treatment followed by mesophilic digestion resulted in higher net energy as well as energy ratio compared to thermophilic digestion alone. The GHG emissions were reduced with Fenton pre-treatment and the highest reduction was observed during mesophilic AD at 20 days of HRT. Energy balance showed that the net energy increased with Fenton pre-treatment (Process 2, comprising Fenton pre-treatment followed by anaerobic digestion). For Process 3 (Process 2 + Fenton pre-treatment of the digestate produced in Process 2, followed by AD) and Process 4 (Process 1 (AD of sludge) + Fenton pre-treatment of the digestate generated in Process 1, followed by AD), the net energy increased compared to the control. The minimum GHG emissions (128 kg CO_2 equivalent/Mg of TDS) were obtained in Process 2.

Relative to the ultrasonication and Fenton pre-treatment, thermal pre-treatment (at 134°C) was the most beneficial in terms of net energy and GHG emissions. The order of pre-treatment efficiency based on energy balance and GHG emissions was thus thermal pre-treatment > Fenton pre-treatment > ultrasonication.

It was demonstrated that the land application of sewage sludge could be a beneficial practice from the GHG emissions perspective. The methodology proposed in this study was more effective/reliable in the estimation of GHG emissions corresponding to land application of sewage sludge as compared to the prevailing ones. This study demonstrates importance of energy and GHG emissions in evaluating a treatment technology for sludge management and in future wil be a point of reference to the researchers in studying these pre-treatment technologies.Thus, evaluating pre-treatment technologies based on the energy and GHG emissions as criteria is likely to influence public opinion and decision-making in selecting the most appropriate sludge management technology.

AVANT PROPOS

PUBLICATIONS DANS CETTE THÈSE

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1. **Pilli, S.,** More, T.T., Yan, S., Tyagi, R.D., Surampalli, R.Y. and Zhang, Tian C**.** Anaerobic Digestion or Co-digestion for Sustainable Solid Waste Treatment/Management. Biosolids for Sustainable Solid Waste Treatment/Management Chapter 9, **ASCE publication**. (**in press**).
2. More, T.T., **Pilli, S.,** Yan, S., Tyagi, R.D., Surampalli, R.Y. and Zhang, Tian C**.** Management of Special Wastes: Biosolids for Sustainable Solid Waste Treatment/Management. Chapter 14, **ASCE publication**. (**in press**).

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TABLE DES MATIÈRES

LISTE DES TABLEAUX

CHAPITRE I

CHAPITRE II, PARTIE 1

CHAPITRE II, PARTIE 2

CHAPITRE II, PARTIE 3

CHAPITRE III, PART 1

CHAPITRE III, PARTIE 2

CHAPITRE IV, PARTIE 1

CHAPITRE IV, PARTIE 2

CHAPITRE V

CHAPITRE VI

LISTE DES FIGURES

CHAPITRE I

CHAPITRE II, PARTIE 1

CHAPITRE II, PARTIE 2

CHAPITRE II, PARTIE 3

CHAPITRE III, PARTIE 1

CHAPITRE III, PARTIE 2

CHAPITRE IV, PARTIE 1

CHAPITRE IV, PARTIE 2

CHAPITRE V

LISTE DES ABRÉVIATIONS

AD: Anaerobic digestion

C_P: Specific heat of sludge

CH_4: Methane

CO_2: Carbon dioxide

COD: Chemical oxygen demand

CST: Capillary suction time

CSTR: Continuous-flow stirred tank reactors

DS: Dry solids

ECP: Extracellular polymers

E_S: Specific energy input

Fe^{2+}: Ferrous ion

Fe^{3+}: Ferric ion

GHGs: Greenhouse gases

GWP: Global warming potential

HRT: Hydraulic retention time

N_2O: Nitrous oxide

P: Power input

PT: Pre-treatment

$Q_{w:}$ Total energy input for ultrasonication

RNA: Ribonucleic acid

SCOD: Soluble chemical oxygen demand

SRT: Solids retention time

TDS: Total dissolved solids

TPT: Thermal pre-treatment

TS: Total solids

TSS: Total suspended solids

TWAS: Thickened waste activated sludge

UASB: Upflow anaerobic sludge blanket

VDS: Volatile dissolved solids

VS: Volatile solids

VSS: Volatile suspended solids

WAS: Waste activated sludge

WWTP: Wastewater treatment plant

Units

g: Gram

ha: Hectare

J: Joules

Kg: Kilo gram

kHz: Kilohertz

kWh: Kilowatt hour

L: Litre

Mg: Mega gram

Mg/yr: mega grams per year

MHz: Megahertz

MJ: Mega joules

Mm: Milli meter

V: Volt

CHAPITRE 1

SYNTHÈSE

1. REVUE DE LITTÉRATURE

1.1 Introduction

Les boues d'épuration (appelées biosolides) sont des résidus collectés dans les différents compartiments des systèmes de traitement des eaux usées (STEPs), notamment dans les décanteurs primaires et/ou secondaires. Le taux de boues d'épuration produites est d'environ 70-90 g/habitant/jr ou de 1 Mg de boue sèche par jour pour 10,000 habitants (Fytili et Zabaniotou, 2008). Ces rejets sont généralement sous forme liquide ou semi-solide, et contiennent entre 0,25 et 12% de solides, dépendamment des opérations et des procédés utilisés dans les STEPs (Metcalf et Eddy, 2003). Au cours de ces dernières années, la production de boues dans les STEPs est devenue une problématique environnementale en pleine croissance au niveau mondial. Les quantités d'eaux usées produites augmentent de plus en plus et les traitements subséquents ont conduit à l'augmentation des volumes des boues d'épuration générées (Metcalf et Eddy, 2003; Le Blanc *et al.,* 2009). Les quantités importantes de boues d'épuration constituent donc un problème environnemental croissant. Les coûts associés à la gestion de ces déchets représentent environ 50-60% des coûts d'exploitation des STEPs (Coma *et al.,* 2013; Pilli *et al.,* 2011). C'est un défi très important dans la gestion des eaux usées (Metcalf et Eddy, 2003).

La gestion des boues (traitement, disposition et/ou réutilisation) permet de convertir la matière organique en dioxyde de carbone (CO_2), méthane (CH_4) et oxyde nitreux (N_2O) (Pilli *et al*., 2014). Le CO_2, CH_4 et N_2O sont donc les principaux gaz à effet de serre (GES) produits lors de la gestion des boues et les STEPs sont considérées comme d'importantes sources d'émissions mineures de ces GES (Bani Shahabadi *et al.,* 2009). Le CO_2 est le premier GES, dont la concentration a commencé à augmenter dans l'atmosphère dès la deuxième moitié du 20^e siècle. Le potentiel de réchauffement global (PRG) a été défini pour estimer et comparer les effets de ces gaz en référence au CO_2 sur un horizon de 100 ans. Les potentiels de réchauffement planétaire du CH_4 et du N_2O sont environ 21 et 310 fois plus élevés que celui du CO_2, respectivement (Gassara *et al.,* 2011). Le niveau alarmant du réchauffement planétaire et les changements climatiques obligent les industries à quantifier les émissions de GES provenant de toutes les sources. L'élimination des boues représente 40% des émissions totales de GES dans une STEP (Brown *et al*., 2010; Shaw *et al*., 2010). Par conséquent, les producteurs de ces contaminants sont contraints de réévaluer leurs stratégies de traitement de ces produits, d'où la nécessité d’utiliser des techniques économiquement efficaces et durables pour la disposition des boues.

1.2 Traitement des boues

L'incinération, l'épandage, l'enfouissement et le compostage sont des stratégies couramment utilisées au cours des dernières années pour gérer les boues d’épuration. Cependant, ces stratégies ne sont pas fiables en raison des impacts négatifs qu’elles ont sur l'environnement. Les problèmes environnementaux, les réglementations de plus en plus strictes et la sensibilisation du public forcent les administrateurs des usines de traitement des eaux usées à réévaluer leurs procédés de gestion de ces boues. Par conséquent, il existe un besoin important de développer des techniques de traitement et de disposition de ces rejets qui soit à la fois abordables d’un point de vue économqiue et durables. Selon de nombreuses recherches, la DA pourrait être la technique la plus rentable et durable pour réduire la quantité de boues produites en raison de la production d'énergie sous forme de biogaz et de son impact environnemental très limité (Alvarez *et al.,* 2010; Khalid *et al.,* 2011; Mata-Alvarez *et al.,* 2011). Les avantages associés à la technique de DA sont notamment, la réduction de la masse des déchets, l'élimination des odeurs, la réduction des agents pathogènes, la faible consommation d'énergie et, de façon plus significative, la production d’énergie sous forme de méthane. Yasui *et al*. (2005 et 2006) ont conclu que la capture d’énergie à partir du méthane produit par la DA contribuerait à réduire la consommation totale de gaz naturel. Cela s’ajouterait à la politique de réduction des émissions de GES et s'inscrirait dans le cadre des nouvelles réglementations en permettant d’atteindreles objectifs du protocole de Kyoto.

1.2.1 Digestion anaérobie des boues

La DA des boues est un processus microbiologique complexe qui convertit les composés organiques dégradables en CH_4 et en CO_2. Il se produit en l’absence d'oxygène. La conversion du substrat en biogaz, principalement du CH_4 et du CO_2, se déroule en quatre étapes, à savoir : l'hydrolyse, l’acidogénèse, l’acétogénèse et la méthanogénèse. Trois différents groupes de micro-organismes (acidogènes, acétogènes et archées méthanogènes) sont responsables de la DA (Figure 1).

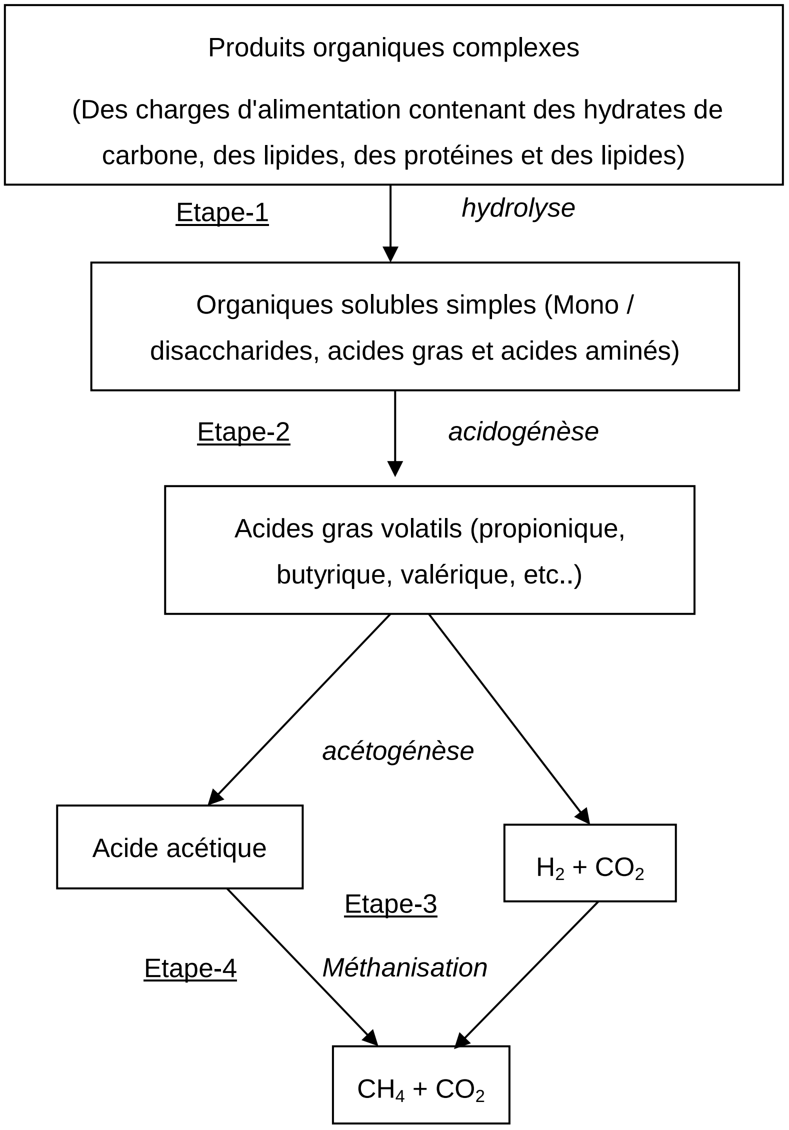

Figure 1. Différentes étapes de la digestion anaérobie

1.2.2 Énergies requises pour la digestion anaérobie

Les besoins énergétiques de la DA sont principalement liés aux besoins lors du pompage des boues, et à l’élévation de la température des composés dans le digesteur, ainsi qu’aux pertes d’énergie à travers les parois du digesteur et aux pertes produites dans la tuyauterie entre la source de chaleur et le digesteur. Keller et Hartley (2003) ont estimé l'énergie totale requise pour le pompage et le mélange de la boue dans le digesteur à environ 0,01 kW/m^3. Les besoins énergétiques dans le DA sont calculés de la façon suivante.

1) l'énergie nécessaire pour élever la température des boues dans le digesteur. Dans la plupart des DA, il est nécessaire de fournir la chaleur à partir d'une source externe afin d'atteindre la température de fonctionnement désirée (environ 35°C). Un bilan thermique est nécessaire pour déterminer les besoins énergétiques d'une installation donnée et pour dimensionner la taille des composants du système de chauffage. La quantité de chaleur (H) nécessaire pour élever la température des boues du digesteur au niveau souhaité peut être calculée à partir de l'équation 1 :

$$H= Q \times Cp \times (T_2-T_1) \qquad (1)$$

où Q est le volume des boues (m^3*/jour); Cp est la chaleur spécifique des boues (4,2 x 103 kJ/*m^3 *°C);* T_2 *est la température des boues dans le digesteur (en °C) et* T_1 *est la température initiale des boues brutes entrant dans le digesteur (en °C).*

2) Les besoins en chaleur sont notamment liés à l'énergie nécessaire pour chauffer les boues à la température désirée et pour compenser les pertes de chaleur dans le milieu environnant. L'intensité des pertes de chaleur dépend de la forme du réacteur et du type de matériau utilisé. Les matériaux de construction ont différents coefficients de transfert thermique. La perte de chaleur au cours de la DA est estimée à 150,84 kWh/m^3 (Metcalf et Eddy, 2003).

1.2.3 Avantages de la digestion anaérobie

Par rapport aux autres méthodes de traitement ou de disposition des boues, la DA des biosolides est une gestion intégrée qui réduit la pollution environnementale. Les principaux avantages de la DA sont la production d'énergie (production de méthane) et de digestat, ayant une valeur fertilisante. Cependant, la conversion en énergie n'est pas toujours positive. À ce propos, les avantages environnementaux, énergétiques ainsi que les avantages du traitement et les avantages socio-économiques de la DA des boues sont discutés ci-dessous (Khalid *et al.,* 2011).

Avantages environnementaux

Les avantages environnementaux de la DA des boues sont:

a) La réduction des agents pathogènes : la DA thermophile produit des boues de catégorie A (Lukehurst *et al*., 2010). L'agence américaine de la protection environnementale (US-EPA) a rapporté que la DA permet de réduire de 90 à 99% les concentrations en coliformes fécaux et en streptocoques fécaux initiallement présents dans les boues.

b) La production de compost stérilisé et riche en nutriments : l'utilisation du digestat pour conditionner les sols permet d'améliorer la croissance des plantes, pouvant être par la suite transformées en engrais organiques ou en combustibles. Ainsi, la DA pourrait réduire la dépendance aux engrais inorganiques par capture et réutilisation des nutriments (Lukehurst *et al.,* 2010).

c) Les émissions de GES : les émissions incontrôlées dans l'atmosphère de méthane, qui est 23 fois plus puissant que le CO_2, à partir des décharges, de la disposition des déchets/boues ou du stockage des boues de fermes d'élevage seraient contrôlées avec l’utilisation de la DA (EPA, 2011). Le méthane capté dans des conditions de contrôle pourrait être reconverti en énergie (cogénération : chaleur et électricité). Cela contribuerait à atténuer l'utilisation des combustibles fossiles et donc à réduire les émissions de GES associées.

Avantages énergétiques de la digestion anaérobie

a) La DA est un processus de production d'énergie (Khalid *et al.,* 2011; Mata-Alvarez *et al.,* 2011; Atandi et Rahman, 2012) .

b) La production de biocarburants (acides gras volatils, méthane, etc) pourrait réduire l'utilisation des combustibles fossiles (Khalid *et al.,* 2011; Mata-Alvarez *et al*., 2011).

c) La DA a une capacité de production énergétique qui peut contribuer à la décentralisation des systèmes de distribution d’électricité (Khalid *et al.,* 2011; Mata-Alvarez *et al.,* 2011; EPA, 2011).

<u>*Avantages socio-économiques*</u>

a) Le méthane produit pendant la DA peut générer des bénéfices financiers directs lorsque de l'électricité est produite (Weiland, 2010).

b) L'énergie et la main-d'œuvre nécessaires pour opérer le digestat peuvent être minimisées (Al-Sedai, 2008).

c) La production d'énergie peut être durable et permet de minimiser les coûts d'opération (Al-Sedaï, 2008).

1.2.4 Inconvénients de la digestion anaérobie

Le processus de minéralisation complète des substrats en CH_4 et en CO_2 est un processus lent, qui nécessite un temps de rétention élevé. En effet, la solubilisation des biopolymères intracellulaires et leur conversion en composés de faibles poids moléculaires (hydrolyse des boues) sont une étape limitante (Pilli *et al.,* 2011). Le faible taux de conversion microbienne lors de la DA entraîne un temps de rétention hydraulique élevé dans le digesteur et nécessite un plus grand volume de digestion, ce qui répresente des inconvénients pour le développement de la technologie. L'indisponibilité de matières organiques solubles et facilement biodégradables, ainsi qu'une faible constante de vitesse de digestion, diminuent la production de méthane (par exemple, la constante de vitessse de digestion est d'ordre de 0,15 j^{-1} pour les boues) (Shimizu *et al.,* 1993). Par conséquent, afin de réduire le temps de rétention dans les digesteurs et d'augmenter la biodégradabilité des boues et la production de biogaz, le prétraitement des boues est suggéré.

1.3 Prétraitement des boues

Le prétraitement des boues libère les matières intracellulaires en rompant la paroi cellulaire microbienne. Cette méthode améliore sensiblement l'efficacité de digestion des boues, réduisant le temps de rétention dans le digesteur et augmentant la production de biogaz (Pavlostathis et Giraldo-Gomez, 1991; Khanal *et al.,* 2007; Appels *et al.,* 2008; Pilli *et al.,* 2011). Le substrat peut être facilement accessible aux bactéries anaérobies après un prétraitement. À ce jour, il existe différentes technologies de prétraitement des boues, telles que les chocs thermique, chimique, mécanique, biologique, physique ou des combinaisons de ces méthodes telles que les prétraitements thermochimique, physico-chimique, biologique et physico-chimique, mécanique et chimique. Le prétraitement des boues améliore leur déshydratation, leur biodégradabilité ainsi que l'efficacité de la DA et la production de biogaz. Avec l'amélioration de la déshydratation des rejets, aucun conditionnement supplémentaire n'est nécessaire. La DA de boues prétraitées permet de réduire davantage la masse de boues à déshydrater. Des recherches approfondies ont permis d'établir la technique de prétraitement la plus efficace et la plus intéressante d'un point de vue économqiue, conduisant à une meilleure digestion/biodégradation des boues. Ces procédés de pré-traitement ont la capacité d'augmenter le taux de biodégradation des boues et de produire davantage de méthane lors de la DA. Les performances ainsi que les avantages et les inconvénients des techniques de prétraitement sont résumés au Tableau 1.

Parmi les techniques de prétraitements existants, les ultrasons et le traitement thermique ont été largement étudiés. Le procédé Fenton est l'une des méthodes de prétraitement oxydatif la plus efficace. Les détails du prétraitement par ultrasons, par prétraitement thermique et du procédé Fenton sont décrits ci-dessous.

Tableau 1. Méthodes de prétraitement des boues

Méthodes de prétraitement	Comparaison avec le contrôle, augmentation en (%)		Dégradation des solides (%)	Avantages	Désavantages
	Biodégradabilité	Production de biogaz			
Ultra-sonication	50–80	10–100	40–70	Augmente la déshydratation, inodore, facile à implanter, haute stabilité opératoire, pas de problèmes de colmatage, récupération d'énergie	Risques d'érosion de la sonotrode, consommation élevée d'énergie.
Prétraitement thermique	60–85	40–100	60–80	Déshydration améliorée, meilleure désinfection de la boue et récupération d'énergie.	Problèmes d'odeurs, de corrosion, faible stabilité opératoire, production de composés toxiques et réfractaires.
Broyage par les billes	15	10	40–60	Facile à opérer, ne dégage pas d'odeurs.	Importante érosion dans la chambre de broyage, colmatage, faible degré de désintégration, faible stabilité opératoire.
Prétraitement Fenton	30–70	10–75	20–45	Déshydratation améliorée, meilleure désinfection de la boue.	Problèmes d'érosion, nécessite de faibles pH et de hautes mesures de sécurité.
Ozonation	10–15	8	36	Déshydratation améliorée, meilleure désinfection de la boue.	Très énergivore, faible degré de désintégration.

1.3.1 Traitement des boues par ultrasons

Le traitement par ultrasons est un procédé émergent efficace, permettant d'améliorer la biodégradabilité des boues. Le traitement par ultrasons est très utile dans les STEPs pour le traitement et la disposition des boues d'épuration (Pilli *et al.,* 2011). Ce procédé consiste en l'application d'une pression acoustique cyclique (compression et détente) de fréquence supérieure à 20 kHz. Le schéma de l'ultrasonication et de ses diverses applications est présenté à la Figure 2. Dépendamment de la fréquence appliquée, ils sont divisés en trois groupes : ultrasons puissants (20-100 kHz), ultrasons à haute fréquence (100 kHz à 1 MHz) et ultrasons de diagnostic (1 à 500 MHz). L'utilisation de ces fréquences dans différents domaines a été résumée par Pilli *et al.* (2011).

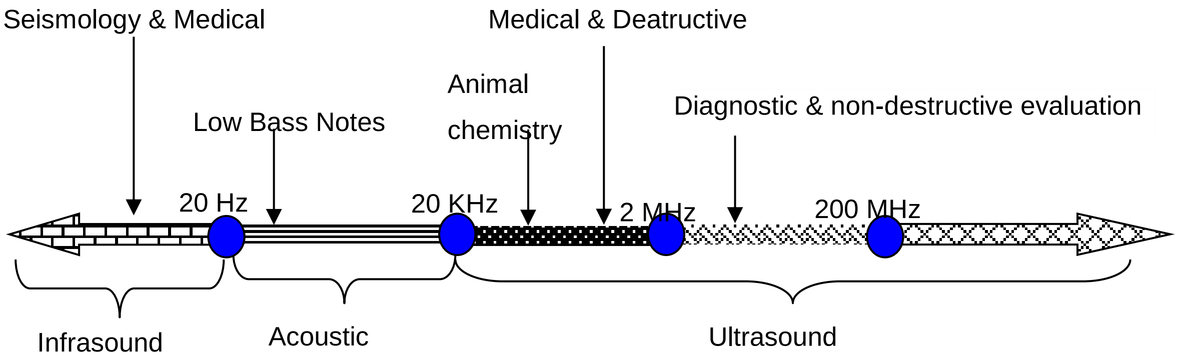

Figure 2. Diagramme des intervalles d'ultrasons

L'objectif de base de la technique par ultrasons est de briser les parois cellulaires des bactéries afin de rendre accessible la matière intracellulaire pour des dégradations ultérieures en CH_4 et en CO_2. Lorsque les ultrasons se propagent dans la boue, ils génèrent des compressions et des réfractions. Les cycles de compression exercent une pression positive sur le liquide en mettant les molécules ensemble, tandis que les cycles de réfractions exercent une pression négative pressant les molécules les unes contre les autres. La pression négative trop importante entraîne la formation de microbulles (bulles de cavitation) dans les régions de réfractions. Ces microbulles grossissent lors des cycles successifs et atteignent des diamètres instables, entraînant une explosion violente des microbulles et produisant des ondes de choc (température d'environ 5,000 °C, pression de 500 atm et durée de vie de quelques microsecondes) (Khanal *et al.,* 2007; Pilli *et al.,* 2011). Le processus par lequel les bulles se forment, se développent et explosent violemment est appelé la cavitation. Les ultrasons par régulation de la température et des autres paramètres opératoires sont présentés à la Figure 3.

L'énergie ultrasonique est convertie en énergie électrique à haute fréquence avec des cristaux piézoélectriques (relier à la chaîne de matériau) attachés à la pièce vibrante (sono-électrode, sonde). Le transducteur (convertisseur) convertit l'énergie électrique ou mécanique produite en ondes sonores. Le booster est un amplificateur mécanique qui augmente la vibration (amplitude) générée par un transducteur (Pilli *et al.,* 2011). L'avertisseur libère des ultrasons dans le liquide. Le booster et la corne sont les principaux composants des appareils d'ultrasons. Le taux de conversion de l'énergie acoustique en énergie thermique peut être calculé selon l'équation 4.2 (*Pilli et al.,* 2011).

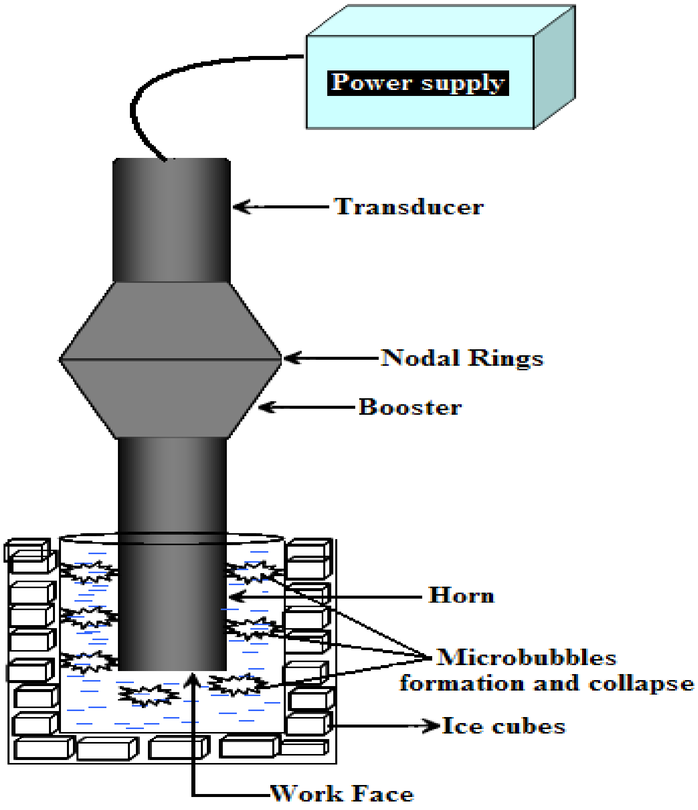

Figure 3. Ultrasons des boues (température contrôlée) (Pilli *et al.,* 2011)

$$Q_{w} = C\ m\ (T-T_0) \quad (2)$$

$$Q_u = P\ t \quad (3)$$

$$\eta(\%) = \frac{Q_w}{Q_u} * 100 \quad (4)$$

T_0 = Température de la boue fraîche; T = Température après traitement par ultrasons; Q_w = Énergie totale; m = Masse d'eau ; C = Chaleur spécifique de l'eau (4.2 kJ/kg.°C); Q_u = Énergie produite; P = Puissance ultrasonique; t = Durée du traitement; η = Rendement.

Les ultrasons améliorent la digestion des boues en brisant les propriétés physiques, chimiques et biologiques de la boue. Le degré de désintégration dépend des paramètres d'ultrasons et des caractéristiques de la boue. L'évaluation des paramètres optimums varie en fonction du type d'appareil à ultrasons utilisé et du type de boue à traiter. La puissance/énergie appliquée pour la désintégration des boues est exprimée de plusieurs manières : a) l'apport d'énergie spécifique ; b) la dose d'ultrasons ; c) la densité des ultrasons et d) l'intensité des ultrasons. Les différentes équations sont présentées au Tableau 2. Par ailleurs, les mécanismes de désintégration ayant lieu durant le traitement des boues par ultrasons sont expliqués par Pilli *et al.* (2011).

Tableau 2. Expressions des boues désintégration

No.	Paramétres	Expression	Unité
1	Apport d'énergie spécifique	$E_S = \frac{P * t}{V * TS}$	kJ/ kg TS ou kWs/kg TS
2	Dose ultrasons	$UD_o = \frac{P * t}{V}$	J/L
3	Densité ultrasons	$UD = \frac{P}{V}$	W/L
4	Intensité des ultrasons	$UI = \frac{P}{A}$	W/cm^2

***Note:** E_S: Énergie spécifique en kWs/kg TS (kJ/kg TS); P: Puissance d'alimentation (kW); T: Temps de sonication (sec); V: Volume des boues (L); TS: Concentration totale en solides (kg/L); A: Surface de la sonde en cm^2*

Les effets des ultrasons sur les propriétés physico-chimiques et biologiques ont été résumés par Pilli *et al.* (2011). Le prétraitement des boues par ultrasons a un effet significatif sur la biodégradabilité de ces dernières au cours de la DA, ce qui a pour effet d'augmenter la production de biogaz et le pourcentage de CH_4 présent dans le biogaz. Des expériences réalisées, aussi bien à l'échelle laboratoire qu'à grande échelle, ont démontré une nette amélioration de la réduction des boues et de la production de biogaz lorsque des ultrasons sont utilisés comme prétraitement. Une baisse d'environ 31% de la quantité des boues peut être obtenue lors de l'application de ce prétraitement à grande échelle. De plus, le traitement par ultrasons améliore la déshydratation des boues. De plus, le traitement par ultrasons accélère la conversion des composés organiques complexes en substrats dégradables et favorise également la croissance des bactéries productrices de méthane. Selon les avis de plusieurs chercheurs, la densité du traitement par ultrasons est un paramètre plus important que le temps de traitement. Les études cinétiques ont conclu que l'effet des paramètres s'inscrit dans l'ordre suivant : pH > concentration des boues > intensité des ultrasons > densité des ultrasons. L'augmentation de la solubilisation de la demande chimique en oxygène (DCO) augmente la production de méthane. Le temps de rétention hydraulique (TRH) du réacteur est réduit et par conséquent, la taille du réacteur est diminuée de manière significative. La réduction des solides volatils est améliorée avec l'augmentation des ultrasons, ce qui augmente l'efficacité de dégradation des boues lors de la DA. L'optimisation des paramètres d'exploitation à partir du bilan de masse et de l'énergie nette est d’une haute importance pour justifier la faisabilité de ce prétraitement à plus grande échelle.

1.3.2 Prétraitement thermique des boues

Le prétraitement par la chaleur est un procédé dans lequel la température de la boue est portée à un degré souhaité pour augmenter de manière significative la désintégration et la solubilisation des matières solides des boues. Le traitement thermique des boues est généralement utilisé pour améliorer leur déshydratation. En outre, ce genre de traitement est considéré comme un procédé de prétraitement permettant d’améliorer la production de biogaz au cours du procédé de DA. L'énergie thermique nécessaire pour élever la température de la boue est généralement produite par injection directe de vapeur, ou encore en utilisant des échangeurs de chaleur. Les boues prétraitées à chaud sont refroidies à la température de la DA et la chaleur est récupérée lors du processus de refroidissement. Cette énergie peut être utilisée pour préchauffer l’alimentation en boue fraîche. La récupération de chaleur augmente de façon significative l'efficacité de l'énergie et réduit le coût de prétraitement de façon significative. La plupart des recherches réalisées sur le prétraitement thermique des boues ont été effectuées en utilisant une large gamme de températures allant de 60 à 270 °C (Climent *et al.,* 2007). Sur la base de la température d’hydrolyse, la température de prétraitement (TPT) a été classée en deux catégories différentes ; à savoir, l'hydrolyse de prétraitement à température supérieure à 100 °C (considérée comme prétraitement thermique à haute température), et la température appliquée au-dessous de 100°C (considérée comme prétraitement thermique de faible température) (Climent *et al.,* 2007). L'effet de l'hydrolyse thermique sur la DA des boues prétraitées à une température supérieure à 100°C a été examiné par Carrere *et al.* (2010) (c.a.d. des méthodes de prétraitement pour améliorer la dégradabilité des boues anaérobies). Les effets du prétraitement thermique sur les propriétés chimiques et physiques, biologiques et le bilan énergétique du procédé intégré (prétraitement et DA thermique) sont résumés par Pilli *et al.* (2014).

<u>Prétraitement thermique à hautes températures</u>

Pendant les années 60 et 70, les traitements thermiques des boues ont été le principal moyen de gestion de ces dernières. Les procédés Porteus et Zimpro sont les deux principaux procédés opérés généralement entre 200 et 250°C. Les problèmes rencontrés avec ces procédés thermiques sont la génération d’odeurs, la production de liquide ayant des concentrations élevées en matières organiques et la corrosion des échangeurs de chaleur. Les projets Porteus et Zimpro ont été arrêtés à la fin des années 60 et/ou au début des années 70.

Avec des conditions d'exploitation modifiées et un prétraitement à faible température, le processus Zimpro est encore en usage au niveau de la déshydratation des boues (Camacho *et al.,* 2008). Diverses combinaisons d'hydrolyse thermique et de techniques acides et alcalines ont émergé au cours des années 80. Ces technologies ont eu pour but de produire des boues pasteurisées, mais aucune d'elles n'a été commercialisée parce qu'elles n'étaient pas économiques et/ou n'amélioraient pas la biodégradabilité. Synox et Protox sont les meilleures illustrations des procédés thermiques combinés permettant d'améliorer la déshydratation. Cependant, ces technologies n'ont pas été commercialisées (Neyens et Baeyens, 2003a).

Au début des années 90, le procédé CAMBI a été développé permettant une hydrolyse thermique efficace. Veolia Water Technologies and Solutions a développé des procédés d'hydrolyse thermique connus sous le nom de Biothelys® permettant d'améliorer la biodégradabilité et la déshydratation des boues. Le procédé Biothelys est la combinaison de l'hydrolyse thermique (procédé d'hydrolyse Thelys^{TM}) et de la DA. CAMBI et Biothelys sont deux procédés commerciaux à hautes températures (TPT).

Prétraitement thermique à faibles températures

Les études sur le prétraitement thermique à faibles températures sont très limitées. Afin de réduire les inconvénients des exigences énergétiques élevées, la formation de composés toxiques réfractaires (composés Amadori et composés mélanoïdines) et la faible biodégradabilité des boues à forte température (> 180°C), Wang *et al.* (1997) ont conclu que la TPT des boues à faible température (60-100°C) améliore la dégradation de la matière organique et la production de méthane de manière significative. Le temps de traitement à faibles températures dure de quelques heures à plusieurs jours (Gavala *et al.,* 2003; Ferrer *et al.,* 2008; Lu *et al.,* 2008; NGES et Liu , 2009; Borges et Chernicharo , 2009; Appels *et al.,* 2010). Les effets du prétraitement thermique sur les propriétés bio-physico-chimiques des boues et sur la production de biogaz ont été résumés par Pilli *et al.* (2014). Les conclusions concernant les effets du prétraitement thermique sont les suivantes : le prétraitement thermique à faibles et hautes températures (TPT) a des effets significatifs sur la biodégradabilité de la boue et améliore la production de biogaz. Les études opérées à l'échelle laboratoire ont permis de conclure est la température optimale pour une meilleure déshydratation et une production optimale de biogaz se situe entre 160 et 170 °C. Des travaux réalisés en laboratoire ont permis de mettre en évidence que la température et le temps optimal de prétraitement et de production de biogaz se situent entre 160 et 180 °C pour une durée allant de 30 à 60 min, respectivement. Les études réalisées à grande échelle ont permis de démontrer que la haute température du prétraitement permet de réduire le temps de rétention et le volume des boues, tout en améliorant la déshydratation des boues et la production de biogaz. Pour une température supérieure à 190 °C, la solubilisation des boues est élevée mais la production de biogaz est faible (la biodégradabilité est réduite) en raison de la formation de composés toxiques réfractaires (composés Amadori et composés mélanoïdines). Les procédés de prétraitement thermique commerciaux, tels que l'hydrolyse thermique CAMBI et le procédé Biothelys améliorent la déshydratation des boues. Une méthode standard d'évaluation de l'efficacité de n'importe quel procédé de prétraitement consiste à calculer le bilan d'énergie et le bilan net de carbone du procédé global, y compris la DA de la boue prétraitée et la production d'énergie à partir du biogaz. L'évaluation du bilan énergétique total et celui net de carbone aideront les décideurs dans le choix de la technique de prétraitement.

1.3.3 Prétraitement par le procédé Fenton

Le réactif utilisé lors du procédé Fenton est un oxydant très fort et ayant un potentiel d'oxydoréduction de +2,33 V. Les radicaux produits sont des oxydants plus puissants que le peroxyde d'hydrogène (+1,36 V) et l'ozone (+2,07 V) (Neyens et Baeyens, 2003b; Erden et Filibeli, 2010; Pham *et al.,* 2010a). Le prétraitement par peroxyde d'hydrogène augmente la réduction des solides de 50 à 60%, produisant ainsi des biosolides de classe A (Cacho Rivero et Sudian, 2006).

Le processus de Fenton est un prétraitement en présence de peroxyde d'hydrogène amélioré par l'ajout de fer ferreux comme catalyseur. Le prétraitement à l'ozone améliore la production de biogaz de 8% par rapport aux procédés de DA traditionnels (Pérez-Elvira *et al.,* 2006). Le prétraitement par le procédé de Fenton est préférable en raison de la complexicité et des coûts élevés du prétraitement par ozone (Cacho Rivero et Sudian, 2006 ; Lydia Cacho Rivero *et al.,* 2006). Le procédé Fenton a été identifié par plusieurs chercheurs comme étant préférable pour prétraiter les boues et augmenter leur biodégradabilité (Pham *et al.,* 2010a; Neyens et Baeyens, 2003b; Erden et Filibeli, 2010). La technologie la plus prometteuse pour la déshydratation des boues est le prétraitement par le procédé Fenton (Zhen *et al.,* 2014). En outre, le procédé Fenton renforce la production de biogaz et minimise le poids des boues pour leur déshydratation, leur transport et leur épandage (Neyens et Baeyens, 2003; Erden et Filibeli, 2010; Pham *et al.,* 2010a).

Les chercheurs ont utilisé la réaction de Fenton comme conditionneur chimique alternatif sur différents types de boues (Mustranta et Viikari, 1993; Lu *et al.,* 2003; Neyens *et al.,* 2003; Buyukkamaci, 2004; Neyens *et al.,* 2004a, b; Dewil *et al.,* 2005; Tony *et al.,* 2008; Pham *et al.,* 2010a). En outre, ce prétraitement a été utilisé pour augmenter la biodisponibilité de la matière organique présentes dans les boues secondaires pour produire le biopesticide *Bacillus thuringiensis* (Pham *et al.,* 2010b). Il a été conclu que le prétraitement des boues par le procédé Fenton améliore la croissance bactérienne et le potentiel entomotoxique. Il a aussi été établi que les boues prétraitées ont donné une meilleure productivité. Pham *et al.* (2011) ont évalué l'effet du prétraitement par Fenton sur la biodégradation du bis(2-éthylhexyl)phtalate (DEHP) et de l'acide 2-éthylhexanoïque présents dans les déchets de boues activées au cours de la production de biopesticide. Ces auteurs ont conclu que la réaction de Fenton a joué un rôle critique dans l'amélioration de la biodisponibilité des composés pour les biopesticides durant la fermentation des boues.

L'oxydation par le procédé de Fenton peut dégrader les substances polymériques extracellulaires, qui représentent jusqu'à 80% de la masse de boues activées (Forlund *et al.,* 1996; Tony *et al.,* 2008). Les traitements avec le réactif Fenton solubilisent une partie des boues mises en solution de matières organiques biodégradables et minéralisent une autre partie en CO_2 et H_2O et les solides. Une faible concentration en H_2O_2 est requise pour produire les ions OH^-, mais une forte concentration en H_2O_2 n'est pas recommandée car le H_2O_2 résiduel se transforme en $OH^\cdot$ comme décrit dans les équations 5 à 7 (Neyens *et al.,* 2003; Bautista *et al*., 2008).

$$H_2O_2 + OH^\cdot \rightarrow HO^\cdot_2 + H_2O \quad (5)$$

$$HO^\cdot_2 + OH^\cdot \rightarrow O_2 + H_2O \quad (6)$$

$$OH^\cdot + OH^\cdot \rightarrow H_2O_2 \quad (7)$$

Dans des conditions acides, la réaction de l'oxydation de Fenton est rapide et exothermique. Au cours de la réaction, le H_2O_2 oxyde le fer Fe^{2+} en Fe^{3+} (équation 8). Le fer ferreux (Fe^{2+}) initie et catalyse la décomposition de l'oxydant, favorisant la génération de radicaux hydroxyles et d'anions hydroxyles (Pham *et al.,* 2010a). Les radicaux hydroxyles réagissent avec les ions Fe^{2+}

en produisant des ions Fe^{3+} et des anions hydroxyles. En présence de composés organiques, les radicaux hydroxyles (RH) réagissent et forment des radicaux organiques ($R^{\cdot}$) (chaîne de propagation). La chaîne de propagation est initiée lorsque les radicaux hydroxyles oxydent les RH par l'abstraction des protons, produisant ainsi des radicaux organiques ($R^{\cdot}$) qui sont très réactifs et peuvent encore être oxydés (Neyens et Baeyens, 2003; Primo *et al.,* 2008; Bautista *et al.,* 2008; Pham *et al.,* 2010a).

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$ (initiation) (8)

$OH^{\cdot} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$ (termination) (9)

$RH + OH^{\cdot} \rightarrow H_2O + R^{\cdot}$ (propagation) (10)

Les radicaux hydroxyles générés pendant des étapes d’ouverture et de propagation réagissent avec des substances organiques cibles. Le radical OH° est le principal réactif de Fenton capable de décomposer les substances organiques via l'oxydation. En fait, diverses réactions entre les radicaux hydroxyles et les polluants ciblés peuvent se produire par le biais de (i) l'abstraction d’hydrogène, (ii) le transfert d'électrons et (iii) l’interaction radical (http://www.lenntech.com/fenton-reaction.htm). Le détail de ces réactions est présenté dans le Tableau 3.

Tableau 3. Réactions entre les radicaux hydroxyles et les polluants ciblés pendant la réaction de Fenton

Type de réaction	Exemples	Description	Références
Addition	$R_2C{=\!=\!=}CR_2 + HO^{\bullet} \rightarrow HO\text{-}C(R)_2 - C^{\bullet}(R)_2$	Au cours de la réaction d'addition, des radicaux hydroxyles ajoutés à un composé non-saturé, aliphatique ou aromatique, forment un radical libre.	Buda *et al.* (2003); Prousek (2007)
Abstraction d'hydrogène	$ArH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O$	Dans cette réaction organique, un radical libre et de l'eau sont formés.	Buda *et al.* (2003); Prousek (2007)
Transfert d'électrons	$HO^{\bullet} + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^{-}$	Dans cette réaction, le radical libre est oxydé	Buda *et al.* (2003); Prousek (2007); http://www.h2o2.com/
Interaction entre radicaux	$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2$	Deux radicaux hydroxyles se combinent pour former un composé stable.	Buda *et al.* (2003); Prousek (2007);

Des études réalisées à l'échelle pilote ont démontré que le prétraitement par le procédé de Fenton avait un fort potentiel, améliorant la déshydratation des boues. Le pH, la température, la concentration en peroxyde d'hydrogène et en ions Fe^{2+} ainsi que le temps de réaction sont des paramètres importants qui influencent l'efficacité du prétraitement par le procédé de Fenton. Le prétraitement à de faibles températures nécessite une haute concentration en réactifs de Fenton et plus de temps de traitement. Le prétraitement à hautes températures requiert de faibles concentrations en réactifs de Fenton et moins de temps de traitement. Le prétraitement par le procédé de Fenton améliore l'efficacité du procédé de digestion anaérobie, mais il n'est pas évident de conclure que ce procédé est bénéfique, étant donné l'énergie déployée.

1.4 Élimination des boues

Les processus de traitement des boues tels que la DA, la digestion aérobie et le compostage ne constituent pas des méthodes d'élimination des boues telles que l'épandage, l'enfouissement et l'incinération. Les méthodes les plus couramment utilisées pour l'élimination des boues sont la mise en décharge, l'incinération et l'épandage (Figure 4) (Kelessidis et Stasinakis, 2012). Les avantages et les inconvénients de cess techniques de disposition sont présentés au Tableau 4. Parmi les différentes options d'élimination de ces rejets, l'application sur des terres agricoles est considérée comme étant la plus économique. Le rapport coût-efficacité est évalué sur la base de la valeur des engrais présents dans les boues. L'élimination des boues se réfère à leur épandage sur ou juste au-dessous de la surface du sol à une profondeur de 15 à 30 cm.

Tableau 4. Différentes voies d'élimination des boues

Méthode de mise au rebut	**Avantages**	**Problèmes**	**Lois et Règlement**
Incinération	Réduction élevée de volume	Coût élevé en capital, génération de réactif ou gaz acides et frais d'exploitation élevés, émissions de CO_2, de N_2O	Loi sur la protection de l'environnement
Application sur des terres agricoles	Faible coût et valeur nutritionnelle (Agriculture)	Exige beaucoup d'espace au sol, problèmes de santé en raison de la présence de pathogènes et de parasites, contamination par des métaux lourds, émissions de CO_2, de CH_4 et de N_2O	Clean Air Act (42 U.S.C. 7401)
Décharge	Moins de contamination environnementale	Production de lixiviat, coût élevé et contamination par des métaux lourds, émissions de CO_2 et de CH_4	Loi sur la protection de l'environnement Loi sur l'assainissement de l'air Loi sur la qualité de l'environnement (Québec)

L'épandage de ces déchets est utilisé comme méthode de gestion des boues dans de nombreux pays depuis de nombreux siècles. Les pourcentages de boues sèches répandues dans différents pays èa travers le monde sont résumés dans le Tableau 5. Lorsque les rejets sont appliqués sur le sol, celui-ci reçoit de la matière organique et des éléments nutritifs provenant des boues. Les processus biologiques qui se produisent subissent des modifications et par conséquent, le flux des gaz à l'interface sol-atmosphère est également modifié. Dans cette perspective, le sol agit soit comme une source soit comme un lavabo pour le carbone. Il existe peu d'études traitant des flux de gaz émis à partir des sols tropicaux sur lesquels des boues ont été épandues, mais beaucoup d'études ont été effectuées sur la température du sol et le climat (Flessa et Beese, 2000; Alvarez *et al.,* 1999; Wong *et al.,* 1998). En outre, l'épandage des boues d'épuration augmente la structure du sol, ce qui améliore sa maniabilité et réduit sa résistance pour la manipulation et le labourage avec des conséquences importantes sur l'économie de carburant et les émissions de GES (Sommers, 1997 ; Brown *et al.,* 2010). L'amélioration des propriétés physico-chimiques du sol permettrait de réduire la gestion et la maintenance nécessaire, ce qui aurait comme conséquence une réduction de GES.

Tableau 5. Production et proportion de boues épandues dans différentes régions du monde

Régions	**Production de boues Sec (Mg/an)**	**Épandage de boues (en % du total des boues)**	**Référence**
Australie	36 000	80	Pritchard *et al.* (2010)
Europe	10 000 000	36	http://ec.europa.eu/environment-2010
États-Unis	7 000 000	50	McClellan and Halden (2010)
Chine	5 000 000	45	Zhu *et al.* (2011)
France	700 000	60	Wang *et al.* (2008b)
Royaume-Uni	1 400 000	58	http://www.biomassenergycentre.org.uk/
Canada	550 000	43	Pilli et al., 2014

En 1977, Sommers a obtenu des données sur la teneur en nutriments présents dans près de 250 échantillons de boues d'épuration ; les taux moyens en N et P étaitent de 5 et de 3% du poids sec des boues d'épuration, respectivement (Sommers, 1997). Clapp *et al.* (1986) ont estimé le rendement des boues d'épuration (tonne/hectare) comme fertilisant pour plusieurs types de cultures, à savoir 38% d'augmentation pour le maïs, 51% pour les céréales et 14% pour les roseaux d'alpiste comparativement aux contrôles de fertilisation par ajout d'azote, de phosphore et de potassium. Les résultats ont été calculés sur une moyenne de 3 à 7 ans d'observations expérimentales réalisées dans des champs. Togun *et al.* (2004) ont signalé une hausse moyenne du rendement de 28,5% pour les tomates. La teneur en carbone des tomates est de 24,8 g C/kg et de 90,9 kg de CO_2/Mg. La préparation du sol et sa maniabilité peut réduire la consommation de carburant de prèes de 5%. Cette hypothèse de la réduction de 5,0% de la consommation de carburant est basée sur la différence de consommation de carburant entre le sol dur et la terre meuble (Moitzi, Weingartmann, *et* Boxberger, 2006). En raison de l'application de boues d'épuration, le sol dur se comportera comme un sol mou. La consommation moyenne de carburant pour le labourage de sol dur est de 12,80 L / ha (Moitzi *et a*l. 2006) et le facteur d'émission pour le carburant est de 2,73 kg CO_2/L de diesel (Gassara *et al.* 2011). Par conséquent, la réduction des émissions de gaz à effet de serre peuvent être calculées en appliquant du compost sur le sol avec une épaisseur moyenne de 53,4 mm.

Une augmentation du rendement des cultures signifie qu'il y a une séquestration élevée du carbone (ou une minimisation des GES) en raison de l'absorption photosynthétique du CO_2 par les plantes et les récoltes D'un autre côté, il a été reporté que l'application de boues d'épuration provoque un flux accru de CO_2, de N_2O et de CH_4 dans l'atmosphère (Fernandes *et al.,* 2005a). Les flux de CO_2, de N_2O et de CH_4 suite à l'épandage des boues ont augmenté de 224,0%, 316,0% et 162,0%, respectivement, par rapport au sol contrôle sans engrais (Fernandes *et al.,* 2005 a&b). Lorsqu'il est appliqué avec une épaisseur de 53,4 mm sur le sol, le compost permet d'économiser environ 0,2513 m^3 d'eau/m^3 de compost (NEBRA, 2008). Il est également mis en évidence que, pour l'utilisation de l'eau pour l'agriculture, près de 9,2462 kWh d'électricité sont nécessaires par mètre cube d'eau. Différents organismes tels que le GIEC, l'EPA, et l'IRC, n'ont pas considérés l'augmentation du flux de CO_2, de N_2O, de CH_4 et l'amélioration de la structure du sol lors de l'estimation des émissions de GES. L'augmentation des flux de CO_2, de N_2O, de CH_4 et l'amélioration de la structure du sol sont pris en compte dans la méthode d'estimation proposée dans cette étude. La liste des organismes gouvernementaux et chercheurs qui ont évalués les émissions de GES au cours de l'épandage de boues est résumée ci-dessous.

Groupe d'experts intergouvernemental sur l'évolution du climat (GIEC)

Les émissions de CO_2 sont considérées comme des sources biogéniques en raison de l'épandage des boues d'épuration ou des bio-solides. Les émissions de CO_2 générées pendant l'application des bio-solides sur les terres agricoles sont considérées comme une source d'émissions de GES ; en raison de l'utilisation de combustibles fossiles au cours du transport des boues d'épuration sur les sites d'application et des véhicules utilisés lors de l'application des biosolides sur les terres (ex. tracteurs, etc). La GIEC a adopté la méthode d'estimation recommandée par l'Organisation de coopération et de développement économique (OCDE). En conséquence, la valeur des émissions de méthane en tant que GES représente 10% du potentiel de gaz qui se dégage lors de l'élimination des boues sur les terres d'agriculture dans les climats humides et est égale à la valeur de 5 kg/Mg de boues sèches solides non traitées. Par ailleurs, le GIEC a adopté les émissions de dioxyde nitreux en raison de l'application de bio-solides dans les sols agricoles tel qu'estimée par Mosier (1996). Selon cette méthode, 1% de l'azote appliqué aux sols agricoles est émis sous forme d'oxyde nitreux par dénitrification.

Émissions de GES : méthodologie d'estimation pour sélectionner la source biogénique par catégorie de recherche d'unité triangulaire (RTI : le RTI (2010) a présenté un projet à l'EPA. Il s'agit d'une méthodologie d'estimation pour sélectionner les catégories de sources biogéniques sur les émissions de GES. Le RTI a estimé la quantité de CO_2 émis à partir de l'épandage des boues d'épuration en supposant une constante de la population de biomasse. Le taux de génération du CO_2 pour l'application des boues sur les terres serait directement proportionnel au taux d'application de carbone sur la terre. Le RTI a examiné uniquement les émissions de CO_2 provenant de l'épandage des matières solides.

Émissions des bio-solides : modèle d'évaluation (BEAM)

Ce modèle a été développé par le Conseil Canadien des Ministres de l'Environnement (CCME) pour permettre aux municipalités d'estimer les émissions de GES à partir des biosolides. Les émissions anthropiques de CO_2 sont considérées pour l'épandage de biosolides. La quantité de carburant utilisé pendant l'épandage de biosolides a été estimée à 3,2 L/Mg de biosolides secs appliqués. Les émissions de CO_2 produites lors de l'application de biosolides sur la terre sont considérées comme des sources biogéniques, et elles ne sont pas incluses dans l'estimation des GES. Pour le modèle BEAM, les émissions de CH_4 provenant de l'application des biosolides sont considérées comme négligeables (Ball *et al.,* 2004; Jones *et al.,* 2005). Les émissions de N_2O provenant de l'épandage des biosolides sont évaluées sur la base de rapport C/N. Si le rapport C/N est > 30, le facteur de conversion de N à N_2O est de 1,57 pour le sol fin ainsi que pour les sols à texture grossière. Si le ratio de C/N est < 30, le facteur de conversion N à N_2O est égal à zéro pour les deux types de sol (SYLVIS Environmental, 2009).

En plus des méthodes suggérées par différents organismes gouvernementaux mentionnées ci-dessus, les émissions de GES au cours de l'application des terres ou de l'application agricole des boues ont également été évaluées au cours de l'analyse du cycle de vie de la gestion des boues par plusieurs autres chercheurs et sont résumées dans le Tableau 6.

Tableau 6. Facteurs de GES à considérer pour l'application terrestre au cours du traitement des boues

Méthodes d'élimination des boues	**Facteurs des émissions de gaz à effet de serre (Kg/Mg de matières sèches)**			**Conclusions**	**Auteurs**
	CO_2	**CH_4**	**N_2O**		
Application en agriculture	NA	NA	NA	Les auteurs n'ont pas tenu compte de l'impact des nutriments sur les GES.	Suh et Rousseaux (2002)
Application sur les terres	NA	NA	NA	Les auteurs ont considéré les facteurs directs d'émissions. Ils n'ont pas considéré les émissions de CH_4 et de N_2O en raison de l'épandage des boues. Les émissions de dioxyde de carbone sont considérées comme des émissions biogéniques et ne sont pas comprises dans les calculs des GES.	Houillon et Jolliet (2005)
Application en agriculture	25	0,012	0,19	Les auteurs ont considéré les avantages de l'azote, ne décrivant pas les émissions de CH_4 et de CO_2 en raison de l'épandage.	Lundin *et al.* (2004)
Application sur les terres	NA	3,18	NA	Les auteurs n'ont pas considéré (évité) les émissions de N_2O et de CO_2 provenant de l'épandage des boues.	Hospido *et al.* (2005)
Application en agriculture	17,2	0,021	0,19	Les auteurs ont considéré les avantages de l'azote. Les autres facteurs sont pris à partir des données d'inventaires sans explication adéquate.	Hong *et al.* (2009)
Application sur les terres	17,2	3,18	NA	Les auteurs ont considéré comme un avantage la teneur en azote présente dans les boues.	Niu *et al.* (2013)

2. PROBLÉMATIQUE

La production des boues est un problème mondialement connu dans les usines de traitement des eaux usées qui génèrent environ 1 Mg de produit sec par 10,000 personnes par jour (Fytili et Zabaniotou, 2006). Les 700 usines de traitement des eaux usées (STEPs) existantes au Québec produisent 230,000 Mg/an de boues sèches (LeBlanc *et al.,* 2008; Perron et Hebert, 2007). Cependant, ce taux de production a augmenté en raison de l'urbanisation et de l'évolution de la population. Par conséquent, la DA a été envisagée comme technologie pour réduire au maximum le volume de rejets à disposer. De plus, un prétraitement a été proposé par plusieurs chercheurs pour faciliter la biodégradabilité et améliorer la disponibilité des matières organiques contenues dans les boues.

L'ultrasonication, le prétraitement thermique et le prétraitement par le procédé Fenton ont été choisis parmi les procédés de traitement existants. En outre, le principal objectif du traitement environnemental est la réduction des émissions de GES, considérées comme une grande menace pour la terre au 21^{e} siècle. Des études ont évalué le procédé de prétraitement pour améliorer la DA basée sur l'augmentation de la production de biogaz en comparaison aux boues non traitées. Dans ce cas, la problématique réside dans le fait que l'énergie requise pour le prétraitement, la DA, la déshydratation et la disposition des boues n'est pas considérée dans l'évaluation de l'efficacité du prétraitement. Pareillement, les émissions de GES ne sont pas considérées dans l'évaluation de l'efficacité du prétraitement. Par conséquent, la présente étude a également permis d'illustrer les difficultés associées au procédé de prétraitement anaérobie et de l'épandage, lesquelles sont décrites dans la section suivante.

2.1 Problèmes liés au procédé de prétraitement

Les procédés de prétraitement ont été évalués en fonction de la production accrue de biogaz lors de la DA par rapport aux boues non traitées (témoin). Ainsi, l'énergie nécessaire pour le prétraitement, la digestion anaérobie, la déshydratation, le transport et l'épandage provient d'autres sources d'énergie telles que les centrales thermique à combustibles fossiles ; lesquelles sont les principaux contributeurs d'émissions anthropiques de GES. De plus, l'énergie récupérée à partir du biogaz produit par la boue prétraitée ne correspond pas forcement à l'apport d'énergie pour le prétraitement, la digestion anaérobie, la déshydratation, le transport et l'épandage.

L’ultrasonication

L’ultrasonication des boues améliore la production de biogaz mais il n'est pas certain que l'apport d'énergie soit supérieur à l'énergie récupérée. Par ailleurs, l'augmentation de la température au cours de l’ultrasonication aurait un effet sur l'énergie nécessaire au cours de la digestion anaérobie, ce qui n'est pas rapporté dans la littérature. Dans ce cas, différentes concentrations de matières solides de boues (boues primaires, secondaires et mixtes) auraient une influence sur l'efficacité de l’ultrasonication et la production de biogaz. L'apport d'énergie et l'énergie récupérée auraient aussi un effet direct sur les émissions de GES.

Le prétraitement thermique

L'énergie nécessaire pour augmenter la température au cours du prétraitement thermique des boues ainsi que sur celle récupérée à partir de la boue préchauffée aurait un effet sur l’énergie totale d’entrée, ce qui n'est pas étudié dans la littérature. Différentes concentrations des matières solides des boues (boues primaires, secondaires et mixtes) auraient une influence sur l'efficacité du prétraitement thermique et la production de biogaz, ce qui n'est pas investigué dans la littérature. L'apport d'énergie aurait aussi un impact direct sur les émissions de GES.

Le prétraitement par Fenton

Le prétraitement des boues par le procédé Fenton augmente la production de biogaz, mais le problème réside dans le fait que l'énergie récupérée à partir des boues prétraitées ne correspond pas forcement à l'énergie totale récupérée. Par conséquent, différentes concentrations de matières solides des boues (boues secondaires) auraient une influence sur l'efficacité de prétraitement par le procédé Fenton et la production de biogaz, ce qui n'est pas étudié dans la littérature. En outre, des études ont été effectuées sur l'effet de ce prétraitement sur les composés biodégradables et non-biodégradables. En fait, le procédé Fenton est un traitement rapide qui réagit avec les composés organiques. De ce fait, l'apport d'énergie au cours de ce prétraitement et celui récupéré à partir de biogaz aurait un effet direct sur les émissions de GES.

2.2 Problèmes liés à la digestion anaérobie

L'énergie nécessaire pour la DA est affectée par la température des boues. De ce fait, l'augmentation de ce facteur après le prétraitement aurait un effet sur l'apport d'énergie, ce qui n'est pas bien expliqué dans la littérature. De plus, la variation de la concentration en matières solides aurait une influence sur l'énergie nécessaire pour la DA. En effet, la combustion du méthane augmente la production de dioxyde de carbone. Par conséquent, l'apport d'énergie et l'énergie récupérée vont affecter directement les émissions de GES.

2.3 Problèmes associés à la déshydratation, au transport et à l'épandage des boues

L'énergie nécessaire pour la déshydratation, le transport et l'épandage serait affectée par le prétraitement des boues. Ainsi, l'apport d'énergie au cours de ces procédés aurait un effet direct sur les émissions de GES. Par ailleurs, les méthodes d'estimation des émissions de ces gaz lors de l'épandage des boues n'ont pas été bien étudiées. En effet, les principales incertitudes du GIEC portaient sur les méthodes d'estimation des émissions de CO_2, de CH_4 et de N_2O provenant de l'épandage des boues d'épuration, qui en fait augmentent la production de la culture et facilitent la récolte qui, par conséquent, augmente la séquestration du carbone. Par contre, l'estimation des émissions de CO_2 provenant des émissions anthropiques ne représente pas la quantité totale de CO_2 produit lors de l'application des boues. En outre, les émissions de méthane ou de protoxyde d'azote peuvent varier considérablement en fonction des types de boues, de la teneur en humidité des boues, des conditions ambiantes et environnementales et aussi en fonction de la variation diurne de la température. Ces facteurs ne sont pas pris en compte dans la méthode d'estimation du GIEC.

Les principales incertitudes de la méthodologie d'estimation des émissions de GES pour certaines catégories de sources biogéniques par unité triangulaire de recherche (OIR) sont le taux de production de CO_2 pour l'épandage des boues. Ce taux est directement proportionnel à la vitesse de carbone à l'unité de traitement du sol. Ce processus donne une surestimation des émissions de CO_2 car elle fournit la conversion complète de carbone des boues d'épuration en CO_2. En pratique, le carbone est converti en CO_2 et en CH_4 en présence de bactéries anaérobies présentes dans le sol. De plus, tel que suggéré plus haut, la fraction de CO_2 et de CH_4 peut varier considérablement en fonction des types de boues, de la teneur en humidité, des conditions environnementales et ambiantes et des variations diurnes de la température.

Les principales incertitudes du modèle d'évaluation des émissions associées aux biosolides (MEEB) sont le CO_2, le CH_4 et le N_2O produits lors de l'épandage (Ritter et Chitikela, 2012). Il y aurait une augmentation de la croissance des plantes et de la production de biomasse, ce qui permettrait de minimiser les émissions de CO_2. En outre, l'épandage de biosolides minimiserait l'entretien du sol et augmenterait la capacité de rétention d'eau. De ce fait, la réduction de l'entretien des sols et l'augmentation de la capacité de rétention d'eau permettrait ainsi de minimiser l'utilisation de machines et la consommation des combustibles fossiles, et réduiront par conséquent les émissions de GES correspondantes. Ces facteurs ne sont pas pris en compte dans l'estimation des émissions de CO_2 dans le MEEB. En se basant sur les deux études décrites ci-dessus, les émissions de méthane provenant de l'épandage de biosolides sont considérées comme négligeables, ce qui sous-estime les émissions de CH_4. D'autre part, Fernandes *et al.* (2005) ont démontré qu'il y avait une augmentation du flux de CH_4 lors de l'épandage de biosolides. Les facteurs utilisés pour évaluer la transformation de l'azote en N_2O (en MEEB) ne permettent pas d'évaluer précisemment les émissions exactes dues à l'épandage de biosolides. En outre, il y aurait plus de flux de N_2O entre l'atmosphère et l'interface du sol dû à l'épandage de biosolides. Ceci doit être pris en compte lors de l'estimation des émissions de N_2O.

Les émissions de GES et l'énergie nécessaire pour le prétraitement, la DA, la déshydratation et l'épandage des boues sont calculées en utilisant le bilan énergétique et le bilan massique. L'évaluation des émissions de GES pour les différentes technologies de prétraitement est susceptible d'influencer l'opinion publique et la prise de décision pour les stations d'épuration.

La méthodologie utilisée pour évaluer les prétraitements aux ultrasons, thermique et par le procédé Fenton sont définis dans les chapitres 2, 3, 4, et 5, respectivement. En outre, une nouvelle méthodologie a été décrite pour évaluer les émissions de GES en raison de l'épandage de boues dans le chapitre 6.

3. HYPOTHÈSES ET OBJECTIFS DE LA RECHERCHE

Le prétraitement des boues améliore leur biodégradabilité ainsi que la production de biogaz. Les émissions de GES avec le prétraitement des boues seraient réduites ou augmentées au cours de la gestion des boues.

3.1 Hypothèses

Les boues sont desproduits inévitables et majeurs issues des procédés de traitement (primaire, secondaire et tertiaire) des eaux usées, et les coûts de gestion des boues représentent environ 50-60% des coûts totaux d'exploitation d'une usine de traitement des eaux usées (Pilli *et al.,* 2011; Coma *et al.*, 2013). La digestion aérobie, la DA et le compostage sont les technologies conventionnelles adoptées pour traiter les boues (Appels *et al.,* 2008). Au cours de ces procédés classiques de traitement, la biomasse est biodégradable en trois principaux GES : le CO_2, le CH_4 et le N_2O. La DA des boues est considérée comme une importante option de traitement de ces dernières associés à la production d'énergie qui peuvent entrer dans le cadre des nouveaux règlements et à l'encontre du protocole de Kyoto pour réduire les émissions de GES (Yasui *et al.,* 2006). En raison de la disponibilité moins importante de matière organique biodégradable dans la boue, l'application des technologies de la DA (processus intensif d'énergie ou processus de consommation d'énergie) est limitée.

Considérant ce problème et la revue de la littérature exposée dans le chapitre 1 partie 2, les faits suivants sont considérés dans la formulation de l'hypothèse. Au cours des dernières années, les chercheurs ont concentré leur attention sur le prétraitement des boues afin d'améliorer la biodégradabilité de celles-ci. La littérature sur les technologies de prétraitement pour améliorer l'efficacité de la biodégradabilité et de la DA est essentielle. Lorsque l'on considère les technologies de prétraitement, les ultrasons, les technologies de prétraitement thermiques et le prétraitement par le procédé Fenton ont émergé comme étant des technologies de traitement prometteuses pour améliorer la biodégradabilité des boues. De l'examen critique de la littérature disponible sur les technologies de prétraitement des boues considérés, il a été conclu que les prétraitements thermique (Appels *et al.,* 2008), les ultrasons (Khanal *et al.,* 2007) et le procédé de Fenton (Dewil *et al.,* 2007) améliorent la production de biogaz.

Cependant, de nombreuses questions restent sans réponse, tel que suit.

- L’amélioration de la production de biogaz en raison de ces prétraitements (procédé Fenton, thermique ou ultrasons) des différentes types de boues (primaire, secondaire, mixte) fournit-elle un bilan énergétique positif ?
- Combien de solides pourraient-être réduits lors de la DA pour l'élimination finale des boues résiduelles, et quel est leur impact sur l'équilibre énergétique et les émissions de GES ?
- De combien s’élève la température au cours des prétraitements des boues aux ultrasons et quelles ont été les conséquences sur l'équilibre énergétique global ?
- Quelles sont les conditions de prétraitement de chaque technologie qui pourrait favoriser un bilan énergétique positif ?
- Quelles sont les conséquences de boues prétraitées suivi d'une DA sur le traitement en aval des boues résiduelles ou le digestat (déshydratation, transport et épandage des digestats sur les terres) ?
- Si les technologies de prétraitements sont intégrées dans le système de traitement des eaux usées, le bilan énergétique global sera-t-il favorable ? Si oui, de combien de fois sera-t-il favorable ?
- Des trois technologies sélectionnées, laquelle génère plus d'énergie et des émissions de GES minimales ?
- La méthodologie disponible pour calculer les émissions de GES pour le cas de l'épandage des boues est-elle suffisamment précise et tient-elle compte de tout le critère influent sur les émissions de GES ?

Compte tenu de ces faits, quatre hypothèses sont proposées.

Hypothèse 1 : De combien la température a augmentée au cours de l’ultrasonication ? L'élévation de la température des boues pendant les prétraitements à ultrasons pourrait augmenter l'énergie nette produite (énergie de sortie-énergie d'entrée) et entraîner une réduction des émissions de GES.

Hypothèse 2 : Le bilan de masse-énergie du prétraitement aux ultrasons suivi d'une digestion anaérobie, de le déshydratation du digestat, du transport et de l'épandage du digestat et leurs émissions de GES correspondantes peut favoriser un processus énergétiquement efficient avec des émissions minimales de GES.

La variation de la concentration de matières solides et du type de boues peut influencer l'énergie et les émissions de GES correspondantes.

Hypothèse 3 : Le bilan de masse-énergie du prétraitement thermique suivi d'une digestion anaérobie, de la déshydratation du digestat, du transport et de l'épandage du digestat et leurs émissions de GES correspondantes peut favoriser un processus énergétiquement efficient avec des émissions minimales de GES.

La variation de la concentration de matières solides et du type de boues pendant le prétraitement thermique et la DA peut influencer le bilan de l'énergie et les émissions de GES correspondantes.

Hypothèse 4 : Le bilan de masse-énergie du prétraitement par le procédé Fenton suivi d'une digestion anaérobie, de la déshydratation du digestat, du transport et de l'épandage du digestat et leurs émissions de GES correspondantes peut favoriser un processus énergétiquement efficient et des émissions minimales de GES.

La variation de la concentration en solides après prétraitement pourrait influencer la digestion anaérobie, l'énergie nette et les émissions de GES correspondantes.

Les faits suivants ont été pris en considération dans la formulation de la 5ème hypothèse. L'épandage des boues est utilisé comme une option d'élimination de ces déchets à travers le monde entier. Les chercheurs ont examiné la teneur en nutriments présents dans les boues dans le but de réduire les émissions de GES en raison du remplacement des engrais commerciaux. Ce fait a été pris en compte dans la méthodologie à appliquer à travers le monde entier et a été accepté par le GIEC. Toutefois, l'épandage des boues améliore les caractéristiques physiques du sol et ses propriétés chimiques et biologiques, il minimise l'application d'engrais minéraux et réduit l'entretien des sols (Singh et Agrawal, 2008). Les applications terrestres des boues augmentent les émissions de GES avec une augmentation du flux de gaz à l'interface sol-atmosphère (Baggs *et al.,* 2000; Fernandes *et al*., 2005a; Fernandes *et al.,* 2005b; Lu e*t al.,* 2012).

De plus, les émissions de GES sont réduites dû : 1) au remplacement des engrais synthétiques, 2) à la séquestration du carbone dans le sol, 3) à la capacité de rétention d'eau supplémentaire du sol, 4) à l'amélioration du labour et du travail des sols et 5) à l’absorption photosynthétique de CO_2 par les cultures. Ces faits n'ont pas été considérés dans les méthodes actuelles utilisées pour estimer les émissions de GES. Par conséquent, considérant toutes les réductions des émissions de GES et les augmentations du flux de gaz, cela pourrait permettre d’estimer les émissions de GES précises en raison de l'épandage de boues.

Hypothèse 5: La prise en compte di pourcentage de carbone séquestré dans le sol, de l'augmentation de la capacité de rétention d'eau du sol, de l'amélioration du travail des sols et de l'augmentation du flux de gaz en raison de l'épandage des boues d'épuration peut permettre d’estimer les émissions nettes de GES provenant de l'épandage des boues.

3.2 Objectifs

L'objectif global de cette étude est d'évaluer les performances des technologies de prétraitement en se basant sur leur bilan énergétique et les émissions de GES.

Les objectifs spécifiques liés qui en découlent sont :

1) L’augmentation de la température des boues au cours de l’ultrasonication et son effet sur le bilan énergétique et les émissions de GES.

2) La DA des boues au cours de l’ultrasonication à différentes concentrations en matières solides ; calcul du bilan de masse-énergie et des GES.

3) La DA des boues prétraitées par le procédé thermique à différentes concentrations en matières solides ; calcul des bilans massiques et énergétiques et des GES.

4) Évaluation du bilan masse-énergie et des émissions de GES au cours du prétraitement par le procédé Fenton, la DA à des températures mésophiles et thermophiles, la déshydratation, le transport et l'épandage.

5) Prétraitement des boues secondaires par le procédé Fenton pour améliorer la DA. Le bilan énergétique des émissions de GES.

6) Méthodologie pour la quantification des émissions de GES au cours de l'épandage des boues.

3.3 Originalité du travail

L'originalité du travail est décrite ci-dessous.

Etudes antérieurs : Il est essentiel de comprendre que la plupart des études antérieures étaient basées sur la production de méthane comme critère et que les autres paramètres tels que les types de boues, la concentration en matières solides, l’énergie et les émissions de GES étaient ignorés. Par conséquent, les données existantes ne suffisaient pas à générer un bilan énergétique et une estimation de GES précis. Donc de définir laquelle de ces technologies pourrait être la meilleure pour assurer l'équilibre énergétique favorable sous certaines conditions opérationnelles tout en minimisant les émissions de GES. Ce problème est bien connu et discuté en détails dans trois articles de synthèse individuellement présentés : chacune des technologies identifiées étant le prétraitement thermique, les ultrasons et l'oxydation par le procédé Fenton. Avant le présent travail, il n'y avait qu’un seul rapport sur l'évaluation des différentes technologies de prétraitement pour améliorer l'efficacité de la digestion anaérobie (en considérant tous les paramètres de fonctionnement du processus) basés sur la production d'énergie et les émissions de GES (Articles 3, 5 et 7). L'originalité de cette recherche est de mener des expériences en tenant compte des paramètres qui manquent dans la littérature, tel que suit.

- Une étude expérimentale comparative sur les boues prétraitées employant les prétraitements par ultrasons, thermiques et le procédé Fenton pour différentes types de boues n’existait pas dans la littérature. Or, cette étude s’avère essentielle pour l'analyse de ces prétraitement du point de vue de l'équilibre énergétique et de l'estimation des GES.

- Une analyse des données considérant les bilans de masse-énergie et les émissions de GES comme critères pour évaluer la gestion des boues, y compris toutes les étapes du processus, n'était pas disponible. Les étapes du procédé comprises dans cette étude sont : le processus de prétraitement des boues (thermique, traitement par ultrasons, Fenton) ; la DA ; la déshydratation des boues ; le transport des boues à épandre et l'épandage des boues.

- De plus, la comparaison des trois technologies de prétraitement utilisant la même base est également une nouveauté de ce travail.

Le présent travail (articles 3, 5) a démontré l'efficacité énergétique et a permis de quantifier les émissions de GES des procédés en tenant compte de divers paramètres tels que le type de boues (3 types) et la concentration en solides. Cette importante information unique, scientifique, et technologique, générée par cette étude, aura une application directe dans les STEPs.

Le prétraitement par le procédé Fenton est une technologie émergente de prétraitement. Pour la première fois, l'effet du prétraitement par le procédé Fenton sur l'efficacité de la DA en considérant le bilan énergétique et les emissions de GES a été étudié dans l'article 7. L'information présentée dans ce travail est cruciale pour la recherche future et les demandes déposées concernant cette technologie.

Une nouvelle méthodologie a été développée et présentée à l'article 8 pour estimer les émissions de GES liées à l'épandage des boues et sera appuyée dans les émissions répétées de GES lors de l'élimination des boues. Une comparaison des différentes méthodologies pour les émissions de GES a démontré que la méthodologie proposée dans cette étude était plus efficace et plus fiable, et que les émissions ou réductions de GES ont varié selon les concentrations en nutriments présents dans la boue. De plus, cette étude définie clairement que les méthodologies disponibles (y compris la méthodologie la plus acceptée par le GIEC) ont tendance à sur- ou sous-estimer les émissions de GES.

4. RÉSULTATS ET DISCUSSION

La présente section est divisée en plusieurs parties reliées entre elles. Cette section présente l'effet de l'augmentation de la température des boues au cours de l'ultrasonication. L'influence de la température lors du prétraitement des boues par ultrasonication sur l'énergie nette et les émissions de GES a également été évaluée. De plus, les bilans masse-énergie et les émissions de GES de l'ultrasonication, du prétraitement thermique et du procédé Fenton ont été évalués en se basant sur les données de la littérature. De plus, des expériences réalisée à l'échelle laboratoire ont été menées afin de démontrer l'effet de l'ultrasonication et du prétraitement thermique des boues primaires, secondaires et mixtes à différentes concentrations en solides totaux. Dans ce cas, les bilans énergétiques et massiques, ainsi que les émissions de GES ont été considérés comme critères d'étude. Des expériences ont également été menées à l'échelle laboratoire avec le procédé Fenton afin d'améliorer l'efficacité de la DA. De plus, une méthodologie améliorée a été proposée pour quantifier les émissions de GES lors de l'épandage des boues. La méthode proposée a, par la suite, été appliquée pour évaluer les émissions de GES liées à l'épandage des boues d'épuration à de faibles, hautes et moyennes concentrations en nutriments (carbone, azote, phosphore). La méthodologie proposée a été comparée avec les méthodes présentées dans la littérature.

4.1 Effet de l'augmentation de la température durant l'ultrasonication sur le bilan énergétique et les émissions de gaz à effet de serre

La méthodologie et la procédure permettant d'évaluer l'effet de l'augmentation de la température des boues pendant le traitement par les ultrasons sur les émissions de GES et le bilan énergétique sont définies dans la section 2 du chapitre 2.

La grande variation de l'augmentation de la température provoquée par les ultrasons selon divers chercheurs dépend de nombreux facteurs tels que l'apport d'énergie par unité de volume, les concentrations en solides totaux, la durée de sonication et la hauteur de corne. Pour cette raison, il est difficile de comparer les résultats rapportés lors de ces différentes études. En raison de cette incertitude, nous avons réalisé le bilan énergétique en supposant deux cas : dans le premier cas, il n'y a pas d'augmentation de température dans la boue après ultrasonication et dans le second cas, la température de la boue augmente de 10°C après traitement aux ultrasons. L'énergie nécessaire pour chauffer la boue jusqu'à 35°C (DA) est plus faible avec une augmentation de température de la boue après traitement aux ultrasons.

Par exemple, pour le cas # 1 à 23 g ST/L, l'énergie nécessaire pour le chauffage de la boue est de 884 kWh/Mg de SST et pour le cas # 2 (à 23 g ST/L), l'énergie requise est de 761 kWh/Mg de SST. À une concentration plus élevée en solides totaux (44 g ST/L), une plus faible quantité d'énergie est nécessaire pour chauffer la boue à 35°C. Cela est attribué au chauffage d'un volume de boues moins important à une concentration élevée en solides totaux. Par exemple, à 23 g ST/L, 1,739 m^3/jour de boues sont nécessaire pour le chauffage, alors qu'à 44 g ST/L, seulement 909 m^3/jour sont nécessaire. De plus, l'augmentation de la température de la boue après traitement aux ultrasons a augmenté le ratio énergétique indépendamment de la concentration en solides totaux et de l'apport d'énergie. Par exemple, l'énergie spécifique à l'entrée était de 641 kJ/kg ST avec 44 g ST/L et le rapport de l'énergie était de 1,37 pour le cas # 1 et de 1,74 pour le cas # 2.

En comparant l'effet de la température (cas 1 et 2) sur les émissions de GES, il est clair que le fait de tenir compte de l'augmentation de la température des boues après traitement aux ultrasons (cas 2) a permis de réduire les émissions de GES. Par exemple, pour un apport d'énergie spécifique de 1,226 kJ/kg ST avec une concentration en solides totaux de boues de 23 g ST/L, les émissions de GES ont été réduites de 37,7% pour le cas # 2 par rapport au cas # 1. De même, à une concentration élevée en solides totaux de 44 g ST/L pour un apport d'énergie spécifique de 641 kJ/kg ST, les émissions de gaz à effet de serre ont été réduites de 34% (cas # 2). Considérant l'augmentation de la température de 10°C pendant l'ultrasonication, l'énergie nette et le rapport d'énergie ont augmenté. Les émissions de gaz à effet de serre étaient également réduites, tenant compte de l'augmentation de la température dans la boue après traitement aux ultrasons.

4.2 Prétraitement thermique des boues d'épuration pour améliorer la digestion anaérobie

La littérature sur le prétraitement thermique des boues d'épuration pour améliorer la DA a été discutée. De plus, sur la base de ces données, le bilan énergétique a été évalué à 1, 2, 3 et 4% (p/v) de concentration en solides totaux (Chapitre 3 partie 1). L'énergie nette (sortie-entrée) et le rapport de l'énergie (production d'énergie/entrée d'énergie) ont augmenté avec l'accroissement de la concentration en solides totaux au niveau du procédé témoin (boues brutes) et des boues prétraitées. Pour des concentrations totales en solides de 1, 2, 3 et 4% (p/v), l'énergie nette et le rapport net de l'énergie étaient plus élevés pour les boues ayant subi un prétraitement thermique en comparaison avec les boues du procédé témoin. Lorsque la concentration en solides totaux était supérieure à environ 1,5% (p/v), l'énergie nette était positive et le rapport d'énergie était supérieur à 1 pour la boue prétraitée à 170°C pendant 30 min. Pour les boues du procédé témoin, l'énergie nette était positive et le rapport de l'énergie était supérieure à 1 à une concentration en solides totaux d'environ 2,2%.

Les résultats rapportés par différents chercheurs ne sont pas dans les mêmes unités et les données de base n'étaient pas fournies pour évaluer et comparer le bilan énergétique. Par conséquent, les données manquantes ont été estimées et le bilan énergétique a été réalisé pour les différents résultats présentés par differents chercheurs dans la littérature. Les données démontrent que pour une concentration en solides totaux supérieure à 3% (p/v), l'énergie nette était positive et le rapport de l'énergie était supérieur à 1 pour la boue prétraitée. Cependant, pour les boues du procédé témoin, les résultats n'étaient pas clairs.

Les résultats rapportés par Kim *et al.* (2003) et Haug *et al*. (1978) pour la DA du procédé témoin sont contradictoires. Au cours de la DA des boues témoins (avec une concentration en solides totaux de 38 g/L), Kim *et al*. (2003) ont rapporté une réduction de 20,1% de matières solides volatiles, ce qui a donné lieu à un rapport d'énergie de 0,47. De plus, Huag *et al*. (1978) ont rapporté pour une concentration en solides totaux de 20,4 g/L que la réduction en matières solides volatiles dans le DA des boues témoins était de 31,8% (rapport d'énergie supérieur à 1). Ainsi, nous avons conclu que les caractéristiques des boues étaient cruciales au cours du prétraitement et de la DA afin d'avoir un procédé énergiquement efficace.

Par ailleurs, les rapports de l'énergie nécessaire à la déshydratation du digestat prétraité, au transport et à l'épandage manquent dans la littérature. Or, ces facteurs sont importants dans l'évaluation de l'analyse du cycle de vie des boues. Ainsi, cette étude est limitée dans son évaluation de l'énergie nette et du rapport d'énergie à différentes concentrations en solides totaux.

4.3 Évaluation du prétraitement par le procédé Fenton des boues pour améliorer la digestion anaérobie

Dans cette section, les données de la littérature sur le prétraitement des boues par le procédé Fenton pour améliorer la digestion anaérobie sont discutées. Sur la base des données obtenues sur le bilan de masse-énergie et de GES, des calculs d'émissions pour la digestion mésophile et thermophile du procédé témoin (sans prétraitement) et du prétraitement des boues par le procédé Fenton à différents temps de rétention des boues ont été réalisés (Chapitre 4 partie 1). Les résultats utilisés dans cette étude pour évaluer le bilan de masse-énergie ont été ceux décrits par Erden et Filibeli (2010).

Pour la digestion mésophile des boues prétraitées par le procédé Fenton, l'énergie nette et le ratio d'énergie ont été plus élevés comparativement au témoin. Les températures thermophiles nécessitent une forte énergie pour augmenter la température de la boue jusqu'à la température de digestion (55 ± 2°C). La production d'énergie et l'énergie nette (énergie de sortie-énergie d’entrée) étaient plus élevées que le contrôle pour la digestion mésophile des boues prétraitées par le procédé Fenton. Pour la digestion thermophile, l'énergie nette était plus élevée pour le contrôle par rapport aux boues prétraitées par le procédé Fenton. De plus, lors de la dégradation accrue des solides des boues prétraitées par le procédé Fenton, l'énergie nécessaire lors de la déshydratation, du transport et de l'épandage était réduite dans les cas de la digestion mésophile et thermophile. Ainsi, le prétraitement par le procédé Fenton suivi d'une digestion mésophile a révélé une énergie nette positive et un ratio d’énergie plus élevé que 1.

Les émissions de GES ont été réduites pendant la DA mésophile pour le procédé témoin et le prétraitement par le procédé Fenton. Cependant, pour le témoin après 15 jours de temps de rétention, les émissions à effet de serre n’étaient pas réduites. En comparaison avec le contrôle, les émissions GES étaient réduites à un taux plus élevé pour les boues prétraitées par le procédé Fenton et ce, pour tous les temps de rétention étudiés. Par exemple, à 15 jours de rétention, les émissions de GES pour le témoin étaient de 44 kg de CO_2 équivalent/Mg de SST, alors que pour les boues prétraitées par le procédé Fenton, les émissions de GHG étaient de -97,8 kg CO_2 équivalent/Mg de SST. Pour la digestion thermophile, les émissions de GES étaient réduites lorsque le système a fonctionné pendant 20 jours (temps de rétention, TR), à la fois pour les boues témoins et les boues prétraitées par le procédé Fenton. La plus forte réduction des émissions de GES a été observée à 20 jours de TR pour une DA thermophile sur les boues témoins et à 30 jours pour la DA thermophile réalisées sur les boues prétraitées par le procédé Fenton.

4.4 Digestion anaérobie des boues subissant des ultrasons à différentes concentrations en matières solides

La méthodologie et la procédure suivies pour évaluer la digestion anaérobie des boues prétraitées aux ultrasons à différentes concentrations en matières solides sont définies dans le Chapitre 2 partie 3.

Les effets du prétraitement aux ultrasons sur la DA ont été étudiés pour les boues (primaires, secondaires et mixtes) provenant du traitement des eaux usées municipales à différentes concentrations en solides totaux. De plus, le prétraitement aux ultrasons, la DA et le processus d'élimination ont été évalués sur la base du bilan masse-énergie et des émissions de GES correspondantes. L'ultrasonication a amélioré la dégradation des solides de la boue (totaux, volatils, en suspension et volatils en suspension). Le bilan de masse a révélé que la boue secondaire traitée aux ultrasons à une concentration de 30 g ST/L a produit le plus faible volume de digestat à déshydrater, transporter et épandre. À 30 g ST/L (boues secondaires traitées aux ultrasons), l'énergie nette (énergie sortie-énergie entrée) maximale étaient de 7,89 kWh/Mg de solides secs totaux (SST), et un ratio d'énergie (sortie/entrée) de 1,0 a été observé. Une diminution des émissions de GES a été observée avec l'augmentation de la concentration des solides totaux présents dans la boue ; soit, 40 g ST/L < 30 g ST/L < 20 g ST/L. Des émissions de GES minimales de 339,6 kg CO_2 équivalent/Mg de SST ont été observées à une concentration en solides totaux de 40 g ST/L pour les boues secondaires.

Pour les boues primaires (contrôle et boues traitées aux ultrasons), l'énergie nette étaient négative, puisque l'apport d'énergie était supérieur à l'énergie récupérée. Les boues primaires contenaient principalement des fibres, des matériaux internes et d'autres matières inorganiques qui n'ont pas conduit à une plus grande production de méthane. Pour les boues secondaires, l'énergie nette étaient positive à une concentration en solides totaux de 30 g ST/L pour les boues traitées aux ultrasons. Les boues secondaires contenaient principalement de la matière organique, ce qui a conduit à une production de biogaz plus élevée. Pour les boues mixtes, l'énergie nette s'approchait du positif à de hautes concentrations en solides de 30 g ST/L pour le procédé témoin et pour les boues traitées aux ultrasons.

Les boues mixtes contiennent de la matière organique et inorganique. Au cours de l'ultrasonication, la matière organique est solubilisée, ce qui conduit à une plus forte production de méthane, mais l'apport d'énergie est plus élevé que l'énergie récupérée. Pour les boues primaires, secondaires et mixtes, les émissions de GES pour le procédé témoin étaient inférieures à celles des boues prétraitées aux ultrasons. En effet, à une concentration de

21,04 g ST/L (boues primaires), les émissions de GES du procédé témoin étaient de 781,2 kg CO_2 équivalent/Mg SST, alors que pour les boues prétraitées aux ultrasons, elles étaient de 1247,8 kg CO_2 équivalent/Mg de SST. À 32,15 g ST/L, les émissions de GES pour le témoin étaient de 454,5 kg CO_2 équivalent/Mg de SST et pour les boues prétraitées, les émissions étaient de 698,0 kg CO_2 équivalent/Mg de SST. À 41,08 g ST/L, les émissions de GES du témoin étaient de 384,5 kg CO_2 équivalent/Mg de SST et celles des boues prétraitées aux ultrasons étaient de 612,9 kg CO_2/Mg de SST.

4.5 Digestion anaérobie des boues prétraitées par voie thermique à différentes concentrations en solides

La description détaillée de la méthodologie et de la procédure pour évaluer la digestion anaérobie des boues prétraitées par voie thermique et ce, à différentes concentrations en matières solides est définie dans le Chapitre 3 partie 2.

L’effet du prétraitement thermique sur l’efficacité de la DA des boues a été étudié pour différentes concentrations en solides totaux (ST) (20, 30 et 40 g ST/L), et à différents temps de digestion (0, 5, 10, 15, 20 et 30 jours) et ce, pour différentes types de boues d'épuration (primaires, secondaires et mixtes). De plus, le procédé de traitement et d’élimination des boues a été évalué sur la base des bilans de masse-énergie et d’émissions de GES. Le bilan de masse a révélé que les boues secondaires prétraitées thermiquement à une concentration de 30,05 g ST/L avaient générées le plus faible taux de digestat (23,39 Mg de SST) et produisaient un volume minimum de digestat pour la déshydratation, le transport et l’épandage.

L'énergie nette et le rapport d’énergie pour les boues prétraitées par voie thermique étaient supérieurs au procédé témoin pour toutes les concentrations en solides étudiées (boues primaires, secondaires et mixtes). L'énergie nette était positive et le rapport d'énergie était supérieur à 1 pour les boues ayant subies un prétraitement thermique et ce, pour toutes les concentrations de solides totaux étudiées. Pour le contrôle, les émissions de GES étaient réduites, avec une augmentation de la concentration en solides totaux des boues. En effet, les émissions de GES étaient réduites dans l'ordre suivant : 40 g ST/L < 30 g ST/L < 20 g ST/L. Des émissions de GES réduites de 73,8 kg de matière sèche CO_2 équivalent/Mg de SST ont été observées à la concentration en solides de 30 g ST/L pour les boues secondaires prétraitées par voie thermique.

Pour les boues primaires (prétraitées par voie thermique), l'énergie nette était positive à des concentrations élevées en solides totaux (> 30 g ST/L). Pour la boue témoin, l'énergie nette était négative, puisque l’énergie d'entrée était supérieure à l’énergie récupérée. Les boues primaires contiennent principalement des fibres et d'autres matériaux inorganiques qui ne conduisent pas à une plus grande production de méthane. Le prétraitement par voie thermique pour améliorer la matière organique soluble a permis d’augmenter la production de méthane et de l'énergie nette. Pour les boues secondaires, l'énergie nette était positive pour des concentrations en solides > 20 g ST/L. Pour les boues témoins et les boues prétraitées thermiquement, l'énergie nette étaient positive, avec une concentration de solides > 30 g ST/L, mais l'augmentation de la concentration en solides de 20 g ST/L à 30 g ST/L a réduit l'énergie nette pour le témoin et les boues prétraitées par voie thermique. Les boues secondaires contiennent principalement de la matière organique qui conduit à une plus forte production de méthane.

L'énergie nette est positive à des concentrations en solides totaux > 20 g ST/L pour les boues mixtes prétraitées par voie thermique. L'augmentation de la concentration en solides de 20 à 30 g ST/L permet l’augmentation de l'énergie nette. Par contre, l'augmentation de la concentration en solides de 30 à 40 g ST/L réduit l'énergie nette. À partir de ces résultats, nous pouvons conclure que le maximum d'énergie nette de 840 kWh/Mg de SST a été obtenu à 30 g ST/L pour les boues secondaires prétraitées par voie thermique. La biodégradabilité maximale (avec un volume minimum de digestat à éliminer) a été obtenue avec des boues secondaires prétraitées par voie thermique à 30 g ST/L.

Avec le prétraitement thermique, les émissions de GES étaient réduites par rapport au contrôle et ce, pour toutes concentrations des solides totaux étudiées. Par exemple, à 20 g ST/L (boues primaires), les émissions de GES pour le contrôle étaient de 752,6 kg CO_2 équivalent/Mg de SST et celles des boues prétraitées par voie thermique étaient de 500 kg CO_2 équivalent/Mg de SST. À une concentration de 30 g ST/L, les émissions de GES du contrôle étaient de 461,0 kg CO_2/Mg de SST et celles du prétraitement thermique étaient de 231,8 kg CO_2 équivalent/Mg de SST. Les émissions de GES ont été réduites pour le contrôle lorsqu’il y avait une augmentation des concentrations en solides totaux.

Pour l'augmentation des concentrations en solides de 20 à 30 g ST/L pour les boues prétraitées thermiquement, les émissions de GES ont été réduites, mais pour des concentrations en solides ≥ 40 g ST/L, les émissions de GES étaient élevées. Par contre, les émissions de GES étaient plus réduites pour les boues secondaires comparativement aux boues primaires et aux boues mixtes. Des émissions de GES minimales de 73,8 kg CO_2 équivalent/Mg de SST ont été observées à 30 g ST/L pour les boues secondaires prétraitées par voie thermique.

4.6 Prétraitement par le procédé Fenton des boues secondaires pour améliorer la digestion anaérobie

La méthodologie et l'explication détaillée des résultats du prétraitement par le procédé Fenton des boues secondaires pour améliorer la digestion anaérobie sont décrites dans le Chapitre 4 partie 2.

Des études réalisées à l'échelle laboratoire sur l'application du prétraitement par le procédé Fenton (PFT) sur les boues secondaires (BS) ont été effectuées pour déterminer son effet sur l'efficacité de la DA. L'effet du FPT sur la DA a été évalué par le calcul du bilan énergétique et des émissions des GES correspondantes. Quatre procédés de traitement ont été évalués : 1) DA des BS (contrôle) ; 2) DA des BS ayant subies le FPT ; 3) processus 2 + PFT du digestat produit dans le procédé 2 suivi par une DA et 4) procédé 1 + PFT du digestat généré dans le processus 1 suivi par une DA.

Les résultats ont révélé que la production de méthane cumulative a augmenté de 15% dans le cas du PFT par rapport au témoin. Le taux de production de méthane dans le contrôle (procédé 1) était de 430 m^3 CH_4/Mg MV dégradé et de 496 m^3 CH_4/Mg MV dégradé pour les boues secondaires PFT (procédé 2). L'énergie nette a augmentée d'un facteur 3 pour le PFT (procédé 2) par rapport au contrôle (procédé 1). L'énergie nette pour le processus 4 a augmentée de 2,5 fois par rapport au procédé 1. Les émissions de GES ont été réduites dans le cas du PFT (procédé 2) en comparaison au contrôle (procédé 1). Les plus basses émissions de GES de 0,128 mg de CO_2/Mg de SST ont été observées dans le cas du procédé 2.

L'énergie nette a été augmentée par le PFT. L'énergie nette du contrôle (procédé 1) était de 91 kWh/Mg de SST, alors que pour les boues PFT (procédé 2), l'énergie nette était de 285 kWh/Mg de SST. L'énergie nette était donc augmentée de 3,1 fois par rapport au témoin. L'énergie nette maximale a été observée pour le procédé 2 avec le PFT (procédé 2) et les émissions de GES ont étés réduites par rapport au contrôle (processus 1). Les émissions de GES pour le contrôle (procédé 1) étaient de 192 kg CO_2/Mg de SST et pour les boues PFT (procédé 2), elles étaient de 128 kg CO_2 équivalent/Mg de SST. Les émissions de GES correspondant au transport et à l'épandage étaient moins importantes pour les boues PFT (procédé 2) par rapport au témoin. La production de méthane, qui a augmenté dans les processus 3 et 4, a augmenté les émissions de GES correspondant à la combustion du méthane comparativement au processus 2. Pour le procédé 2, les émissions de GES étaient réduites par rapport au contrôle (procédé 1). L'émission minimum de GES a été observée dans le procédé 2.

4.7 Méthodologie pour la quantification des émissions de gaz à effet de serre au cours de l'épandage des boues

La description détaillée de la mise au point d'une nouvelle méthodologie pour estimer les émissions de GES au cours de l'épandage de boues est décrite dans le Chapitre 5.

Dans ce travail, les différentes méthodes décrites dans la littérature permettant d’estimer les émissions de GES liées à l'épandage des boues d'épuration sont résumées et leurs inconvénients y sont présentés. Aussi, une meilleure méthodologie est proposée pour évaluer les émissions de GES liées à l'épandage des boues d'épuration. De plus, en utilisant la méthodologie proposée, les émissions de GES liées èa l'épandage de boues d'épuration à faible, haute et moyenne concentrations en nutriments (carbone, azote et phosphore) ont été évaluées. Les résultats révélent que les émissions de GES sont substantiellement diminuées lorsque les boues d'épuration contenant une concentration élevée en éléments nutritifs sont épandues.

Les calculs des émissions de GES dues à l'épandage des boues d'épuration utilisant des méthodologies différentes ont démontré une variabilité des émissions de GES. Les méthodologies GIEC et RTI ont révélé que les émissions de GES étaient réduites avec une diminution de la concentration en nutriments dans les boues d'épuration.

Dans la méthodologie du GIEC, l'estimation des émissions de GES était directement liée aux concentrations en nutriments de carbone et d'azote avec des facteurs établis par défaut. La méthodologie RTI prédit des émissions de GES plus élevées, car on suppose que les émissions de CO_2 sont directement liées à la teneur en carbone présente dans les boues d'épuration. Par conséquent, les émissions de GES sont plus faibles pour des boues à faible concentration en carbone (nutriments) et elles sont plus élevées pour des boues d’épuration ayant une concentration élevée en carbone.

Cependant, les méthodologies GIEC et RTI ne prennent pas en compte le remplacement de l'engrais synthétique, la séquestration du carbone et l'amélioration des caractéristiques du sol (augmentation de la capacité de rétention d'eau, amélioration du labourage du sol et de la circulation des véhicules), qui sont des facteurs responsables de la réduction des émissions de GES. La méthodologie BEAM a révélé des réductions plus importantes de GES, où les émissions de GES étaient les plus faibles et ce, pour toutes les concentrations en nutriments étudiées. Dans la méthodologie proposée, les émissions de GES estimées ont diminué avec l'augmentation de la concentration en éléments nutritifs. Depuis que nous avons considéré tous les facteurs (tel que décrit dans la Section 4), les émissions de GES sont représentatives conformément à la concentration en éléments nutritifs présents dans les boues d'épuration épandues. Par conséquent, les calculs des émissions de GES effectués selon la méthodologie proposée ont révélé que l'estimation des émissions de GES était plus efficace et plus représentative.

4.8 Comparaison des prétraitements aux ultrasons, thermique et Fenton basée sur le bilan masse-énergie et les émissions de GES

4.8.1 Bilan massique DA

Le bilan de masse pour les prétraitements aux ultrasons, thermique et par le procédé Fenton ont été décrits au Chapitre 2, partie 3; au Chapitre 3, partie 2 et au Chapitre 4, partie 2, respectivement. Dans la présente section, une comparaison des résultats des prétraitements aux ultrasons, thermique et par le procédé Fenton est présentée au Tableau 7. En supposant que 40 Mg de matières sèches entrent dans le procédé de prétraitement et de la DA, la quantité de matières restantes après la DA pour le transport et l'épandage était de 20,02 Mg pour les boues secondaires traitées aux ultrasons. La réduction de la quantité de digestat dans le cas de la boue traitée aux ultrasons était due à la réduction des matières volatiles (64,18%) au cours de la digestion anaérobie. Basé sur le bilan de masse, le procédé de prétraitement aux ultrasons était plus efficace dans la réduction de la quantité de boues. Cependant, l'apport d'énergie par gramme de ST était plus élevé par rapport aux autres procédés de prétraitement. Basé sur le bilan de masse, l'ordre des processus de prétraitement en termes de réduction de la quantité de boue était le suivant : ultrasons > prétraitement thermique > prétraitement par le procédé Fenton.

Tableau 7. Comparaison des bilans de masses pour les procédés de prétraitement

Description	Ultrasonification		Prétraitement thermique		Prétraitement Fenton	
Entrée d'énergie **(kWh/Mg de SST)**	0 (Contrôle)	1595	0 (Contrôle)	713	0 (Contrôle)	491
% de dégradation des solides volatils après un TRH de 30 jours	53.67	64.18	51.46	57.95	51.46	52.76
Volume de méthane produit (mL)	6651	9013	6408	8984	6408	7223
Poids de solides volatils dégradés durant la DA (Mg)	16.55	19.88	14.90	16.61	14.90	14.56
Solides secs restants après centrifugation qui seront transportés et appliqués à la terre (Mg)	23.45	20.22	25.1	23.39	25.1	25.43

***Note:** La masse de solides secs entrant la DA est de 40 Mg; Solides totaux 30 g/L*

4.8.2 Bilan énergétique

Les bilans énergétiques des prétraitements aux ultrasons, thermique et Fenton ont été décrits dans le Chapitre 2, partie 3; dans le Chapitre 3, partie 2 et dans le Chapitre 4, partie 2, respectivement. La comparaison du bilan énergétique pour les prétraitements aux ultrasons, thermiques et par le procédé Fenton sont résumés au Tableau 8. L'énergie requise par Mg de SST pour l'ultrasonication était 1595 kWh, ce qui était significativement plus élevée comparativement au prétraitement thermique et au procédé Fenton. L'énergie récupérée pour les boues secondaires traitées aux ultrasons était de 1915 kWh/Mg de SST, mais le bilan énergétique net était faible comparativement à celui du prétraitement thermique et du prétraitement par le procédé Fenton en raison de l'apport élevé en énergie requise pour ces procédés. Une énergie nette maximale de 840 kWh/Mg de SST a été observée pour les boues secondaires à 30 g ST/L prétraitées thermiquement, puisque que l'énergie récupérée était 1909 kWh/Mg de SST et l'apport énergétique était de 1609 kWh/Mg de SST. Basé sur l'équilibre énergétique, les processus de traitement ont été classés selon l'ordre suivant : prétraitement thermique > prétraitement par le procédé Fenton > ultrasonication.

Tableau 8. Comparaison du bilan énergétique des prétraitements

Description	Bilan énergétique					
	Ultrasonification		Prétraitement thermique		Prétraitement Fenton	
Entrée d'énergie dans le prétraitement	0	1595	0	713	0	491
DA	975.4	48.0	943	50	943	427
Déshydratation	59.5	51.26	63.62	59.3	63.6	64.5
Transport	40.9	35.3	43.75	40.78	43.7	44.3
Épandage	206	178	221	206	221	224
(a) Énergie totale entrée	1282	1907	1271	1069	1271	1250
(b) Sortie d'énergie	1262	1915	1362	1909	1362	1535
Énergie nette = (**b-a**)	-19.71	7.89	91	840	91	285
Ratio d'énergie Sorties/ Entrée	0.98	1.0	1.07	1.79	1.07	1.23

Note: *énergie-kWh/Mg de SST, solides totaux- 30g/L*

4.8.3 Bilan massique GES

Les émissions de GES pour les prétraitements aux ultrasons, thermiques et par le procédé Fenton ont été décrites dans les Chapitres 2, 3 et 4, respectivement, dans les parties 3, 2 et 2. La comparaison des résultats d'émissions de GES pour l'ultrasonication, les prétraitements thermique et par le procédé Fenton est résumée au Tableau 9. Une réduction des émissions de GES de 73,8 kg CO_2 équivalent/Mg de SST a été observée pour les boues secondaires prétraitées thermiquement. La réduction des émissions de GES était significativement plus élevée dans le cas des boues secondaires prétraitées thermiquement comparativement à celles traitées aux ultrasons et par le procédé Fenton. Le prétraitement thermique a réduit les émissions de GES (-445,1 Kg CO_2 équivalent/Mg de SST) en raison de l'augmentation de l'énergie nette, qui a remplacé l'énergie des combustibles fossiles et des émissions de GES correspondantes.

Basé sur les émissions de GES, les processus de prétraitement ont été classés dans l'ordre suivant : prétraitement thermique > prétraitement par le procédé Fenton > ultrasonication. Par conséquent, en se basant sur le bilan de masse-énergie et les émissions de GES, le prétraitement thermique des boues secondaires a été bénéfique.

Tableau 9. Comparaison des émissions de GES pour les prétraitements

Description	**Émissions GHG (Kg CO_2 équivalent/Mg de SST)**					
	Ultrasonification		**Prétraitement thermique**		**Prétraitement Fenton**	
	0	**Sonifiées**	**0**	**thermique**	**0**	**Fenton**
Émissions nettes de GES dues aux entrées et sorties d'énergie	10.45	-4.18	-48.0	-445.1	-48.0	-150.7
Émissions de GES durant la DA (émissions biogéniques)	229.2	295.1	304.8	397.6	304.8	250.6
Émissions de GES pendant la combustion du méthane	292.0	442.4	314.6	441.0	314.6	354.5
Émissions de GES durant le transport	11.3	9.76	12.1	11.3	19.3	19.3
Émissions de GES dues à l'épandage	66.8	57.6	71.5	66.7	-94	-95
Émissions de GES totales sans considerer les émissions biogéniques de CO_2	380.2	505.6	350.2	73.8	192	128

Note: *énergie-kWh/mg de SST, solides totaux- 30g/L*

5. CONCLUSION ET RECOMMANDATIONS

5.1 Conclusion

1. L'augmentation de la température des boues au cours de l'ultrasonication a un effet direct sur l'énergie nette et les émissions de GES. Par exemple, l'énergie nette était de 459,5 et de 724,7 kWh/Mg de matières sèches totales pour le contrôle (sans ultrasons) et pour les boues prétraitées par ultrasonication, respectivement.

2. Le prétraitement thermique des boues améliore l'efficacité de la DA. L'énergie nette était positive (production d'énergie - l'apport d'énergie ≥ 1) lorsque la concentration en matières solides totale était supérieure à 1,5% (p/v). À une concentration en ST de 2 %, l'énergie nette est de 2010 kWh/Mg de solides secs .

3. Le prétraitement par le procédé Fenton suivie de la digestion mésophile a révélé une énergie nette et un rapport d'énergie plus élevé que la digestion thermophile (Énergie nette était de 2653,5 kWh/Mg de solides totaux secs et le taux d'énergie est de 3,13). Les émissions de GES ont été réduites avec le procédé de Fenton. La meilleure réduction a été observée avec un TRH de 20 jours au cours de la digestion mésophile.

4. Le bilan énergétique a démontré que l'énergie nette maximale pour les boues secondaires prétraitées par ultrasonication a été atteinte à une concentration de 31,45 g ST/L. Les émissions de GES ont été réduites avec une augmentation de la concentration en matières solides pour les boues primaires, secondaires et mixtes.

5. L'énergie nette était positive et le taux d'énergie était supérieur à 1 pour les boues secondaires et mixtes prétraitées par le procédé thermique à différentes concentrations en matières solides. Pour les boues primaires, l'énergie nette était positive et le rapport énergie était supérieur, avec une concentration en matières solides de > 30 g ST/L. Un taux maximum d'énergie a été observé à 30 g ST/L pour les boues secondaires prétraitées thermiquement. Pour le cas des boues non traitées (contrôle), les émissions de GES étaient réduites, avec une concentration plus élevée en matières solides des boues. Les émissions de GES étaient abaissées dans le cas des boues prétraitées par le procédé thermique en comparaison au témoin.

6. Le bilan énergétique a démontré que l'énergie nette avait augmenté avec le prétraitement par le procédé Fenton (procédé 2). Les émissions de GES ont été réduites dans le cas du prétraitement par le procédé Fenton en comparaison du contrôle (procédé 1). Les plus faibles émissions de GES de 0,128 kg de CO_2/Mg du total de matières sèches (TDS) ont été observées dans le cas du procédé 2.

7. D'après la littérature, il est clair que l'épandage des boues d'épuration pourrait résulter en une amélioration des émissions de GES. À des concentrations élevées en nutriments contenus dans les boues, les émissions de GES sont supérieures en comparaison aux boues à faibles concentrations en éléments nutritifs. Les émissions de GES résultants des calculs effectués selon la méthodologie proposée ont révélé que l'estimation des émissions de GES est plus efficace et plus représentative.

5.2 Recommandations

Des études réalisées à l'échelle laboratoire sur le traitement des boues par ultrasonication, par prétraitement thermique et par le procédé Fenton pour améliorer la DA à différentes concentrations en matières solides ont été évaluées dans cette recherche. Une étude réaliée à grande échelle (échelle préindustrielle) sur le processus de prétraitement thermique est nécessaire pour évaluer les émissions de GES et le bilan énergétique. Une analyse technico-économique du processus de prétraitement thermique, basée sur des essais réalisés à grande échelle, est nécessaire. La réduction et l'augmentation des émissions de GES au cours de l'épandage du digestat (générés par la DA des boues prétraitées) doivent être évaluées expérimentalement pour valider la méthodologie mentionnée dans cette étude. Le type de boues (primaires, secondaires ou mixtes) appliqué lors l'épandage aura également un effet sur les émissions de GES. En outre, le type de traitement (DA) et la durée du traitement des boues (temps de rétention des matières solides) ont également eu un impact sur les émissions de GES au cours de l'épandage des boues. De plus, le type de boues et de prétraitement influencent principalement la communauté microbienne du sol, ce qui affecte la dégradation des matières solides et des matières organiques. Par conséquent, l'épandage des boues à différentes concentrations en nutriments et leur effet sur la séquestration du carbone dans le sol doit être étudié afin de déterminer les émissions de GES. Aussi, la capacité supplémentaire de rétention d'eau, l'amélioration et l'entretien du sol, l'absorption et la photosynthèse de la récolte ainsi que la variation du flux de gaz dans le sol et l'atmosphère doivent être étudiées.

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CHAPITRE II

ULTRASONICATION OF SLUDGE

PARTIE 1

ULTRASONIC PRETREATMENT OF SLUDGE: A REVIEW

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RÉSUMÉ

L’ultrasonication est un procédé de prétraitement mécanique émergent, très efficace permettant d’améliorer la biodégradabilité des boues. Il est également très utile dans les usines de traitement des eaux usées pour le traitement et la gestion des boues d’épuration. Elle améliore la digestion des boues en perturbant leurs propriétés physiques, chimiques et biologiques. En effet, le degré de désintégration dépend en premier lieu des paramètres de sonication et en deuxième lieu des caractéristiques des boues. Par conséquent, l'évaluation optimale de ces paramètres varie selon le type de sonicateur et de boues à traiter. Les installations à grande échelle de traitement aux ultrasons ont révélé qu'ils permettent une augmentation de 50% de la production de biogaz. De plus, l'évaluation de la balance énergétique a montré que le rapport moyen du gain net d'énergie et de l'électricité consommée par le dispositif à ultrasons est de 2,5. En fait, cet article de synthèse résume les avantages de l’ultrasonication des boues, l'effet des paramètres de sonication, l’impact des caractéristiques des boues sur la désintégration des boues, ainsi que l'augmentation de la production de biogaz dans un digesteur anaérobie. Cette recherche a montré qu’il existe peu de travaux de recherche effectués sur ce sujet et, également un manque de données expérimentales. La comparaison de l’ultrasonication avec d'autres méthodes de prétraitements est nécessaire pour évaluer la meilleure technologie de prétraitement sur les plans économiques et environnementaux pour le traitement et la gestion des boues. Les paramètres optimaux de l’ultrasonication varient en fonction des caractéristiques des boues.

Mots-clés: digestion anaérobie; traitement biologique des eaux usées; cavitation; boues activées; ultrasonication.

ABSTRACT

Ultrasonication is an emerging and very effective mechanical pretreatment method to enhance the biodegradability of the sludge, and it would be very useful to all wastewater treatment plants in treating and disposing sewage sludge. Ultrasonication enhances the sludge digestibility by disrupting the physical, chemical and biological properties of the sludge. The degree of disintegration depends on the sonication parameters and also on sludge characteristics, therefore the evaluation of the optimum parameters varies with the type of sonicater and sludge to be treated. The full scale installations of ultrasonication have demonstrated that there is 50% increase in the biogas generation, and in addition evaluation of energy balance showed that the average ratio of the net energy gain to electric consumed by the ultrasound device is 2.5. This review article summarizes the benefits of ultrasonication of sludge, the effect of sonication parameters, impact of sludge characteristics on sludge disintegration, and thereby the increase in biogas production in anaerobic digester. Due to uncertainty in the unit representation by many researchers and nonavailability of the data, comparison of these results is complicated. Comparison of ultrasonication with other pretreatment options is necessary to evaluate the best economical and environmental pretreatment technology for sludge treatment and disposal. The optimum parameters for the ultrasonication vary with sludge characteristics.

Keywords: anaerobic digestion; biological wastewater treatment; cavitation; waste activated sludge; ultrasonication.

1. INTRODUCTION

The rapid growth of industrialization and urbanization in the 21st century has resulted in production of unmanageable quantity of sludge from wastewater treatment plants (WWTPs). The sludge management is the major issue of wastewater treatment plant, as it costs 60% of the total plant capital cost [1] and the laws for sludge disposal are becoming increasingly stringent. With increase in global warming and climate change, the greenhouse gases (GHGs) emissions from the waste sector are of increasing concern. In Canada, GHGs from the waste sector have increased by 15% from 1990 to 2006 [2]. The existing WWTPs in Canada are producing 670 000 Mg/yr of dry sludge [3], and the production rate is expected to increase further in the future. Incineration, ocean discharge, land application and composting are the common sludge disposal methods used over the years. These common sludge disposal methods are no longer reliable due to the economical constraints and the negative impacts on environment. Due to environmental and economical constraints, there is a need for affordable and sustainable technologies for sludge treatment and disposal. With extensive research on sludge treatment, many researchers have proposed anaerobic digestion (AD) of sludge as the efficient and sustainable technology for sludge treatment. The benefits associated with AD technology are huge, which include mass reduction, odour removal, pathogen reduction, less energy use, and more significantly, the energy recovery in the form of methane.

The AD of sludge is a complex process that converts degradable organic compounds to methane (CH_4) and carbon dioxide (CO_2) in the absence of elemental oxygen with a series of microbiological process. The conversion pathway of the substrate to biogas (mainly CH_4 and CO_2) occurs in four stages, namely, hydrolysis, acidogenesis, acetogenesis and methanogenesis by three different groups of bacteria. The first group involves hydrolytic and acidogenic bacteria, which hydrolyse the complex substrates (carbohydrates, lipids, proteins, etc) to dissolved monomers (sugars, fatty acids, amino acids, etc.) and further to CO_2, H_2, organic acids and alcohols. The second metabolic group of bacteria is hydrogen producing acetogens that convert the simple monomers and fatty acids to acetate, H_2, and CO_2. The third group is methanogenic bacteria that utilize the H_2, CO_2 and acetate to produce CH_4 and CO_2. This complete microbial digestion process of the substrate to CH_4 and CO_2 is a slow process and requires high retention time. In particular, intracellular biopolymers solubilisation and conversion to the lower molecular weight compounds of solid degradable organics such as sludge through hydrolysis is a rate limiting step [4,5]. The conventional anaerobic digestion process with four stages is presented in Figure1.

The lower microbial conversion rates during conventional AD process results in high hydraulic retention time in the digester and larger digester volume, which are the prime drawbacks of the conventional AD technology. The nonavailability of the readily biodegradable soluble and organic matters and lower digestion rate constant (i.e., first order digestion rate constant 0.15 day^{-1} for sludge) [6] necessitates the pretreatment of sludge. Pretreatment of sludge is required to rupture the cell wall and to facilitate the release of intracellular matter into the aqueous phase to increase biodegradability and to enhance the anaerobic digestion with lower retention time and with higher biogas production [7-9] With the advancements in various sludge pretreatment techniques like thermal, chemical, mechanical, biological and physical and several combinations such as physico-chemical, biological-physicochemical, mechanical-chemical and thermal-chemical, biodegradability of sludge can be enhanced by several orders; however, economical constraints of these technologies have limited their scale-up and lab-to-field implementation.

Extensive research has been carried throughout the world to establish the best economically feasible pretreatment technology to enhance the digestibility of sludge. The ultrasonication is an emerging and promising mechanical disruption technique for sludge disintegration due to several inherent merits like efficient sludge disintegration (> 95%, [10]), improvement in biodegradability [9], improved biosolids quality [9], increase in methane percentage in biogas [9,11], no chemical addition [12], less retention time [13], sludge reduction [14] and energy recovery (1kW of ultrasound energy generates 7kW of electrical energy including losses [11]. The order of pretreatment efficiency for enhancement of methane generation is: ultrasonic lysis (20 W, 9 kHz, 30 min) > thermal pretreatment by autoclave (120°C, 30 min) > thermal pretreatment with hot water (60°C 30 min) > freezing (-10°C, 15 h) [15]. This paper presents an extensive review of the ultrasonic pretreatment of sludge to enhance the AD, and to compare the results of the full-scale and lab-scale implementation.

2. ULTRASONICATION

In early days of sonar, the sound waves are used for anti-submarine warfare, results in the killing of fish by the sound waves, has given the birth of ultrasound method of destroying or inactivating biological cells. Hughes et al. [16] and Alliger [17] have studied the mechanism of ultrasound interaction with microbial cells and observed that the brief exposure to ultrasound can cause thinning of cell wall attributed to releasing of the cytoplasm membrane from the cell wall. The ultrasound is cyclic sound pressure (compression and expansion) with a frequency greater than 20 kHz. The ultrasound range diagram with various applications at different frequency is shown in Figure 2.

Depending on the frequency, it is divided into three regions: power ultrasound (20–100 kHz), high frequency ultrasound (100 kHz–1 MHz), and diagnostic ultrasound (1–500 MHz). Ultrasound application in medicine started during the Second World War as ultrasound massage to substitute for hands of the masseur in patients who has suffered from fractures [18]. With advancements in technology and sophistication, ultrasound (> 20 kHz) is used in several fields. Ultrasound ranging from 20-100 kHz is used in chemically important systems in which chemical and physical changes are desired [19,20]. The ultrasound ranging from 1-10 MHz is used in different fields, like animal navigation and communication, detection of cracks or flaws in solids and under water echo location, fetal scanning, detection of pelvic abnormalities, treating benign and malignant tumors etc. [19, 21,22]. Biological cell disruption for the recovery of intracellular materials is achieved by ultrasonication [22-24], and further full scale application for municipal sludge disintegration was evaluated by Hogan et al. [25]. The acoustic waves between 20 Hz and 20 kHz are the audible range, while hearing varies with the individual and the age. The acoustic waves less than 20Hz down to 0.001 Hz is used in seismology [26], medical application [27] [ballistocardiography and seismocardiography to study the mechanics of the heart], and also in charting rock and petroleum formations below the earth [26].

2.1 Cavitation phenomena induced by ultrasound

The basic goal of ultrasound technique is to spiflicate bacterial cell walls and to facilitate intracellular matter available for subsequent degradation to CH_4 and CO_2 in AD. When the ultrasound wave propagates in sludge medium, it generates compressions and rarefactions, the compression cycles exert a positive pressure on the liquid by pushing the molecules together and the rarefaction cycle exerts a negative pressure by pulling the molecules from one another. Because of this excessively large negative pressure, microbubbles (cavitation bubbles) are formed in the rarefaction regions. These microbubbles grow in successive cycles and reaches to an unstable diameter that collapse violently producing shock waves (temperature of around 5000°C and pressure of 500 atmospheres at a lifetime of few microseconds) [14,28,29-34]. This process by which the bubbles form, grow and undergo violent collapse is known as cavitation. Representation of development and collapse of the cavitation bubble is shown in Figure 3.

2.2 Factors influencing the cavitation phenomena

The sludge disintegration efficiency is essentially based on the cavitation phenomena and the factors influencing the cavitation that influence the efficiency of disintegration are shown in the Table 1.

2.3 Ultrasound generation and disintegration mechanism

Ultrasound is generated by two techniques magnetostrictive and piezoelectric. In magnetostrictive technique, the electrical energy is converted to mechanical energy (or vibration) with a magnetic coil attached to vibrating piece like nickel and Terfenol-D [44]. In the piezoelectric technique, the electrical energy is converted to high frequency electric energy with piezoelectric crystals (rely to material strain) attached to the vibrating piece (sonotrode, probe or horn). The transducer (converter) converts the electrical or mechanical energy to sound waves and the booster is a mechanical amplifier that increases the vibration (amplitude) generated by transducer [9,45]. The horn delivers the ultrasound waves into the liquid. Therefore transducer, booster and horn are the major components in ultrasound equipment. Ultrasonication of sludge with temperature control and sonication components is shown below in Figure 4.

Holding or affixing the transducer, booster and horn together is called as stack assembly and the stack is clamped at nodal points as shown in Figure 4. The two most common places to clamp or to hold the total system is at the transducer or at the booster nodal ring. Similar to the booster, the horn which delivers the motion to the sludge often amplifies the motion even further. In addition, the horn is usually half a wavelength long, but full wavelength designs are also common depending upon the application. The intensity of sonication can be controlled by altering the power input and is based on the probe design. This is a very important parameter in ultrasonication and will determine the magnitude of the gain or mechanical amplification of the vibration. The conversion efficiency of sound energy to thermal energy can be calculated as shown in the eqs. (1-3) [46].

$$Q_{w} = C\ m\ (T - T_0) \tag{1}$$

$$Q_u = P\ t \tag{2}$$

$$\eta(\%) = \frac{Q_w}{Q_u} * 100 \tag{3}$$

T_0 = Temperature of fresh sludge; T = Temperature after ultrasonication; Q_w =Total energy; m = Mass of water; C = Specific heat of water (4.2 kJ/kg °C); Q_u = Actual energy produced; P = Ultrasound power; t = Ultrasound duration; η = Efficiency.

Sludge Disintegration

The applied power/energy supplied for sludge disintegration is expressed in many ways,

a) Specific energy input, b) ultrasonic dose, c) ultrasonic density and d) ultrasonic intensity and the expressions are given in the Table 2.

The expected disintegration mechanisms during ultrasonic disintegration of sludge are as follows [9, 33, and 49]:

a) Hydro-mechanical shear forces

b) Oxidising effect of $^{\cdot}OH$, $^{\cdot}H$, $^{\cdot}N$, and $^{\cdot}O$ produced under the ultrasound radiation

c) Thermal decomposition of volatile hydrophobic substances in the sludge

d) Increase of temperature during ultrasonic activated sludge disintegration

The induce cavitation that occurs during ultrasonication results in sudden and violent collapse of huge number of microbubbles, which generates powerful hydromechanical shear forces in the bulk liquid surrounding the bubbles [9,34,49-51]. The high temperature produced during the bubble collapse (implosion) decomposes water (H_2O) into extremely reactive hydrogen atoms (H^+), and hydroxyl radicals ($^{\cdot}OH$) and in the cooling phase these radicals will recombine to form hydrogen peroxide and molecular hydrogen [9,33,49,52-56]. The oxidising effect of $^{\cdot}H$, $^{\cdot}N$ and $^{\cdot}O$ is less than $^{\cdot}OH$ [49, 53, 54, and 57]; therefore the effect of $^{\cdot}H$, $^{\cdot}N$ and $^{\cdot}O$ is neglected during the ultrasonication. The effect of the volatile hydrophobic substances is neglected as their quantity is very low in the sludge [49]. Considering the temperature effect on solubilisation, at higher temperature the sludge solubilisation is very low and needs longer time to attain the solubilisation of sludge (temperature raised to 80°C in 1 hr produces low solubilisation and a low degree of disintegration in the sludge, where the sonication is a short period of time). Therefore, sludge disintegration is expected to occur in two ways, mainly by hydro-mechanical shear forces and the oxidising effect of $^{\cdot}OH$.

Wang et al. [49] have evaluated the effect of $^{\cdot}OH$ and hydro-mechanical shear forces on sludge disintegration. The effect of hydroxide radical was evaluated by addition of the $NaHCO_3$ to the sludge prior to sonication. The oxidation effect of hydroxide ion on sludge solubilisation was slightly higher by the addition of $NaHCO_3$, but the slight enhancement was due to the increase in the pH of the sludge. This shows that the oxidation effect of the hydroxide radical on sludge solubilisation is negligible. Therefore, the disintegration of the sludge occurs mainly by hydro-mechanical shear forces produced by cavitation bubbles. The sludge disintegration by hydro-mechanical shear forces and hydroxide radical follows a first order reaction. The total reaction constant "u" is calculated as follows (Eq. 4) [49].

$$u = u_{^{\cdot}OH} + u_{HSF} \qquad (4)$$

Where, $u_{^{\cdot}OH}$ is the reaction constant under oxidising effect; u_{HSF} is the reaction constant under effect of hydro-mechanical shear forces. Neglecting the effect of hydroxide radical oxidation effect, then the reaction constant is $u = u_{HSF}$. The reaction rate constant of hydroxide radical increases with increase in ultrasonic density; for example, the contribution of the oxidising effect of hydroxide radical increased from 19.15% to 25.86%, with increase in ultrasonication density from 0.384 W/mL to 0.72 W/mL [49].

2.4 Evaluation of ultrasound disintegration

The ultrasound de-agglomerates the biological flocs and disrupts the large organic particles into smaller size particles. The shear force produced by high pressure wave breaks down bacterial cell wall and releases the intracellular substances into aqueous phase. This changes the physical, chemical and biological properties of sludge during pretreatment by ultrasonication. Therefore, the degree of sludge disintegration is to be evaluated based on the changes in physical (particle size distribution, turbidity, settleability, mass composition and microscopic examination), chemical (increase in SCOD, protein concentration, polysaccharide content of the supernatant, nitrate-nitrogen and release of NH_3) and biological (heterotrophic count and specific oxygen uptake rate) properties.

2.4.1 Physical changes

The physical parameters of the sludge have a significant effect on AD, so the evaluation of the physical parameters after sonication is essential for operation of AD. Further, physical evaluation is used as qualitative measurement of sludge disintegration. Particle size analysis, sludge settleability, mass composition, microscopic image, turbidity, and sludge dewaterability are some of the techniques used to judge the degree of ultrasonic disintegration. Particle size is analysed by various techniques depending upon size of particles. The different techniques are sieves, sedimentation, electrozone sensing, microscopy, laser diffraction [58,59]. Ultrasonication disintegrates sludge particles to a very smaller size, and laser diffraction is usually used for particle size analysis. The turbidity of sludge changes with increase in sonication parameters (ultrasound density, ultrasound intensity, and sonication time) and it is measured by using a turbidity meter, with NTU units. The sludge dewaterability is measured based on the capillary suction time (CST) and specific resistance of filtration (SRF), [13, 60-65].

2.4.1.1 Particle size

The particle solubilisation rate is governed by the size of particles in the waste, and methane production in the mature digester is proportional to the net rate of particle size solubilisation [5,51,66]. Ultrasound pretreatment is very effective in reducing the particle size of sludge and the efficiency of size reduction is dependent upon the sonication duration [13,67-70], ultrasonication density [12,41,61,64,71-75], sonication power [41,59,62,73], sludge volume and sludge characteristics [12,47,66,69,72,73]. With increase in sonication time the particle size reduces gradually; for example, the particle size reduces from 165 μm to 135 μm and 85 μm with a sonication time of 0.49 and 1.6 min, respectively [13]. Similarly, Biggs and Lant [68] observed a particle size reduction of 125 mm to 10 mm after 5 min sonication (50 W, 100 ml). Gonze et al. [69] observed a similar reduction trend initially but beyond a sonication of 10 min the particle size has increased gradually with further increase in sonication time. At 0.5 min @ 3.9 kJ/L, 1 min @7.8 kJ/L, 3 min @ 23.4 kJ/L and 6 min @ 46.8 kJ/L, the particle size was reduced from 66.9 μm to 55.1, 42.6, 24.2, 18.1 μm, respectively, but beyond a sonication time of 10 min the particle was increased gradually to 19.5, 20.6, and 31.9 μm at 10 min @78 kJ/L, 20 min @ 156 kJ/L and 60 @ 468 kJ/L min, respectively.

The increase in the particle size at higher sonication time is due to re-flocculation of the particles. Initially the flocs are reduced but increase in sonication time further causes more release of intracellular polymers due to cell lysis that are favourable for re-flocculation [64,67,69,76,77]. The biopolymers released are thought to be the glue that holds bioflocs together and they form functional groups such as hydroxyl and negatively charged carboxy groups [78]. The mean particle size reduction also increases with increase in sonication densities. At densities of 0.52 W/mL, the mean particle is reduced from 51 μm to 15 μm and 51 μm to 19 μm at 0.33 W/mL, respectively [72]. Low power level has no effect on floc size reduction by sonication. With increase in power level, the floc size reduction increases with increase in ultrasonication density and sonication time. For example, the floc size reduces from 94 μm to less than 3 μm with a sonication density of 0.22 W/mL and 0.44 W/mL, respectively, [61]. At constant power level of 0.33 W/mL, with increase in sonication time reduces the floc size to 22 μm and 10 μm with a sonication time of 20 min and 40 min, respectively [61]. At constant sonication time of 60 min, the particle size reduction was less than 3 μm at 0.33 W/mL and 0.44 W/mL. Microscopic examination reveals that structural integrity of floc will be destroyed completely after 60 min of sonication, so further increase in sonication time or power level cannot disintegrate the floc. There thus exist an optimum power level and sonication time for sludge disintegration [61].

Chu et al. [71] has studied the effect of sonication on the raw sludge and flocculated sludge. The size reduction in AD of the flocculated sludge after sonication was more than 50% of the sonicated raw sludge. The average surface charge of the sludge reduces due to sonication. The sonication will split the floc particles into several small particles with negatively charged surfaces. For example, due to flocculation, the ζ- potential of sludge has been increased from -14 to 18mV, following sonication has reduced the ζ- potential to + 4mV, while in the original sample the ζ- potential was -14mV [71]. Mao et al. [12] evaluated the effect of sonication on particle size reduction in primary and secondary sludge; the sludge disintegration was more in the secondary sludge compared to primary sludge. A reduction of 85% particle size has been observed in secondary and 71% in primary within 20 min of sonication. The higher reduction in the secondary sludge is expected, as it contains mostly the biomass (microbial cells), but the primary sludge consists predominantly readily settleable solids comprising fibres and less degradable cellulosic material.

The increase in sonication density has also increased the disintegration efficiency; more particles are disintegrated at higher sonication densities (73% at 4 W/mL and 60% at 2 W/mL) [12]. Bougrier et al. [47] evaluated the effect of ultrasonic treatment on particle size distribution ranging from 0.4 to 1000 μm of waste activated sludge (WAS) using 20 kHz frequency at different specific energy inputs. Particle sizes less than 1μm have been observed to increase with increase in specific energy supplied. For example, Es = 14, 550 kJ/kg TS, particles of 1μm occupied 1.5% of the whole volume, whereas they occupied 0.1% in the untreated sample. However, the volume occupied by larger particle greater than 100 μm has also been increased due to re-flocculation [69]. Akin et al. [66] studied the effect of sonication on particle size at different total solids concentration (TS) in the sludge. The size reduction was more for the lower TS sludge (2% TS content decreased by 6.5 fold at 0.67 W/mL, 240 min sonication), and a similar degree of reduction requires more ulrasonication density in the higher TS Sludge (4% needs 1.03 W/mL and 6% needs 0.83 W/mL).

The effect of sonication on particle size is compared using the uniformity coefficient ($dp_{60}\backslash dp_{10}$), and dp_{10}. Ultrasonication has been reported to increase uniformity coefficient of sludge by five fold and decreases in particle size gradually with increase in specific energy [33,69]. For example, the uniformity coefficient and dp_{10} of sludge changed from 3.3 to 17 and 30.5 μm to 1.2 μm, respectively at E_s = 7200 kJ/L [63]. The micro-flocs (< 4.4 μm) shows less susceptibility to sonication than macro-flocs (> 4.4 μm), as macro-flocs have the larger surface area exposed to sonication than the micro-flocs which have more binding forces, such as cells [41]. El-Hadji et al. [64] observed that with an increase in specific energy (E_s) input, the volume occupied by the smaller particles size (≤ 28 μm) was more than 90%. A particle with a size larger than 4.4 μm (including, $4.4 < d \leq 50$ μm, $50 < d \leq 125$ μm and $d \geq 125$ μm) exhibited more disruption than micro-flocs (< 4.4 μm) [41]. The effect of particle size distribution on CST (Capillary suction time) and SRF (specific resistance to filtration) was observed by Jin et al. [79] and Feng et al. [65] and they derived a strong correlation between the particle size and CST/SRF. The correlation coefficient between dp90 and CST was in the range of 0.8248 [79] to 0.9436 [46]. The ultrasonication breaks up small particles more effectively than larger one [46,63, 64] and the particle size and energy dose were inversely related with a correlation coefficient of 0.996 at the significance level 0.01 [46].

2.4.1.2 Dewaterability of sludge

Ultrasonication has both positive and negative effects on sludge dewaterability. Lower power level with less sonication time increases dewaterability, but decreases the degree of disintegration as there is no cell lysis. FitzGerald et al. [80] studied the effect of different sonication intensities on sludge dewaterability and observed a correlation between sonication and CST (suspended and total solids effects the dewaterability after sonication). Quarmby et al. [60] observed that dewaterability of the sludge decreases with an increase in ultrasonication intensity (CST increased gradually with increased in ultrasonication intensity) but anaerobic digestion of sludge has a positive effect on dewaterability, that is, dewaterability of the digested sludge increased with sonication (CST decreased). With an increase in sonication time, the dewaterability of sludge decreased gradually (CST increased from 197.4 to 488.9 sec with 60 min of sonication; the bound water content also increased by four-folds at higher power level, 0.33 W/mL), because a greater increase in the amount of small particles formed after sonication resulted in a larger surface area for holding water [61]. Gonze et al. [69] summarized that CST of sludge decreased (dewaterability of sludge increased) with lower sonication power level and less sonication time, but with an increase in sonicaion time at same power level, the CST value increased. This is due to the fact that the flocs did not reduce to smaller particles at lower power levels and with less sonication time, the lower level settings favoured the sludge dewaterability.

The dewaterability of the sludge deteriorates with increase in ultrasonication intensity due to cell lysis and release of biopolymers from extracellular polymeric substances (EPS) and bacteria into aqueous phase [81]. It was stated that EPS will reduce the activated sludge dewaterability [82]. The dewaterability of sludge increases by adding flocculent to sludge before sonication [83]; by addition of flocculent will reduces the sludge water content by around 80% [84]. For example, the specific filtration resistance (SFR) of the sludge is reduced from 3.59×10^{12} m/kg to 0.43×10^{12} m/kg by addition of 100 ppm flocculent and a sonication power dose of 500 W/m^2 for 30 secs. So, sonication can reduce the flocculent dose by 20-50% and increases the dewaterability of sludge [83]. In comparison to results of the above authors, Na et al. [63] observed that CST will increase initially at specific energy in the range of 0-800 kJ/L and with further increase in specific energy the CST decreases gradually. Apart from specific energy input, CST reduction is also a function of sonication time and sludge volume. As the specific energy used by previous authors were lower than the specific energy used by Na et al. [63], so dewaterability may increase with increase in specific energy at higher level.

The sludge dewaterability is favourable at CST less than 20 secs [85, 86]. Dewaterability of sludge can be expressed in terms of bound water, i.e. if the bound water content of the sludge increases then dewaterability decreases. With increasing input power, the bound water content of the sludge increases. For example, at 0.33 W/mL, the bound water content has been reported to increase by four-fold and thus reducing the dewaterability of the sludge [84]. Bound water content of original sludge is 3.8 kg/kg DS, and at power level of 0.11 W/ml the bound water increases to 5.9 kg/kg DS. Further at a power level of 0.33 W/mL, the bound water has increased to 11.7 kg/kg DS [84]. At higher input power, the sludge particles are disintegrated to smaller size with higher surface area causing adsorption of more water and thereby increasing the bound water [61].

The relation between the sludge dewaterability and the degree of disintegration has been evaluated by many researchers. The sludge dewaterability will increase when the degree of sludge disintegration lies between 2 and 5%. When the degree of disintegration is less than 2%, the change in sludge floc structure is very limited and when it is more than 5%, the fine particles are more which increases the bound water content [88]. Feng et al. [65] evaluated the sludge dewaterability considering the extracellular polymeric substance concentration. The optimum specific energy for the better sludge dewaterability observed is 800 kJ/kg TS, the EPS concentration is 400-500 mg/L and particle size range is 80-90 µm. When the specific energy is less than 4400 kJ/kg TS, the sludge dewaterability enhanced slightly and with dosages greater than 4400 kJ/kg TS, the dewaterability dropped significantly. At specific energy dose ranging from 0-2200 kJ/kg TS, the sludge dewaterabilty increases. Beyond the specific energy 22000 kJ/kg the dewaterability of sludge deteriorates [65]. Further the dewaterability of sludge can be expressed in terms of CST and EPS of the sludge [62,65,89]. A correlation coefficient (R) of 0.9576 for EPS and CST, and 0.8314 for EPS and SRF has been reported (Feng et al., 2009b). Similarly, Wang et al. [62] found a good correlation coefficient of 0.9233, between EPS and CST. Houghton and Stephenson [89] have derived a quadratic relationship between EPS and CST with coefficient of determination (R^2) of 0.9687.

Feng et al. [65] evaluated the effect of specific energy on EPS release and found that with increase in specific energy, the release of EPS increases in the solution. The EPS concentration in the sludge sample increases the viscosity of the sludge [62]. Moreover, the EPS forms a thin layer on the surface of the filtering media that acts as a barrier for the water, and thus dewaterability of the sludge decreases [84] as the specific energy increases.

2.4.1.3 Settleability of sludge

The settleability of sludge changes with increase in specific energy. Feng et al. [46] have suggested a specific energy of 1000 kJ/kg TS is optimum for improving the WAS settleability. The settleability of WAS is improved, when the specific energy is less than 1000 kJ/kg (at lower specific energy the flocs are disrupted slightly, which improves the settleability), and when the specific energy is greater than 5000 kJ/kg TS, the settleability of WAS deteriorates due to complete breakdown of flocs and increase of EPS concentration in the sample [46]. The settling velocity for the activated sludge floc ranges from 5 m/hr to 30 m/hr, with fastest settling flocs densities ranging from 1.065 to 1.60 g/mL [90]. Chu et al. [61] concluded that ultrasonic treatment has no influence on sludge settleability, which contradicts the changes in particle size and floc structure after ultrasonication [46,63,64], and the established effects of ultrasonication on sludge [91]. The change in mass composition was evaluated by Feng et al. [46], and concluded that there is a strong correlation between specific energy input (Es) and TDS. The optimum solids concentration range for the better sludge settleability was given by [41], and the optimal solids content ranges from 2.3% and 3.2%. Further, Show et al. [41] observed an optimal TS range of 23 000–32 000 mg/L, and Zhang et al. [92] calculated the efficiency as "Energy efficient = (I * surface area of probe * sonication time)/$\mathrm{SCOD}_{\mathrm{increase}}$". With TS = 20 910 mg/L and 30 min sonication, Zhang et al. [92] has observed the highest energy efficiency as 166.7 kWh/kg $\mathrm{SCOD}_{\mathrm{increase}}$.

2.4.1.4 Microscopic examination of sludge

Ultrasonication disintegrates the sludge flocs and lysis the cell wall of the microbes. The microscopic image evaluation of microbes before and after disintegration of sludge can be used to evaluate the degree of disintegration [61]. Microscopic image evaluation provides information at cellular level of the sludge disintegrated by ultrasound [93]. The change in the structural integrity of flocs and breakdown of microbial cell walls can be observed at different sonication time [93]. With increase in sonication time complete breakdown of the flocs and cell wall will occur. For example, at 2 min of sonication the structural integrity of the flocs and filaments are significantly disrupted without appreciable destruction of bacterial cells, and at 10 min of sonication the flocs are completely disintegrated and filament-like structures with a few scattered bacterial cells, and at 30 min of sonication, more or less the complete break-up of cell walls have been observed [93]. Dewil et al. [85] have concluded that ultrasound treatment reduces average size of flocs and produces abundance of separate cells and abundant short pieces of filaments (Actinomyces). In contrast to the above studies on microscopic image evaluation, Feng et al. [46] visualised that even at high energy dose 26,000 kJ/kg TS, neither the floc structure nor the microbial cells were totally disintegrated. This indicates that the ultrasonication has significant effect on microbial disruption, but the efficiency of the disruption is not clear. Still extensive future research is required is in this area to evaluate the effect of ultrasonication on microbial disruption at different specific energy input and sonication time.

2.4.1.5 Change in turbidity

The turbidity of sludge increases with increase in specific energy [33,46,63,64,75]. The lower ultrasonic frequency (20 kHz) gives high sludge disintegration efficiency, while the higher reduction in particle size during disintegration increases the turbidity of the sludge [33]. El-Hadj et al. [64] represented the effect of specific energy on aqueous phase turbidity graphically. The turbidity of the supernatant sludge decreased for specific energy less than 5000 kJ/kg TS and with specific energy greater 5000 kJ/kg TS, the turbidity increased drastically as release of micro particles into supernatant [46]. The energy doses less than 1000 kJ/kg TS cannot disrupt large amounts of organic matter into the supernatant thus turbidity of sludge does not increased, indicating that the minimum energy required to disrupt the sludge is 1000 kJ/kg TS [46, 47,69].

The evaluation of physical parameters gives a relative measurement of sludge disintegration efficiency. Still extensive research is needed between sonication parameters and their effects on physical parameters of sludge. In real field application, the changes in the physical parameters will play a major role in evaluating the sludge disintegration efficiency. The effect of ultrasonication on sludge physical parameters was evaluated by different authors as summarized in the Table 3.

2.4.2 Chemcial evaluation

The sludge is a complex substrate which contains various types of micro-organisms; the cell wall strength of these micro-organisms varies from each other. Chemical evaluation is 90% more quantitative and mainly focuses on sludge disintegration efficiency [9]. The “degree of disintegration (DD)” parameter was proposed by Kunz and Wagner [94] to quantify the sludge disintegration efficiency which is shown in the Eq. (5) [95].

$$DD = \left[\frac{COD_f - COD_i}{COD_{NaOH} - COD_{NaOHo}}\right]\left[\frac{COD_{NaOH*}}{COD_{\mathrm{homogenization}}}\right] \times 100\,(\%) \qquad (5)$$

Where, COD_f is the final COD of supernatant after ultrasound treatment (mg/L), COD_i is the initial COD (supernatant COD, untreated) of the sample (mg/L), COD_{NaOH} is the COD of the supernatant at 22 hr after addition of 1 M NaOH (mg/L), COD_{NaOHo} is the COD of supernatant just after addition of 1 M NaOH (mg/L), COD_{NaOH*} is the COD of original sample right after addition of 1 M NaOH (mg/L) and $COD_{homogenization}$ is the COD of original sample after homogenization.

In the above equation (COD_f-COD_i) is the soluble COD release by disintegration and (COD_{NaOH-} - COD_{NaOHo}) represents the soluble COD by chemical disintegration. Chemical disintegration NaOH) is assumed to disintegrate completely. Therefore, it is used as reference COD [9,12,33,47,48,56,61,62,69,71,94-99]

The ratio of COD_{NaOH*} and $COD_{homogenization}$ represents the COD of the sample before and after addition of 1 M NaOH in the ratio of 1:3.5 at 20°C. Further Muller has modified Eq. (5) to calculate degree of disintegration (DD_{COD}) [95] as follows:

$$DD_{COD}=\left[\frac{COD_{ultrasound}-COD_{original}}{COD_{NaOH}-COD_{original}}\right]\times 100\,(\%) \tag{6}$$

The $COD_{ultrasound}$ is supernatant COD of the sonicated sample (mg/L); $COD_{original}$ is supernatant COD of original sample (mg/L) and COD_{NaOH} is the maximum COD release in the supernatant after NaOH digestion (sludge and 1 M NaOH, ratio of 1:2 for 10 min at 90°C).

2.4.2.1 Soluble COD assessment

Ultrasonication disintegrates both cellular and extracellular matter and, organic debris and extracellular polymeric substances (EPS) of the sludge. The SCOD of sludge increases due to solubilisation of solid phase matter and increase in the concentration of organic matter and EPS in aqueous phase. Therefore, SCOD can be used as a parameter to evaluate the sludge disintegration. Apart from SCOD, ammonium nitrogen and nitrate nitrogen and EPS concentrations (polysaccharides, proteins, nucleic acids, lipids and other polymeric compounds) are also important parameters in chemical evaluation after sludge sonication. Almost all the researchers have applied SCOD as a parameter to evaluate the sludge disintegration efficiency. However, comparison of these results is very difficult, because the sludge disintegration depends on various factors like, sludge type, TS content, power supply, frequency, ultrasonic density, temperature, ultrasonication duration, sludge characteristics, etc. Ultrasonication has no effect on the total COD (TCOD) of the sludge, therefore the ratio of SCOD/TCOD represents the release of the organic matter from solid state to liquid state after ultrasonication. Tiehm et al. [33], Rai et al. [98], Bougrier et al. [47] and Nickel & Neis [100], used the degree of disintegration (DD_{COD}) modified by Muller (Modified version from Kunz and Wagner, [94]) for evaluating the disintegration efficiency as shown in Eq. (6).

Shimizu et al. [6] evaluated the solubilisation of WAS at different sonication times. To achieve a solubilisation rate of 75-80%, a minimum of 90 min ultrasonication time is required and at least 30 to 40 min of ultrasonication is required to get 50% solubilisation [6]. Tiehm et al. [13] reported that after 96 sec of ultrasonication, the disintegration was more than 30%. With increase in sonication intensity the SCOD concentration of the WAS increases [60]. For example, at a sonication intensity of 111 W.min, the increment in SCOD concentration was 9.6% and at 356 W.min, the SCOD concentration increased by 15% [60]. A linear correlation was observed between degree of disintegration and applied ultrasonic intensity. The degree of disintegration was more than doubled by increasing the intensity from 6 to 18 W/cm^2 [48]. The higher mechanical shear forces produced at higher intensities ruptures the cell walls of microorganisms and thereby will increase the solubilisation of the COD. This in turns increases the degree of disintegration.

Further, Wang et al. [31] evaluated the effect of sonication time on sludge disintegration and found that the concentration of soluble COD, protein, and carbohydrate in the sludge or supernatant of sludge increases gradually with increase in sonication time. The ultrasonication increases the concentration of COD, protein, and carbohydrates by breaking the flocs and disrupting the cell walls of the bacteria that releases the extracellular organic compounds contained in the bacterial flocs. The dry matter of the bacteria contains about 50-60% of proteins [69]. The observed COD and carbohydrate concentration increment in the sludge with respect to increment in sonication time was relatively less when compared with protein concentration and carbohydrate concentration in the supernatant. For example, at 40 min sonication the concentration of COD, protein and carbohydrate in the supernatant was 1040 mg/L, 6000 mg/L and 1800 mg/L, respectively [31]. The ratio of sludge solubilisation is defined as the concentration of the organic substances such as protein, carbohydrates and COD in the supernatant after pretreatment to the total organic substance before pretreatment multiplied by 100 [31].

The disintegration efficiency can also be evaluated based on the release of components such as protein, polysaccharides, and DNA. Ultrasonication disintegrates flocs, lysis the microbial cells, which results in release of EPS and other components. The release rate of these components is not the same during the ultrasonication [81]. The protein release was higher than polysaccharides and DNA. The rate of increase was more within 20 min of sonication and beyond this the release of proteins was slower [81]. A similar trend was observed with polysaccharides and DNA. The released DNA is denatured with increase in ultrasonication density (> 0.528 W/mL). In addition, increasing sonication time increases the temperature of the bulk solution and thereby denatures the released DNA [81].

Considering the performance of the disintegration and the energy input together, the optimum specific energy for sludge disintegration is 50 kJ/kg TS. A further increase in (> 50 kJ/kg TS) specific energy may slow down the increment rate of protein, polysaccharides and DNA [81] The ultrasound disintegration of sludge has been reported to increase the concentration of Ca^{+2} and Mg^{+2} into the aqueous phase. The rate of increase was higher initially and decreased with the time. The smaller particles of the sludge formed during the disintegration, absorbs the calcium and magnesium ions and decreases the concentration of Ca^{+2} and Mg^{+2} ions in the aqueous phase of the solution [81]. Ca^{+2} and Mg^{+2} released during the sonication are linked to biopolymers (protein).

The effect of total solids concentration on degree of disintegration was evaluated by Nels et al. [48]. Increase in TS, the solubilisation of SCOD increased leading to an optimum, beyond which solubilisation of SCOD decreased due to attenuation effect [12,48]. For example, the SCOD has increased from 1000 mg/L to 1800, 4000, 5800 and 3200 mg/L at the TS content of 0.98%, 1.7%, 2.6% and 3.6% w/v, respectively [66]. Higher solids in the liquid produces more cavitation sites and more hydro mechanical shear forces due to implosion of more bubbles formed, and beyond the optimum concentration the homogeneous distribution of the acoustic waves are disrupted by absorption effects [48]. The degree of disintegration is lower at higher specific input, therefore the effect of ultrasonic density is more significant than specific energy input (A contradictory statement when compared with previous studies, saying that specific energy is more important than ultrasonication density for higher sludge disintegration) [62,97].

The protein concentration in the supernatant increases with increase in specific energy input at all TS content [66]. The increase of protein concentration in the supernatant was higher initially and decreased with prolong sonication [66]. At higher TS content the protein release was deteriorated due to the decreasing cavitational effect in the sludge. Show et al. [41] evaluated the effect on SCOD solubilisation with increase in ultrasonication density and TS content of the sludge. The release of SCOD in the supernatant increased with increase in ultrasonication density. At constant energy input, the optimum TS concentration range lies between 2.3% and 3.2%. To evaluate the optimal solid content range, the ultrasound disruption index D (a relationship between the disruption efficiency and the solids content) is proposed which can be calculated as:

$$D = \gamma\ (S/E) \tag{7}$$

Where, D is the ultrasound disruption index, S (mg/L) is the SCOD released in the supernatant by disruption, E (kWh/kg DS) is specific energy consumption to sonicate 1 kg dry solids of the sludge and S/E is the slope for SCOD versus specific energy input and γ is the correlation coefficient relative to sonication density, γ is regarded as 1 [41].

A new parameter, kWh/kg SCOD, has been introduced to evaluate the degree of disintegration which considers sludge characteristics and lysis efficiency [92]. Evaluating the ultrasonication of sludge with the new index parameter, the optimum operational parameters are TS in the range of 20-30 g/L, sound intensity of 158-251 W/cm^2 and sonication time of 5-15 min [92]. A positive correlation ($R = 0.993$, $P < 0.01$) between SCOD and the applied energy dosage was observed by [46]. The optimum value for complete disintegration was not found as the soluble COD went on increasing with increase in specific energy input (even at 26, 000 kJ/kg TS) [46].

Tiehm et al. [33] evaluated the effect of ultrasound frequency, specific energy input and theoretical resonant cavitation bubble size on the degree of sludge disintegration. With increase in frequency the degree of disintegration decreased gradually (DD_{COD} = 80% at 41 kHz and DD_{COD} = 7% at 3217 kHz). The effect of bubble radius on degree of disintegration was calculated by considering the equation $R_r \approx 3.28\ f_r^{-1}$, where R_r is the resonant bubble radius in mm and f_r is the resonance frequency in kHz [101]. The degree of the disintegration increases logarithmically with the bubble radius (> 4 μm) [33].

The effect of input power and the temperature rise of the bulk solution were evaluated by [61] and it was observed that with an increase in power level from 0.11 W/mL to 0.33 W/mL at 120 min sonication, the total COD solubilised was 2% and 20% in the supernatant, respectively. At power level of 0.33 W/mL, the ratio of BOD/TCOD increased from 66% to 80% [61].

Considering the effect of ultrasonication on temperature, sufficient results are not available to justify an effect. The rise in temperature will leads to higher saturated vapour pressure, which will make it harder for the vapour bubble to collapse and thus decreases the intensity of cavitation [88], and hence the disintegration efficiency. Huan et al. [88] evaluated the effect of temperature on ultrasonication of sludge. The temperature of sludge increases with increase in sonication time and increases the efficiency of ultrasonication. For example, at 4 W/ml-1 min sonication with (kept at 20°C) and without temperature control the percentage degree of disintegration was 9% for both the cases, but at 0.8 W/ml- 5 min sonication, the percentage degree of disintegration was more for the uncontrolled sample (27%). For the control sample the degree of disintegration was 23%.

The effect of temperature in the bulk solution was evaluated at different power level. With increase in power level and sonication time, the temperature of the bulk solution increased gradually which resulted in an increase in the SCOD/COD ratio [61]. The effect of ultrasonic density on sludge disintegration was evaluated [62]. A low disintegration was observed due to increase in the temperature of the sludge to 65°C in one hour. With ultrasound density of 0.768 W/mL, the SCOD of the sludge increased from 52 mg/L to 2581 mg/L, 7509 mg/L and 8912 mg/L in 5 min, 15 min and 20 min, respectively, [62]. The SCOD solubilisation rate decreased with longer sonication time.

The effect of high power and short retention time and low power and long retention time on sludge disintegration was evaluated by Gronroos et al. [97] and found no difference on SCOD released. Therefore, the optimization of the ultrasonication energy consumption is necessary for a favourable degree of disintegration. The degree of disintegration increased with an increase in dry solids (DS) content of the sludge due to the higher concentration of microbes that could be disrupted. However, the optimum DS will vary for every reactor configuration, so as to enable ultrasonic wave propagation and cell disruption. The factors limiting to achieve a maximum DS value are reactor size, transducer type, viscosity of the sludge, temperature of the sludge and polymer concentration (if polymers are added) [97]. Based on the transmutative power function model, it was concluded that power index of the sonication time was higher than that of the sonication energy density, i.e., low density and long sonication time was more efficient than the high density and less time [88]. The transmutative power function model was derived by assuming that the ultrasonic sludge disintegration as the dependent variable and its increase slows down gradually with sonication time or ultrasonication density. Generally ultrasonic sludge disintegration lies between 0 and 1. The model was expressed as:

$$DD_{COD} = 1- (1/ 1+ k\, C^{l}\, E^{m}\, t^{n}) \qquad (8)$$

Where, DD_{COD} is the degree of disintegration (%); C is the sludge concentration (g/L); E is the ultrasonic density (W/mL); t is the sonication time (min); l, m and n are the indices of the sludge concentration, ultrasonication density and sonication time, respectively; k is the reaction rate constant depending on the ultrasonic reactor.

The solubilisation effect during in the ultrasonication in the primary and secondary sludge was evaluated [12]. The solubilisation of SCOD was higher in the secondary sludge (SCOD increased 4 times in the primary sludge and 7.7 times in the secondary sludge) and linear correlation was observed between SCOD and sonication time for primary and secondary sonicated sludge [12]. The SCOD solubilisation increases with increase in sonication densities, that is, the SCOD increased by 1.2 times, 2.3 times and 4.8 times at 2 W/mL, 3 W/mL and 4 W/mL, respectively at the same specific energy input [12]. Bougrier et al. [47] evaluated the effect of specific energy (kJ/kg TS) on COD solubilisation. With increase in specific energy input the SCOD increased. The rate of solubilisation was higher initially between specific energy of 0-8000 kJ/kg TS, beyond which increase in specific energy reduces the rate of total solid solubilisation [47]. The soluble COD ratio (SCOD/TCOD) increased from 4 to 32% with increase in specific energy from 0 to 10 000 kJ/kg TS, and the optimum solubilisation occurred at a specific energy of 10 000 kJ/kg TS [47].

2.4.2.1.1 Kinetic model for Ultrasonic sludge disintegration

The effect of sonication parameters and sludge characteristics on SCOD solubilisation is evaluated by developing the kinetic model. The SCOD is assumed as dependent variable and sludge concentration, pH, ultrasonic intensity, ultrasonication time and ultrasonic density as independent variables [49]. The SCOD solubilisation rate and percentage degree of disintegration can be calculated as:

$$\frac{d(SCOD+)}{dt} = k$$

(9)

$$\frac{d(SCOD\%)}{dt} = u \qquad (10)$$

Where, 'k' and 'u' are given as: $k = k_o\ [I]^{\alpha}\ [pH]^{\beta}\ [D]^{\gamma}\ [C]^{\delta}$ and $u = u_0\ [I]^{\varphi}\ [pH]^{v}\ [D]^{\lambda}\ [C]^{\theta}$. 'I' is the ultrsonication intensity, 'D' the ultrasonic density, 'C' is sludge concentration. α and φ are the influence indexes for ultrasonic density, β and v are the influence indexes of pH, λ and γ are the influence indexes for sludge concentration, δ and θ are the influence indexes for the sludge concentration, k_0 and u_0 are the intrinsic kinetics constants and are related to reaction temperature as follows:

Where k_0 and u_0 is defined as $k_0 = A \exp\left(\frac{-\Delta E_a}{RT}\right)$ (11)

The kinetic model can be analysed using multivariable linear regression method. Wang et al. [49] showed that magnitude of each parameter on SCOD solubilisation can be arranged in the order of: sludge pH > sludge concentration > ultrasonication intensity > ultrasonic density.

The sonication time has a large effect on biomass inactivation efficiency. It is observed that the biomass inactivation occurs after 10 min of sonication [56]. Similarly, Chu et al. [61] has reported at 20 min sonication biomass inactivation using low sonication density. The above two studies reveal that inactivation of sludge is dependent on the ultrasonication density. Further, Zhang et al. [56] observed following linear relations between the degree of sludge disintegration and cell lysis with increase in ultrasonication density in the range of 0.1-1.5 W/mL.

DD_{COD} = 38.7 x ultrasonication density (12)

Where DD_{COD} is the degree of disintegration (%); ultrasonicaiton denisity (W/mL)

Nucleic acids = 81 + 523 x power density (13)

Where Nucleic acids mg/L; power density W/mL.

The disintegration of sludge by ultrasonication results in increase of SCOD, supernatant protein and nucleic acids concentration [56]. The reported increase rate of supernatant protein and nucleic acids concentration is linear and can be expressed as follows:

Nucleic acids concentration (mg/L) = 15 + 114 x sonication time (14)

DD_{COD} = 1.2 x Sonication time (15)

SS reduction = 0.875 x sonication time (16)

Where nucleic acids mg/L; sonciation time in min; SS reduction in %

Evaluating the effect of disintegration and VS reduction, Zhang et al. [56] observed that VS reduction and degree of disintegration overlaps, which implies that these two parameters are interchangeable. The VS and COD represents the organic matter of the sludge, therefore the increase of the supernatant organic can be correlated with the VS reduction [56]. The degree of disintegration increases with increase in specific energy. At Es =10,800 kJ/L, the ratio of SCOD/TCOD has increased from 9% to 62%. Similarly, an increment in DD_{COD} of 80% at specific energy input of 4000 kJ/L has been reported [63]. Nels et al. [48] observed a maximum of 32% increment in DD_{COD} at Es of 12,000 kJ/kg with dry solids (DS) content of 34.4 g/kg of WAS. Khanal et al. [102] have reported that optimum power input for the highest SCOD release is 35 kJ/g TS or at 3% TS content.

2.4.2.2 Protein assessment

Proteins are important building block of the bacteria that are responsible for many different functions in the living cell, for example, proteins that catalyze chemical and biochemical reactions within living cell and outside. In WAS, about 70–80% of the extracellular organic carbon is in the form of proteins and saccharides [103,104,105,106,107]. Wang et al. [62] have done the quantification of sludge disintegration (particularly WAS) by protein measurement. Akin et al. [66] measured the coefficient of determination (R^2) for protein increase ($\Delta_{protien}$), DD_{COD1} and DD_{SCOD2} with respect to biogas yield (Δ_{biogas}), which are used to evaluate the sludge disintegration. For example, the combined coefficients of 0.97 for $\Delta_{protien}$/ Δ_{biogas} were higher than that of 0.54 for DD_{COD1}/ Δ_{biogas}, and 0.83 for DD_{SCOD2}/ Δ_{biogas}.

Wang et al. [81] examined the release of protein in aqueous phase at different sonication times. The protein concentration has been found more predominant than DNA and polysaccharide in the aqueous phase of the sonicated sludge. The rate of release of protein was very high during the initial 20 min of sonication, while polysaccharide and DNA concentration dropped after 20 min of sonication. Feng et al. [46] has observed that the protein concentration increases with increase in energy input. An increment of 97% in the protein concentration was observed at energy input of 26000 kJ/kg TS. Further, with high energy input the concentration of proteins is observed to increase. However, the protein measurement is not common and the calculation of ultrasound disintegration efficiency by protein measurement is not yet well accepted. Therefore, COD measurement will continue to measure the ultrasound disintegration efficiency due to its simplicity and easiness in daily operation.

2.4.2.3 NH_3 assessment

Ultrasonication increases organic nitrogen and ammonia concentration in sludge samples [9,46,47,51]. Therefore, NH_3 assessment can also be used to evaluate the degree of disintegration. Bougrier et al. [47] evaluated the effect of sonication on organic nitrogen solubilisation. At a specific energy of 15000 kJ/kg TS, the organic nitrogen solubilisation is 40% and the maximum solubilisation occurs at a specific energy input of 10, 000 kJ/kg TS [47]. With the increase of specific energy input and TS content of WAS, the release of ammonia nitrogen concentration increases [108]. The total nitrogen solubilisation increased linearly with increase in specific energy above 3600 kJ/kg TS, and a solubilisation of 19.6% was achieved at specific energy input of 108,000 kJ/kg TS [109]. The ammonia-N concentration increases due to the disintegration of bacterial cells and release of intracellular organic nitrogen into the aqueous phase, which is subsequently hydrolyzed to ammonia [51].

Feng et al. [46] have observed the changes in ammonium nitrogen and nitrogen concentration after ultrasonication at different specific energy input. The nitrate nitrogen concentration increased at ultrasonication energies higher than 5000 kJ/kg TS, while the increase of nitrate nitrogen concentration was smaller than ammonium nitrogen at similar conditions due to generation of hydroxyl radicals through acoustic cavitation [46,52]. Further the disintegration of organic nitrogen from non-biological debris is also an important contribution to ammonia nitrogen. The correlation between nitrogen data and subsequent anaerobic digestion test are required to understand the effect of ultrasonication and the release of ammonia in aqueous phase. At present, convincing conclusions are not yet reported to evaluate the disintegration efficiency of the sludge by ultrasonication [9]. The quantification of chemical parameters by various authors is tabulated in the Table 4.

2.4.2.4 Biological Evaluation

The ultrasonication disrupts the flocs and breaks-up the cell wall of bacteria. The breakdown of bacterial cell walls by disruption can be assessed by using biological utilization tests. Considerable amount of the WAS contains aerobic and facultative bacteria. The oxygen utilization rate (OUR) is used to characterise the microbiological activity. For example, if the OUR = 0, then all the bacterial cells are disrupted and the degree of disintegration is 100%. Thus, effectiveness of sludge disintegration by ultrasonication can be measured by OUR measurement. The term degree of inactivation (DD_{OUR}) was introduced by [98], which is similar to DD_{COD} for evaluating the degree of disintegration. The DD_{OUR} is calculated using the expression of Eq. (17).

$$DD_{OUR}(\%) = \left[1 - \frac{OUR_{sonicated}}{OUR_{orginal}}\right] \times 100 \tag{17}$$

Where, $OUR_{sonocated}$ is the oxygen uptake rate of sonicated sludge, $OUR_{original}$ is the oxygen uptake rate of the original sample (without sonication), and OUR can be represented by Eq. (18).

$$\mathrm{OUR} = -\frac{\mathrm{d}[\mathrm{O}_2]}{\mathrm{dt}} \tag{18}$$

The DD_{OUR} have been observed to increase rapidly with increase in specific energy input up to 40 kJ/g TS, beyond which it retards the DD_{OUR} increase rate [98]. Chu et al. [61] used the heterotrophic plate count and OUR (oxygen utilization rate) to evaluate ultrasound disintegration efficiency. With increase in sonication time, the survival ratio (ratio of viable bacteria density levels after sonication to those of original sample) of the heterotrophic bacteria decreased. For example, the survival ratio reached a value of 44% for heterotrophic bacteria and 3% for total coliform at a sonication density of 0.33 W/mL for 120 min. With increase in specific energy input, the specific oxygen uptake rate (SOUR) increases and reaches an optimum; beyond which increase in specific energy decreases the SOUR of the sludge exponentially due to inactivation of microbes [51,61,88].

At low ultrasonic densities, the floc gets disrupted, but the cell lysis does not occur, so the SOUR increases initially. A maximum of 65% degree of inactivation was observed by Akin et al. [66], and the degree of inactivation based on SOUR was found to decline by 60% at a specific energy of 10 kW/g TS at 2% TS content. Similar trend was observed for higher TS concentrations (4% & 6%) in the sludge [51]. Huan et al. [88] have evaluated the relationship between the sludge microbial activity and degree of disintegration. When the sludge disintegration degree was 0-20%, microbial activity was enhanced significantly and SOUR increased by 20-40%, when the degree of disintegration was 20-40%, SOUR increased less than 20%. This indicates that some cell wall of the bacteria gets damaged prior to increase in microbial activity and when degree of disintegration reaches more than 40%, the cell lysis occurs which results in decrease of microbial activity [88]. An approximate relation between SOUR and degree of disintegration was evaluated by Huan et al. [88], which can be expressed as $DD_{SOUR} = -3.75\ DD_{COD}^2 + 0.75\ DD_{COD} + 0.21$.

3. EFFECTS OF ULTRASONICATION ON SLUDGE DEGRADABILITY AND METHANE PRODUCTION IN ANAEROBIC DIGESTER

The primary aim of ultrasonication is to increase the sludge biodegradability to enhance the methane production at lower HRT in anaerobic digester. Over the decades many authors have evaluated the effect of ultrasonication parameters on the sludge degradability and increased methane production. The order of pretreatment efficiency for enhancement of methane generation is: ultrasonic lysis (20 W, 9 kHz 30 min) > thermal pretreatment by autoclave (120°C, 30 min) > thermal pretreatment with hot water (60°C 30 min) > freezing (-10°C, 15 h) [15,106]. The intracellular biopolymers solubilisation and conversion to the lower molecular weight compounds of sludge through hydrolysis is a rate limiting step [4, 5], and usually the hydrolysis of complex organics is catalyzed by extracellular enzymes (such as amylases, proteinases, lipases, and nucleases) [74,112,113]. Ultrasonication induces cavitation, which lysis the cell walls of microbes and releases the intracellular components into the aqueous phase. Therefore, the sonication parameters affecting cavitation will affect the sludge digestion. The increased VS reduction directly translates into increased methane generation during the anaerobic digestion and less stabilized biosolids to be disposed of.

3.1 Effects on sludge digestibility and methane

The effect of sonication density, sonication intensity and sonication time on sludge disintegration and increase in digestibility was evaluated by various authors. Shimizu et al. [6] evaluated the effect of sonication on AD of sludge in continuous digesters and found increased biogas production rate for sonicated sludge at lower HRT. For example, at 2.5 days retention time, the digestibility improved to 60% and the gas conversion efficiency improved to 40%. The gas production rate was increased till the retention time was less than 2.5 days [6]. The digestion rate of WAS and the hydrolysis rate of the biopolymers released from the WAS follows the first order kinetics, with rate constants of 0.16 d^{-1} and 1.2 d^{-1}, respectively [6]. The conversion efficiency of WAS to CH_4 is greatly improved in a two phase AD process when compared with single phase AD system [6].

Tiehm et al. [13] evaluated the effect of AD of sludge after ultrasonication by conducting batch experiments at different HRTs of 22, 26, 12 and 8 days. The percentage VS reduction in the AD after pretreatment was on the higher side compared to the untreated sample (at 22 d). The VS reduction in untreated sample was 45.8% and in the pre-treated sample VS reduction is 50.3% at a residence time of 22d. The VS concentration in the effluent is always 10% less than that of the conventional AD effluent [13]. Ultrasonication of sludge was observed to enhance VS reduction and biogas production in AD. For example, the biogas production for the disintegrated sludge at 22 days residence time is 36.36 L/d and at 8 days, the biogas production is 100 L/d with the volatile solids reduction of 50.3% and for the control the volatile reduction is only 45.8% at 8 days retention time. The ultrasonicaton of sludge increases the degradation rate of sludge, which allows for shorter retention time. For example, higher removal rate at shorter retention time, i.e., decrease of HRT from 16 to 4 days, was observed by Nels et al. [48]. The degradation rate of VS at 4 days HRT increased by 30% as compared to the control.

The effect of sonication time and frequency of sonication was evaluated by Muller [33] and found that with increase in pretreatment, the VS reduction in AD digester increases gradually. For example, the VS reduction in the control sample is 21.5%, and that of 30 min sonicated sample the VS reduction increased to 27.3% in the digester, an increment of 27% compared to the control. For the sample sonicated for 150 min, the VS reduction increased to 33.7%, an increment of 56.7% compared to the control [33]. The percentage biogas production of the sonicated sludge increased with increase in sonication time, and the methane percentage in the biogas increased simultaneously. Compared to the control, 8.59% increment in methane content in biogas is observed at sonication time of 150 min [33]. Evaluating the effect of frequency, with increase in ultrasound frequency the degree of disintegration decreased and the VS degradation also reduced [33].

The effect of energy input on sludge solubilisation and subsequent anaerobic digestion was evaluated by [60], and observed that the biogas production in the solubilised sludge will increase by 15% in the sonicated sludge at 356 W.min compared to control. Moreover, the effect of sonication on volatile fatty acids and their effect on AD were evaluated by Quarmby et al.[60].

The volatile fatty acids (VFAs) concentration in the digester of the control sample increased from 1100 mg/L (initial VFAs in the sludge) to 1400 mg/L on the second day. After the digestion the VFA got reduced to 86 mg/L. For the sample sonicated with 356 W.min, the VFAs had been increased to 1300 mg/L after sonication and in the digester, it was increased to 1800 mg/L which was 22% more compared to the control [60]. The acetic acid in the digester was analysed to evaluate the activity of the methanogenic bacteria in the digester [60]. The increment of acetic acid of the control sample was increased from 550 mg/ L to 770 mg/L, only 33%, and that in the sonicated sample with 356 W.min, the increment was 80%, increased from 520 mg/L to 940 mg/L [60].

The effect of sonication time on the sludge disintegration and the subsequent AD (batch test) was also evaluated by Wang et al. [31]. The percentage increment of methane increased gradually with increase in sonication time. For example, the methane amount increased by 12, 31, 64 and 69% on 11th day, corresponding to the sonication time of 10, 20, 30 and 40 min, respectively [31]. Therefore, the optimum pretreatment time for enhancing the AD efficiency of WAS should be approximately 30 min [31]. The protein, carbohydrates and VFAs degradation followed a similar trend during AD. The concentration of these organic substances increased initially with 24 hr (the protein concentration), 12 hr (carbohydrates and VFAs digestion), thereafter, the concentration decreased gradually. The methane yield of the sonicated sludge is directly related to the increase in VFA (in particular acetate) concentration [13]. The specific methane yield decreased with increase in HRT, e.g., at 15 HRT the methane yield is 61% more compared to control whereas it was 41% higher compared to control at 25 days HRT. The increase in specific methane yield is due to increase in the net surface area of the particles and solubilisation of complex organic matter. The effect of ultrasonic density (0.2 W/mL) on methane production of the excess sludge has been evaluated [97]. The observed methane production in the sonicated sludge was 8-17 times more than that of the control sample during 19 days assays. The methane production per kg of SCOD in the sample was same for 2.5 and 10 min sonication samples, suggesting that SCOD in these samples was equally degradable despite differences in its quantities. The methane production in the anaerobic batch studies of the treated sludge (0.3 W/mL, 30 min) is 10-20% more compared to untreated sludge [97].

The effect of specific energy input on biogas production is evaluated by Bougrier et al.[47]. The biogas production increased with increase in specific energy input. For example, the biogas production for untreated sample is 20.5 mL and for the sonicated sludge, the biogas has increased to 23, 25.6, 25.7, 31.2 and 32.8 mL at the specific energy of 660, 1350, 2700, 6950 and 14547 kJ/kg TS, respectively. However, at higher energies the biogas production was almost the same, and for 7000 and 15000 kJ/kgTS the biogas production was same. For untreated sample about 97% of biogas is produced from the particulate matter, whereas for sonicated sludge (Es = 7000 kJ/kg TS) the biogas produced from the particulate matter was 60% only [47]. The total amount of biogas increased because solids contained in the particulate part of the sludge were made soluble by ultrasonication, which are more available in the soluble fraction for the bacteria.

The effect of feed/inoculum ratio on anaerobic digestion of the sonicated sludge is evaluated by Braguglia et al. [114]. The biogas production rate increases with increasing the food/inoculum (F/I) ratio. For example, a maximum gain of 25% (biogas) was observed when the F/I ratio is 0.5 [114]. The ultrasonication pretreatment considerably enhanced the hydrolysis reaction rate constant from 0.06-0.17 d^{-1} (untreated) to 0.13-0.23 d^{-1} (sonicated) [114]. The changes in the sludge characteristics have direct relation with methane production, i.e., the rate of methane production is directly proportional to the net rate of particle size solubilisation in an anaerobic digestion [56].

The effect of sonication on hydrolysis, acidogenesis and methanogenesis and their relation was evaluated by Mao and Show [73]. The sonication appeared to be ineffective in relation to acidogenesis reaction rates (almost constant), but it provided a better buffering capacity to diminish the adverse effect of acidification [73]. The hydrolysis rate was enhanced by 19 to 75% for digesters fed with sonicated sludge at different sonication densities (0.18-0.52 W/mL) [73]. Therefore, the promoted biochemical reactions by sonication treatment during hydrolysis and acidogenesis was mainly attributed to the accelerated hydrolysis of complex organics, but not so much to the acidogenesis of soluble organics. The digesters fed with sonicated sludge were able to provide an amenable environment in enhancing hydrolysis of complex organics (leading to improved subsequent hydrolysis limitation) and in promoting methanogenic biomass growth, there by facilitating the initial methanogenesis limitation.

3.2 Full-scale application

Ultrasonication of sludge in enhancing COD reduction in the AD are limited for full-scale application due to its scale-up from small scale experimental studies. Sonic Ltd., has developed a full-scale ultrasound system capable of enhancing the AD. The full-scale trials and full-scale installation around the world were done using Sonix^{TM} (is a new technology utilising highpowered, concentrated ultrasound for conditioning sludges). Avounmouth, Wessex water, UK, have installed an ultrasound system for treating the domestic and industrial mixed sludge (i.e., population equivalent of 1,200,000). The TS and VS reduction of the untreated sludge in the digesters was 40 and 50%, respectively and that of sonicated sludge was 60 and 70%, respectively [25]. Similarly, Sonix^{TM} system was installed in many plants in UK, US and Australia. Observed biogas production rate in these installations increased by 40-50% (approximately) compared with control, and the approximate VS reduction rate increased by 30-50% [25]. The effects of ultrasonication on the increment in the sludge digestibility evaluated by different authors have been summarized in the Table 5.

Barber [11] have presented the details of full-scale part-stream ultrasound plants (Germany, Austria, Switzerland, Italy, and Japan), where the biogas increased by 20-50% (volume/kg fed), VS reduction improved by 20-50%, and dewatering of the sludge was improved by 3-7%. In a typical full-scale installation, the biogas production rate, VS reduction rate, and dewatering was increased by 22%, 22%, and 5-7%, respectively [11]. The energy and mass balance over a typical digester (1200 m^3, HRT- 20 days, sludge temperature 15^oC, and flow rate 200 m^3/d at 5% DS) installed with ultrasound of 2.5 $W/m^2/K$, operating at temperature 35^oC revealed that energy produced is more than energy consumed, i.e., 1 kW of ultrasound used will generate 7 kW of electrical energy after losses [11]. Xie et al. [115] evaluated that full-scale installation of ultrasound ('V' shape reactor volume 3.5 L, 20 kHz, 6 kW, housing five donut shaped horns stacked one over the other at a spacing of 5 cm each) for treating mixed sludge (primary and secondary sludge). In the above installation about 15-58% increase in biogas production was observed under strictly controlled conditions, with an average of 45%. Evaluating the energy balance showed that the average ratio of the net energy gain (NEG) to electric energy consumed by the ultrasound device in the operation was 2.5 (assumed every cubic meter of the methane gas generates 2.2 kWh).

4. FUTURE PERSPECTIVES

Ultrasonication of sludge has significant effects on physical, chemical and biological properties of sludge. Evaluation of physical, chemical and biological parameters will give the efficiency of ultrasonication (or disintegration of sludge by ultrasonication). The physical parameters like, particle size, turbidity, and dewaterability of sludge effected by ultrasonication and the ultrasonication parameters. The particle size of the sludge decreases with increase in ultrasonication but beyond a certain point, ultrasonication will increase the particle size due to reflocculation. The particle size reduction varies with change in sludge characteristics and sonication parameters; therefore, the optimum ultrasonication parameters and sludge characteristics should be evaluated for each case. This can be done by mass and energy balance of the full system.

The chemical parameter evaluation is the more quantitative, and in real application, the chemical parameters (SCOD, protein concentration, ammonia concentration, VS concentration, etc. plays a major role in evaluating the efficiency of the ultrasonication. The SCOD, protein, and ammonia concentration of the sludge increase with an increase in ultrasonication, and further increase in sonication has very little effect on these solubilisation parameters. Using high ultrasonic power with short time is as effective as low ultrasonic power with long retention time. For non-homogeneous sludge, high power and short retention and for homogenous sludge, high sonication time with low power will be more effective.

The ultrasonication of sludge is one of the emerging technologies for the sludge pretreatment to increase the biodegradability, but still extensive research on optimizing the methane yield (i.e the net energy yield is more than energy input) is required for the full-scale application. There are more than 50 publications available, yet there is no generalised method to evaluate the efficiency of the pretreatment process. Various authors have expressed the effect of sonication parameters in different units and method of evaluation has to be standardised to compare the results of various authors. Since the cavitation is the basic phenomena of ultrasonication, the factors influencing cavitation will have a significant effect on the ultrasonication. There is a need to evaluate the predominance of each factor (acoustic cavitation, agitation, and local heating) during the ultrasonication and their effect on degree of disintegration. The authors have evaluated the effect of ultrasonic disintegration efficiency based on the COD solubilisation and degree of disintegration, but still there is no clear picture about the effect of COD solubilisation and the specific energy input, ultrasonication density and the sonication. Also, there is a need to evaluate the correlation between these parameters. Researchers have evaluated the effect of sonication based on the VS reduction and increase in the biogas production; still uncertainties exist in judging the efficiency. Increase in viscosity of the sludge due to ultrasonication and the effect of viscosity on the performance of AD has to be evaluated.

The effect of transient cavitation (occurs when ultrasonic intensity is equal to 10 W/cm^2) and stable caviatation (non-inertial cavitation; occurs when ultrasonication intensity is between 1-3 W/cm^2) on biodegradability of sludge and increase in methane content needs to be explored further before its successful implementation. The major disadvantage of AD is an increase in alkalinity, and therefore the release of calcium and magnesium ions during ultrasonication has a significant effect. The correlation between the amount of calcium ion and magnesium released from the sludge flocs during the sonication and their effect on AD is required for estimating the efficiency of the AD. The effects of biopolymers addition on sonication and AD has to be evaluated along with correlation with the sludge digestibility. It is also important to establish to what extent ultrasound treatment could influence each of the degradation steps for digester control and performance improvement. The sludge pH has significant effect on the disintegration efficiency; therefore, the effect of sludge pH on sludge disintegration and the AD needs to be documented. The correlation between the sludge pH and the sonication parameters and AD efficiency is necessary in full-scale application. A standard method for evaluating the efficiency of any pretreatment process is by evaluating the net energy balance and calculating the net carbon saving.

5. CONCLUSION

The pretreatment of the sludge by ultrasonication has a significant effect on the sludge biodegradability during the anaerobic digestion that increases biogas generation as well as percentage of methane in the biogas. Both laboratory-scale and full-scale experiments have shown a great increment in sludge reduction and biogas production of the sonicated sludge in the AD. Almost 31% reduction in sludge cake can be achieved in full-scale application and also it will increase the dewaterability of sludge. The ultrasonication of sludge accelerates the conversion of complex organics into degradable substrate and it also promotes the growth of the methane-producing bacteria. The opinion of many researchers is that the effect of ultrasonic density is supposed to be more vital than the sonication time. The studies with the kinetic model have concluded that the effect of parameters is in the order of pH > sludge concentration > ultrasonication intensity > ultrasonic density. Mass and energy balance on full-scale studies showed that 1 kW of ultrasonic energy used generates about 7 kW of electrical energy after losses. Thus, higher amount of capital and operating cost can be overcome with significant reduction in the size of digesters and operating at lower HRT, which will give a significant boost to sludge management at wastewater treatment plants.

The rate of biogas production is directly proportional to the net rate of solubilisation. With increase in COD solubilisation, methane production will increase. Also, this will decrease the required HRT in the reactor, and thereby reducing the overall size of the reactor significantly. Volatile solids reduction increases with increases in ultrasonication, which will increase the degradation efficiency of the sludge in AD. Optimization of operating parameters (specific energy input, soldis concentration, anaerobic biodegradability, and digestion time), based upon net mass and energy balance is of utmost important to justify the feasibility of full-scale application.

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Table 1. Factors influencing the cavitation phenomena

No.	Factors	Influence on cavitation phenomena
1.	Gas and particulate matter	Presence of gas/air in the liquid will lower the cavitational threshold and reduces the intensity of the shock wave released, as much of the shock wave will be utilized to collapse the gas bubbles. Particulate matters, especially like trapped vapour gas nuclei in their crevices and recesses, will reduce the cavitation effect [18].
2.	External applied pressure	Increasing the external pressure raises the rarefaction pressure, which increases the cavitation collapse intensity [35, 36].
3.	Solvent viscosity	If the natural cohesive forces acting in the liquid are lower, then they will suppress [37] the negative pressure in the expansion or rarefaction cycle. Therefore to increase the cavitation threshold the natural cohesive forces need to be increased by increasing the viscosity of liquid.
4.	Solvent surface tension	The addition of surfactant to an aqueous solution certainly facilitates the cavitation. Increase in solvent viscosity and surface tension, reduces the rate of microbubble formation but increases the intensity of bubble collapse. With addition of surfactants will reduces the solvent surface tension and facilities bubble nucleation (i.e., fewer microbubbles are formed), [35, 38].
5.	Solvent vapour pressure	If the vapour pressure of the liquid is low, then it is difficult to induce cavitation in the liquid. Because, low vapour will enter into the bubble and results in low cavitation [37].
6.	Applied frequency	The rarefaction phase is shortened by increasing the frequency of irradiation, but to maintain an equivalent amount of cavitational energy into the system the power should be increased. That is at higher frequency more power is required to maintain same cavitational effect [35, 39, 40].
7.	Temperature	The cavitation threshold increases with decrease in temperature of bulk solution. With increase in temperature, the solvent reaches the solvent boiling point and produces larger number of cavitation bubbles concurrently, which acts as barrier to sound transmission and nullify the effectivity of ultrasound energy [38]
8.	Sonication density	Increase in sonication density increases the sonication effects on the sludge as given by the equation, $P_A = \sqrt{2I\rho C}$, [41]; Where P_A= acoustic pressure, I = intensity, ρ = density, C = velocity of sound in the medium
9.	Acoustic intensity	Increasing the sonication intensity increases the sonication effects, and it is directly proportional to the square root of the amplitude (P_A) of the acoustic wave divided by the density of the liquid (ρ) and the speed of sound in the liquid (c). $I = \frac{P_A^2}{2\rho c}$ [36,42]
10.	Types of ultrasound Cavitation	The collapse of the cavitation bubbles produces high velocity waves and temperature, causing inter-particle collision and the rupture of cell wall. Depending on bubble types, the ultrasound cavitation is classified as transient or stable (non-inertial cavitation). Transient is believed to occur at 10 W/cm^2 and the later at 1-3 W/cm^2 [37]; The stable bubbles bound to have significant long term effect. The transient and stable bubble growth is explained by bubble growth time by Abramov [43]; $\tau_g = 0.75 T+(i-1) T$; T = 1/f, where τ_g is the bubble growth time, \`f\` is the ultrasound frequency , \`T\` is the period of ultrasound wave and \`i\` is number of acoustic cycles the bubble experienced.

Table 1. Continutation..

No.	Factors	Influence on cavitation phenomena
11	Attenuation	The intensity of the ultrasound is attenuated as it progress through the medium. The attenuation is inversely proportional to the frequency of the ultrasound (i.e., energy is dissipated in form of heat which is not considered in the bulk medium). High power and high frequency is required to have the same intensity at the lower depth for a given sample.
12	Field type	The standing wave field is pronounced with more acoustic cavitation than a progressive field [37]

Table 2. Expression for sludge disintegration

No.	Parameter	Expression	Unit	Reference
1	Specific energy input	$E_S = \frac{P*t}{V*TS}$	kJ/kg TS or kWs/kg TS	[46]
2	Ultrasound dose	$UD_o = \frac{P*t}{V}$	J/L	[33]
3	Ultrasound density	$\mathrm{UD} = \frac{\mathrm{P}}{\mathrm{V}}$	W/L	[33]
4	Ultrasound intensity	$\mathrm{UI} = \frac{\mathrm{P}}{\mathrm{A}}$	W/cm^2	[48]

Note: E_S: Specific energy in kWs/kg TS (kJ/kg TS); P: Power input (kW); T: Sonication time (sec); V: Volume of sludge (L); TS: Total solids concentration (kg/L); A: Surface area of the probe in cm^2

Table 3. Change in physical parameters of sludge due to ultrasonication

Sonication condition				Physical parameters									
Frequ-ency (kHz)	Time (min)	Density (W/mL)	Power Input	Particle size reduction (μm)		Settleability SVI (mL/g)		Turbidity NTU		Dewaterability (CST) secs		Reference	Comments
				Initial	Final	Initial	Final	Initial	Final	Initial	Final		
31	a) 0.49 b) 1.6	NA	3.6 kW	165	a) 135 b) 85	NA	NA	NA	NA	NA	NA	[13]	Particle size reduced with increase in sonication time
16 -20	7.2	NA	a) 111W.min b) 356W.min	NA	NA	NA	NA	NA	NA	766.1	a) 852 b) 904	[60]	Dewaterability deteriorated with increase in ultrasonication (US) intensity
20	120	a) 0.11 b) 0.33	0.110 kW	98.9	a) 97.5 b) 4	NA	NA	NA	NA	197.4	a) 188 b) 304	[51]	Particle size reduced and dewaterability deteriorated with increase in US density
20	20	0.33	NA	400	48	NA	NA	NA	NA	NA	NA	[70]	Particle size reduced with increase in US density
20	a) 60 b) 3 c) 6 d) 10	NA	0.26 kW	66.9	a) 31.9 b) 24.2 c) 18.1 d) 19.5	218	a) 155 sonication @ 39 kJ/L b) 125 sonication @ 156 kJ/L	NA	NA	NA	NA	[59]	The settleability of the sludge reduced with increase in specific energy input

Table 3. Continuation..

Sonication condition				Physical parameters									
Frequ-ency (kHz)	Time (min)	Density (W/mL)	Power Input	Particle size reduction (µm)		Settleability SVI (mL/g)		Turbidity NTU		Dewaterability (CST) secs		Reference	Comments
				Initial	Final	Initial	Final	Initial	Final	Initial	Final		
20	20	a) 2 b) 3 c) 4	0.2 kW	48 (primary sludge)	a.16 b.14 c.12	NA	NA	NA	NA	NA	NA	[12]	The reduction of particle size is more in secondary sludge than primary sludge at same energy input
	20	a) 2 b) 3 c) 4	0.2 kW	48(secondary sludge)	a.10 b.7 c.6	NA	NA	NA	NA	NA	NA		
20			0.225 kW	31.99	a) 19.6[1] b) 18.5[2] c) 17.6[3] d) 12.7[4]	NA	NA	NA	NA	NA	NA	[36]	Increasing the ultrasonication resulted in smaller size particles
20	a) 5 b) 30	0.528	0.3-1.2 kW	NA	NA	NA	NA	NA	NA	82	a)344 b)520	[52]	The dewaterability of the is deteriorated due to sonication
NA	30	a) 0.25 b) 0.35 c) 0.50	NA	NA	NA	a) 140 b) 130 c) 118	a)65 b)85 c)70	NA	NA	NA	NA	[62]	Increasing in ultrasonication density will reduce the settleability of the sludge
28		NA	a) 600 kJ/L b) 7200 kJ/L	85	4	NA	NA	35	370	50-55	a)68 b)7	[53]	The turbidity and particle size reduction increased with increase in Power input

Table 3. Continuation..

Sonication condition				Physical parameters									
Frequ-ency (kHz)	Time (min)	Density (W/mL)	Power Input	Particle size reduction (µm)		Settleability SVI (mL/g)		Turbidity NTU		Dewaterability (CST) secs		Reference	Comments
				Initial	Final	Initial	Final	Initial	Final	Initial	Final		
20	240	a) 0.67 b) 1.28 c) 2.2 d) 3.22	2.2 kW	209 (2%TS)	a)32.4 b)28.5 c)22.6 d)18.1	NA	NA	NA	NA	NA	NA	[56]	The particle size reduction is less at higher TS content
		a) 0.44 b) 1.03 c) 1.87 d) 2.24		217 (4% TS)	a)185.1 b)36.7 c)33.4 d)38.2	NA	NA	NA	NA	NA	NA		
30	a) 2 b) 10	0.012	0.05-0.4 kW	65	a)68 b)41.2	NA	NA	NA	NA	NA	NA	[70]	The particle size reduction is more with increase in sonication time
20	1	a) 0.18 b) 0.33 c) 0.52	1.5 kW	51	a)29-38 b)19-29 c)15-21	NA	NA	NA	NA	NA	NA	[63]	Increase in sonication density resulted in more particle size reduction
20	NA	NA	0.07 kW	33.8	10-13.26	NA	NA	NA	With increase of E_S		Increased	[54]	Increasing the E_S input the particle size reduction
20	15	a) 0.18 b) 033 c) 0.52	a) 0.09 kW b) 0.166 kW c) 0.26 kW	49	a) 19 b)13 c) 9	NA	NA	NA	NA	NA	NA	[41]	Increasing power input and sonication density resulted in more particle size reduction

Table 3. Continuation..

Frequency (kHz)	Time (min)	Density (W/mL)	Power Input	Physical parameters								Reference	Comments
				Particle size reduction (μm)		Settleability SVI (mL/g)		Turbidity NTU		Dewaterability (CST) secs			
				Initial	Final	Initial	Final	Initial	Final	Initial	Final		
20	240	a) 0.67 b) 1.28 c) 2.2 d) 3.22	2.2 kW	209 (2%TS)	a)32.4 b)28.5 c)22.6 d)18.1	Sonication condition	NA	NA	NA	NA	NA	[56]	The particle size reduction is less at higher TS content
		a) 0.44 b) 1.03 c) 1.87 d) 2.24		217 (4% TS)	a)185.1 b)36.7 c)33.4 d)38.2	NA	NA	NA	NA	NA	NA		
30	a) 2 b) 10	0.012	0.05-0.4 kW	65	a)68 b)41.2	NA	NA	NA	NA	NA	NA	[70]	The particle size reduction is more with increase in sonication time
20	1	a) 0.18 b) 0.33 c) 0.52	1.5 kW	51	a)29-38 b)19-29 c)15-21	NA	NA	NA	NA	NA	NA	[63]	Increase in sonication density resulted in more particle size reduction
20	NA	NA	0.07 kW	33.8	10-13.26	NA	NA	NA	With increase of E_S		Increased	[54]	Increasing the E_S input the particle size reduction
20	15	a) 0.18 b) 033 c) 0.52	a) 0.09 kW b) 0.166 kW c) 0.26 kW	49	a) 19 b)13 c) 9	NA	NA	NA	NA	NA	NA	[41]	Increasing power input and sonication density resulted in more particle size reduction

Table 3. Continuation..

Sonication condition				**Physical parameters**									
				Particle size reduction (μm)		**Settleability SVI (mL/g)**		**Turbidity NTU**		**Dewaterability (CST) secs**			
Frequ-ency (kHz)	**Time (min)**	**Density (W/mL)**	**Power Input**	**Initial**	**Final**	**Initial**	**Final**	**Initial**	**Final**	**Initial**	**Final**	**Refere nce**	**Comments**
20	1	a) 0.18 b) 033 c) 0.52	a) 0.09 kW b) 0.166 kW c) 0.26 kW	49	a)32 b)24 c)13	NA	NA	NA	NA	NA	NA	[64]	Similar observations as Show et al. [41]
20	NA	E_S a) 800 b) 2200 c) 4400 d) 17600 e) 26000 f) 35000	0.3-2 kW	94.75	a)88.4 f)61.29	NA	NA	NA	NA	94.2	a)83.1 b)89.6 c)112 d)260 e)339 f)673.4	[55]	With lower E_S input the dewaterability of the sludge increased, further increase in E_S deteriorated the sludge dewaterability
20	NA	E_S a) 24700 b) 49500 c) 98900 d) 163300	0.1 kW	NA	NA	171	a)118 b)81 c)47 d)26	171	a)770 b)1040 c)1520 d)1790	NA	NA	[66]	The turbidity and SVI increased with increase in E_S input

Table 4. Quantification of chemical parameters

No.	Sludge	TS	Ultrasonic density or intensity	S_E Input/ frequency	Time (min)	Chemical parameters %COD Solubilisation	DD (%)	SCOD (mg/L)		Protein (mg/L)		(%) Nitrogen Solubilisation		Reference
								Initial	Final	Initial	Final			
1	MS	NA	NA	NA	1.6	NA	30	630	2270	NA	NA	NA	NA	[13]
2	WAS	NA	NA	NA	90	75-80	NA	NA	NA	NA	NA	NA	NA	[6]
3	WAS	6-7%	111 W.min	NA	NA	NA	NA	1509	1654	NA	NA	NA	NA	[60]
	WAS		356 W.min	NA	NA	NA	NA	1509	1755	NA	NA	NA	NA	
4	WAS	3.3-4%	NA	NA	a) 10	NA	NA	60	a) 280	110	a)1200	NA	NA	[31]
					b) 20				b) 520		b)3000			
					c) 30				c) 900		c)5500			
					d) 40				d)1080		d)6000			
5	SAS	2.3%	NA	NA	1	90	NA	100	10000		NA	NA	NA	[110]
6	WAS	2.59%	1.8 (W/cm^2)	(kHz) a)41	240	NA	a)80	NA	NA	NA	NA	NA	NA	[33]
				b)207			b)47							
				c)360			c)25							
				d)616			d)15							
				e)1068			e)10							
				f)3217			f)7							

Table 4. Continuation..

No.	Sludge	TS	Ultrasonic density or intensity	S_E Input/ frequency	Time (min)	Chemical parameters								Reference
						%COD Solubilisation	DD (%)	SCOD (mg/L)		Protein (mg/L)		(%) Nitrogen Solubilisation		
								Initial	Final	Initial	Final			
6	WAS	2.59%	1.8 (W/cm^2)	NA	a)7.5 b)30 c)60 d)150		a)0.0 b)4.7 c)13.1 d)23.1	NA	NA	NA	NA	NA	NA	[33]
7	WAS	38 (g/L)			120	18.4		2250	5000	NA	NA	NA	NA	[111]
8	AS		68.4 (W/cm^2)	(kJ/L) 160	NA	NA	9-20			NA	NA	NA	NA	[59]
9.	ES	2.45%	1.25 W/mL	(kJ/kg TS) a)3000 b)14,900	NA	NA		1300	a)2600 b)4050	NA	NA	NA	NA	[94]
9.	WAS	0.48%		(kJ/kg TS) a)8000 b)24000 c)40000 e)64000	NA	NA	a)4.2 b)8 d)10 e)25	NA	NA	NA	NA	NA	NA	[91]

Table 4. Continuation..

No.	Sludge	TS	Ultrasonic density or intensity	S_E Input/ frequency	Time (min)	Chemical parameters								Reference
						%COD Solubilisation	DD (%)	SCOD (mg/L)		Protein (mg/L)		(%) Nitrogen Solubilisation		
								Initial	Final	Initial	Final			
10	PS				20	NA	NA	1020	3980	NA	NA	NA	NA	[12]
		%	4	NA										
		a)0.98	(W/mL)					1020	a)2700					
		b)1.7							b)3000					
		c)2.6							c)4300					
		d)3.6							d)5600					
	SS		4	NA	20	NA	NA	670	5260	NA	NA	NA	NA	
		%	(W/mL)											
		a)1.02						670	a)4260					
		b)1.65							b)6800					
		c)2.88							c)9000					
		d)3.75							d)4400					
11	WAS	1.85%	NA	(kJ/kg TS)				NA	NA	NA	NA	NA	NA	[36]
				a)1000		a)8	a)14							
				b)15000		b)35	b)55							

Table 4. Continuation..

No.	Sludge	TS	Ultrasonic density or intensity	S_E Input/ frequency	Time (min)	Chemical parameters								Reference
						% COD Solubilisation	DD (%)	SCOD (mg/L)		Protein (mg/L)		(%) Nitrogen Solubilisation		
								Initial	Final	Initial	Final			
11	WAS	1.85%	NA	(kJ/kg TS) a)0 b)660 c)1355 d)2700 e)6951 f)14547	NA	NA	NA	NA	NA	NA	NA	TKNs/TKN a)3.1 b)8.6 c)11.3 d)15.6 e)29.4 f)44.7	N-NH_4^+/ TKN a)2.3 b)4.1 c)4.6 d)5.7 e)11.3 f)18.2	[36]
12	WAS	2.6%	5-18 (W/cm^2)	NA	1.06	NA	7.5 – 18	NA	NA	NA	NA	NA	NA	[37]
13	WAS	3%	0.768 (W/mL)	NA	a)5 b)15 c)20	NA	NA	52	a)2581 b)7509 c)8912	38.8	a)800 b)2300 c)3300	NA	NA	[93]
14	BS	NA	0.5 (W/mL)		a)10 b)15 c)20 d)30	NA	a)18 b)23 c)26 d)30	410	a)1100 b)1700 c)2700 d)3250	400	a)1800 b)2200 c)2400 d)2700	NA	NA	[45]
15	ES	NA	NA	kJ/kg MLVSS 1.15 x 10^5		44.7	NA	166	10260	70	4701	NA	NA	[92]

Table 4. Continuation..

No.	Sludge	TS	Ultrasonic density or intensity	S_E Input/ frequency	Time (min)	Chemical parameters								Reference
						%COD Solubilisation	DD (%)	SCOD (mg/L) Initial	SCOD (mg/L) Final	Protein (mg/L) Initial	Protein (mg/L) Final	(%) Nitrogen Solubilisation		
16	WAS	(%) a)2 b)4 c)6	NA	kWs/g TS 5	NA	NA	NA	1.80	a)2.4 b)3.2 c)1.8	NA 0.08 0.06	NA 0.80 0.44	NA	NA	[56]
17	SS	2.47(%)	a)0.18 b) 0.33 c) 0.52 (W/mL)	NA	1	NA	NA	523	a)723 b)890 c)1002	NA	NA	NA	NA	[63]
18	Sewage sludge	30.48 (g/L)	NA	kJ/kg TS a)5000 b) 1500		a)6 b)16	a)12 b)31	NA	NA	NA	NA	NA	NA	[53]
19	WAS	2%	NA	kWs/g TS a)1.7 b)5.09 c)10.19 d)20.37 e)40.75	10 30 60 120 240	NA	NA	126	a)3800 b) 5917 c)7800 d) 8300 e)12200	242	a)700 b) 950 c)1449 d) 1948	NA	NA	[40]

Table 4. Continuation..

No.	Sludge	TS	Ultrasonic density or intensity	S_E Input/ frequency	Time (min)	Chemical parameters								Reference
						%COD Solubilisation	DD (%)	SCOD (mg/L)		Protein (mg/L)		(%) Nitrogen Solubilisation		
								Initial	Final	Initial	Final			
19	WAS	4%	NA	kWs/g TS a)0.53 b)1.59 c)3.18 d)6.36 e)12.73	10 30 60 120 240	NA	NA	380	a)1850 b)3800 c)4400 d)6350 e)9936	138	a)510 b)740 c)1400 d)1750 e)1917	NA	NA	[40]
19	WAS	6%	NA	kWs/g TS a)0.36 b)1,08 c)2.16 d)4.34 e)8.65	10 30 60 120 240	NA	NA	420	a)1800 b)2000 c)3900 d)4500 e)7129	161	a)390 b)600 c)890 d)1295 e)1617	NA	NA	[40]
20	WAS	14.46 g/L	NA	kJ/kg TS a)0 b)500 c)1000 d)5000 e)11000 f)18000 g)26000	NA	NA	NA	110	a)110 b)150 c)180 d)300 e)790 f)1300 g)1468	538	a)538 b)600 c)610 d)820 e)870 f)900 g)1000	NA	$N\text{-}NH_4^+$ a)12 23 b)20 c)27 d)34 e)37 f)42	[65]

WAS – waste activated sludge; MS – mixed sludge; SAS – surplus activated sludge; AS- activated sludge; ES- excess sludge; PS- primary sludge; SS-secondary sludge; BS- biological sludge.

Table 5. Increment in the sludge digestibility

No.	Type of sludge	Sonication parameters				SRT (d)	% increment with respect to control				Reference
		Power (kW)	Specific energy	Sonication time (min)	Sonication density or intensity		VS reduction	Biogas production	Methane yield	Methane content	
1	Mixed sludge	3.6	NA	1.6	NA	22	9.8	NA	NA	NA	[13]
2	WAS	NA	Batch studies		a)111 W.min b)356 W.min	NA	NA	a)11.5 b)15	NA	NA	[60]
			Pilot plant studies		a)111 W.min b)356 W.min	a)7.3 b)1.37	NA	NA	NA	a)1.01 b)2.60	
3	WAS	0.2	NA	a)10 b)20 c)30 d)40	NA	11	NA	NA	a)12 b)31 c)64 d)69	NA	[31]
4	SAS	9	NA	1	NA	19	NA	NA	47	5-10	[110]
	Primary sludge	NA	NA	NA	NA	a)15 b)25	NA	NA	a)61 b)41	NA	
5	WAS	NA	NA	a)7.5 b)30 c)60 d)150	NA	8	a)5.58 b)26.97 c)46.04 d)56.74	a)-4.7 b)15.7 c)30.7 d)41.64	NA	a)1.14 b)4.93 c)7.2 d)8.6	[33]
6	WAS	0.047	kJ/g VS 3.4-5	1.5	NA	a)8 b)10 c)12	a)-3.25 b)-8.60 c)0.00	NA	NA	a)0.58 b)23 c)-0.129	[116]
7	WAS	NA	NA	120	NA	7	89.75	20.67	19.94	NA	[111]
8	Excess sludge	Methane production assays		a)2.5 b)10	0.2 W/mL	19	NA	NA	a)8.5 times b)17 times	NA	[94]
		AD		30	0.3 W/mL	19			10-20		
9	WAS	0.025	kJ/kg TSs a)660 b)1350 c)2700 d)6950 e)14547	NA	NA	NA	NA	a)12.9 b)24.87 c)25.36 d)52.19 e)60.00	NA	NA	[36]

Table 5. Continuation..

No.	Type of sludge	Sonication parameters				SRT (d)	% increment with respect to control				Reference
		Power (kW)	Specific energy	Sonication time (min)	Sonication density or intensity		VS reduction	Biogas production	Methane yield	Methane content	
10	WAS	3.6	NA	1.6	5-18 W/cm^2	a)18 b)8	a)31.2 b)41.1	a)13.6 b)22	NA	NA	[37]
11	SS	1.5	NA	1	a)0.18 b)0.33 c)0.52 W/mL	4	a)14.86 b)22.97 c)25.67	a)148 b)205.7 c)102		a)3.02 b)10.9 c)12.5	[74]
12	WAS	NA	NA	1.5	10 W/cm^2	a)16 b)8	a)30 b)40.2	a)10.5 b)16.1	NA	NA	[91]

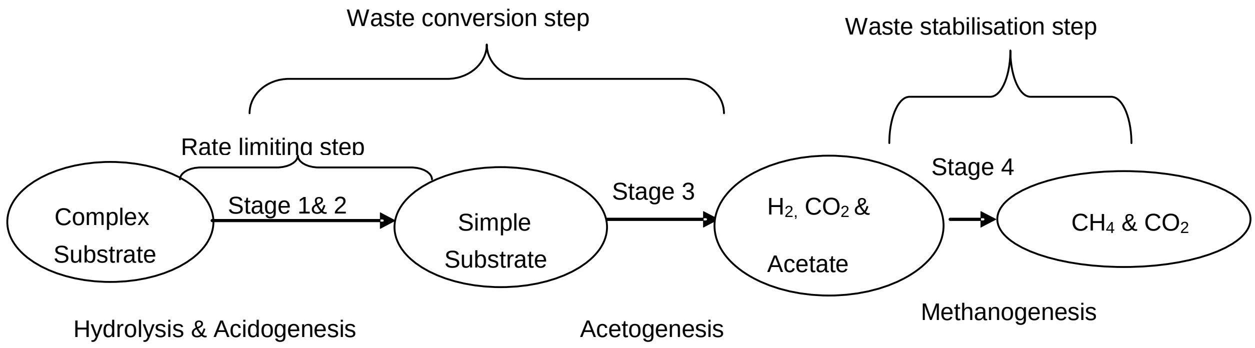

Figure 1. Different stages of anaerobic digestion

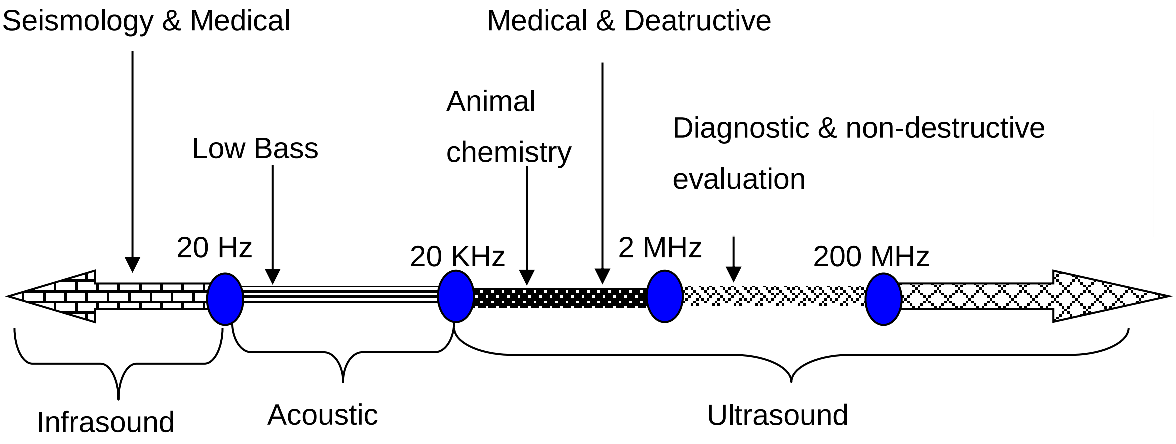

Figure 2. Diagram of ultrasound range

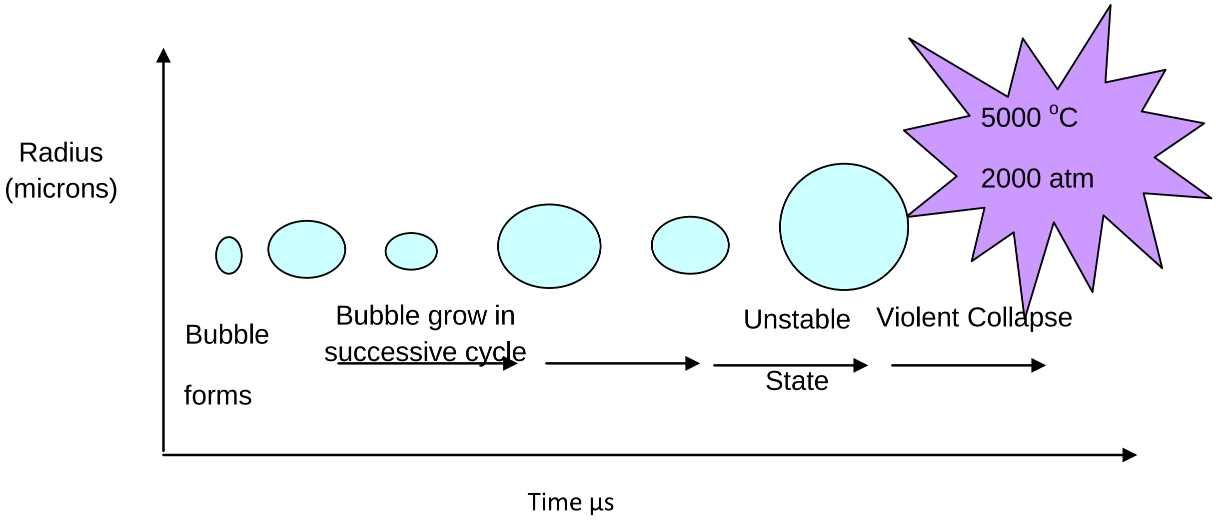

Figure 3. Development and collapse of the cavitation bubble

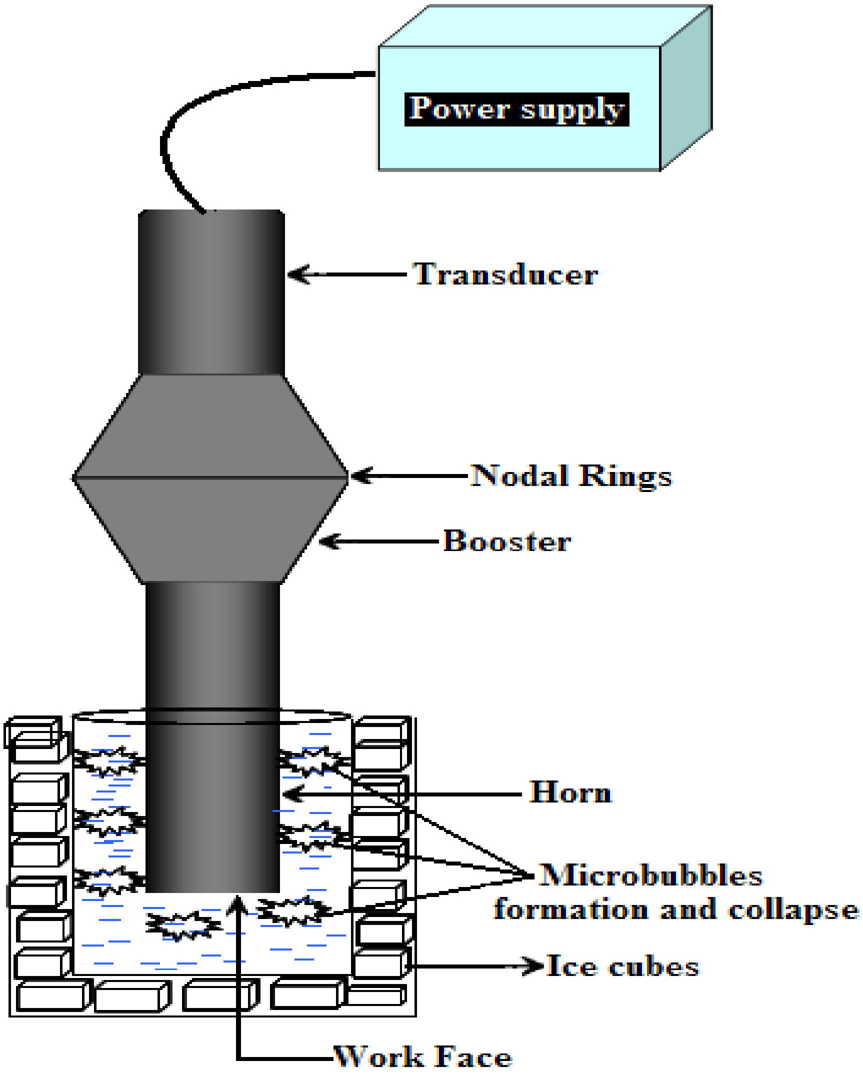

Figure 4. Ultrasonication of sludge (temperature controlled)

PARTIE 2

ENERGY BALANCE AND GREENHOUSE GAS EMISSIONS DURING ANAEROBIC DIGESTION OF ULTRASONICATED SLUDGE

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Bioprocess and Biosystems Engineering (under review)

RÉSUMÉ

Ces travaux évaluent les émissions de gaz à effet de serre (GES) au cours de l'ultrasonication, la digestion anaérobie (DA) des boues à ultrasons, la déshydratation des boues, le transport et l'épandage du digestat de boue basé sur les bilans massiques et énergétiques. Le bilan masse-énergie a été effectué sur les boues non traitées montrant ainsi que la libération de l'énergie est positive, le rapport de l'énergie (énergie sortie/énergie entrée) est supérieur à 1. Les émissions de GES sont réduites avec l'augmentation de la concentration en matières solides et à faible apport d'énergie à ultrasons au cours de l'ultrasonication. En effet, l'augmentation de la température au cours de la sonication réduit l'apport d'énergie, augmente l'énergie nette, le rapport d'énergie et diminue les émissions de GES.

Mots-clés: digestion anaérobie; ultrasonication; émissions de gaz à effet de serre; apport spécifique d'énergie; énergie nette; rapport d'énergie.

ABSTRACT

This manuscript presents the greenhouse gas (GHG) emissions during the ultrasonication pre-treatment, anaerobic digestion (AD) of the ultrasonicated wastewater sludge, dewatering, transportation and land application of the digestate based on mass-energy balance. The mass and energy balance assessment was also conducted for the untreated sludge. It was found that the energy release was positive, the energy ratio (energy output/energy input) was greater than one and GHG emissions were reduced for the ultrasonicated sludge at high solids concentrations and low ultrasound energy inputs. Thus, it can be concluded that increased sludge temperature during sonication will reduce the energy input, increase the net energy and energy ratio and reduce GHG emissions.

Keywords: anaerobic digestion, ultrasonication, greenhouse gas emissions, specific energy input, net energy, energy ratio.

1. INTRODUCTION

Global warming and climate change have made it essential to quantify greenhouse gas emissions (GHGs) from each and every source and to implement necessary actions for reducing these emissions. Sludge generated during the wastewater treatment processes converts to CO_2, CH_4 and N_2O (three principal GHGs) during treatment, disposal and/or reuse. The GHG production during sludge treatment and end-use processes can constitute up to 40% of the total GHG emissions associated with wastewater treatment [1-3]. Sludge generated during the wastewater treatment is disposed of on land as fertilizer, landfilled or incinerated, all of which contribute to GHG production [2]. The factors, such as environmental problems, increasing stringent sludge disposal regulations, economical sludge disposal and increasing public awareness of the different sludge disposal options are forcing the wastewater treatment plant operators to re-evaluate their sludge management strategies. In recent years, researchers have focused their attention on sludge pre-treatment, aiming to enhance its biodegradability. When considering the pre-treatment options, ultrasonication, thermal and Fenton have emerged as promising treatment technologies, based on their potential to enhance sludge biodegradability [3-6]. Sludge pre-treatment followed by anaerobic digestion (AD) has been considered as one of the beneficial options for stabilizing the sludge [4-6]. Among the various available pre-treatment techniques, ultrasonication is an emerging and promising mechanical disruption technique for sludge disintegration, due to several inherent merits, including efficient sludge disintegration, improvement in biodegradability, improved solids quality, and increased biogas production [4-10].

Based on the increased biogas production, several researchers [4-10] have concluded that ultrasonication pre-treatment enhances the energy recovery during the AD of the pre-treated sludge. However many questions remain unanswered:

i. Is enhanced production of biogas due to sludge pre-treatment (ultrasonication) or does sludge provide positive energy balance?

ii. By how much can the amount of solids be reduced during anaerobic digestion for final residual sludge disposal and what is their impact on energy balance and GHG emissions?

iii. By how much is temperature increased during sludge ultrasonication pre-treatment and what are the consequences on overall energy balance?

iv. Under which pre-treatment conditions could each technology favor a positive energy balance?

v. What are the consequences of sludge pre-treatment followed by anaerobic digestion of pre-treated sludge on downstream processing of residual sludge or the digestate (dewatering, transportation and digestate application to land)?

vi. Will the overall energy balance be favorable?

Moreover, during ultrasonication, the solids concentration affects the ultrasonication efficiency as well as the energy input during AD. Therefore, it is essential to compute the energy balance for ultrasonication and AD process in relation to sludge solids concentration. In addition, mass-energy and GHG emissions as criteria for evaluating sludge management efficiency, including all process steps, are not presently available. These process steps include: (i) sludge pre-treatment process (ultrasonication), (ii) anaerobic digestion, (iii) sludge dewatering, (iv) sludge transportation to the land site and (v) land application of sludge. Therefore, this study aims to compute the mass-energy balance and GHG emissions for sludge management with ultrasonication pre-treatment.

2. PROCEDURE TO EVALUATE MASS-ENERGY BALANCE OF THE PROCESS OF ULTRASONICATION OF SLUDGE, AD AND LAND APPLICATION OF DIGESTED SLUDGE

The overall pathway (or process steps) considered for evaluating the mass-energy balance and the corresponding GHG estimation is presented in Figure 1. As can be seen, five main steps are considered for evaluating the mass-energy balance, namely (1) sludge ultrasonication, (2) anaerobic digestion, (3) dewatering, (4) transportation and (5) land application. The mass-energy balance is computed using Microsoft Excel 2003, based on the adopted and design values presented in Table 1.

2.1 Ultrasonication of sludge

Sludge ultrasonication (Step 1) enhances sludge biodegradability [5-8, 10-13] by solubilizing the suspended solids. During AD, biodegradable carbon is converted to biomass, CO_2 and CH_4. The optimum ultrasonication parameters (ultrasonication time and ultrasonication density) for achieving maximum biodegradability of the secondary sludge were determined in line with the work of Pham et al. [14]. During ultrasonication, sludge temperature is increased, and thus affects the cavitation and the energy requirement for the AD process. The specific energy (SE) input for sludge ultrasonication can be calculated by applying Eq. (1). Specific energy input at different sonication times and sonication intensities, evaluated by Pham et al. [14], is considered for evaluating the mass-energy balance (Table 1).

$$SE = \frac{\mathrm{P\,t}}{\mathrm{V\,TS}} \tag{1}$$

Where SE is the specific energy input in (kJ/kg TS); P is the power input (kW); t is the ultrasonication time (sec); V is the volume of sludge (m^3); and TS is the total solids concentration (kg/m^3).

Calculation of the temperature increase during sludge ultrasonication

As mentioned above, the increased sludge temperature during ultrasonication may significantly affect its biodegradability. The cavitation threshold increases with the increase in bulk temperature up to 60°C, while a further increase in temperature reduces the cavitation impact. As the temperature increases, the liquid (solution) reaches its boiling point and simultaneously produces a large number of cavitation bubbles, which act as a barrier to the ultrasound wave's transmission and nullify the effect of the ultrasound energy [5, 15]. On the other hand, an increase in sludge temperature during ultrasonication [16-18] will reduce the energy requirements for heating the sludge to 35°C (the temperature required for anaerobic digestion process). This will affect the net energy gain of the combined process (ultrasonication followed by AD), as the energy required would otherwise be produced by fossil-fired power plants (significant GHG contributors).

From the total energy input during ultrasonication, a part of the energy is transformed into thermal energy (heat energy), which eventually increases the sludge temperature. The total energy input into the system during ultrasonication is given below:

$$E_s = E_\alpha + E_C + E_{ab} + E_{ts} \tag{2}$$

E_s - total energy input into the sludge during ultrasonication (W/mL)

E_α - energy dissipated into the sludge sample (responsible for sludge temperature rise)

E_C - energy required for the cavitation

E_{ab} - energy absorbed by the sludge (for disintegration)

E_{ts} - energy transmitted through the sludge (to overcome the attenuation effect)

The total energy required for different fractions of sonication has not been evaluated; therefore, extensive research is needed to understand the energy efficiency of different functions in the ultrasonication system. Due to the cavitation threshold, the temperature increase during ultrasonication should be maintained below 60°C. The raw sludge temperature generally varies between 10 and 15°C, whereas anaerobic digester is operated at a designed temperature (either mesophilic 35−40°C or thermophilic 55−60°C). Therefore, sludge temperature needs to be raised to the desired level. Thus, the rise in sludge temperature during ultrasonication can substantially reduce the amount of energy required to produce the desired temperature increase. The theoretical relationship between sludge temperature increase (Δt) and power required (p) is represented by Eq. 3 [19].

$$\Delta T = T_f - T_i = \frac{p\,t}{C_p\,M} \tag{3}$$

where T_f is the final sludge temperature (°C); T_i is the initial sludge temperature(°C); p is the power required for increasing the sludge temperature (W); C_p is the specific heat of the sludge (4.2 kJ /kg °C); M is the mass of sludge used (kg); and t is the ultrasonication duration (sec).

Various researchers [16-18] have observed an increase in sludge temperature during ultrasonication. However, to date, no correlation has been established between ultrasonication power input and increase in sludge temperature. There are also contradictory results on the temperature increase during sludge ultrasonication. Many researchers reported an increase in sludge temperature [10, 16, 20-23], whereas several others observed a negligible temperature increase during sludge ultrasonication [17, 24, 25].

The percentage of power diverted towards heating the sludge (or producing the required temperature increase) is evaluated in this study using Eq. 3. In order to calculate the fraction of power utilized to increase the sludge temperature during ultrasonication, the power input and the corresponding sludge temperature increase (ΔT) were adopted from Chu et al. [16] and Feng et al. [17]. Subsequent calculations revealed that the percentage of power utilized to increase the sludge temperature contributed less than 0.12% of the total power input (723 W for the ultrasonication time of 50 s). These results indicate that the calculated fraction of power utilized for increasing the sludge temperature was the lowest. At a higher total solids content

(4% w/v), the sludge volume and the attenuation effect reduce the effect on the fraction of the power dedicated to the temperature increase during ultrasonication. In conclusion, there is a large variation in the temperature increase due to ultrasonication, as reported by various researchers, and depends on many factors, such as energy input per unit volume, solids concentration, sonication duration and horn height. Therefore, it is difficult to compare the results reported in extant studies.

Due to this uncertainty, in this study, the energy balance was performed by assuming two cases. In Case 1, there is no temperature increase in sludge after ultrasonication, while an increase by 10°C in the sludge temperature after ultrasonication is assumed in Case 2.

2.2 Anaerobic digestion of ultrasonicated sludge

The aerobic biodegradability of the ultrasonicated sludge at different solids concentrations (Table 1) was evaluated in the previous work by Pham et al. [14] and the data were adopted for evaluating the mass-energy balance during AD of sludge. Considering biodegradability data reported by Pham et al. [14], the methane produced in the AD was evaluated according to Eq. 4. Moreover, various researchers reported that, during anaerobic digestion, the amount of volatile solids reduced was 10% higher than that of the total solids degraded [26-28]. Therefore, in order to obtain the amount of volatile solids biodegraded during the AD process, the amount of 10% was added to the total solids biodegraded. The values of volatile solids degraded based on the calculation at different solids concentrations and at different specific energy inputs during sonication are shown in Table 2. Based on the results obtained by Pham et al. [14], anaerobic digestion time (solids retention time) was set at 20 days. The volume of methane calculated (according to Eq. 4) based on the volatile solids degraded (or biodegradability of sludge) at different solids concentrations and different specific energy inputs is presented in Table 2. During sludge digestion, mainly CO_2 and CH_4 gases are produced, while N_2O is mainly produced during nitrification and de-nitrification process. Therefore, N_2O production during the AD of sludge was not considered. Carbon dioxide emissions from the biological pathway are considered as biogenic CO_2 emissions. Therefore, this is not taken into account in national protocols due to the fact that they are considered (by convention) “carbon neutral” (i.e., global warming potential is assumed to be equal to zero) [28]. The CO_2 generated during methane combustion for energy recovery was considered as potential GHG. The design inputs required to perform the energy balance for anaerobic digestion of ultrasonicated sludge and control sludge are given in Table 1.

Methane produced (m^3/day) = $VS_{reduction}$ (kg/m^3) x 0.5 (m^3 CH_4/kg $VS_{destroyed}$) x V (volume of sludge, m^3/day) (4)

where $VS_{reduction}$ is volatile solids reduction during AD, and the methane produced 0.5 m^3 per kg of VS destroyed was adopted from Barber [9].

2.3 Dewatering, transportation and land application of the digested sludge

It is assumed that digestate is dewatered (Step 3) using the centrifuge to increase solids concentration. The supernatant of centrifuged sludge (wastewater) is sent back to the wastewater treatment unit by gravity. The energy required for dewatering the digestate using centrifuge is given in Table 1. Transportation of dewatered solids (Step 4), or the quantity of diesel required for the vehicles to transport the solids from wastewater treatment plant (WWTP) to the land application site, was considered. The distance between the WWTP and the land application site to which the dewatered solids are transported was set to 50 km [29]. The diesel consumption rate of the waste collection vehicle is 35 L per 100 km and GHG emission values are equivalent to 2730 g CO_2/L of diesel, 0.12 g CH_4/L of diesel, and 0.08 g N_2O/L of diesel [29]. The energy required for spreading the dewatered solids on to the land (Step 5) is presented in Table 1. The CO_2, CH_4, and N_2O emissions from the land-applied digestate are estimated using the factors reported in Table 1. The GHG emissions in various process steps (the energy consumed during ultrasonication pre-treatment, anaerobic digestion, dewatering of the digested sludge, transportation, and land application) were evaluated the using national emission intensity coefficient (0.53 kg CO_2/kWh, as determined by Environment Canada study based on the Resources for the Future (RFF) model).

3. RESULTS AND DISCUSSION

3.1 Mass balance for ultrasonication of sludge, anaerobic digestion, dewatering, transportation and land application of digestate

The results of the mass balance for different solids concentrations and different specific energy inputs are summarized in Table 2. An increase in specific energy input during sludge ultrasonication increased the volatile solids degradation (or reduction) compared to the control, irrespective of the solids concentration. For example, at 23 g TS/L, for the control samples, the volatile solids reduction of 37.4% was obtained, compared to 41.3% and 66% for SE 1226 kJ/kg

TS and SE 10370, respectively. The increased volatile solids degradation was due to the increased solubilization of sludge organic matter with increased SE input [14].

From the mass balance (Table 2), it is clear that the digestate obtained for dewatering, transportation and land application pertaining to the ultrasonicated sludge (at different specific energy inputs) is lower than that for the corresponding control. The minimum weight of sludge (or digestate) generated for dewatering, transport, and land application was measured at 23.8 tonnes (Table 2) at the specific energy input of 10370 kJ/kg TS.

3.2 Comparison of Case 1 and Case 2 based on the energy required for heating sludge at different solids concentrations

The impact of Case 1 and Case 2 on the energy required for heating the sludge to 35°C (the temperature required for the anaerobic digestion) is shown in Figure 2. As can be seen, this energy requirement reduces with the increase in sludge temperature after ultrasonication (Fig. 2). More specifically, for Case 1 and Case 2, at 23 g TS/L, the energy required for heating the sludge was 884 kWh/t and 761 kWh/t of dry solids, respectively. At a higher solids concentration (44 g TS/L), comparatively lower amount of energy was required to heat the sludge to 35°C. This was attributed to the need to the heat a smaller sludge volume at high solids concentrations. For example, at 23 g TS/L, it is necessary to heat 1739 m^3/day of sludge, whereas, at 44 g TS/L, only 909 m^3/day is required.

3.3 Effects of solids concentrations on energy requirements and GHG emissions

3.3.1 Effects of solids concentration on the net energy

The total energy input (for sonication, anaerobic digestion, dewatering, transportation and land application), energy recovered and the net energy recovered, corresponding to different specific energy inputs during sonication for 23, 33 and 44 g TS/L, are presented in Figure 3a, 3b, and 3c, respectively. With the increase in the total energy input, the energy recovered also increased compared to the control (without sonication), irrespective of the solids concentration. For example, at 23 g TS/L, for the control, the energy recovered was 993 kWh/t of dry solids, for SE 1226 kJ/kg TS the energy recovered was 1570 kWh/t of dry solids, and for SE 13070 kJ/kg TS, it was 2508 kWh/t of dry solids. Due to the high volatile solids degradation, methane generation increased, along with the recovered energy. However, for a small increase in the total energy input, there was no increase in the energy recovery. In other words, for a specific energy input of 3457 and 3678 kJ/kg TS, the energy recovered remained constant (Fig. 3a), as the volatile solids reductions remained constant (Table 2).

The net energy (energy recovered − total energy input) at different specific energy inputs during sludge sonication for different solids concentrations revealed that, at low solids concentrations, the net energy was negative. This is due to the fact that, at low solids concentrations (corresponding to high sludge volume), the energy required to heat the sludge is very high (Fig. 2) compared to the energy recovered. At low solids concentrations (23 g TS/L), with the increase in specific energy input during sonication, the energy balance was increasingly negative (Fig. 3a). However, considering the 10°C increase in the temperature of the ultrasonicated sludge, higher net energy was observed at all solids concentrations. At higher solids concentrations and lower specific energy inputs during sonication, the net energy was positive (Fig. 3c). For example, at 44 g TS/L, the net energy for the control was -131.4 kWh/t TS, and at the specific energy input of 641 kJ/kg TS, the net energy was 459.5 kWh/t TS with no increase in the sonicated sludge temperature. With the temperature increase of 10°C during sonication, the net energy increased to 724.69 kWh/t TS. However, at a higher specific energy input (5420 kJ/kg TS), the net energy became negative (-925.8 kWh/t TS).

At 33 g TS/L, the net energy was negative for the control. More specifically, the net energy was -309.44 kWh/t TS of the control and -496.49 kWh/t TS at the specific energy input of 3135 kJ/kg TS for a 0°C increase in the sonicated sludge temperature. However, considering the sonicated sludge temperature increase of 10°C, the net energy was comparatively higher, but still negative (-142.95 kWh/t TS). The data for specific energy inputs are available only at high energy inputs, when the net energy is negative. Therefore, further experiments are required at lower specific energy inputs and at 33 g TS/L to evaluate the domain of positive net energy with respect to the input energy for sonication. Moreover, an increase in the energy input increases the solids solubilization; however, beyond a certain energy input (optimum), there is no impact on sludge solubilization. Therefore, at high solids concentrations with low specific energy inputs during sonication, the net energy balance is positive (Fig 3c).

3.3.2 Effects of solids concentrations on the energy ratio

The energy ratio (energy output/energy input) at different specific energy inputs for different solids concentrations is presented in Figure 4a, 4b, and 4c. The energy ratio for the sonicated sludge was greater than the control at all solids concentrations. On the other hand, as the specific energy input increased, the energy ratio became lower than that obtained for the control. For example, with the specific energy input of 10370 kJ/kg TS and at the solids concentration of 23 g TS/L, the energy ratio was 0.55 (ultrasonicated), whereas the energy ratio for the control was 0.58. Similarly, at 44 g TS/L, the energy ratio was more than one up to specific energy input of 1923 kJ/kg TS during sonication (Figure 4c). Moreover, an increase in the sludge temperature after ultrasonication increased the energy ratio irrespective of the solids concentration and the energy input. For example, at the specific energy input of 641 kJ/kg TS and 44 g/L TS, the energy ratio was 1.37 (Case 1) and 1.74 (Case 2) (Fig 4c). At a higher specific energy input, the energy ratio was less than one, irrespective of the solids concentration (Figure 4a, 4b, and 4c). As mentioned above, at the solids concentration of 33 g TS/L, low specific energy input data need to be generated. Therefore, the low specific energy input during sonication and high solids concentrations should be preferable for achieving a positive net energy balance or an energy ratio greater than one.

3.3.3 Effects of solids concentrations on GHG emissions

The total GHG emissions at different specific energy inputs during sonication and for different solids concentrations are presented in Figure 5a, 5b, and 5c. As can be seen, an increase in the specific energy input increased the energy demand, but did not generate a corresponding high amount of methane, which substantially enhanced the total GHG emissions irrespective of specific energy input during sonication and sludge solids concentration (Figure 5). Comparing the effects of temperature (Case 1 and Case 2) on the GHGs, it is clear that considering the increase in sludge temperature after sonication (Case 2) will reduce the GHGs (Figure 5). For example, at the specific energy input of 1226 kJ/kg TS and the sludge solids concentration of 23 g/L TS, the GHGs produced in Case 2 are reduced by 37.7%, compared to Case 1. Similarly, at a high solids concentration (44g TS/L) for the specific energy input of 641 kJ/kg TS, the GHG emissions were reduced by 34% (Case 2). Moreover, it is also evident that, at low specific energy inputs and high solids concentrations, GHGs are reduced compared to the control (Figure 5).

Based on the maximum sludge biodegradability during ultrasonication, Pham and coworkers [14] concluded that 23 g TS/L with 10362 kJ/kg TS energy input during ultrasonication was the optimum condition. The amount of methane generated (11804 m^3, Table 2) under these conditions (as computed in this work) was also the greatest. However, this study has established that, when considering the mass-energy balance of ultrasonicated as well as non-sonicated sludge followed by anaerobic digestion (considering the biodegradability or volatile solids degraded) and downstream steps (sludge dewatering, transportation and land application of the digestate) at the solids concentration of 44 g TS/L and at a lower specific sonication energy input (641 kJ/kg TS), a positive energy balance can be achieved, with the energy ratio greater than one and reduced GHG emissions. Therefore, making conclusions based solely on biodegradation and the increase in methane generation may be misleading with respect to the energy recovery, the energy ratio and GHGs emissions.

4. CONCLUSION

Computations based on the data reported in the extant literature revealed that there was no correlation between ultrasonication power input and the increase in the sludge temperature. The theoretical calculations performed in this work demonstrated that the percentage of power utilized to increase sludge temperature during sludge ultrasonication was the lowest. Mass-energy balance of ultrasonication, AD, dewatering, transportation, and land application of sludge reveal that high solids concentrations (44 g TS/L) and low ultrasound energy inputs (641 kJ/kg TS) were favorable. The net energy and the energy ratio of the ultrasonicated sludge were greater than those obtained for the control at all solids concentrations (23, 33 and 44 g TS/L). When the effect of the sludge temperature increase of 10°C during ultrasonication was assessed, both the net energy and the energy ratio increased. The GHG emissions are reduced at high solids concentrations (44 g TS/L) and low ultrasound energy inputs (641 kJ/kg TS). GHG emissions are also reduced when the sludge temperature is increased after ultrasonication.

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Table 1. Operating parameters considering in evaluating mass-energy balance and GHGs

Parameter	Value	Unit	Reference
Mass of sludge to be treated	40000	Kg dry TS /day	Assumed
Total solids concentration	23, 33, 44	g TS/L	
Specific energy input at 23 g TS/L			
(i) 20 min sonication time 0.27 W/ cm^2	1226	kJ/kg TS	[14]
(ii) 40 min sonication time 0.75 W/ cm^2	3457		
(iii) 60 min sonication time 0.27 W/ cm^2	3678		
(iv) 60 min sonication time 0.75 W/ cm^2	10370		
Specific energy input for 33 g TS/L			
(v) 40 min sonication time 0.52 W/ cm^2	3235	kJ/kg TS	[14]
Specific energy input for 44 g TS/L	641	kJ/kg TS	[14]
(vi) 20 min sonication time 0.27 W/ cm^2	1807		
(vii) 20 min sonication time 0.75 W/ cm^2	1923		
(viii) 60 min sonication time 0.27 W/ cm^2	5421		
60 min sonication time 0.75 W/ cm^2			
Temperature of			
Control sludge	10	°C	
Sonciated sludge	20	°C	Assumed
Anaerobic digestion temperature	35	°C	[30]
Density of sludge	1000	Kg/m^3	[30]
Heat loss during anaerobic digestion	150.84	kJ/day m^3 of reactor volume	[30]
Mixing and pumps power requirement : Control	10	W/ m^3 reactor volume	[9, 31]
Sonicated sludge	6.5		
Methane production rate for control	0.499	m^3 CH_4/kg VS destroyed	[9, 32]
Methane production rate for sonicated sludge	0.73		[9, 32]
Heating value of methane	31.79	MJ/m^3 CH_4	[30]
Volumetric mass of methane	0.714	kg CH_4/m^3	[30]
Energy required for land application		kWh/Mg of dry solids	[33]
Land application of sludge			
CH_4 emissions	3.18	kg CH_4/Mg of dry solids	[31]
CO_2 emissions	17.2	kg CO_2/Mg of dry solids	[1,26]
N_2O emissions	0.03	Mg of CO_2 equivalent/Mg of dry solids	[1,34]

Note : Global warming potential for CH_4 and N_2O used was 28 and 265 respectively

Table 2. Mass balance of control and sonicated sludge at different solids concentration

Description	23 g TS/L					33 g TS/L		44 g TS/L				
	Specific energy input (kJ/kg TS)					Specific energy input (kJ/kg TS)		Specific energy input (kJ/kg TS)				
	0	1226	3457	3678	10370	0	3235	0	641	1807	1923	5421
Mass of dry solids (kg) entering AD	40000					40000		40000				
%Volatile solids degradation at HRT 20 days	37.4	41.3	42.6	42.6	66	37.90	44.63	36.2	44.8	43.2	42.5	43.4
Volume of methane Produced (m^3)	4673	7387	7619	7619	11804	4736	7982	4523	8013	7726	7601	7762
Weight of Volatile degraded during AD (kg)	9163	10118	10437	10437	16170	9286	10934	8869	10976	10584	10413	10633
Digestate dry solids remaining after centrifugation, which will be transported and land applied	30837	29882	29563	29563	23830	30714	29066	31131	29024	29416	29587	29367

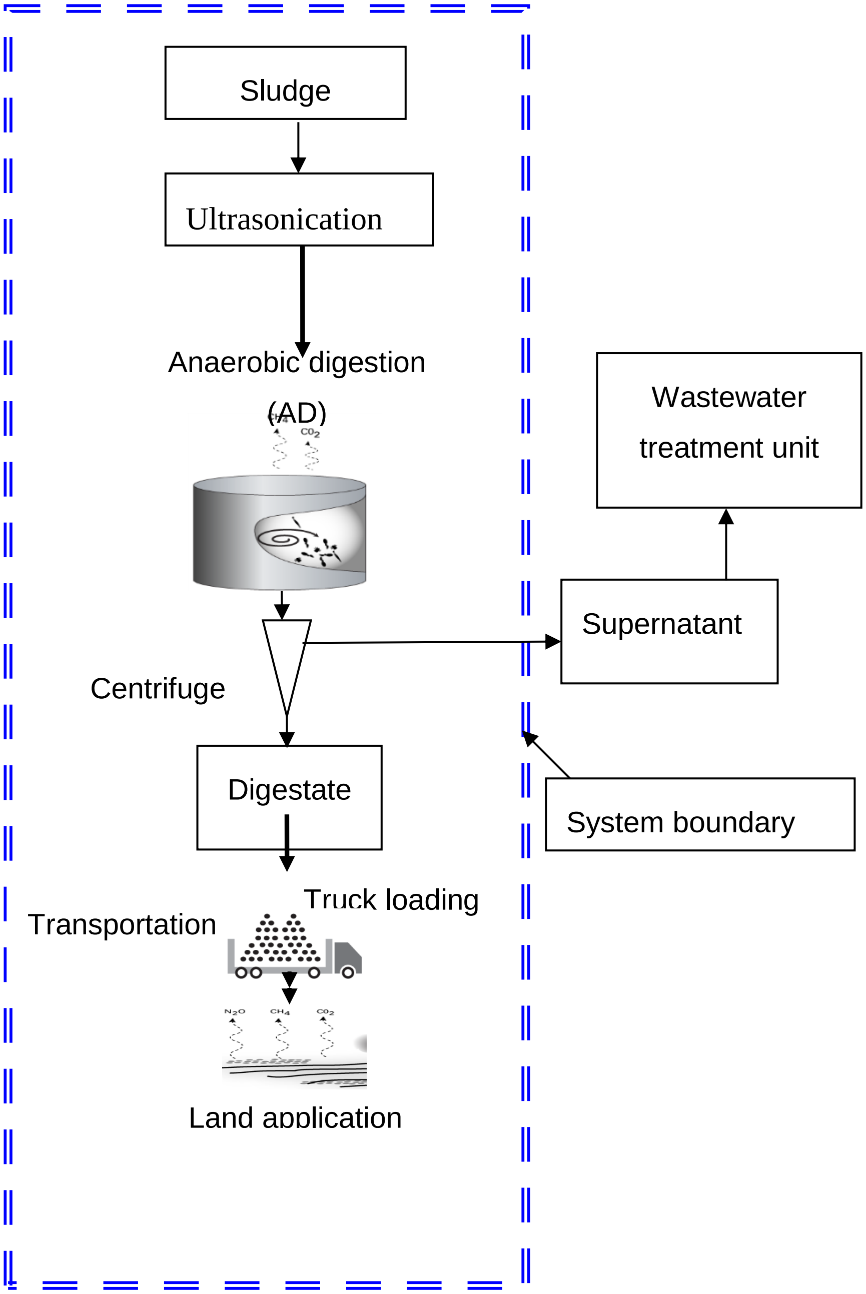

Figure 1. Pathway (or system boundary) considered for evaluting mass-energy balance and GHGs

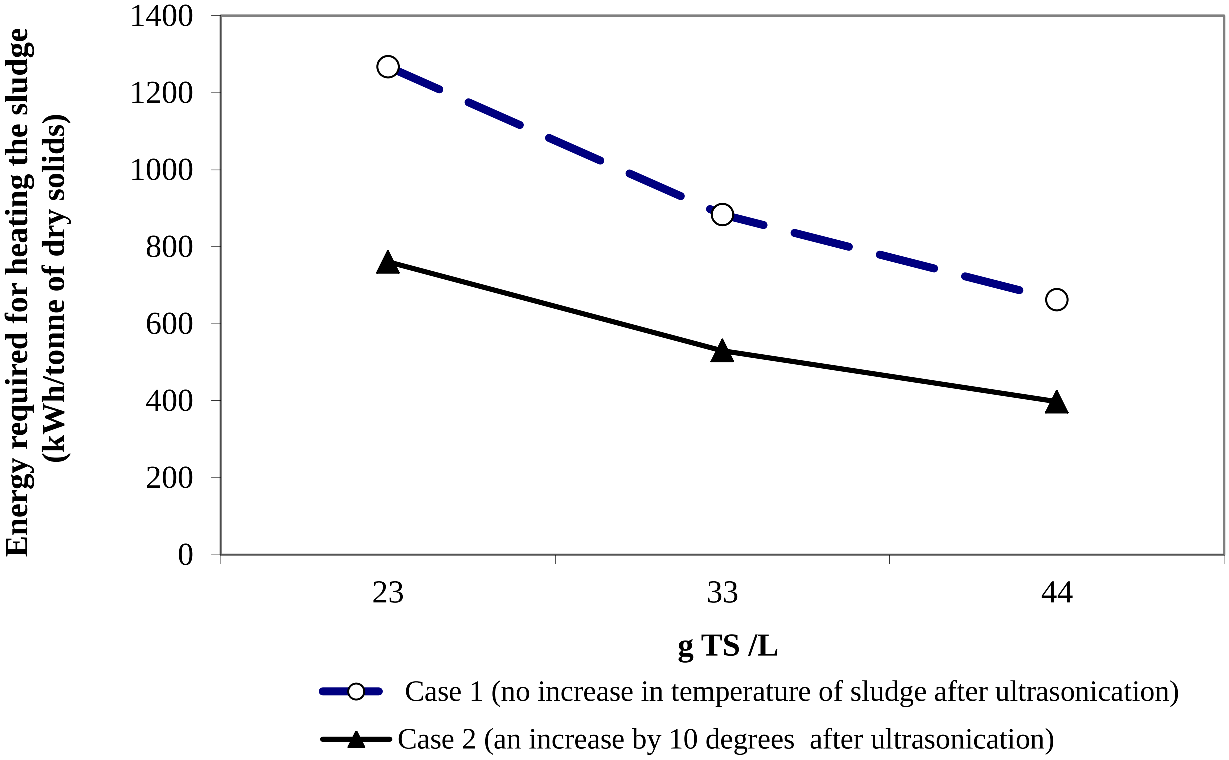

Figure 2. Effect of rise in sludge temperature during ultrasonication on the energy requirement for heating the sludge to 35°C required for AD

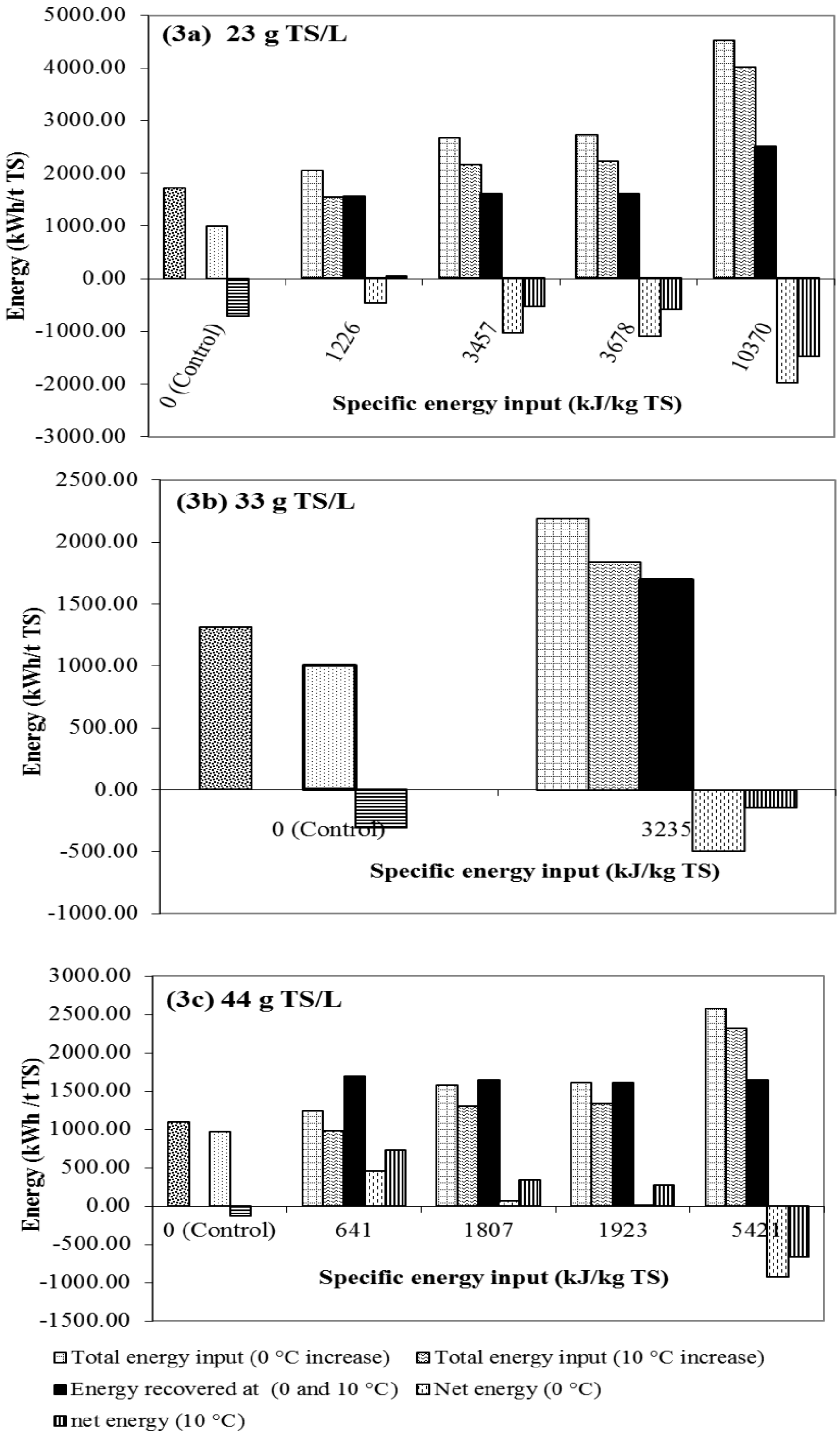

Figure 3. Effect of increase in temperature during ultrasonication

Note: case 1 no increase in temperature of sludge after ultrasonication; Case 2 an increase by 10 degree after ultrasonication

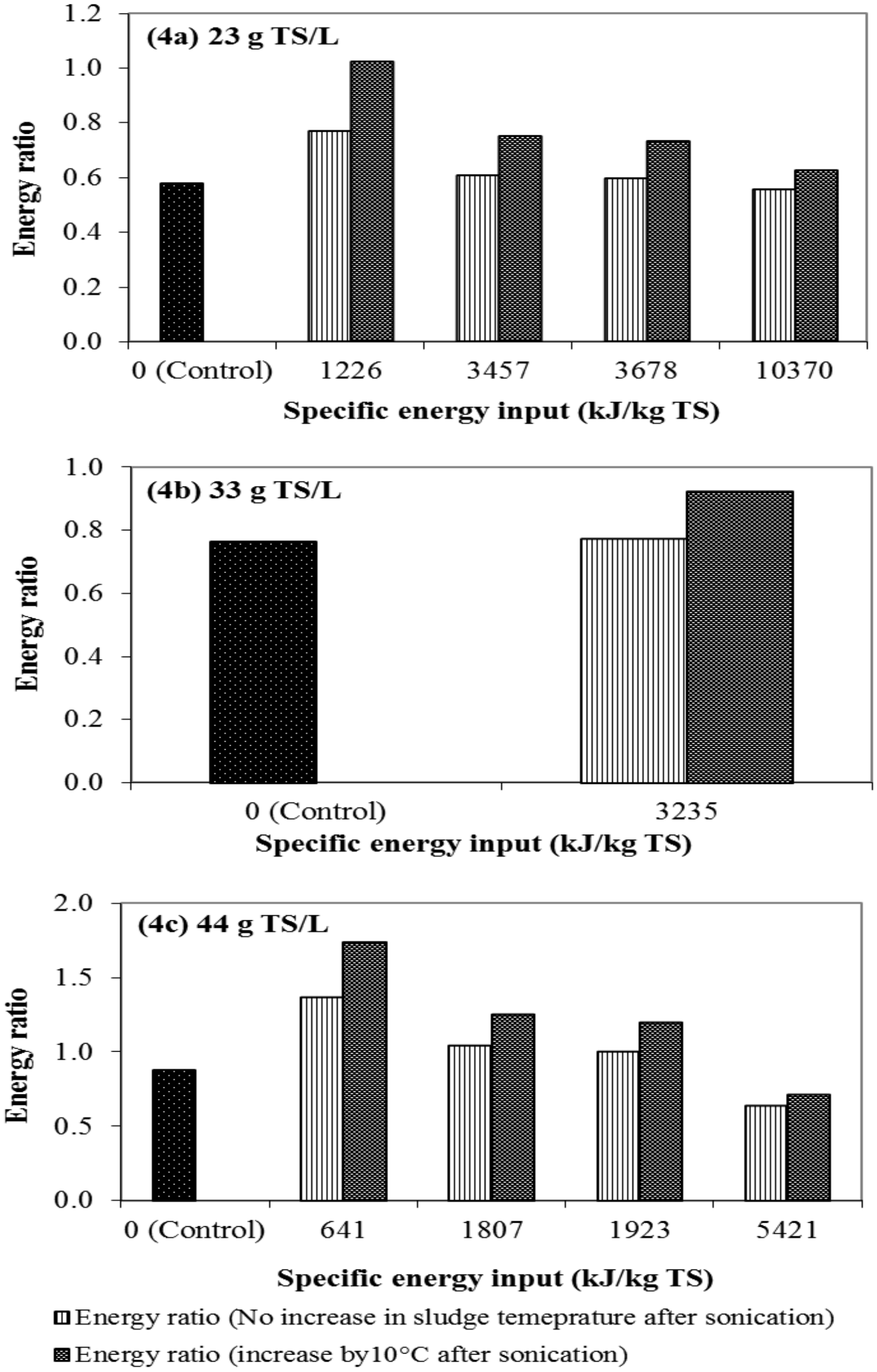

Figure 4. Effect of rise in temperature during ultrasonication on the energy ratio at different solids concentration and at different specific energy input during ultrasonication

Note: case 1 no increase in temperature of sludge after ultrasonication; Case 2 an increase by 10 degree after ultrasonication

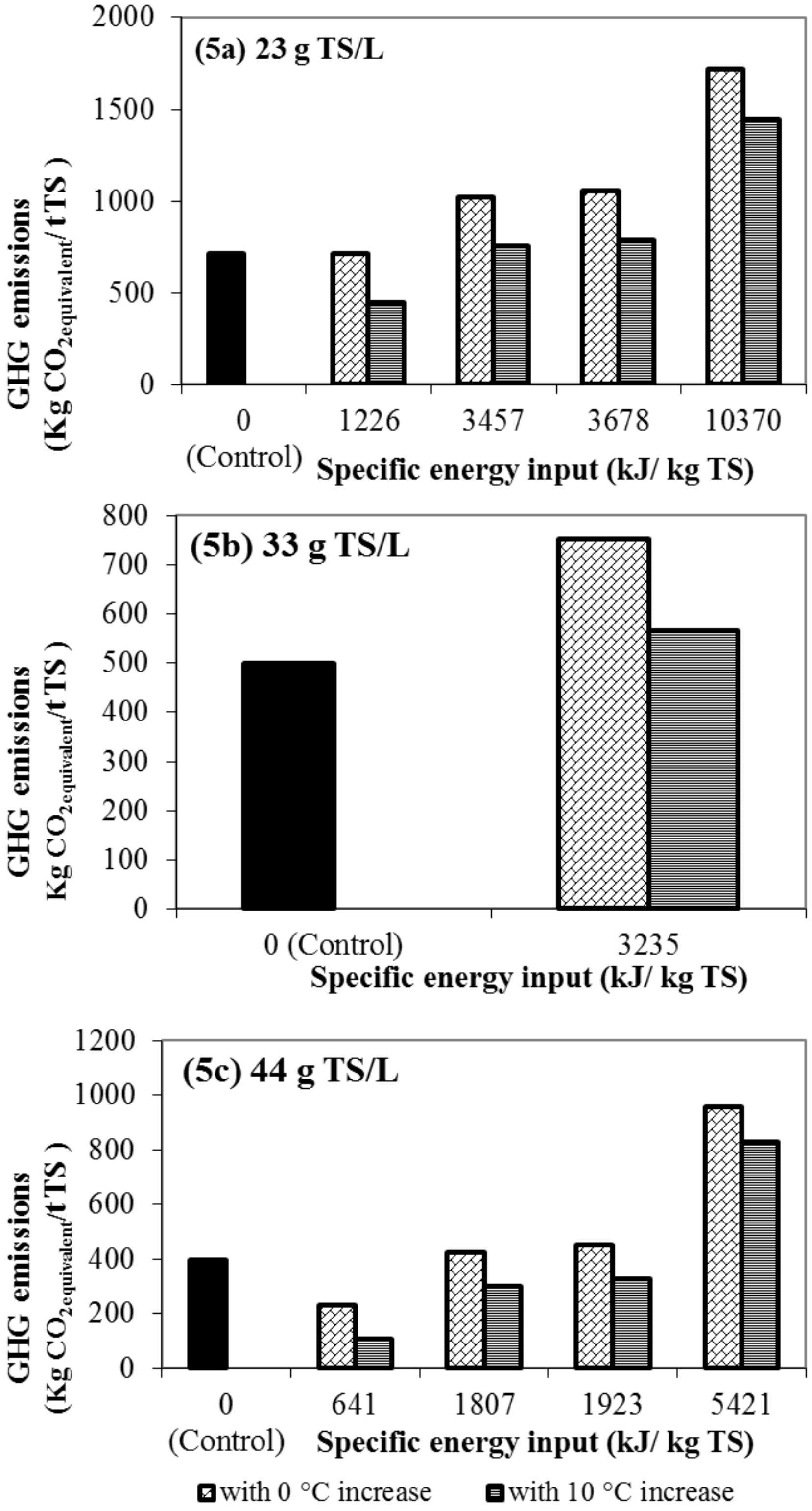

Figure 5. Effect of rise in temperature during ultrasonication on the GHG emissions at different solids concentration and at different specific energy input during ultrasonication

PARTIE 3

ANAEROBIC DIGESTION OF ULTRASONICATED SLUDGE AT DIFFERENT SOLIDS CONCENTRATIONS - COMPUTATION OF MASS-ENERGY BALANCE AND GREENHOUSE GAS EMISSIONS

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RÉSUMÉ

Les effets du prétraitement aux ultrasons sur la digestion anaérobie (DA) ont été étudiés pour les boues issues du traitement des eaux usées municipales (primaires, secondaires et mixtes) et ayant différentes concentrations en solides totaux. En outre, le prétraitement aux ultrasons, la DA et le processus d'élimination ont été évalués sur la base du bilan massique d'énergie et de gaz à effet de serre correspondants (GES). La dégradation des solides présents dans la boue secondaire traitée aux ultrasons était de 60,07% et de 51,43% pour le contrôle pour un temps de rétention de 30 jours. Le bilan de masse a révélé que la boue secondaire prétraitée aux ultrasons à une concentration de 31,45 g ST/L produit un digestat minimum (20,2 Mg de boues sèches) devant être déshydratés, transportés et épandus. À 31,45 g ST/L (boues secondaires traitées aux ultrasons), une énergie nette (énergie de sortie-énergie d'entrée) maximale de 7,89 kWh/Mg de solides totaux secs (TDS) et un ratio d'énergie (sortie/entrée) de 1,0 ont été observés. Une diminution des émissions de GES a été mise en évidence avec l'augmentation de la concentration en solides totaux présents dans la boue (soit 40 g ST/L < 30 g ST/L < 20 g ST/L). Des émissions de GES minimales de 339,6 kg CO_2/Mg de TDS ont été observées à une concentration en solides de 42,06 g ST/L pour les boues secondaires. Le prétraitement aux ultrasons est efficace et bénéfique pour l'amélioration de l'efficacité de la DA des boues secondaires.

Mots-clés: ultrasonication; digestion anaérobie; bilan masse-énergie; émissions de gaz à effet de serre.

ABSTRACT

Two cases of anaerobic digestion (AD) of sludge, namely (i) with pre-treatment and (ii) without pre-treatment, were assessed using mass-energy balance and the corresponding greenhouse gas (GHG) emissions. For a digestion period of 30 days, volatile solids degradation was 51.4% for the control (without ultrasonication) and 60.1% for the ultrasonicated sludge, respectively. Mass balance revealed that the quantity of digestate required for dewatering, transport and land application was the lowest (20.2×10^6 g dry sludge/day) for ultrasonicated secondary sludge at 31.4 g TS/L. Furthermore, for ultrasonicated secondary sludge at 31.4 g TS/L of total dry solids (TDS), the maximum net energy (energy output − energy input) was 7.89×10^{-6} kWh/g and the energy ratio (output/input) was 1.0. GHG emissions were also reduced (i.e., at 40.0 g TS/L < at 30.0 g TS/L < at 20.0 g TS/L) with the increase in the sludge solids concentration. Ultrasonication pre-treatment proved to be efficient and beneficial for enhancing anaerobic digestion efficiency of the secondary sludge when compared to the primary and mixed sludge.

Keywords: ultrasonication, anaerobic digestion, mass-energy balance, greenhouse gas emissions.

1. INTRODUCTION

In the last two decades, biomass has been the most commonly used renewable source for energy production. Sludge is a biomass produced during primary, secondary and tertiary treatment of municipal wastewater. It is also used as a valuable resource for renewable energy production. Sewage sludge is produced in large quantities around the world. In the USA, approximately 6.2×10^{12} g of dry sewage sludge is produced annually (Karbo, 2010). Sludge quantity is expected to increase in the future due to the population growth and increasingly stringent environmental regulations. Wastewater sludge without proper treatment and disposal poses a great danger to the environment. Moreover, sludge biomass is converted to carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) (three principal greenhouse gases (GHGs)) during sludge treatment, disposal and/or reuse. The treatment and disposal of sludge accounts for around 50-60% of the total wastewater treatment plant (WWTP) operating costs (Coma et al., 2013). Sludge management accounts for approximately 40% of the GHG emissions from a WWTP (Brown et al., 2010). Moreover, global warming and climate change have made it important to quantify GHG emissions from each and every source, along with implementing necessary strategies for reducing these emissions.

Anaerobic digestion (AD) of sludge is the most commonly used biological process to generate renewable energy, reduce sludge quantity and decrease GHG emissions. Recovery of energy from the produced biogas will offset fossil fuel usage and decrease GHG emissions. AD of sludge is the microbial degradation process that converts biodegradable organic compounds to CH_4 and CO_2 in the absence of oxygen. The degradation process occurs in four steps, comprising of hydrolysis, acidogenesis, acetogenesis and methanogenesis. Among these four steps, biological hydrolysis has been identified as the rate-limiting step due to the non-availability of the biodegradable organic matter in the sewage sludge. This results in longer hydraulic retention time and greater digester volume, as well as produces a lesser volume of biogas, which are all considered the prime drawbacks of the current AD technology (Carrere et al., 2010). Therefore, to enhance the biodegradability and to reduce the retention time, various pre-treatment processes have been studied (Carrere et al., 2010). During the pre-treatment, three specific stages occur, (1) rupture of sludge floc, (2) cell lysis and release of intracellular matter, and (3) breakage of intracellular matter into proteins, lipids, carbohydrates, etc. (Pilli et al., 2011). Liberating the intracellular matter fractions of sludge into the aqueous phase increases its biodegradability and AD efficiency (enhanced biogas production).

Among various sludge pre-treatment methods, sludge ultrasonication followed by AD proved to be the most promising sustainable technology for sludge treatment with increased biogas production and higher solids reduction (Carrere et al., 2010; Dhar et al., 2012). Ultrasonication pre-treatment increases biogas production (Carrere et al., 2010). However, it is not entirely clear whether the energy produced from the biogas will correspond to the energy input for the treatment process (ultrasonication pre-treatment, AD, dewatering, and land application). Thus, sludge management processes (ultrasonication pre-treatment followed by AD, dewatering, and land application) need to be evaluated based on the net energy (energy output − energy input) or energy ratio (energy output/energy input). The mass-energy balance and GHG emissions will also help the decision-makers in identifying the most optimal system in line with the local legislation and economical reasons. The energy input for ultrasonication, required for increasing sludge temperature to the digestion temperature (35°C), transportation and land application of the digestate will influence the energy balance (Pilli et al., 2011). Increase in the sludge temperature during ultrasonication has thus far not been considered when evaluating the pre-treatment process efficiency (Barber, 2005; Salsabil et al., 2010).

Thus, given these shortcomings, the primary goal of this research was to evaluate the effectiveness of the sludge ultrasonication pre-treatment (primary, secondary and mixed sludge) used for enhancing the AD efficiency by computing the energy balance and the corresponding GHG emissions. Moreover, the effect of different solids concentrations on the sludge management process was also evaluated (Fig. 1).

2. EXPERIMENTAL SETUP AND PROCEDURE

2.1 Wastewater sludge

Wastewater sludge used in the study was collected from the wastewater treatment facility, Communauté urbaine de Québec (CUQ) (Beauport, Québec City, Canada). Sludge total solids (TS) were concentrated by gravity settling, followed by centrifugation at 1600 × *g* for 3 min in a Sorvall RC 5C, plus Macrocentrifuge (rotor SA-600). Different concentrations (20.0, 30.0 and 40.0 TS g/L) were obtained by diluting the concentrated sludge with demineralized water, which was later homogenized in a WaringTM blender for 30 seconds. Handling sludge was difficult at above 40.0 TS g/L, because its viscosity was very high at high solids concentrations. The characteristics of the sludge used in this work (without pre-treatment) are presented in Table 1.

2.2 Ultrasonication

Sludge with different total solids concentrations (20.0, 30.0 and 40.0 g/L) was ultrasonicated using ultrasonic homogenizer Autotune 750 W (Cole-Parmer Instruments, Vernon Hills, IL, US). The available operating frequency of the ultrasonic equipment was 20 kHz. The platinum probe with a tip diameter of 25 mm was used and the length of the probe dipped inside the sludge volume was 2 cm (Pham et al., 2009). Sludge volume of 200 mL was taken in a 500 mL beaker for ultrasonication. The preliminary experiments were conducted to evaluate the increase in temperature of the secondary sludge after ultrasonication without temperature control. The specific energy input (SE) required during ultrasonication was calculated according to the Eq. 1 (Pham et al., 2009).

$$SE = \frac{\mathrm{P\,.\,t}}{\mathrm{V\,.\,TS}} \qquad (1)$$

Where *SE* is the specific energy input kJ/kg TS, P is the power input (kW), t is the ultrasonication time (s), V is the volume of sludge (L), and TS is the total solids concentration (g/L).

2.3 Anaerobic digestion of the pre-treated and non pre-treated sludge

Sludge (with and without pre-treatment) volume of 0.75 L was inoculated with 0.05 L of anaerobic sludge collected from the anaerobic digester (Valcartier, Québec, Canada). The anaerobic sludge was collected in tanks and stored at 4°C prior to use. AD was performed in 1 L septic bottles placed in a water bath at 35°C. The working volume of each bottle was 0.80 L. The water level in the water bath was adjusted to the sludge height in the bottles. In order to maintain anaerobic conditions, the air from the headspace of the bottles was removed by sparging the nitrogen gas through sludge for 2 min. The bottles were mixed manually (twice a day) to minimize the effects of settling during AD. The initial pH of sludge was adjusted to 7 using NaOH solution (4 N). The AD was conducted for 30 days. The digested sludge samples of the control and the ultrasonicated sludge were taken on the 5th, 10th, 15th, 20th and 30th day to evaluate the total solids (TS), volatile solids (VS), suspended solids (SS), and volatile suspended solids (VSS) degradation. Sample volume of 0.07 L was collected at 0, 120, 240, 360, 480 and 720 hours for the analysis by transferring the digested solids into a measuring cylinder with the minimum exposure time of 15 s. Nitrogen gas was immediately sparged into bottles for 2 min to maintain anaerobic conditions for further AD.

2.4 Dewaterability

Capillary-suction-time (CST) was used to measure the dewaterability. CST was determined by using the CST instrument (Triton electronics, model 304 M CST, Dunmow, Essex) with a 10-mm diameter reservoir (Scholz, 2006). The CST values of the raw sludge, ultrasonicated sludge and anaerobically digested sludge were evaluated.

2.5 Sludge disposal

Land application of dewatered sludge was considered as a disposal option in this study (Fig. 1). A distance of 50 km between the WWTP and the land application site was considered (usually 80.0% of agricultural lands are located no more than 50 km away from a WWTP (Gassara et al., 2011)) when evaluating the energy input and the corresponding GHG emissions. For transporting dewatered sludge, using 3-axle semi-trailer vehicles, 35.0 L of diesel/100 km was required (Gassara et al., 2011). The GHG emission values corresponding to diesel consumption were equivalent to 2730.0 g CO_2/L, 12.0 × 10^{-2} g CH_4/L, and 8.0 × 10^{-2} g N_2O/L (Gassara et al., 2011). Furthermore, during the energy balance, 351.7 × 10^{-6} kWh/g of TDS (Wang et al., 2008) was used as the energy required during land application of dry solids of the digestate.

2.6 Mass-energy balance

Mass balance was evaluated by measuring the total mass entering the anaerobic digester and the corresponding mass that was converted into biogas and the remaining digestate transferred for dewatering and land application. The energy balance was evaluated for the process depicted in Fig. 2. The parameters used for evaluating the energy balance are discussed below.

Total energy input = ∑energy content of fuels, electricity, and steam used in different processes (ultrasonication, AD, dewatering, transportation and land application).

Energy output = Energy obtained from methane produced using combined heat and power generation unit.

The efficiecny of combined heat and power plant is up to 90% (i.e., 35% electricty and 65% heat) (Al Seadi, 2008)

Net energy = energy output - energy input (2)

Energy ratio = energy output/energy input (3)

2.7 GHG emissions

The energy required for ultrasonication pre-treatment, AD, dewatering, truck loading, transportation and land application was generated from the fossil fuels, which contribute to the GHG emissions, and are considered their major sources. GHG emissions corresponding to energy utilization in the various process steps (Fig. 2) were computed using national emission intensity coefficient 530.0 g CO_2/kWh (developed by Environment Canada study based on the Resources for the Future (RFF) model). During anaerobic digestion, sludge biomass is biodegraded to CO_2 and CH_4. CO_2 emissions from the biological pathway were considered biogenic emissions and are not taken into account in national protocols due to the fact that they are considered (by convention) as “carbon neutral” (with the global warming potential equal to zero) (Pradel and Reverdy, 2012). However, the CO_2 produced (Eq. 4) during the methane combustion was considered. Land application of digestate produces CO_2, CH_4, and N_2O. The factors for estimating CO_2, CH_4, and N_2O emissions due to the land application were evaluated by Brown et al. (2010), who reported 25.0×10^{-2} g CO_2 per g of TDS (i.e., carbon sequestration due to land application of sludge), 7.0×10^{-2} g CO_2 equivalent per g of TDS, and 3.0×10^{-2} g CO_2 equivalent per g of TDS, respectively.

$CH_4 + 2\ O_2 \text{ ---->} CO_2 + 2\ H_2O + \text{energy}$ (4)

2.8 Analytical methods

The analysis of the TS, VS, SS, VSS, pH, nitrogen, phosphorus, total carbon, total and soluble chemical oxygen demand (SCOD), and total chemical oxygen demand (TCOD) were carried by applying the standard methods (APHA, 2006). These parameters were measured for raw, ultrasonicated, digested and dewatered sludge. The biogas produced during the AD process was collected and analyzed using Gas chromatograph (Shimadzu GC 14A) as per Cui and Jahng (2006). The biogas volume was measured based on the water displacement (Fig. 1). The energy recovered from the methane gas generated during AD was evaluated using the heating value of methane, which is equal to 35.8 MJ/m^3 CH_4 (Tervahauta et al., 2014).

3. RESULTS AND DISCUSSION

3.1 Increase on temeprature of sludge after ultrasocniation

Sludge temperature increase during ultrasonication at various sonication times (ranging from 5 to 30 min) is presented in Fig. 3. As can be seen, in general, sludge temperature increased gradually as the ultrasonication time increased. In fact, the increase in sludge temperature during ultrasonication was directly proportional to the sonication time (Fig. 3), which is in line with the values reported in extant literature. For example, Chu et al. (2001) reported a temperature increase from 4°C to above 60°C after 120 min of sonication. In addition, the rise in sludge temperature at different solids concentrations followed the 20.0 g TS/L > 30.0 g TS/L > 40.0 g TS/L pattern. At a high solids concentration (40.0 g TS/L), sludge temperature in the beaker was not uniform after ultrasonication. Moreover, the temperature of sludge adjoining the surface of the horn was higher; while that at the periphery of the beaker was lower (a temperature difference of 8°C was observed between the center and the periphery of the sample after ultrasonication). This difference is due to the attenuation effect at high solids concentrations (40 g TS/L) (i.e., the ultrasonic waves decay as they propagate through the material). In another study, the authors reported that the effect of ultrasonication on sludge solubilization deteriorated at high solids concentrations (Mao et al., 2004). Moreover, Pilli et al. (2011) reported that the rise in sludge temperature above 60°C would decrease the ultrasonication efficiency. In this experiment, sludge temperature increased above 50°C after 15 min of ultrasonication (Fig. 3). Therefore, ultrasonication time of 15 min was considered in this study. The power input (kJ) value for 15 min ultrasonication was recorded by the ultrasonication instrument.

3.2 Effect of ultrasonciation on sludge solubilisation at different solids concentration

The variation in SCOD due to ultrasonication (of 15 min duration) was observed for the primary, secondary and mixed sludge at different solids concentrations and was summarized in Fig. 4. In general, after ultrasonication for 15 min, the SCOD increased irrespective of the type of sludge and the sludge solids concentration (Fig. 4a-c). In the primary sludge, increasing the solids concentration from 20.0 to 30.0 and 40.0 g TS/L increased the SCOD by 1.14 and 1.12 times, respectively. The SCOD/TCOD ratio increased from 0.04 to 0.12, 0.03 to 0.08, and 0.02 to 0.06, at 20.0, 30.0 and 40.0 g TS/L, respectively. The SCOD/TCOD ratio denotes the release of organic matter from a solid phase to the aqueous phase (Grübel and Suschka, 2014). In the primary sludge, increasing the amount of solids did not increase the SCOD/TCOD ratio. For the secondary and mixed sludge, the SCOD and the SCOD/TCOD ratio increased after ultrasonication. Similar to the primary sludge, for the secondary and mixed sludge, the SCOD/TCOD ratio did not increase with an increase in the solids concentrations. Thus, these results confirm that ultrasonication pre-treatment increases the SCOD, irrespective of the type of sludge (Fig. 4). The increase in SCOD, after ultrasonication, was mainly due to the release of intracellular matter from the cells into the aqueous phase due to the cell lysis (i.e., organic matter progressed from solid to aqueous phase). At ~20.0 g TS/L, the SCOD increased by 2.7, 3.6 and 3.3 times for primary, secondary and mixed sludge, respectively, (Fig. 4) after ultrasonication. Compared to the primary and mixed sludge, the SCOD increase was higher for the secondary sludge, due to the higher organic matter content (proteins, carbohydrates, humic substances, nucleic acids, etc.) in the latter (Smith et al., 2009). More efficient disintegration (i.e., 33% increase compared to the control) was observed in the secondary sludge (Neis et al., 2000; Na et al., 2007).

The SCOD/TCOD ratio increased from 0.02 to 0.10 for the secondary sludge at 31.4 g/L, after ultrasonication. The increased SCOD/TCOD ratio represents the increase in the organic matter content from the solid phase to the aqueous phase. Mao et al. (2004) observed that, after 20 minutes of sonication (0.44 W/mL), the SCOD increased from 1.02 mg/L to 3.98 g/L and from 0.67 mg/L to 5.26 mg/L for primary and secondary sludge, respectively. At high solids concentrations, attenuation effects (when the prorogation of ultrasonication waves is restricted) decrease the breakdown of cell walls (Pilli et al., 2011). In the primary and the secondary sludge, at high solids concentrations of 3.6 and 3.7% (w/v), ultrasonication effect was weak due to the attenuation effect (Mao et al., 2004).

Na et al. (2007) reported that the disintegration of sludge (cell lysis) increased with the increase in specific energy input. In this study, specific energy input decreased with the increase in solids concentrations (i.e., for the primary sludge, the specific energy input at 20.0, 30.0 and 40.0 g TS/L was 8543, 5617 and 4396 kJ/kg TS, respectively). The effect of each parameter on SCOD solubilization follows the sludge pH > sludge concentration > ultrasonication intensity > ultrasonic density pattern (Pilli et al., 2011). Therefore, to enhance the solubilization at high solids concentrations, high specific energy input is required.

The variations in SS and VSS for primary, secondary and mixed sludge, due to ultrasonication, at different solids concentrations are presented in Fig. 5. In general, the SS and VSS decreased with ultrasonication, irrespective of the sludge type and solids concentration. Comparing the effect of ultrasonication on SS solubilization at solids concentrations 30.0 and 40.0 g TS/L, the percentage SS solubilization was lower in the latter case (i.e., it decreased from 19.0% at 30.0 g TS/L to 13.0% at 40.0 g TS/L, for secondary sludge after ultrasonication). VSS solubilization showed a similar trend. Show et al. (2007) also reported SS and VSS solubilization for the ultrasonicated secondary sludge, indicating that the increase in SCOD and the SS reduction was limited at high solids concentrations. According to Pilli et al. (2011), this phenomenon was mainly due to the diminution of ultrasonication waves, which is also observed in this study (rise in the sludge temperature decreased during ultrasonication at 40.0 g TS/L, due to the diminution of ultrasonic waves).

3.3 Anaerobic digestion of sludge with different solids concentration

Degradation of solids (TS, VS, SS, and VSS) at different retention times, during the AD for primary, secondary, and mixed sludge, is presented in Fig. 6 to 8. As can be seen, in general, there was a gradual decrease in the solids concentration during the 30 days of digestion, irrespective of the type of sludge and solids concentration. In the case of the primary sludge, the decrease in the solids concentration was always enhanced for the ultrasonicated sludge when compared to the control sludge (Fig. 6). After 30 days of digestion, the VS was reduced from 23.1 to 11.4 g VS/L and from 23.1 to 10.2 g VS/L in the control and ultrasonicated primary sludge, respectively. In addition, for the ultrasonicated sludge, the VS reduction was 5.5% higher at 30.0 g TS/L when compared to the value pertaining to 20.0 g TS/L. The VS reduction diminished by -2.5% at 40.0 g TS/L when compared to the 20.0 g TS/L case. A similar trend was observed for the primary sludge (without pre-treatment). Finally, for 20.0, 30.0 and 40.0 g TS/L, the VS reduction was 15.8, 9.4 and 8.8% higher, respectively, for the ultrasonicated sludge when compared to the control sludge during five days of digestion (Fig. 7).

Similar to the primary sludge (with pre-treatment), VS degradation for the secondary and mixed sludge was enhanced with ultrasonication when compared to the control sludge, irrespective of the solids concentration. After 30 days of digestion, the VS reduction at 30.0 TS/L was 5.8% and 4.2% higher when compared to the 20.0 g TS/L for the secondary and the mixed sludge, respectively (Fig. 8). In addition, when the solids concentration was increased to 40.0 g TS/L, VS degradation was lower than that of 20 g TS/L (-1.7% and -4.1% in the secondary and mixed pre-treated sludge, respectively). A similar trend was observed for the control, secondary and the mixed sludge. The reduction in solids degradation at high solids concentrations was due to the diminution of ultrasonic waves and its effects on sludge solubilization.

For the ultrasonicated secondary sludge and the mixed sludge, the solids concentration reduction was always enhanced when compared to the control sludge during the initial five days of digestion. Volatile solids reduction was 19.0, 17.0 and 12.0% higher for the ultrasonicated secondary sludge when compared to the control sludge (without pre-treatment) at 20.0, 30.0 and 40.0 g TS/L, respectively. A similar trend was observed for the mixed sludge. Neis et al. (2000) observed increased VS degradation rate after four days of HRT compared to 16 days. Moreover, the degradation rate was increased by 30% when compared to the control sludge. Increased degradation of the ultrasonicated sludge was also observed by Theim et al. (1997). According to Mao and Show (2007), hydrolysis was rapid in the anaerobic digester fed with the ultrasonicated sludge and was mainly due to easily available degradable substrate for micro-organisms. Moreover, the contact between the biomass and substrate increased for the sonicated sludge because it was possible to overcome the inhibition of substrate diffusion across the bound biosolids (Mao and Show 2007). Therefore, the authors concluded that sludge ultrasonication enhances solids degradation and reduces the retention time.

3.4 Methane production during anaerobic digestion of different types of sludge at different solids concentration

The cumulative methane production, during a 30-day-long AD, for the control and ultrasonicated primary sludge is presented in Fig. 9a. As can be seen, the methane percentage ranges from 48.0 to 58.0%, 50.0 to 62.0%, and 51.0 to 58.0% for the primary, secondary and mixed sludge, respectively. Moreover, in both the control and ultrasonicated sludge, the cumulative methane production increased with the increase in digestion time, irrespective of the solids concentration. After 30 days of digestion, cumulative methane production for ultrasonicated primary sludge was 1.2, 1.2 and 1.1 times higher compared to the control, at 20.0, 30.0 and 40.0 g TS/L, respectively (Fig. 9a). However, during five days of retention time, at 20.0, 30.0 and 40.0 g TS/L, cumulative methane production for the ultrasonicated primary sludge was 5.29, 4.2 and 2.95 times higher, respectively, when compared to the control. Finally, cumulative methane production was lower at 40 g TS/L compare to 30 g TS/L (Fig. 9a). The solubilisation was low at higher solids concentration (40 g TS/L) due to attenuation effect.Moreover, decrease in particle size increases the diffusion of particles in the liquid ((Mao and Show 2007) and also increases the contact with micororganisms, which was not absorved at high solids concentration.

The cumulative methane production for secondary and mixed sludge is presented in Fig. 9b and c, respectively. In general, it was higher in the secondary and the mixed ultrasonicated sludge when compared to the control sludge. When compared to the control, after 30 days, cumulative methane production was 1.3, 1.5 and 1.2 times higher for the ultrasonicated secondary sludge at 20.0 30.0 and 40.0 g TS/L, respectively. Similarly, for cumulative methane production, the ultrasonicated mixed sludge was 1.3, 1.4 and 1.2 times higher when compared to the control sludge (Fig. 9c).

Similar to the primary sludge, cumulative methane production for the ultrasonicated secondary sludge and mixed sludge was higher when compared to the control sludge (without pre-treatment). More specifically, after five days of digestion, cumulative methane production was 4.0, 6.2 and 3.6 times higher for the ultrasonicated secondary sludge when compared to the control at 20.0 30.0 and 40.0 g TS/L, respectively (Fig. 9b). In addition, cumulative methane production in the secondary sludge was higher when compared to the primary sludge and mixed sludge (Fig 9b). The increased methane production in the secondary sludge is due to higher sludge solubilization during ultrasonication. Moreover, secondary sludge mainly contains microbial cells, whereas primary sludge contains fibers, inorganic materials, etc. Thus, it contains twice as much total protein when compared to the primary sludge (Wilson and Novak, 2009). Pre-treatment introduces cell matter (lipids, proteins, carbohydrates, etc.) into the liquid phase due to the breakage of flux and cell lysis. It was also reported that, by increasing the soluble organics, the ultrasonicated sludge would exhibit an enhanced diffusion of substrate among the bulk solution, particle surface area and bacteria communities (Mao and Show, 2007). For primary sludge, the biopolymers and organics are predominantly present in the solid phase, compared to the liquid phase. Finally, as, when compared to the secondary sludge, the soluble organics were not improved for the primary and the mixed sludge, the accesses of biodegradable substrate to the microorganisms was reduced.

At different sonication densities (0.18, 0.33, and 0.52 W/mL), biogas production was enhanced when compared to the control sludge (Mao and Show, 2007). For the control sludge, biogas production was 1540 mL and for the sonicated sludge at 0.18, 0.33, 0.52 W/mL, biogas production was 1840 mL, 2150 mL and 2350 mL, respectively. Tiehm et al. (2001) reported that biogas production increased from 16.0 to 122.0% due to sludge ultrasonication (after 22 days of digestion). A similar trend, i.e., from 12.0 to 69.0%, was also observed by Wang et al. (1999), after 11 days of digestion. Increasing the solids concentration had a negative effect on sludge solubilization as well as methane production. The results observed in this study correspond well with the values reported in extant literature. From the above results and discussion, it is evident that the cumulative methane production for the ultrasonicated sludge was enhanced when compared to the control sludge (without pre-treatment).

3.5 Mass-energy balance

3.5.1 Mass balance

To evaluate the mass-energy balance, a WWTP having treatment capacity of 47000 m^3 of wastewater treated per day was considered (which corresponds to Bonnybrook WWTP in Calgary, Canada). Sludge production rate during secondary wastewater treatment was considered to be 0.225×10^{-3} Mg of TDS/m^3 of treated wastewater (Ghazy et al., 2011). Thus, the quantity of secondary sludge generated per day was 40 Mg. The conclusions of the computations for the mass balance of the control sludge and ultrasonicated primary sludge at different solids concentrations are summarized in Table 2.

In general, the digestate obtained from the AD of the ultrasonicated sludge (at different solids concentrations) was lower when compared to the control (primary, secondary and mixed sludge). The digestate obtained after AD of the ultrasonicated primary sludge (at 21.2 g TS/L) was 24.02 Mg, and it was 25.46 Mg for the control sludge. A minimum quantity of the digestate (20.22 Mg of dry solids) was produced for ultrasonicated secondary sludge (SE-5742 kJ/kg TS) at solids concentration of 31.4 g TS/L, required for dewatering, transport, and land application (Table 2). Furthermore, the increase in solids concentration did not result in a reduction of the quantity of digestate. This was due to the lower solids reduction at higher solids concentrations (Table 2), i.e. the VS degradation for ultrasonicated secondary sludge was 64.2% at 42.1 g TS/L and was 56.7% at 31.4 g TS/L. From the mass balance, it is clear that ultrasonication enhanced the digestion and reduced the quantity of sludge that needs to be managed for land application.

3.5.2 Energy balance

The (i) total energy input for the ultrasonication pre-treatment, AD, dewatering, transportation and land application, (ii) the energy recovered, and (iii) the net energy values are presented in Table 3 for the primary, secondary and mixed sludge at different solids concentration. In general, for primary sludge, the net energy (at the end of 30 days of AD) was higher for the control when compared to the ultrasonicated sludge, irrespective of the solids concentration. While the total energy recovered was higher for the ultrasonicated sludge when compared to the control, the energy input was much higher for the ultrasonication pre-treatment and the net energy was thus lower. With ultrasonication, the energy required during AD, dewatering, transportation, and land application was reduced when compared to the control (irrespective of the solids concentration in the primary sludge).

The net energy for the control (after 30 days of digestion) was higher than for the ultrasonicated sludge. The energy output of the ultrasonicated secondary sludge at 31.4 g TS/L was 1915.2 kWh/Mg of TDS, while the energy input was 1907.3 kWh/Mg of TDS. In this case, both solids degradation and methane production were higher. Moreover, the energy input required for dewatering, transportation, and land application was due to the lower quantity of digestate produced. At higher solids concentration, similar trend was observed for the secondary and mixed sludge. When the values for the primary, secondary and mixed sludge were compared, a maximum net energy 7.9 kWh/Mg of TDS was observed for the ultrasonicated secondary sludge, which is primarily due to higher solids degradation and higher energy outputs.

Pre-treatment is less effective for primary sludge (Appels et al., 2008), since it contains fiber, inert materials, and other inorganic matter, which does not lead to higher methane production. Secondary sludge mainly contains organic matter, which leads to higher biogas production; therefore, the net energy was positive. For the mixed sludge, the net energy was approaching positive value at high solids concentration (31.6 g TS/L) for both the control and the ultrasonicated sludge. On the other hand, for the mixed sludge, the net energy was negative at all solids concentrations. In addition, the SCOD was not enhanced when compared to the secondary sludge. However, sludge ultrasonication enhances the organic matter solubilization and thus leads to higher methane production. Nonetheless, the energy input was higher than the energy recovered.

The energy ratio for the control (for the primary and mixed sludge) was greater than that pertaining to the ultrasonicated sludge at all solids concentrations evaluated in this study. For the primary sludge, at 21.0 g TS/L, the energy ratio was 0.48, compared to 0.37 obtained for the ultrasonicated sludge. Similarly, at 19.9 g TS/L, the energy ratio was 0.60 and 0.49, for the mixed and the ultrasonicated sludge, respectively (Table 3). For the ultrasonicated secondary sludge, at 31.4 g TS/L, the energy ratio was greater than that obtained for the control. At 31.4 g TS/L, the energy ratio for the secondary sludge (with and without pre-treatment) was 1 and 0.97, respectively. When the solids concentration was increased to 42.1 g TS/L, the energy ratio was higher for the control when compared to the ultrasonicated secondary sludge. At 41.7 g

TS/L, the energy ratio of the secondary sludge (with and without pre-treatment) was 0.86 and 0.97, respectively. During ultrasonication pre-treatment at high solids concentration, sludge solids solubilization was low, resulting in low methane production and energy output. Moreover, the energy input was very high for the ultrasonication, which resulted in lower energy ratio compared to that pertaining to the control.

The results of the energy ratio computation at different retention times are presented in Fig. 10. It is evident that the energy ratio for the ultrasonicated sludge was greater at 5, 10 15 and 20 days retention time (Fig. 10). In addition, when the retention time was increased to 30 days, with the exception of 31.4 g TS/L (for the ultrasonicated secondary sludge), the energy ratio for the control was greater than that obtained for the ultrasonicated sludge (primary, secondary and mixed sludge). As noted above, the energy ratio for ultrasonicated secondary sludge and control was 1.0 and 0.98, respectively. On the other hand, at 20-day retention time, the energy ratio for the ultrasonicated secondary sludge and control was 0.98 and 0.6, respectively. In other words, increasing the retention time from 20 to 30 days has resulted in a meager 2.0% increase in the energy ratio for the ultrasonicated sludge. Thus, ultrasonicated secondary sludge at 31.4 g TS/L (at 30 days retention time) is more beneficial than primary and mixed sludge, based on solids degradation, increased methane production, net energy and energy ratio.

3.6 Dewaterability

Dewaterability, which is measured in terms of CST, for the control, ultrasonicated and anaerobic digestate at all solids concentrations for primary, secondary and mixed sludge was measured and is summarized in Table 4. In general, the CST was reduced for the ultrasonicated primary sludge when compared to the control, irrespective of the solids concentration. Increasing the solids concentration gradually increased the CST for the control and the ultrasonicated primary sludge. Similarly, for the control and the ultrasonicated secondary and mixed sludge, the CST increased with the increase in solids concentration. Comparing to secondary and mixed sludge, the CST for the primary sludge was lower. The reduction in CST (or enhancement in sludge dewaterability) due to ultrasonication was due to the breakage of sludge flocs and of extracellular polymeric substance (EPS) resulting from cell lysis (Feng et al., 2009). With the specific energy input of 800 kJ/kg TS, the CST was reduced from 94.2 to 83.1 s for waste-activated sludge (at 1.2% solids content w/v) (Feng et al., 2009). In addition, increasing the specific energy input > 4400 kJ/kg TS has decreased the dewaterability of sludge due to the smaller particle and larger surface (Feng et al., 2009). The effect of AD on the CST was measured for all cases (Table 4), In general, the CST was gradually reduced after AD. From the results, it is clear that AD reduces the CST value and thus increases the digestate dewaterability. The reduction of organic matters (mainly proteins) in the loosely bound fractions of EPS has been attributed to the reduction in dewaterability after AD (Xu et al., 2011). Increase in dewaterability after anaerobic digestion contributes to the reduction of energy input for dewatering. However, CST reduction observed in this study cannot be related to the centrifugation. Thus, further full-scale studies are required in order to better understand this phenomenon.

3.7 GHG emissions

The energy required and the corresponding GHG emissions in the ultrasonication process, AD, dewatering, transportation, and land application were evaluated for primary, secondary and mixed sludge and the results are summarized in Table 5. For primary sludge, the GHG emissions for the control were 1.60, 1.64 and 1.59 times lower than the ultrasonicated primary sludge at 20.0, 30.0 and 40.0 g TS/L, respectively. With increasing solids concentration, the GHG emissions for the control and the ultrasonicated primary sludge were reduced. In addition, the GHG emissions corresponding to energy utilization during AD, transportation, and land application were reduced at higher solids concentration. Similarly, for secondary and mixed sludge, the GHG emissions increased due to ultrasonication, irrespective of solids concentration (Table 5). The net energy was positive and the energy ratio was 1.0 for the ultrasonicated secondary sludge at 31.4 g TS/L; however, the net GHG emissions were higher compared to the control. Since the GHG emissions corresponding to methane combustion resulted in higher GHG emissions (Table 5), the minimum GHG emissions (339.6 kg CO_2 equivalent/Mg of TDS) were observed for the secondary sludge at 42.1 g TS/L.

4. CONCLUSION

In general, it can be concluded that sludge ultrasonication was favorable for the secondary sludge at 30.0 g TS/L. Increasing the solids concentration had a negative effect on the temperature increase during ultrasonication. In this study (at 20, 30 and 40 g TS/L), the optimum sludge (secondary) concentration was 31.4 g TS/L based on sludge solubilization, and volatile solids degradation during AD. Cumulative methane production increased with the increase in sludge solids concentration for untreated primary, secondary and mixed sludge.

From the mass balance, the lowest quantity of the digestate subjected to dewatering, transport and land application was observed at 31.4 g TS/L for the ultrasonicated secondary sludge. Energy balance showed that the maximum net energy 7.89 kWh/ Mg of TDS and the energy ratio 1.0 were observed at 31.4 g TS/L for the ultrasonicated secondary sludge. GHG emissions were reduced with increasing solids concentration (for the primary, secondary and mixed sludge). Finally, ultrasonication followed by AD enhanced sludge dewaterability.

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Table 1. Sludge characteristics

	Total solids (g/L)	VS (g/L)	SS (g/L)	VSS (g/L)	Total Carbon kg/kg of dry solids	TN	TP	pH	TCOD (g/L)	SCOD (mg/L)
						g/kg of dry solids				
Primary sludge	21.04 (±0.21)	15.45 (±0.06)	19.53 (±0.18)	14.17 (±0.11)	0. 53	31.2	1.02	6.71 (±0.01)	22.43 (±0.47)	915.5 (±2.5)
	32.15 (±0.18)	23.13 (±0.25)	30.61 (±0.20)	21.96 (±0.13)				6.67 (±0.02)	33.56 (±0.38)	925.8 (±3.4)
	41.08 (±0.18)	30.15 (±0.12)	41.43 (±0.08)	28.85 (±0.40)				6.69 (±0.02)	44.65 (±0.38)	928.6 (±2.6)
Secondary sludge	20.64 (±0.36)	15.89 (±0.02)	18.78 (±0.38)	14.79 (±0.34)	0.42	52.4	1.4	6.77 (±0.02)	23.54 (±0.47)	780.2 (±0.5)
	31.45 (±0.42)	24.24 (±0.03)	29.81 (±0.41)	22.18 (±0.23)				6.67 (±0.01)	34.60 (±0.38)	781.2 (±0.9)
	42.06 (±0.35)	32.36 (±0.02)	40.49 (±0.28)	28.98 (±0.04)				6.68 (±0.02)	45.51 (±0.38)	782.1 (±0.7)
Mixed sludge	19.98 (±0.82)	14.78 (±0.02)	18.57 (±0.38)	13.61 (±0.34)	0.46	48.5	1.32	6.87 (±0.01)	22.64 (±0.47)	805.2 (±0.5)
	31.59 (±0.29)	23.35 (±0.03)	29.35 (±0.14)	22.20 (±0.23)				6.86 (±0.03)	33.45 (±0.38)	817.5 (±0.6)
	41.67 (±0.61)	30.86 (±0.03)	38.96 (±0.27)	29.08 (±0.20)				6.82 (±0.03)	44.71 (±0.18)	810.3 (±0.6)

Table 2. Mass balance of the control and ultrasonicated sludge at different solids concentration

Description	**Primary sludge**						**Secondary sludge**						**Mixed sludge**					
Mass of dry solids (Mg) entering AD (assumed)	**40**						**40**						**40**					
TS (g/L)	**21.04**		**32.15**		**41.08**		**20.64**		**31.45**		**42.06**		**19.98**		**31.59**		**41.67**	
Specific energy input (kJ/kg TS)	0 (C)	8583	0 (C)	5617	0 (C)	4396	0 (C)	8750	0 (C)	5742	0 (C)	4294	0 (C)	9039	0 (C)	5717	0 (C)	4334
%Volatile solids degradation at HRT 30 days	47.7	51.19	50.54	56.64	46.24	49.5	51.4	58.41	53.67	64.18	47.16	56.68	48.31	55.92	51.43	60.07	44.5	51.81
Volume of methane Produced mL	4063	4852	5367	6296	4456	4927	5777	7702	6651	9013	4963	6147	5289	6725	5580	7562	4306	5209
Weight of Volatile degraded during AD (Mg)	14.01	14.98	14.53	15.98	13.50	14.66	15.83	17.95	16.55	19.88	14.51	17.39	15.34	16.52	16.10	17.75	13.68	15.32
Digestate dry solids remaining after centrifugation, which will be transported and land applied (Mg)	25.99	25.02	25.46	24.02	26.50	25.34	24.17	22.05	23.45	20.22	25.49	22.61	24.66	23.48	23.90	22.25	26.32	24.68

Note: C is control without ultrasonication; Mg is mega gram

Table 3. Energy balance of the control and ultrasonicated sludge at different solids concentration

Description	**Primary sludge**						**Secondary sludge**						**Mixed sludge**					
TS (g/L)	**21.04**		**32.15**		**41.08**		**20.64**		**31.45**		**42.06**		**19.98**		**31.59**		**41.67**	
Specific energy input (kJ/kg TS)	**0 (C)**	**8583**	**0 (C)**	**5617**	**0 (C)**	**4396**	**0 (C)**	**8750**	**0 (C)**	**5742**	**0 (C)**	**4294**	**0 (C)**	**9039**	**0 (C)**	**5717**	**0 (C)**	**4334**
	Energy (kWh/Mg of TDS)																	
Ultrasonication	0	2380	0	1560	0	1220	0	2431	0	1595	0	1192.9	0	2510.8	0	1588.1	0	1203.9
AD	1458.9	71.8	954.1	46.9	746.7	36.7	1486.2	71.7	975.4	48.0	729.3	36.7	1535.3	75.5	971.0	47.96	736.1	36.2
Dewatering	65.9	63.4	64.5	60.9	67.2	64.2	61.3	56.0	59.5	51.26	65.2	57.3	65.2	59.5	62.9	56.4	68.0	62.6
Transportation	45.3	43.6	44.4	41.9	46.2	44.2	42..14	38.4	40.9	35.3	44.8	39.4	44.8	40.9	43.2	38.8	46.8	43.0
Land application	228.5	219.9	223.8	211.2	233.0	222.8	212.5	193.8	206.2	178.0	226.1	198.8	226.0	206.4	218.0	195.6	235.9	217.0
(a) Total energy input	1797.6	2778.7	1286.9	1920.9	1093.0	1587.9	1802.1	2790.4	1281.9	1907.3	1065.4	1524.7	1871.3	2893.2	1295.1	1926.8	1086.8	1562.6
(b) Energy output	864.4	1747.5	1144.6	1338.0	947.0	1047.0	1227.6	1636.6	1262.2	1915.2	1038.1	1306.1	1123.9	1429.1	1185.8	1607.0	915.1	1107.0
Net energy = (**b-a**)	-934.2	-2030.8	-146.5	-582.9	-146.1	-541.0	-574.6	-1153.8	-19.71	7.89	-27.3	-218.6	-747.4	-1464.1	-109.3	-319.8	-171.7	-455.7
Energy ratio Energy input/energy output	0.48	0.37	0.89	0.70	0.87	0.66	0.68	0.59	0.98	1.0	0.97	0.86	0.6	0.49	0.92	0.83	0.84	0.71

Note: C is control without ultrasonication; negative sign indicates increase energy input; Mg is mega gram; TDS is total dry solids

Table 4. CST of the primary, secondary and mixed sludge at different solids concentration

Description	Solids concentration (gTS/L)	Sample type	CST
Primary sludge	21.04	Control	770 (±2)
		Ultrasonicated	660 (±4)
		Control after AD	680 (±3)
		Ultrasocniated after AD	550 (±6)
	32.15	Control	989 (±6)
		Ultrasonicated	790 (±5)
		Control after AD	740 (±7)
		Ultrasonicated after AD	589 (±4)
	41.08	Control	1300 (±12)
		Ultrasonicated	1106 (±10)
		Control after AD	1000 (±12)
		Ultrasonicated after AD	880 (±8)
Secondary sludge	20.64	Control	790 (±6)
		Ultrasonicated	590 (±4)
		Control after AD	640 (±3)
		Ultrasonicated after AD	450 (±2)
	31.45	Control	1006 (±12)
		Ultrasonicated	890 (±14)
		Control after AD	840 (±9)
		Ultrasonicated after AD	617 (±8)
	42.06	Control	1600 (±14)
		Ultrasonicated	1400 (±12)
		Control after AD	1368(±6)
		Ultrasonicated after AD	1187(±14)

Table 4. Continutation

Description	Solids concentration (gTS/L)	Sample type	CST
Mixed sludge	19.98	Control	649 (±12)
		Ultrasonicated	527 (±9)
		Control after AD	545 (±6)
		Ultrasonicated after AD	460 (±10)
	35.59	Control	890 (±14)
		Ultrasonicated	729 (±12)
		Control after AD	780 (±8)
		Ultrasonicated after AD	633 (±15)
	41.67	Control	1349 (±14)
		Ultrasonicated	1198 (±10)
		Control after AD	1109 (±8)
		Ultrasonicated after AD	961 (±6)

Table 5. GHG emissions for control and ultrasonicated sludge at different solids concentration

Description	**Primary sludge**						**Secondary sludge**						**Mixed sludge**					
TS (g/L)	**21.04**		**32.15**		**41.08**		**20.64**		**31.45**		**42.06**		**19.98**		**31.59**		**41.67**	
Specific energy input (kJ/kg TS)	**0 (C)**	**8583**	**0 (C)**	**5617**	**0 (C)**	**4396**	**0 (C)**	**8750**	**0 (C)**	**5742**	**0 (C)**	**4294**	**0 (C)**	**9039**	**0 (C)**	**5717**	**0 (C)**	**4334**
	GHG emission (kg CO_2 equivalent/Mg of TDS)																	
Net GHG emission due to energy input and out put	495.1	926.2	77.6	308.9	77.42	286.7	303.5	611.5	10.45	-4.18	14.47	115.9	597.2	776.0	57.95	169.5	91.02	241.51
GHG emissions during AD (biogenic emissions)	234.2	258.2	253.2	285.4	218.8	232.5	283.7	322.2	229.2	295.1	195.5	227.7	117.4	317.3	243.0	280.2	187.5	217.9
GHG emissions during CH_4 combustion	194.4	238.2	263.4	309.1	218.8	241.9	283.6	378.1	292.0	442.4	239.8	301.7	168.9	330.1	273.9	371.2	211.4	255.7
GHG emissions during transportation	12.5	12.1	12.3	11.6	12.8	12.2	11.7	10.6	11.3	9.76	12.4	10.9	11.9	11.3	12.0	10.74	13.0	11.9
GHG emissions during land application	74.1	71.3	72.5	68.4	75.5	72.2	68.9	62.8	66.8	57.6	73.3	64.4	70.3	66.9	70.65	63.4	76.5	70.3
Total GHG emission Without considering biogenic CO_2 emissions	781.2	1247.8	425.9	698.0	384.5	612.9	668.6	1063.0	380.2	505.6	339.6	492.9	848.2	1184.3	414.5	615.0	391.8	579.5

Note: C is control without ultrasonication; negative sign indicates reduction in GHG emissions; Mg is mega gram; TDS is total dry solids

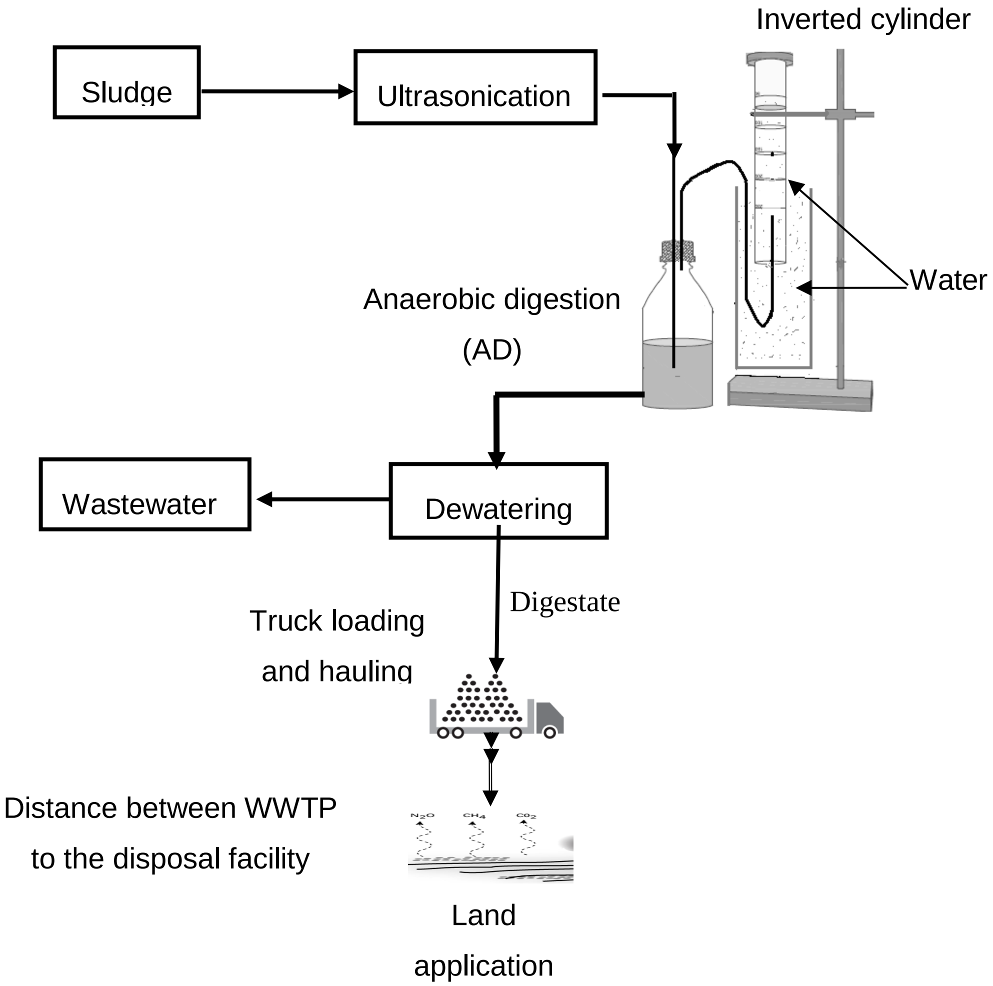


Figure 1. Experiment setup for the evaluating the mass-energy and GHG emissions

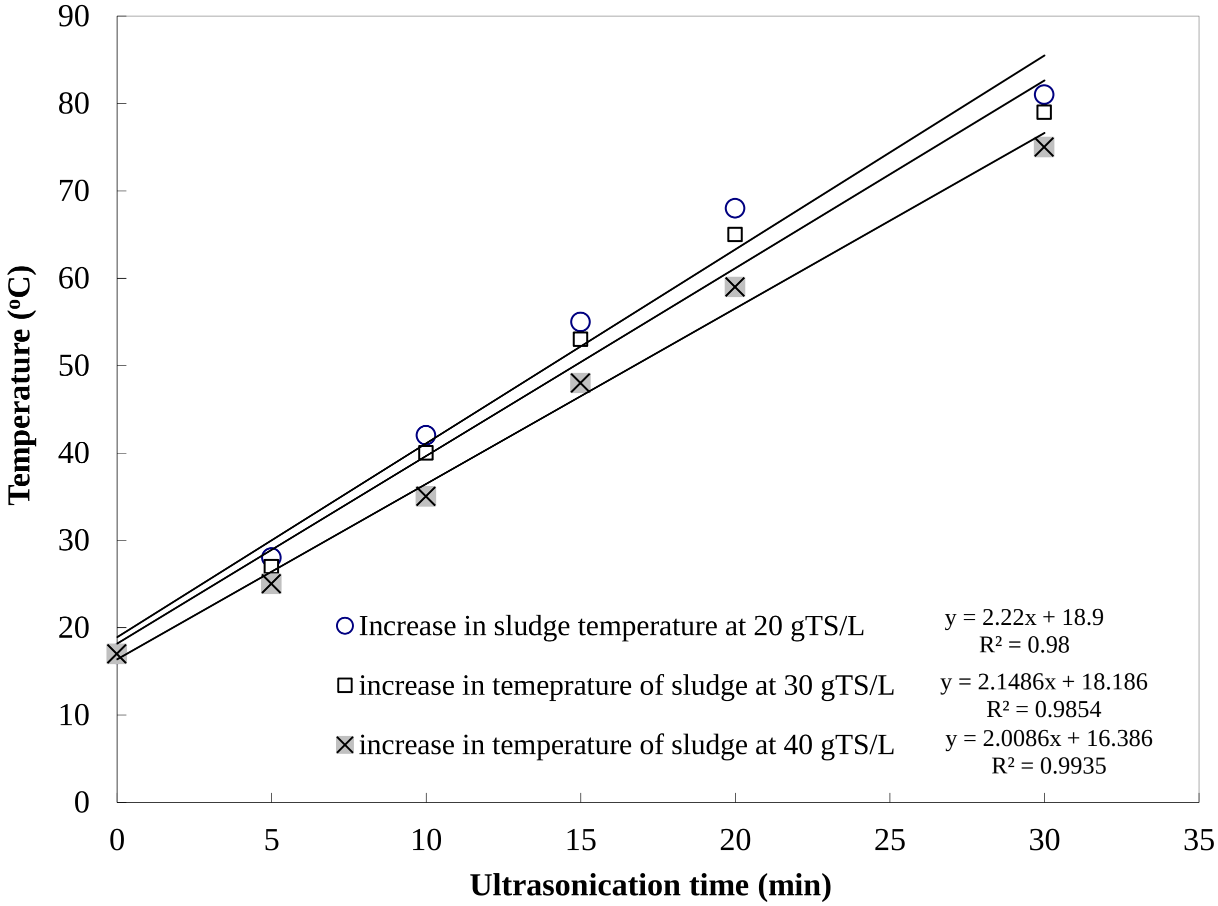


Figure 2. Rise in temperature of sludge during ultrasonication

Note: "E" is the energy required for the process (generated from fossil fuels)

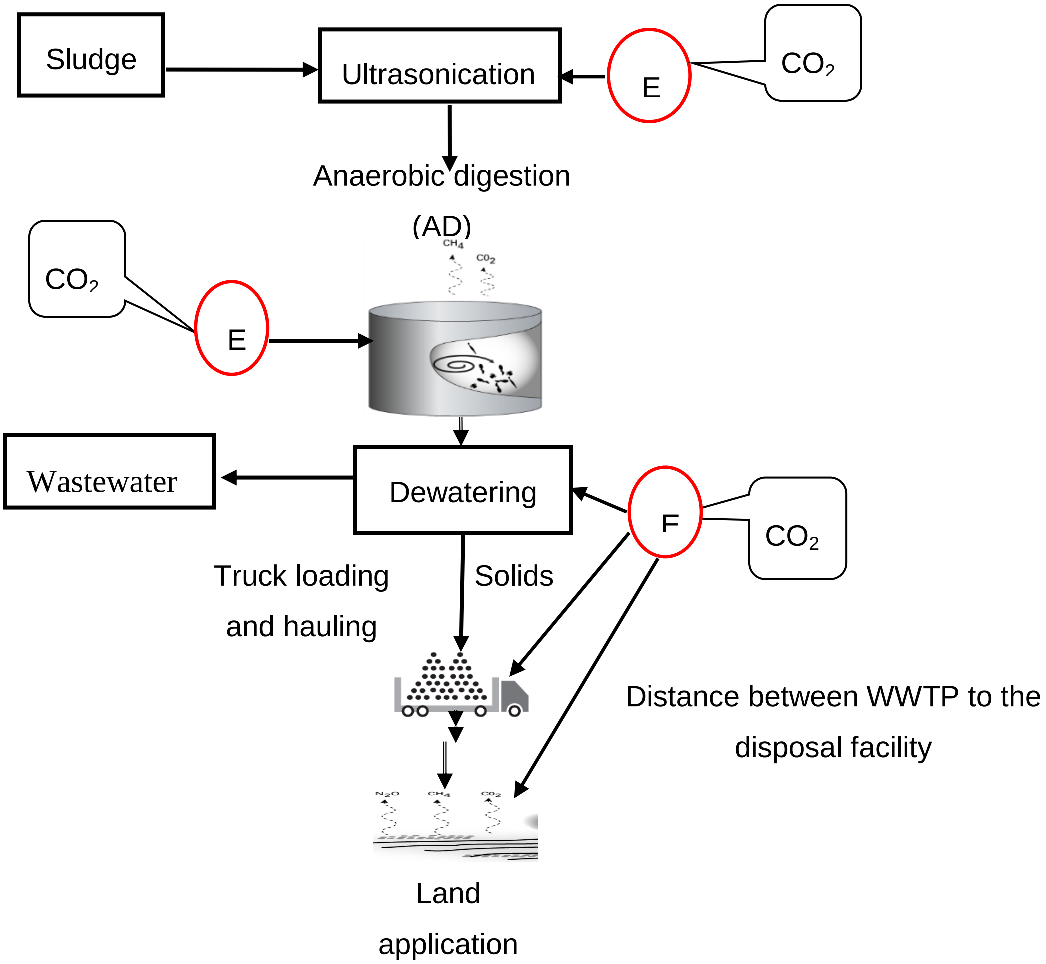


Figure 3. Associated GHG emissions during sludge management

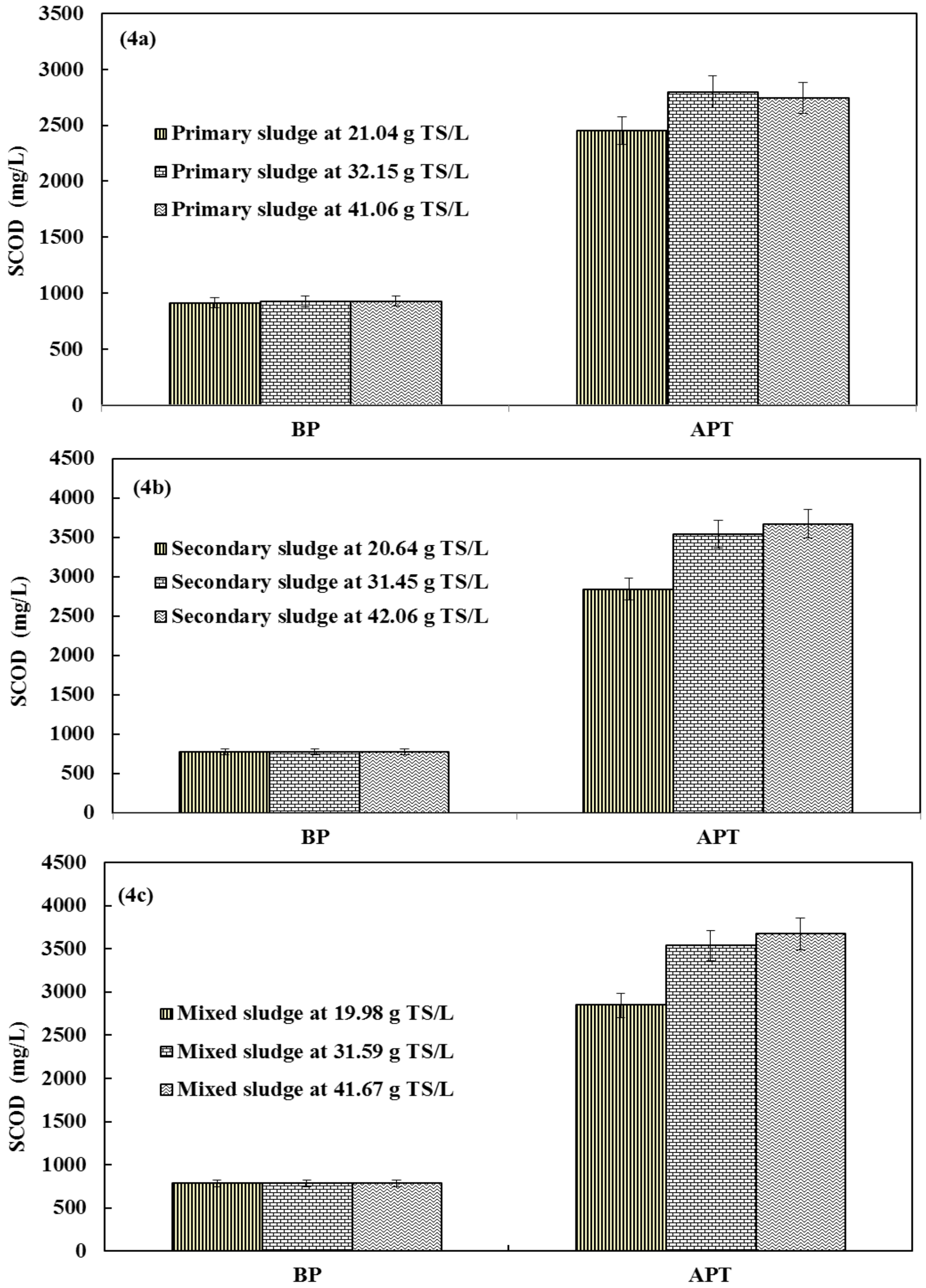
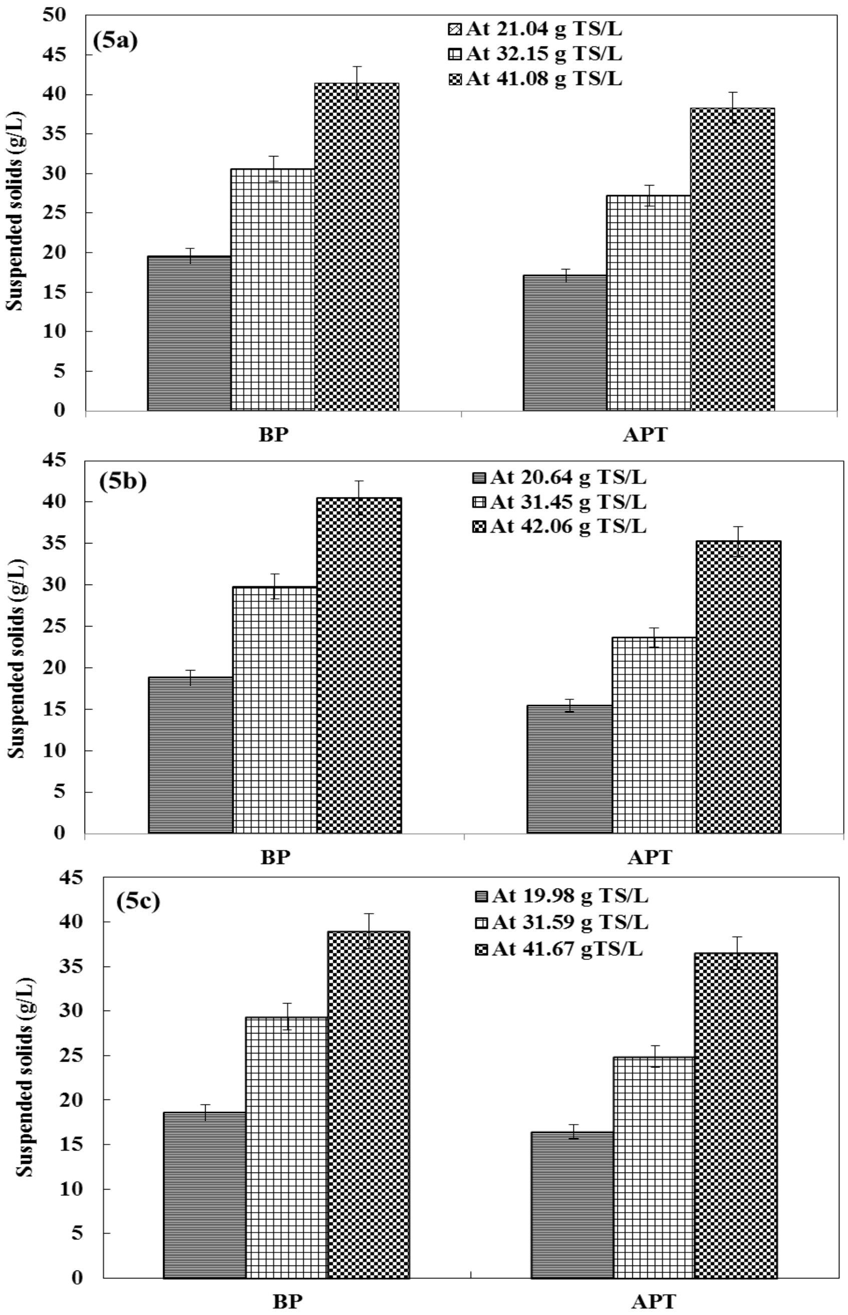


Figure 4. Soluble COD increase due to solubilisation after ultrasonication

Note: BP is before pre-treatment; APT is after pre-treatment; "4a" is SCOD increase for primary sludge; "4b" SCOD increase for secondary sludge; "4c" SCOD increase for mixed sludge



Note: BP: before pre-treatment; APT: after pre-treatment; "5a" is suspended solids solubilisation for primary sludge; "5b" suspended solids solubilisation for secondary sludge; "5c suspended solids solubilisation for mixed sludge

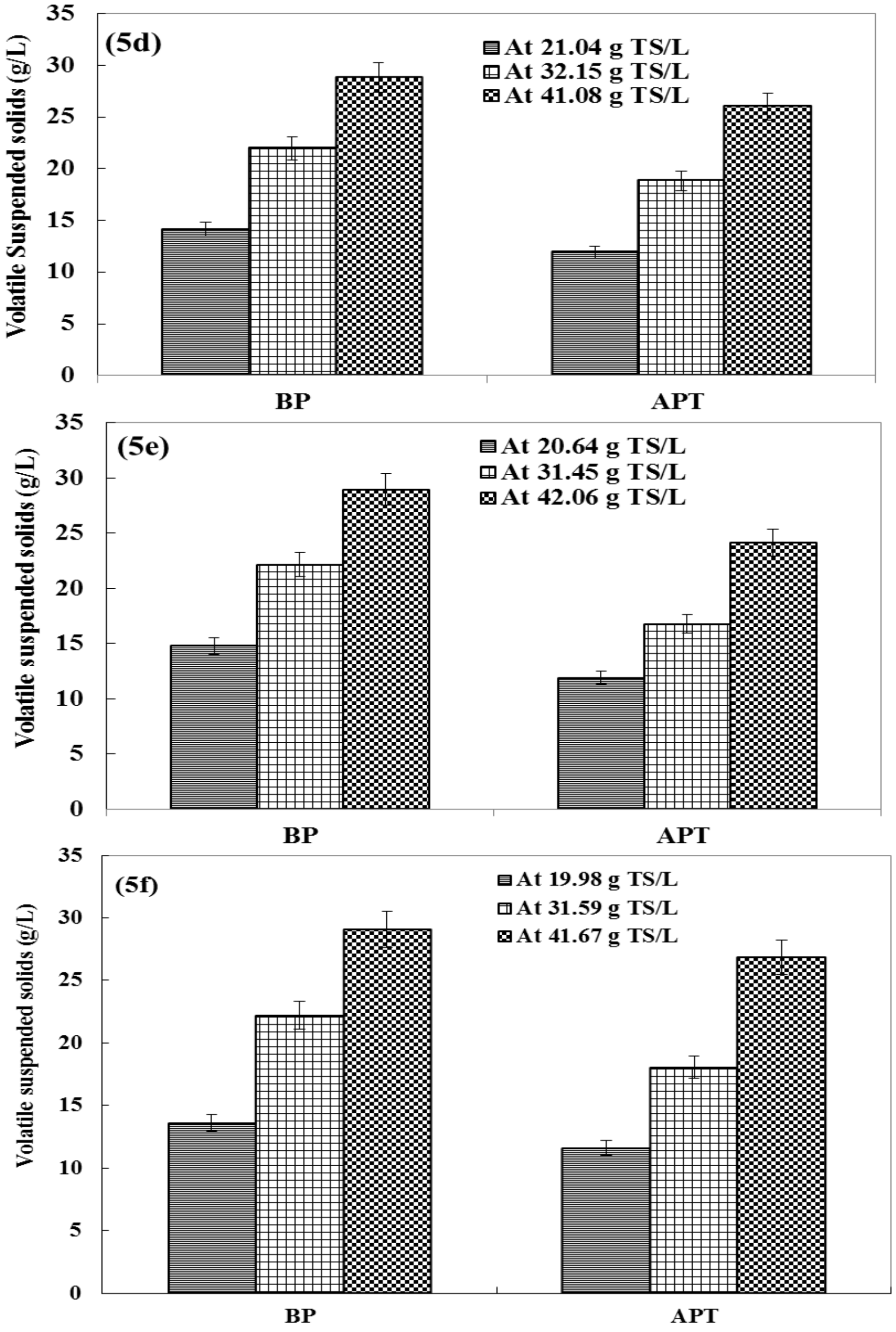


Figure 5. Reduction in suspended solids and volatile suspended solids due to ulrasonication

Note: BP: before pre-treatment; APT: after pre-treatment; "5d" is volatile suspended solids solubilisation for primary sludge; "5e" is volatile suspended solids solubilisation for secondary sludge; "5f" is volatile suspended solids solubilisation for mixed sludge

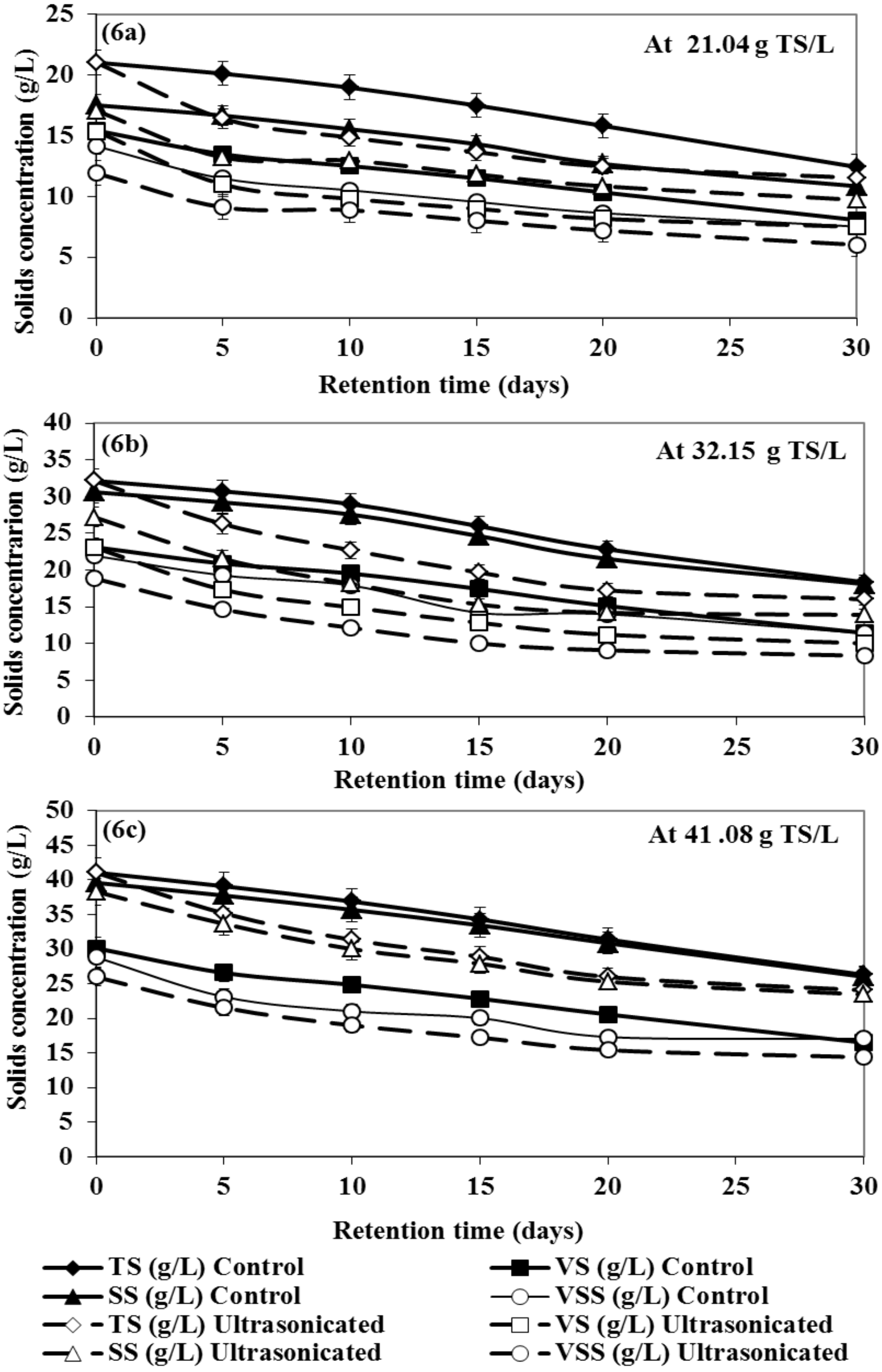


Figure 6. Solids degradation of primary sludge during anaerobic digestion

Note: "6a" is solids degradation at 21.04 g TS/L; "6b" is solids degradation at 32.15 g TS/L; "6c" is solids degradation at 41.08 g TS/L

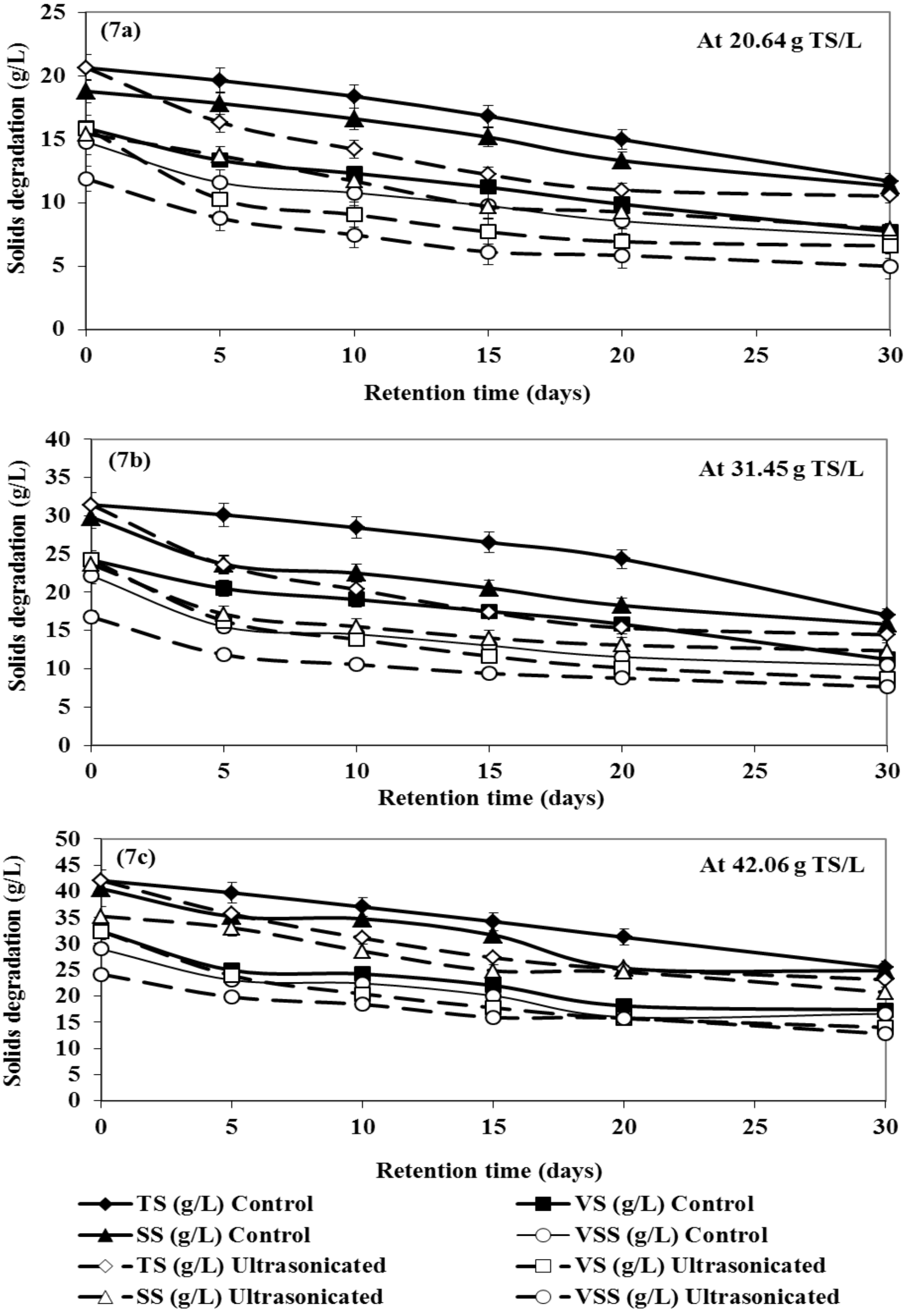


Figure 7. Solids degradation of secondary sludge during anaerobic digestion

Note: "7a" is solids degradation at 20.64 g TS/L; "7b" is solids degradation at 31.45 g TS/L; "7c" is solids degradation at 42.06 g TS/L

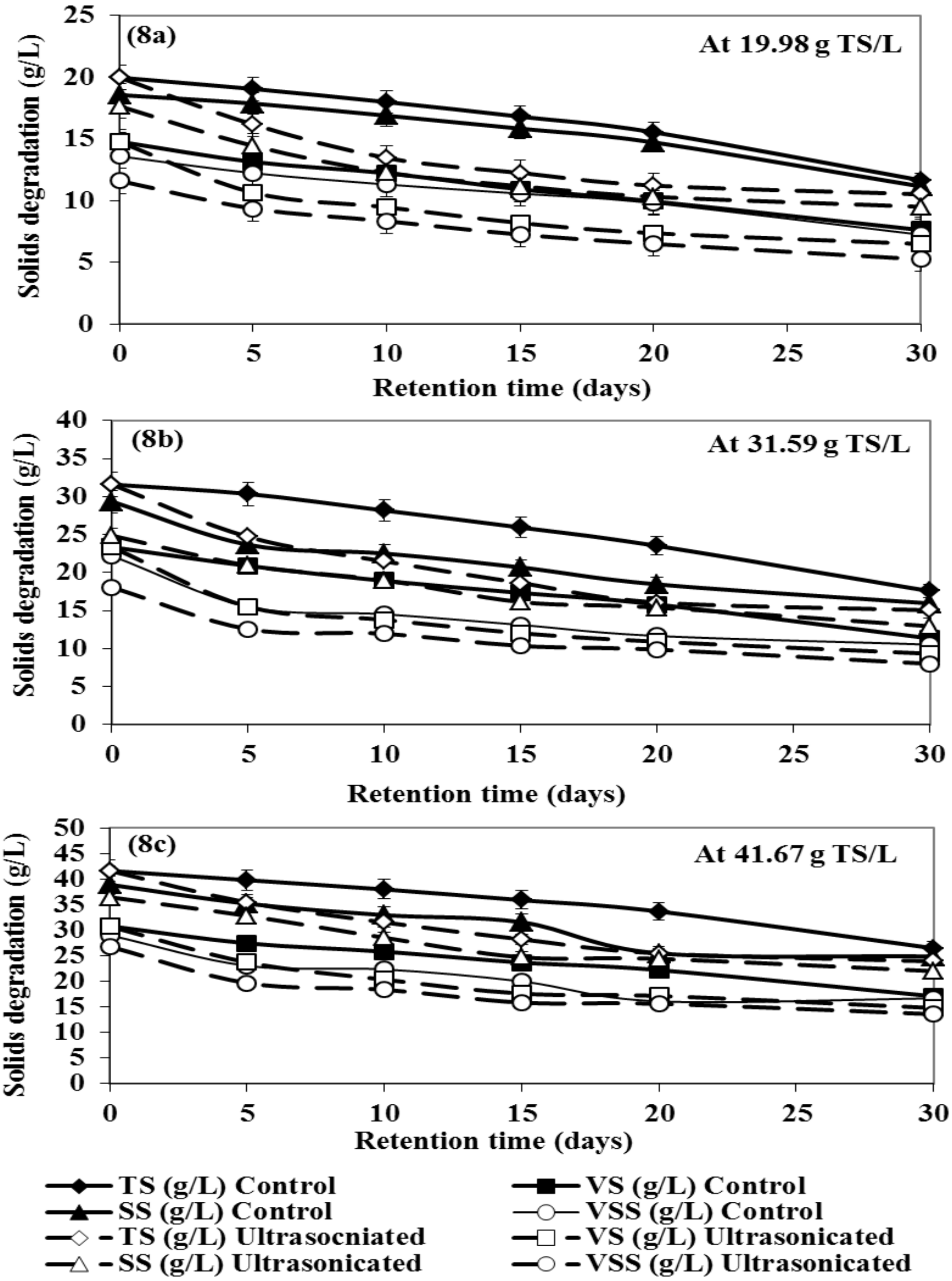


Figure 8. Mixed sludge solids degradation during anaerobic digestion

Note: "8a" is solids degradation at 19.98 g TS/L; "8b" is solids degradation at 31.59 g TS/L; "8c" is solids degradation at 41.67 g TS/L

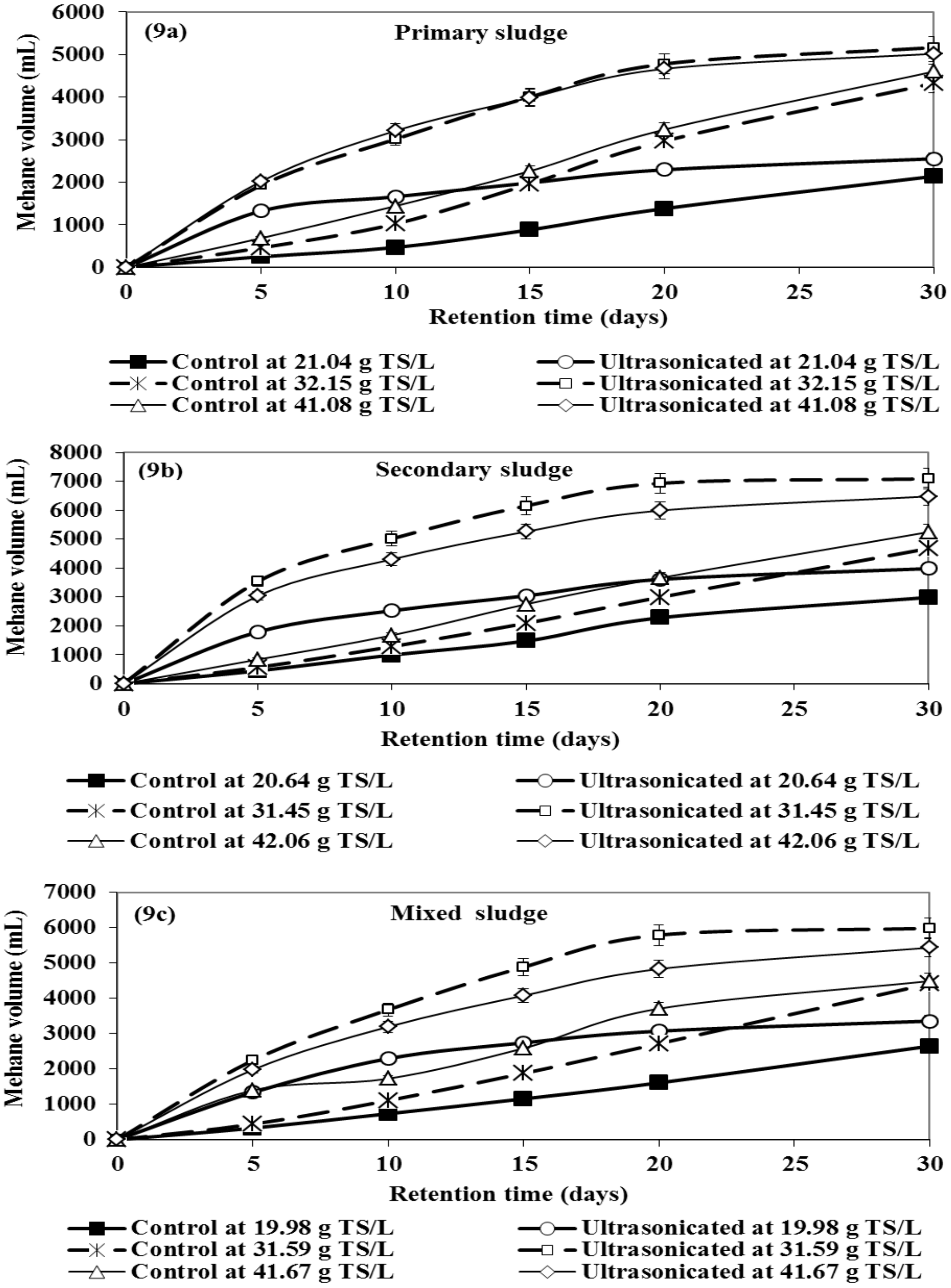


Figure 9. Methane production during AD at different retention time for different sludge and solids concentrations

Note: "9a" is the cumulative methane production of primary sludge; "9b" is the cumulative methane production of secondary sludge; "9c" is the cumulative methane production of mixed sludge

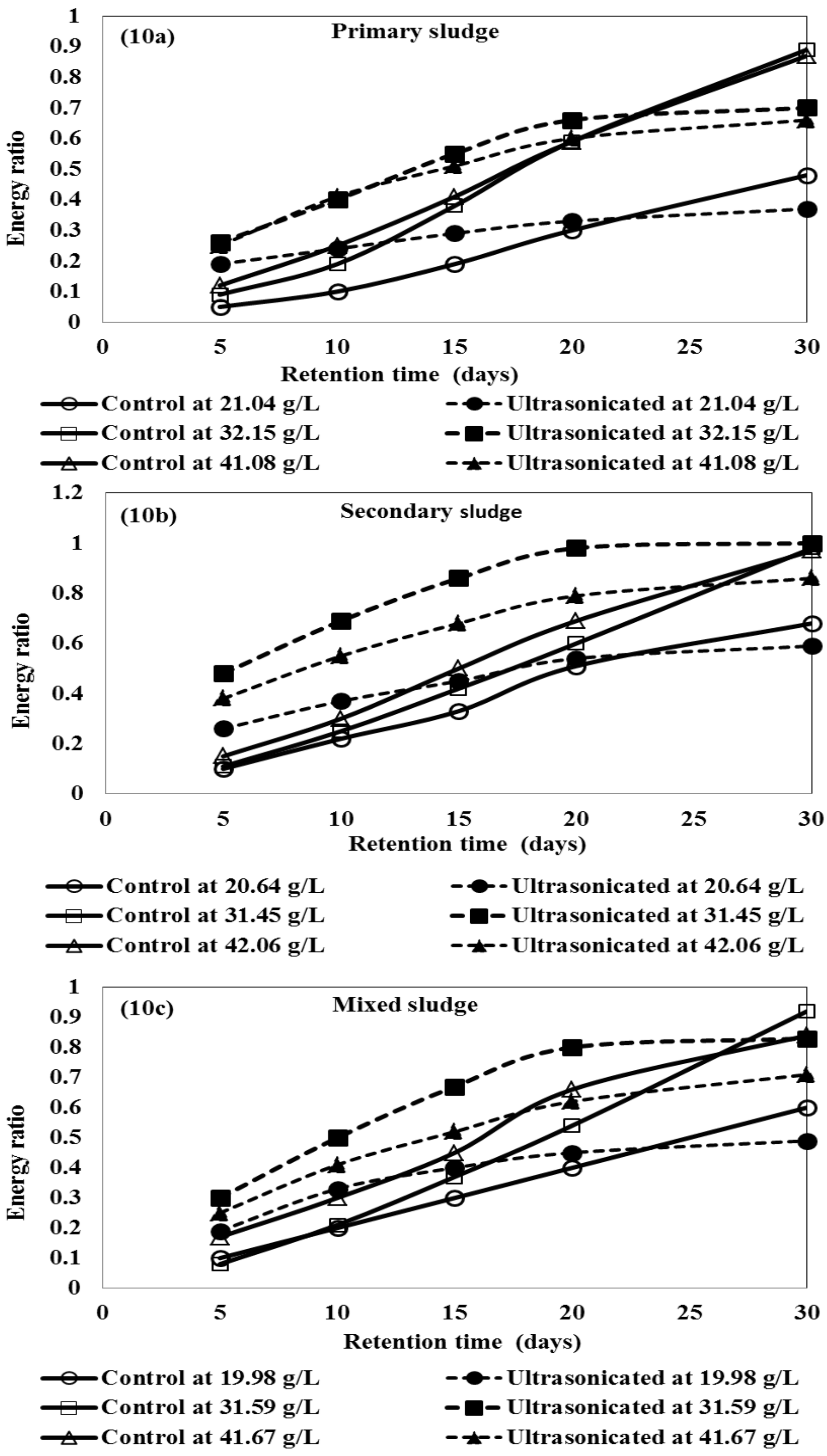


Figure 10. Energy ratio at different solids concnetration

CHAPITRE III

THERMAL PRE-TREATMENT OF SLUDGE

PARTIE 1

THERMAL PRE-TREATMENT OF SEWAGE SLUDGE TO ENHANCE ANAEROBIC DIGESTION: A REVIEW

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RÉSUMÉ

Cette revue traite de l'effet du prétraitement thermique (PT) à haute et basse température sur la déshydratation des boues, la digestion anaérobie (DA) et la production de biogaz. La DA des boues traitées par PT a mis en évidence une diminution du temps de rétention des boues, une augmentation de la production de biogaz, une dégradation des matières organiques, une amélioration de la déshydratation et une diminution du volume de digesteur par rapport à la DA conventionnelle des boues. Il en résulte que le bilan énergétique du procédé de prétraitement thermique (PT) a montré que ce dernier est durable et qu'il permet d'obtenir un bilan d'énergie net positif et une concentration en matières solides supérieure à 3%. L'énergie nette et le rapport de l'énergie du prétraitement et de la DA augmentent avec la hausse de la concentration en matières solides totales.

Mots-clés: digestion anaérobie; traitement biologique des eaux usées; boues activées; prétraitement thermique.

ABSTRACT

This review summarizes the effect of high and low temperature thermal pre-treatment (TPT) on sludge dewaterability, anaerobic digestion (AD) and biogas production efficiencies. The AD of the TPT sludge have demonstrated the following observations: sludge retention time is reduced, increased biogas generation, higher organics degradation, improved dewaterability, and lower digester volume than the conventional AD of sludge. Energy balance of the TPT process showed energetically self sustainable and produced surplus energy at solids concentration greater than 3%. Net energy and energy ratio of TPT and AD revealed that net energy and energy ratio are increased with increase in total solids concentration.

Keywords: anaerobic digestion; biological wastewater treatment; waste activated sludge; thermal pre-treatment.

1. INTRODUCTION

The unmanageable quantity of sludge is generated in the 21st century from the wastewater treatment plants (WWTPs) due to high water demand by an increasing population, industrialisation, urbanisation and also due to higher level of wastewater treatment. In Canada, in the province of Quebec, 230000 mega grams per year (Mg/yr) of dry sludge is generated from the existing 700 municipal wastewater treatment plants (LeBlanc et al., 2009; Perron and Hebert, 2007) and production rate is expected to increase in the future. Sludge management (treatment and disposal) is responsible for 60% of the total WWTP operation cost (Sridhar et al., 2011). Sludge is also a major problem for the environmental engineers as it is a heterogeneous medium largely consisting of water (>90%) and solids (<10%). Further, sludge disposal laws are becoming increasingly strict. The common sludge disposal techniques like incineration, landfill, and land application used over the years are neither economical nor sustainable, and generate huge amounts of greenhouse gases (GHGs). Therefore, sludge generators are constrained to re-evaluate their sludge management strategies; resulting in a need to *achieve* cost effective and sustainable technologies for sludge treatment and disposal. From the extensive research on sludge treatment technologies, many researchers concluded that anaerobic digestion (AD) is efficient and a sustainable technology for sludge treatment/disposal (Pilli et al., 2010). The benefits associated with AD technology are high, which include mass reduction, odour removal, pathogen reduction, less energy use, flexibility towards the waste composition and more significantly, the energy recovery in the form of biogas (Metcalf and Eddy, 2003; Appels et al., 2008 & 2010).

Anaerobic digestion of sludge is a microbiological process that converts degradable organic compounds to methane (CH_4) and carbon dioxide (CO_2) in the absence of elemental oxygen. Mainly, the process occurs in four stages as described in Appels et al. (2008). The microbiological conversion of sludge to CH_4 and CO_2 by three groups of microorganisms is a slow process and requires high retention time and larger digester volume. In particular, solubilisation of intracellular biopolymers and there conversion to lower molecular weight compounds of degradable organics through hydrolysis is a rate limiting step in the AD process (Appels et al., 2008; Pilli et al., 2011). The lower digestion rate (i.e., first order digestion rate constant 0.15 day^{-1} for sludge, Shimizu et al., 1993) due to non-availability of the readily biodegradable organic matter for anaerobic digestion, necessitates pre-treatment of sludge. Pre-treatment of sludge enhances the biodegradable organic carbon by rupturing the cell wall and releasing the intercellular matter in aqueous phase, which enhances the digestion rates, reduces the retention time and increases the biogas production (Khanal et al., 2007; Pilli et al., 2010). Various pre-treatment techniques like thermal, chemical, mechanical, biological, physical and several combinations such as thermo-chemical, physico-chemical, biological-physicochemical, and mechanical-chemical have been studied by many researchers. However, economic constraints have limited the scale-up and commercialisation of these technologies.

To establish an economically feasible pre-treatment technology for enhancing sludge degradability extensive research has been carried out around the world. The TPT technology is a well-established and commercially implemented technology. The several inherent merits of TPT technology are: higher volatile solids reduction (235% > control) during AD or enhanced biodegradability (Jeong et al., 2007; Carrere et al., 2008; Bougrier et al., 2008), increase in dewaterability (60-80% improvement, Odeby et al., 1996), 60% increase in methane production (Valo et al., 2004; Carrere et al., 2008; Bougrier et al., 2008), destruction of pathogens (Potts, 2007), the most effective treatment as per energy considerations (Kepp et al., 2000; Perez-Elvira et al., 2008), reduces the auxiliary fuel consumption for sludge dewatering, low transportation due to lower residual sludge after AD, produces class A bio-solids (Climent et al 2007; Camacho et al., 2008). Due to inherent advantages and commercial applicability of sludge thermal pre-treatment, this article attempted to present a systematic review of the extensive research on TPT of sludge and consequent impact on AD process including biogas generation and energy balance of the process (thermal pre-treatment + anaerobic digestion).

2. THERMAL PRE-TREATMENT AT DIFFERENT TEMPERATURE

Thermal pre-treatment (heat pre-treatment) is a process where the temperature of sludge is raised to a desired temperature to significantly increase the disintegration and solubilisation of sludge solids. Thermal treatment of sludge is usually used for improving dewaterability; further, thermal treatment is considered as pre-treatment process to enhance the biogas production during anaerobic digestion process. The thermal energy required to raise the temperature of sludge is generally achieved through direct injection of steam or passing the steam through heat exchangers. The hot pre-treated sludge is cooled to anaerobic digester temperature and the heat is recovered during the cooling process, which can be used to pre-heat the feed (fresh) sludge. The heat recovery significantly increases the energy efficiency and significantly reduces the cost of pre-treatment. Most of the research on pre-treatment has been done using a wide range of temperature from 60 to 270°C (Climent et al., 2007). Based on the hydrolysis temperature, the TPT has been classified in two different categories, i.e., the hydrolysis (pre-treatment) temperature above 100°C (considered as high temperature thermal pre-treatment) and the temperature applied below 100°C (considered as low temperature thermal pre-treatment) (Climent et al., 2007). The effect of thermal hydrolysis on AD of the pre-treated sludge at temperature greater than 100°C was reviewed by Carrere et al. (2010) (i.e. pre-treatment methods to improve sludge anaerobic degradability), but the effect of thermal pre-treatment on the physical, chemical properties, biological properties, and energy balance of the process (integrated thermal pre-treatment and anaerobic digestion) are not considered. Therefore, detailed research findings on these aspects of sludge thermal pre-treatment at different temperature (high temperature and low temperature) are presented and discussed in this review.

2.1 High Temperature Thermal Pre-Treatment Process

During 60's and 70's sludge heat treatment was the major emphasis. Porteus and Zimpro, two main processes operating at temperature typically between 200-250°C were installed (Camacho et al., 2008). The problems encountered in these processes include: odour generation, high strength liquors production, and corrosion in heat exchangers. Porteus and Zimpro projects were closed during late sixties, and/or early seventies. With modified operating conditions and pre-treatment at lower temperature, the Zimpro process is still in use to enhance the dewaterability of sludge (Camacho et al., 2008). Further, various combination of thermal hydrolysis with acid and alkaline based technologies emerged during mid 80's to produce pasteurized sludge, but none of these processes were commercialised because they were not economical and could not improve the biodegradability. Synox and Protox are the best illustrations of the combined thermal process to improve the dewaterability, which are not successfully commercialised (Neyens and Baeyens 2003).

Further, CAMBI process was developed for efficient thermal hydrolysis during early 90's. Veolia Water Solution and Technologies developed thermal hydrolysis processes known as BIOTHELYS®, to enhance the biodegradability and dewaterability of sludge. BIOTHELYS® process is the combination of thermal hydrolysis (Thelys ™ hydrolysis process) and anaerobic digestion. Both CAMBI and BIOTHELYS® are commercial high temperature TPT processes. The process configurations of both the models, which are widely established, are explained below.

2.1.1 CAMBI Thermal Hydrolysis Process

CAMBI thermal hydrolysis is a three step process and mainly consists of three units. The first unit is a preheated tank, which eliminates the problems of pumping under pressure and corrosion in heat exchangers. The second unit is a steam reactor, where steam is introduced under pressure and third unit is a flash tank, where the reactor pressure is rapidly released (Figure 1). Sludge is pre-dewatered to around 14% to 18% dry solids (DS) content before feeding into the preheated tank. The pre-dewatered sludge is continuously fed into preheated tank where the temperature of sludge is raised to nearly 100°C. Temperature in the pre-heated tank is maintained by directing the return steam from the second reactor and the flash tank. In the steam reactor, sludge is heated by direct steam addition for 20-30 min (steam pressure 12 bars) in batch mode to achieve temperature of 150 to 160°C and pressure of about 8 to 9 bars. The pressure in the reactor is reduced to 2 bars before discharging the heated sludge into the flash tank and the released steam is re-circulated to the preheated tank. Releasing the pressure rapidly from the steam reactor and flashing sludge to flash tank (third unit) enables the cells to rupture. Sludge in the flash tank cools down to about 100°C. Further, the hydrolysed sludge is cooled down to anaerobic digester temperature (35°C). Technical information of the CAMBI process is available in the European patent number EP0784504 (method for hydrolysis of organic materials). The advantages of CAMBI process are; sludge retention time in the anaerobic digester is reduced from 15-30 days (conventional) to 10-12 days, 50% digester volume is saved in comparison with conventional digestion, high biogas production, improved dewaterability (30-40% DS content can be achieved), and pasteurized sludge (ready to use in agriculture) (Camacho et al., 2008). Further, the process was successful in eliminating corrosion, scaling problems and difficult to degrade filtrate chemical oxygen demand (COD). The performance of CAMBI process installed at various WWTPs is given on the website http://www.cambi.no.

2.1.2 BIOTHELYS® *Process*

The thermal hydrolysis (Thelys ™ hydrolysis process) followed by anaerobic biological treatment is the BIOTHELYS®, which is the result of a decade's development work by Veolia Water Solutions and Technologies. The BIOTHELYS® process configuration is shown in Figure 2. The main objective of this process is to enhance the biodegradability of sludge by solubilising the organic matter, and enhancing the biogas production in the anaerobic digester. The process mainly contains hydrolysis reactor where the dewatered sludge (15-16% dry solids) is added into the hydrolysis reactor. Sludge is heated through direct steam injection for 30-60 min, the temperature inside the reactor reaches around 150-180°C. The hydrolysed sludge is with drawn using the residual pressure in the reactor and is cooled down to anaerobic digester temperature (35°C). To recover the energy, two or more batch hydrolysis reactors are parallelly operated in batch mode; the released flash steam is used for preheating another hydrolysis reactor. The hydrolysed sludge is less viscous and easier to pump with enhanced dewaterability. The advantages of the BIOTHELYS® process include: the anaerobic digestion of the hydrolysed sludge reduces the quantity of sludge up to 80% higher as compared to conventional anaerobic digestion (without hydrolysis), increases biogas production, decreases the retention time, requires low digester volume, and can be operated continuously and is a secure process (www.veoliawaterst.com/biothelys/en/applications.htm).

2.2 Low Temperature Thermal Pre-Treatment Process

The studies on low temperature thermal sludge pre-treatments are very limited. In order to overcome the drawbacks of high energy requirements, toxic refractory compounds formation (amadori and melanoidins compounds), and low biodegradability of sludge at high (>180°C) thermal treatments, Wang et al. (1997a) concluded that TPT of sludge at lower temperature (60-100°C) enhances organic matter degradation and methane production significantly during anaerobic digestion. The treatment time at lower temperature lasted from hours to several days (Gavala et al., 2003; Ferrer et al., 2008; Lu et al., 2008; Nges and Liu, 2009; Borges and Chernicharo, 2009; Appels et al., 2010).

3. EFFECT OF THERMAL PRE-TREATMENT ON SLUDGE CHARACTERISTICS

During thermal pre-treatment, sludge particles and cells are subjected to rapid increase in temperature, which causes them to rupture and release the water-soluble cell components. At high temperature, the released soluble organic contents will undergo chemical and physical reactions. Therefore, many researchers evaluated the effect of TPT with respect to the changes in physical (particle size distribution, turbidity, settleability, mass composition and microscopic examination), chemical (increase in soluble chemical oxygen demand (SCOD), nitrate nitrogen, NH_3, protein, polysaccharides content of the supernatant) and biological (destruction of pathogens, heterotrophic count and change in specific oxygen uptake rate) properties. These changes substantially influence the anaerobic digestion, methane production during anaerobic digestion and therefore, are discussed in this section.

3.1 Effect of High Temperature Thermal Pre-Treatment on Sludge Characteristics

3.1.1 Physical Changes

Physical changes during the thermal pre-treatment of sludge can be used as qualitative measurement for evaluating the efficiency of thermal hydrolysis. Sludge dewaterability, sludge settleability, mass composition, and turbidity are some of the techniques used to evaluate the effect of thermal hydrolysis. The extracellular polymers (ECP) are thought to influence the dewaterability of sludge (Houghton et al., 2000; Houghton et al., 2001; Neyens and Baeyens, 2003). Increased levels of ECP in the activated sludge make sludge more difficult to dewater. Extracellular polymers (containing up to 98% water; either associated with the bacterial cell wall or in suspension) are extremely hydrated and prevent desiccation of the bacterial cells under environmental conditions (Houghton et al., 2000). An excellent review on thermal sludge pre-treatment processes and possible role of ECP to improve dewaterability is presented by Neyens and Baeyens (2003).

Bound water and intracellular water in sludge are difficult to dewater. Chemical conditioning can release the bound water but the intracellular water is very difficult to release. Thermal treatment releases both the bound as well the intracellular water due to several physical and chemical reactions that take place during thermal hydrolysis. Further, a rapid temperature increase causes sludge particles and microorganisms to rupture and then releasing the intracellular water. The increased molecular activity at high temperature causes the particles to collide with each other resulting in a breakdown of the gel-like structure that releases the bound water (this process is so called syneresis). With release of bound water and intracellular water, sludge dewaterability is enhanced (Chu et al., 1999). In this context, Fisher and Swanswick (1971) and Anderson et al. (2002) observed that thermal treatment at temperature greater than 150°C enhanced the dewaterability. The results of various researches on enhancement of dewaterability with TPT are summarized in Table 1.

CAMBI thermal hydrolysis enhances the dewaterabiltiy and dry solids up to 40% w/w can be obtained. Similarly, dewaterability could be enhanced by BIOTHELYS® process, i.e., 28-35% dry solids after centrifugation and 35-50% with filter press. Full scale installation of CAMBI process at WWTPs concluded that dewaterability of sludge was enhanced remarkably (10 to

12% higher than the conventional) (Norli, 2006). Fernandez-Polanco et al. (2008) observed that the centrifugation characteristics of hydrolyzed sludge (direct steam injection) were much better than those of the fresh sludge. They also observed that solids disintegration and sludge filterability increased with pre-treatment temperature but the biodegradability of sludge decreased at high temperature. The optimum pre-treatment conditions for better solid-liquid separation during centrifugation and for greater methane productivity were 170°C and 30 min. Also, the temperature and treatment time are important parameters in enhancing the dewaterability; temperature greater than 150°C and treatment time of 30 min showed better dewaterability. From the above discussion, it is clear that sludge dewaterbility is deteriorated (or not much improves) when the treatment temperature is less than 150°C (this is due to sludge solids solubilisation and production of small particles). The dewaterability is improved with treatment temperature greater than 150°C due to the modification of sludge structure and release of linked water.

3.1.2 Chemical Changes

Ssludge is a complex material which contains various types of micro-organisms with general approximate composition (w/w) of 10% carbohydrates, 50% protein, 10% lipid and 30% others including ribonucleic acid (RNA) and fibre (Li and Nokie 1987; Li and Nokie, 1992). The cell wall strength of these microorganisms varies from each other, and the temperature required to break the cell wall to release the intracellular compounds will vary from microorganisms to microorganisms. The rapid rise of temperature (cooking of cells) causes physical-chemical reactions, which releases the bound water, intracellular water and also solubilises organic particulates (carbohydrates, lipids, and proteins or lower molecular weight compounds). The chemical changes during the TPT at high and low temperatures thermal pre-treatment reported in the literature are summarised in Table 2 and 3.

3.1.2.1 COD solubilisation

The soluble COD increased with increase in temperature and treatment time (Valo et al., 2004; Carrere et al., 2008; Bougrier et al., 2006). The COD solubilisation was linearly related to the treatment temperature (60-170°C) (Carrere et al., 2008). The thermal treatment time has very little impact on sludge solubilisation (Bougrier et al. 2006). The solubilisation of COD and VS increased with increase in temperature in the range of 110 to 220°C, COD (Mottet et al., 2009). Perez-Elvira et al. (2010) evaluated the performance of thermal hydrolysis of mixed sludge (at

170°C and 30 min) at pilot-plant and observed 4 times higher soluble COD in the supernatant (which increased from 7.8% to 29%).

Bougrier et al. (2008) evaluated the effect of TPT temperature (95°C-210°C) on five different sludge samples (generated from urban, industrial and slaughterhouse wastewaters) and concluded that the solids solubilisation level (measured by evaluating the total suspended solids (TSS)/ total solids (TS) ratio and volatile suspended solids (VSS/TSS ratio)) increased with increase in temperature. Takashima (2008) examined the combination of different process configurations for treatment and anaerobic digestion of sewage sludge (1: control or digestion with no thermal treatment, 2: pre-treatment followed by digestion, 3: anaerobic digestion followed by thermal treatment and recycling of the treated sludge to anaerobic digestion, 4: anaerobic digestion followed by thermal treatment and 2nd stage anaerobic digestion) by incorporating TPT (120°C for 1 hr). They observed that the dissolved solids concentration increased from 0.4 g/L (control) to 4.4-6.2 g/L, which implies that a significant portion of the digested sludge was solubilised through thermal pre-treatment. Further, the volatile solids (VS) destruction increased by 4.5, 6.6, and 9.9 times for pre, post, and interstage-treatment, respectively compared to the control, i.e., interstage-treatment (anaerobic digestion- thermal treatment- anaerobic digestion) > post-treatment (thermal treatment of the anaerobic digested sludge and recycled to AD) > pre-treatment (thermal treatment before anaerobic digestion) >control.

The effect of treatment time and temperature on COD solubilisation reported in the literature is summarised in Table 2. A comparison of these results is very difficult, because *the solubilisation of sludge varies with treatment temperature,* treatment time, suspended solids concentration and the type of sludge. Further, to compare the impact of treatment time and treatment temperature (100°C-200°C) on COD solubilisation, for a given sludge solids concentration, time-temperature (min-°C) was considered as a parameter. Relation between the time-temperature and percentage COD solubilisation of WAS is presented (Figure 3) for the available literature data. There was a linear correlation between the time-temperature factor and percentage COD solubilisation. The slope of the line decreased with total sludge solids concentration. However, to obtain a perfect relationship between time-temperature and COD solubilisation, further, COD solubilisation data are required at different solids concentration for a given treatment temperature and time.

3.1.2.2 Carbohydrate solubilisation

The effect of treatment time and temperature on carbohydrate solubilisation reported in the literature is summarised in Table 2. The soluble carbohydrate concentration increased until 130°C and further increase in temperature decreased the carbohydrate solubilisation. For example, the carbohydrate concentration increased from 0.13 g eqGluc/L to 1.04 g eqGluc/L when sludge was treated at 130°C, whereas, at 170°C the carbohydrate concentration decreased to 0.78 g eqGluc/L (Bougrier et al., 2008). The decrease in carbohydrate concentration could be explained as follows; the carbohydrate concentration was measured by spectrophotometry by quantifying the carbonyl group, with increasing temperature the released carbohydrates reacted with other carbohydrates ("burnt sugar" reactions) or with proteins (Maillard reactions) and thus the carbonyl groups disappeared, therefore, the compounds could not be quantified (Bougrier et al., 2008). Mottet et al. (2009) evaluated thermal hydrolysis of waste activated sludge at different temperatures 110°C, 165°C and 220°C (heated in electric mode) and 165°C (heated with steam) and observed that the carbohydrates solubilisation strongly decreased from 15% at 165°C to 1.2% at 220°C. The decrease in carbohydrates concentration was mainly due to reaction with components to form products, which were slowly biodegradable (Muller, 2000; Bougrier et al., 2008).

3.1.2.3 Protein solubilisation

The effect of treatment time and temperature on protein solubilisation reported in the literature is summarised in Table 2. The soluble protein concentration increased with increase in temperature. An increase in soluble protein concentration from 0.31 eqSAB/L (BSA = bovine serum albumin) (control sludge) to 5.9 eqSAB/L in sludge treated at 170°C was observed (Bougrier et al., 2008). An increase in $N\text{-}NH_4$ (from 95.2 mg/L to 655 mg/L) was observed as a consequence of protein solubilisation during thermo-chemical pre-treatment of microbial biomass at 140°C for 30 min and pH 12 (or addition of 26.1 g of NaOH/L) (Penaud et al. 1999).

Mottet et al. (2009) evaluated thermal hydrolysis of waste activated sludge at different temperatures 110°C, 165°C and 220°C (heated in electric mode) and 165°C (heated in steam mode) and observed increased protein solubilisation with increasing temperature. Waste activated sludge treated at 165°C with steam mode observed high protein solubilisation compared with electric mode (40.2% with steam and 34.5% in electric mode). Wilson and Novak (2009) observed that protein solubilisation increased with increase in temperature, but beyond 150°C caused reduction in the protein size.

3.2 Effect of Low Temperature Thermal Pre-Treatment on Sludge Characteristics

3.2.1 Low Temperature Effect on Dewaterability

The effect of low temperature thermal pre-treatment on sludge dewaterabulity was evaluated by various researchers (Mustranta and Vikari, 1993; Lin and Shien 2001; Barjenbruch and Kopplow, 2003) and concluded that sludge dewaterability is reduced after thermal pre-treatment. A decrease in sludge dewaterability after low temperature pre-treatment is due to increase in liquid temperature, which will lower liquid viscosity and promotes sludge filterability (Lin and Shien 2001). The change in dewaterability after thermal pre-treatment reported in the literature are summarised in Table 1.

3.2.2 Low Temperature Effect on Chemical Changes

The chemical changes in terms of COD, carbohydrates and proteins during low temperature treatment reported in the literature are summarised in Table 3.

3.2.2.1 COD solubilisation at low temperature thermal pre-treatment

Wang et al. (1997a) evaluated the organic matter solubilisation in the range of 60-120°C and 5 to 60 min treatment time and concluded that solubilisation reached equilibrium at 60°C in approximately 30 min which was in agreement with other researchers (Brooks and Grad, 1968; Wang et al., 1988). Vlyssides and Karlis (2004) evaluated the COD solubilisation and VSS reduction during thermal hydrolysis at temperature ranging from 50 to 90°C and pH 8 to 11. At all conditions, the COD solubilisation increased significantly (at pH ≥ 10 and temp ≥ 80, 80% solubilisation was achieved). Moreover, change in the temperature (50°C to 90°C) and pH (10 to 11) affected significantly the VSS reduction (due to maillard reactions, as the treatment time was greater than 2 hr). For example, at pH 8, the VSS reduction was 17% at 50°C and 24% at 90°C; at pH 11 the VSS reduction was 17% at 50°C and 43% at 90°C. Vlyssides and Karlis (2004) also defined a correlation between soluble COD production and VSS reduction (a = d(COD)/d(VSS)). The correlation coefficient “a” depends on the material to be hydrolysed. The value of “a” for hydrocarbons, proteins, and lipids was 1.2, 2.0 and 2.5, respectively (Vlyssides, 1987).

Ferrer et al. (2008) evaluated the mixed sludge solubilisation by analysing the TDS (total dissolved solids). An increase of VDS (volatile dissolved solids)/VS ratio from 0.05 to 0.44-0.48 (an increase of 780%) resulted after sludge TPT at 70°C for 48 hrs. Similarly, a negligible (or limited) increase in soluble COD at 70°C for 1hr treatment was observed by Appels et al. (2010). Lower temperature thermal pre-treatment requires longer treatment time for sludge solids solubilisation. From the above discussion and from the literature data presented in Table 3 we can conclude that low temperature and longer treatment time showed increased SCOD concentration and the solubilisation percentage was very low. But, comparing the results of low temperature and high temperature using time-temperature factor (Table 2 and 3), it can be concluded that high temperature with shorter treatment time is beneficial to achieve high COD solubilisation.

3.2.2.2 Carbohydrate solubilisation at low temperature thermal pre-treatment

At low temperature TPT the carbohydrate solubilisation increases with temperature. The carbohydrate solubilisation of WAS at 60°C, 80°C and 100°C was 15%, 20% and 21%, respectively (Jeong et al., 2007). Appels et al. (2010) revealed that after TPT of secondary sludge (with initial soluble carbohydrate concentration of 136 mg Glu-eq/L) at 70°C, 80°C, and 90°C for 60 min the concentration of soluble carbohydrates was 144, 721, 1094 mg Glu-eq/L, respectively. The effect of treatment time and temperature on carbohydrates solubilisation is summarised in Table 3.

3.2.2.3 Protein solubilisation at low temperature thermal pre-treatment

Increase in protein solubilisation of waste activated sludge with temperature was observed by various researchers. For untreated WAS sludge, the soluble protein was 2% (of the total protein), whereas with treatment at 60°C, 80°C and 100°C for 30 min the soluble protein was 12%, 20% and 18% of the total protein, respectively (Jeong et al. 2007). At low temperature longer treatment time is required to release the protein and other materials from the microbial cells. Moreover, the soluble protein concentration increased with increase in treatment temperature (the concentrations reported are tabulated in Table 3).

4. EFFECT OF THERMAL PRE-TREATMENT ON ANAEROBIC DIGESTION

The primary aim of sludge TPT is to increase sludge biodegradability and methane production at lowest possible residence time in an anaerobic digester. Over the decades many researchers have evaluated the effect of low temperature (treatment time in days) and high temperature (treatment time in hours) TPT on sludge degradability to increase the biogas production. The performance of anaerobic digestion based on the biogas production, increased biodegradability, COD degradation, TSS reduction, VS solids reduction, and methane production was evaluated by various researchers at low and high temperatures are summarised in Tables 4 and Table 5, and discussed below.

4.1 High Temperature Pre-Treatment Effect on AD

The biodegradability (based on the methane production) of thermal pre-treated waste activated sludge was enhanced through hydrolysis or by splitting complex organic compounds (Stuckey and McCarty, 1978). The anaerobic sludge biodegradability increased with pre-treatment temperature (Carrere et al., 2008). However, the biodegradability of WAS decreased at higher pre-treatment temperatures (>200°C) due to formation of Amadori and melanoidins compounds. Bougrier et al. (2008) also concluded that the WAS biodegradability slightly decreased (but stayed higher than the untreated) at temperature ≥ 190°C due to toxic refractory compounds formation (Amadori and melanoidins compounds). Pre-treatment temperature greater than 175°C enhanced the WAS solubilisation but not the biogas production (Stuckey and Mc Carty, 1978; Haug et al., 1983). Pre-treatment at 170°C by direct steam injection for 30 min resulted in increased biodegradability (in terms of specific methane production or mL CH_4/ g VS_{added}) of the pre-treated WAS than the non-treated WAS (Perez-Elvira et al., 2008; Fernandez-Polanco et al., 2008; and Donoso-Bravo et al., 2010 & 2011). Wett et al. (2010) compared disintegration of WAS using mechanical ball milling and thermo-pressure-hydrolysis (THD) (with a pressure of 19-21 bar and feeding sludge was continuously pre-treated at 170-180°C for 60 min) on a full-scale plant and concluded that the biogas production increased by 75% in THD (biogas production increased from 247 L to 443 L per kg volatile suspended solids (VSS) with and without treatment, respectively) and 41% (265 L to 415 L per kg VSS with and without treatment, respectively) in ballmilling pre-treatment.

The increase in biodegradability could be linearly correlated to COD solubilisation for treatment temperature up to 190°C. Sludge that was poorly biodegradable (initially) exhibited a higher impact of TPT than that the easily biodegradable sludge (Carrere et al., 2008; Bourgrier et al., 2007). The poorly biodegradable WAS showed 78% increase in methane production after treatment at 170°C (i.e., from 128 to 228 mL CH_4/g VS added), whereas only 23% increase was observed when initially easily biodegradable waste activated sludge was treated at 190°C (254 mL CH_4/g VS added). Mottet et al. (2009) observed that heating mode (electrical or steam mode) had no significant impact on the WAS anaerobic biodegradability.

To overcome the formation of toxic compounds, rapid TPT (170°C) with short retention time of 60 sec was studied (Dohanyos et al. 2004), which enhanced the biogas production from 0.26 L/g COD_{inlet} (untreated sludge) to 0.39 L/g COD_{inlet} (pre-treated sludge). Batch anaerobic digestion of sludge pre-treated at 120°C for 1 hr resulted in increase of cumulative methane gas production by 2.4-3.0 times compared to non-treated sludge (Takashima, 2008). In their continuous experiment (for 91 days), an average methane production for the control was 0.168 - 0.004 L/g VS fed. For post-treatment (thermal treatment of the anaerobically digested sludge and recycled to AD) and inter-stage treatment (anaerobic digestion- thermal treatment-anaerobic digestion), the average methane production was increased by 21% and 17% compared with the control, respectively. The effect of sludge type, pressure, pre-treatment temperature, and treatment time were optimized by Fernandez-Polanco et al. (2008). They also studied the continuous anaerobic digestion of the pre-treated mixed sludge (170°C, 30 min) under mesophilic and thermophilic conditions, 445 L/kg VS_{added} of biogas production was observed in the mesophilic reactor (55% increment in CH_4 production over raw sludge) and 405 L/kg VS_{added} of biogas production was recorded in thermophilic reactor (48% increment in CH_4 production over raw sludge).

Wang et al. (2009) investigated the performance of anaerobic sequencing batch reactor (ASBR) with thermally hydrolysed sewage sludge and observed ASBR performed better than the continuous-flow stirred tank reactors (CSTR). The anaerobic digestibility and the rate of degradation of thermally hydrolysed sludge in a full scale mesophilic digester increased significantly (40% higher biogas production in nearly half the time for thermally hydrolysed sludge at residence time of 12 days and 20 days for the control sludge) (Perez-Elvira et al., 2010). In the context of characterising the effluent colour of the liquor produced during the pre-treatment process, Dwyer et al. (2008) studied the effect of temperature (lowering the temperature from 165°C to 140°C) on biodegradability of secondary sludge and also on TPT effluent colour produced during the pre-treatment and concluded that decreasing the temperature from 165°C to 140°C didn’t reduce biodegradability, but colour of the effluent liquor was reduced, i.e. the TPT effluent colour decreased from 12,677 mgPtCo (platinum-colbat units)/L to 3837 mgPtCo/L.

Based on the report of various researchers, the TPT of WAS in temperature range of 120°C to 170°C for 30 to 60 minutes resulted in increase of various parameters in the following range: increase in methane production from 22 to 43%, methane content of biogas increased from 40 to 70%, total solids reduction up to 59%, increase in volatile solids degradation up to 23% and

COD reduction up to 75% (Valo et al., 2004; Skiadas et al., 2005; Bougrier et al., 2008; Jeong et al., 2007). Thus, based on various research reports presented and discussed here, the condition for WAS pre-treatment to obtain maximum biodegradability and biogas generation was 165-170°C for 30 minutes (Li and Noike, 1992; Stuckey and McCarthy, 1984). The pre-treatment under optimum conditions (i.e. 165-170°C) also increased the ease of dewatering (Fernandez-Polanco et al. 2008; Mottet et al, 2009).

4.2 Low Temperature Effect on Anaerobic Digestion

In general, sludge anaerobic biodegradability (biogas production) increased with treatment temperature (60-100°C); however, higher treatment time was required at low temperature. Paul et al. (2006) studied the effect of TPT at temperature below 100°C by performing respirometric test on the solubilised COD and showed that only 40-50% of the soluble COD was biodegradable at hydraulic retention time of 24 hr (Paul et al., 2006). Borges and Chernicharo (2009) evaluated the effect of TPT (75°C for 7 hr) on sludge generated from an UASB reactor. They observed 50% higher anaerobic biodegradability (and increase in biogas production) than the untreated sludge. Ferrer et al. (2008) pre-treated sludge at 70°C for 9, 24, 48 and 72 hr and observed increased biodegradability (the biogas production increased by 30% both in batch tests and in semi-continuous experiments) under thermophilic anaerobic conditions.

The methane generation increased with increase in temperature and pH during sludge pre-treatment (Vlyssides and Karlis, 2004). At 50°C, pH 8 for 10 hrs pre-treatment methane generation was 0.07 L CH_4/g VSS loading. At 90°C, pH 11 for 10 hr pre-treatment, methane generation increased to 0.28 L CH_4/g VSS loading. The organic matter destruction increased remarkably during anaerobic digestion of pre-treated sludge at a temperature between 80°C - 100°C (Hiraoka et al., 1984). Wang et al. (1997a) reported that continuous AD of WAS pre-treated at temperature below 100°C (30 min, pH 7) increased methane generation by 30%. Moreover, the organic matter destruction of thermal treated WAS in anaerobic digestion followed the following order with respect to temperature: 100°C > 80°C > 60°C > control (Wang et al., 1997b).

Gavala et al. (2003) evaluated the effect of mesophilic and thermophilic digestion of pre-treated (70°C) primary and secondary sludge, and concluded that the effect of pre-treatment showed very positive effect on methane production rate upon subsequent thermophilic digestion of primary sludge (Table 4). But in the case of secondary sludge, it was reported that the methane production rate was mostly influenced in mesophilic digestion followed by thermophilic digestion. Further, it was concluded that the selection of the pre-treatment duration and temperature during subsequent anaerobic digestion depends on the ratio of primary to secondary sludge. For the primary sludge (pre-treated at 70°C for 1-4 days), methane generation increased during mesophilic and thermophilic digestion by 9.2-16.2% and 37.9-85.9%, respectively. For the secondary sludge (pre-treated at 70°C for 1-4 days), methane generation during mesophilic and thermophilic digestion increased by 43-145% and 4-58%, respectively (Gavala et al., 2003). Pre-treatment of sludge for 2 days at 70°C found to be more efficient than control i.e., 28% and 61.7% higher VSS removal for primary and secondary sludge during AD, respectively, than the untreated sludge (Skiadas et al., 2005).

Ferrer et al. (2008) observed initial biogas production for 9 hr, 24 hr, and 48 hr of pre-treated sludge (70°C and pH 7), which was almost 50% higher compared to the control. Ferrer et al. (2008) also stated that lower solids retention time for thermophilic anaerobic digestion of thermally pre-treated are more efficient in terms of energy production, but less efficient in terms of effluent stabilisation. Low temperature TPT of sludge in enhancing the anaerobic digestion efficiency follows the following order 100°C > 80°C > 60°C > control, and required longer treatment time (more than 8 hr). Lower the temperature higher is the required sludge treatment time for enhancing the anaerobic digestion efficiency. Thus in general, with only exception of Wang et al., (1997a) low thermal pre-treatment (50°C-100°C) enhances sludge biodegradability but requires longer treatment time (more than 8 hr) to enhance the biogas production.

5. ENERGY BALANCE OF THERMAL PRE-TREATMENT PROCESS

The primary purpose of TPT is to enhance biogas generation and to have self sustainable energy for the treatment process. From the values reported in the literature, discussed above and summarised in Tables 4 and 5, it is clear that most of the researchers have reported biogas production in terms of per kg of VS_{added} or per kg of COD_{added}. Moreover, the solids concentration of sludge, TPT conditions (treatment time and temperature) and anaerobic digestion conditions are not similar to compare the results presented in the literature. With this information it is not possible to evaluate the energy balance or energy ratio of the pre-treatment and anaerobic digestion process. In order to perform the energy calculation values of sludge solids (SS, VS, and VSS) degraded are required along with amount of biogas generated. Few researchers have provided these and were used for energy calculations as discussed below.

5.1 Computation of energy balance at different solids (TS) concentration.

In order to evaluate the energy balance following three process steps is considered (Figure 1). The first step considered in the pre-treatment process is heating sludge from 12°C to 170°C (the optimum temperature adopted from Fernandez-Polanco et al. 2008; Perez-Elvira et al., 2010) and maintain 170°C for 30 min. The efficiency of the boiler is considered as 90% (http://hpac.com/heating/maximizing-small-boiler-efficiency) to increase sludge temperature to 170°C. In the second step it is considered that heat energy (85%, Lu et al., 2008) is recovered from the heated sludge before adding into the anaerobic digester using heat exchangers (to heat the incoming sludge). In the next (third) step of anaerobic digestion the hydraulic retention time considered for AD of sludge (with and with out pre-treament) in anaerobic digester is given in Table 6. The heat loss is assumed 5% (2-8%) of sludge heating requirement (Zupancic and Ros, 2003) for the hydraulic retention time (HRT) (control and TPT) considered (Table 6). It is also assumed that the produced biogas is used for mixing sludge (Van Haandel and Van Der Lubbe, 2012; Nayono, 2009), and the energy required in compressing the biogas is negligible and therefore, it is not considered in computations of the energy balance. The parametric values considered for energy evaluation are provided in Table 6. The energy recovered during the process is (a) heat energy was recovered using heat exchangers, (b) the energy generated from the biogas in process step 3. The energy balance evaluated for the process (with and without pre-treatment) and is presented in Figure 5.

The energy balance was evaluated at 1, 2, 3, 4% w/v total solids concentration and presented in Figure 5. The net energy (output - input) and energy ratio (energy out put/energy input) is increased with increase in total solids concentration for the control (raw sludge) and the pre-treated sludge (Figure 5). Moreover, the energy ratio also increased with increase of total solids concentration. At total solids concentration 1%, 2%, 3% and 4% (w/v %) the net energy and energy ratio was higher for the thermal pre-treated sludge when compared with the control sludge. When the total solids concentration was greater than ~1.5% (w/v), the net energy was positive and energy ratio was greater than 1, for the pre-treated sludge (at 170°C for 30 min). For the control sludge the net energy was positive and energy ratio was greater than one at ~2.2% total solids concentration (Figure 5). Different treatment temperatures and treatment times will have different effects on the energy ratio, therefore, further research is required for TPT at higher total solids concentration (TS > 4% w/v) followed by anaerobic digestion. The commercialised technologies CAMBI and BIOTHELYS® also concluded that the energy generated is self sustainable to operate the processes. However, detailed energy balance is not available in the literature. Moreover, the energy required for dewatering, transportation and land application of the pre-treated digestate was not considered. Thus, consideration of reduction in energy requirement during dewatering, transportation and land application of the thermal pre-treated digestate may render a positive energy balance when compared with control.

5.2 Computed energy balance for the literature results

As said before, the results reported by different researchers are not in the same units and basic data are not provided to evaluate and compare the energy balance. Therefore, missing data were assumed from Table 6 and energy balance was performed for various data of researchers presented in the literature. The obtained results are summarised in Table 7. The results show that at solids concentration greater than 3% w/v, the net energy was positive and energy ratio was greater than one for the pre-treated sludge. But for the control sludge the results are unclear. The results reported by Kim et al. (2003) and Haug et al. (1978) for the control anaerobic digestion are contradictory. During the anaerobic digestion of the control sludge (with total solids concentration of 38 g/L), Kim et al. (2003) reported 20.1% volatile solids reduction, which resulted in energy ratio 0.47 (Table 7). Further, Huag et al. (1978) reported (with total solids concentration of 20.4 g/L), the volatile solids reduction in control anaerobic digester was 31.8% (energy ratio greater than 1, Table 7). Thus we can conclude that sludge characteristics are very critical during the pre-treatment and anaerobic digestion to have an energy efficient process. Moreover, the energy required for dewatering the pre-treated digestate, transportation and land application is missing in the literature, which are important factors in evaluating the life cycle analysis. Therefore, this article was limited to evaluate the net energy and energy ratio at different sludge solids concentration (TS).

5.3 Full scale thermal sludge pre-treatment and anaerobic digestion

A full scale plant of thermal sludge pre-treatment and anaerobic digestion treating 3200 Mg of DS/year showed that there was a net energy gain of 223 KW, which was higher than the conventional treatment (175 KW) and the treated sludge proved to be of high fertilizer value (Kepp et al., 2000). Perez-Elvira et al. (2008) demonstrated a full-scale feasibility study of the thermal hydrolysis and concluded that there was 30% increase in biogas production which eventually produces surplus energy in gas engine (i.e. 246 KW of energy). The economic value associated with the surplus energy generated was 384.64 $/yr. Yang et al. (2010) reported contradictory results while comparing with other literature data; they stated that the input energy during pre-treatment was very high compared to the energy generated from the biogas. For example, the energy input for heating sludge to 150°C was 2699.7 kJ/kg WAS and the energy generated from biogas was only 105.2 kJ/kg WAS.

5.4 Energy balance of low temperature thermal pre-treatment

Low temperature thermal pre-treatment requires longer treatment time and increase of biogas generation is not high compared with high temperature thermal pre-treatment. The energy balance at low temperature treatment has not been reported. Therefore, extensive research on energy balance is needed. Lu et al. (2008) is the only study that evaluated and reported the energy balance for low temperature thermal pre-treatment. They observed that the extra energy required for pre-treatment step will be covered by the energy produced from the extra methane generation and there would be a significant surplus energy of 2.17 kJ/d.

6. FUTURE PERSPECTIVES

The research on the effect of lower temperature on the chemical parameters (proteins, carbohydrates and lipids) and its corresponding effect on anaerobic digestion are still at laboratory scale. Further studies are necessary to have an energy efficient TPT process. The alkalinity of sludge plays a major role during AD of sludge; therefore the release of calcium and magnesium ions during TPT may have a significant effect on AD. The resultant effects of greenhouse gas emissions (GHGs), global warming and climate change have made it obligatory to quantify GHG emissions from every source. Still extensive research on optimizing the treatment parameters for enhancing the methane yield (i.e to increase the net energy yield) is required for energy efficient process. Research on TPT is evaluated since 1960, yet there is no generalised method to evaluate the efficiency of the pre-treatment process. There is a need to standardise to evaluate the treatment process and measuring parameters to compare the results of various authors. Full-scale installation and the pilot plant studies have evaluated the energy balance for the pre-treatment process, but the net energy evaluation of the process including the energy reduction for dewatering and sludge volume reduction are factors those need to be considered. A standard method for evaluating the efficiency of any pre-treatment process is by calculating the total energy balance and the net carbon balance of the total process (including anaerobic digestion of the pre-treated sludge, energy generation from the biogas). Evaluating the total energy balance and the net carbon balance will help decision makers in choosing the pre-treatment technology.

7. CONCLUSION

The low and high temperature thermal pre-treatment (TPT) of sludge has significant effect on sludge biodegradability during anaerobic digestion process in enhancing the biogas generation. Lab scale studies have concluded that 160-170°C is the optimum temperature for better dewaterability and biogas production. The optimum pre-treatment temperature and time for higher biogas production is in the range from 160°C to 180°C and 30 to 60 min, respectively. Full-scale studies proved that high temperature pre-treatment will reduce sludge retention time and sludge volume, increase dewaterability, and biogas production. At temperature > 190°C sludge solubilisation is higher but biogas production is lower (biodegradability is reduced) due to formation of toxic refractory compounds (Amadori and melanoidins compounds).

Commercial thermal pre-treatment process, CAMBI thermal hydrolysis and BIOTHELYS® process enhances dewaterability. Based on energy balance of the process, it was concluded that the energy requirement during pre-treatment step will be covered by the energy produced from the extra methane generated. With increased solids concentration the net energy and energy ratio is increased. At high solids concentration (4% w/v TS) the net energy was positive and energy ratio greater than 1 for the control sludge. When solids concentration was greater 1.5% w/v, the net energy was positive and energy ratio was greater than 1 for the thermal pre-treated sludge. In WWTPs, the total solids, thermal treatment time, treatment temperature, need to be optimised to increase the net energy and energy ratio before implementation of TPT technique.

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Abbreviations list

AD: anaerobic digestion

ASBR: anaerobic sequencing batch reactor

BSA: bovine serum albumin

CH_4: methane

COD: chemical oxygen demand

CO_2: carbon dioxide

CST: capillary suction time

CSTR: continuous-flow stirred tank reactors

DS: dry solids

ECP: extracellular polymers

GHGs: greenhouse gases

Mg/yr: mega grams per year

MJ: mega joules

PT: pre-treatment

RNA: ribonucleic acid

SCOD: soluble chemical oxygen demand

ΔSCOD : Difference in intial and final SCOD after thermal pre-treatment

SRT solids retention time

TPT: thermal pre-treatment

TDS: total dissolved solids

THD: thermo pressure hydrolysis

HRT: hydraulic retention time

TS: total solids

TSS: total suspended solids

TWAS: thickened waste activated sludge

VS: volatile solids

VDS: volatile dissolved solids

VSS: volatile suspended solids

WAS: waste activated sludge

WWTPs: wastewater treatment plants

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Table 1. Impact of thermal pre-treatment on sludge dewaterability

Sludge type	**Temperature and treatment time**	**Increase in dewaterability**	**Reference**
Sewage sludge	200-250°C and 0.5 hr	52% dry solids in sludge cake	Lumb (1951)
WAS	100-225°C and 0.5 hr	Dewaterability increased with increase in temperature, dewaterability at 225°C was significantly higher than lower temperature	Haug et al. (1978)
Dewatered sewage sludge	175°C and 1 hr	Thermo-chemical liquidized dewatered sludge was centrifuged to 42.3% w/w.	Sawayama et al. (1995)
Anaerobically digested *sludge*	175°C and 1 hr	Thermo-chemical liquidized dewatered sludge was centrifuged to 52.3% w/w.	Sawayama et al. (1996)
WAS	190°C and 0.24-1 hr	Capillary suction time (CST) of sludge increased until 130°C and started to decrease after that. CST of sludge decreased from 1330 s to 31 s at 190°C pre-treatment.	Bougrier et al. (2008)
WAS	170°C	Dry matter up to 50% was obtained after dewatering	Jung and Jungjohann (1996)
WAS	70 and 90°C and 1 hr	At 90°C the specific filtration resistance (R) reduced from 470 x 10^{12} m/kg to 190 x 10^{12} m/kg and to 19 x 10^{12} m/kg with 15 mM H_2O_2 concentration. At 70°C R decreased to 375 x 10^{12} m/kg and 125 x 10^{12} m/kg with 15 mM H_2O_2 concentration.	Mustranta, and Vikari (1993)
Sewage sludge	80°C	CST reduced from 48 sec to 27 sec with thermal pre-treatment and 14 sec with thermal pre-treatment and polymer addition.	Lin and Shien (2001)

Table 1. Contunation..

Sludge type	**Temperature and treatment time**	**Increase in dewaterability**	**Reference**
Surplus Sludge	90 and 121°C and 1 hr	At 90°C dewatering performance was higher than 121°C pre-treated sludge; i.e., the change of suction time at 90°C was -7% and that at 121°C was 10%.	Barjenbruch and Kopplow (2003)
Mixed sludge	170°C for 30 min	The dewaterability was measured using centrifugation (270 g for 1 min) and filtration tests (Millipore, with 2 bar pressure, volume filtered with respect to time). The quantity of water removed was 84% (thermally pre-treated sludge), which was nearly twice to that of fresh mixed sludge (43%).	Perez-Elvira et al. (2010)

Table 2. Chemical changes during the high temperature thermal treatment

Sludge type	TS (g/L)	Treatment		Time-temp	SCOD (mg/L)				Protein (mg/L)				Carbohydrate (mg/L)				Reference
		Time (min)	Temp (°C)		Before	After PT	ΔSCOD	% S*	Before	After PT	Δprotein	% S*	Before	After PT	Δ Carbohydrate	% S*	
WAS	29.7	30	100	3000	959.2	7810	6850.8	17.9	--	--	--	--	--	--	--	--	Haug et al. (1978)
WAS	29.7	30	135	4050	959.2	9840	8880.8	22.6	--	--	--	--	--	--	--	--	
WAS	29.7	30	175	5250	959.2	18600	17640.8	42.7	--	--	--	--	--	--	--	--	
WAS	29.7	30	200	6000	959.2	18500	17540.8	53.9	--	--	--	--	--	--	--	--	
WAS	29.7	30	225 at pH 12	6750	959.2	22000	21040.8	54.7	--	--	--	--	--	--	--	--	
WAS	29.7	120	175 at pH 1.2	21000	959.2	21100	20140.8	48.4	--	--	--	--	--	--	--	--	
WAS	--	30	120	5250	1192.1	5694.1	4502	43.7	282.24	2039.9	1757.68	34.4	42.78	361.988	319.208	41.8	Li and Noike (1992)
WAS	--	30	150	5250	1192.1	6166.4	4974.29	41.0	282.24	2333.8	2051.59	41.9	42.78	443.82	401.04	48.4	
WAS	--	60	170	3600	1192.1	7932.1	6740.01	49.7	282.24	2467.5	2185.27	44.3	42.78	332.25	289.47	46.6	
WAS	--	30	175	4500	1192.1	8793	7600.89	55.2	282.24	2649.6	2367.36	48.0	42.78	418.08	375.3	50.8	

Table 2. Contunation..

Sludge type	TS (g/L)	Treatment		Time-temp	SCOD (mg/L)				Protein (mg/L)				Carbohydrate (mg/L)				Reference
		Time (min)	Temp (°C)		Before	After PT	ΔSCOD	% S*	Before	After PT	Δprotein	% S*	Before	After PT	Δ Carbohydrate	% S*	
WAS	17.8	30	130 at pH 10	10200	700	10600	9900	63	--	--	--	--	--	--	--	--	Bougrier et al. (2006)
WAS	,,	30	170	5250	700	9200	8500	63	--	--	--	--	--	--	--	--	
WAS	17.7	30	150	3900	1100	4900	3800	39	--	--	--	--	--	--	--	--	
WAS	,,	30	170	5100	1100	6300	5200	56	--	--	--	--	--	--	--	--	
WAS	17.1	60	130	7800	396.9	3719	3322.1	25.3	--	--	--	--	--	--	--	--	Valo et al. (2004)
WAS	,,	60	150	9000	396.9	6453.3	6056.4	43.9	--	--	--	--	--	--	--	--	
WAS	,,	60	170	10200	396.9	10353	9956.1	59.5	--	--	--	--	--	--	--	--	
WAS	--	30	120	3600	302.52	2499.3	2196.74	24.2	124.31	1416.8	1292.49	23.1	47.16	275.08	227.92	35	Jeong et al. (2007)
WAS	--	30	150	4500	302.52	1794.9	1492.43	17.8	124.31	1180.9	1056.59	19	47.16	163.47	116.31	20.8	
WAS	--	30	170	5100	302.52	1815.1	1512.6	18	124.31	1230.7	1106.36	19.8	47.16	188.63	141.47	24	
WAS		30	180	5400	302.52	1764.7	1462.17	17.5	124.31	1243.1	1118.79	20	47.16	161.9	114.74	20.6	
PS	60.0	120	130	15600	6200	9300	3100	12.17	48	500	452	3.31	--	--	--	--	Wlson and Novak (2009)
PS	,,	120	150	18000	6200	11500	5300	15.05	48	2280	2232	15.10	--	--	--	--	
PS	,,	120	170	20400	6200	13000	6800	17.02	48	2400	2352	15.89	--	--	--	--	
PS	,,	120	190	22800	6200	14200	8000	18.59	48	2750	2702	18.21	--	--	--	--	
PS	,,	120	220	26400	6200	17000	10800	22.25	48	2750	2702	18.21	--	--	--	--	

Table 2. Contunation..

Sludge type	TS (g/L)	Treatment		Time-temp	SCOD (mg/L)				Protein (mg/L)				Carbohydrate (mg/L)				Reference
		Time (min)	Temp (°C)		Before	After PT	ΔSCOD	% S*	Before	After PT	Δprotein	% S*	Before	After PT	Δ Carbohydrate	% S*	
WAS	,,	120	130	15600	830	6800	5970	9.71	429	460	31	1.42	--	--	--	--	Wlson and Novak (2009)
WAS	,,	120	150	18000	830	10200	9370	14.57	429	2300	1871	7.08	--	--	--	--	
WAS	--	30	150	4500	302.52	1794.9	1492.43	17.8	124.31	1180.9	1056.59	19	47.16	163.47	116.31	20.8	
WAS	--	30	170	5100	302.52	1815.1	1512.6	18	124.31	1230.7	1106.36	19.8	47.16	188.63	141.47	24	
WAS		30	180	5400	302.52	1764.7	1462.17	17.5	124.31	1243.1	1118.79	20	47.16	161.9	114.74	20.6	
WAS	,,	120	150	18000	830	10200	9370	14.57	429	2300	1871	7.08	--	--	--	--	
WAS	,,	120	170	20400	830	11850	11020	16.93	429	2800	2371	8.62	--	--	--	--	
WAS	,,	120	190	22800	830	14050	13220	20.07	429	2900	2471	8.92	--	--	--	--	
WAS	,,	120	220	26400	830	16800	15970	24.00	429	3250	2821	10.00	--	--	--	--	
WAS	99.8	5	170	850	7376	45000	37624	41.66	2200	23000	20800	54.83	733	7600	6867	57.62	Donoso-Bravo et al. (2011)

Table 2. Contunation..

Sludge type	TS (g/L)	Treatment		Time-temp	SCOD (mg/L)				Protein (mg/L)				Carbohydrate (mg/L)				Reference
		Time (min)	Temp (°C)		Before	After PT	ΔSCOD	% S*	Before	After PT	Δprotein	% S*	Before	After PT	Δ Carbohydrate	% S*	
WAS	,,	10	170	1700	7376	53000	45624	49.06	2200	27000	24800	64.36	733	10500	9767	79.60	
WAS	,,	15	170	2550	7376	55000	47624	50.92	2200	33000	30800	78.67	733	9300	8567	70.50	
WAS	,,	25	170	4250	7376	55000	47624	50.92	2200	32000	29800	76.28	733	7000	6267	53.07	
WAS	76.8	5	170	850	4829	30000	37624	30.06	1950	13000	11050	34.39	629	7500	6871	69.01	Donoso-Bravo et al. (2011)
WAS	,,	10	170	1700	4829	36000	25171	36.07	1950	15500	13550	41.00	629	6800	6171	62.57	
WAS	,,	15	170	2550	4829	35000	31171	35.07	1950	16000	14050	42.32	629	8500	7871	78.21	
WAS	,,	25	170	4250	4829	37500	30171	37.58	1950	18000	16050	47.61	629	7200	6571	66.25	
WAS	,,	30	170	5100	4829	42000	32671	42.08	1950	17000	15050	44.97	629	8300	7671	76.37	

Note: S* is solubilisation percentage; Δ is the difference between the SCOD before and after pre-treatment;

-- is not applicable, ,, is similar value

Table 3. Chemical changes during the low temperature thermal treatment

Sludge type	TS	Treatment		Time - temp	SCOD (mg/L)				Soluble Protein (mg/L)				Soluble Carbohydrate (mg/L)				Reference
		Time (min)	Temp (°C)		Before	After PT	ΔSCOD	% S*	Before	After PT	Δprotein	% S*	Before	After PT	Δ carbohydrate	% S*	
TWAS	--	15	70	1050	400	650	250	0.45	125	864	739	2.51	136	139	3	0.04	Soluble proteins as mg BSA-eq/L carbohydrates as mg Glu-eq/L
TWAS	--	30	70	2100	400	800	-320	0.72	125	1293	1168	3.96	136	130	-6	-0.08	
TWAS	--	60	70	4200	400	1150	750	1.36	125	1155	1030	3.49	136	144	8	0.1	
TWAS	--	15	80	1200	400	1350	950	1.72	125	388	263	0.89	136	164	28	0.35	
TWAS	--	30	80	2400	400	2050	1650	2.98	125	900	775	2.63	136	208	72	0.88	
TWAS	--	60	80	4800	400	8200	7800	14.1	125	2736	2611	8.85	136	721	585	7.17	
TWAS	--	15	90	1350	400	1600	1200	2.17	125	748	623	2.11	136	165	29	0.35	Appels et al. (2010)
TWAS	--	30	90	2700	400	7200	6800	12.3	125	2495	2370	8.03	136	722	586	7.18	
TWAS	--	60	90	5400	400	10250	9850	17.8	125	3162	3037	10.3	136	1094	958	11.74	Soluble
WAS	--	30	60	1800	302.52	1089.1	786.54	10.8	124.31	791.1	666.79	11.28	47.16	83.31	36	15.6	
WAS	--	30	80	2400	302.52	1865.5	1563.02	18.5	124.31	1280.4	1156.08	20.6	47.16	165.05	117	21.0	Jeong et al. (2007)
WAS	--	30	100	3000	302.52	1774.7	1472.18	17.6	124.31	1149.9	1025.55	18.5	47.16	175.26	128	22.3	

Note : S* is solubilisation percentage; Δ is the difference between the SCOD before and after pre-treatment; -- is not applicable

Table 4. Effect of low temperature thermal pre-treatment on biogas generation rate

Temperature ˚C	Hydrolysis time (hr)	Increase in biogas generation rate	Methane produced	Reference
100	0.5	14% increase in biogas is observed	Secondary sludge - control 510 mL/day Pre-treated, secondary sludge 579 mL/day	Haug et al. (1978)
60	1	30% increase in biogas at organic loading of 3 kg –VS/m^3 d	Waste activated sludge - control 217 mL/g VS$_{added}$ Pre-treated 283 mL/g VS$_{added}$	Hiraoka et al. (1984)
100	1	More than 50% increase is expected at organic loading of 3 kg –VS/m^3 d	Waste activated sludge - control 217 mL/g VS$_{added}$ Pre-treated 344 mL/g VS$_{added}$	
60	NA	52.1% increase in methane generation at 8 days HRT	Waste activated sludge - control 585 mL/L day Pre-treated 344 mL/L day	Wang et al. (1997a)
70	24 and 96	Pre-treating the primary sludge for 4 days the methane generation rate increased by 16.2% and at 7.7%, when pre-treated for 7 days	Primary sludge- control 21.4 mmol CH_4/g VS Pre-treated for 4 days 24.8 mmol CH_4/g VS Pre-treated for 7 days 23.1 mmol CH_4/g VS	Gavala et al. (2003)
70	24 and 96	For secondary sludge at 4 days pre-treatment the methane generation rate increased by 144.6% and at 1 day pre-treatment 25.9%	10.7 mmol CH_4/g VS Pre-treated for 4 days 8.5 mmol CH_4/g VS Pre-treated for 1 day	
70	48	The methane generation from pre-treated primary and secondary sludge is enhanced by 11% and 37.5% than untreated primary and secondary sludge, respectively.	Primary sludge - Control 144.6 mL/L day, pre-treated 162 mL/L day Secondary sludge –control 40 mL/L day, pre-treated 55 mL/L day	Skiadas et al. (2005)

Table 4. Contunation..

Temperature °C	Hydrolysis time (hr)	Increase in biogas generation rate	Methane produced	Reference
70	9	68.6% increment in biogas production is observed	Control (secondary sludge) 0.35 L/day, Pre-treated (secondary sludge) 0.59 L/day	Climent et al. (2007)
70	9	Biogas production increased up to 30% both in batch tests and in semi-continuous experiments. The rate of biogas production is around 0.63 L/L day, and the methane content in the biogas is around 64%.	Control (mixed sludge) (0.22 L/gVS_{added}) Pre-treated (mixed sludge)0.28–0.30 L/gVS_{added})	Ferrer et al. (2008)
70	0.5	The pre-treatment of the primary sludge resulted up to 48% increase of methane potential and up to 115% increase of methane production rate.	Control (primary sludge) 13.5 mmol CH_4/g VS Pretreated (primary sludge) 20.1 mmol CH_4/g VS	Lu et al. (2008)
75	7	Seven hours of thermal pre-treatment at 75°C led to 50% increase in biogas production	Waste activated sludge - control 62.5 mL/day, Waste activated sludge - Pre-treated 93.6 mL/day	Borges and Chernicharo (2009)
70	48	Methane yield Increased from 5% at thermophlic digestion. At mesohilic digestion the methane yield increased by 4.6%	Mixed sludge - control 247±9 Nml CH_4/g VS_{added}. Pre-treated 264±8 Nml CH_4/g VS_{added}. Mixed sludge- control (mesophilic digested) 254±9 Nml CH_4/g VS_{added} Pretreated 268±7 Nml CH_4/g VS_{added}	Nges and Liu (2009)
50	48	Methane yield Increased from 6.25% at thermophlic digestion. At mesohilic digestion the methane yield increased by 11%.	Mixed sludge- control 247±9 Nml CH_4/g VS_{added}. Pre-treated 268±6 Nml CH_4/g VS_{added}. Mixed sludge- control (mesophilic digested) 254±9 Nml CH_4/g VS_{added}. Pretreated 284±8 Nml CH_4/g VS_{added}	Nges and Liu (2009)

Table 4. Contunation..

Temperature °C	Hydrolysis time (hr)	Increase in biogas generation rate	Methane produced	Reference
50	48	Methane yield Increased from 6.25% at thermophlic digestion. At mesohilic digestion the methane yield increased by 11%.	Mixed sludge- control 247±9 Nml CH_4 /g VS_{added}. Pre-treated 268±6 Nml CH_4/g VS_{added}. Mixed sludge- control (mesophilic digested) 254±9 Nml CH_4/g VS_{added}. Pretreated 284±8 Nml CH_4/g VS_{added}	Nges and Liu (2009)
50 -65	12-48	Pre-treatment temperature had a very clear affect on methane yield. The degradability was increased at thermophilic temperature, which was increased from 21% to 49% with temperature increased from 50 to 65°C , respectively.	For secondary sludge, approximately 160 mL/g VS_{added} at 50°C was observed and approximately 300mL/g VS_{added} at 65°C, respectively.	Ge et al., (2011a)
50-70	Over different periods of 15 months	At 50°C pre-treatment during period 1 for186 days, thermophilic pre-treatment did not offered any advantage over mesophilc pre-treatment. But increasing the pre-treatment temperature to 60°C and 65°C (period 2, 100 days and period 3, 67 days respectively) showed improved performance, i.e., VS destruction increased from 35% to 42% and 50% respectively. Further increase in pre-treatment temperature to 70°C (Period 4, 68 days), there was no increase in VS reduction.	Comparing the hydrolysis coefficient in mesophilic and thermophilic pre-treatment systems, the hydrolyis coefficient of the secondary sludge is enhanced at pre-treatment of 60-70°C .	Ge et al., (2011b)
70-90	0.25 to 1hr	Biogas production increased significantly with treatment at temperature of 90°C when compared with 70°C treatment temperature	Biogas 377.56 mL/g organic dry solids degraded, at 90°C And at 70°C 35.32 mL/g ODS for secondary sludge.	Appels et al. (2010)

Table 5. Effect of high temperature thermal pre-treatment on biogas generation rate

Temperature ˚C	Hydrolysis time (hr)	Increase in biogas/methane generation rate	Methane produced	Reference
175	0.5	60-70% increase in the biogas production	Control 406 mL/day Pre-treated 641 mL/day	Haug et al. (1978)
110	0.3	Thermal pre-treatment of combined sludge (45% primary sludge, 45% excess sludge) at 110°C enhanced 25% higher biogas compared to the control sludge.	Control 0.9 dm^3/day biogas Pre-treated 0.95 dm^3/day biogas	Bien et al. (2004)
130 at pH 10	1.0	During the batch thermophilic digestion (20d), the biogas production increased by 74%	Control 88 mg/g COD_{added} Pre-treated 154 mg/g COD_{added}	Valo et al. (2004)
170	1.0	During the batch thermophilic digestion for 20d, the methane production increased by 61%	Control 88 mg/g COD_{added} Pre-treated 142 mg/g COD_{added}	Valo et al. (2004)
170	0.5	During the batch anaerobic digestion (24d), the methane production increased by 76%	Control 221 mL/g COD_{added} Pre-treated 331 mL/g COD_{added}	Bougrier et al. (2007)
170	0.5	During the anaerobic digestion in CSTR (20d), the methane production increased by 51% .	Control 145 mL/g COD_{added} Pre-treated 256 mL/g COD_{added}	Bougrier et al. (2006)
120	0.5	The methane gas production for thermally pretreated WAS increased from 22.4 to 42.9% (at 10d HRT)	Control 185 mL/day Pretreated 230 mL/day	Jeong et al. (2007)
170	0.5	78% increase in methane production (HRT:17d to 24 d)	Control 128 mL CH_4/g VS_{added} Pre-treated to 228 mL CH_4/g VS_{added}	Carrere et al. (2008)

Table 5. Contunation..

Temperature °C	**Hydrolys is time (hr)**	**Increase in biogas/methane generation rate**	**Methane produced**	**Reference**
190	0.5	Biogas production is improved by 23% at 190°C pre-treatment (17d to 24d HRT)	Control 128 mL CH_4/g VS_{added} Pre-treated to 228 mL CH_4/g VS_{added}	Carrere et al. (2008)
180	1.0	Pre-hydrolysing WAS by Thermo-Druck-Hydrolyse process (TDH), biogas production increased from 90.32 L/kgCOD to 162.82 L/kgCOD (20-30d HRT)	Control 206.5 mL CH_4/g VS_{added} Pre-treated to 254.0 mL CH_4/g VS_{added}	Phothilangka et al. (2008)
175	0.5	Compared the performance of anaerobic sequencing batch reactor (ASBR) and continuous-flow stirred tank reactors (CSTR) for the digestion of thermally hydrolyzed sewage sludge. The daily biogas production of ASBR is 15% and 31% higher than the CSTR at 20 and 10 days hydraulic retention time respectively.	At 20 days ASBR 273 mL CH_4/g COD_{added} CSTR 235 mL CH_4 /g COD_{added} At 10 days ASBR 256 mL CH_4/g COD_{added} CSTR 207 mL CH_4/g COD_{added}	Wang et al. (2009)
165	0.5	The methane production has increased by 30.3% at 165°C (steam mode) (22d HRT)	Control 165 mL/COD_{inlet} pre-treatmenmt 215 mL/COD_{inlet}	Mottet et al. (2009)
170	0.5	The biogas production is enhanced by 40% in half time, compared to a conventional digester (20-30d)	Control 250 mL CH_4 /g VS_{added} pre-treatmenmt 365 mL CH_4/g VS_{added}	Perez-Elvira et al. (2010)
170-180	1.0	With thermal hydrolysis the biogas production was increased by 75% and with mechanical ball milling the biogas production was increased to 41%, respectively when compared with control (14d-20d HRT)	247 L to 443 L/kg VSS_{added} load due to TDH pre-treatment 265 L to 415 L per kg VSS_{added} ball milling	Wett et al. (2010)

Table 6. Parametric values considered in the energy analysis

Description	Value	Units	Reference
Sludge to be treated	40000	Kg dry solids per day	Assumed
Temperature of sludge before pre-treatment	12	°C	Wastewater treatment plant, Quebec city
Anaerobic digestion temperature	35	°C	Metcalf and Eddy (2003)
Specific heat of sludge	4200	$kJ/m^3\ ^oC$	Metcalf and Eddy (2003)
Density of sludge	1000	Kg/m^3	Metcalf and Eddy (2003)
Retention time (HRT)			Fernandez-Polanco et al. (2008); Perez-Elvira et al., (2010)
Control sludge	20	Days	
Pre-treated sludge	12		
Heat loss of AD	5 (2-8)	% of sludge heating requirement	Zupancic and Ros (2003)
Methane production rate	0.499	$m^3\ CH_4/kg\ VS_{destroyed}$	Metcalf and Eddy (2003)
Heating value of methane	31.79	$MJ/m^3\ CH_4$	Metcalf and Eddy (2003)
Thermal pre-treatment temperature	170	°C	Fernandez-Polanco et al. (2008); Perez-Elvira et al., (2010)
Recovery of heat energy from the pre-heated sludge using heat exchangers	85	%	Lu et al., (2008)
Volatile solids reduction for non-pretreated sludge	45	%	Metcalf and Eddy (2003)
Volatile solids reduction for pretreated sludge	65	%	Haug (1977)

Table 7. Computation of energy ratio for the data adopted from the different authors

Total solids g/L	Pre-treatment Temperature (°C)	Pre-treatment time (min)	Energy input kWh/Mg dry solids	Energy recovered kWh/Mg dry solids	Net energy kWh/Mg dry solids	Energy ratio	Reference
20.4	NT	NT	741.3	946.5	205.2	1.28	Haug et al. (1978)
20.4	170	30	1454.5	1247.9	-206.5	0.86	
40.7	NT	NT	371.6	1009.6	638.1	2.72	Haug et al. (1983)
30.7	175	30	966.5	1683.8	717.3	1.74	
44.8	NT	NT	910.7	1279.8	369.1	1.41	Ferrer et al. (2008)
48.1	70	1440	839.1	1025.7	186.5	1.22	
58.9	70	2880	686.1	828.9	142.7	1.21	
68.2	70	540	592.1	1024.5	432.4	1.73	
38 .0	NT	NT	1209.8	563.7	-646.0	0.47	Kim et al. (2003)
38.0	120	30	502.2	967.6	465.4	1.93	
12.5	NT	NT	1209.8	957.0	-252.8	0.79	Valo et al. (2004)
7.0	170	30	4101.2	1507.3	-2593.9	0.37	
10.9	130	30	1927.4	1022.6	-904.8	0.53	

Note : NT- no pre-treatment (or control)

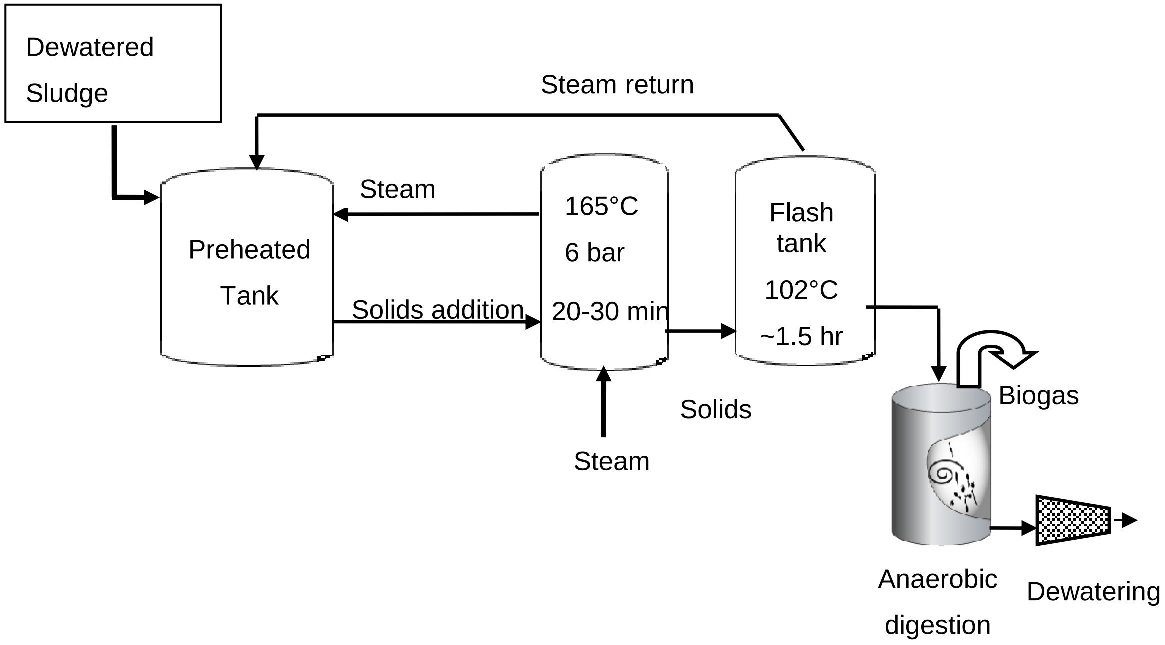

Figure 1. Thermal hydrolysis process flow diagram (Cambi Process)

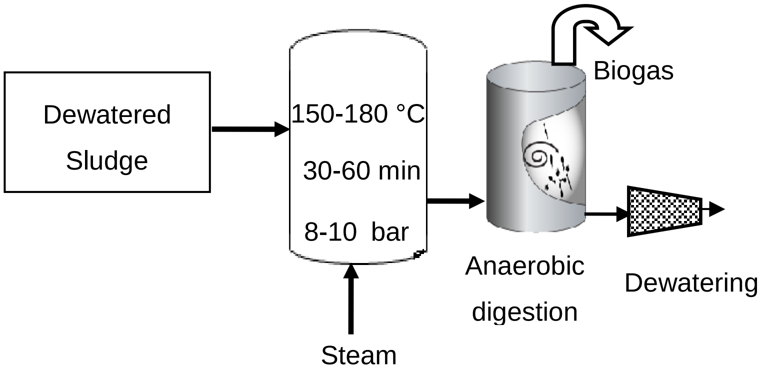

Figure 2. Thermal hydrolysis process flow diagram (BIOTHELYS®)

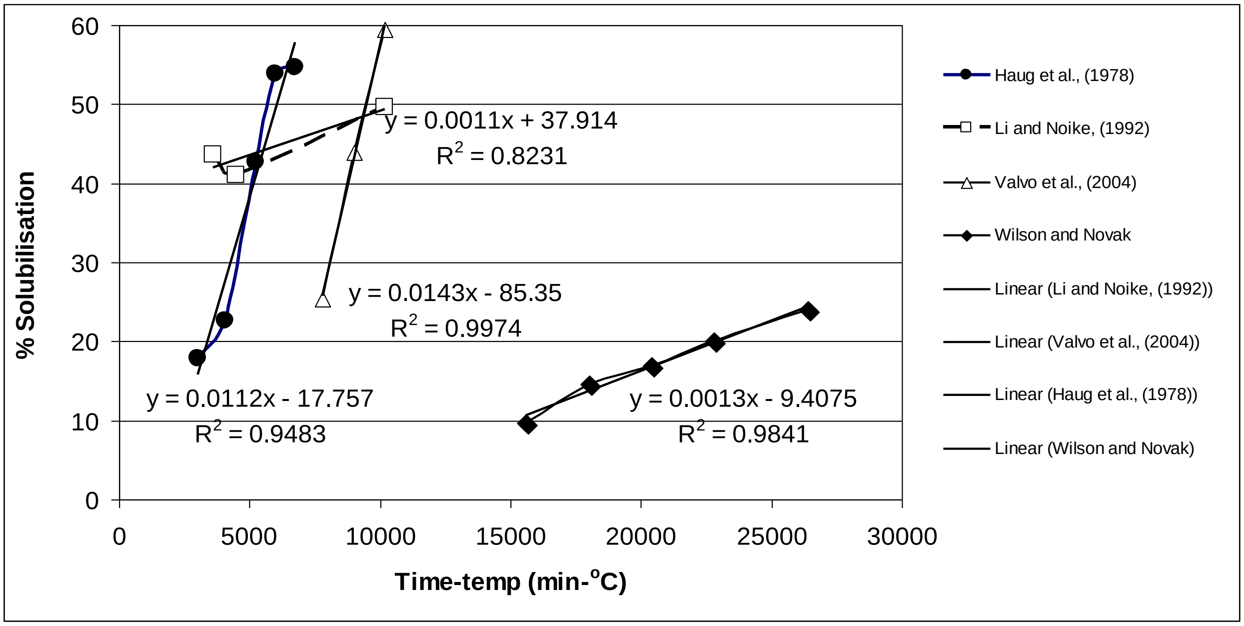

Figure 3. Solubilisation of WAS at different time-temperature

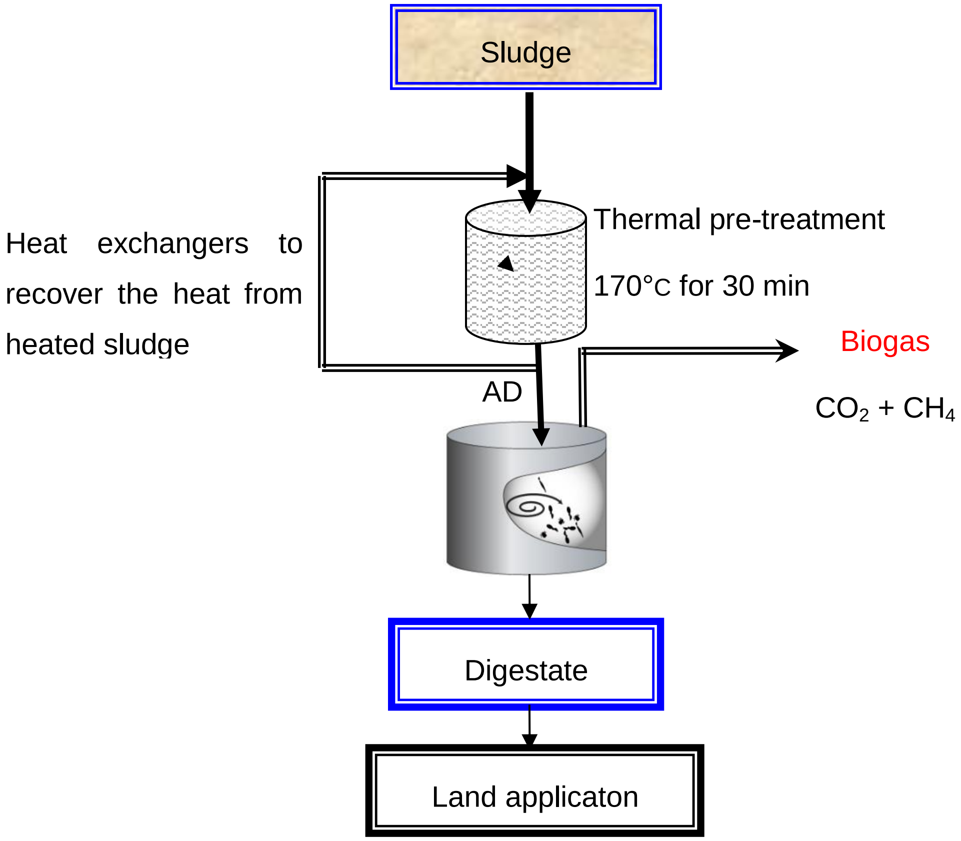

Figure 4. Thermal pre-treatment and anaerobic digestion process considered for energy balance

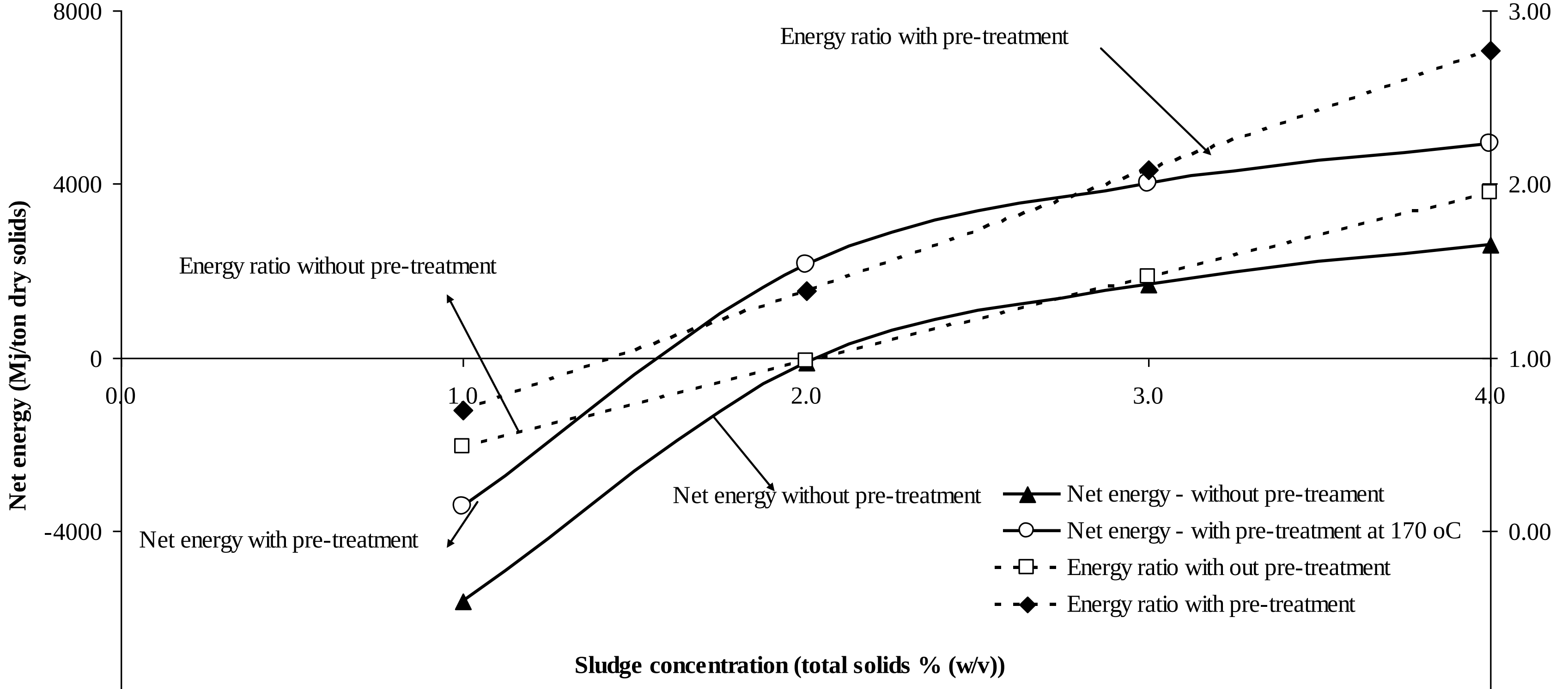

Figure 5. Net energy (output-input) generated at different sludge solids concentration

PARTIE 2

ANAEROBIC DIGESTION OF THERMAL PRE-TREATED SLUDGE AT DIFFERENT SOLIDS CONCENTRATION-COMPUTATION OF MASS-ENERGY BALANCE AND GREENHOUSE GAS EMISSIONS

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RÉSUMÉ

L’effet du prétraitement thermique sur l’efficacité de la digestion anaérobie des boues a été étudié pour différentes concentrations en solides totaux (ST) (20, 30 et 40 g ST/L) et à divers temps de digestion (0, 5, 10, 15, 20 et 30 jours) pour plusieurs types de boues d'épuration (primaires, secondaires et mixtes). En outre, le processus de traitement et d’élimination des boues a été évalué sur la base des bilans de masse-énergie et de gaz à effet de serre correspondants (GES). Le bilan de masse a révélé que les boues secondaires prétraitées thermiquement à une concentration de 30,0 gTS/L avaient généré le plus faible digestat (23,39 Mg de matières sèches). L'énergie nette (énergie d'entrée - sortie d'énergie) et le ratio de l'énergie (énergie de sortie/énergie d'entrée) pour les boues prétraitées thermiquement étaient supérieurs au contrôle dans tous les cas. Des émissions de GES minimales de $73{,}8 \times 10^{-3}$ g CO_2/Mg de matières sèches totales (TDS) ont été observées à une concentration en solides totaux de 30,0 g ST/L pour les boues secondaires ayant subi un prétraitement thermique. Le prétraitement thermique des boues est énergétiquement avantageux et il diminue le temps de digestion de 10 jours pour les boues secondaires prétraitées par ce même procédé.

Mots-clés: prétraitement thermique; digestion anaérobie; bilan de masse-énergie; émissions de gaz à effet de serre.

ABSTRACT

The effect of thermal pre-treatment on sludge anaerobic digestion (AD) efficiency was studied at different total solids (TS) concentrations (20.0, 30.0 and 40.0 g TS/L) and digestion times (0, 5, 10, 15, 20 and 30 days) for primary, secondary and mixed wastewater sludge. Moreover, sludge pre-treatment, AD and disposal processes were evaluated based on a mass-energy balance and corresponding greenhouse gas (GHG) emissions. Mass balance revealed that the least quantity of digestate was generated by thermal pre-treated secondary sludge at 30.0 g TS/L. The net energy (energy output-energy input) and energy ratio (energy output/energy input) for thermal pre-treated sludge was greater than control in all cases. The reduced GHG emissions of 73.8×10^{-3} g CO_2 equivalent/g of total dry solids were observed for the thermal pre-treated secondary sludge at 30.0 g TS/L. Thermal pre-treatment of sludge is energetically beneficial and required less retention time compared to control.

Keywords: thermal pre-treatment; primary sludge; secondary sludge; mixed sludge; net energy; energy ratio.

1. INTRODUCTION

Sludge is an inevitable and a major product of the (primary, secondary and tertiary) wastewater treatment processes. Large quantities of sludge are being produced annually by wastewater treatment plants (WWTPs) all over the world. Sludge treatment and disposal has become a foremost problem, and sludge production is expected to increase significantly in the future, due to the increasing stringent environmental regulations. Moreover, sludge management costs are around 50-60% of the total wastewater treatment plant operating costs (Pilli et al., 2011; Coma et al., 2013). The most commonly used sludge treatment methods are aerobic digestion, anaerobic digestion (AD), and composting (Hanjie, 2010; Arthurson, 2008). Further, incineration, landfill, and land application are the most commonly used sludge disposal methods. During sludge treatment, disposal and/or reuse (as fertilizer or biotransformation), the biomass is biodegraded or converted to carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), which are the principal greenhouse (GHG) emissions. An alarming level of global warming and climate change has made it essential to quantify GHG emissions generating from every source. Sludge treatment, disposal and/or reuse accounts for approximately 40% of the total GHG emissions from a WWTP (Brown et al., 2010).

AD of sludge is considered an important sludge treatment option that can fit into the framework of new regulations and meet the Kyoto protocol (to reduce GHG emissions) (Yasui et al., 2006). AD reduces sludge quantities and generates biogas (energy recovered from the biogas can offset the fossil fuel energy and the corresponding GHG emissions). Moreover, it has very limited adverse environmental impact (Khalid et al., 2011; Mata-Alvarez et al., 2011). AD is the microbial degradation process, where the substrate is broken down to produce CO_2 and CH_4 and it is capable of preserving nutrients (Appels et al., 2008; Mata-Alvarez et al., 2011). The substrate conversion to CO_2 and CH_4 occurs in four stages (hydrolysis, acidogenesis, acetogenesis and methanogenesis) by three different groups of microorganisms (acidogenic, acetogens and methanogenic archae). It is well known that hydrolysis of sludge is a rate limiting step (Appels et al., 2008; Pilli et al., 2011). Complex substrates present in sludge require longer retention time (for hydrolysis) and larger digester volume. Pre-treatment of sludge releases the intracellular matter by rupturing the microbial cell wall, which substantially enhances the digestion rate, reduces the retention time and increases the biogas production (Appels et al., 2008; Pilli et al., 2011).

There are various pre-treatment technologies like thermal, chemical, mechanical, biological, physical and several combinations such as thermo-chemical, physico-chemical, biological-physicochemical, and mechanical-chemical. The thermal hydrolysis process has more advantages over other pre-treatment technologies (Pilli et al., 2014). Thermal hydrolysis produces Class A pathogen-free biosolids as defined by United States CFR 40 part 503.32 US EPA (Gianico et al., 2013). To date, there are no studies on evaluating the thermal pre-treatment technology for enhancing biogas production based on mass-energy balance and GHG emissions at different solids concentrations of primary, secondary, and mixed municipal wastewater sludge. Sludge solids concentration can affect the energy required during AD, dewatering, transportation, and land application as well as corresponding GHG emissions. Therefore, the objective of the present study was to assess the effect of thermal pre-treatment in enhancing AD on the basis of mass-energy balance and corresponding GHG emissions at different solids concentrations of primary, secondary, and mixed municipal wastewater sludge.

The overall process considered in this study is presented in Fig. 1.

2. MATERIAL AND METHODS

2.1 Wastewater sludge

Primary, secondary and mixed sludge was collected from a wastewater treatment facility, Communauté urbaine de Québec (CUQ) (Beauport, Québec City, Canada). The wastewater treatment facility includes unit processes such as primary clarification, secondary biological treatment (without nutrient removal) and tertiary treatment. After gravity settling for 2 h, the total solids concentration of settled sludge (primary, secondary, mixed sludge) was ~15.0 g/L. Further, sludge solids concentration was increased by centrifugation at 1600×*g* for 3 min in a Sorvall RC 5C plus Macrocentrifuge (rotor SA-600). The sediments of the centrifuged sludge were diluted with demineralised water to obtain desired solids concentrations of 20.0, 30.0 and 40.0 total solids (TS) g/L and were homogenized in a Waring TM blender for 30 s. Sludge (primary, secondary and mixed) characteristics are presented in Table 1.

2.2 Thermal pre-treatment of the sludge

Thermal pre-treatment of sludge was carried out in a lab scale thermal hydrolyser (total capacity of 8×10^{-3} m^3) at 134-140°C and 3.4 bar for 30 min. Sludge temperature was first increased to

134°C and then the temperature was allowed to further increase to 140°C for 30 min. The temperature of 134°C was concluded effective in solubilising organic matter of secondary sludge (Gianico et al., 2013). The optimum treatment time for thermal pre-treatment to enhance AD is in the range of 30-60 min (Pilli et al., 2014). Therefore, treatment time of 30 min was considered in our study. Sludge of volume 4 L after centrifugation was directly added to the hydrolyser.

The energy required for heating sludge from 10°C to 134°C and to maintain at 134°C for 30 min was calculated as per Eq. 1. Heat energy was considered to be recovered (85%) from the heated sludge (134°C) using heat exchangers (to heat the incoming sludge), prior to its addition into the anaerobic digester (at 35°C) (Lu et al., 2008; Pilli et al., 2014).

$$E = Q \times Cp \times (T_2 - T_1) \tag{1}$$

Where, E is the energy required for heating sludge (kJ/day), Q is the volume of sludge (m^3/day), Cp is the specific heat of sludge (4.2×10^3 kJ/m^3 °C), T_2 temperature of sludge in the tank (°C); and T_1 temperature of raw sludge entering the tank (°C).

2.3 Anaerobic digestion

Anaerobic digestion was performed at mesophilic temperature (35°C) in a water bath. Septic glass bottles (with provision to collect biogas) having capacity of 1×10^{-3} m^3 with working volume of 8×10^{-4} m^3 were used. To maintain the constant temperature, the water level in the water bath was adjusted to the upper level of sludge height in the bottles. Anaerobic sludge (1×10^{-4} m^3) was collected from Valcartier, Québec, Canada in aseptic conditions and was refrigerated at 4°C, which was used as inoculum. To remove the air from the head space and to ensure anaerobic conditions, the nitrogen gas was sparged through the bottles for 2 min. To minimise the effects of settling during AD, the bottles were mixed manually twice a day. During the digestion pH of the samples were adjusted to 7 with NaOH solution. To evaluate the effect of thermal pre-treatment on solids degradation at a different retention time during AD, the digested sludge samples (75×10^{-6} m^3) of control and thermal pre-treated sludge were collected on 5th, 10th, 15th, 20th and 30th day of the digestion. The digested sludge samples were collected by transferring the samples into a measuring cylinder with a minimum exposure time of 15 s. Nitrogen gas was immediately sparged into bottles for 2 min to maintain anaerobic conditions for further AD.

2.4 Dewaterability

Capillary-suction-time (CST) was used to measure the dewaterability. CST was determined by using the CST instrument (Triton electronics, model 304 M CST, Dunmow, Essex) with 10-mm diameter reservoir (Scholz, 2006). Dewatering (belt press or centrifugation) requires higher energy; therefore, estimation of dewaterability of the pre-treated anaerobic digested sludge was necessary for calculating the energy balance and GHG emissions.

2.5 Sludge disposal

The land application of dewatered sludge digesate was considered as a disposal option in the present study (Fig. 1). In computations, the distance between the WWTP and land application site was considered as 50 km, since agriculture lands are located 50 km away from the industrial area (Gassara, et al., 2011). Dewatered sludge was transported by using 3 axle semi-trailer vehicles, and they had consumed 35 L of diesel/100 km (Gassara et al., 2011). GHG emission values corresponding to diesel use for transportation were equivalent to 2730 g CO_2/L of diesel, 12×10^{-2} g CH_4/L of diesel, and 8×10^{-2} g N_2O/L of diesel (Gassara et al., 2011). Further, it was also considered the energy required during land application of the dewatered sludge was evaluated based on the factor as 351.68×10^{-6} kWh/g of total dry solids (TDS) (Wang et al., 2008).

2.6 Mass-energy balance

The total mass entering into AD, corresponding mass that was converted into biogas and the remaining digestate transferred for dewatering were measured for evaluating the mass balance of the process. The parameters used for the energy balance evaluation were as described here.

Total energy input = ∑energy containing in fuels, electricity, and steam used in the process for thermal pre-treatment, AD, dewatering, transportation and land application.

Energy output = Energy obtained from the CH_4 produced using cogeneration unit (combined heat and power)

Net energy = energy output- energy input (2)

Energy ratio = energy output / energy input (3)

2.7 GHG emissions

The energy required for thermal pre-treatment, AD, dewatering, transportation and land application was generated from fossil fuels. This will correspond to GHG emissions. National emission intensity coefficient 530 g CO_2/kWh (developed by Environment Canada study based on the Resources for the Future (RFF) model) is used to compute GHG emissions corresponding to energy utilization in the various process steps (Fig. 1). During the energy recovery, CH_4 combustion will generate CO_2 (Eq. 4). Principal GHG emissions are CO_2, CH_4, and N_2O from the land applied of digestate and they are estimated using the factors as specified by Hospido et al. (2005), Hong et al. (2009), and Brown et al. (2010), i.e. 17×10^{-4} g CO_2 per g of TDS, 3×10^{-3} g CH_4 per g of TDS, and 3×10^{-2} g CO_2 equivalent per g of TDS, respectively. During the AD, the biomass is biodegraded to CO_2 and CH_4, but CO_2 emissions from biological pathway are considered as biogenic emissions. Therefore, CO_2 emissions from the AD are not taken into account in national protocols due to the fact that they are considered (by convention) as “carbon neutral” (global warming potential equal to zero) (Pradel and Reverdy, 2012).

$$CH_4 + 2\,O_2 \text{ ----> } CO_2 + 2\,H_2O + \text{energy} \qquad (4)$$

2.8 Analytical methods

The analysis of total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), pH, soluble chemical oxygen demand (SCOD), and total chemical oxygen demand (TCOD) were carried out as per the standard methods (APHA, 2006). All the data presented was representative of all samples measured in triplicates. The percentage error of the data presented in Fig. 2 to 6 was less than 5%. The biogas produced during the AD was collected and analysed using Gas chromatograph (Shimadzu GC 14A) as per the procedure given by Cui and Jahng (2006). The volume of biogas was measured based on the water displacement. Using the heating value of CH_4 (35.8 MJ/m^3, Tervahauta et al., 2014), the energy recovered from the CH_4 was evaluated.

3. RESULTS AND DISCUSSION

3.1 Effect of thermal pre-treatment on (priamry, secodnary and mixed) sludge solubilisationat different solids concentrations

The variations in SCOD observed for primary, secondary and mixed sludge at different solids concentrations are summarised in Fig. 2. In general, thermal pre-treatment (at 134°C for 30 min) had increased SCOD, irrespective of the type of sludge and sludge solids concentrations (Fig. 2a-c). Moreover, increase in SCOD was also observed with the increase in sludge solids concentration, after thermal pre-treatment of sludge (in all the cases). Compared to the primary sludge, the SCOD was approximately 1.5 and 1.3 times higher for the secondary and the mixed sludge, respectively . The increase of SCOD concentration after thermal pre-treatment was attributed to the de-agglomeration and transfer of organic substances from non-soluble material into soluble materials. Thermal pre-treatment of sludge breaks the polymeric network ending with the release of mainly extracellular and possibly intracellular materials such as polysaccharides, protein including smaller amounts of DNA and RNA into the soluble phase (Ekicioglu et al., 2006). Secondary sludge contains a higher content of organic matter (proteins, carbohydrates, humic substances, nucleic acids, etc.) as compared to the primary sludge (Smith et al., 2009). Therefore, SCOD was higher in the secondary sludge when compared to the primary and mixed sludge. The increase in the SCOD observed in the present study was in concurrence with the literature reports (Gianico et al., 2013; Bougrier et al., 2006).

The variations in SS and VSS before/after thermal pre-treatment are summarised in Fig. 3. In general, thermal pre-treatment (at 134°C for 30 min) reduced SS and VSS concentrations, irrespective of the type of sludge and sludge solids concentrations (Fig. 3a-f). The percentage of SS and VSS reduction was 19.9% and 18.3%, respectively in the primary sludge. Similarly, the SS and VSS reduction was 29.6% and 32.3% for secondary sludge and was 28.5% and 29.5% for the mixed sludge, respectively. Increasing the solids concentrations, the SS and VSS reduction did not increase. The SS reduction was 29.6%, 25.4% and 16.4%, respectively, during the thermal pre-treatment of the secondary sludge at 20.0, 30.0 and 40.0 g TS/L. The reduction of the SS and VSS was due to the cell lysis and release of intracellular matter into the liquid phase. Secondary sludge mainly contains microbial mass compared to primary and mixed sludge (Smith et al., 2009). At higher solids concentrations, the thermal pre-treatment was not as effective when compared to the lower solids concentrations. Therefore, the SS and VSS reduction was relatively lower at higher solids concentration. The possible reason for the decline in the SS reduction at high solids concentration was due to inhomogeneous mixture and mixing of sludge during the pre-treatment. Extent of disintegration during thermal pre-treatment depends upon several factors including treatment time, temperature, (Pilli et al., 2014) sludge concentration, and mixing. Increasing the treatment time has increased the SS solubilisation (Jayashree et al., 2014). Degree of disintegration was 14.0% and 13.0% at 20.8 and 41.4 g TS/L, respectively at 134°C for 20 min (Gianico et al., 2013). Thus, the degree of disintegration was lower at high solids concentrations.

3.2 Anaerobic digestion of primary, secondary and mixed sludge at different solids concentration

Solids degradation during AD of the primary sludge at different solids concentrations for 30 days are summarised in Fig. 4. In general, there was a gradual decrease in the solids concentrations in all cases during 30 days of AD. The VS degradation was higher by 3.8% at 30.0 TS/L and 2.2% at 40.0 g TS/L, compared to the 20.0 g TS/L. Thermal pre-treatment increased the rate of solids degradation during 5-10 days of AD. The degradation rate was 260.0 g/m^3 day^{-1} and 390.0 g/m^3 day^{-1} for the control and the thermal pre-treated sludge, respectively at 20.0 g TS/L during 5 days of digestion. Increasing the solids concentration increased the degradation rate during 5 days of digestion, i.e. the degradation rate was 500 g/m^3 day^{-1} at 30.0 g TS/L and 760 g/m^3 day^{-1} at 40.0 g TS/L. However, there was no significant difference in solids degradation for thermal pretreated or untreated sludge at the end of AD (30 days). For primary sludge (control) at 30.0 g TS/L, the VS degradation was 47.9%, whereas, it was 50.4% for thermal pre-treated sludge.

The secondary and mixed sludge degradation at different solids concentrations are summarised in Fig. 5 and 6, respectively. Similar to that of the primary sludge, there was a gradual decrease in the solids concentration in the secondary and the mixed sludge during 30 days of AD. The degradation rate in the secondary and the mixed sludge was high for the thermally pre-treated sludge during the initial 5 days of digestion. The VS degradation was 50.3%, 57.9%, and 54.9%, respectively, for the primary, secondary and the mixed sludge at 30.0 g TS/L after 30 days of digestion. The decrease in solids concentration was due to the degradation of the organic matter (Pilli et al., 2014). The total protein and soluble protein content was 13.4 and 0.03, and 31.2 and 0.40 g/L of the primary and the secondary sludge, respectively (Wilson and Novak, 2009). Therefore, the easily available soluble organic matter for secondary sludge was high compared to the primary and the mixed sludge. Thermal pre-treatment increased the available organic matter to the anaerobic microorganisms, which enhanced the rate of degradation during the initial 5 days of digestion for the thermal pre-treated sludge. At the end of digestion (30 days) the easily available organic matter was not avaialable for the thermally pre-treated sludge. For the control case, the micro-organisms have hydrolysed the cells and digested the organic matter. Gianico et al. (2013) also had observed a reduction in volatile solids degradation at a higher organic loading rate.

3.3 Methane production during anaerobic digestion of different types of sludge at different solids concentration

The cumulative CH_4 production for control and thermal pre-treated of primary sludge during AD for 30 days is evaluated (Fig. 7a). An increase in the CH_4 percentage after thermal pre-treatment was insignificant (Table 2). In general, the cumulative CH_4 volume increased with the increasing digestion time. Thermal pre-treatment (at 134°C for 30 min) increased the cumulative CH_4 volume, irrespective of sludge solids concentrations. For example, the cumulative CH_4 production was 21.12×10^{-4} m^3/g of VS added for the control (primary sludge) at 20.8 g TS/L and was 30.46×10^{-4} m^3/g of VS added for thermal pre-treated sludge at 20.6 g TS/L for 30 days (Fig. 7a). Increasing solids concentrations increased the cumulative CH_4 volume. The cumulative CH_4 production rate was 4.77×10^{-4}, 5.08×10^{-4}, and 4.73×10^{-4} m^3/g of VS added for 20.0, 30.0 and 40.0 g TS/L, respectively. At a high solids concentration (40.0 g TS/L) sludge solubilisation was lower (i.e. the available biodegradable matter was lower for the microorganisms for the CH_4 production).

Similarly, the cumulative CH_4 volume production for the secondary sludge and mixed sludge are increased as digestion time was increased (Fig. 7b and c, respectively). For thermally pre-treated (at 134°C for 30 min) secondary and mixed sludge, the cumulative CH_4 was greater than the control at all solids concentrations. The cumulative CH_4 volume of the secondary sludge (control and pre-treated sludge) was higher when compared to the primary and mixed sludge. The cumulative CH_4 production was 38.7×10^{-4}, 51.25×10^{-4} and 45.93×10^{-4} m^3, respectively, for the untreated primary, secondary and mixed sludge at the 40.0 g TS/L, for 30 days digestion. A similar trend was observed for the thermally pre-treated primary, secondary, and mixed sludge. The cumulative CH_4 production was 5.08×10^{-4}, 5.41×10^{-4}, and 5.06×10^{-4} m^3/g of VS added for thermally pre-treated primary, secondary and mixed sludge (for 30 days). Higher CH_4 production for the secondary sludge was observed because of higher organic matter content present in the secondary sludge when compared to the primary or mixed sludge. The available soluble proteins (for the microorganisms) in the secondary sludge were approximately 2.0 times higher than the primary sludge (Wilson and Novak, 2009). Moreover, during the thermal pre-treatment, cell lysis releases the cell matter (proteins, carbohydrates, lipids, etc.) into the liquid phase thus increasing the biodegradability of sludge (Pilli et al., 2014). The higher CH_4 production in the pre-treated primary, secondary and mixed sludge was due to the cell lysis and the availability of organic matter to the microorganisms. These results are in line with other findings in the literature (Braguglia et al., 2011; Gianico et al., 2013). The specific biogas production was 6.6×10^{-4} and 8.3×10^{-4} m^3/g of VS degraded for the control and the thermal pre-treated sludge, respectively (Gianico et al., 2013). The increased CH_4 production for thermally pre-treated sludge was due to increased degradation of solids. The VS degradation during mesophilic AD was 39.0% and 41.0% for the control and thermal pre-treated waste activated sludge (Bougrier et al., 2007).

3.4 Mass-energy balance of anaerobic digestion of different types of sludge at different solids concentration

3.4.1 Mass balance

The WWTP plant has the capacity to treat an average daily flow of 17.8×10^4 m^3/day wastewater and a sludge production rate of 225 g of TDS/m^3 of wastewater treated (Ghazy et al., 2011) which was used in computing mass-energy balance of sludge (with and without pre-treatment). The results of mass balance of sludge (with and without pre-treatment) for primary, secondary, and mixed sludge at different solids concentration are summarised in Table 3. For primary sludge, the volatile solids reduction was higher for the thermally pre-treated sludge when compared to the control at all solids concentrations. Therefore, the digestate obtained was lower for the thermally pre-treated sludge when compared to control. Increasing the solids concentration decreased the percentage increase in volatile solids reduction. The percentage error of the volatile solids reduction was less than 1% (Fig.4). Thus, from the results it is clear that the volatile solids reduction was higher for the thermally pre-treated primary sludge when compared to the untreated sludge. Therefore, the digestate obtained from the AD of thermal pre-treated sludge (at different solids concentrations) for dewatering, transportation and land application was lower. Similar trends were observed for the secondary and mixed thermally pre-treated sludge. The volatile solids reduction was higher for the secondary sludge compared to the primary and mixed sludge. Therefore, the digesate volume produced for the thermally pre-treated secondary sludge was also lower. The least quantity of the digestate generated was

23.4×10^6 g of TDS/day (after 30 days of digestion) to dewater, transport, and land application for thermal pre-treated secondary sludge at solids concentration of 30.0 g TS/L (Table 2).

3.4.2 Energy balance

The total energy input for thermal pre-treatment, AD, dewatering, transportation and land application, and energy recovered at different solids concentration for primary secondary and mixed sludge are presented in Table 4. The energy input required for dewatering, transportation and land application was reduced to thermal pre-treated sludge irrespective of solids concentration (for primary, secondary and mixed sludge) (Table 4). The reduction in energy input for the thermal pre-treated sludge was due to the less quantity of digestate to handle (i.e. higher solids degradation). The reduction in energy input for the thermal pre-treated sludge was due to the less quantity of digestate to handle (i.e. higher solids degradation). The net energy of the thermal pre-treated primary sludge was greater than the control irrespective of solids concentrations. The net energy for the control was -8.68×10^{-4}, -2.54×10^{-4}, and -2.93×10^{-4} kWh/g of TDS at 20.0, 30.0 and 40.0 g TS/L, respectively. For thermal pre-treated primary sludge it was -2.31×10^{-4}, 3.74×10^{-4}, 3.13×10^{-4} kWh/g of TDS at 20.0, 30.0 and 40.0 g TS/L, respectively. The net energy of the thermal pre-treated secondary sludge and the mixed sludge was greater than the control at all solids concentrations (Table 4).

Increasing the solids concentration from 20.0 g TS/L to 30.0 g TS/L, increased the net energy for the control and thermal pre-treated sludge. However, increasing the solids concentration beyond 30.0 g TS/L caused the net energy to decrease, i.e. at 30.0 g TS/L (secondary sludge), for control, the net energy was 0.91×10^{-4} kWh/g of TDS and at 40.6 g TS/L the net energy was 0.34×10^{-4} kWh/g of TDS. Similarly, for thermal pre-treated sludge the net energy was 8.4×10^{-4} kWh/g of TDS at 29.9 g TS/L (secondary sludge) and the net energy was 6.89×10^{-4} kWh/g of TDS at 40.1 g TS/L. At a high solids concentration the energy output was lower compared to the energy input. This is primarily due to the lower solids degradation and the subsequent lower CH_4 volume.

For thermally pre-treated primary sludge, the net energy was positive at solids concentrations $\geq$ 30.0 g TS/L. For control the net energy was negative since energy input was greater than the energy recovery. For thermally pre-treated secondary sludge and mixed sludge, the net energy was positive at solids concentration $\geq$ 20.0 g TS/L. For the secondary sludge (control) the net energy was positive at solids concentration $\geq$ 30.0 g TS/L. The net energy of the mixed sludge (control) was negative irrespective of the solids concentration. The maximum net energy 840 ×

10^{-6} kWh/g of TDS was obtained at 30.0 g TS/L for thermal pre-treated secondary sludge (Table 4). Moreover, the maximum biodegradability (i.e. minimum digestate to dispose) was observed for the thermal pre-treated secondary sludge at 30.0 g TS/L. Therefore, thermal pre-treatment was energetically beneficial at 30.0 g TS/L for the secondary sludge compared to the primary and the mixed sludge at different solids concentrations (20.0, 30.0 and 40.0 g TS/L).

The energy ratio of the thermal pre-treated primary sludge was greater than the control at all solids concentrations (for the primary, secondary and the mixed sludge). For the primary sludge the energy ratio for thermally pre-treated case was greater than one at a solids concentration ≥ 30.0 g TS/L (Table 4). At low solid concentrations of 20.0 g TS/L the energy recovered was not greater than energy input. The energy ratio of the thermal pre-treated secondary and the mixed sludge was greater than one at all solids concentrations (20.0, 30.0 and 40.0 g TS/L). Increasing the solids concentration from 30.0 g TS/L to 40.0 g TS/L, the energy ratio was reduced for the primary, secondary and the mixed sludge. For example, the energy ratio for the mixed sludge was 1.51 and 1.55 at 30.0 and 40.0 g TS/L, respectively. From the results it was clear that the energy ratio was highest for the thermal pre-treated secondary sludge compared to the thermal pre-treated primary and the mixed sludge. The maximum energy ratio of 1.79 was observed (at 30.0 g TS/L) for the thermal pre-treated secondary sludge.

3.4.3 The energy ratio at different retention times

The energy ratio computed at the different retention times (5, 10, 15, 20 and 30 days) of the primary sludge (with and without pre-treatment) and at different solids concentrations are summarised in Fig. 8a. In general, the energy ratio increased with the increasing retention time. The energy ratio of the thermal pre-treated primary sludge was greater than the control irrespective of solids concentration and retention time (Fig. 8a). At a low solids concentration (of 20.0 g TS/L) the energy ratio was greater than the control, but less than one (0.84) for the thermal pre-treated primary sludge. Increasing the solids concentration to ≥ 30.0 g TS/L the energy ratio was greater than one (i.e. the energy output was greater than the energy input) for the thermal pre-treated primary sludge. The energy ratio of the secondary and the mixed sludge (with and without pre-treatment) at different retention times and solids concentrations are summarised in Fig. 8b and c. The energy ratio increased with increasing retention time and was greater than control for the thermally pre-treated secondary sludge and mixed sludge. For thermally pre-treated secondary sludge at solids concentrations ≥ 30.0 g TS/L the energy ratio was greater than one at 10 days retention time (Fig. 8b). In the case of thermally pre-treated mixed sludge, the energy ratio was greater than one at 15 days retention time (Fig. 8c). From the above results it is clear that the thermally pre-treated secondary sludge required lower retention time (10 days) to have a positive energy balance (i.e. energy output was greater than energy input). For thermally pre-treated primary sludge, 20 days retention time and solids concentration ≥ 30.0 g TS/L was required to have a positive energy balance (which was energetically beneficial). For thermally pre-treated mixed sludge (30.0 g TS/L) a retention time of 15 days was required to have an energy ratio greater than one. Thus, it was clear that the thermally pre-treated secondary sludge at 30.0 g TS/L was more beneficial than primary and mixed sludge based on the biodegradability (less volume of digesate to dispose), increased CH_4 production, net energy and energy ratio.

3.5 Dewaterability of the control, thermal pre-treated sludge and the anaerobic digestate

The dewaterbility measured in terms of CST for the control, thermal pre-treated and anaerobic digestate for primary, secondary and mixed sludge is summarised in Table 5. In general, the CST of the thermally pre-treated sludge was reduced when compared to control irrespective of the solids concentrations. The CST increased with increasing solids concentrations for the primary sludge (with and without pre-treatment). Similarly for the secondary and mixed sludge (with and without pre-treatment) the CST increased with increasing solids concentrations. Increased temperature of sludge increased the physical-chemical reactions along with an increase in the release of bound water and intracellular water from the cells of sludge sludge (Pilli et al., 2014). The release of the bound water and intracellular water increased sludge dewaterability (Pilli et al., 2014). The results of CST after thermal pre-treatment are in line with the literature (Bougrier et al., 2007; Perez-Elvira et al., 2010). AD reduced the CST irrespective of the types of sludge and solids concentrations. The CST of the thermal pre-treated secondary sludge before AD was 210 (±14) and after AD was 186 (±8). The reduction of organic matter (primarily proteins) in the loosely bound fractions of extracellular polymers substances has attributed to the reduction in CST after AD (Xu et al., 2011). Increase in dewaterability was not considered in our calculations, because the projections of CST values for centrifugation are not truly representative. The energy reduction of centrifuging the digestate after AD needs to be established.

3.6 GHG emissions for control and thermal pre-treated sludge at different solids concentration for primary, secondary and mixed sludge

The GHG emissions corresponding to energy utilisation for thermal pre-treatment, AD, dewatering, transportation, and land application were evaluated for all the cases and are summarised in Table 6. . In general, GHG emissions with thermal pre-treatment sludge are reduced compared to the control case irrespective of the solids concentrations. For primary sludge (with and without pre-treatment), the GHG emissions were reduced with increasing solids concentrations. The energy input for the primary sludge (without pre-treatment) was in the following order 40.0 < 30.0 < 20.0 g TS/L. However, the net energy was in the following order 30.0 < 40.0 < 20.0 g TS/L. Therefore, the GHG emissions corresponding to the net energy was in the following order 30.0 < 40.0 < 20.0 g TS/L. A similar trend was observed for the secondary and the mixed sludge (with and without pre-treatment).

The net GHG emissions decreased with increasing solids concentration for the primary sludge (with and without pre-treatment). In the case of the secondary sludge, GHG emissions for the control decreased with increasing solids concentration. For the thermal pre-treated secondary sludge GHG emissions were lower at 30.0 g TS/L when compared to 40.0 g TS/L. A similar trend was observed for the mixed sludge. Increasing the solids concentration (for thermally pre-treated secondary and mixed sludge) from 30.0 to 40.0 g TS/L, reduced the net energy and resulted in GHG emissions. Compared to the primary and the mixed sludge the GHG emissions were reduced for the secondary sludge since the energy output was greater than the energy input. The lowest GHG emissions 73.8×10^{-3} g CO_2 equivalent /g of TDS were observed at 30.0 g TS/L for the thermal pre-treated secondary sludge. Therefore, the thermal pre-treatment of sludge followed by AD decreases the GHG emissions.

4. CONCLUSION

Based on a mass-energy balance evaluation, thermal pre-treatment of sludge to enhance AD efficiency was favourable. From the mass balances, the least quantity of the digestate produced to dewater, transport and land application was observed at the 30.0 g TS/L for thermal pre-treated sludge. The energy balance showed that the maximum net energy was 8.4×10^{-4} kWh/g of TDS at 30.0 g TS/L for the thermal pre-treated secondary sludge. At 30 days, the net energy was positive and the energy ratio was greater than one for thermal pre-treated secondary and mixed sludge at all solids concentrations. For the primary sludge, the net energy was positive.

The energy ratio was greater than one at solids concentrations ≥ 30.0 g TS/L. The maximum energy ratio (1.79) was observed at 30.0 g TS/L for thermal pre-treated secondary sludge. At 30.0 g TS/L, for the primary treated sludge at 20 days, secondary treated sludge at 10 days, and mixed treated sludge at 15 days digestion was required to have a positive net energy and an energy ratio greater than one. For the untreated sludge (control), GHG emissions were reduced with the increasing sludge solids concentration. GHG emissions of thermal pre-treated sludge were also reduced compared to the untreated one (control).

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Table 1. Waterwater sludge characteristics

	TS	VS	SS	VSS	Total Carbon	TN	TP	pH	TCOD	SCOD
	(g/L)	(g/L)	(g/L)	(g/L)	kg/kg of TDS	g/kg of TDS			(g/L)	(mg/L)
Primary sludge	20.84 (±0.32	13.90 (±0.08)	16.94 (±0.16)	11.26 (±0.12)	0. 58	38.2	0.98	6.74 (±0.01)	22.43 (±0.37)	937.3 (±6.5)
	30.45 (±0.15)	20.34 (±0.35)	26.35 (±0.22)	17.34 (±0.23)				6.67 (±0.02)	34.15 (±0.48)	920.5 (±8.2)
	39.76 (±0.16)	26.24 (±0.10)	35.61 (±0.10)	23.37 (±0.38)				6.68 (±0.01)	42.32 (±0.41)	935.4 (±6.4)
Secondary sludge	20.14 (±0.34)	14.90 (±0.06)	17.08 (±0.34)	14.60 (±0.33)	0.42	51.4	1.38	6.75 (±0.01)	23.87 (±0.67)	815.4 (±6.5)
	30.05 (±0.42)	21.76 (±0.02)	26.98 (±0.40)	19.31 (±0.21)				6.68 (±0.02)	33.34 (±0.68)	820.2 (±4.9)
	40.61 (±0.33)	29.28 (±0.02)	37.33 (±0.22)	26.70 (±0.04)				6.68 (±0.04)	43.21 (±0.68)	809.4 (±6.7)
Mixed sludge	20.09 (±0.72)	14.00 (±0.06)	16.41 (±0.34)	11.33 (±0.31)	0.49	53.6	1.12	6.84 (±0.03)	22.94 (±0.37)	858.2 (±4.5)
	30.80 (±0.25)	21.38 (±0.08)	27.15 (±0.12)	18.70 (±0.20)				6.89 (±0.04)	33.16 (±0.41)	873.5 (±6.1)
	40.98 (±0.51)	28.36 (±0.08)	37.28 (±0.23)	25.60 (±0.18)				6.85 (±0.01)	43.55 (±0.46)	873.5 (±5.6)

Note: total solids (TS); volatile solids (VS); suspended solids (SS); volatile suspended solids (VSS); total nitrogen (TN); total phosphorus (TP); total chemical oxygen demand (TCOD); soluble chemical oxygen demand (SCOD); total dry solids (TDS)

Table 2. Methane percentage of control and pre-treated sludge

Solids concentration		Methane percentage Primary Sludge	 Secondary Sludge	 Mixed sludge
20 g/L	Control	45.4 (±1.02)	49.8 (±1.23)	49.5 (±0.96)
	Pre-treated	47.6 (±0.86)	54.5 (±0.89)	51.3 (±0.92)
30 g/L	Control	50.8 (±0.91)	56.6 (±1.15)	52.5 (±0.84)
	Pre-treated	52.6 (±1.22)	60.4 (±1.01)	57.4 (±0.91)
40 g/L	Control	50.3 (±0.85)	54.6 (±0.98)	53.4 (±0.73)
	Pre-treated	50.8 (±0.77)	57.7 (±0.86)	54.4 (±0.87)

Table 3. Mass balance of the control and thermal pre-treated sludge at different solids concentration

Description	**Primary sludge**						**Secondary sludge**						**Mixed sludge**					
Mass of TDS (Mg) entering AD (assumed)	**40**						**40**						**40**					
Total solids	**20 g TS/L**		**30 g TS/L**		**40 g TS/L**		**20 g TS/L**		**30 g TS/L**		**40 g TS/L**		**20 g TS/L**		**30 g TS/L**		**40 g TS/L**	
	C	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**
%Volatile solids degradation at HRT 30 days	44.07	48.3	47.89	50.35	46.23	47.35	51.56	54.56	51.46	57.95	48.46	52.57	49.94	50.61	53.08	54.89	47.0	48.55
Volume of methane Produced (m^3)	4051	6230	4901	6758	3686	5877	5479	8074	6408	8984	5045	7451	3711	7068	5732	7854	4483	6485
Weight of Volatile degraded during AD (Mg)	11.81	12.37	12.80	13.32	12.21	12.41	15.26	15.80	14.90	16.61	13.98	15.21	10.76	14.17	14.74	15.52	13.01	13.59
Digestate dry solids remaining after centrifugation, which will be transported and land applied (Mg)	28.19	27.63	27.20	26.68	27.79	27.59	24.74	24.20	25.1	23.39	26.02	24.79	29.24	25.83	25.26	24.48	26.99	26.41

Note: C is control without thermal pre-treatment; TPT is thermal pre-treatment; TDS is total dry solids

Table 4. Energy balance of the control and Thermal pre-treated sludge at different solids concentration

Description	Primary sludge						Secondary sludge						Mixed sludge					
Total solids	**20 g TS/L**		**30 g TS/L**		**40 g TS/L**		**20 g TS/L**		**30 g TS/L**		**40 g TS/L**		**20 g TS/L**		**30 g TS/L**		**40 g TS/L**	
	C	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**
	Energy (kWh/Mg of dry solids)																	
Thermal pre-treated sludge	0	1034	0	704	0	538	0	1602	0	713	0	532	0	1067	0	709	0	529
AD	1360	73	931	50	713	38	1407	75	943	50	698	38	1411	75	920	50	692	37
Dewatering	71.46	70.06	68.96	67.64	70.46	69.95	62.71	61.35	63.62	59.3	65.97	62.85	74.13	65.47	64.05	62.06	68.42	66.96
Transportation	49.14	48.17	47.42	46.51	48.45	48.1	43.12	42.18	43.75	40.78	45.37	43.22	50.98	45.02	44.04	42.67	47.05	46.05
Land application	248	243	239	235	244	243	218	213	221	206	229	218	257	227	222	215	237	232
(a) Total energy input	1728	1469	1286	1103	1076	936	1731	1453	1271	1069	1038	849	1793	1480	1250	1079	1044	912
(b) Energy output	861	1238	1041	1477	783	1249	1164	1716	1362	1909	1072	1583	789	1502	1218	1669	953	1378
Net energy = (**a- b**)	-868	-231	-254	374	-293	313	-566	263	91	840	34	689	-1004	22	-32	589	-92	466
Energy ratio Energy input/energy output	0.5	0.84	0.81	1.34	0.73	1.33	0.67	1.18	1.07	1.79	1.03	1.77	0.44	1.01	0.97	1.55	0.91	1.51

Note : (C) is control with out ultrasonication; negative sing indicates increase energy input

Table 5. CST of the primary, secondary and mixed sludge at different solids concentration

Description	Solids concentration (g TS/L)	Sample type	CST
Primary sludge	20	Control	754 (±13)
		Thermal pre-treated	160 (±15)
		Control after AD	602 (±14)
		Thermal pre-treated after AD	148 (±7)
	30	Control	989 (±18)
		Thermal pre-treated	190 (±12)
		Control after AD	718 (±10)
		Thermal pre-treated after AD	165 (±12)
	40	Control	1240 (±12)
		Thermal pre-treated	306 (±10)
		Control after AD	1084 (±12)
		Thermal pre-treated after AD	280 (±18)
Secondary sludge	20	Control	856 (±16)
		Thermal pre-treated	90 (±14)
		Control after AD	628 (±13)
		Thermal pre-treated after AD	84 (±8)
	30	Control	1006 (±12)
		Thermal pre-treated	210 (±14)
		Control after AD	820 (±19)
		Thermal pre-treated after AD	186 (±8)
	40	Control	1578 (±18)
		Thermal pre-treated	340 (±10)
		Control after AD	1238(±15)
		Thermal pre-treated after AD	301 (±12)
Mixed sludge	20	Control	709 (±16)
		Thermal pre-treated	303 (±15)
		Control after AD	545 (±13)
		Thermal pre-treated after AD	284 (±14)
	30	Control	876 (±16)
		Thermal pre-treated	315 (±14)
		Control after AD	754 (±12)
		Thermal pre-treated after AD	303 (±13)
	40	Control	1401 (±15)
		Thermal pre-treated	358 (±12)
		Control after AD	1053 (±12)
		Thermal pre-treated after AD	321 (±10)

Note: control is without pre-treatment

Table 6. GHG emissions for control and thermal pre-treated sludge at different solids concentration

Description	**Primary sludge**						**Secondary sludge**						**Mixed sludge**					
	GHG emission (kg CO_2 equivalent/Mg of TDS)																	
TS (g/L)	**20 g TS/L**		**30 g TS/L**		**40 g TS/L**		**20 g TS/L**		**30 g TS/L**		**40 g TS/L**		**20 g TS/L**		**30 g TS/L**		**40 g TS/L**	
	C	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**	**C**	**TPT**
Net GHG emission due to energy input and out put	459.8	122.5	129.8	-198.3	155.2	-165.7	300.1	-139.3	-48.0	-445.1	-18.1	-365.4	532..3	-11.7	17.2	-312.4	48.6	-247.1
GHG emissions during AD (biogenic emissions)	239.3	314.8	233.1	307.6	178.9	279.5	323.6	436.5	304.8	397.6	245.0	354.4	219.2	382.1	272.6	347.5	217.7	308.4
GHG emissions during CH_4 combustion	198.9	285.9	240.6	341	180.9	288.5	268.9	396.3	314.6	441.0	247.7	365.7	182.2	347.0	281.4	385.5	220.1	318.3
GHG emissions during transportation	13.6	13.3	13.1	12.9	13.4	13.3	11.9	11.7	12.1	11.3	12.6	12.0	14.1	12.5	12.2	11.81	13.0	12.7
GHG emissions during land application	80.3	78.7	77.5	76.0	79.2	78.6	70.5	69.0	71.5	66.7	74.2	70.7	83.3	73.6	72.0	69.8	76.9	75.3
Total GHG emission Without considering biogenic CO_2 emissions	752.6	500.4	461.0	231.8	428.8	214.7	651.5	337.7	350.2	73.8	316.3	82.9	811.9	421.3	382.7	154.6	358.6	159.3

Note: C is control; negative sign indicates reduction in GHG emissions; TPT is thermal pre-treatment; Mg is mega gram; TDS is total dry solids

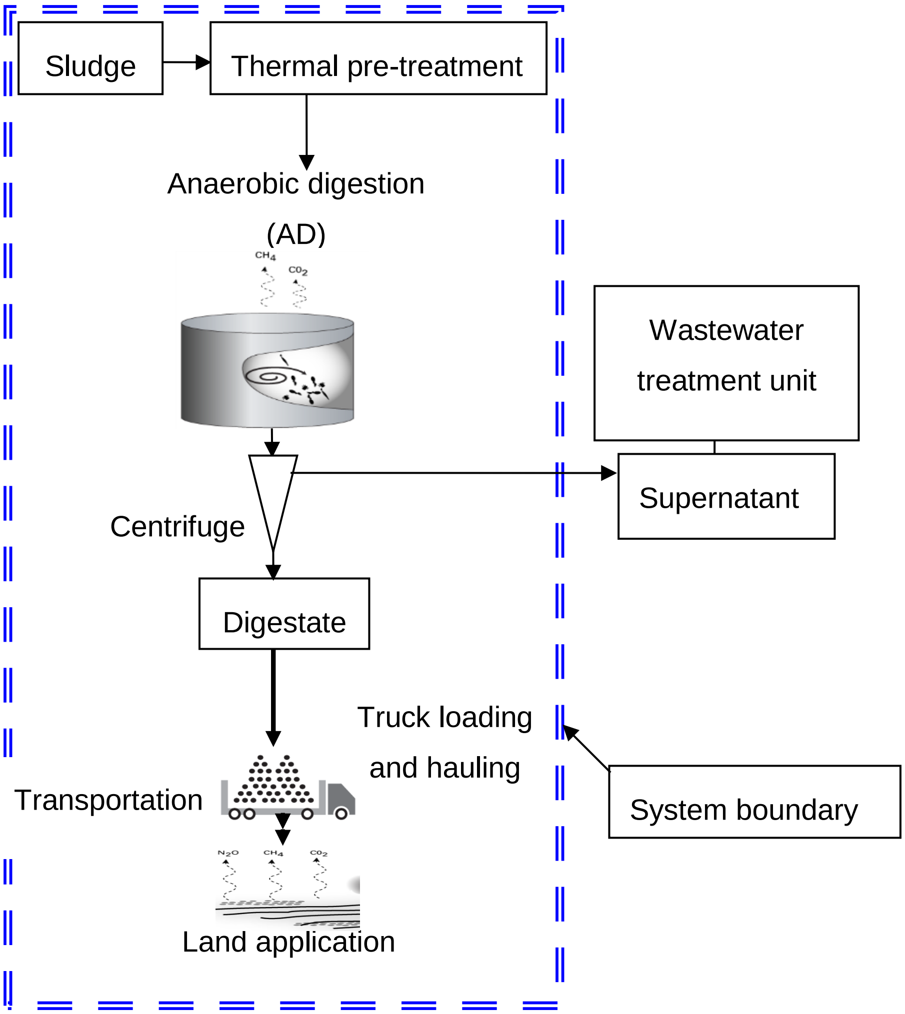


Figure 1. Pathway (or system boundary) considered for evaluting mass-energy balance and GHGs

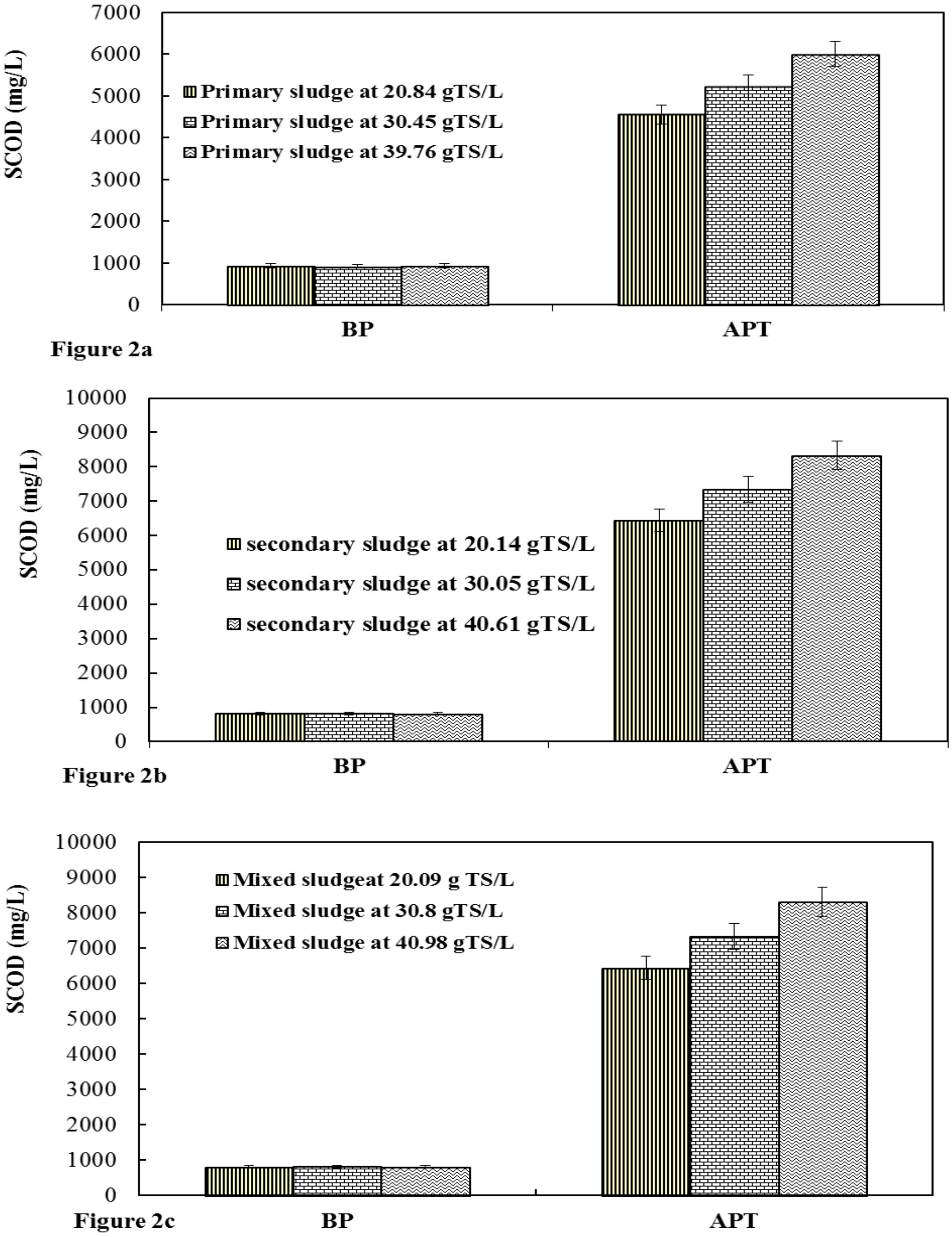


Figure 2. SCOD before and after thermal pre-treatment at different solids concentrations

Figure 2a – primary sludge; Figure 2b – secondary sludge; Figure 2c – mixed sludge.

Note: BP is before pre-treatment; APT is after pre-treatment

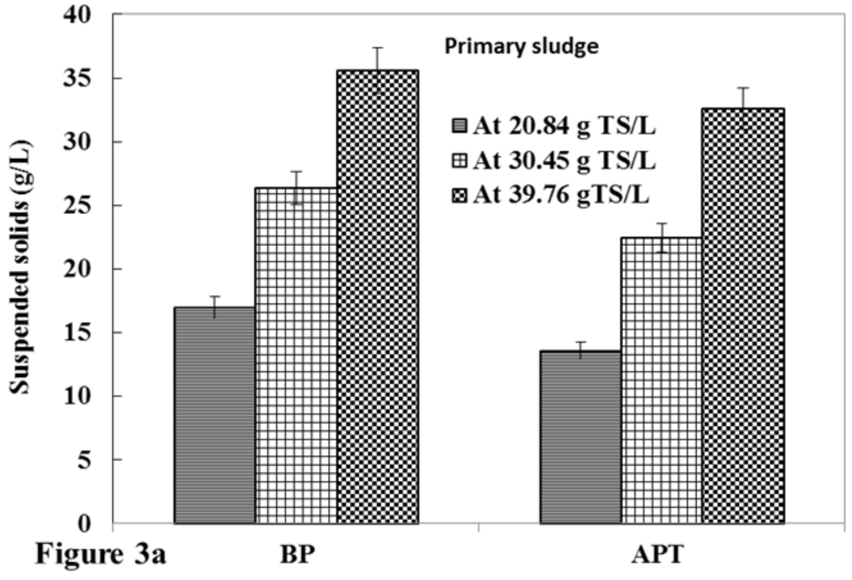


Figure 3a

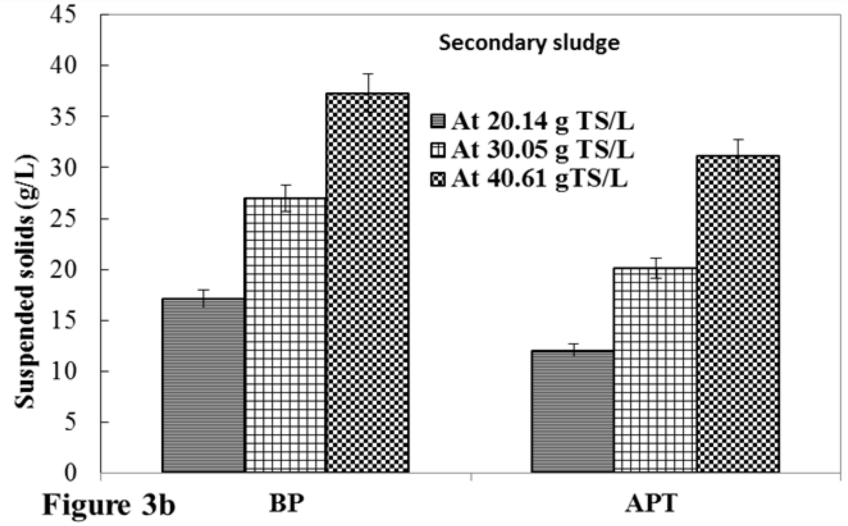


Figure 3b

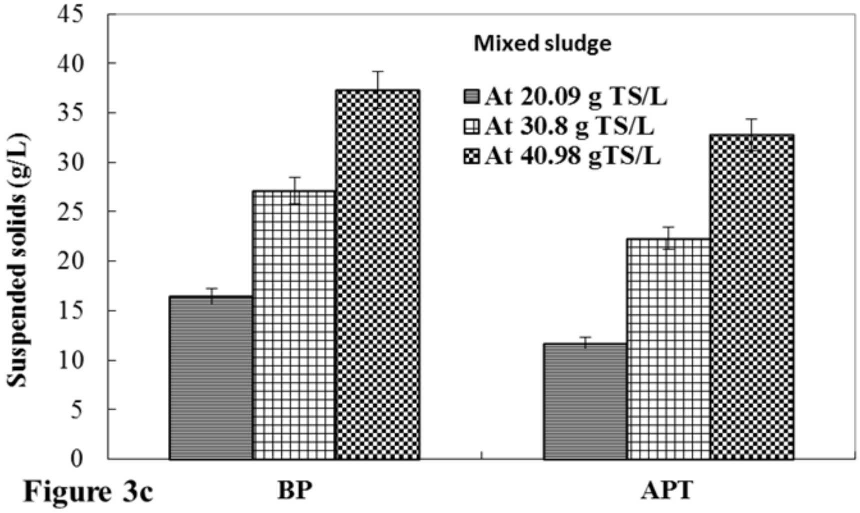


Figure 3c

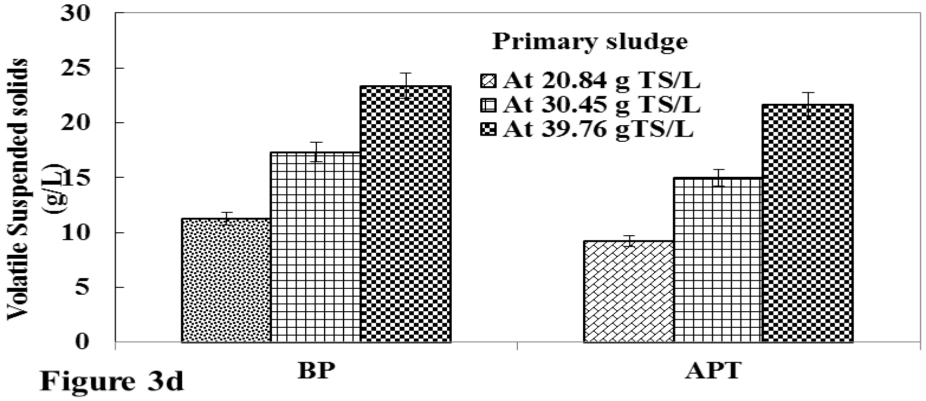


Figure 3d

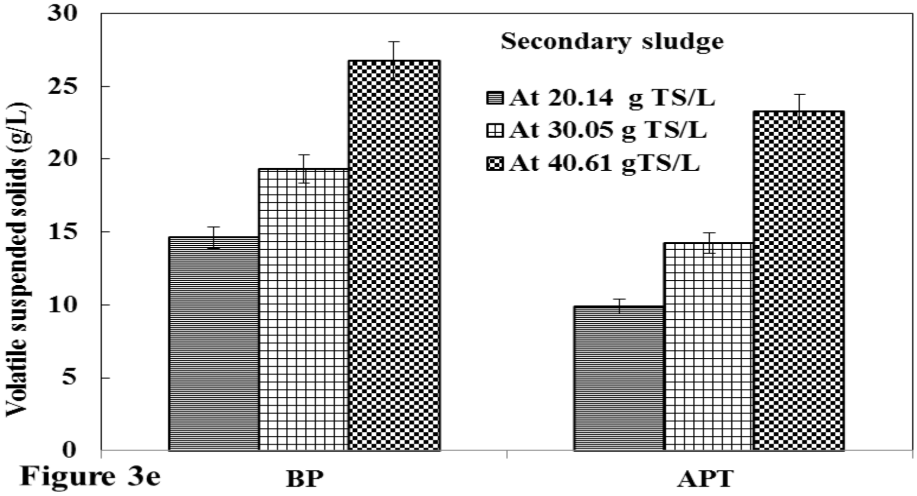


Figure 3e

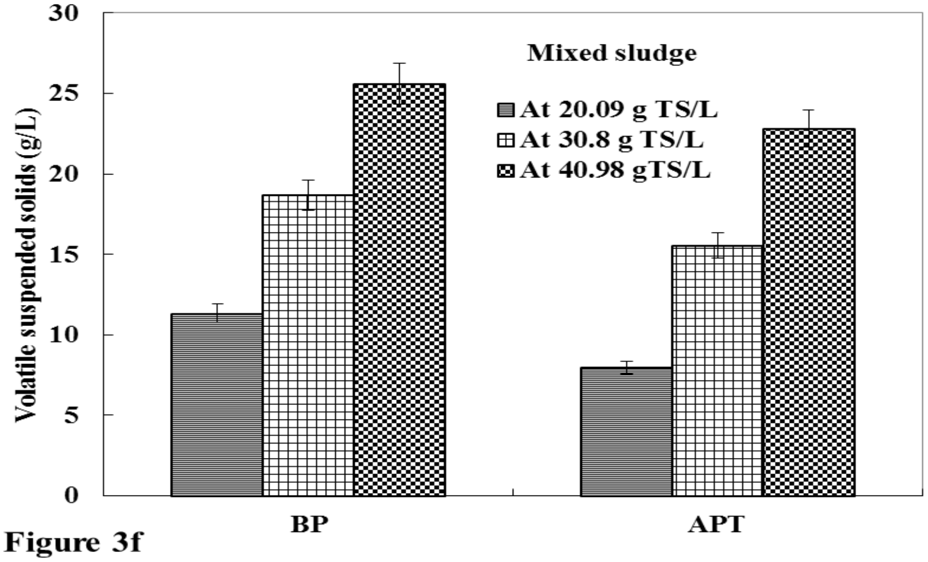


Figure 3f

Figure 3. SS and VSS reduction during thermal pre-treatment of sludge at different solids concentrations

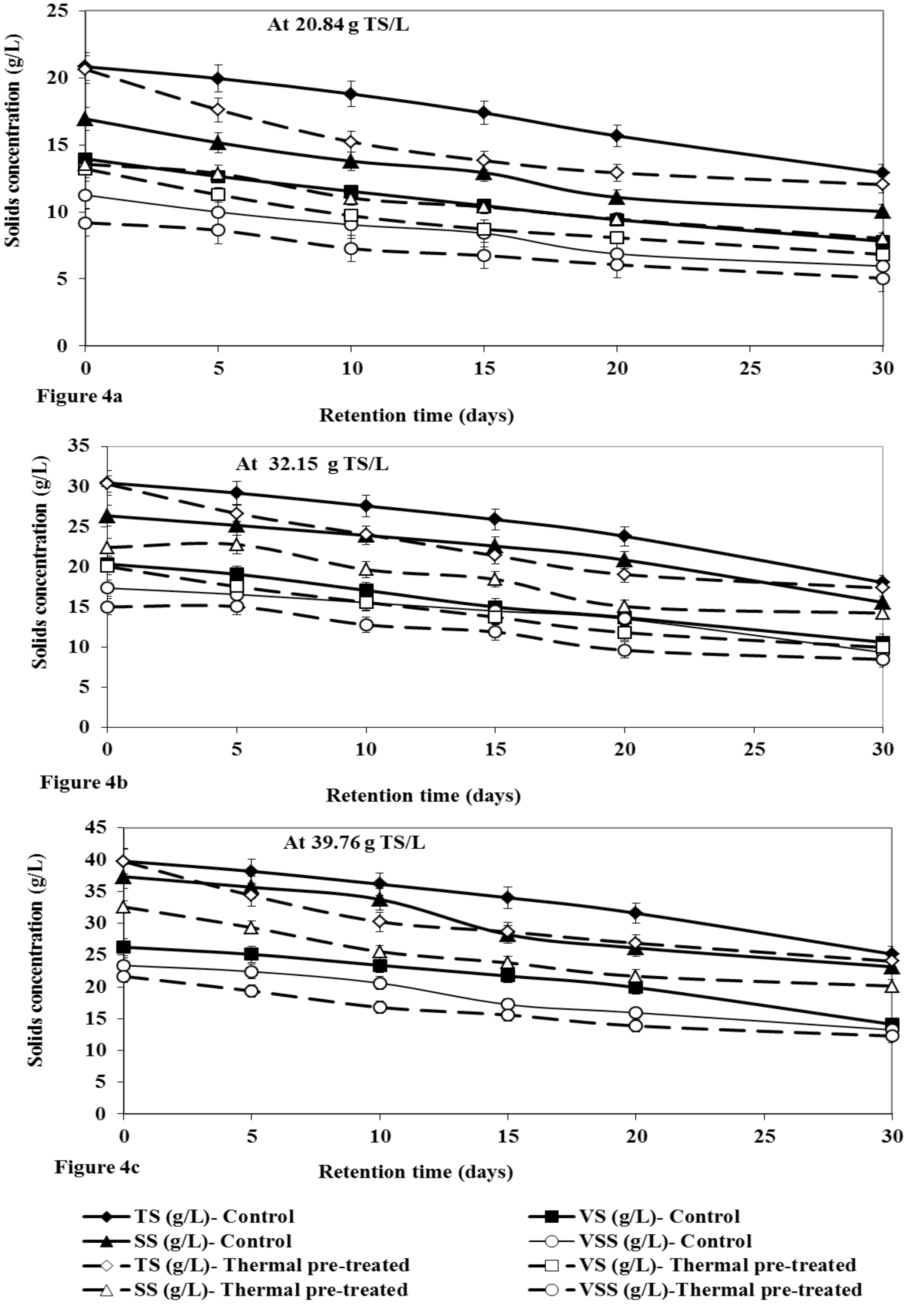


Figure 4. Primary sludge solids degradation during anaerobic digestion

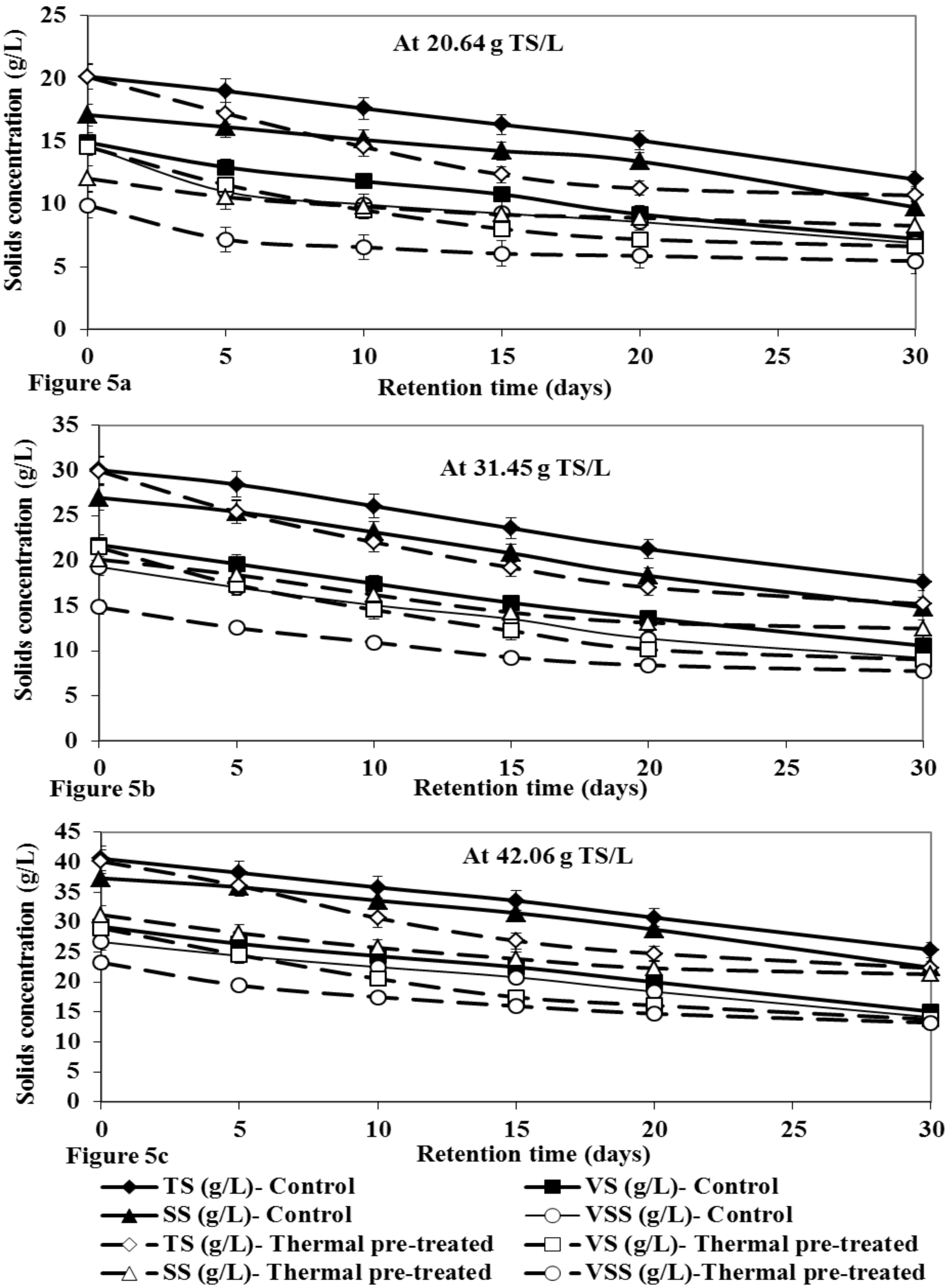


Figure 5. Secondary sludge solids degradation during anaerobic digestion

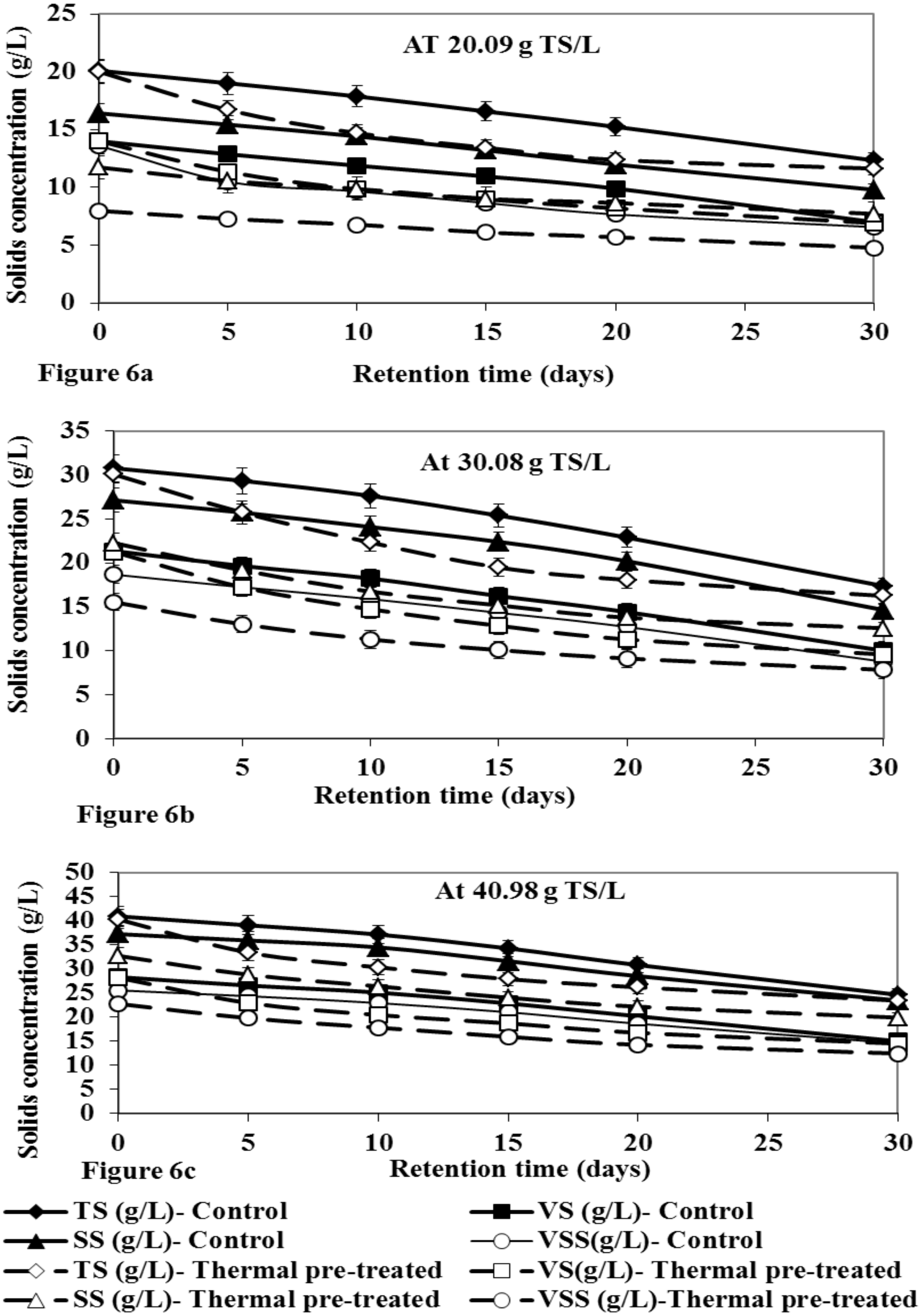


Figure 6. Mixed sludge solids degradation during anaerobic digestion

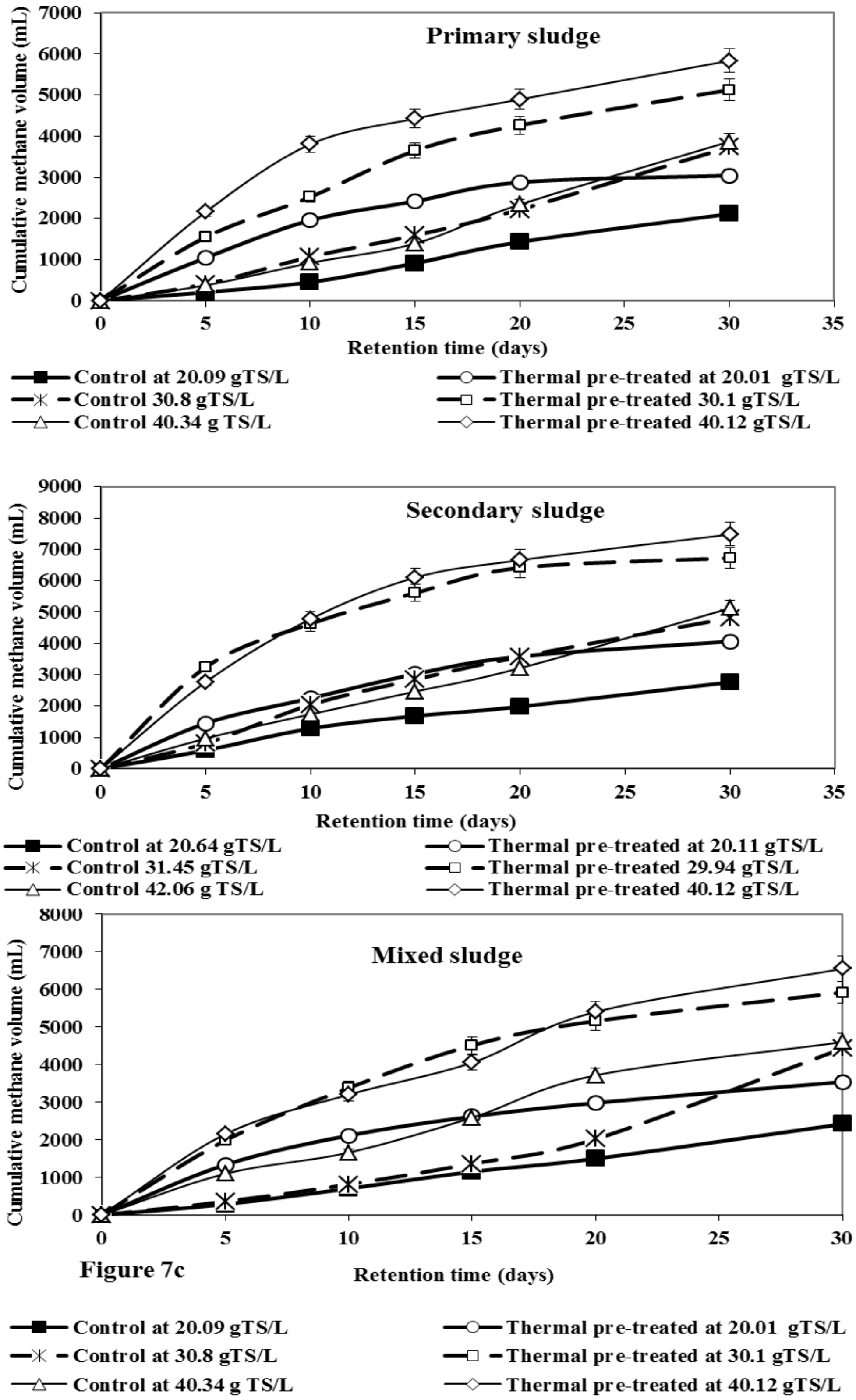


Figure 7. Cumulative methane production during anaerobic digestion at different solids concentration

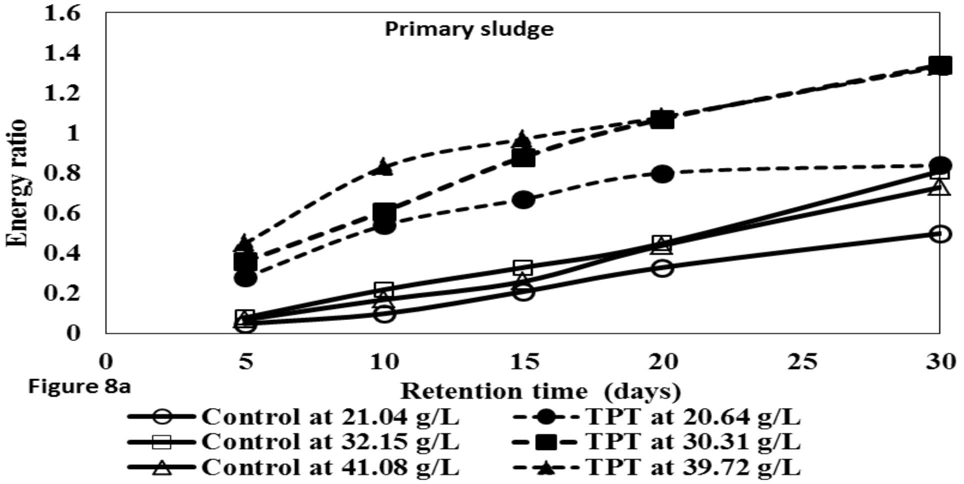


Figure 8a

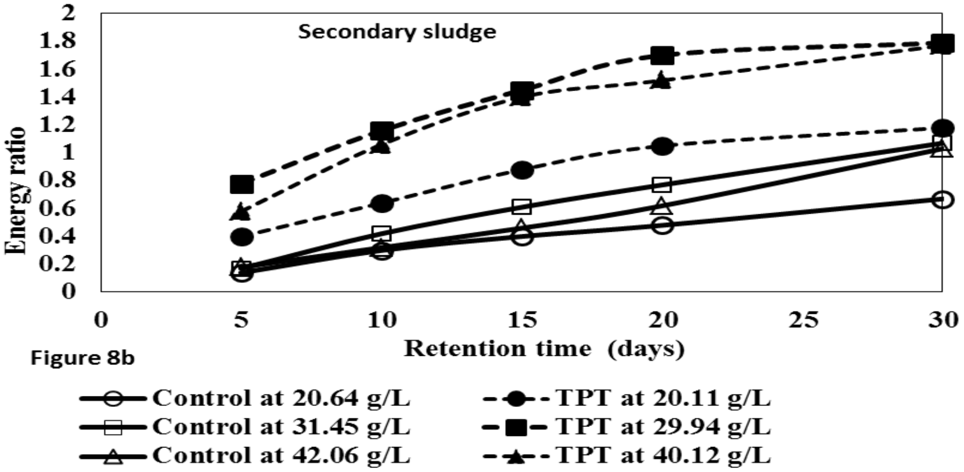
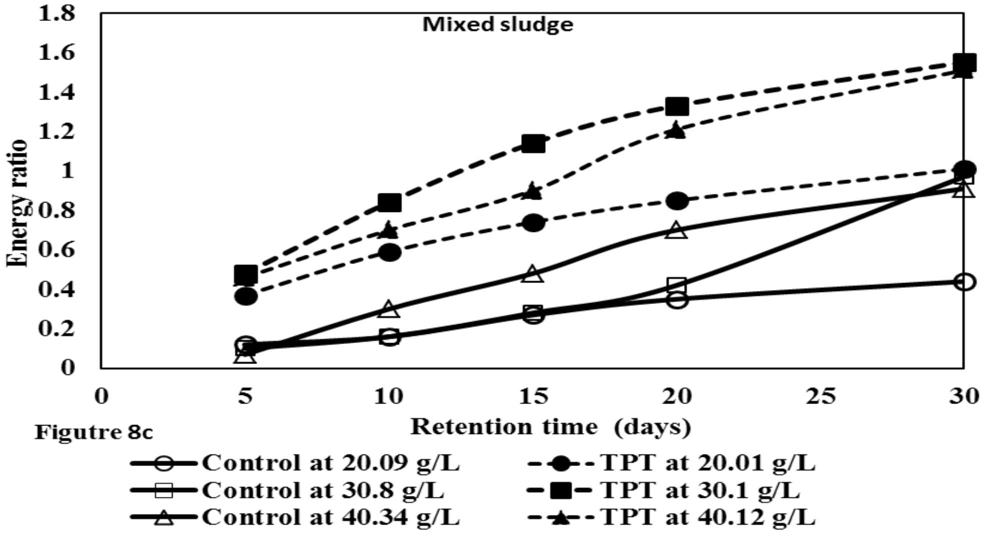


Figure 8b



Figutre 8c

Figure 8. Cumulative methane production during anaerobic digestion at different solids concentration

CHAPITRE IV

FENTON PRE-TREATMENT OF SLUDGE

PARTIE 1

OVERVIEW OF FENTON PRE-TREATMENT OF SLUDGE TO ENHANCE ANAEROBIC DIGESTION EFFICIENCY

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RÉSUMÉ

La disponibilité du substrat présent dans les boues d'épuration limite l'efficacité du procédé de digestion anaérobie. Par conséquent, un prétraitement des boues est nécessaire pour augmenter la biodégradabilité des matières solides et pour améliorer la digestion anaérobie. Dans ce cadre, on s’intéresse aux procédés d'oxydation avancés, en particulier, le prétraitement par la méthode de Fenton qui est reconnu pour être efficace pour améliorer la biodégradabilité des boues. En fait, cette revue résume les principales applications de prétraitement par le procédé de Fenton, effectuées pour la désintégration et la déshydratation des boues, et met en évidence leurs effets sur la digestion mésophile et thermophile. Des études ont été faites afin de montrer l'effet du prétraitement par le procédé de Fenton afin d’améliorer la digestion anaérobie (augmentation de la production de biogaz et réduction des matières solides) des boues d'épuration. Une étude a été effectuée sur le bilan masse - énergie et la production de gaz à effet de serre (GES) lors de la digestion mésophile et thermophile des boues sans et avec prétraitement par le procédé de Fenton à différents temps de rétention.

Mots-clés: digestion anaérobie; usine de traitement biologique des eaux usées; déshydratation; prétraitement par Fenton; bilan masse-énergie; émissions de gaz à effet de serre.

ABSTRACT

Availability of the biodegradable matter in wastewater sludge limits the anaerobic digestion (AD) process efficiency. Therefore, sludge pre-treatment is required to increase sludge solid degradability and, in turn, AD efficiency. Advanced oxidation processes, particularly Fenton pre-treatment, are emerging as popular methods aiming to enhance sludge biodegradability. This review summarizes the major findings of Fenton pre-treatment application in sludge disintegration and dewaterability, and elucidates the impacts on both mesophilic and thermophilic digestion. Efforts are made to understand the effect of the Fenton pre-treatment of wastewater sludge on enhancing AD efficiency (increased biogas production and solids reduction) and outline the future research direction. A case study of mass-energy balance and greenhouse gas (GHG) emission computations for mesophilic and thermophilic digestion of control (without pre-treatment) and Fenton pre-treatment sludge at different sludge retention times is also illustrated.

Keywords: Fenton pre-treatment; sludge biodegradability; sludge dewaterability; anaerobic digestion.

1. INTRODCUTION

Sludge generation in wastewater treatment plants (WWTPs) is a significant global environmental problem. The existing WWTPs in Canada generate around 750,000 Mg of sludge annually on a dry weight basis (GE AES Greenhouse Gas Services, 2008), and sludge production rate is expected to increase in the near future. Sludge management cost presently contributes up to 60% to the total operational cost of WWTP (Appels et al., 2010; Pilli et al., 2011). The organic matter present in sludge is biodegraded (or converted) to CO_2, CH_4 and N_2O during sludge management (treatment or disposal), which are the principal greenhouse gases (GHGs). Population growth and urbanization are expected to result in an increasing wastewater generation and consequently sludge volume. Solid waste and wastewater treatment accounts about 3% of the total global anthropogenic GHG emissions (Bogner et al., 2008). Sludge management accounts for 40% of the total GHG emissions from a WWTP (Brown et al., 2010; Shaw et al., 2010). Energy required during sludge management is generated from fossil fuel power plants, as the biggest contributors to GHG emissions. Greenhouse gas concentrations in the atmosphere are increasing by burning fossil fuels (anthropogenic emissions), as well as due to other natural causes (such as volcanic eruptions, forest firing, etc). Increasing GHGs concentrations in the atmosphere has resulted in global warming and climate change. Thus, the alarming extent of global warming and climate change has made it necessary to quantify GHG emissions pertaining to each source.

To reduce sludge quantity, several biological sludge treatment processes are presently used, including composting, aerobic digestion and anaerobic digestion (AD) (Zhang, 2010). Among these biological treatments, AD is claimed to be the most cost-effective, due to the energy recovery in the form of biogas and its very limited adverse environmental impact (Alvarez et al., 2010; Khalid et al., 2011; Mata-Alvarez et al., 2011). Recovering the energy from sludge will offset the fossil fuel derived energy and corresponding GHG emissions. Treating the mixed sludge (7.7 mega gram (Mg) total solids (TS)/day of primary sludge and 3.7 Mg-TS/day secondary sludge) in a mesophilic anaerobic digester (at HRT of 52 days) and capturing energy from the produced methane (94,500 Nm^3/day) will contribute in reducing 3% of the total natural gas consumption by the citizens. This is equivalent to a reduction of 1000 Mg of GHG emissions every year and can fit into the framework of new regulations, as well as meet the Kyoto protocol requirements (Yasui et al., 2005; Yasui et al., 2006). AD is the microbial degradation process where the substrate is broken down to produce CO_2 and CH_4 in the absence of elemental oxygen. The substrate conversion to CO_2 and CH_4 occurs in four stages (hydrolysis, acidogenesis, acetogenesis and methanogenesis) by three different groups of microorganisms (acidogenic, acetogens and methanogenic archae). Anaerobic digestion of sludge is a slow process, as the complex substrates present in sludge necessitate longer retention time (for sludge hydrolysis) and require larger digester volume. In order to reduce the retention time in anaerobic sludge digesters and to increase sludge biodegradability, sludge pre-treatment has been suggested (Khanal et al., 2007). Pre-treatment of sludge releases the intracellular matter by rupturing the microbial cell wall, which substantially enhances the digestion rate, reduces the retention time and increases the biogas production (Pavlostathis and Giraldo-Gomez, 1991; Khanal et al., 2007; Pilli et al., 2010).

The pre-treatment processes presently used to enhance sludge biodegradability are chemical (Fenton pre-treatment, hydrogen peroxide, ozone pre-treatment, etc.), thermal, physical, mechanical, biological and physical-chemical treatment processes. Hydrogen peroxide, Fenton reagent, and ozone are commonly used chemicals for advanced oxidation process (Cacho Rivero et al., 2006; Tokumura et al., 2007; Erden and Filibeli, 2010), capable of oxidizing the complex organic substrates. Fenton reagent produces highly oxidizing radicals, as having oxidation-reduction potential of +2.33 V, the radicals are stronger oxidants than hydrogen peroxide (+1.36 V), and ozone (+2.07 V) (Neyens and Baeyens, 2003; Erden and Filibeli, 2010; Pham et al., 2010a). Hydrogen peroxide pre-treatment will increase the solids reduction by 50 to 60%, producing class A biosolids (Cacho Rivero and Sudian, 2006). Fenton process enhances the hydrogen peroxide pre-treatment process due to the addition of ferrous iron as a catalyst. In the study conducted by Pérez-Elvira et al. (2006), biogas production was enhanced by 8% with ozone pre-treatment, compared to conventional AD. Given the expense and complexity of ozone pre-treatment, Fenton pre-treatment is preferable (Cacho Rivero and Sudian, 2006; Cacho Rivero et al., 2006). The oxidation−reduction potential of the Fenton process has been suggested as the means of pre-treating sludge and increasing its biodegradability (Pham et al., 2010a; Neyens and Baeyens, 2003; Erden and Filibeli, 2010). The most promising technology among the advanced oxidation processes for sludge dewatering is the Fenton pre-treatment (Zhen et al., 2014). Moreover, Fenton pre-treatment enhances biogas production and minimizes sludge weight (Neyens and Baeyens, 2003; Erden and Filibeli, 2010; Pham et al., 2010a) that needs to be dewatered, transported and subjected to land application. Thus, an assessment of the effectiveness of Fenton pre-treatment in enhancing the AD of sludge is worthy and more relevant than that of the other advanced oxidation process. Therefore, a comprehensive overview of the data published in the extant literature is presented on the Fenton pre-treatment of sludge with the aim of enhancing AD. Furthermore, the energy balance of the combined process chain of Fenton sludge pre-treatment, subsequent AD of sludge (with and without pre-treatment), dewatering of the digestate, and transportation and land application of the dewatered digestate was conducted.

2. FENTON PRE-TREATMENT

Fenton's reagent having strong oxidizing radicals is used for chemical oxidation of organic and inorganic contaminants or substrates (Neyens and Baeyens, 2003; Andrews et al., 2006; Eskicioglua et al., 2008; Seol and Javandel, 2008; Pham et al., 2010a). Today, Fenton's reagent is used for treating different types of industrial waste, wastewater, contaminated soil, sludge containing toxic organic compounds, etc. Fenton's reagent is typically applied as a reagent, as it is effective in increasing biodegradability (wastewater and wastewater sludge), organic pollution reduction, toxicity reduction, BOD/COD removal, chemical precipitation, odor and color removal (Andrews et al., 2006; Comninellis et al., 2008; Eskicioglua et al., 2008; Pham et al., 2010a; Kumar and Pal, 2012).

Researchers have used Fenton's reaction as an alternative chemical conditioner for different sludge types (Mustranta and Viikari, 1993; Lu et al., 2003; Neyens et al., 2003; Buyukkamaci, 2004; Neyens et al., 2004a, b; Dewil et al., 2005; Tony et al., 2008; Pham et al., 2010a). It was used to increase the bioavailability of the organic matter from the secondary sludge to produce *Bacillus thuringiensis*-based bio-pesticides (Pham et al., 2010b). Extant evidence indicates that Fenton pre-treatment of sludge enhanced the bacterial growth and entomotoxic potential. In addition, Fenton pre-treated sludge gave higher productivity when compared to the control and ultrasonicated sludge. Pham et al. (2011) evaluated the effect of Fenton pre-treatment on biodegradation of bis(2-ethylhexyl) phthalate (DEHP) and 2-ethylhexanoic acid in the waste-activated sludge (WAS) during bio-pesticide production. The authors concluded that Fenton reaction played a critical role in the improvement of bioavailability of the compounds for biopesticide fermentation of sludge.

Fenton oxidation can degrade extracellular polymeric substances, which represent up to 80% of the activated sludge mass (Forlund et al., 1996; Tony et al., 2008). Treatment with Fenton reagent will solubilize (i.e., a part of the sludge volume is solubilized to biodegradable organics) and mineralize (whereby a part of the sludge volume is mineralized to CO_2 and H_2O) the WAS solids. Although H_2O_2 is required to produce OH^- ions, high concentration of H_2O_2 is not recommended because residual H_2O_2 transforms into $OH^·$ Scavenger, as depicted in Eq. (1) to (3) (Neyens et al., 2003; Bautista et al., 2008).

$H_2O_2 + OH^· \rightarrow HO^·_2 + H_2O$ (1)

$HO^·_2 + OH^· \rightarrow O_2 + H_2O$ (2)

$OH^· + OH^· \rightarrow H_2O_2$ (3)

The Fenton reaction under acidic conditions is rapid and exothermic. During the reaction, hydrogen peroxide oxidizes iron catalyst (Fe^{2+}) to Fe^{3+}, as shown in Eq. (4). The ferrous iron (Fe^{2+}) initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals and hydroxyl anions (Pham et al., 2010a). The hydroxyl radicals will react with Fe^{2+}, leading to chain termination given by Eq. (5), producing Fe^{3+} and hydroxyl anion. In the presence of organics (RH), the hydroxyl radicals will react and form organic radicals ($R^·$). This process is referred to as chain propagation, which is initiated when the hydroxyl radicals oxidize organics (RH) by abstraction of proton-producing organic radicals ($R^·$), which are highly reactive and can be further oxidized (Neyens and Baeyens, 2003; Primo et al., 2008; Bautista et al., 2008; Pham et al., 2010a).

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^· + OH^-$ (chain initiation) (4)

$OH^· + Fe^{2+} \rightarrow OH^- + Fe^{3+}$ (chain termination) (5)

$RH + OH^· \rightarrow H_2O + R^·$ (chain propagation) (6)

The hydroxyl radicals generated during chain initiation and chain propagation will react with target organic substances. The OH·radical is the main reactant of the Fenton oxidation process, capable of decomposing organic substances via oxidation. Actually, various reactions between the hydroxyl radicals and the targeted pollutants can occur through (i) addition, (ii) hydrogen abstraction, (iii) electron transfer, and (iv) radical interaction (http://www.lenntech.com/fenton-reaction.htm). The details of these reactions are given in Table 1.

3. PARAMETERS THAT INFLUENCE FENTON TREATMENT OF SLUDGE

The main parameters influencing the Fenton reaction are H_2O_2 concentration, iron concentration, reaction time, temperature, and pH (Bautista et al., 2008).

3.1 H_2O_2 concentration

During the Fenton reaction, H_2O_2 concentration is required for producing the required quantity of hydroxyl ions. The organic materials are indiscriminately oxidized by the hydroxyl radicals produced during the Fenton reaction (Maletzky et al., 1999). Therefore, for any waste/wastewater/contaminated soil/sludge to be treated, it is important to profile the H_2O_2 concentration during the Fenton reaction in the laboratory (Maletzky et al., 1999; Ramaswamy et al., 2009; Pham et al., (2010b, 2011). If H_2O_2 is not added in the required quantity, the targeted reduction in toxicity, COD, etc. cannot be achieved. This is essential in, for example, toxicity reduction in the industrial wastewater. In addition, while H_2O_2 concentration will initially reduce the COD, no reduction in toxicity will be achieved, as it requires further addition of H_2O_2. The limitations of H_2O_2 concentration are summarized in Table 2.

3.2 Iron type and concentration

Iron acts as the catalyst for generating the hydroxyl radicals during the Fenton reaction. Although the iron concentration required during the Fenton reaction varies with the type and concentration of waste, in general, the minimum concentration (minimal threshold) needed to accelerate the reaction, regardless of the organic material concentration, is 3-15 mg Fe/L (Ramaswamy et al., 2009; Maletzky et al., 1999). Researchers have used different types of iron salts (Fe^{2+} and Fe^{3+}) to catalyze the Fenton reaction, whereby the catalytic cycle begins with an abundance of H_2O_2 and organic matter (http://www.h2o2.com). Some researchers have suggested utilizing Fe^{2+} salts for catalyzing the Fenton reaction. More recently, iron nano particles were used as a catalyst in the modified Fenton reaction process (Jofri et al., 2013).

3.3 pH effect

The pH of the wastewater/sludge/contaminated soil is very important to obtain the desired treatment or toxicity reduction. If the pH is not controlled, the iron catalytically decomposes the peroxide into oxygen and water. During the Fenton reaction, the organic matter is converted to organic acids and pH declines (Neyens and Baeyens, 2003; Pham et al., 2010b, 2011). Therefore, pH reduction during the Fenton reaction needs to be controlled to optimize the treatment efficiency. Multistage treatment is the preferred means of controlling the pH for the Fenton reaction (Neyens and Baeyens, 2003).

3.4 Temperature

Temperature is also an important parameter for the Fenton reaction to obtain the desired treatment. The reaction rate increases with the increase in temperature up to 40°C. However, beyond this temperature, the accelerated decomposition of H_2O_2 to oxygen and water will occur (Neyens and Baeyens, 2003). During Fenton reaction, temperature of the solution will increase when treating with high H_2O_2 concentration (between 10 and 20 g/L) (http://www.h2o2.com). On the other hand, Neyens and Baeyens (2003) observed that sludge dewaterability increased with Fenton pre-treatment at high temperatures (70 to 90°C) and with short reaction time. Therefore, the reaction temperature required to obtain the desired treatment need to be optimized for each waste material.

3.5 Reaction time

To reduce the desired toxicity concentration, COD, or the amount of harmful compounds, the reaction time is very important during the Fenton treatment (Neyens and Baeyens, 2003). The pH and temperature may increase during the reaction, which may inhibit the efficiency of the Fenton reagent (http://www.h2o2.com). Therefore, reaction time has to be scheduled for higher treatment efficiency and optimized for each waste material.

The limitations of H_2O_2 concentration, iron concentration, reaction time, temperature, and pH are summarized in Table 2. Fenton reagent (for *in situ* treatment of soil and groundwater contamination) is limited due to optimum pH, explosive reactions, organic vapor generation and contaminant migration (In-Situ Oxidative Technologies Inc.). Therefore, to overcome the limitations of the Fenton reagent, modified Fenton reagent process was developed by the addition of chelating agents (Ahuja et al., 2007; Lewis et al., 2009). The modified Fenton reaction is not rapid, does not produce organic vapors, and it is effective at neutral pH (Ahuja et al., 2007; Lewis et al., 2009). It is presently mainly used for *in situ* treatment of soil and groundwater contamination.

4. EFFECT OF FENTON PRE-TREATMENT ON SLUDGE CHARACTERISTICS

Sludge disintegration with Fenton reagent results in numerous changes in its physical and chemical characteristics. Therefore, the effects of Fenton pre-treatment are evaluated based on the changes in physical and chemical characteristics, which will influence AD of the pre-treated sludge. The efficiency of Fenton pre-treatment was evaluated by the dewaterability, anaerobic biodegradability, AD efficiency, and biogas generation (Neyens and Baeyens, 2003; Neyens et al., 2004; Dewil et al., 2005; Pham et al., 2010a; Dhar et al., 2011; Erden and Filibeli, 2011).

4.1 Changes in physical characteristics of sludge

Changes in dewaterability, viscosity, and particle size concentration were used to evaluate the effects of Fenton pre-treatment on the sludge physical characteristics.

4.1.1 Dewaterability

Fenton pre-treatment enhances sludge dewaterability (Pere et al., 1993; Lu et al., 2001; Lu et al., 2003; Neyens et al., 2002; 2003; 2004a; 2004b; Buyukkamaci 2004; Dewil et al., 2004; 2005; Erden and Filibeli 2010; Pham et al., 2010a, b; Zhen et al., 2013). It is exhibited in two ways: (i) it degrades EPS proteins and polysaccharides, reducing the EPS water retention characteristics, and (ii) acidification and oxidation by free hydroxyl radicals, will lead to changes in interparticle interactions between sludge flocs and their components (Neyens et al., 2004b; Pham et al., 2010a). Fenton pre-treatment effects on sludge dewaterability are summarized in Table 3. Fenton reagent component (H_2O_2 and Fe^{2+}) concentrations, reaction time and other parameters (pH and temperature) will influence sludge dewaterability (Neyens et al., 2002; 2003; 2004a; 2004b; Zhen et al., 2013). Dewaterability can be classified as (i) easily dewaterable, CST (capillary suction time) /SS (suspended solids %) ≤ 30 seconds/ (%w/w) suspended solids and specific resistance filtration (SRF) ≤ 1012.5 m/kg, (ii) average dewaterability CST/SS ≈ 30-150 s/%, SRF ≈ 1012.5 -1014.5 m/kg, (iii) poorly dewaterable CST/SS ≥ 150 s/%, SRF ≥ 1014.5 (Spinosa and Vesilind, 2001). It is, however, not possible to classify Fenton pre-treated sludge as easily, average or poorly dewaterable based on the data reported in the literature.

Published dewaterability results may not be compared directly to the different Fenton sludge pre-treatment studies, as they have used different units to express the Fenton reagent concentration (for example, mg of H_2O_2/L of sludge, mg of H_2O_2/kg of TS, mg of H_2O_2/kg VSS, mg of H_2O_2/kg of SS, etc.). Buyukkamaci (2004) reported the optimum concentration of H_2O_2 and Fe^{2+} as 6000 and 5000 mg/L, respectively, at pH 3.5. In these conditions, the specific resistance to filtration and CST of sludge (20 g/L of SS) are reduced with Fenton pre-treatment

(Table 3). Similarly, Tony et al. (2008) reported the optimum concentration of H_2O_2 and Fe^{2+} as 21 mg/g DS (dry solids) and 105 mg/g DS, respectively, at pH 6, which is optimal for obtaining higher dewaterability (Table 3). Recently, Zhen et al. (2014) showed an optimum concentration of 178 mg of H_2O_2/g VSS and 211 mg Fe^{2+}/g VSS at pH 3.8 for enhancing the dewaterability of WAS at 3.01% TS (w/v) (Table 3).

Pham et al. (2010a) observed enhanced dewaterability due to the increase in aggregation of sludge flocs, as the particle size increased after Fenton oxidation (due to acidic pH, and generation of ferric hydroxide and ferric hydroxo complexes). At low temperatures (55 ^{o}C), high hydrogen peroxide concentration (150 mM/L of sludge, 3% w/v TS) and long reaction time (4 h, at pH 3) is required to obtain a better sludge dewaterability. In contrast, at pH 3 and a reaction temperature of 80-90°C, very low hydrogen peroxide concentration (15 mM/L of sludge at 3% w/v TS) is sufficient to obtain satisfactory sludge dewaterability (Mustranta and Viikari, 1993; Neyens and Baeyens, 2003). The results pertaining to the optimum pH required during the Fenton pre-treatment are contradictory. Mustranta and Viikari (1993) reported the optimum pH of 2.5-3 to enhance the dewaterability of the WAS. In contrast, Lu et al. (2003) claimed that pH 2-7 has no significant effect on dewaterability during the Fenton pre-treatment of WAS. Tony et al. (2008) proposed pH 6 as the optimum for the Fenton pre-treatment to enhance the dewaterability of the aluminum-based wastewater sludge. Zhen et al. (2014) found that pH 3.8 was optimal during Fenton treatment for enhancing the dewaterability of WAS. Thus, from the foregoing discussion, there is no consensus regarding the pH at which the Fenton pre-treatment will influence sludge dewaterability the most. At low temperatures, longer treatment time is required for improving dewaterability and, at high temperatures (80-90°C), less time and a minimum Fenton concentration are required to obtain satisfactory sludge dewaterability. However, Fenton pre-treated sludge dewaterability is increased because of the increase in the particle size after the oxidation.

4.1.2 Viscosity

Acidification (pH 3-3.5) during the Fenton pre-treatment will result in a decrease in electrostatic repulsion between flocs. Consequently, the exposed cross-sectional area of solids was lower (Pham et al., 2010). Therefore, the resistance to flow was reduced leading to lower viscosity. Moreover, acidification will also hydrolyze the EPS components, resulting in instability of extracellular polymers. Oxidation by free hydroxyl radicals will lead to changes in interparticle interactions between sludge flocs and their components. During Fenton reaction, oxidative–

reductive depolymerization takes place and causes cleavage of linkages in the polymeric backbone of the extracellular polymers (Pham et al., 2010). In general, a variety of organic macromolecules in the EPS matrix will have different potential for binding together the floc matrix and sustain good floc strength (Pham et al., 2010). However, during Fenton reaction, changes in the composition or removal of specific compounds will lead to changes in the floc strength. Thus, degradation of EPS and interaction cleavage due to free hydroxyl radicals and acid hydrolysis during Fenton reaction will diminish the strength of sludge flocs, resulting in a decrease in apparent viscosity (Pham et al., 2010).

Fenton pre-treatment process resulted in a decrease in pseudoplasticity of sludge (Pham et al., 2010a). The disintegration of sludge flocs, degradation of EPS interaction cleavage due to hydroxyl radicals and acid hydrolysis generated during Fenton oxidation are the main reasons for a decrease in the cohesiveness of sludge fluid (flow consistency index K of Fenton-oxidized sludge was lower than that of untreated sludge) and an increase in flowability (flow behaviour index (n) of Fenton-oxidized sludge was higher than untreated sludge) (Pham et al., 2010a). The evolution of viscosity as a function of time and solids concentration was presented by Pham et al. (2010a). The apparent viscosity of the Fenton pre-treated sludge decreased from 121.8 to 79.9 mPa s at a constant shear rate (3.67 s^{-1}) over a period of 102 min. However, the decrease was not continuous, as at 60 min, the apparent viscosity increased to 120 mPa s. Production of ferric hydroxide during Fenton reaction induced more flocculation, which resulted in a temporary increase in the apparent viscosity at 60 min. It clear that decrease in viscosity during Fenton pre-treatment is mainly due to the operating conditions, i.e., acidification and oxidation by free hydroxyl radicals (Pham et al., 2010).

4.1.3 Particle size concentration

Fenton pre-treatment increases particle size due to acidification and formation of ferric hydroxide and ferric hydroxide complexes (Pham et al., 2010). The volume occupied by large particles (above 250 μm) for the Fenton pre-treated sludge was in the range of 0.89-5.63% at 10-40 g/L total solids concentration (Pham et al., 2010). Acidification and formation of ferric hydroxide and ferric hydroxide complexes (during Fenton reaction) have resulted in coagulation and flocculation to from larger particles (Pham et al., 2010). Comparing ultrasonication with Fenton pre-treatment, Pham et al. (2010) observed that the mean particle size in the ultrasonicated sludge decreased, whereas, for Fenton pre-treated sludge, the particle size increased due to re-aggregation. Moreover, the volume percentage of small particles (below 10 μm) was the highest (0.54%-0.38% for 10-40 g/L) for the ultrasonicated sludge. Further, Pham et al. (2010) evaluated fractal dimension index Df (to determine the degree of compactness of sludge flocs) and observed that Df was 1.6, 1.5 and 1.3 for raw sludge, ultrasonicated sludge and Fenton pre-treated sludge, respectively. In contrast, Erden and Filibeli (2010) observed a particle size reduction for the Fenton pre-treated sludge (9.6%) compared to the control. The percentage reduction (9.6%) was of a rate corresponding to the experimental error. Moreover, the concentration of Fenton reagent used by Erden and Filibeli (2010) (0.004 g Fe^{2+}/g TS and 0.06 g H_2O_2/g TS) is relatively high, compared to Pham et al. (2010), who used H_2O_2/g SS and H_2O/Fe^{2+} = 150. Thus, further studies are required to better understand changes in particles at different Fenton concentrations.

4.2 Changes in sludge chemical characteristics

Chemical characteristics of sludge due to Fenton pre-treatment were evaluated based on sludge disintegration, changes in the concentration of SCOD/BOD, and microorganism components (or cellular components) (i.e., carbohydrates, proteins, lipids, and other ribonucleic acids and fibers) in the supernatant.

4.2.1 Sludge disintegration

Fenton pre-treatment is used as a sludge disintegration technique (Erden and Filibeli, 2010). The diverse microorganisms present in sludge will have different cell wall strength. Disintegration is a phenomenon where the microbial cells in sludge are disrupted and the cell walls destroyed. This results in the release of cell components (mainly intracellular matter) into the liquid phase. Disintegration of sludge due to the Fenton pre-treatment will cause solubilization and mineralization of sludge solids (Erden and Filibeli, 2010). The soluble COD of sludge increases due to solubilization of suspended solids and thus increases the concentration of organic matter and EPS in the liquid phase. Therefore, SCOD can be used as a parameter to evaluate sludge disintegration by Fenton pre-treatment process. Solubilization will enhance the biodegradable organics and mineralization results in a part of sludge being converted to carbon dioxide and water (Erden and Filibeli, 2010). Kim et al. (2013) concluded that the increased solubilization of organics due to pre-treatment (ultrasonication and alkaline pre-treatment) does not represent a 100% increase in biodegradability. In other words, some of the soluble organics are converted to refractory soluble organics, which are non-biodegradable. Therefore, these parameters are also important in evaluating the chemical changes after sludge disintegration or Fenton pre-treatment.

The results pertaining to secondary sludge disintegration at different H_2O_2 and Fe^{2+} concentrations showed that the degree of disintegration (DD) increased with increasing H_2O_2 concentration (Erden and Filibeli, 2011). The maximum degree of disintegration (25.3%) was observed at 60 g H_2O_2/kg TS and 4 g Fe^{2+}/kg TS (at concentrations exceeding 60 g H_2O_2/kg TS, DD decreased due to mineralization of the soluble organics). Further, at 4 g Fe^{2+}/kg TS and 60 g H_2O_2/kg TS, Erden and Filibeli (2011) observed an increase in dissolved organic carbon and total nitrogen in sludge supernatant by 75.74% and 60.60%, respectively. The DD was evaluated using Eq. (7) (Muller, 2000; Erden and Filibeli, 2011).

$$DD = \frac{(SCOD_T - SCOD_U)}{(SCOD_a - SCOD_U)} \; x\, 100\,\% \qquad (7)$$

where $SCOD_a$ is the soluble chemical oxygen demand that has to be determined by an alkalic total fusion process and $SCOD_u$ and $SCOD_T$ are the soluble COD of the untreated and pre-treated sludge, respectively.

At an optimum concentration of 0.01 mL H_2O_2/g SS, 150 $[H_2O_2]_0/[Fe^{2+}]_0$, at 25°C and for 60 min treatment duration, solubilization of the secondary sludge (at 25 g/L TS) was 70% (Pham et al., 2010b). The highest solubilization (81%) for the secondary sludge was observed at 0.01 ml H_2O_2/g SS, 150 $[H_2O_2]_0/[Fe^{2+}]_0$, 25 g/L TS, at 70°C for 120 min (Pham et al., 2010b).

4.2.2 Concentration of SCOD and BOD

The SCOD concentration increased from 179 mg/L (without pre-treatment) to 1023 mg/L (with Fenton pre-treatment) (Dewil et al., 2005). Similarly, at different H_2O_2/ Fe^{2+} concentrations, Dewil et al. (2007) observed increases in SCOD and BOD concentration in the liquid phase of the secondary sludge at solids concentration of 0.54% (w/v). For example, the BOD/COD ratio in the supernatant of the control (without treatment) was 0.48, which increased to 0.56, 0.56, and 0.58 at 5g H_2O_2/kg DS, 25 g H_2O_2/kg DS, and 50 g H_2O_2/kg DS, respectively, with a ratio of 0.07 g Fe^{2+} per gram of H_2O_2. The ds (dissolved solids)/$ds_{control}$ ratio in the liquid phase increased from 1 to 4.06 and 6.67 at 0.186 and 0.372 g H_2O_2/g Fe^{2+}/100 mL sludge, respectively (Neyens et al., 2002). Similarly, the organic matter concentration also increased with the increase in H_2O_2 concentration (Neyens et al., 2002). The addition of 0.037 g H_2O_2/g Fe^{2+}/100 mL of sludge yielded a considerable release of dissolved solids and organic matter in the liquid phase (a three- to four-fold increase relative to the concentration in the control). Thus, in general, Fenton pre-treatment increases the SCOD, BOD, and nitrogen content in the liquid phase of sludge, but there is a need for further research to evaluate the optimum Fenton pre-treatment conditions for sludge solubilization at which AD efficiency is increased.

4.2.3 Concentration of microorganism components

Sludge is a complex material containing different types of microorganisms. The general approximated composition of the microorganisms is protein (50%), lipids (10%) carbohydrates (10%) and other constituents (30%), including ribonucleic acid (RNA) and fiber (Pilli et al., 2014). Fenton pre-treatment results in the destruction of microbial cells and leads to the release of intercellular composition into the sludge liquid phase (Lu et al., 2003). It is estimated by evaluating the BOD/COD ratio (i.e., increased organic matter), nitrogen (N) and phosphorus (P) concentration in the liquid phase (or supernatant). A four-fold increase in the organic matter release into the liquid phase was observed with the addition of 0.037 g H_2O_2/100 mL (Neyens et al., 2002). The evolution of N-components as a result of Fenton reaction was summarized by Neyens et al. (2002), who noted that the ammonia nitrogen of untreated sludge in liquid phase was 105 mg N/L, increasing to 220 mg N/L after Fenton reaction. Similarly, the Kjeldahl nitrogen concentration increased from 15 mg N/L to 314 mg N/L after Fenton reaction. Furthermore, Neyens et al. (2003) evaluated pilot scale Fenton pre-treatment by adding 25 g H_2O_2/kg dry solids and 1.67 g Fe^{2+}/kg solids and observed increased nitrogen and phosphorus concentrations in the liquid phase. More specifically, the Kjeldahl nitrogen concentration increased from 104.2 mg N/L to 149.6 mg N/L, while phosphorus concentration increased from 3 mg P/L to 4.3 mg P/L. On the other hand, the concentration of ortho-phosphates decreased from 12.9 to 5.1 mg P/L due to the partial precipitation of $FePO_4$. Nonetheless, further work is required in order to establish the effect of Fenton concentrations on the release of organic matter and the resulting effect on biogas production/volatile fatty acids during AD.

5. FENTON PRE-TREATMENT EFFECT ON ANAEROBIC DIGESTION

Many researchers have established that the Fenton pre-treatment enhances sludge biodegradability, and improves AD with increased biogas production (Dewil et al., 2007; Lee and Shoda, 2008; Dhar et al., 2011; Erden and Filibeli, 2010, 2011). Biodegradability is an important parameter in evaluating AD efficiency. Fenton pre-treatment enhances sludge biodegradability in two ways: (i) the hydroxyl radicals break the microbial cell membrane, leading to oxidative decomposition of the cell walls, which results in the release of the organic substances into the liquid phase, (ii) the hydroxyl radicals will partially oxidize the recalcitrant compounds and thus change into biodegradable compounds (Neyens et al., 2004). Release of cellular matter into the liquid phase (due to pre-treatment) enhances sludge biodegradability and thus increases biogas production during AD. As mentioned above, not all soluble matter produced by pre-treatment is biodegradable and does not result in enhanced AD efficiency (Kim et al., 2013). From the findings reported by Kim et al. (2013), it is clear that sludge biodegradability is not directly proportional to the solubilization of sludge solids by the pre-treatment.

Recent studies on Fenton pre-treatment of WAS aiming to enhance biogas production are summarized in Table 4. When compared with the control sludge digestion, AD efficiency increased in the Fenton pre-treated sludge (Dewil et al. 2007, Erden and Filibeli, 2010, 2011). Literature review conducted as a part of this investigation revealed paucity of studies on AD of the Fenton pre-treated sludge. Moreover, the reported AD efficiency results cannot be compared directly, as different units were used and sludge composition was not reported. For example, Dewil et al. (2007) failed to report the total solids or volatile solid concentration of sludge. The authors used an organic dry solids percentage as a base for evaluating the digestion efficiency, while Erden and Filibeli (2010, 2011) used volatile solids percentage.

To compare sludge biodegradability, Taricska et al. (2008) summarized the volatile degradation during AD for a given initial volatile solids concentration in sludge ranging from 60% to 85% and for a solid retention time of 10 to 60 days. The authors reported that sludge characterized by lower volatile solids concentration exhibited a lower volatile solids reduction, i.e., at 55% initial volatile solids concentration the degradation was only 35% after 30 days retention time (Taricska et al., 2008). For example, Dewil et al. (2007) utilized sludge that contained less than 60% organic dry solids and, during AD, 8.8% reduction was measured for control after 8 days of solids retention time. Similarly, Erden and Filibeli (2010, 2011) used sludge with only 55% volatile solids, whereby the volatile solids reduction of 34% was measured for the control, after the retention time of 30 days. Therefore, the initial volatile solids content of sludge is vital for an efficient anaerobic digestion. From the above discussion, it could be generally concluded that Fenton pre-treatment of WAS enhanced biogas production. Nonetheless, further research is required to obtain optimum Fenton pre-treatment conditions for enhancing sludge solubilization, biodegradability and AD efficiency. Moreover, further analysis of the effect of initial volatile solids concentration in sludge on Fenton pre-treatment process and AD is required.

6. MASS AND ENERGY BALANCE AND GHG EMISSIONS DURING SLUDGE MANAGEMENT WITH OR WITHOUT FENTON PRE-TREATMENT

6.1 Assumption and parametric values considered for mass and energy balance and GHG emissions

As mentioned earlier, several studies (Table 4) clearly demonstrated that Fenton pre-treatment of wastewater sludge enhanced methane generation (due to increased biodegradability) when the treated sludge was subjected to AD. However, it is still not clear whether the energy recovered from the produced methane will be lower or higher than the total energy input for the combined process of pre-treatment and AD. The empirical evidence on the mass and energy balance of the combined process of pre-treatment and AD is scarce.

Therefore, an attempt was made to perform mass-energy balance in the combined process of Fenton pre-treatment of WAS and AD at mesophilic and thermophilic conditions of the pre-treated sludge. The data used in this study to evaluate mass-energy balance was adopted from Erden and Filibeli (2010). For mesophilic AD, the initial dry solids concentration of sludge was 4.2% (w/v) for the control and 4.6% for the Fenton pre-treated sludge. For thermophilic AD, the initial DS for control as well as Fenton pre-treated sludge was 4.2% (w/v) (Erden and Filibeli, 2010). Different solids retention times (from batch data) i.e., 15 days, 20 days, 25 days and 30 days were considered during mass and energy balance computations. All other data are listed in Table 5. The overall process pathway considered in the mass and energy balance in this work is given in Fig. 1.

The energy ratio and the net energy are important parameters that indicate if the process is energetically beneficial. If the energy ratio (output/input) is greater than one, the energy recovery is greater than the energy input. Net energy refers to the difference between the energy recovered and the energy input. To calculate the energy ratio, net energy and GHG emissions, the following steps are considered. In Step 1, the energy required for the WAS pre-treatment (energy required for mixing sludge) and the energy content of the chemicals required is evaluated. The energy required for mixing (60 min) during Fenton pre-treatment is considered as 30 kW/1000 m^3 of the reactor volume (i.e., an average of 20-40 kW/10^3 m^3 of reactor volume) (Spinosa and Vesilind, 2001). The quantity of chemicals used during the Fenton pre-treatment is set at 60 g H_2O_2/kg dry solids and 0.07 g Fe^{2+}/g H_2O_2 (the optimum concentration reported by

Erden and Filibeli, 2010). The energy embedded in the hydrogen peroxide is 7.7 kWh/kg of H_2O_2 (Munter 2001) and in Fe^{2+} is 6.94 kWh/kg of Fe^{2+} (Hammond and Jones, 2008).

AD is considered in Step 2. The energy required to increase the temperature of the incoming pre-treated sludge (12°C) to the mesophilic digester temperature (35±2°C) and thermophilic digester temperature (55±2°C), and the energy required to compensate the heat loss from the digester during the AD process are considered in this step. It was assumed that the biogas produced during AD was re-circulated for sludge mixing (Van Haandel and Van Der Lubbe, 2012; Nayono, 2009). Moreover, the volume of methane produced and the energy recovered was also evaluated. Dewatering the digested sludge was considered in Step 3, and the energy required for dewatering the digested solids is given in Table 5.

Transportation of dewatered solids (Step 4) or the quantity of diesel required for the vehicles to transport the solids for land application was considered. The distance between WWTP and the land application site to which the dewatered solids need to be transported was set at 50 km (Gassara et al., 2011). The diesel consumption rate of the waste collection vehicles was 3.5 L per 100 km and GHG emission values were 2730 g CO_2/L of diesel, 0.12 g CH_4 /L of diesel, and 0.08 g N_2O/L of diesel (Gassara et al., 2011).

The land application of the dewatered sludge solids was considered in Step 5. The energy required for spreading the dewatered solids across the land is considered in evaluating the energy input (Table 5). The GHG emissions corresponding to the energy consumed during Fenton pre-treatment, dewatering of the digested sludge, transportation, and land application was evaluated using the national emission intensity coefficient 0.53 kg CO_2/kWh (developed by Environment Canada study based on the Resources for the Future (RFF) model). GHG emissions during anaerobic digestion, methane combustion, and from vehicles during transportation and land application are also considered in the calculation of GHG emissions.

6.2 Results of Mass- Energy balance and GHG emissions

The results of computations pertaining to mass and energy balance, based on degradation of DS in mesophilic and thermophilic AD are summarized in Fig. 2 and 3 and Table 6. The mass balance of the control and Fenton pre-treatment sludge at 15 days retention time for mesophilic and thermophilic digestion is presented in Fig. 2. As can be seen, DS degraded in the Fenton pre-treated sludge was higher than in the control for mesophilic as well as thermophilic digestion (Fig. 2). Similarly, the amount of DS left after AD of the Fenton pre-treated sludge was lower than in the control. This difference will have impact on the reduction of the energy required for dewatering, transportation and land application.

A summary of the energy balance of the control and Fenton pre-treated sludge at different retention times for mesophilic and thermophilic digestion is presented in Fig. 3. The DS degradation was increased with retention time for all the cases, but the net energy did not increase with increased retention time (Fig. 3). During mesophilic digestion, the net energy and the energy ratio were higher in the Fenton pre-treated sludge. Thermophilic temperatures require high energy for increasing the sludge temperature to the digestion temperature (55±2 °C). The energy output and net energy (energy output − energy input) is higher than the control for the Fenton pre-treated with mesophilic digestion. For thermophilic digestion, the net energy is higher for the control when compared with Fenton pre-treated sludge. However, the total energy output is higher than the total energy input for all the cases. Moreover, increased solids degradation for the Fenton pre-treated sludge, and the energy required during dewatering, transportation and land application is reduced for both mesophilic and thermophilic digestion. Thus, Fenton pre-treatment followed by mesophilic digestion resulted in higher net energy and energy ratio.

The GHG emission for the mesophilic and thermophilic digestion of the control and Fenton pre-treated sludge at different retention times is presented in Table 6. CO_2 emissions from biological pathway are considered as biogenic CO_2 emissions; therefore, they are not taken into account in national protocols as they are considered (by convention) as “carbon neutral” (i.e., their global warming potential is assumed to be equal to zero) (Pradel and Reverdy, 2012). GHG emissions are reduced during mesophilic AD for the control and the Fenton pre-treatment. However, at 15 days retention time, GHG emissions were not reduced for the control. When compared with the control, GHG emissions were reduced at a higher rate for the Fenton pre-treated sludge at all retention times. For example, at 15 days retention time, the GHG emissions for the control are 44 kg CO_2 equivalent/Mg of DS, whereas for the Fenton pre-treated sludge the GHG emissions are -97.8 kg CO_2 equivalent/Mg of DS. For thermophilic digestion, the GHG emissions reduced when the system was operated at 20 days retention time for both the control and the Fenton pre-treated sludge. The highest reduction in GHG emissions was observed at 20 days HRT for the control—thermophilic AD and 30 days for the Fenton—pre-treated thermophilic AD. Therefore, it can be concluded that GHG emissions are reduced with Fenton pre-treatment and the highest reduction was observed at 20 day HRT during mesophilic AD.

It must be pointed out that these computations are based on a specific sludge with and without Fenton treatment. In general, the net energy and the energy ratio will depend on the type of sludge, sludge solids concentration, initial biodegradability of sludge, etc. Therefore, it is necessary that the mass and energy balance be computed for specific conditions of sludge and the pre-treatment process.

7. FUTURE PERSPECTIVE

The Fenton pre-treatment of sludge is one of the emerging technologies for sludge pre-treatment to increase its biodegradability. Nonetheless, extensive research on methane production optimization is required for a full-scale application. The effect of Fenton pre-treatment on the chemical compounds (protein, carbohydrates, nitrogen, etc.) present in the sludge and its corresponding effect on AD have not been studied. Moreover, AD of Fenton pre-treated sludge at different solids concentration for primary, secondary and mixed sludge is required to obtain an energy efficient process. Single stage (i.e., Fenton pre-treatment of sludge followed by AD), and multistage (i.e., pre-treating the digestate of control and Fenton pre-treated, and followed by AD) Fenton pre-treatment of sludge aimed at enhancing AD need to be evaluated based on the mass-energy balance. Modified Fenton's reagent utilization for sludge pre-treatment has not been studied, and the effect on enhancing AD needs to be established. Both pilot scale and full-scale studies using Fenton pre-treated sludge need to be evaluated based on the mass-energy balance. Evaluating the total mass-energy balance and the net carbon balance will help the decision makers in choosing the most optimal pre-treatment technology.

8. CONCLUSION

Lab scale and pilot scale studies showed that Fenton pre-treatment had high potential in enhancing sludge dewaterability. The pH, temperature, concentration of hydrogen peroxide, Fe^{2+}, and the reaction time are important parameters that influence Fenton pre-treatment efficiency. Low pre-treatment temperature requires high Fenton concentration and more treatment time. On the other hand, high pre-treatment temperature required low Fenton concentration and less treatment time. Although Fenton pre-treatment enhances AD process efficiency, it is not clear whether the process is energetically feasible. Using the data available, the mass-energy balance computation of the pre-treatment and AD processes was performed.

The computation results established that Fenton pre-treatment enhances the methane production and the energy output/input ratio for both mesophilic and thermophilic digestion. Greenhouse gas emissions are also reduced with AD of Fenton pre-treated sludge for mesophilic and thermophilic digestion.

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Abbreviation list

AD: Anaerobic digestion

BOD: biochemical oxygen demand

CH_4: methane

CO_2: Carbon dioxide

COD: chemical oxygen demand

CST: Capillary suction time

ds: dissolved solids

DD: degree of disintegration

DS: dry solids

Fe^{2+}: Ferrous ion

GHG: greenhouse gases

H_2O_2 : hydrogen peroxide

kg: kilogram

kW: kilowatt

kWh: kilowatt hour

mL: milliliter

N_2O: Nitrous oxide

NH_3: Ammonia

ODS: Organic dry solids

RFF: Resource for Future

SCOD: soluble chemical oxygen demand

$SCOD_u$: soluble COD of untreated sludge

$SCOD_m$: soluble COD of Fenton pre-treated

SRF: specific resistance to filtration

SS: suspended solids

VS: Volatile solids

VSS: Volatile suspended solids

WAS: Waste activated solids

WWTP: wastewater treatment plant

WWTPs: wastewater treatment plants

ΔODS: difference of organic dry solids

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Table 1. The reactions between the hydroxyl radicals and the targeted pollutants during Fenton reaction

Reaction type	Example	Description	Reference
Addition	$R_2C{=}{=}{=}CR_2 + HO^\bullet \rightarrow HO\text{-}C(R)_2 - C^\bullet(R)_2$	During the addition reaction hydroxyl radicals adds to an unsaturated compound, aliphatic or aromatic to form a free radical product.	Buda et al., (2003); Prousek, (2007);
Hydrogen abstraction	$ArH + HO^\bullet \rightarrow R^\bullet + H_2O$	In this reaction an organic free radical and water are formed.	Buda et al., (2003); Prousek, (2007);
Electron transfer	$HO^\bullet + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^-$	In this reaction free radical is oxidised	Buda et al., (2003); Prousek, (2007); http://www.h2o2.com
Radical recombination	$HO^\bullet + HO^\bullet \rightarrow H_2O_2$	Two hydroxyl radicals react to combine or disproportionate to form a stable compound.	Buda et al., (2003); Prousek, (2007); http://www.h2o2.com

Table 2. Limitations of the parameters affecting the Fenton reaction

Parameter	limitations	Reference
H_2O_2 concentration	The H_2O_2 concentration required in general for occurrence of hydroxyl radical can be very low < 10-25 mg L^{-1} H_2O_2 or 1 part Fe per 5-25 parts of H_2O_2 (wt/wt). For sludge solubilisation the optimum concentration of H_2O_2 is 0.01 mL H_2O_2/g SS, and $[H_2O_2]_0/[Fe2^+]_0$ ratio of 150 is required.	Ramaswamy et al., (2009); Maletzky et al., (1999); Pham et al., (2010b, 2011)
Iron type and concentration	For the desired end products, the typical concentration required is: 1 part Fe per 10-50 parts of substrate	Ramaswamy et al., (2009); Maletzky et al., (1999); http://www.h2o2.com
pH	Various researchers have evaluated the effect of pH during the Fenton treatment, the optimal pH for obtaining the desired treatment is in the range of 3 to 6.	Neyens and Baeyens, (2003); Pham et al., (2010b, 2011)
Temperature	Most favourable temperature for Fenton treatment is in the range of 20-40°C.	http://www.h2o2.com; Neyens and Baeyens, (2003)
Reaction time	For maximum solubilisation and increase biodegradability of sludge reaction time of 20 min is required (Pham et al., (2010b)	Neyens and Baeyens, (2003); (Pham et al., (2010b); http://www.h2o2.com

Table 3. Effect of Fenton pre-treatment on sludge dewaterability

Sludge type	pH	Total Solids concentration (%) w/v	Fenton reagent concentration		Effect on dewaterability	Reference
			H_2O_2	Fe^{2+}		
WAS at 70°C (Sulphite pulp, paper mill)	3.0	3.0	60 mM	0.2 mM	Untreated SRF = 6200 x 10^{12} m/kg treated SRF = 35 x 10^{12} m/kg	Mustranta and Viikari (1993)
WAS at 70°C (neutral sulphite semi-chemical pulp, board mill)	3.0	2.8	30 mM	0.1 mM	Untreated SRF = 144 x 10^{12} m/kg treated SRF = 19 x 10^{12} m/kg	
WAS at 70°C (Sulphite plup mill)	3.0	3.1	30 mM	0.1 mM	Untreated SRF = 2400 x 10^{12} m/kg Pre-treated SRF = 71 x 10^{12} m/kg	
WAS at 70°C (sulphite pulp, paper mill) pilot scale activated sludge plant	3.0	3.0	15 mM	0.05 mM	Untreated SRF = 355 x 10^{12} m/kg treated SRF = 123 x 10^{12} m/kg	
WAS	NA	3.0	3 g/L	6 g/L	reduction of SRF(%) : control 4% and pre-treated 96%	Liu et al. (2001 & 2003)
Municipal sewage sludge	3.0	6 .0	0 mg/mL	0.01 mg/L	CST (sec) = 68.0 (30.98% DS)	Neyens et al. (2002)
		(DS content)	0.04	0.0083	59.9 (31.78%DS	
			0.37	0.0063	37.9 (39.10%DS)	
			1.86	0.0060	33.4 (39.24%DS)	
			3.72	0.0060	23.6 (39.86%DS)	
			37.2	0.0059	50.9 (40.18%DS)	
Municipal sewage sludge	3.0	6.0	0 mg/mL	0.01 mg/L	CST (sec) = 68.0 (30.98% DS)	Neyens et al. (2002)
			0.037	0.083	57.2 (32.50%DS)	
			0.372	0.060	34.6 (38.82%DS)	
			1.860	0.060	32.5 (39.45%DS)	
			3.72	0.057	21.7 (40.85%DS)	
			37.2	0.057	43.9 (42.1%DS)	

Table 3. Continutation

Sludge type	pH	Total Solids concentration (%) w/v	Fenton reagent concentration		Effect on dewaterability	Reference
			H_2O_2	Fe^{2+}		
Municipal sewage sludge	3.0	6.0	25.0 g/kgDS	1.67 g/kgDS	Improved dewaterability with a 30% reduction of sludge volume, and a 30% increase of the cake DS content when compared with the untreated sludge sample	Nayens et al. (2003)
WAS	3.5	2.00	6.0 g/L	5.0 g/L	Untreated SRF = 9.162 x 10^{10} m/kg treated SRF = 6.149 x 10^{9} m/kg CST for untreated =30.5 s CST for Pre-treated = 15.7 s	Buyukkamaci (2004)
WAS	3.0	4.0	25 g/kg DS	1.67 g/kg DS	Untreated %(w/w)DS in filter cake = 22.58 g/kg DS, % DS in filter cake = 40.31	Dewil et al. (2005)
WAS	3.0	NA	0.0	0.0	Untreated DS% (W/W) 0.08	Dewil et al. (2007)
			5.0 g/kg DS	0.35 g/kgDS	0.15	
			25.0 g/kg DS	1.75 g/kg DS	0.44	
			50.0 g/kg DS	3.50 g/kg DS	0.65	
Aluminium-based sludge	6.0	2.8 g/L (SS)	105 mg/gDS	21 mg/g DS	CST reduction efficiency of 48% was achieved.	Tony et al. (2008 & 2009)
Waste activated sludge	3.8	3.01	178 mg/g VSS	211 mg/g VSS	CST reduction efficiency of 98.25% was achieved.	Zhen et al. (2013)

Note: NA: Not applicable

Table 4. Effect of Fenton pre-treatment on biogas production

Sludge	Pre-treatment conditions	AD	Biogas production	Conclusion	Reference
WAS	0.07 Fe^{2+} /g of H_2O_2 5 mg H_2O_2/kgDS, 25 mg H_2O_2/kgDS and 50 mg H_2O_2/kg DS, pre-treated for 60 min.	Lab scale at 37°C for 8 days	Blank = 644 mL/g ΔODS Pre-treated with H_2O_2 5 (mg/kgDS) = 632 mL/g ΔODS 25 (mg/kgDS) = 655 mL/g ΔODS 50 (mg/kgDS) = 668 mL/g ΔODS	Pre-treatment with the Fenton reagent positively influenced the biogas formation during anaerobic digestion. The biogas production increased with increasing dosage of H_2O_2.	Dewil et al. (2007)
WAS	NA	Lab scale at 35°C for 5 days	NA	25.4% reduction in VS was obtained operated with a 5 day sludge retention time. VS reduction was 1.53 times greater than in the control reactor.	Kaynak and Filibeli (2008)
WAS	0.067 g Fe^{2+}/ g H_2O_2, and 60 g H_2O_2/kg dried solids (DS), pre-treated for 60 min.	First stage (55±2°C) Second stage (37±2°C) for 30 days	The specific methane production Control –first stage- 400 mL CH_4/gVS Control –Second stage 544.6 mL CH_4/gVS Pre-treated –first stage 547.3 mL CH_4/gVS Pre-treated-second stage 561.1 mL CH_4/gVS	Fenton pre-treatment provided 1.4 and 1.2 times higher methane production in first stage of digestion and second stage of digestion, respectively, at the end of 30 day operation.	Erden and Filibeli (2010)
WAS	4 g Fe^{2+}/kg TS and 60 g H_2O_2/kg TS, pre-treated for 60 min.	37°C for 30 days	Cumulative methane production for 55 days control-327 mL pre-treated-390 mL	With Fenton pre-treatment 19.4% higher methane production was achieved compared to raw sludge.	Erden and Filibeli (2011)

Note : ODS = organic dry solids; DS = dry solids; NA= not applicable; A = mg of H_2O_2/mg dissolved S^{2-}; B = mg of $FeCl_2$/mg dissolved S^{2-}

Table 4. Continutation

Sludge	Pre-treatment conditions	AD	Biogas production	Conclusion	Reference
WAS	Fenton pre-treatment for 30min followed by mechanical pre-treatment (pressuring the reactor to 75± 1 Psi for 30 min)	37±1°C for 30 days	Control - 226 ± 4 ml CH_4/g VS_{Sadded}	30 days of digestion, cumulative methane volume was 8-10% higher for all pre-treatment conditions compared to the control test.	Dhar et al. (2011)
	(i) A = 0.6; B = 1.5		(i) 258 ± 1 mL CH_4/g VS_{Sadded}		
	(ii) A = 1.5; B = 1.5		(ii) 254 ± 1 mLCH_4/g VS_{Sadded}		
	(iii) A = 0.6; B = 3		(iii) 253 ± 4 mL CH_4/g VS_{Sadded}		
	(iv) A = 1.5; B =2.5		(iv) 260 ± 1 mL CH_4/g VS_{Sadded}		
	(v) A = 2; B = 2.5		(v) 254 ± 3 mL CH_4/g VS_{Sadded}		
	(vi) A = 2; B = 3		(vi) 251 ± 6 mL CH_4/g VS_{Sadded}		

Note : ODS = organic dry solids; DS = dry solids; NA= not applicable; A = mg of H_2O_2/mg dissolved S^{2-}; B = mg of $FeCl_2$/mg dissolved S^{2-}

Table 5. Parametric values used in calculations

Descrition	Value	Units	Reference
Volume of sludge to be treated	1000	m^3	Considered m^3
Temperature of sludge	12	°C	Wastewater treatment plant, Quebec
Temperature of Fenton pre-treated sludge	12	°C	
Anaerobic digestion temperature Mesophilic thermophilic	35 55	°C °C	Erden and Filibeli (2010)
Specific heat of sludge	4200	kJ/m^3 °C	Metcalf and Eddy (2003)
DS degraded at 20 days retention time Mesophilic control Mesophilic Fenton pre-treated Thermophilic control Thermophilic Fenton pre-treated	60.70 69.56 64.28 64.76	% % % %	Erden and Filibeli (2010)
Heating value of methane	31.79	MJ/m^3 CH_4	Metcalf and Eddy (2003)
HRT	15, 20 25 and 30	Days	Erden and Filibeli (2010)
Energy required for dewatering	101.4	kWh/dry Mg biosolids	Brown et al. (2010)
Distance between the WWTP and land application site	50	km	Assumed
Energy required for land application of dry solids	351.68	kWh/dry Mg biosolids	Wang et al. (2008)
GHG emissions from land application			
CH_4 emissions	3.18	Kg CH_4/dry Mg biosolids	Hospido et al. (2005)
CO_2 emssions	17.20	Kg CO_2/dry Mg biosolids	Hong et al. (2009)

Table 6. GHG emissions for control and Fenton pre-treated sludge at mesophilic and thermophilic digestion

	Mesophilic digestion								**Thermophilic digestion**							
	Control				**Fenton pre-treated**				**Control**				**Fenton pre-treated**			
	Retention time (days)				**Retention time (days)**				**Retention time (days)**				**Retention time (days)**			
Description	**15**	**20**	**25**	**30**	**15**	**20**	**25**	**30**	**15**	**20**	**25**	**30**	**15**	**20**	**25**	**30**
	GHG emissions Kg CO_2 equivalent/Mg of DS				**GHG emissions Kg CO_2 equivalent/Mg of DS**				**GHG emissions Kg CO_2 equivalent/Mg of DS**				**GHG emissions Kg CO_2 equivalent/Mg of DS**			
Net GHG emission due to energy input and out put	-389.6	-934.4	-987.2	-904.3	-799.7	-1572.3	-1502.8	-1406.4	-190.5	-1282.1	-1210.5	-1214.3	-620.2	-1117.5	-1272.4	-1422.4
GHG emissions during AD (biogenic emissions)	254.7	405.4	420.7	396.6	437.0	650.4	630.7	600.4	278.6	590.1	567.5	567.6	475.3	616.5	660.6	702.7
GHG emissions during CH_4 combustion	381.9	607.8	630.8	594.6	655.2	975.2	945.6	900.3	417.8	884.8	850.6	851.0	712.7	924.4	990.6	1053.6
GHG emissions during transportation	9.7	7.6	7.4	7.1	8.7	5.9	5.8	5.7	8.7	6.9	6.9	6.7	7.8	6.8	6.8	6.4
GHG emissions during land application	42.0	33.0	32.0	31.0	38.0	25.6	25.2	24.7	38.0	30.0	30.0	29.0	34.0	25.6	29.6	28.0
Total GHG emission With out considering biogenic CO_2 emissions	**44.0**	**-286.0**	**-317.1**	**-271.6**	**-97.8**	**-565.7**	**-526.2**	**-475.8**	**274.1**	**-360.4**	**-323.0**	**-327.6**	**134.3**	**-160.7**	**-245.4**	**-334.3**

Note : Negative sign indicate reduction in GHG emissions; GHG emissions from biogenic source are as “carbon neutral” (i.e, global warming potential is equal to zero) Pradel and Reverdy.

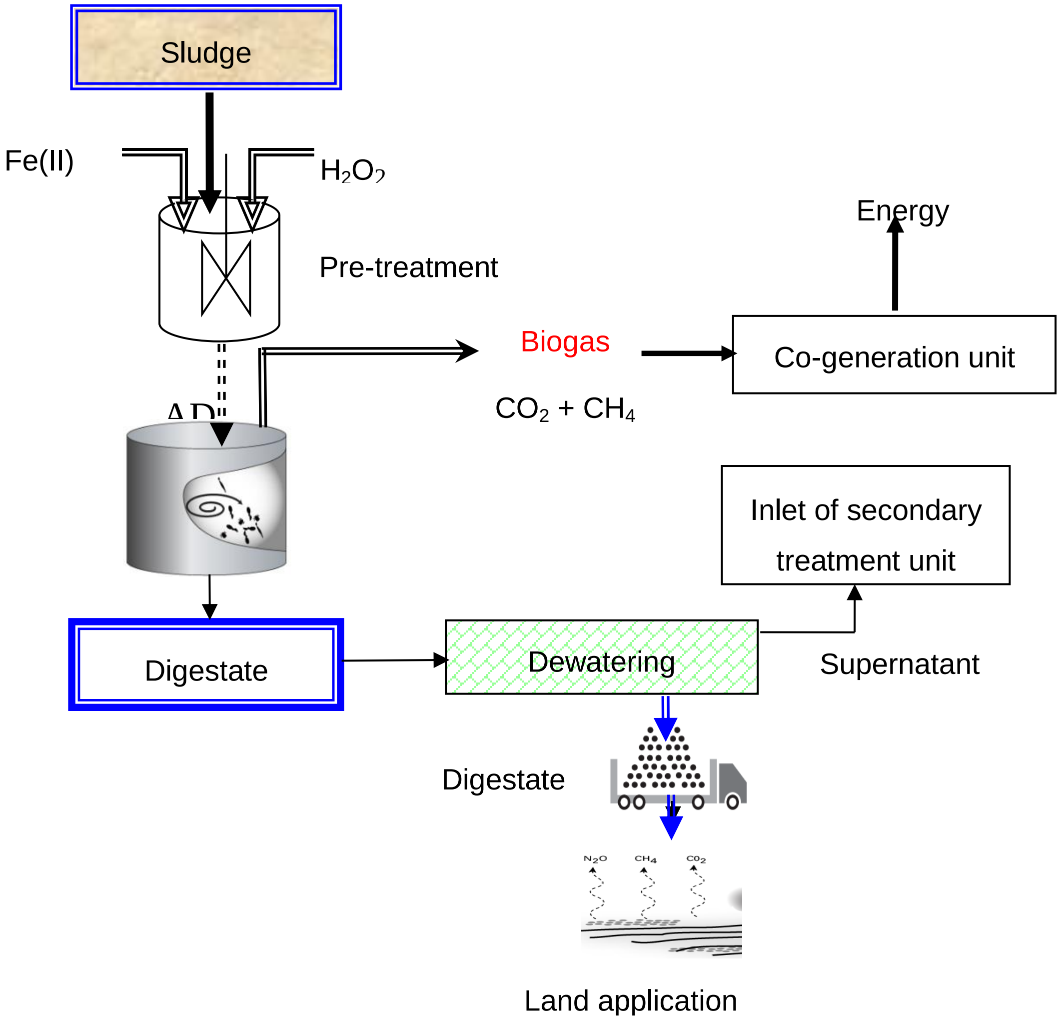

Figure 1. Pathway of sludge management with Fenton pre-treatment

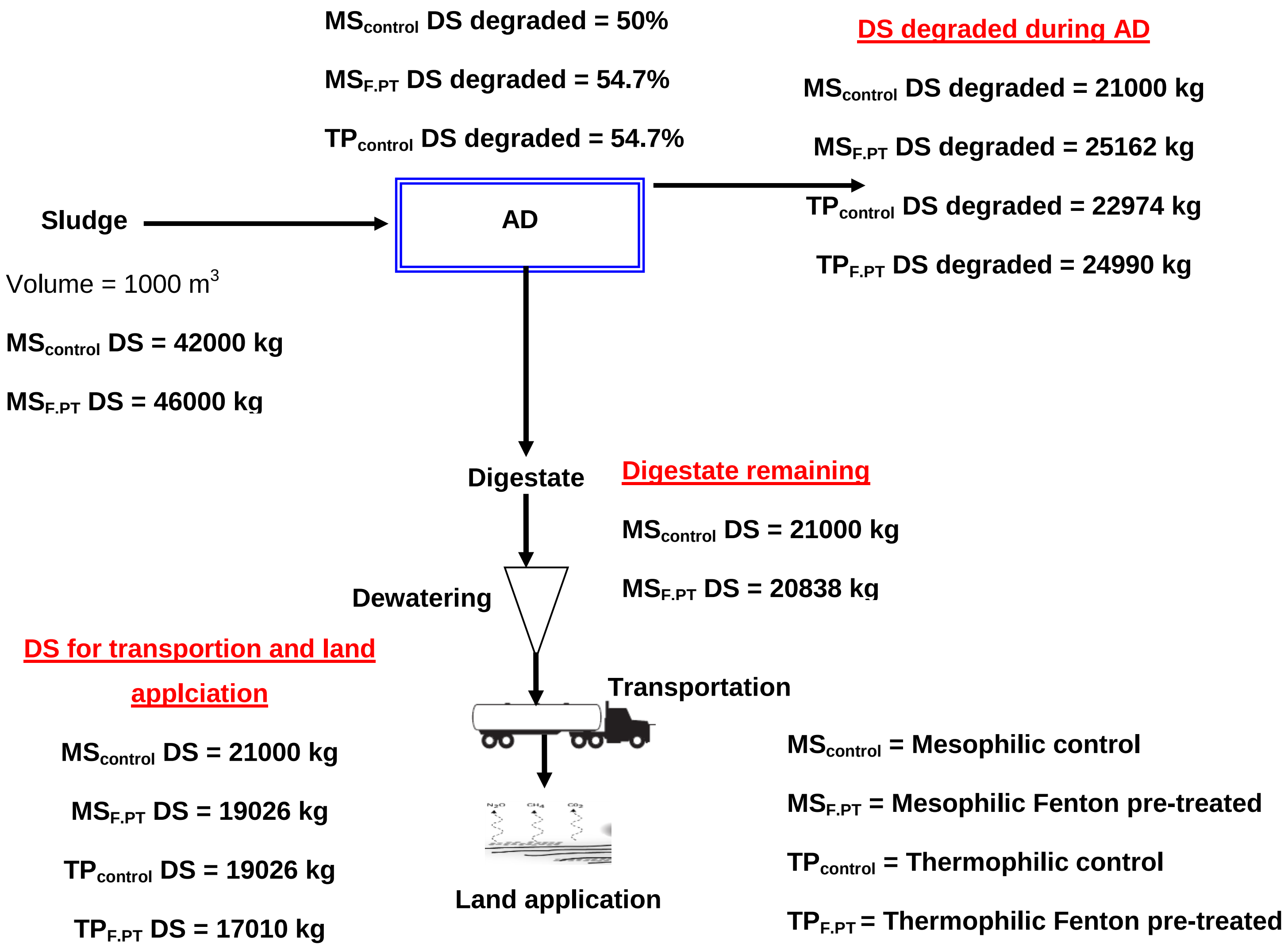

Figure 2. Mass balance for the control and Fenton pre-treated sludge at mesophilic and thermophilic digestion

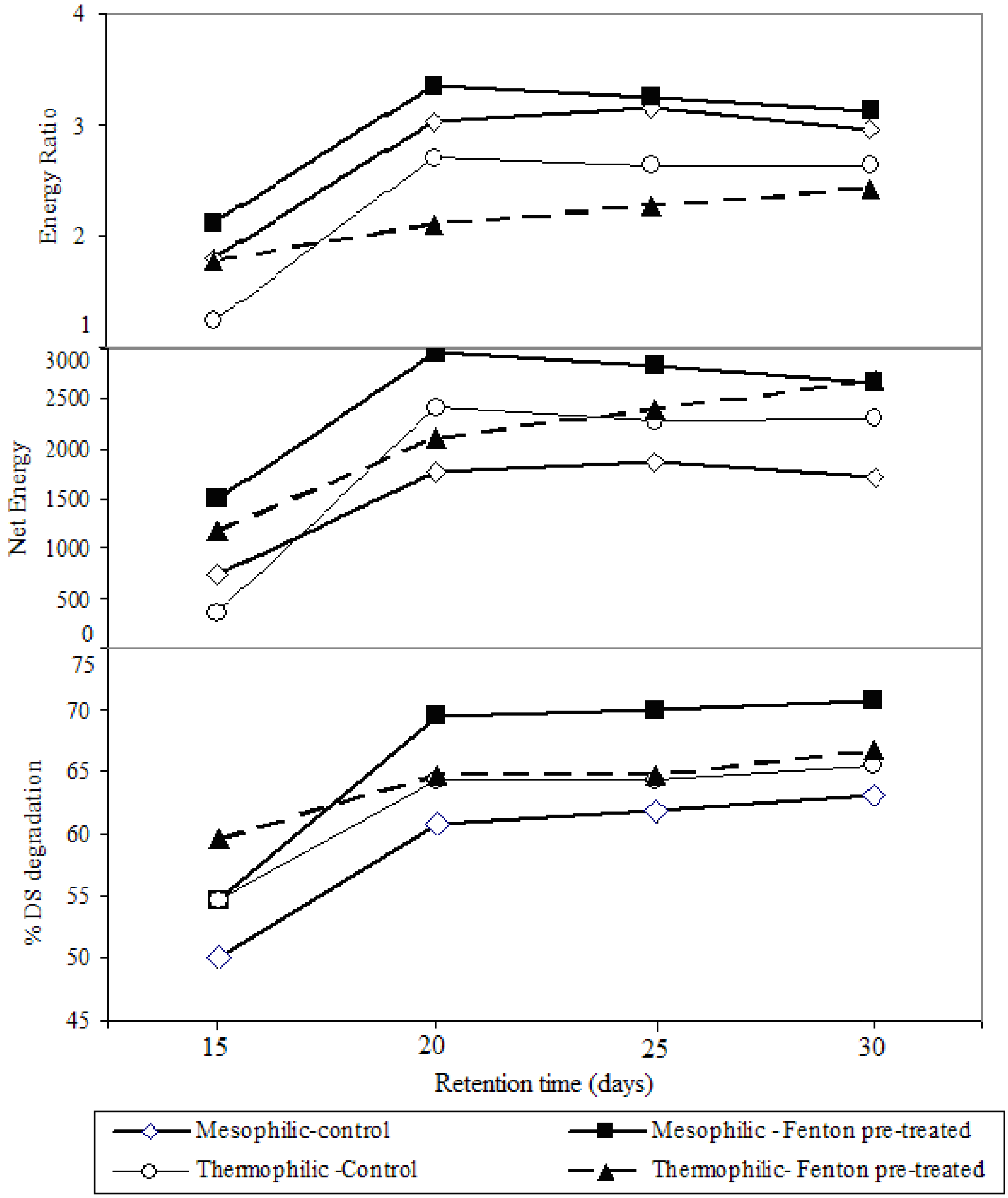

Figure 3. Energy balance for control and Fenton pre-treated sludge at mesophilic and thermophilic digestion

PARTIE 2

FENTON PRE-TREATMENT OF SECONDARY SLUDGE TO ENHANCE ANAEROBIC DIGESTION: ENERGY BALANCE AND GREENHOUSE GAS EMISSIONS

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RÉSUMÉ

Des expériences réalisées à l'échelle laboratoire concernant l'application du prétraitement Fenton (FPT) sur les boues secondaires (SS) ont été effectuées pour déterminer son effet sur l'efficacité de la digestion anaérobie (DA). L'effet du FPT sur la DA a été évalué par le calcul du bilan d'énergie et de production de gaz à effet de serre (GES) correspondant. Quatre procédés de traitement ont été évaluées: (i) Procédé 1- DA de SS (contrôle); (ii) Procédé 2- DA de la SS ayant subi le FPT; (iii) le Procédé 3- il s'agit du Procédé 2 + prétraitement Fenton du digestat produit dans le procédé 2, suivi par une DA (iv) Procédé 4- il s'agit du procédé 1 + prétraitment Fenton du digestat généré dans le Procédé 1, suivi par une DA. Les résultats ont révélé que la production de méthane cumulative a été augmentée de 15% dans le cas du prétraitement Fenton par rapport au témoin. Le taux de production de méthane dans le contrôle (Procédé 1) était de 430 m^3 CH_4/Mg VS dégradé et il était de 496 m^3 CH_4/Mg VS dégradé pour les boues secondaires prétraitées par le procédé Fenton (Procédé 2). L'énergie nette a été augmentée d'un facteur de 3,1 pour le prétraitement Fenton (Procédé 2) par rapport au contrôle (Procédé 1). L'énergie nette pour le Processus 4 a été augmentée de 2,5 fois par rapport au Procédé 1. Les émissions de GES ont été réduites dans le cas du prétraitement par le procédé Fenton (Procédé 2) en comparaison au contrôle (Procédé 1). Les plus basses émissions de GES de 0,128 Mg de CO_2/Mg du total de matières sèches (TDS) ont été observées dans le cas du Procédé 2. Le prétraitement par le procédé Fenton (principalement Procédé 2) est un processus rentable, en raison de la récupération d'énergie et des faibles émissions de GES.

Mots-clés: prétraitement Fenton; digestion anaérobie; digestat; bilan énergétique; émissions de gaz à effet de serre.

ABSTRACT

Laboratory scale experiments on Fenton pre-treatment (FPT) application to the secondary sludge (SS) were carried out to determine its effect on the anaerobic digestion (AD) efficiency. The effect of FPT on AD was evaluated by computing energy balance and corresponding greenhouse gas (GHG) emissions. Four treatment processes were evaluated: (i) Process 1 − AD of SS (control); (ii) Process 2 − AD of the Fenton pre-treated SS; (iii) Process 3 − Process 2 + Fenton pre-treatment of the digestate produced in Process 2, followed by AD (iv) Process 4 − Process 1 + Fenton pre-treatment of the digestate generated in Process 1, followed by AD. The results revealed that the cumulative methane production was increased by 15% in Fenton pre-treatment compared to the control. The methane production rate in the control (Process 1) was 430 m^3 CH_4/Mg VS degraded and it was 496 m^3 CH_4/Mg VS degraded for Fenton pre-treated SS (Process 2). The net energy was increased 3.1 times with Fenton pre-treatment (Process 2), when compared to the control (Process 1). The net energy for Process 4 increased 2.5 times compared to Process 1. The GHG emissions were reduced in Fenton pre-treatment (Process 2) compared to the control (Process 1). The lowest GHG emissions of 0.128 Mg CO_2 equivalent/Mg of total dry solids (TDS) were observed in the Fenton pre-treated sludge (Process 2). Thus, Fenton pre-treatment process (mainly Process 2) is cost-effective, due to energy recovery and decreased GHG emissions.

Keywords: Fenton treatment; anaerobic digestion; energy balance; greenhouse gas emissions.

1. INTRODUCTION

In recent years, sewage sludge production during wastewater treatment in wastewater treatment plants (WWTPs) has become a global environmental problem. The annual sludge production of the existing WWTPs in USA and Canada is estimated at 6515 × 10^3 and 550 × 10^3 Mg total dry solids (TDS) per year, respectively (LeBlanc et al. 2008). In China, sludge production steadily increased from 11 × 10^6 to 21 × 10^6 Mg per year from 2005 to 2010 (sludge with 80% water content) (Liu et al., 2013). Sharp rise in sludge production in the near future is expected due to high water demand caused by rapidly increasing population, industrialization, and urbanization, as well as due to higher levels of wastewater treatment. The cost associated with sludge management is around 50-60% of the total WWTPs operating costs (Pilli et al., 2011; Coma et al., 2013). In developed countries, the most common sludge treatment methods are aerobic digestion, anaerobic digestion (AD) and composting (Arthurson, 2008; Hanjie, 2010); and the most common disposal methods are incineration, landfill, or land application. Depending upon the environmental conditions during sludge treatment and disposal, the organic matter present in sludge is transformed to CO_2, CH_4, and N_2O. These gases are considered as the principal greenhouse gases (GHGs). Carbon dioxide was used as the basis to compute the level of relative contribution to global warming potential of each gas. The global warming potential of CH_4 and N_2O for 100 years is about 28 and 265 times, respectively, more powerful than CO_2 (Stocker et al., 2013). Alarming rates of global warming and climate change have made it obligatory to quantify GHG emissions from every source. The sludge management accounts for 40% of the total GHG emissions from a WWTP (Brown et al., 2010; Shaw et al., 2010).

Among the biological treatment processes, AD is considered the most cost-effective, due to the energy recovery in the form of biogas and its very limited adverse environmental impact (Alvarez et al., 2010; Khalid et al., 2011; Mata-Alvarez et al., 2011). According to Yasui et al. (2005, 2006), by capturing the energy from the methane produced during AD, the total natural gas consumption can be reduced and a significant reduction in the annual GHG emissions can be achieved. This process can follow the framework of new regulations and meet the Kyoto protocol requirement to reduce GHG emissions. AD of sludge is a slow process due to the complex nature of sludge and requires longer retention time (Carrère et al., 2010). The non-availability of the easily biodegradable matter in sludge reduces biogas production and increases the digestion time during AD. Therefore, aiming to increase the biogas production and to reduce digestion time, various pre-treatment technologies have been studied by different authors (Carrère et al., 2010).

Sludge pre-treatment facilitates the release of intracellular matter by rupturing the cell walls in to the aqueous phase to increase the biodegradability and biogas production. The various pre-treatment processes that are studied with the aim of enhancing AD efficiency (increasing biogas production and achieving reduction in retention time) can be classified as chemical (Fenton pre-treatment, hydrogen peroxide, ozone pre-treatment, etc.), physical, mechanical, biological and physico-chemical treatment processes. Hydrogen peroxide, Fenton reagent, and ozone are commonly used chemicals for advanced oxidation process (Cacho Rivero et al., 2006; Tokumura et al., 2007; Erden and Filibeli, 2010). These chemicals are capable of oxidizing the complex organic substrates. Fenton reagent produces highly oxidizing radicals, having oxidation-reduction potential of +2.33 V. These radicals are stronger oxidants than hydrogen peroxide (+1.36 V) and ozone (+2.07 V) (Neyens and Baeyens, 2003; Erden and Filibeli, 2010; Pham et al., 2010a).

Fenton pre-treatment (FPT) increases biogas (methane and carbon dioxide) production (Dewil et al., 2007; Kayanal and Fibeli, 2008; Erden and Filibeli, 2010 and 2011). However, it is presently not clear whether the energy recovered from the produced methane will be equivalent to the energy input required for the pre-treatment process and AD. Thus, the aim of the present study was to evaluate the effectiveness of Fenton pre-treatment of secondary sludge for enhancing the AD efficiency by computing energy balance and corresponding GHG emissions. Moreover, four treatment process configurations (Process 1-4) are considered in this study (Fig. 1).

2. MATERIALS AND METHODS

2.1 Wastewater sludge

Secondary wastewater sludge was collected from municipal wastewater treatment plant (WWTP) Communauté urbaine de Québec (CUQ) (Beauport, Quebec City, Canada). The WWTP consists of primary clarification, secondary biological treatment (without nutrient removal) and tertiary treatment. The total solids (TS) of the collected sludge after gravity settling was measured at ~1.5 g/L and TS concentration was increased by centrifugation at 1600 × *g* for 3 min (Sorvall RC 5C plus Macrocentrifuge (rotor SA-600)). The concentrated sludge obtained after centrifugation exceeded 30 TS g/L; therefore, it was diluted with demineralized water to achieve the required TS concentration of 30 g/L, as well as homogenized in a WaringTM blender for 30 s. The sludge was stored at 4^{o}C for further use.

2.2 Fenton treatment of sludge

Initially, the pH of sludge samples was adjusted to pH 3 using 10 N-H_2SO_4. In the second step, H_2O_2 and $FeSO_4$ stock solution (60 g H_2O_2/kg TS and 0.07 g Fe^{2+}/g H_2O_2, respectively) was added to the acidified sludge samples (of 1 L volume) to initiate the Fenton oxidation reaction. Next, the samples were stirred at 150 rpm for 1 h at ambient temperature to carry out the Fenton oxidation. Moreover, the digestates produced from Process 1 and 2 after 30 days of digestion were centrifuged to achieve total solids concentration of 30 g/L. The Fenton pre-treatment of the concentrated digestates generated from Process 2 and Process 1 was carried out as described in Fig. 1 (corresponding to Process 3 and Process 4, respectively).

2.3 Anaerobic digestion

AD was performed in 1000 mL digester glass bottles placed in a water bath at 35 °C having a provision to collect biogas. The working volume of each digester bottle was 800 mL. Each digester bottle was inoculated with anaerobic sludge (100 mL) collected from Valcartier, Quebec, Canada. The AD was carried out for 30 days. The AD of the Fenton pre-treated digestate (i.e., digestate generated from Process 1 and Process 2 after 30 days of digestion) was also performed in glass bottles (Fig. 2). The water level in the water bath was adjusted to the sludge height in the bottles. To remove the air from the headspace of the bottles and maintain the anaerobic conditions, the nitrogen gas was sparged through sludge for 2 min. The bottles were mixed manually twice a day to minimize the effects of settling during AD. The initial pH of sludge was adjusted to 7 with NaOH solution (4 N). Pre-treatment enhances the AD and reduces the retention time (Pilli et al., 2011). Therefore, to evaluate the degradation, total solids (TS), volatile solids (VS), suspended solids (SS), and volatile suspended solids (VSS) were analyzed for all processes (1-4) at different digestion times (day 0, 5, 10, 15, 20 and 30). Samples were collected for analysis by transferring the digested sludge from the bottles into a beaker. Upon collecting the samples, the digested sludge was returned into the bottles for further digestion and anaerobic conditions were maintained by sparging nitrogen.

2.4 Dewaterability

Fenton pre-treatment of sludge enhances its dewaterability (Neyens and Baeyens, 2003; Zhen et al., 2014). Sludge dewatering requires higher energy; therefore, dewaterability determination of the pre-treated anaerobic digested sludge was necessary for evaluating the energy balance and GHG emissions. Capillary-suction-time (CST) was used to measure the dewaterability. The CST was determined by using a CST instrument (Triton electronics, model 304 M CST, Dunmow, Essex) with 10-mm diameter (Electronics, 1998; Scholz, 2005).

2.5 Sludge disposal

Land application of dewatered sludge digestate was considered in this study (Fig. 1). In Quebec, more than 80% of the farmers or agricultural lands are located no more than 50 km away from the industries (Gassara et al., 2011). Therefore, in this study, the same distance between the WWTPs and the land application site was adopted. To evaluate the energy balance, it was considered that dewatered sludge was transported using 3-axle semi-trailers vehicles, which consumed 35 L of diesel/100 km (Gassara et al., 2011). GHG emissions values corresponding to diesel use were equivalent to 2730 g CO_2/L of diesel, 0.12 g CH_4/L of diesel, and 0.08 g N_2O/L of diesel (Gassara, 2011, 1178-1185). Further, the energy required during the land application of TDS was set at 351.68 kWh/Mg of TDS (Wang et al., 2008). The CO_2, CH_4, and N_2O emissions due to the land application of digestate were evaluated based on -0.25 Mg CO_2/Mg of dry solids (negative sign indicate reduction of GHG emissions), 0.07 Mg CO_2 equivalent/Mg of TDS, and 0.03 Mg CO_2 equivalent/Mg of TDS, respectively (Brown et al., 2010).

2.6 Energy balance

The energy balance was evaluated for Process 1 and 2. For Process 3 and 4, the energy balance was evaluated for Stage 1 (AD of the control and Fenton pre-treated sludge) and Stage 2 (the digestate generated from Process 1 and 2 after 30 days was further Fenton pre-treated and digested for another 30 days). The parameters that were used for evaluating the energy balance are described below.

Total energy input = ∑energy containing in the chemicals, fuels, and electricity, used in the process for Fenton pre-treatment, AD, dewatering, transportation and land application (1)

Energy output = energy obtained from the methane produced.

The energy from the methane was recovered by using cogeneration unit (combined heat and power).

Net energy = energy output-energy input (2)

Energy ratio = energy output/energy input (3)

For computing the energy balance, wastewater treatment plant having treatment capacity of 47000 m^3 of wastewater per day was considered (corresponding to Bonnybrook WWTP, Calgary, Canada). The sludge production rate during secondary wastewater treatment was considered as 0.225×10^{-3} Mg of TDS/m^3 of treated wastewater (Ghazy et al., 2011; Ghazy et al., 2009). Thus the quantity of secondary sludge generated per day was 40 Mg. The energy embedded in the hydrogen peroxide was set at 7.7 kWh/kg of H_2O_2 (Munter 2001) and in Fe^{2+} 6.94 kWh/kg of Fe^{2+} (Hammond and Jones, 2008) was considered in evaluating the energy input during Fenton pre-treatment.

2.7 GHG emissions

The energy required for Fenton pre-treatment, AD, dewatering, transportation and land application was generated from the fossil fuels, contributing to the GHG emissions. The GHG emissions in various process steps (Fig. 1) corresponding to energy utilization were computed using national emission intensity coefficient 0.53 kg CO_2 equivalent/kWh (developed by Environment Canada study based on the Resources for the Future (RFF) model). During AD, the biomass was biodegraded to CO_2 and CH_4. The methane combustion generated CO_2 (Eq. 4). Land application (forest land) of sewage sludge also generated GHG emissions. Land application of sludge refers to the spreading of sludge on or just below the soil surface. Brown et al. (2010) provided factors for determining the potential GHG emissions for AD followed by land application of sludge. The CO_2, CH_4, and N_2O emissions from the land application of digestate were estimated using these factors, namely -0.25 Mg CO_2 equivalent per Mg of TDS (i.e., carbon sequestration due to the land application of sludge), 0.07 Mg CO_2 equivalent per Mg of TDS, and 0.03 Mg CO_2 equivalent per Mg of TDS, respectively. Carbon dioxide emissions generated from biological pathways were considered as biogenic emissions. Therefore, CO_2 emissions during AD were not taken into account in national protocols, as they are considered (by convention) “carbon neutral” (global warming potential equal to zero) (Pradel and Reverdy, 2012).

$CH_4 + 2O_2 \text{ ----> } CO_2 + 2H_2O + \text{energy}$ (4)

2.8 Analytical methods

The analyses of TS, VS, SS, VSS, pH, soluble chemical oxygen demand (SCOD), and total chemical oxygen demand (TCOD) were carried out for Process 1-4, following the standard methods (APHA, 2006). The biogas produced during the AD was collected and analyzed using Gas chromatograph (Shimadzu GC 14A) as per the procedure given in the Cui and Jahng (2006). The biogas volume was measured based on the water displacement method. The energy recovered from the methane was evaluated by considering the heating value of methane of 35.8 MJ/m^3 CH_4 (Tervahauta et al., 2014). All the data are presented in Table 1 and Fig. 3 is representative of all samples measured in triplicates. The percentage error of data presented in Fig. 3 is less than 5%.

3. RESULTS AND DISCUSSION

3.1 Solubilisation of SS and Fenton pre-treated SS and anaerobic digestate (generated from process 1 and 2)

The characteristics of secondary sludge (control, Process 1), Fenton pre-treated sludge (Process 2), digestate generated from Process 1, digestate produced from Process 2 and Fenton pre-treated of the digestate (Process 3 and 4) are presented in Table 1. The efficiency of Fenton pre-treatment was assessed in terms of SS, VSS, and organic matter (SCOD) solubilization (Mohapatra et al., 2011). From the results (Table 1) it is clear that solubilization of SS, VSS and SCOD was improved by Fenton pre-treatment. The suspended solids of raw sludge were decreased from 26.98 g SS/L to 21.27 g SS/L (21% solubilization), and VSS was decreased from 19.31 g VSS/L to 14.46 g VSS/L (25% solubilization). Moreover, the SCOD of the raw sludge increased from 0.82 g/L to 7.8 g/L. Similar trend was observed by Dewil et al. (2007), i.e., with Fenton pre-treatment (50 g H_2O_2/kg DS) the SCOD increased from 0.42 to 2.5 g/L. Sludge yielded a considerable release of dissolved solids and organic matter in the liquid phase (three to four folds of the concentration in the control) by addition of 0.037 g H_2O_2/ g Fe^{2+}/100 mL (Neyens et al., 2002). The increase of SCOD was due to the SS and VSS solubilization during the Fenton pre-treatment. Further, based on these results, it is clear that digestate (generated from Process 1 and 2) percentage solubilization of the SS and VSS was lower compared to the secondary sludge solubilization (raw sludge used in Process 1). The SS of the digestate (control) was reduced from 25.66 g SS/L to 23.34 g SS/L (9% solubilization) and VSS solubilization was only 12%. For Fenton pre-treated digestate (generated from Process 2), the solubilization of SS was 8% only. A decrease in the solids solubilization was expected, since most of the biodegradable solids were solubilized and degraded during AD.

3.2 Anaerobic digestion

The AD efficiency was evaluated based on TS, VS, SS, and VSS solids degradation, which was assessed on the 5th, 10th, 15th, 20th, and 30th day during AD and the results are summarized in Fig. 3. From Fig. 3b, it is clear that the solids degradation was much faster for the Fenton pre-treated sludge. At solids retention time (SRT) of 5 days, the VS solids percentage degradation in the control (Fig. 3a) was 9.74%, compared to 14.73% for Fenton pre-treated sludge (Fig. 3b). The overall total solids degradation after 30 days increased by 3% for Fenton pre-treated sludge compared to the control. Therefore, it is clear that Fenton pre-treatment enhances solids degradation and reduces retention time. However, energy balance computations still need to be carried out to determine the solids retention time at which AD can be energetically beneficial, as discussed later in this manuscript.

The digestate of the control and Fenton pre-treated sludge was further subjected to Fenton pre-treatment and AD (Fig. 1) (Process 3 and 4). The solids degradation (TS, VS, SS, and VSS) on the 5th, 10th, 15th, 20th, and 30th day during AD (of Stage 2, as described in Fig. 1) is represented in Fig. 3c and 3d. As can be seen, the Fenton pre-treated digestate generated from Process 1 was more degradable compared to Fenton pre-treatment of the digestate generated from Process 2. The percentage total solids degradation (after 30 days of HRT) for Process 4 (Fig. 3c) was 28.25%, while 19.32% was obtained for Process 3. The biodegradable solids are degraded during Stage 1; therefore, during Stage 2, the solids degradation was not high for Process 3 and 4. After evaluating single- and two-stage digestion of the Fenton pre-treated sludge, Erden and Filibeli (2010) concluded that, in the first stage, solids reduction in the Fenton pre-treated sludge was twice as high as that in the control. However, during the second stage, control digestion improved (Erden and Filibeli, 2010).

3.3 Methane production during anaerobic digestion

The methane percentage obtained from the GC analysis, for the control and Fenton pre-treated sludge, was 56.6 (±0.23)% and 58.6 (±0.38)%, respectively. The increase in the methane percentage after Fenton pre-treatment was not substantial. Similarly, the methane percentage for Process 3 and 4 (of Stage 2 AD, as described in Fig. 1) was 52.4 (±0.15)% and 52.8 (±0.13)%, respectively. The cumulative methane production during AD for four treatment processes is presented in Fig. 4. Comparing control and Fenton pre-treated sludge, it is evident that the cumulative methane production was higher in the latter (Process 2). More specifically, at 30 days HRT, the cumulative methane volume for control was 4.8×10^{-3} m^3 at an average production rate of 0.430 m^3 CH_4/kg VS destroyed, whereas for Fenton pre-treated sludge, the cumulative methane volume was 5.6×10^{-3} m^3 at an average production rate of 0.496 m^3 CH_4/kg VS destroyed. Thus, Fenton pre-treatment enhanced methane production by 15% compared to the raw sludge digestion. These results are in line with those reported by Erden and Filibeli (2011), where 19.4% higher methane production was obtained compared to raw sludge. The increase in the SCOD increases the methane production (Erden and Filibeli, 2011). Erden and Filibeli (2010) concluded that the specific methane production increased during the first 20 days of digestion in the digester containing Fenton pre-treated sludge. During Fenton pre-treatment, cell lysis initially occurs and releases extra cellular polymeric substance (EPS), which is further broken down into the fractions (proteins, carbohydrates, lipids, etc.). These proteins are degraded during the operation time in the digesters and produce biogas. For the Fenton pre-treated sludge (Process 2), the methane production for FPT was higher at all retention times compared to the control (Process 1) (Fig. 4).

During Stage 2 AD (Fig. 1), higher methane production was observed for Process 4 compared to Process 3 (Fig. 4). For Process 3, during Stage 1, FPT has solubilized the SS and has enhanced the methane production (due to high solids degradation, Fig. 3b) during AD. Furthermore, during Stage 2, the solids that are not easily biodegraded were subjected to FPT, resulting in solubilization and methane production (due to biodegradation of solids, as shown in Fig. 3c). On the other hand, during Stage 2 of Process 4, solids were subjected to AD and the methane production was not high (due to low solids degradation, see Fig. 3a). The solids that are not biodegraded during AD (Stage 1, for 30 days) were subjected to FPT, resulting in solids solubilization and increased methane production due to biodegradation of solids in Stage 2 of AD (Process 4). The cumulative methane volume produced during Stage 2 AD of Process 4 at 30 days retention time was 3.57×10^{-3} m^3 at an average production rate of 0.574 m^3 CH_4/kg VS destroyed. In contrast, the cumulative methane volume produced during Stage 2 AD of Process 3 at 30 days retention time was 2.48 × 10^{-3} m^3 at an average production rate of 0.462 m^3 CH_4/kg VS destroyed. Therefore, from the results, it is clear that Fenton pre-treatment enhances methane production; moreover, it enhances the solids degradation of the digestate as well as the corresponding methane production. The efficiency of four treatment processes in generating methane followed the Process 3 > Process 4 > Process 2 > Process 1 pattern. However, in terms of the m^3 CH_4/kg VS destroyed, Process 3 > Process 2 > Process 4 > Process 1 was noted.

3.4 Energy balance of the different process

Energy balance of Process 1 and 2 was evaluated by assuming 40 Mg of TDS per day to be treated during AD process. The energy input for AD, Fenton pre-treatment, dewatering the digested solids, transporting the dewatered solids from the WWTP to the land application site and during land application was calculated. The energy output from the methane was calculated based on the energy value given in section 2.8. The net energy computed for Process 1 and 2 is presented in Table 2. The energy balance of Stage 1 of Process 3 and 4 was evaluated by assuming 40 Mg of TDS, while, for Stage 2, the solids generated after 30 days of digestion (from Process 1 and 2, respectively) were considered.

The energy input for the AD was higher for the control sludge compared to the pre-treated sludge, since the sludge temperature after Fenton pre-treatment increased from 12 (±2)°C to 25 (±3)°C. For the control, the energy input for increasing the sludge temperature to that required for digestion was 893 kWh/Mg of TDS, while it was 378 kWh/Mg of TDS for the Fenton pre-treated sludge. The energy required for dewatering, transportation and land application was not reduced for the Fenton pre-treated sludge (Process 2) as compared to the control (Process 1) (Table 2). For the control (Process 1), the total VS solids mass was 28.96 Mg (and 11.04 Mg inert solids) and, during AD, 14.9 Mg of VS were digested. On the other hand, for the Fenton pre-treated sludge, the total VS mass was 27.6 Mg (and 12.4 Mg inert solids) and, during AD, 14.56 Mg of VS were digested. Therefore, the amount of solids that remained after AD digestion for the control and Fenton pre-treated sludge was measured at 25.1 Mg and 25.44 Mg, respectively. While the solids degradation was higher in Process 2, the quantity of the digestate produced was high (due to the high percentage of inert solids) compared to the control. Furthermore, the energy input (Table 2) for dewatering, transportation and land application was further reduced in Process 3 and 4 due to the lower digestate mass. The quantity of digestate generated from Process 1 was measured at 25.1 Mg of TDS (i.e., out of 40 Mg of TDS 51.46% VS was degraded during AD), and the digestate generated from Process 4 was measured at 19.99 Mg of TDS (i.e., out of 25.1 Mg of TDS, 35% VS was degraded). Therefore, the energy required for dewatering the solids generated from Process 3 and 4 was lower than that required for Process 1 and 2.

With Fenton pre-treatment (for Process 2), at 30 days retention time, the net energy increased, i.e., the net for the control (Process 1) was 91 kWh/Mg of TDS and was 285 kWh/Mg of TDS for Process 2. The net energy increased 3.1 times for Process 2 compared to Process 1. Therefore, these results demonstrated that Fenton pre-treatment enhanced the AD efficiency and it was energetically beneficial. In addition, for Process 3 and 4, the net energy increased compared to Process 1. At 30 days retention time, the net energy for Process 3 (i.e., 30 days digestion for Stage 1 and further 30 days for Stage 2) was 182 kWh/Mg of TDS total dry solids, compared to 231 kWh/Mg of TDS for Process 4. The net energy for Process 3 was lower than that obtained in Process 2, since the energy input for Fenton pre-treatment and AD is twice as high (Table 2) compared to that of Process 2. Moreover, the energy recovery for Process 3 (during the two stages) was not equivalent to the energy input. Similarly, for Process 4, the net energy was low compared to Process 2. The maximum net energy was observed in Process 2 (Table 2). Thus, Fenton pre-treatment (i.e., Process 2) will be energetically beneficial compared to two-step Fenton pre-treatment (Process 3). As a two-stage process, Process 4 is more beneficial compared to the control.

The energy ratio was higher for the Fenton pre-treated sludge (Process 2) than the control (Process 1). Evaluation of the energy ratio at different solids retention times revealed that Process 2 is more beneficial compared to Process 1 (Fig. 5). For example, at 20 days digestion, for Process 1, the energy ratio was 0.78, while it was 0.96 for Process 2. More specifically, the total energy input for Process 1 was 1308 kWh/Mg of TDS and the energy recovery was 1011 kWh/Mg of TDS. In contrast, for Process 2, the total energy input was 1291 kWh/Mg of TDS and the energy recovery was 1238 kWh/Mg of TDS. The energy ratio of Process 3 and 4 was high compared to Process 1. For example, in Process 3, at 15 days digestion (i.e., 30 days digestion during Stage 1 + 15 days digestion for Stage 2), the energy ratio was 0.73, and was 0.69 for Process 4. The increased energy ratio was due to higher solids degradation and methane production. More specifically, for Process 3, the solids have degraded from 40 Mg of TDS to 15.03 Mg of TDS during the two-stage digestion. Thus, in order for the energy ratio to exceed one and the net energy to be positive, a minimum of 30 days solids retention time is required.

The following order was observed with respect to increasing energy ratio: Process 2 > Process 4 > Process 3 > Process 1.

3.5 Dewaterbility of the sludge (control, FPT, Fenton treated digestate)

Dewaterability, measured in terms of CST, was 1006 (±12) s and 120 (±15) s, for the control and Fenton pre-treated, respectively. Zhen et al. (2014) observed a 97.7% CST reduction with Fenton pre-treatment (H_2O_2 178 mg/g of VSS and Fe^{2+} 211 mg/g of VSS). The release of sludge-bound water due to the disintegration of sludge flocs, cell lysis and breakdown of the EPS during Fenton pre-treatment has reduced the CST (Zhen et al., 2014; Erden and Filibeli 2010). It is clear that the Fenton pre-treatment process reduces the CST and hence increases the sludge dewaterability. The dewaterability of anaerobic digestate after 30 days digestion for the control and the Fenton pre-treated sludge was 820 (±19) s and 106 (±8) s, respectively. AD of sludge (both control and Fenton pretreated sludge) further improved sludge dewaterability (reduced the CST). The increase in sludge dewaterability after AD was due to the solids reduction (% VS degradation for the control after 30 days digestion was 51.46%). The CST of the Fenton pre-treated digestate generated from Process 1 and 2 was 145 (±12) s and 87 (±11) s, respectively. The CST of the digestate generated after AD in Process 1 and 2 was further reduced to 138 (±6) s and 80 (±8) s, respectively. Fenton pre-treatment of digestate has reduced the CST value as well as increased dewaterability. The increase in dewaterability (or reduction in the CST value) after the AD process will reduce the energy requirement during dewatering. In the calculation performed here, increase in dewaterability was not considered, because the CST projections for centrifugation are not truly representative. The energy reduction resulting from centrifuging the digestate after AD thus needs to be established.

3.6 GHG emissions for the control and Fenton treated sludge

The GHG emissions corresponding to energy utilization for Fenton pre-treatment, AD, dewatering, transportation and land application was evaluated for four processes considered in this study (Fig. 1) and the results are summarized in Table 3. With Fenton pre-treatment (Process 2), GHG emissions were lower compared to the control (Process 1). The GHG emissions for the control (Process 1) and for Fenton pre-treated sludge (Process 2) were 0.192 Mg CO_2 equivalent/Mg of TDS and 0.128 Mg CO_2 equivalent/Mg TDS, respectively. The energy recovery and land application are the factors responsible for the reduction in GHG emissions

(Table 3) in Process 2. For Process 3 and 4, the GHG emissions corresponding to methane combustion are high compared to Process 1 and 2 (i.e., for Process 1 and Process 3, the GHG emissions corresponding to methane combustion were measured at 0.314 Mg CO_2 equivalent/Mg TDS and 0.513 Mg CO_2 equivalent/Mg TDS, respectively). GHG emissions will be lower than those computed in this study due to land application of sludge, if factors such as fertilizer value of sludge, carbon sequestration in soil, additional water holding capacity of soil, improved tillage and workability of soils, and photosynthetic absorption of CO_2 by crops, are considered (Pilli et al., 2014). However, these factors were not measured in this study, as the fertilizer value of the sludge was not determined. Moreover, the energy output (generated from methane) was greater than the energy input, which resulted in a reduction in the GHG emissions pertaining to Process 2 compared to Process 1. The increased energy input (during Stage 2) in Process 3 and 4 resulted in increased GHG emissions compared to Process 2. The minimum GHG emission levels were observed in Process 2. Thus, in terms of reducing GHG emissions, the following order was observed: Process 2 > Process 4 > Process 3 > Process 1.

4. CONCLUSION

In general, it can be concluded that Fenton pre-treatment of sludge was favorable, based on the energy balance and GHG emissions. The sludge solids solubilization and solids degradation was enhanced by Fenton pre-treatment. Cumulative methane production increased with Fenton pre-treatment and the methane production rate for the Fenton pre-treated sludge was 0.496 m^3/kg VS destroyed. The energy balance showed that the net energy was increased with Fenton pre-treatment (Process 2). The energy ratio for Process 2 was greater than that of Process 1, 3 and 4. At different retention times, the energy ratio for Process 2 was high compared to Process 1. AD had enhanced the dewaterability of the control and Fenton pre-treated sludge, while land application of Fenton pre-treated sludge (process 2) reduced GHG emissions. Minimum GHG emissions of 128 kg CO_2 equivalent/Mg of TDS were achieved in Process 2. Based on the energy balance and GHG emissions, Process 2 is favorable and further pilot studies are required to establish the most optimal process characteristics. In addition, further studies on Fenton pre-treatment of the digestate generated at different digestion times (e.g., 5, 10, 15 and 20 days) are also required to establish the lower digestion time for the two-stage process.

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Table 1. Sludge characteristics before and after Fenton pre-treatment

Description	Control	FPT	Digestate		FPT of the digestate	
			Control (A)	FPT (B)	Generated from (A)	Generated from (B)
TS (g/L)	30.05 (±0.18)	30.86 (±0.20)	31.04 (±0.15)	30.81 (±0.25)	30.76 (±0.13)	30.64 (±0.28)
VS (g/L)	21.76 (±0.14)	21.21 (±0.11)	18.94 (±0.16)	18.79 (±0.12)	17.21 (±0.10)	18.38 (±0.13)
SS (g/L)	26.98 (±0.28)	21.27 (±0.23)	25.66 (±0.26)	27.88 (±0.21)	23.34 (±0.29)	25.53 (±0.31)
VSS (g/L)	19.31 (±0.24)	14.46 (±0.22)	17.85 (±0.27)	17.44 (±0.26)	15.77 (±0.28)	15.65 (±0.20)
TCOD(g/L)	33.84 (±0.31)	33.02 (±0.27)	33.83 (±0.23)	34.05 (±0.33)	33.65 (±0.28)	31.33 (±0.30)
SCOD (g/L)	0.82 (±0.08)	7.80 (±0.11)	1.50 (±0.07)	1.80 (±0.33)	6.54 (±0.25)	7.43 (±0.26

Note: Control is without pre-treatment; FPT is Fenton pre-treatment

Table 2. Energy balance for the different process

Description	Process-1	Process-2	Process-3	Process-4
	Energy (kWh/Mg of TDS)			
Fenton treatment	0	491	982*	491
AD				
i. Energy required to increase the temperature of sludge to AD temperature	893	378	756*	1271*
ii. Heat loss	50	49	98*	99*
iii. Total energy input during AD (i+ii)	943	427	854*	1370*
Dewatering	63.6	64.5	39.5	50.7
Transportation	43.7	44.3	27.2	34.8
Land application	221	224	137	175.8
(a) Total energy input	1271	1250	2040	2123
(b) Energy output (heat (55%) and power (30%) recovered)	1362	1535	2222	2353
Net energy = (**b-a**)	91	285	182	231
Energy ratio Energy input/energy output	1.07	1.23	1.08	1.11

Note: negative sing indicates increase energy input; Mg is mega gram; TDS is total dry solids; AD: anaerobic digestion; * indicates that for process 3 and 4, stage 1 and stage 2 AD was combined during computations.

Table 3. GHG emissions evaluated for different process

Description	GHG emissions (kg CO_2/Mg of TDS)			
	Process-1	**Process-2**	**Process-3**	**Process-4**
Net GHG emission due to energy input and out put	-48.0	-150.7	-96.5	-122.2
GHG emissions during AD (biogenic emissions)	304.8	250.6	392.5	511.4
GHG emissions during CH_4 combustion	314.6	354.5	513.3	543.6
GHG emissions during transportation	19.3	19.3	7.5	9.6
GHG emissions during land application	-94	-95	-58	-75
Total GHG emissions without considering biogenic CO_2 emissions	192	128	366	356

Note: negative sign indicates reduction in GHG emissions; Mg is mega gram; TDS is total dry solids

Table 4. GHG emissions evaluated for different process

Description	**GHG emissions (kg CO_2 equivalent/Mg of TDS)**			
	Process-1	**Process-2**	**Process-3**	**Process-4**
Net GHG emission due to energy input and out put	-48.0	-150.7	-96.5	-122.2
GHG emissions during AD (biogenic emissions)	304.8	250.6	392.5	511.4
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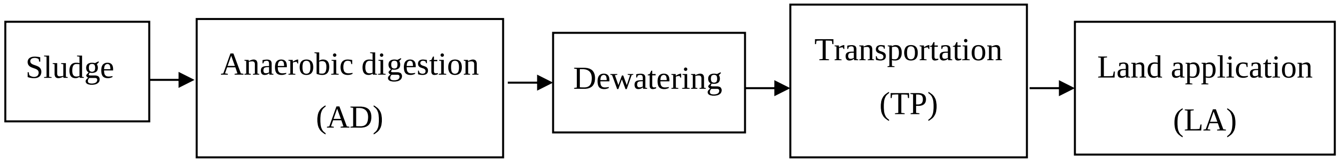
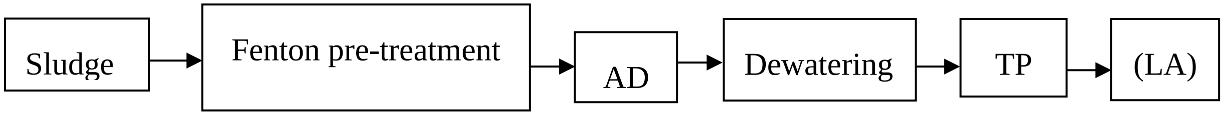
GHG emissions during transportation	19.3	19.3	7.5	9.6
GHG emissions during land application	-94	-95	-58	-75
Total GHG emissions without considering biogenic CO_2 emissions	192	128	366	356

Note: negative sign indicates reduction in GHG emissions; Mg is mega gram; TDS is total dry solids



(i) Process-1



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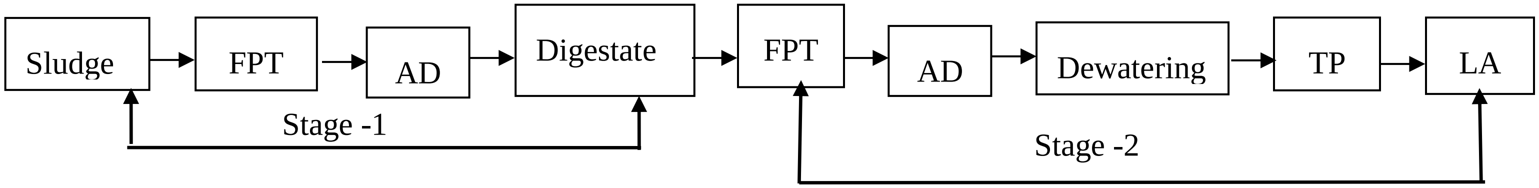
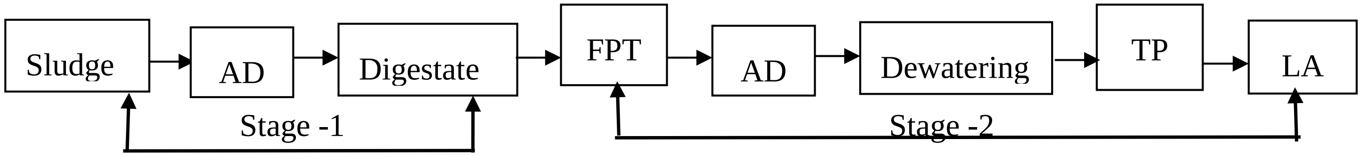


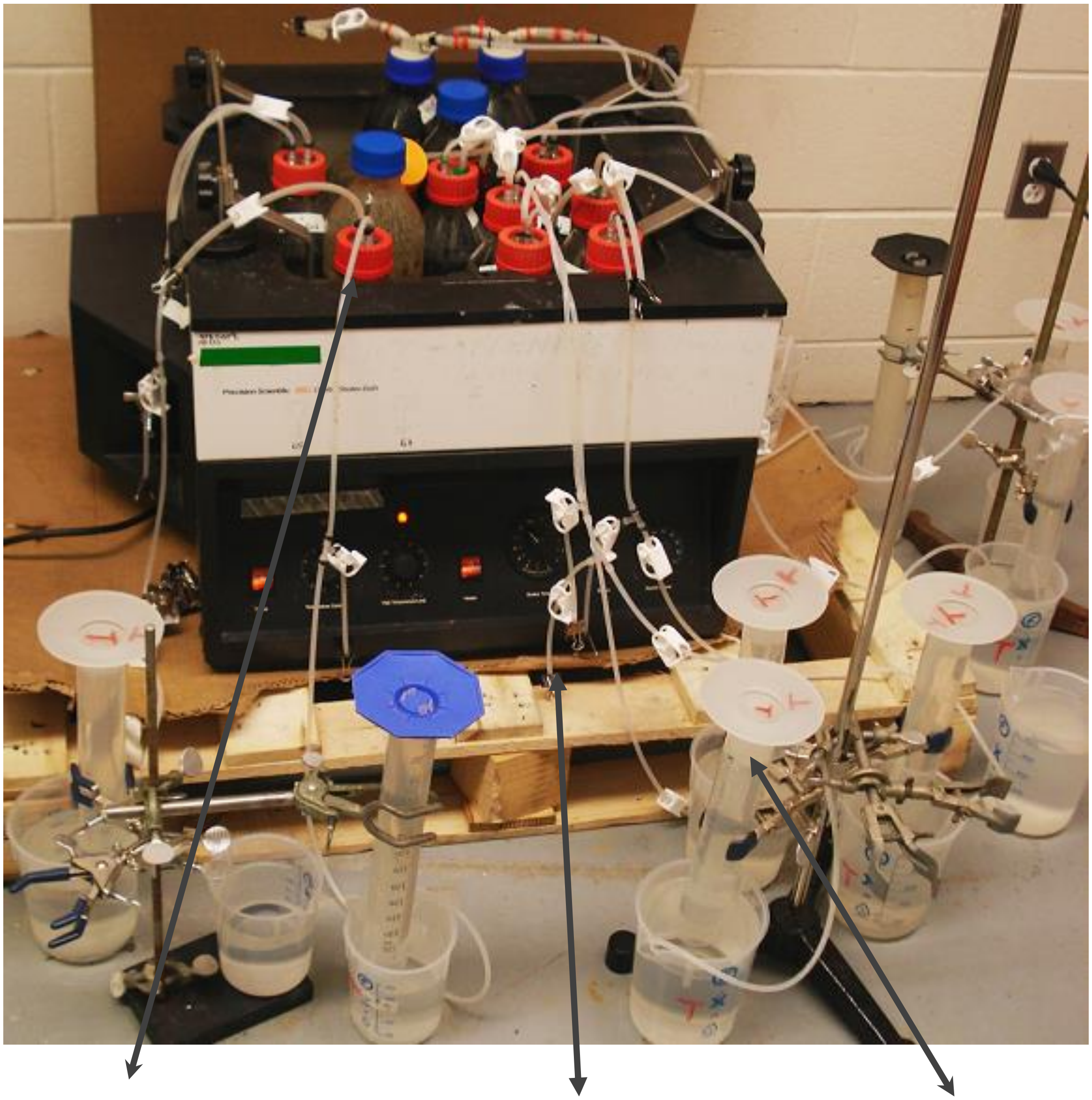
(iii) Process-3



(iv) Process-4

Figure 1. Four process configurations considered in this study for evaluting energy balance and GHGs

Note : AD: anaerobic digestion; FPT: Fenton pre-treatment; TP: transportation; LA: land application



Biogas collection

Water displacement

Sceptic glass bottles

Figure 2. Anaerobic digestion setup

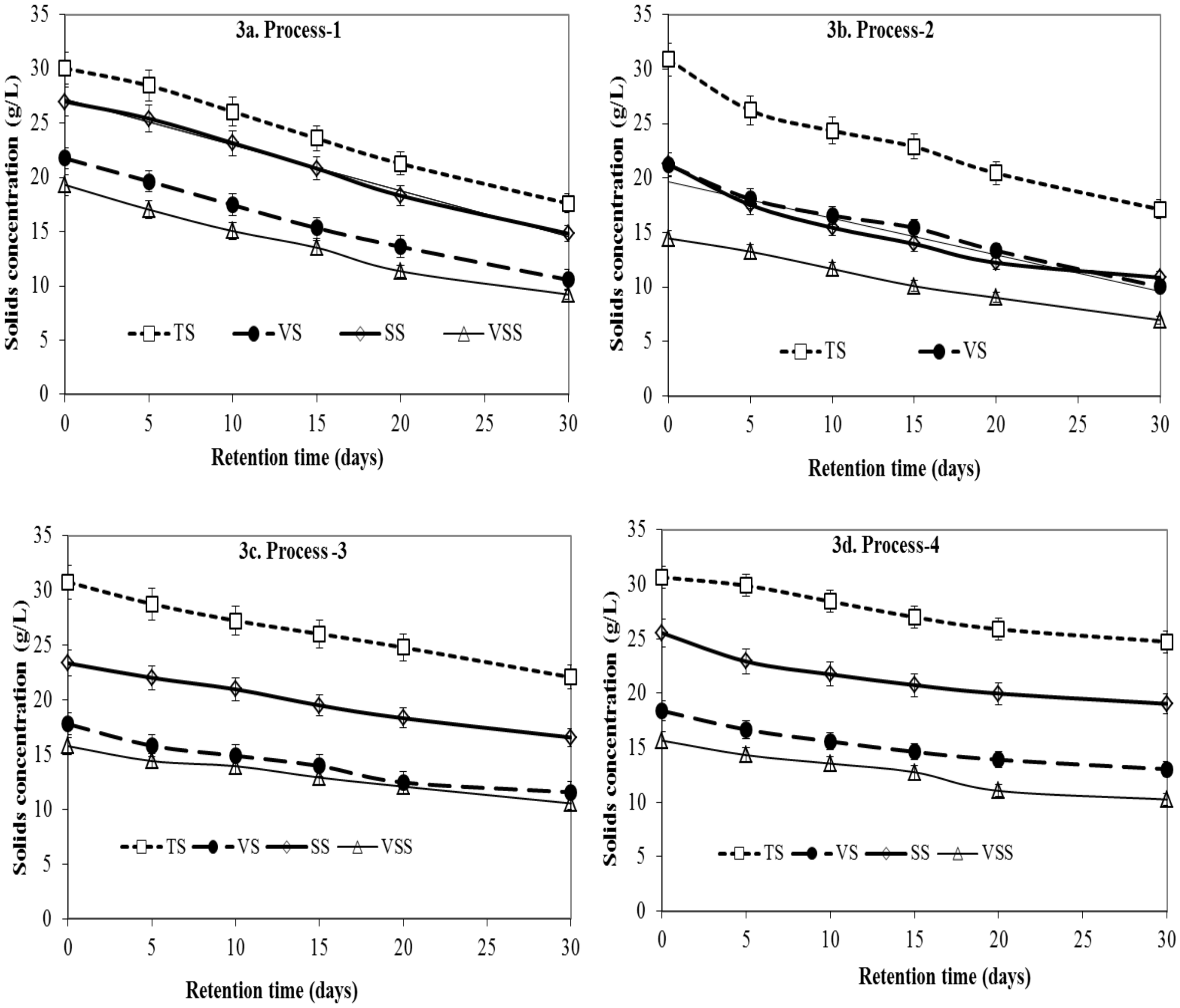


Figure 3. Solids degradation during anaerobic digestion

Note: Fig. 3a is the solids degradation of process 1; Fig. 3b is the solids degradation of process 2; Fig. 3c is the solids degradation for second stage of process 3; Fig. 3d is the solids degradation for second stage of process

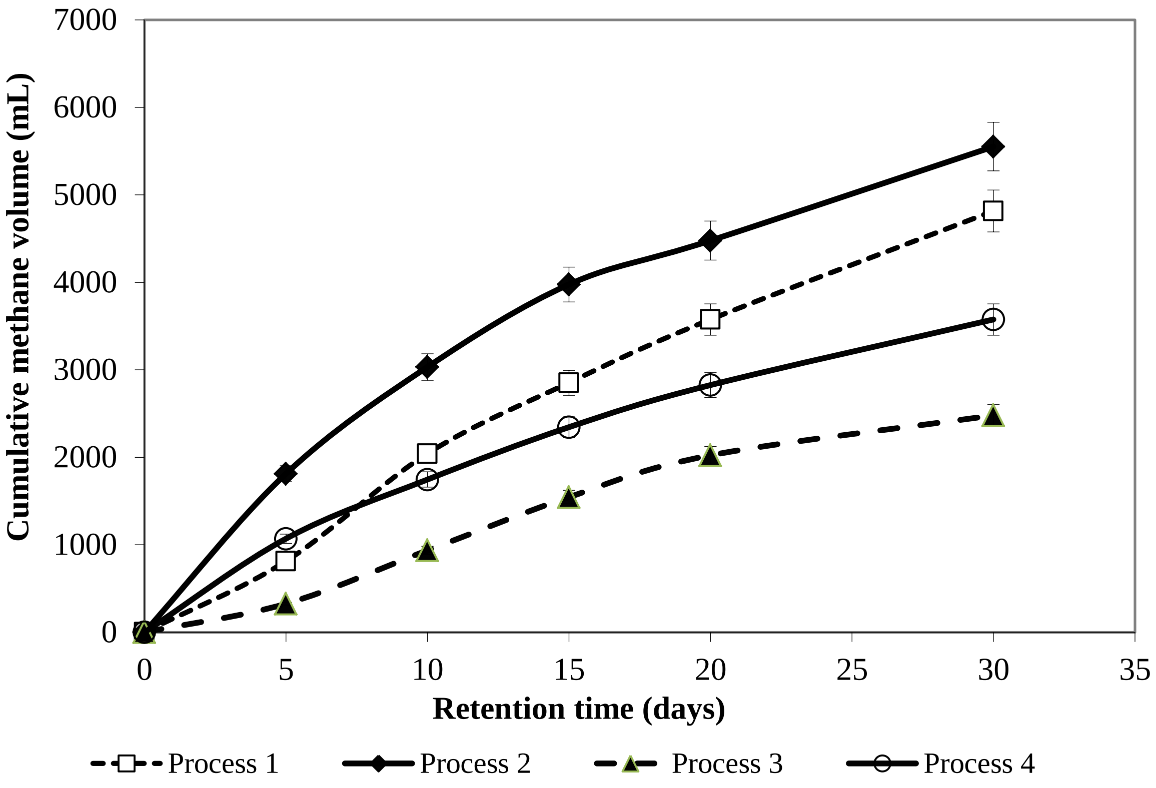


Figure 4. Cumulative methane production during anaerobic digestion

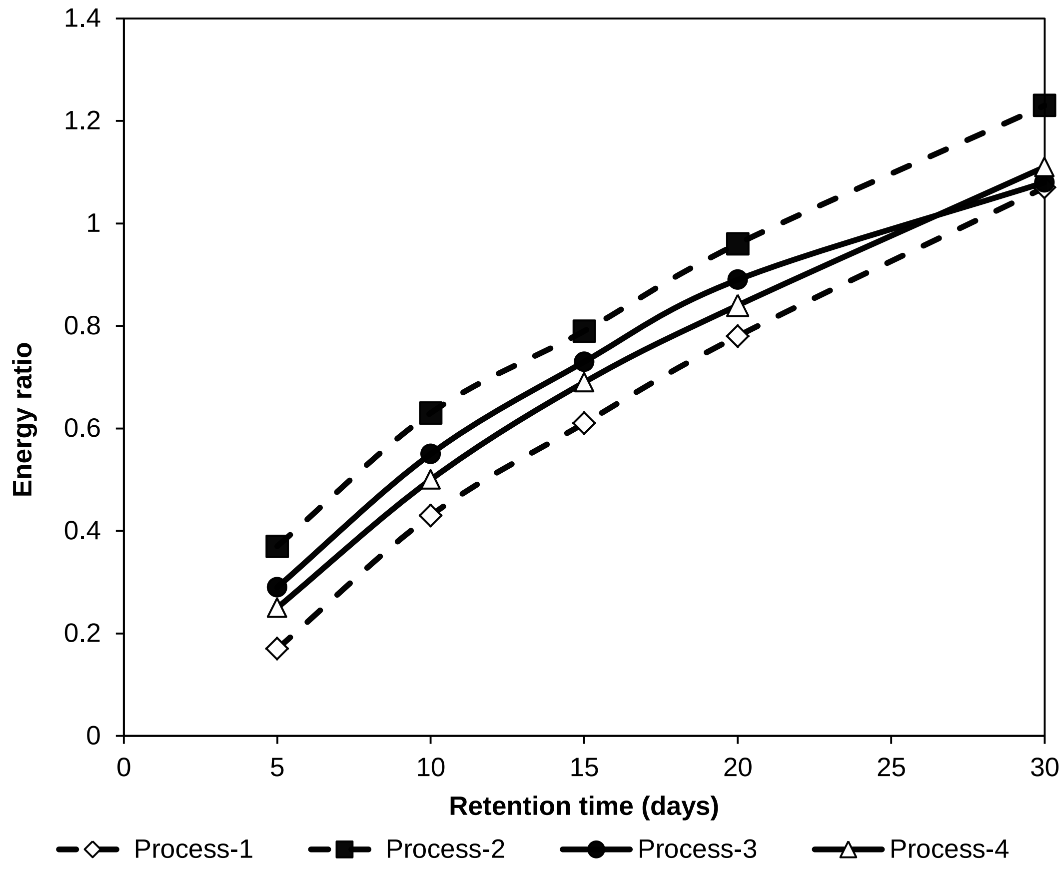


Figure 5. Energy ratio at different solids concentrations

Note: for process 3 and 4, stage 1 and stage 2 are included

CHAPITRE V

LAND APPLCIATION OF THE SLUDGE

METHODOLOGY FOR THE QUANTIFICATION OF GREENHOUSE GAS EMISSIONS DURING LAND APPLICATION OF SEWAGE SLUDGE

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RÉSUMÉ

L'épandage des boues d'épuration améliore les propriétés physiques, chimiques et biologiques des sols, ce qui minimise l'application d'engrais minéraux et réduit l'entretien du sol. Dans ce travail, différentes méthodes décrites dans la littérature permettant d’estimer l’émission des gaz à effet de serre (GES) liées à l'épandage des boues d'épuration sont résumées et leurs inconvénients sont présentés. En outre, une meilleure méthodologie permettant d’évaluer les émissions de GES liées à l'application des boues d'épuration a été proposée. De plus, en utilisant la méthodologie proposée, les émissions de GES lors de l'épandage de boues d'épuration à faible, haute et moyenne concentrations en nutriments (carbone, azote et phosphore) ont été évaluées. Les résultats ont révélé que les émissions de GES sont sensiblement diminuées lorsque les boues d'épuration contenant une concentration élevées en éléments nutritifs sont épandues. La méthode proposée a été comparée avec celles présentées dans la littérature.

Mots-clés: boues d'épuration; émissions de gaz à effet de serre; épandage; digestion anaérobie; digestat; concentration en éléments nutritifs.

ABSTRACT

Land application of sewage sludge improves soil physical, chemical and biological properties, minimizes the mineral fertilizer application and reduces maintenance of soil. In this work, various methods to estimate greenhouse gas (GHG) emissions due to land application of sewage sludge described in the literature were summarized and their limitations were presented. Moreover, an improved methodology to evaluate GHG emissions due to the land application of sewage sludge was proposed. Further, based on the proposed methodology, GHG emissions due to land application of sewage sludge at lower, higher and average concentrations of nutrients (carbon, nitrogen and phosphorus) were assessed. The results revealed that GHG emissions substantially decreased when higher nutrients containing sewage sludge were applied to land. For methodologies presented in the literature, GHG emissions or reductions due to land application did not change with nutrients concentrations of sewage sludge. However, based on the proposed methodology GHG emissions or reductions varied according to sludge nutrients concentrations.

Keywords: sewage sludge; greenhouse gas emissions; land application; anaerobic digestion; digestate; nutrient concentration.

1. INTRODUCTION

The reduction of greenhouse gas (GHG) emissions is the prime focus and goal of several researchers, scientists, industrialists, and municipalities. The radiatively active trace gases in the Earth's atmosphere are called greenhouse gases (GHGs), which principally include water vapor, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3) (Gohar and Shine, 2007). The CO_2 is used as the basis to calculate the level of relative contribution to global warming potential of each gas. Based on per molecule, the global warming potential of CH_4 and N_2O for 100 years is about 28 and 265 times, respectively, more powerful than CO_2 (Stocker et al., 2013). According to the Intergovernmental Panel on Climate Change (IPCC), population growth, deforestation, factory farming, biomass degradation (from the wastewater treatment plants and during sludge management) and the widespread use of fossil fuels create an excess of GHG emissions. These GHGs while in the atmosphere absorb radiations emitted to ground and thus contribute to the global warming and climate change. Alarming level of global warming and climate change arising from unprecedented release of GHGs has made it essential to quantify GHG emissions from every source.

The sewage sludge is an unavoidable byproduct collected from different stages of the wastewater treatment process. In general, specific sludge production varies widely from 35 to 85 g dry solids per population equivalent per day during the wastewater treatment (Ginestet and Camacho, 2007). From the existing wastewater treatment plants (WWTPs) the annual sludge production in USA and Canada is 6 515 $x10^3$ and 550 $x10^3$ Mg dry solids per year, respectively (LeBlanc et al., 2009). In Europe, during the last decade the sewage sludge production has increased significantly (Heres et al., 2005; Fytili and Zabaniotou, 2008). In china from 2005 to 2010 sludge production steadily rose from 11 $x10^6$ to 21 $x10^6$ Mg per year (sludge with 80.0% water content) (Liu et al., 2013). In Taiwan, the prevalence of the public sewage system could reach to 36.0% of the population by 2014, and the sewage sludge production could reach up to 1040 Mg/day (Wang et al., 2013). The sewage sludge production has increased by 45.0% in France (i.e. 58 $x10^4$ Mg dry solids per year in 2001 to 13 $x10^5$ Mg dry solids per year in 2005) (Pradel and Reverdy, 2012). Moreover, the sewage sludge production is expected to increase in the future due to industrialization, population increase, greater volume of water used, higher levels of wastewater treatment and increased stringent laws for wastewater treatment and disposal.

In general, the common sludge treatment methods are aerobic digestion, anaerobic digestion followed by dewatering, and composting, and the common disposal methods are incineration, landfill, or land application (Figure 1). Sludge disposed by different methods in different countries is given in Table 1. Sludge treatment and disposal contribute to GHG emissions (Pradel and Reverdy, 2012). During sludge treatment, disposal, and/or reuse (as fertilizer, biotransformation), the sewage sludge is metabolized to soluble or gaseous end-products mainly consisting of CO_2, CH_4 and N_2O (depending upon the environmental conditions). These three gases are considered as the principal GHGs emitted during sludge treatment and disposal routes. Sludge management (treatment, disposal and/or reuse) may account for approximately 40.0 % of the total GHG emissions from a wastewater treatment plant (Brown et al., 2010). GHG emissions from sludge treatment in wetlands are 17×10^{-3} Mg CO_2 equivalent/population equivalent and for the untreated sludge are 0.162 Mg CO_2 equivalent/population equivalent (Uggetti et al., 2012). Landfilling of the sewage sludge will contribute GHG emissions of 0.297 Mg CO_2 equivalent/Mg of sludge in Taiwan (Wang et al., 2013). Among the various disposal methods land application of sludge is the most common method in practice around the world (Table 1).

Land application of sewage sludge

Sewage sludge contains a substantial amount of organic matter rich in nutrients such as carbon (C), nitrogen (N), phosphorous (P), and also provides macro nutrients such as potassium and sulphur, and micronutrients such as copper and zinc (Singh and Agrawal, 2008; Wang et al., 2008a; Bettiol and Ghini, 2011;). The N and P content in the sewage sludge reported by various researchers are summarized in Table 2. The concentration of N and P present in the sewage sludge varies depending upon the original effluent composition and the treatment method (Quilbé et al., 2005). An extensive study on the sewage sludge composition (nutrients composition) was conducted by Basta (1995). It was reported that the sewage sludge consists mainly of partially decomposed organic matter (30.0-60.0%) and other significant amount of nutrients required by the plant that include N (0.5-10.0%), P (1.0-6.0%), sulphur (0.5-1.5%), calcium (1.0-20.0%), magnesium (0.3-2.0%) and micronutrients such as iron (0.1-5.0%), copper, manganese, and zinc (< 0.2%), nickel, boron, cobalt, and molybdenum (< 0.05%) (Basta, 1995). The cost effectiveness of the land application is evaluated based on the fertilizing value (nutrient content) of sludge. Therefore, land application of sewage sludge is considered to be the most economical (Champagne, 2007; Laboy-Nieves et al., 2008; Singh and Agrawal, 2008; Lu et al., 2012).

The organic carbon content has been reported in the range of 17.5-25.3% w/w (average 21.4% w/w) of the dry mass for the aerobically digested sludge and in the range of 6.8-28.5% w/w (average of 17.6%) of dry mass for anaerobically digested sludge (Parker and Sommers, 1983). Depending on sludge solids content, the organic form of the N available is around 50.0-90.0% of the total N of sludge (average total nitrogen is 3.9% on a dry basis) (Sommers, 1977). The N components (have been identified as proteinaceous, amino acids, and hexosamines) of sludge are predominantly organic in nature (Epstein, 2002). The P content of sludge has been often closer to half of the N content (Johannesson, 1999). Moreover, the crop's requirement of P is just 1/10-1/5 of the N requirement (Johannesson, 1999).

The land application of the sewage sludge refers to spreading sludge on or just below the soil surface with tilling depth of 15-30 cm (Delgado et al., 2011; Epstein, 2002; Lu et al., 2012; Wang et al., 2008b). Moreover, the land application of the sewage sludge is practiced in many countries for centuries (Jiménez et al., 2010; Singh and Agrawal, 2008). In general, research on land application of the sewage sludge has focused on its effects on plant development (Singh and Agrawal, 2008; Wang et al., 2008b) and also on soil contamination due to heavy metals (Bettiol and Ghini, 2011; Haynes et al., 2009; Wang et al., 2008b). However, very limited studies are available pertaining to GHG emissions due to land application of the sewage sludge.

2. ADVANTAGES AND DISADVANTAGES OF LAND APPLICATION OF SEWAGE SLUDGE

2.1 Advantages

The land application of sewage sludge reduces the need for chemical fertilizers and pesticides, increases the crop production and improves soil structure (i.e. enhancement of workability andlower resistance to ploughing and tilling) (Aggelides and Londra, 2000; Haynes et al., 2009; Singh and Agrawal, 2008; Torri and Lavado, 2008; Wang et al., 2008b). Therefore, fossil fuel (energy) usage in the production of chemical fertilizers and pesticides will be reduced along with corresponding GHG emissions. The fossil fuel (energy) required by the tractors for ploughing, tilling and other activities during irrigation will also be reduced as well as the corresponding GHG emissions. The physical properties of soil such as soil aggregate stability, water holding capacity, porosity and humus content are increased with sewage sludge amendment (Singh and Agrawal, 2008). On the other hand, land application of sewage sludge decreases bulk density and erosion of the soil. With sewage sludge amendments the soil organic carbon, electrical conductance, cation exchange capacity and N and P are increased (Singh and Agrawal, 2008). The land application of sewage sludge has the potential to increase soil carbon stores and gain credits for carbon sequestration (Singh and Agrawal, 2008; Sylvis, 2009). The use of compost on soils results in 8.0% of the compost carbon (this equates to 0.13 Mg CO_2 equivalent/dry Mg wastewater solids) being sequestered for 100 years (Recycled Organics Unit, 2006). A larger mass of carbon sequestration (0.25 Mg CO_2 equivalent/dry Mg wastewater solids) was estimated at biosolids land reclamation sites in British Columbia (Sylvis, 2009). Sewage sludge also modifies the soil's biological properties (Singh and Agrawal, 2008; Torri and Lavado, 2008; Wang et al., 2008b). Biological properties of soil basically govern the dynamics of the microbiotia, which control the soil ecosystem and its functioning, that is, humus formation, organic matter decomposition, nutrient cycling, physical and other functions..

2.2 Disadvantages

The land application of sewage sludge requires relatively less capital, which is generally lower than other sludge management technologies, however, the process can be labour intensive (Shammas and Wang, 2009). The land application of sewage sludge is limited during rainy and snowing weather conditions. Public opposition and odour problems also limit the land application of sewage sludge. The presence of contaminants (metals, etc.) in sludge may also limit the land application. Moreover, the land application of sewage sludge should not affect the groundwater, surface watercourses, wells and other environmentally sensitive features. Contrary to the positive effect of land application of sewage sludge on the microbial activity, there are reports that find a reduction in microbial activity (Baggs, and Rees, 2000; Fernandes et al., 2005a; Fernandes, Bettiol, Cerri, and Camargo, 2005b; Lu et al., 2012). The land application of sewage sludge and its effect on the microbial activity were investigated by researchers by measuring the flux of gases (CO_2, CH_4 and N_2O) at the soil–atmosphere interface (Baggs et al., 2000; De Urzedo et al., 2013; Fernandes et al., 2005a, 2005b; Lu et al., 2012; Ruíz-Valdiviezo et al., 2013). The land application of sewage sludge will provide organic matter and nutrients to the soil, but on the other side the biological processes undergo altercations, and as a consequence, the flux of the gases at the soil–atmosphere interface is also changed.

Sludge land applications increase GHG emissions with increased flux of gases at the soil–atmosphere interface (Baggs et al., 2000; Fernandes et al., 2005a, 2005b; Lu et al., 2012). Emerging contaminants (endocrine-disrupting compounds), antibiotics and heavy metals present in sewage sludge will affect the soil microbial flora, and as a consequence will affect the flux of gases at the soil–atmosphere interface.

3. METHODS IN LITERATURE TO QUANTIFY GHG EMISSIONS DUE TO LAND APPLICATION OF SEWAGE SLUDGE

The estimation methods used by government bodies and researchers to evaluate GHG emissions during the land application of sewage sludge are summarized in Table 3. The methane or nitrous oxide emissions will vary vastly depending upon the types of sludge, prevailing moisture content, the ambient environmental conditions and also on the diurnal temperature variations. These factors are not considered in the IPCC estimation methodology. CO_2 emissions due to land application are considered as biogenic emissions (IPCC, 2007), (since they are generated from biological pathways) and they were not taken into account, due to the fact that they are considered (by convention) ‘carbon neutral’ (global warming potential equal to zero). Indirect CO_2 emissions due to fossil fuel utilization during land application are considered. RTI International has estimated the CO_2 emissions from the land application of sewage sludge by assuming a constant biomass population (dying and decaying biomass equalling new biomass growth). The CO_2 generation rate for the land application will be directly proportional to the carbon application rate to the land treatment unit. This methodology gives an overestimation of CO_2 emission, as it presumes the complete conversion of carbon content of sewage sludge to CO_2.

The biosolids emissions assessment model (BEAM) was developed by SYLVIS environmental for the Canadian Council of Ministers of the Environment to allow municipalities to estimate GHG emissions from biosolids management. Anthropogenic CO_2 emissions are considered for the land application of biosolids, that is, fuel burned for hauling and transporting biosolids to farm fields and during the land application process (e.g. using tractors and spreaders). The fuel used during the land application of biosolids as 3.2 L/Mg dry biosolids applied. CO_2 emissions from land due to biosolids are considered as biogenic sources and they are not included in GHG estimation. In BEAM, CH_4 emissions from land application of biosolids are considered negligible based on the studies by Bal and Scott (2004) and Jones and Skiba (2006). Methane emissions from storage of biosolids before land application are considered in this methodology. The N_2O

emissions from the land application of the biosolids are evaluated as given in Table 3. Reducing the soil maintenance and increasing the water holding capacity will minimize machinery usage and fossil fuels and corresponding GHG emissions. These factors are not considered in estimating CO_2 emissions. Increased microbial activity in air pockets formed in the soil will increase the CH_4 emissions. N to N_2O conversion factors are used in estimating N_2O, which will not present the exact emissions due to the land application of sewage sludge. There will be increased N_2O flux between atmosphere and soil interface due to the land application of sewage sludge, which need to be considered in estimating N_2O emissions.

Several other researchers have evaluated GHG emissions during the life cycle analysis of sewage sludge management (considering land application or agriculture application as sludge disposal option) (Table 3). Lundin, and Zetterlund (2004) have considered P and N presented in sludge replaces mineral fertilizer. Energy savings due to the replacement of mineral N (by sewage sludge) was less than the energy required for the pasteurization, transportation and spreading of sewage sludge. These resulted in higher CO_2 and N_2O emissions due to the land application of sewage sludge. However, it was assumed that CH_4 emissions due to the land application were −0.012 kg/Mg of dry solids without explaining the details. Fernandes et al. (2005a) concluded that there will be increased flux of CO_2 and N_2O gases from the land applied of sewage sludge. On the other hand, some of the N and P present in sewage sludge will be utilized by plants as a source for their development. It is unclear if the land application of sewage sludge corresponds to either GHG emissions or GHG reductions. Moreover, the sewage sludge application will change the physical properties of the soil, which will affect GHG emissions. Therefore, in this study a methodology was developed (by considering possible factors responsible for GHG reductions and GHG emissions) to evaluate precise net GHG emissions due to the land application of sewage sludge.

4. PROPOSED METHODOLOGY FOR THE QUANTIFICATION OF GHG EMISSIONS DUE TO LAND APPLICATION OF SEWAGE SLUDGE

There are many limitations in GHG estimation methods (Table 3). In this proposed methodology, net GHG emissions (GHG reductions-GHG emissions) due to the land application are considered. The land application of sewage sludge reduces GHG emissions due to the following reasons: (i) replacing the synthetic fertilizers, (ii) carbon sequestration in soil, (iii) additional water holding capacity of soil, (iv) improved tillage and workability of soils and (v) photosynthetic absorption of CO_2 by crops. On the other hand, the land application of sewage sludge increases the flux of gases (CO_2, CH_4 and N_2O) at the soil–atmosphere interface. Further, the energy required during the land application of sewage sludge will contribute to GHG emissions. Therefore, the net GHG emissions due to the land application of sewage sludge are evaluated using Equation (1).

Net GHG emissions = (increased flux of gases + GHG emissions corresponding to energy requirement during land application) - sum of GHG reductions (1)

4.1 Reduction of GHG emissions due to replacement of synthetic fertilizers

The type of sludge and the N and P contents on the dry basis were presented in Table 2. The US Department of Agriculture and University of Minnesota have conducted extensive research on the use of sewage sludge from crop production and revealed that land-applied sewage sludge produces high crop yields and high-quality crops similar to commercial fertilizer. Fossil fuels are mainly used during chemical fertilizer production, which is accountable for GHG emissions. During fertilizer application to soil, various fossil fuel-consuming machinery is also used, further contributing to GHG emissions. The land application of sewage sludge will minimize the use of chemical fertilizers and machinery, thereby offseting fossil fuels and thus reducing GHG emissions. The production of 1 kg N synthetic fertilizers produce a total of 5465 g of CO_2 equivalents (Flessa et al., 2002) and 1 kg of P synthetic fertilizer generates 165 g CO_2 equivalents (Wood and Cowie, 2004). The N present in organic fertilizers normally exists in two forms: (i) ammonium- N, which is readily available for plant uptake and (ii) organic-N compounds, which are less available to plants. Therefore, the amount of ammonium-N relative to the total N content will determine the N availability in the organic fertilizer. The N availability also depends upon the moisture content of sludge. In general, the N-nutrient value of organic fertilizers varies in the range of 20.0–50.0% of the available total N content (http://www.northwaymushrooms.com/organic-fertilizers-a-valuablecommodity/). Therefore, N available for the plants was considered as 30.0%. In the case of P, organic fertilizers can generally be considered as 100.0% available (i.e. each kg of P applied in organic fertilizer can replace 1 kg P from chemical fertilizer) (http://www.northwaymushrooms.com/organic-fertilizers-a-valuable-commodity/). The GHG reductions(Mg CO_2 equivalent/yr) due to synthetic fertilizer replacement by sewage sludge are evaluated as per Equation 2.

GHG reductions due to N replacement + reductions due to P replacement

$$= \frac{W_s \times 5465 \times 0.3 \times \%N + W_s \times 165.1 \times \%P}{10^5} \qquad (2)$$

Where "W_s" Mg/yr of dry sewage sludge applied to the land, %N and %P represent the amount contained in sewage sludge on dry weight basis.

4.2 GHGs reduction due to carbon sequestration in soil

The average organic carbon content of aerobically digested sludge is 21.4% w/w and that for anaerobically digested is 17.6% w/w (Parker and Sommers, 1983). When sludge is applied to the land, the organic matter immediately begins to decompose by the soil microbes as well as by those in sludge, provided that the temperature is above freezing and there is sufficient moisture. Determination of carbon sequestration from sewage sludge to soil is difficult, because of the many factors that affect the longevity of the sequestration, that is, tilling, precipitation, air, runoff, soil temperature, pH, etc. Most of the carbon of sewage sludge applied to the soil will eventually be converted to CO_2 and CH_4 depending upon the aerobic and anaerobic pockets, but some carbon remains in the organic matter. To the best of our knowledge, there are no reports available to date on this value (i.e. carbon remained in the organic form in the soil). When sewage sludge compost is applied to soils, it is assumed that 8.2% carbon of the compost remains in the soil for 100 years or more (NEBRA, 2008). Even though sewage sludge and sewage sludge compost are entirely two different things, however, the application of sewage sludge in the soil will eventually undergo aerobic, facultative and anaerobic degradation process by the soil and sludge microbes, similar to a composting operation. Therefore, in the absence of the real data of carbon sequestration from sewage sludge, the same percentage (as that of compost) of carbon can be assumed as carbon sequestration credit for direct sewage sludge application to soil. This GHG reductions (Mg CO_2 equivalent/yr) can be calculated as per Equation (3).

GHG reductions due to carbon sequestration

$$= (44/12) \times W_s \times 0.082 \times O_C \qquad (3)$$

Where, "W_s" Mg/yr of dry sewage sludge applied on land, O_C organic carbon content in sewage sludge (g/g).

4.3 GHGs reductions due to additional water holding capacity of soils

Land application of sewage sludge improves the soil structure. The organic matter present in sewage sludge will improve water holding capacity of the soil. Depending upon the region, soil type, soil texture and compost application rate, the compost can save more than 30.0% of irrigation water and thereby reduces GHG emissions related to the electrical energy requirement for supplying that extra water through irrigation systems (Compost Australia). The application of compost can save between 0.13 and 0.95 mL of water per hectare per year, depending on crop and soil types (Compost Australia, http://www.wmaa.asn.au/lib/pdf/05_d/ca/dca_1212_capabilitystatement.pdf).

A mixture of sewage sludge and fly ash applied to the soil increased the water holding capacity from 53.0% to 58.5% (Veeresh et al., 2003). In the absence of practical study of the extra water holding capacity of the soil due to sewage sludge application to agricultural land, the same degree of water holding capacity as that of the compost can be assumed for the computation. Irrigation water requirements will significantly reduce due to the compost application. When sewage sludge compost with a thickness of 53.40 mm is applied over the soil, it will save 0.251 m^3 of water/m^3 of sludge compost (NEBRA, 2008). Moreover, it is reported that 9.25 kWh electricity is required per cubic metre of water for agricultural use (E2, 2007). If the water content of sludge before land application is X%, sludge bulk density is Y kg/m^3, then GHGs reduction (Mg CO_2 equivalent/yr) due to irrigation water saving due to application of Ws Mg/yr of dry sewage sludge can be calculated as per Equation (4).

GHG reductions due to water holding capacity of soil.

$$= \frac{\kappa \times W_s \times 100 \times 9.25 \times 0.251}{(100 - X) \text{ x } Y} \tag{4}$$

Where, “κ” is the national emission intensity coefficient 0.53 x10^{-3} Mg CO_2 equivalent/kWh (developed by Environment Canada study based on the Resources for the Future (RFF) model)

4.4 GHGs reductions due to improved tillage and workability of soils

Due to the availability of nutrients, sewage sludge will restore the health of the soil by building organic matter and tilth, and it will also improve the soil’s physical and chemical properties (Torri and Lavado, 2008). The change in physical and chemical properties will reduce the management and maintenance required due to the fact that the machinery will pass through the soil (after sewage sludge application) more easily. This will result in the reduction in the fossil fuel consumption from machinery and therefore will result in lower GHG emissions. There are no available quantitative data on this aspect, but it is assumed that the improvement of tillage and workability will reduce the tractor fuel consumption by 5.0%. This assumption of 5.0% reduction in fuel consumption is based upon the difference in fuel consumption between hard soil and soft soil (Moitzi and Boxberger, 2006). Due to the sewage sludge application the hard soil will behave like a soft soil. The average fuel consumption of hard soil is 12.80 L/ha (Moitzi et al., 2006) and emission factor for fuel is 2.73 kg CO_2/L of diesel (Gassara et al., 2011). Therefore, GHG reductions (Mg CO_2 equivalent/yr) when sludge is applied with an average thickness of 53.40 mm can be calculated as per Equation (5).

GHG reductions due to improved tillage and workability

$$= \frac{2.73 \times W_s \times 0.05 \times 12.8}{(100 - X) \times Y \times 5.34} \tag{5}$$

Where, "W_s" Mg/yr of dry sewage sludge applied to land, water content of sludge before land application is X%, Y is sewage sludge bulk density kg/m^3.

4.5 GHGs reductions due to photosynthetic absorption of CO_2 by crops

It was concluded that the land application of sewage sludge produce high crop yields and high-quality crops similar to commercial fertilizers (based on three to seven years of field study by the US Department of Agriculture and University of Minnesota). Clapp (1986) reported increased yield for several crops with sewage sludge land application as fertilizer compared to commercial NPK (nitrogen, phosphorus and potassium) fertilizers, (38.0% increase for corn fodder, 51.0% for grain and 14.0% of reed canary grass). Similarly, Togun and Dris (2003) reported an increase of 28.0% yield of tomato due to sewage sludge land application (tomato yield increased from a typical average of 14.40 Mg/ha yield to 18.50 Mg/ha). The effect of sewage sludge amendment on growth, yield and heavy metal accumulation in plants is reported by various researchers and is summarized by Singh and Agrawal (2008). An increase in crop yield signifies higher carbon sequestration (or GHG minimization) due to photosynthetic CO_2 absorption by plants and crops. The land application of sewage sludge was studied by Kharub (2012) and reported a positive effect on the emergence and growth of Abelmoschus esculentus. Thus, an increase in the yield of plants growth and crops due to sewage sludge application will reduce GHG emissions compared to the control (without sewage sludge application). The extra carbon sequestration will be due to additional growth of plants (leaves, stem, branches, etc.) and for additional yield of crops (fruits, grains, etc.). If sewage sludge is applied on dry basis (Ws in Mg/yr) with an average thickness of 53.40 mm, GHGs reduction (Mg CO_2 equivalent/yr) due to additional photosynthetic absorption of CO_2 can be calculated as given by Equation (6)

GHGs reduction due to additional photosynthetic absorption of CO_2 by surplus growth of plants (leaves, stem, branches, etc.) and crops (i.e., fruits, grains, etc.)

$$= [\text{¢}_1(a_1-b_1) + \text{¢}_2(a_2-b_2)] \times \frac{W_s}{(100-X) \times Y \times 5.34} \times \frac{44}{12} \tag{6}$$

Where, "W_s" Mg/yr of dry sewage sludge applied on land, "¢_1" is the carbon content in the plant (kg/kg weight of plants without crops) and "¢_2" is the carbon content in the crops (kg/kg weight of crops), "a_1" is a yield of plant (kg/ha) and "a_2" is the yield of crops (kg/ha) after land application of sewage, "b_1" is yield of plants without crops (kg/ha) and "b_2" is yield of the crops (kg/ha) before (or without) land application of sewage sludge.

4.6 Increased GHG emissions due to land application of sewage sludge

The function of soil ecosystems is governed by the dynamics of its microbiota. The land application of sewage sludge will change the dynamics of soil microbiota. The microbiota have a very essential role in organic matter degradation. Reduction or increase in microbiota due to sewage sludge land application will affect the nutrient cycling (Giller and McGrath, 1998). Few studies are available on the flux of gases in sewage sludge applied to tropical soils (Alvarez and Lavado, 1999; Blechschmidt and Hüttl, 1999; Flessa and Beese, 2000). Soil respiration, metabolic quotient and soil enzyme activity are the important parameters or indicators to evaluate the effect of sewage sludge application on soil microbial activity (Bettiol and Ghini, 2011). The application of sewage sludge has been reported to cause an increased flux of CO_2, N_2O and CH_4 to the atmosphere (Bettiol and Ghini, 2011; Chiaradia et al., 2009; Fernandes et al., 2005a, 2005b). The flux of CO_2, N_2O and CH_4 with sludge land application are increased by 224.0%, 316.0% and 162.0%, respectively, compared with the control soil without any fertilizers (Fernandes et al., 2005a, 2005b). Similarly, when soils are amended with chemical fertilizers the flux of CO_2, N_2O and CH_4 to the atmosphere is increased by 85.0%, 45.0% and 106.0%, respectively, compared with the control soil without any fertilizers. Fernandes et al. (2005a) observed the flux of CO_2, N_2O and CH_4 to the atmosphere with sewage sludge application as

115.10 mg $C.m^{-2}$ h^{-1}, 8.60 mg $N.m^{-2}$ h^{-1} and 0.05 µg $C.m^{-2}$ h^{-1}, respectively. Therefore, GHG emissions (Mg CO_2 equivalent/yr) into the atmosphere due to land application of sewage sludge with an average thickness of 53.40 mm can be calculated as per Equation (7). Further, it was also considered the energy required during sewage sludge land application as 351.68 kWh/Mg of dry sludge solids (Wang et al., 2008a).

GHG emissions due to microbial mineralization

$$= 24\times365\times[A\times10^{-9}\times(\frac{44}{12})+B\times10^{-9}\times(\frac{44}{28})+C\times10^{-12}\times(\frac{16}{12})]\times\frac{W\times10^{8}}{(100-X)\times Y} \qquad (7)$$

Where, A is the net increase in the CO_2 flux (mg $C.m^{-2}$ h^{-1}) with respect to control (i.e., without sewage sludge or without fertilizer application), B is the net increase in the N_2O flux (mg $N.m^{-2}$ h^{-1}) with respect to the control (i.e., without sewage sludge or fertilizer application), C is the net increase in the methane flux (µg $C.m^{-2}$ h^{-1}) with respect to the control (i.e., without sewage sludge or fertilizer application) due to the application of fertilizers or sewage sludge; "W" is Mg of dry sewage sludge applied to land.

Therefore the net GHG emissions due to the land application of sewage sludge are evaluated as per Equation 8.

Net GHG emissions = [GHG emissions due to microbial mineralization (equation 7) + energies required during land application]–[Equation 2 + Equation 3 + Equation 4 + Equation 5 + Equation 6]. (8)

The negative value of Equation 8, will indicate savings in GHGs whereas, a positive value will indicate GHG emissions due to land application of sewage sludge.

5. HYPOTHETICAL CASE STUDY FOR ESTIMATING GHG EMISSIONS FROM LAND APPLICATION OF SLUDGE

In order to evaluate whether the land application of sewage sludge would result in either GHG emissions or reductions, a hypothetical case study has been presented based on the literature values. In this case, it was considered that the WWTP had a treatment capacity of 20 million gallons of wastewater per day (75708 m^3/day). The sludge production rate is considered as 0.225×10^{-3} Mg of dry solids/m^3 of treated wastewater (Ghazyand Dichtl, 2011). Considering

45.0% (w/v) total volatile solids degraded during anaerobic digestion (Metcalf and Tchobanoglous, 2004), the weight of the digestate required for land application was calculated. Chemical composition of anaerobic digested sludge (ranging from lower to higher concentration) was adopted from Sommers (1977). Further, three possibilities were considered to evaluate the GHGs emissions for land application of the digested solids. Case 1: with lower percentage of carbon, N and P. Case 2: with higher concentration of organic carbon, N and P. Case 3: average concentration of organic carbon, N and P (Table 4). The nutrients concentrations in sewage sludge defined by various researchers (Table 2) fall within the range of cases 1, 2 and 3. Further, it also evaluated GHG emissions based on the available methodologies in the literature and the results are compared with the present study (Table 6).

The carbon content in the plant and carbon content in the crops (as required in Equation 6) are not available for sewage sludge application. Therefore, for the evaluation of GHGs reduction due to the photosynthetic absorption of CO_2 by crops, the data increase in the yield of tomato after compost application were considered from Togun et al. (2003). The typical carbon content of tomato is 24.80 g C/kg of tomato or 90.90 kg CO_2 equivalent/Mg of tomato (Ministry of Agriculture and Forestry, http://www.mpi.govt.nz/mafnet/rural-nz). In case 2, due to non-availability of suitable data, a rational figure of 10.0% increase in the crop yield (compared to case 1) was assumed. An increase in the flux of gases in the soil–atmosphere interface at different nutrients concentrations is not available. Therefore, it was considered that there was a similar effect on gas fluxes at the soil–atmosphere interface by different nutrients concentrations.

5.1 GHG emissions and reductions at different nutrients concentrations

The computations of net GHG emissions (GHG reductions-GHG emissions) at different nutrients concentrations are summarized in Table 5. The GHG reduction, GHG emission and net GHG emissions for cases 1, 2 and 3 are presented in Figure 2. In case 1 at lower nutrients concentrations, GHG reductions due to the replacement of fertilizers represent only −40.88 Mg CO_2 equivalent/yr, since the reductions are directly proportional to the nutrients concentrations (N and P) in the sludge. In cases 2 and 3, the GHG reductions corresponding to the fertilizer replacement were −1414.97 and −53.74 Mg CO_2 equivalent/yr, respectively, that is, the maximum GHG reduction was observed for sludge with high nutrients concentrations (case 2). GHG reductions due to the carbon sequestration were proportional to the amount of carbon content in sewage sludge, therefore at high nutrients concentrations (case 2) the carbon sequestration was high (−515.81 CO_2 equivalent/yr). In cases 1 and 3, the carbon sequestration was relatively low compared with the case 2 (Table 5). Due to non-availability of the data at different nutrients concentrations and their effect on water holding capacity, improved tillage and photosynthetic absorption of CO_2 by crops, similar factors were assumed (for cases 1, 2 and 3) which resulted in similar GHG savings. However, further studies are required to establish the data. GHG emissions corresponding to the energy utilization were directly proportional to the volume of the digestate applied to the soil. Therefore, GHG emissions corresponding to the energy utilization were similar to cases 1, 2 and 3 (Table 5). GHG emissions corresponding to the increase flux of gases were similar at different nutrients concentrations (since a similar flux factor was assumed).

At lower nutrients concentrations (case 1) GHG emissions corresponding to the energy required during land application represent 62.0% of the net GHG emissions (Table 5). Moreover, GHG emissions corresponding to the increased flux of gases in the soil–atmosphere interface are 33.0% of the net GHG emissions. Thus GHG reductions due to digestate application represents only 5.0% of the net GHG emissions. In case 1, the GHG reductions due the replacement of fertilizers were only −40.88 CO_2 equivalent/yr, because of the lower nutrients concentrations in the digestate, but increased flux has resulted in GHG emissions of 493.23 CO_2 equivalent/yr. Thus, the overall balance represents increased GHG emissions for case 1. With increased nutrients concentrations (case 2), GHG emissions corresponding to the energy required during land application represent only 25.0% of the net GHG emissions, whereas GHG emissions corresponding to increased flux represent 14.0% of the net GHG emissions. At higher nutrients concentrations in sludge, the GHG reductions corresponding to the replacement of synthetic fertilizer are 44.0% of the net GHG emissions. GHG reductions corresponding to carbon sequestration represent 16.0% of the net GHG emissions. The sum of GHG emissions and reductions due to the land application of the digestate with higher nutrients concentrations was greater than the sum of GHG emissions. Therefore, the overall balance of higher nutrients concentrations result in GHG reductions. The land application of sewage sludge having average nutrients concentrations (case 3) will result in increased GHG emissions (Table 5). At average nutrients (case 3) concentrations the major factor for GHG reductions was due to carbon sequestration −259.10 CO_2 equivalent/yr. The sum of GHG reductions and emissions are −340.63 Mg CO_2/yr and 1259.14 CO_2 equivalent/yr, respectively. The net GHG emissions for case 3 were 918.51 CO_2 equivalent/yr. Therefore, the land application of digestate possessing lower nutrients concentrations results in net GHG emissions. The replacement of synthetic fertilizers and carbon sequestration represents the highest percentage of GHGs savings compared with other parameters (i.e. GHGs reduction due to additional water holding capacity, improved tillage and photosynthetic absorption of CO_2 by crops) (Table 5).

5.2 GHG Comparison of different methodologies to quantify GHG emissions due to the land application of sewage sludge

Computation of GHG emissions due to the land application of sewage sludge by employing different methodologies exhibited variable GHG emissions (Table 6). IPCC and RTI methodologies revealed that GHG emissions decreased with a decrease in the concentrations of nutrients in sewage sludge (Table 6). In IPCC methodology (Eggleston and Tanabe, 2006), estimation of GHG emissions is linked directly to nutrients (C, N) concentration with default factors (Table 3). RTI's methodology predicted the highest GHG emissions (Table 6); because it is assumed that CO_2 emissions are directly related to the carbon content of sewage sludge (Table 3). Therefore, GHG emissions are lower at a lower carbon (nutrient) concentration and higher at a higher carbon concentration of sewage sludge. The IPCC and RTI methodologies do not take into account the replacement of the synthetic fertilizer, carbon sequestration and improved characteristic of soil (increased water holding capacity, improved tillage and movement of vehicles), which are the factors responsible for the reduction in GHG emissions.

The BEAM methodology revealed higher GHG reductions (Table 6). The lowest GHG emissions are due to various assumptions, that is, (i) carbon sequestration is 25.0% of the dry sewage sludge applied, (ii) fertilizer credit for N is assumed as 4 and (iii) fertilizer credit for phosphorus as 2. Moreover, GHG emissions were also lower when the BEAM methodology was used by employing default values (i.e. 4.0% N and 1.5% P content present in sewage sludge) (Table 6). Moreover, the methodology developed by BEAM did not consider the increased water holding capacity of the soil, improved tillage and movement of vehicles and increased crop production due to the land application of sewage sludge. GHG emissions studies conducted by Hospido et al. (2005) and Niu et al. (2013) indicated an increase in GHG emissions due to sewage sludge land application, whereas GHG emissions studies conducted by Lundin et al. (2004) and Hong et al. (2009) revealed a decrease in GHG emissions due to sewage sludge land application. It was considered that CH_4 and N_2O emissions are reduced in these studies (Hong et al., 2009; Lundin et al., 2004). These authors have assumed a value of −0.012 kg CH_4/Mg of dry solids and −0.190 kg N_2O/Mg of dry solids (Table 3) for estimating GHG emissions without explaining the details. In the proposed methodology, the estimated GHG emissions decreased with increased nutrients concentrations.

In the proposed methodology the factors responsible (defined in Section 4) for GHG emissions are considered. Therefore, GHG emissions are representative in accordance with nutrients concentrations of sewage sludge applied to the land. Computations of GHG emissions performed according to the proposed methodology revealed that the estimation of GHG emissions was more effective and representative.

6. LIMITATIONS AND FUTURE PERSPECTIVE

It is imperative to note that the nutrient content of sewage sludge is unpredictable. The release of nutrients in available form that plants can use may not occur at the right plant growth stage. Moreover, sewage sludge nutrient content, their solubility and nutrient release rates, in general, are lower than inorganic fertilizers. On the whole, the nutrients in sewage sludge are both more diluted and much less readily available to plants. In case of a shorter time frame, nutrients of sewage sludge will not be available to the plants and therefore will not contribute to GHG savings. However, for a longer time frame, all the nutrient content of sewage sludge will eventually be available to plants and thus the calculation of GHGs saving would yield more or less realistic values.

Organic fertilizers from compost and other sources (such as sewage sludge) can be quite variable from one batch to the next. Therefore, without testing each batch, the amount of the applied nutrients cannot be accurately known. Therefore, the consideration of compost derived data for calculating additional water holding capacity of soils due to land application of sewage sludge may not give accurate results. The type of sludge (primary, secondary or mixed) applied to agriculture land will also affect GHG emissions. Moreover, the type of sludge treatment process (aerobic or anaerobic) and treatment duration (solids retention time) will also affect GHG emissions. The type of sludge and the type of treatment mainly influence the background microbial community of the soil, which affects the degradation of sludge solids or organic matter after sludge is land applied.

The availability of N and P of sewage sludge for plants needs to be established. The carbon percentage sequestrated in the soil, increased water holding capacity of soil and increase in the flux of gases due to land application of sewage sludge vary with type of soil, moisture content of the soil and atmospheric conditions. Therefore, further study of these components is required to estimate either GHG emissions or reductions. The carbon content of the plants and the crop, before and after sewage sludge application is required to estimate the GHG reductions. Further, the antibiotics and other emerging contaminants, which are present in sewage sludge at the nano-concentrations will impact the soil microbiota and also the flux of gases at the soil–atmosphere interface. Thus, data need to be generated on the impacts of emerging contaminants on the gas flux at the soil–atmosphere interface.

7. CONCLUSION

Different methodologies to evaluate GHG emissions due to the land application of sewage sludge presented in the literature are summarized. A progressed methodology to evaluate GHG emissions was proposed. Based upon the proposed methodology, it was clear that increased nutrients concentrations in sewage sludge substantially sequestrated GHG emissions. The land application of sewage sludge proved to be beneficial in reducing GHG emissions only at high nutrients concentrations (39.0% organic carbon, 17.6% N and 14.3% P) with sequestration in GHG emissions (−699 kg CO_2 equivalent/yr). A comparison of different methodologies for GHG emissions showed that the methodology proposed in this study was more effective and reliable, that is, GHG emissions or reductions vary according to the nutrients concentrations of the sludge.

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Table 1. Percent wastewater sludge disposed by different methods

Region	Year	Land Application (%)	Incineration (%)	Land-Filling (%)	Compost [a](%)	Others (%)	Ref.[a]
USA	-	52.0	22.0	17.0	9.0	-	[1]
Canada		43.0	47.0	4.0		6.0	[2]
Western Canada	-	66.0	-	4.0	27.0	-	[1]
Japan	-	-	80.0	-	-	-	[1]
China	2010	48.5	3.5	34.5	-	13.5	[3]
Australia	2011	55.0	15	30.0	15.0	-	[4]
France	2008	60.0	-	-	-	-	[5]
U.K.	2005	69.0	14.0	5.0	1	9.0	[6]
Denmark	2007	59.0	16.0	6.0	-	19.0	[5]
Sweden	2009	24.0	1.0	24.0	33.0	18.0	[5]
Germany	2008	28.0	51.0	-	17.5	3.5	[5]
Italy	2005	23.0	3.0	42.0	21.0	11.0	[5]
Belgium	2008	14.0	53.5	-	-	32.5	[5]
Netherlands	2006	-	67.0	4.5	13.0	15.5	[5]
Greece	2008	1.0	46.0	38.0	-	15.0	[5]

[a] [1] = LeBlanc et al. (2008); [2] = Roy et al. 2011; [3] = Chen et al. (2012); [4] = http://www.biosolids.com.au/benefits-land-application.php; [5] = Kelessidis and Stasinakis (2012) and [6] = Maisonnave et al., (2002); Compost is mainly applied to agriculture land or used for hoticulture. Other applicatins: used in cement industry, bricks, etc.

Table 2. Nitrogen and phosphorus content in the sewage sludge

Type of sludge	Nitrogen content	Phosphorus content	Reference
Sewage sludge	NA	1.2% to 9.5%	Furrer (1984)
Secondary sludge	3.8%	2.2%	Smith (1996)
Fermented sludge	3.9% (average)	2.5% (average)	Sommers (1977)
Anaerobic sludge	32 to 96 g N/kg dry mass	24 to 47 g P_2O_5/kg dry matter	Johannesson (1999)
Anaerobic sludge	15 g N/kg dry matter	78 g P_2O_5/kg dry matter	Quilbé et al.(2005)
Thermally stabilized sewage sludge	19 g N/kg dry matter	22 g P_2O_5/kg dry matter	
Aerobic sludge	48 g N/kg dry matter	25 g P/kg dry matter	Sigua et al. (2005)
anaerobic sludge	40 g N/kg dry matter (pH 11; calcium hydroxide treated)	22 g P/kg dry matter	
Cake biosolids	39 g N/ kg dry matter	33 g P/kg dry matter	
Secondary sludge	21 to 50 g N/kg dry matter	16 to 31 g P/kg dry matter	Fernandes et al. (2005a)
Sewage sludge	2.3%	1.1%	Wang et al. (2008b)
Sewage sludge	7 mg TN/kg dry matter	17 g TP/kg dry matter	Wang et al. (2008c)
Sewage sludge	2.8 to 5.1%	0.8 to 3.0%	Chan (2009)
Sewage sludge	30 g TN/kg dry matter	10 g P/kg dry matter	Franco et al. (2010)
Sewage sludge	2.3%	0.4%	Keskin et al. (2010)
Sewage sludge	47 g N/kg dry matter	< 1 g P_2O_5/kg dry matter	Lakhdar et al. (2010)
Sewage sludge	1.4%	0.8%	Kabir et al. (2012)

Note : NA: not applicable

Table 3. Methodologies to estimate GHG emissions

Method	Gases included	Parameters used	Limitations of the methods
IPCC	CO_2 emissions from vehicles used for transport and during land application of sewage sludge. CH_4 and N_2O emissions following sludge land application. Indirect N_2O emissions.	10.0% of CH_4 potential or 5 kg CH_4/Mg raw dry solids 1.0% of total nitrogen applied Indirect N_2O emissions = application rate (kg N applied) x $Frac_{GASM}$ x EF_4 Where $Frac_{GASM}$ is the fraction of the added N that will volatilize (default value is 0.20) and EF_4 is a conversion factor (default value is 0.01) for the fraction of N that volatilizes what will convert to N_2O.	This method does not account for any benefits of land application of sewage sludge (IPCC, fourth Assessment Report by Bonger et al., 2009). Increase in the flux of gases (CO_2, CH_4, and N_2O; Fernandes et al., 2005b) following the land application are not considered. Emissions reduction resulting from offsetting fertilizer use was not considered.
Research triangular institute (RTI)	CO_2 emissions following land application of sewage sludge. The emissions will be directly proportional to the carbon application rate to the land.	GHGs emissions = $M_W \times TS_W \times CC_W \times \left(\frac{44}{12}\right)$ Mg CO_2/year The MW = annual mass of waste applied to the land treatment unit (Mg/yr, wet basis); TS_W = Total solids content of waste material applied to the land (kg dry solids/kg wet solids) CC_w = Carbon content of sewage sludge applied to the land (kg C/kg dry solids) 44 = Molecular weight of CO_2 (kg/kg-mol) 12 = Molecular weight of carbon (kg/kg-mol)	This process gives an overestimation of CO_2 emissions as it presumes the complete conversion of carbon content of sewage sludge to CO_2. Following the land application, carbon will be converted into CO_2 and CH_4 due to the presence of anaerobic pockets within the land. Increased in the flux of gases (CO_2, CH_4, and N_2O; Fernandes et al., 2005b) following the land application of sewage sludge are not considered. Emissions reduction resulting from offsetting fertilizer use was not considered.

Table 3. Continutation

Method	Gases included	Parameters used			Limitations of the methods
Lundin et al. (2004)	Positive benefits of nitrogen and phosphrous (18 kg of phosphrous/Mg of dry solids) are considered. N_2O and NO_3 are likely to be released when the organically bound nitrogen in sludge is mineralised.	GHG emission factors (kg/Mg of dry solids) $\underline{CO_2}$ 25.00	$\underline{CH_4}$ -0.01	$\underline{N_2O}$ -0.19	CH_4 and CO_2 emissions due to sludge land application are not described. An increase in the flux of gases (CO_2, CH_4, and N_2O; Fernandes et al., 2005b) following the land application are not considered. The negative value was not defiend by the authors.
Hospido et al. (2005)	Benefits of nitrogen 17.87 kg N/Mg of dry solids and phosphrous 14.32 kg P/Mg of dry solids) due to sludge application was considered.	$\underline{CO_2}$ NA	$\underline{CH_4}$ 3.18	$\underline{N_2O}$ NA	There was no explaination for the values utilised for evaluating the GHG emissions. The authors did not consider (avoided) CO_2 and N_2O emissions from the land application of sludge.
Hong et al. (2009)	Positive benefits of nitrogen are considered. The other factors are taken from inventory data without proper explanation.	$\underline{CO_2}$ 17.20	$\underline{CH_4}$ -21.30	$\underline{N_2O}$ -0.19	The authors have not considered carbon sequestration due to land application of sludge. Moreover, authors have not included increased flux of gases at soil-atmosphere interface due to the land application of sludge. Comapare to Lundin et al. (2004) and Hospido et al. (2005) the methane emission factor was different. The representation of negative sign was not mentioned.
Niu et al. (2013)	Positive benefits of the nitrogen content present in sludge was considered. Further explanation of the factors was detailed.	$\underline{CO_2}$ 17.2	$\underline{CH_4}$ 3.18	$\underline{N_2O}$ NA	Authors have considerd CO_2 emissions values from Hospido et al. (2005) and CH_4 factor from Hong et al. (2009) but they have not included N_2O emissions. There was no explained behind the assumption considered in computing GHG emissions

Table 3. Continutation

Method	Gases included	Parameters used	Limitations of the methods
This study	- CO_2, CH_4 & N_2O emissions and reductions are considered	Details of these parameters used are explained in the section 4. The parameter (or factors) considered in evaluating GHG emissions due to land application of sludge are as follows. (i) Increased GHG emissions due to increased flux of gases at soil-atmosphere (ii) Replacement of the synthetic fertilizers (iii) Carbon sequestration in the soil (iv) Additional water holding capacity of the soil (v) Improved tillage and workability of the soil (vi) Photosynthetic absorption of carbon by crops	Since there are gaps in the knowledge associated with land application of sewage sludge. Few of the parameters are considered from sewage sludge compost. Moreover, we have not included the GHG emissions during sludge generation, dewatering and during the transportation of dewatered sludge to the land application site.

Table 4. Parameters considered for evaluation of GHGs during land application of the sludge digestate

Parameter	Quantity	Unit	Reference
Volume of wastewater	75708	m^3/day	Assumed
Sludge production rate	0.225	kg of dry solids/ m^3 of wastewater treated	Ghazy et al. (2009); Ghazy et al. (2011)
Sludge produced during wastewater treatment	17034.30	kg dry solids/day	Calculated
Volatile solids content in the sludge	65	%	Metcalf et al. (2004)
Total dry solids degraded during AD	40	%	Metcalf et al. (2004)
Digestate for land application	12051.77	Kg dry solids/day	Calculated
<u>Case 1. low percentage of</u>		(w/w)	
Organic carbon			
Nitrogen	18	(%)	McFarland (2001);
Phosphrous	0.5	(%)	Sommers (1977)
	0.5	(%)	
<u>Case 2. high percentage of</u>			
Organic carbon			
Nitrogen	39	(%)	
Phosphrous	17.6	(%)	McFarland (2001);
	14.3	(%)	Sommers (1977)
<u>Average nutrient concentration</u>			
Organic carbon			
Nitrogen	28.5	(%)	McFarland (2001);
Phosphrous	9.05	(%)	Sommers (1977)
	7.4	(%)	
<u>Digestate applied on the land</u>			
Thickness	53.4	mm	NEBRA (2008)
Water content of sludge before land application	70	%	McFarland (2001)
Bulk density of sludge	1020	kg/m^3	McFarland (2001)

Table 5. Net GHG emissions due to sewage sludge land application at different nutrient concentrations

		Case 1	Case 2	Case 3
		GHG emission (Mg CO_2 equivalent/yr) at		
	Description	**Low nutrient concentration**	**High nutrient concentration**	**Average nutrient concentration**
I.	GHG reductions due to replacement of fertilizers	-40.88	-1414.97	-53.74
II.	GHG reductions due to carbon sequestration	-2.38	-515.81	-259.10
III.	GHG reductions due to additional water holding capacity	-17.71	-17.71	-17.71
IV.	GHG reductions due to improved tillage	-0.05	-0.05	-0.05
V.	GHG reductions due to photosynthetic absorption of CO_2 by crops	-10.03	-10.03	-10.03
VI.	**Sum of the reductions (I+II+III+IV+V)**	-71.05	-1958.58	-340.63
VII.	GHG emissions due to increased flux	439.23	439.23	439.23
VIII.	GHG emissions due to energy utilization	819.91	819.91	819.91
IX.	**Sum of the GHG emissions (VII+VIII)**	1259.15	1259.15	1259.15
	Net GHG emissions due to land application of digestate	1188.10	**-699.43**	918.51
	The reduction in net GHG emissions compared to case 1	-	**158.0%**	22.0%

Note: Negative sign indicates a reduction in GHG emissions; positive sign indicates increased GHG emissions

Table 6. Comparison of GHG estimation methodologies due to land application of sewage sludge

Description			**GHG reductions**	**GHG emissions**	**Net GHG emissions**	**Reference**
			Mg CO_2 equivalent/yr			
Case 1: Organic carbon 18.0%, nitrogen 0.5% and phosphorus 0.5%			NA	686	686	**IPCC**
			NA	2903	2903	**RTI**
			-1496	1030	-465	**BEAM**
			-71	1259	1188	**This study**
Case 3: Organic carbon 28.5%, nitrogen 9.1% and phosphorus 7.4%			NA	1882	1882	**IPCC**
			NA	3159	3159	**RTI**
			-8085	4629	-3456	**BEAM**
			-340	1259	919	**This study**
Case 2: Organic carbon 39.0%, nitrogen 17.6% and phosphorus 14.3%			NA	3078	3078	**IPCC**
			NA	6290	6290	**RTI**
			-14745	8228	-6516	**BEAM**
			-1988	1259	-699	**This study**
Default values of 4.0% N and 1.5% P			-4046	2503	-1543	**BEAM**
GHG emissions (kg/Mg of dry solids)						
CO_2	**CH_4**	**N_2O**				
25.00	-0.01	-0.19	-223	110	-112	Lundin et al. (2004)
NA	**3.18**	**NA**	NA	392	392	Hospido et al. (2005)
17.2	**-21.30**	**-0.19**	-224	75	-148	Hong et al. (2009)
17.2	**3.18**	**NA**	NA	467	467	Niu et al. (2013)

Note: NA means not applicable; IPCC is an intergovernmental panel on climate change; RTI is research triangular institute; BEAM is biosolids emissions assessment model; negative sign indicates a reduction in GHG emissions; positive sign indicates increased GHG emissions

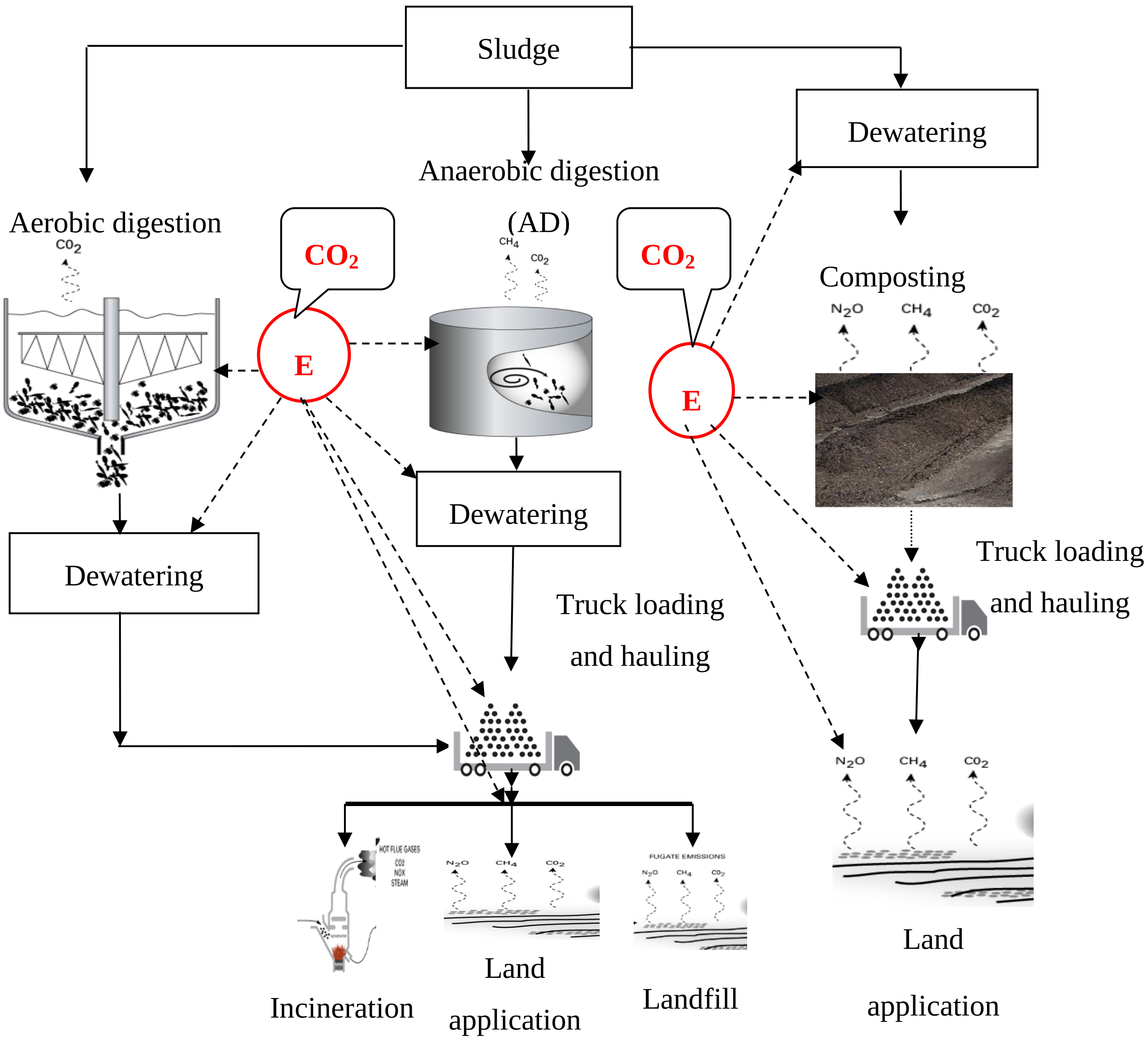
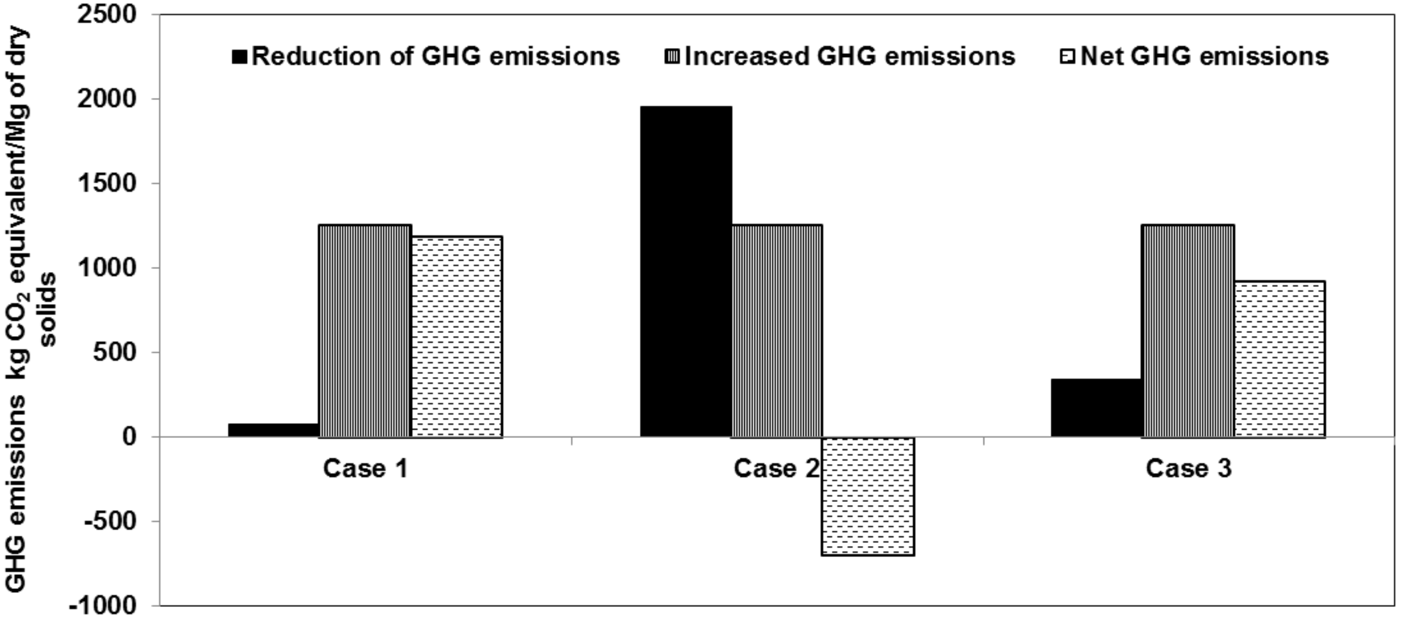


Figure 1. The sludge management with most common treatment process

Note : "E" is the energy required for the process (generated from fossil fuels)



Case 1: lower nutrients concentrations in the sludge **Case 2: higher nutrients concentrations in the sludge**

Case 3: Average nutrients concentrations in the sludge

Figure 2. Net GHG emissions due to the land application of sewage sludge with different nutrients concentrations

CHAPITRE VI

COMPARISON OF PRE-TREATMENT PROCESSES

COMPARISON OF ULTRASONICATION, THERMAL AND FENTON PRE-TREATMENT PROCESS BASED ON MASS-ENERGY AND GHG EMISSIONS

1.1 Introduction

One of the main objectives of the thesis was to evaluate different pre-treatment technologies/process to enhance Anaerobic Digestion (AD) efficiency based upon biogas production, solids (suspensed solids (SS), total solids (TS), volatile solids (VS), and volatile suspended solids (VSS)) degradation, methane generation, composition of biogas, energy generation and greenhouse gas (GHG) emissions. Ultrasonication and Fenton pre-treatment technologies are emerging technologies, whereas, thermal pre-treatment is a commercially available technology. However, there is no energy balance information (whether it is energy favorable or energy demanding system) on these pre-treatment technologies aiming to enhance AD efficiency. Additionally, there were no studies available to understand these emerging technologies with respect to energy generation and GHG emissions. Therefore, each technology had to be studied separately (with respect to type of sludge, sludge solids concentration, time of biodegradation) to generate the required set of data. Moreover, the glaring technology gap has been clearly discussed and well documented in three different state-of-the-art technology review articles Chapter 2 (part-1), Chapter 3 (part-1) and Chapter 4 (part-1). Thus, for the first time ever, these technologies were exclusively explored through rigorous experimental work (and experimentally measured) to demonstrate whether these technologies are energy efficient or energy consuming processes (Chapter 2 (part-3), Chapter 3 (part-2), and Chapter 4 (part-2)). In addition, these three pretreatment technologies (ultrasonication, thermal and Fenton pretreatment) have been compared and their comparative performance evaluation was included in this chapter.

1.2 Solubilisation

Pre-treatment of sludge facilitates the release of intracellular matter by rupturing the cell walls into the aqueous phase to increase sludge solubilisation. The pre-treatment efficiency of sludge solubilisation is evaluated by the soluble chemical oxygen demand (SCOD)/total chemical oxygen demand (TCOD) ratio (Pilli et al*.,* 2015a). The SCOD/TCOD ratio denotes the release of organic matter from a solid phase to the aqueous phase. Ultrasonication, thermal and Fenton pre-treatment enhances sludge solubilisation. The effect of sludge solubilisation by ultrasonication, thermal and Fenton pre-treatment at different solids concentration was discussed in the Chapter 2 (part-3), Chapter 3 (part-2), and Chapter 4 (part-2) respectively. For ultrasonication pre-treatment (at specific energy (SE) input 5742 kJ/kg TS), the SCOD/TCOD ratio increased from 0.02 to 0.10 for the secondary sludge at 31.45 g TS/L. For thermal pre-treatment (134 ^{o}C for 30 min) the SCOD/TCOD ratio increased 0.02 to 0.22 for the secondary sludge at 29.94 g TS/L. With Fenton pre-treatment (at pH 3.5 and 60 g H_2O_2/kg TS and 0.07 g Fe^{2+}/g H_2O_2) the SCOD/TCOD ratio increased from 0.02 to 0.24 for the secondary sludge at 30.81 g TS/L. The order of pre-treatment efficiency for enhancing sludge solubilisation was Fenton pre-treatment > Thermal pre-treatment > ultrasonication. During Fenton pre-treatment acidification (to pH 3.5) with sulfuric acid and Fenton oxidation had lead higher solubilisation compared to thermal and ultrasonication pre-treatment. Thermal pre-treatment was conducted at a lower temperature (140 ^{o}C for 30 min) and in Chapter 3, part 1 it was clearly mentioned that increasing the temperature (above 170 ^{o}C) increases the sludge solubilisation. Similarly, for ultrasonication high SE input is required for sludge solubilisation (Chapter 2, (part 1)). In terms of solubilisation, Bougrier et al. (2006) also observed that the thermal pre-treatment (at 170 ^{o}C) was better than sonication (SE 6250 kJ/kg TS). However, the increased solubilisation due to pre-treatment does not represent a 100% increase in biodegradability (Kim and Lee 2012; Kim et al., 2013).

1.3 Methane production

From Chapter 2 (part 3), Chapter 3 (part 2), and Chapter 4 (part 2) it is clear that Ultrasonication, thermal and Fenton pre-treatment enhances methane production. At different solids concentration the cumulative production of methane was enhanced compared to the control. The cumulative methane production was 7086, 6729 and 5552 m^3/g VS added for the ultrasonication, thermal and Fenton pre-treated secondary sludge. The order of pre-treatment efficiency for enhancing methane production was ultrasonication > thermal > Fenton pre-treatment. In this study weak solublisation of COD and high biodegradability was observed for ultrasonication pre-treatment. This confirms results obtained by Bougrier et al. (2006). Thermal pre-treatment enhanced sludge solublisation by breaking the microbial cells walls (no active microbes), but methane production was low due to not well-adapted inoculum or low symbiotic relationship between acetate-forming and methane forming bacteria. Acetate-forming (acetogenic bacteria) and methane-forming bacteria grow in a symbiotic relationship.

Acetogenic bacteria reproduce very slowly (usually greater than 3 days) (Gerardi, 2003). Anaerobic sludge volume of 50 mL was used as inoculum for AD of control, ultrasonication, thermal and Fenton pre-treated sludge. Cumulative methane production decreases by decreasing the inoculum volume (Braguglia et al., 2006). Formation of refractory compounds or consumption of Fenton reagent by the reduced compounds of sludge and low inoculum ratio (0.066) has led to low methane production. Therefore, substrate to inoculum ratio on methane production need to be established for thermal and Fenton pre-treated sludge. Further studies are required to understand the effect of sludge solubilisation (pre-treatment) on the symbiotic relationship.

1.4 Mass balance

The mass balance for ultrasonication, thermal and fenton pre-treatment at different solids concentrations was presented in chapter 2 (part 3), chapter 3 (part 2), and chapter 4 (part 2), respectively. In this section, comparison of the results of ultrasonication, thermal and fenton pre-treatment are summarized in Table 1. To evaluate mass balance of the anaerobic digestion 40 mg of dry solids was assumed. The quantity of solids remained after AD for transportation and land application was 20.02 mg for ultrasonicated secondary sludge. The reduction in quantity of digestate in case of the ultrasonicated sludge was due to the higher reduction in volatile solids (64.18%) than the other methods during anaerobic digestion. As explained earlier, the methane production was higher for the ultrsonicated sludge compared to the thermal and fenton pre-treated sludge. Based on the mass balance, ultrasonication pre-treatment process was more efficient in reducing the quantity of sludge. But the energy input per g of TS was very high as compared to other pre-treatment process. Based on mass balance, the order of reduction in quantity of sludge for different pre-treatment process was as ultrasonication > thermal pre-treatment > fenton pre-treatment.

Table 1. Comparison of mass balance for pre-treatment processes

	Total solids 30 g/L					
Description	**Ultrasonication**		**Thermal pre-treatment**		**Fenton pre-treatment**	
Energy input kWh/Mg of TDS	0*	1595	0*	713	0*	491
%Volatile solids degradation at HRT 30 days	53.67	64.18	51.46	57.95	51.46	52.76
Volume of methane Produced (mL)	6651	9013	6408	8984	6408	7223
Weight of Volatile degraded during AD (Mg)	16.55	19.88	14.90	16.61	14.90	14.56
Digestate dry solids remaining after centrifugation, which will be transported and land applied (Mg)	23.45	20.22	25.1	23.39	25.1	25.43

Note : 0* is control with zero energy input

1.5 Energy balance

The energy balance at different solids for different type of sludge for ultrasonication, thermal and Fenton pre-treatment has been described in in Chapter 2 (part 3), Chapter 3 (part 2), and Chapter 4 (part 2), respectively. Comparison of energy balance for ultrasonication, thermal and Fenton pre-treatment processes are summarized in Table 2. The energy required during ultrasonication for Mg of total dry solids was 1595 kWh, which was significantly higher than the thermal (713 kWh) and Fenton (491 kWh) pre-treatment. The energy recovered from methane combustion for the ultrasonicated, thermal and Fenton pre-treated sludge was 1915 1909 and 1535 kWh/Mg of total dry solids, respectively. Thus, the net energy balance was low (7.89 kWh/Mg of dry solids) for the ultrasonicated sludge. The energy output for thermal and Fenton pre-treatment was lower than the ultrasonicated process, but the net energy was higher for the thermal (840 kWh/Mg of dry solids) and Fenton pre-treatment (568 (840 kWh/Mg of dry solids) compared to ultrasonication pre-treatment (7.89 kWh/Mg of dry solids). Compared to the control the net energy was enhanced irrespective of sludge pre-treatment process. The maximum net energy 840 kWh/Mg of total dry solids was observed for thermal pre-treated secondary sludge at 30 g TS/L. Based on energy balance (in the order of higher net energy), the pre-treatment process were in the following order thermal pre-treatment > Fenton pre-treatment > ultrasonication.

Table 2. Comparison of energy balance for pre-treatment processes

Description	Energy balance					
	Ultrasonication		Thermal pre-treatment		Fenton pre-treatment	
	kWh/Mg of TDS					
Energy input for pre-treatment kWh/Mg of TDS	0	1595	0	713	0	491
AD	975.4	48.0	943	50	943	427
Dewatering	59.5	51.26	63.62	59.3	63.6	64.5
Transportation	40.9	35.3	43.75	40.78	43.7	44.3
Land application	206	178	221	206	221	224
(a) Total energy input	1282	1907	1271	1069	1271	1250
(b) Energy output	1262	1915	1362	1909	1362	1535
Net energy = (**b- a**)	-19.71	7.89	91	840	91	285
Energy ratio Energy output/energy input	0.98	1.0	1.07	1.79	1.07	1.23

Note: Total solids- 30 g/L

1.6 GHG emissions

In Chapter 2 (part 3), Chapter 3 (part 2), and Chapter 4 (part 2), GHG emissions for ultrasonication, thermal and Fenton pre-treatment at different solids concentrations have been described. The comparison of results of GHG emissions for ultrasonication, thermal and Fenton pre-treatment processes are summarized in Table 3. The energy output (generated from the combustion of methane) was equal to energy input for the ultrasonicated pre-treatment process. Therefore, there was no net energy to replace fossil fuels and no reduction of GHG emissions. Moreover, when methane is combusted CO_2 is produced. Thus, GHG emissions are increased with ultrasonication pre-treatment. For thermal and Fenton pre-treatment processes the net energy was 840 and 285 kWh/Mg of TDS, respectively. Replacing the energy dervived from fossil fuels with the energy produced (from methane) will account for the redcution of GHG emissions. The reduced GHG emissions were 73.8 kg CO_2 equivalent/Mg of TDS was observed for the thermal pre-treated secondary sludge. The reduction in GHG emissions was significantly higher in case of thermal pretreated secondary sludge as compared to ultrasonication and

Fenton pre-treatment process. The thermal pre-treatment have reduced the GHG emissions (-445.1 Kg CO_2 equivalent/Mg of total dry solids) due to increased net energy. The pre-treatment process for reducing GHG emission were in the following order : thermal pre-treatment > Fenton pre-treatment > ultrasonication. However, based on the proposed methodology in Chapter 5 it was clear that increased nutrients concentration in the digestate will substantially reduce GHG emissions (Pilli et al., 2015b). Therefore, further studies are required to estimate the nutrients concentration in the digestate after centrifugation of the digested sludge. Since pre-treatment solubilizes sewage sludge and releases the nutrients into water phase (Pilli et al., 2011), but during AD nutrient mineralization is possible (Appels et al., 2008).

Table 3. Comparison of GHG emission for pre-treatment processes

	Total solids (30 g TS/L)					
Description	**Ultrasonication**		**Thermal pre-treatment**		**Fenton pre-treatment**	
	0 (C)	Sonicated	0 (C)	Thermal pre-treated	0 (C)	Fenton pre-treated
	GHG emissions (kg CO_2 equivalent/Mg of TDS)					
Net GHG emission due to energy input and out put kWh/Mg of TDS	10.45	-4.18	-48.0	-445.1	-48.0	-150.7
GHG emissions during AD (biogenic emissions)	229.2	295.1	304.8	397.6	304.8	250.6
GHG emissions during CH_4 combustion	292.0	442.4	314.6	441.0	314.6	354.5
GHG emissions during transportation	11.3	9.76	12.1	11.3	19.3	19.3
GHG emissions during land application	66.8	57.6	71.5	66.7	-94	-95
Total GHG emission Without considering biogenic CO_2 equivalent emissions	380.2	505.6	350.2	73.8	192	128

1.7 Conclusion

All three pre-treatment technologies enhanced sludge solubilisation and increased AD efficiency. In terms of solubilisation, ultrasonication pre-treatment performance was better than the thermal or Fenton pre-treatment processes. In terms of methane production, all three pre-treatment technologies enhanced methane production. The methane production for the pre-treated sludge was higher than their respective control sludge. Ultrasonication pre-treatment was more efficient in terms of increased methane production compared to thermal and Fenton pre-treated sludge. Further studies are required to establish the data on methane production by increasing the inoculum ratio for the thermal and Fenton pre-treated sludge. Based on the mass balance, the quantity of residual sludge (digestate) left after anaerobic digestion for disposal is reduced with all pre-treatment processes. The minimum quantity of the digesate was observed for the ultrasonicated sludge. Based on energy balance performed under experimental conditions, thermal pre-treatment was the most energy efficient process. The maximum net energy was 840 kWh/Mg of TDS at 30.0 g TS/L for the thermal pre-treated secondary sludge. For ultrasonication process the energy input is very high compared to thermal and Fenton pre-treatment process, which lowers the net energy in spite of highest energy recovered from combustion of methane. Compared to the control GHG emissions were also reduced for thermal pre-treatment process. The order of pre-treatment processes based on mass-energy balance and GHG emissions is as follows: thermal pre-treatment > Fenton pre-treatment > ultrasonication.

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