Université du Québec
Institut National de la Recherche Scientifique
Centre Eau, Terre et Environnement

DÉVELOPPEMENT D'UN PROCÉDÉ DE TRAITEMENT D'OXYDATION SONO-ÉLECTROCHIMIQUE DE POLLUANTS ORGANIQUES D'INTÉRÊT ÉMERGENT DE TYPE PHARMACEUTIQUE

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Thèse présenté pour l'obtention du

grade de Philosophiae doctor (Ph.D.) en sciences de l'eau

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REMERCIEMENTS

Cette thèse a été réalisée au Laboratoire d'Électro-technologies Environnementales et Procédés Oxydatifs (LEEPO) du Centre Eau, Terre et Environnement de l'Institut National de la Recherche Scientifique (INRS-ETE), Université du Québec. Je tiens à exprimer à Monsieur le Professeur Patrick Drogui, ma profonde gratitude pour avoir accepté de diriger ces travaux. Je le remercie de m'avoir soutenu, orienté tout au long de mes travaux.

Je voudrais aussi remercier ma codirectrice, Professeure Satinder Kaur Brar pour avoir voulu m'accompagner jusqu'au bout en acceptant de diriger et juger ce travail.

Je suis particulièrement reconnaissante et honorée de l'intérêt qu'ont porté à cette thèse en acceptant d'en être les rapporteurs, Messieurs les Professeurs Trong-On Do de l'Université Laval, Simon Barnabé de l'Université du Québec à Trois-Rivières et Guy Mercier de l'INRS-ETE.

Je n'oublie pas de citer le stagiaire Laurent Nguyen, pour sa contribution, son investissement et sa collaboration dans ce projet de recherche.

Je remercie vivement l'ensemble des membres du LEEPO, du groupe Assainissement et Valorisation et le personnel de l'INRS pour leur aide précieuse lors de mes travaux de recherche. Que Arnaud De Conink et Oumar Dia soient remerciées pour leur sympathie et leur collaboration lors des essais menés au laboratoire. Je ne peux nommer ici toutes les personnes qui de près ou de loin m'ont aidées et encouragées mais je les en remercie vivement. Mille fois merci à vous tous !!!

Enfin, un gros merci est adressé à ma famille pour son soutien permanent et ses encouragements.

RÉSUMÉ

Depuis quelques années, l’explosion démographique et les activités humaines ont entraîné dans l’environnement l’apparition de divers types de polluants organiques d’intérêt émergents (POE). La pollution de l’environnement par les POE représente un défi majeur auquel doivent inéluctablement faire face les scientifiques et les gestionnaires de l’environnement. Ces composés organiques sont pour la plupart réfractaires, non oxydables ou difficilement oxydables biologiquement et chimiquement. Au nombre des composés organiques émergents se trouvent les produits pharmaceutiques, les hormones et les produits de soins personnels. Le risque potentiel associé à la présence de ces produits est actuellement au cœur des débats. Les recherches actuelles visent donc à limiter la contamination de l’environnement par ces POE en proposant des technologies hybrides d’oxydation avancée. L’objectif de ce projet est d’évaluer l’efficacité d’un procédé de traitement d’oxydation sono-électrochimique US-EO (combinaison de procédés d’ultrasons (US) et d’électro-oxydation (EO)) pour l’élimination des POE. Le développement d’un tel procédé pourrait constituer une avenue potentielle de traitement tertiaire des composés organiques persistants des eaux usées résiduaires de type municipal, domestique et industriel. La génération d’espèces oxygénées réactives (EORs) ($HO\cdot$, $HO_2\cdot$ et $O\cdot$) et l’utilisation d’électrodes catalytiques à forte surtension en oxygène et dont la surface est continuellement renouvelée par des forces de cisaillement très puissantes induites par l’implosion des bulles de cavitation (générées par les ultrasons) constituent les deux éléments clés pour oxyder plus efficacement les POE, soit directement sur la surface des électrodes ou indirectement par les EORs. Cet effet de synergie permet de produire *in situ* des espèces oxygénées réactives très puissantes telles que les radicaux hydroxyles ayant la capacité de dégrader efficacement les composés organiques réfractaires jusqu’à leur minéralisation. Le réacteur cylindrique, en verre ou plexiglas, est constitué de deux électrodes concentriques et est muni d’un transducteur céramique (un disque piézoélectrique de 4 cm de diamètre) installé dans le fond du réacteur. La cathode est un cylindre en déployé de métal de titane, de rayon 12 cm et de hauteur 16 cm. L’anode placée au centre, est un cylindre en métal déployé de titane recouvert d’oxyde de plomb (PbO_2) de rayon 8 cm, de hauteur 16 cm. Les travaux préliminaires ont d’abord consisté à évaluer le caractère adiabatique de la cellule sono-électrochimique (US-EO) et de son potentiel

d'oxydation, lequel potentiel a été respectivement comparé avec celui du procédé sonochimique seul (US) et du procédé d'électroxydation seule (EO). Pour ce faire, la p-nitrosodimethylaniline (RNO) a été utilisée pour évaluer la capacité de production des espèces oxygénées réactives (notamment les radicaux hydroxyles). Un taux de blanchissement de RNO allant jusqu'à 90% a été enregistré.

Ces résultats ont par la suite permis d'exploiter le procédé hybride US-EO pour le traitement d'une solution synthétique contaminée par un polluant organique persistant tel que la carbamazépine (CBZ), puis pour le traitement des effluents réels artificiellement contaminés par la CBZ. L'évaluation de la performance d'une cellule US-EO pour le traitement des eaux usées synthétiques contaminées par la CBZ a été basée sur une série d'optimisation de certains paramètres opérationnels. Les différents paramètres inhérents à ce procédé tels que l'intensité de courant, le temps de traitement et la puissance calorifique ont été évalués en termes d'efficacité de dégradation du polluant. Le recours à l'utilisation d'un logiciel de plan d'expérience en premier lieu a permis de décrire les différents processus de dégradation et d'évaluer les effets propres à chaque paramètre ainsi que les interactions éventuelles. Dans les conditions optimales, un taux de dégradation de la CBZ (C_0 = 10 mg L^{-1}) allant jusqu'à 90% peut être enregistré en appliquant une intensité de courant de 4,86 A pendant 177 min et en imposant une puissance ultrasonore de 38,3 W. Les conditions optimales ont par la suite été appliquées pour le traitement tertiaire des effluents d'eaux usées municipales contaminées par 10 µg CBZ L^{-1}. Les rendements d'élimination de CBZ, COT, COD et de la couleur étaient de 93%, 60%, 93% et 86%, respectivement. De même, la toxicité (bactérie *Vibrio fisheri*) des effluents municipaux a complètement été réduite suite à l'application du procédé US-EO. Dans l'optique d'élargir le spectre d'activité d'oxydation du procédé EO-US à d'autres types de polluants pharmaceutiques, des travaux additionnels ont été entrepris afin de vérifier les performances du procédé pour la dégradation de l'ibuprofène (IBU) et de la chlortétracycline (CTC). Des taux d'abattement de CTC allant jusqu'à 98% ont été enregistrés dans les eaux réelles de type municipal articiciellement contaminées. La CTC a pu être éliminée à la fois par oxydation directe à l'anode (au moyen des radicaux $^{\bullet}OH^{\cdot}$) et par oxydation indirecte par l'intermédiaire de médiateurs, tels que l'acide hypochloreux produit en solution suite à l'oxydation des ions chlorures. Des taux d'abattenment se situant entre 84 et 90 % ont été enregistrés dans le cas de l'IBU.

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ACE	Acétaminophène
CBZ	Carbamazépine
CytR	Cytarabine
COD	Carbone organique dissous
COT	Carbone organique total
CTC	Chlortétracycline
DBO	Demande biologique en oxygène
DBO_5	Demande biochimique en oxygène (5 jrs)
DIA	Diazépame
DIC	Diclofénac
DCO	Demande chimique en oxygène
EE2	17α Éthinyl estradiol
E1	Estrone
E2	17β estradiol
EIS	Spectroscopie d'impédance
EO	Électrooxidation
EO-US	Electro-sonochimie
EOR	Espèces oxygénées réactives
HAP	Hydrocarbures aromatiques polycycliques
H&G	Huiles et graisses totales
HMA	Hydrocarbures monocycliques aromatiques
HH	Hydrocarbures halogénés
IBU	Ibuprofène
K_{ow}	Coefficient de partage octanol-eau
LD	Limite de détection
LC-MS	Liquid chromatography-mass spectrometry
MEB/SEM	Microscopie électronique à balayage
POE	Polluants organiques émergents

PCC	Plan central composite
PSR	Plan de surface de réponse
US	Ultrason
UV-VIS	Ultraviolet - Visible

PARTIE I: SYNTHÈSE

CHAPITRE 1 SYNTHÈSE

1.1 INTRODUCTION

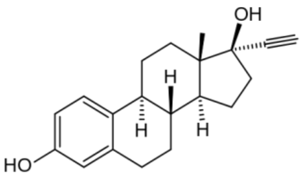
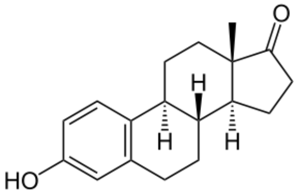
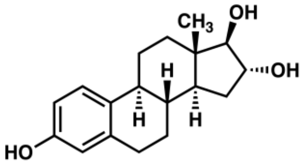
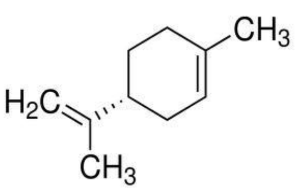
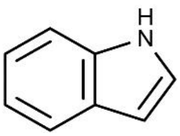
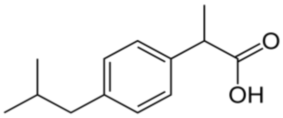
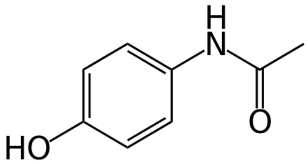
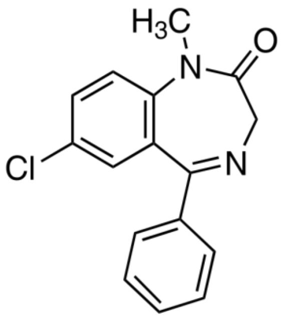
Les polluants organiques émergents (POE) sont des composés organiques réfractaires et pour la plupart, non oxydables ou difficilement oxydables biologiquement et chimiquement. Bon nombre de ces substances organiques rentrent dans la catégorie des composés appelés perturbateurs endocriniens, lesquels sont à l'origine de nombreuses perturbations de la faune marine (féminisation de la population et disparition de la faune) et constituent un risque pour la santé humaine (naissance prématurée, malformation des organes génitaux etc.). Ayant un caractère hydrophobe très marqué ces composés s'adsorbent plus facilement sur des matières particulaires. Ainsi, on les retrouve très souvent dans des matrices solides ou liquides telles que les eaux usées, eau de surface, les sédiments marins, les sols et quelques déchets industriels. Les POEs sont aussi retrouvés en concentrations très faibles dans les eaux traitées issues de stations d'épuration municipale. Pour faire face à cette problématique environnementale, l'équipe de recherche du Laboratoire d'Électro-technologies Environnementales et Procédés Oxydatifs (LEEPO) de l'INRS-ETE a mis au point des procédés de dégradation de divers types de POEs (pharmaceutique, pesticide et hormone etc.) contaminés en eau et autres matrices. La plupart de ces procédés mettent en œuvre une technique d'oxydation avancée en utilisant des électrodes catalytiques. Depuis ces dernières années, les procédés d'oxydation sono-électrochimique ont suscité beaucoup d'intérêt, principalement grâce à leur faible coût, leur simplicité de mise en œuvre, leur faible production de boues, mais surtout en raison de leur grande efficacité.

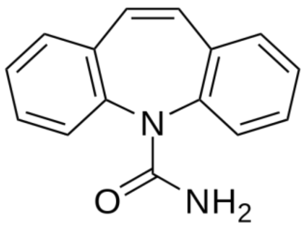
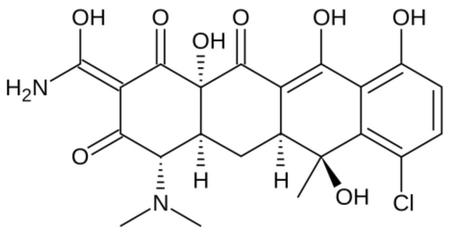
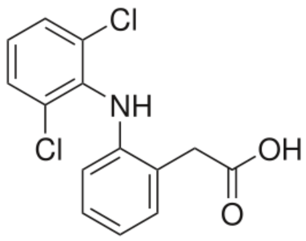
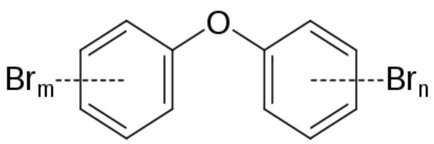
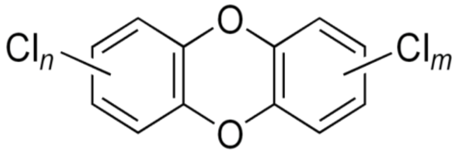
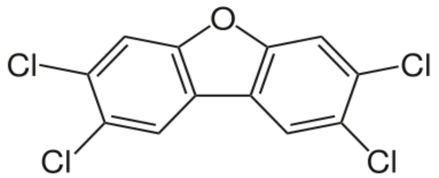
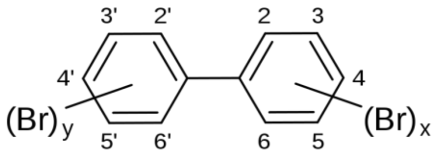
1.2 LES POLLUANTS ORGANIQUES D'INTÉRÊT ÉMERGENTS ET LEUR EMISSION DANS L'ENVIRONNEMENT

1.2.1 Définition et caractéristiques des polluants organiques d'intérêt émergents

Il est bien difficile de trouver une définition précise du terme « polluant organique d'intérêt émergent ». Ce terme assez générique regroupe les polluants d'origine chimique, biologique qui peuvent être d'origine industrielle, agricole, domestique ou naturelle. Les polluants d'intérêt émergents constituent une famille de composés complexes, avec des propriétés et des comportements variés. Ce sont très souvent des composés retrouvés dans l’environnement du fait de l’amélioration de la surveillance et du développement des techniques analytiques. En effet, grâce aux avancées technologiques et au progrès des méthodes d’analyse, de nombreux composés sont détectés dans les différentes matrices environnementales. Il s’agit bien souvent de molécules, pas nécessairement d’usage nouveau, mais nouvellement recherchées et pour lesquelles les données sont rares. Parmi ces polluants émergents sont notamment concernés certains stéroïdes, des médicaments soumis ou non à des prescriptions médicales (antibiotiques, hormones) à usage humain ou vétérinaire, les produits de dégradation de détergents non ioniques (composés du nonyl- et octyl-phénol), des désinfectants, des phtalates, des retardateurs de flamme, des antioxydants, les nanoparticules, etc. Les POEs forment une famille de composés chimiques constitués d’atomes de carbone et d’hydrogène dont la structure moléculaire comprend au moins un cycle aromatique fusionné (de cinq à six atomes de carbone) comme dans le tableau 1.1.

Tableau 1. 1 Structure moléculaires des POEs parentaux les plus communs

Stéroïdes et hormones	Ethinylestradiol (EE2) 	Estrone (E1) 	Estriol 
Produits soins personnel	d-Limonene 	Indole 	
Produits pharmaceutiques	Ibuprofène 	Acétaminophène 	Diazépame 
	Carbamazépine	Diclofénac	

	 Chlortétracycline 	
Produits à retard de flamme	Polybromodiphényléther  Polychlorodibenzo-p-dioxine 	Dibenzofurane  Polybromobiphényle 

La plupart de ces substances identifiées sont connues ou suspectées pour avoir des effets sur les fonctions endocriniennes et posent donc des problèmes vis-à-vis de la santé ou des écosystèmes. Pour un grand nombre de ces composés, il existe peu de données relatives à leur devenir, leur comportement dans l'environnement et les effets probables qu'ils peuvent avoir sur les êtres vivants ne sont pas encore bien définis.

1.2.2 Source d'émission des POE dans l'environnement

La présence de POE dans l'environnement peut donner lieu à plusieurs types de réactions de dégradation, entrainant la formation ou l'apparition de produits de transformation aux propriétés nouvelles. Peu d’études se sont intéressées au devenir des polluants émergents lors de l’incinération. Les principales conséquences observées suite à la présence de certains de ces composés (bisphénol A, phtalates, retardateurs de flamme, etc.) lors de l’incinération sont l’augmentation du taux de formation de dioxines, furanes et de composés chloro aromatiques. Les polluants entrent dans l’environnement par deux grandes voies qui sont les sources ponctuelles et les sources diffuses (Miao et al., 2005a; Drogui et al., 2007). Les sources ponctuelles sont des points d’entrée fixes des contaminants; elles sont plus faciles à maîtriser (Lefebvre et al., 2006; Chowdhury et al., 2010). Les sources ponctuelles peuvent être des effluents des stations d’épuration, des eaux usées industrielles, des eaux usées domestiques et des lixiviats des décharges (Naddeo et al., 2009c; Oller et al., 2011). Les sources diffuses quant à elles ne constituent pas des points fixes d’entrée, elles sont ainsi moins faciles à contrôler. Les voies d’entrées dites sources diffuses sont par exemple, les eaux de ruissellement, le lessivage des sols et les eaux souterraines (Satyawali et al., 2008; Sires et al., 2012). En plus des effluents des stations d’épuration, il existe d’autres voies d’entrée des polluants émergents dans l’environnement. Ces dernières sont souvent liées à l’utilisation des composés et à leur mode d’application. Par exemple, les antibiotiques à usage vétérinaire peuvent être dispersés par les excréments des animaux (Metcalfe et al., 2003; Stamatelatou et al., 2003), les composés contenus dans les produits à usage ménager peuvent entrer dans l’environnement par les lixiviats des décharges municipales (Miao et al., 2005a). A l’inverse, de nombreuses études ont évalué le devenir de plusieurs polluants émergents dans le cadre du stockage des déchets. La lixiviation dépend évidemment du type de composé considéré et des conditions environnementales. En particulier, la présence de carbone organique dissous dans les lixiviats, qui dépend du type de déchet enfoui et de son niveau de biodégradation, influe fortement sur l’élution par adsorption et donc sur la quantité de composés lixiviés. Par ailleurs, les processus de biodégradation de ces composés au sein d’un massif de déchet ne sont pas encore totalement connus : certaines études ont donné lieu à des résultats contradictoires. Ceci pourrait être dû aux difficultés analytiques liées à la détection de ces composés et surtout de leurs métabolites. En effet, en l’absence de procédures standardisées, les méthodes employées et les composés recherchés varient d’une étude à l’autre, ce qui influe sur les résultats. De manière analogue, la présence de micropolluants émergents dans les eaux usées et l’efficacité des stations d’épuration pour leur élimination ont été largement étudiées (Li et al., 2011). Les principaux procédés pouvant avoir lieu sont la sorption, le stripping (ou volatilisation) et la dégradation biologique. Les taux d'élimination observés, variables selon les composés et le type de traitement, sont relativement élevés. Les procédés avancés comme l'ozonation, la filtration sur charbon actif et l'osmose inverse, assurent un traitement complémentaire de certains composés généralement mal retenus par les procédés biologiques et permettent d'atteindre des rendements d'élimination supérieurs à 70% (Metcalfe et al., 2003; Bound et al., 2006; Esplugas et al., 2007). Cependant, puisque ces polluants sont actifs à des concentrations extrêmement faibles (plusieurs dizaines de ng.L^{-1}), des traitements complémentaires doivent être envisagés. Par ailleurs la question du devenir de la fraction non biodégradable et du transfert de pollution doit être soulevée: ces substances ont tendance à se concentrer dans les boues d'épuration, qui peuvent être épandues. Il est donc nécessaire de considérer la nature et l'utilisation des composés afin d'identifier leurs différentes voies d'entrée.

1.2.3 Toxicité des POE

La présence des contaminants dans l'environnement entraîne des interrogations notamment sur les effets qu'ils peuvent avoir sur l'écosystème. Ainsi, de nombreuses études sont effectuées afin d'identifier les effets probables sur la flore et la faune. Dans la littérature, les études de toxicité les plus rencontrées sont les évaluations d'effet de toxicité aigüe. Cette dernière est étudiée *invivo*, chez l'animal après exposition à des doses relativement élevées ou in vitro, avec des tests sur des cultures cellulaires. Les effets des contaminants sur les humains sont difficiles à étudier car l'expérimentation sur l'humain est limitée. L'impact des polluants sur les hommes est, en général, mis en évidence par des études épidémiologiques ou estimé en fonction des tests sur les animaux et les cellules.

Des exemples d'effets mis en évidence sont présentés dans le tableau 1.2 suivant.

Tableau 1. 2 Effets des POEs sur des organismes aquatiques

Composé	Effets	Organimes	Référecens
Anti-inflammatoires (ibuprofène, diclofenac…)	Cytotoxicité Inhibition de la bioluminescence	Truite arc en ciel Vibrio Fischeri	(Mutiyar et al., 2013; Laurenson et al., 2014)

Antibiotique (tétracycline)	Inhibition de la croissance	Algues	(Xie et al., 2011)
Antiépileptique (carbamazépine)	Atténuation humorale et la réponse cellulaire	Poissons	(Basta et al., 2008)
Hormone stéroïde (17β-oestradiol)	Perturbateur endocrinien : Baisse de fécondité, effet sur la différenciation sexuelle	Poissons	(Laurenson et al., 2014)

1.2.4 Réglementation des POE

Les polluants organiques émergents sont des substances d’origine industrielle ou pharmaceutique, susceptibles d'avoir une action toxique à faible dose dans un milieu donné. Selon différentes règlementations et directives, plus d'un millier de substances peuvent être considérées comme micropolluants sur les 100 000 couramment utilisées dans l’industrie, l’agriculture ou pour des usages domestiques. Quant aux polluants émergents, ils ne sont actuellement pas tous inclus dans les réglementations ni dans les programmes de surveillance des milieux aquatiques. Ils ont été identifiés par la communauté scientifique à partir de l'examen de données (éco) toxicologiques et d'occurrence dans l'environnement. Il s'agit notamment des hormones, des additifs pour plastiques, des nouveaux pesticides et de leurs métabolites, des composés pharmaceutiques, des produits de soins corporels ou de tout autre nouveau composé pour lesquels les connaissances actuelles sont insuffisantes pour évaluer le risque de leur présence dans l'environnement.

Les législations sont la conséquence de risques croissants de détérioration de la qualité de l'eau douce et des pénuries d'eau que connaissent différentes régions dans le monde. Une tendance forte vers la réglementation des POE est observée depuis plusieurs années dans plusieurs pays. L’application des législations et des normes est en émergence ou en vigueur selon les problématiques propres à chaque pays.

L’Union européenne fait figure de proue dans la réglementation imposant la réduction progressive des rejets de substances prioritaires, c’est-à-dire celles présentant un risque significatif pour l’environnement aquatique, de même que la suppression des substances "dangereuses prioritaires", c’est-à-dire celles qui sont persistantes, bioaccumulables et toxiques.

En effet, le Parlement européen et le Conseil ont adopté, le 20 novembre 2001, la décision n°2455/2001/CE qui établit une liste de 33 « substances ou groupes de substances prioritaires » dans le domaine de l'eau (directive-cadre européenne sur l'eau (DCE)).

Tableau 1. 3 Liste des substances prioritaires dans le domaine de l'eau (CE, 2001)

1	Alachlore	12	Di(2-éthylhexyl)phtalate	23	Nickel et ses composés
2	Anthracène	13	Diuron	24	Nonylphénols
3	Atrazine	14	Endosulfan	25	4-(para)-nonylphénol
4	Benzène	15	Fluoranthène	26	Pentachlorobenzène
5	Diphényléthers bromés	16	Hexachlorobenzène	27	Pentachlorophénol
6	Cadmium et ses composés	17	Hexachlorobutadiène	28	Hydrocarbures aromatiques polycycliques
7	$C_{10\text{-}13}$-chloroalcanes	18	Hexachlorocyclohexane	29	Simazine
8	Chlorfenvinphos	19	Isoproturon	30	Composés du tributylétain
9	Chlorpyrifos	20	Plomb et ses composés	31	Trichlorobenzène
10	1,2-Dichloroéthane	21	Mercure et ses composés	32	Trichlorométhane
11	Dichlorométhane	22	Naphthalène	33	Trifluraline

Au Canada, il existe la Loi canadienne sur la protection de l'environnement – 1999 (LCPE) qui est l'élément principal du cadre législatif fédéral visant à protéger l'environnement canadien et la santé humaine. La Loi a catégorisé environ 23 000 substances existantes selon leur persistance, leur bioaccumulation et leur toxicité intrinsèque pour l'environnement. En 2012, 393 substances étaient classées « Haute priorité », car elles sont positives sur les trois critères cités ci-dessus.

La Stratégie pancanadienne sur la gestion des effluents d'eaux usées municipales du Conseil canadien des ministres de l'Environnement (CCME) (2009), vise les effluents rejetés dans les eaux de surface par les ouvrages d'assainissement. Plusieurs études sont effectuées dans les effluents au Québec et au Canada par le MDDEFP, Santé Canada et Environnement Canada. Ces tests sont réalisés afin de mesurer les quantités, la dangerosité et la toxicité de différentes substances sur les milieux aquatiques et la santé humaine. En cas de détection d'une substance dangereuse, la plupart des recommandations visent une élimination à la source ou une élimination directement dans l'effluent des usines par le biais d'un traitement adapté.

Au Québec, sur le territoire de l'agglomération de Montréal, l'élimination des eaux usées se fait principalement via les réseaux d'égout municipaux. Les rejets dans les ouvrages d'assainissement et certains cours d'eau sont assujettis aux exigences du Règlement 2008-47 de la Communauté métropolitaine de Montréal (CMM), mais ce sont les municipalités de la CMM qui sont chargées de son application (CMM, 2008). Les normes de rejet de ce règlement sont en vigueur depuis le 1er janvier 2012. Celles-ci visent à prévenir ou à contrôler le rejet, dans les réseaux d'égout ou les cours d'eau, de 62 substances pouvant nuire au bon fonctionnement des ouvrages d'assainissement municipaux (égouts et stations d'épuration) ou pouvant causer préjudice à la qualité de l'environnement. Sur les 62 contaminants inscrits au règlement 2008-47 (CMM, 2008), 14 sont identiques aux 33 substances de la Directive-Cadre européenne sur l’eau (DCE).

1.3 STRATÉGIES ENVIRONNEMENTALES DE TRAITEMENT DES POLLUANTS ORGANIQUES EMERGENTS

Les rejets industriels, urbains et domestiques présentent des caractéristiques physico-chimiques, biologiques et écologiques très variables. Cette diversité explique les efforts consentis actuellement dans la recherche de technologies de traitement adapté à chaque situation. Pour ce faire, des méthodes chimiques, physico-chimiques, physiques et biologiques sont étudiées et leur couplage est souvent envisagé.

1.3.1 Traitements conventionnels

Traitement biologique

Les procédés de décontamination biologiques sont les plus couramment utilisés en assainissement des eaux résiduaires. En effet, ces procédés où les bactéries sont les principaux acteurs de la dégradation sont relativement peu coûteux et aisés à mettre en place. Leur efficacité pour l’élimination des polluants plus difficilement biodégradables peut être améliorée par utilisation de microorganismes spécifiques et par fixation de ceux-ci sur des supports, ce qui leur permet de mieux supporter les chocs toxiques et les débits très variables (Sarayu et al., 2012). Généralement économique, le traitement biologique est choisi lorsque l’effluent contient des composés biodégradables et non toxiques (Guieysse et al., 2014). Deux voies sont possibles pour réaliser la transformation des composés organiques: la voie aérobie si l'oxygène de l'air est associée et la voie anaérobie si la dégradation s'effectue à l'abri de l'air (en milieu réducteur).

Le traitement biologique aérobie est le procédé le plus adéquat pour traiter à grande échelle un effluent constitué de composés biodégradables. Parmi les composés toxiques aromatiques, le phénol est l'un des composés qui a été largement étudié par voie biologique aérobie. La biodégradation de ce composé peut être réalisée avec des boues activées de station d'épuration urbaine (Pant et al., 2007). Des taux de dégradation du phénol de plus de 98% peuvent être obtenus en moins de trois jours (Oller et al., 2011). En revanche, en présence d'effluent à faible concentration de composés biodégradables, le traitement biologique conventionnel n'est pas très efficace, car les vitesses de dégradation sont faibles et les substances à éliminer persistent. Les systèmes d'épuration à biomasse fixée sont particulièrement bien adaptés à l'élimination de composés difficilement biodégradables en faible concentration.

Le traitement anaérobie est très intéressant pour des effluents organiques à forte concentration (DBO > 500 mg L^{-1}) générés par exemple par des industries agroalimentaires. Il offre de nombreux avantages (comparativement au traitement aérobie): faible production de boues qui sont stabilisées, production d'un gaz combustible comme sous-produit, le méthane. La biodégradation des POE par voie anaérobie est moins étudiée. Longtemps considérée comme irréalisable, les récents résultats montrent qu'il y a un potentiel réel des flores anaérobies à dégrader ces composés (Ho et al., 2012; Sarayu and Sandhya, 2012). Des taux de dégradation de 56.4, 36.3, 71.3, 64.6% des estrone (E1), 17β-estradiol (E2), bisphenol A (BPA) et 4-tert-octylphenol (4t-OP) ont été enregistrés par Balest et al. (2008) en appliquant un traitement biologique conventionnel par boue activée. Cependant, en utilisant un traitement aérobie par bio-filtration (biomasse fixée sur un sur support granulaire), le taux d'éliminer peut atteindre 62.2, 68, 91.8, 77.9%, respectivement. Les procédés aérobies favorisent le développement des microorganismes qui décomposent les polluants. Le 17a-ethinylestradiol (EE2) a également été soumis au traitement par voie biologique aérobie en utilisant des bactéries nitrifiantes (De Gusseme et al., 2009). Des taux de dégradation d'EE2 de 99% ont été obtenus en imposant un temps de rétention de six mois avec des eaux usées synthétique ayant une concentration initiale de 8,3 ng L^{-1}.

Traitements physicochimiques

Les traitements physico-chimiques lors du traitement des eaux ou eaux usées ont pour objectif la séparation des particules solides, des huiles, des acides gras... (Lefebvre and Moletta, 2006)

Le processus de coagulation-floculation facilite l'élimination des solides en suspension et des particules colloïdales (Sires and Brillas, 2012). On l'utilise dans l'étape d'une séparation solide-liquide : clarification, flottation ou filtration. La coagulation est la déstabilisation de particules colloïdales par addition d'un réactif chimique. La floculation est l'agglomération de particules déstabilisées en micro floc et ensuite en flocons plus volumineux que l'on appelle flocs. On peut ajouter un autre réactif appelé floculant ou adjuvant de floculation pour faciliter la formation de flocs. Les facteurs qui peuvent améliorer la coagulation-floculation sont le gradient de vitesse, le temps et le pH. Le temps et le gradient de vitesse sont importants pour augmenter la probabilité de chocs entre les particules. Le pH est un facteur très important pour l'élimination des colloïdes (Satyawali and Balakrishnan, 2008). L'exploitation de ces procédés est en général plus coûteuse et ils produisent davantage de boues. Leur principal avantage réside dans leur réponse pratiquement immédiate à toute variation importante de charge. Les traitements physico-chimiques permettent de concevoir des stations compactes et de faible encombrement que l'on rend peu apparentes en les incluant dans des bâtiments fermés.

La filtration membranaire est un procédé physique qui complète ou remplace l'étape de clarification. L'eau circule sous pression à travers des membranes qui peuvent être de nature organique (polymère de synthèse) ou de nature minérale (type céramique). Ces procédés sont classés selon le diamètre des pores sur les parois des fibres (Schafer et al., 2011). Les membranes de microfiltration (de l'ordre de 100 nanomètres) permettent la rétention des bactéries, des parasites, des levures, des particules à l'origine de la turbidité (eau trouble en raison de matières en suspension). Les membranes d'ultrafiltration (de l'ordre de 10 nanomètres) arrêtent en plus les virus, les colloïdes. Les membranes de nano filtration (de l'ordre de 1 nanomètre) retiennent le calcium et la plupart des pesticides (Ersahin et al., 2012; Ylitervo et al., 2013). Enfin, l'osmose inverse utilise des membranes plus denses (de l'ordre de 0,1 nanomètre) qui stoppent aussi les ions métalliques. Cette dernière technique est appliquée au dessalement de l'eau de mer et à la production d'eau ultra pure et d'eau de processus (Ersahin et al., 2012).

Le charbon actif en grain est largement utilisé pour la filtration gravitaire rapide ou lente (filtres sandwich) dans des adsorbeurs fixes ou mobiles. Le traitement par filtre charbon actif est basée sur d'absorber les matières organiques. Les polluants organiques de l'eau sont par nature très variés allant de micropolluants tels que des pesticides aux substances organiques naturelles (Delgado et al., 2012; Mezohegyi et al., 2012). Le traitement de l'eau nécessite alors l'utilisation d'un charbon actif en grain dont la structure poreuse permet l'adsorption de cette large gamme de composés (Suhas et al., 2007). Le charbon actif en grain (CAG) doit posséder un nombre de pores suffisants afin que les molécules puissent être transportées vers les sites d'adsorption. Lorsque le charbon actif est saturé, il convient de le changer.

Différents procédés physicochimiques ont été proposés pour l'élimination des POEs de type pharmaceutiques. Une étude récente de Vergili (2013) utilisant un procédé de nano filtration (membrane de type FM NP010) a été effectuée pour le traitement d'eau potable artificiellement contaminée par la carbamazépine (CBZ), le diclofénac (DIC) et l'ibuprofène (IBU). Des taux d'élimination de CBZ variant entre 31 - 39% ont été enregistrés, alors que des pourcentages d'élimination se situant entre 55 et 65% ont été enregistrés pour le DIC et le IBU et ce, en imposant une pression hydrostatique de 12 bar et une vitesse de circulation de 3 L min^{-1}. L'adsorption sur charbon actif a également été étudiée pour l'élimination de différents types de POEs (17α-ethinyl estradiol (EE2), 5-fluorouracil (5-Fu), Cytarabine (CytR)) (Kovalova et al., 2013). Un taux d'enlèvement allant jusqu'à 90% a été enregistré pour chaque polluant en injectant respectivement une concentration de charbon actif de 18, 70, and 87 mg L^{-1} en fonction du type de polluant étudié. Il est important de mentionner que les traitement physicochimiques ne dégradent par les polluants, mais se limitent à transfert de polluant d'une phase à une autre.

1.3.2 Traitements alternatifs

Les traitements conventionnels ne permettent pas une élimination complète des polluants émergents. Initialement, les stations de traitement des eaux usées ont été construites pour l'abattement du phosphore, de l'azote, des composés carbonés arrivant à des concentrations de l'ordre du mg L^{-1} (Drogui et al., 2007). Les traitements conventionnels des stations épurations ne sont pas adaptés aux polluants émergeants. Avec pour objectifs de réduire les effets sur l'environnement causés par les polluants rejetés par les effluents des stations d'épuration, différents procédés dits 'Procédés d'Oxydation Avancés' (POA) ont été plus spécifiquement étudiés et développés. Le principe des POA repose sur la formation d'espèces radicalaires oxydantes réactives, les radicaux qui pourront décomposer les molécules biorécalcitrantes et les rendre potentiellement plus biodégradables ou les transformer en composés minéraux (Sarayu and Sandhya, 2012). Par exemple, les radicaux hydroxyles peuvent oxyder un grand nombre de composés organiques avec une vitesse d'oxydation largement supérieure à celle de l'ozone (109 fois plus élevée) (Ternes et al., 2003; Esplugas et al., 2007). Les radicaux libres sont des espèces hautement actives susceptibles de réagir avec la quasi-totalité des molécules organiques. Ces composés réagissent avec les doubles liaisons –C=C- et attaquent les noyaux aromatiques, composants majeurs des composés réfractaires (Gogate et al., 2004). Ces POA ont été appliqués pour la décoloration des eaux (Hsing et al., 2007), la dégradation de produits phytosanitaires et pharmaceutiques ((Ikehata et al., 2006), le traitement des eaux usées industrielles (Martinez-Huitle et al., 2006a), le traitement de lixiviat d'enfouissement sanitaire et pour le traitement de boues municipales (Flotron et al., 2003), etc. Ces techniques peuvent être employées soit comme technique de prétraitement oxydatif conduisant à des composés facilement biodégradables, soit comme méthode de traitement tertiaire pour l'élimination ou la minéralisation complète des polluants résiduels (Drogui et al., 2007; Ho et al., 2012). La plupart de ces technologies ont été développées et appliquées qu'à l'échelle laboratoire, d'autres par contre comme le couplage O_3/H_2O_2 ont fait leur preuve à l'échelle industrielle.

Les procédés photochimiques

Au cours des années récentes, les technologies photochimiques sont devenues très attractives et sont susceptibles de remplacer les techniques de traitement conventionnelles telles que la biodégradation et l'adsorption sur charbon actif. Les procédés photochimiques basés sur les radiations UV sont simples d'utilisation, propres et peu couteuses (Kumar, 2011). De plus, ces technologies ont la particularité d'assurer à la fois la désinfection et le traitement des contaminants. Lors de la photolyse directe, les radiations UV absorbées par les molécules de l'eau permettent la génération des espèces oxydantes puissantes telles que les radicaux hydroxyles (·OH) et le peroxyde d'hydrogène (H_2O_2) (Ishihara et al., 2007). Cependant, l'application des radiations UV lors du traitement des eaux usées est généralement affectée par plusieurs facteurs tels que la qualité des eaux, le coût de la maintenance ainsi que le coût énergétique (Grabowska et al., 2012). Liu et al. (2004) ont démontré le potentiel de la photochimie pour la dégradation de divers types de POEs tels que l'Estrone et le 17β-estradiol

(3-20 mg L^{-1}). Un taux de dégradation jusqu'à 50% pour l'Estrone et 90% pour le 17β-estradiol a été enregistrée pour chacun des polluants sous irradiation UV (λ= 254 nm, 30 W).

Couplage peroxyde/ultraviolet (H_2O_2/UV) et couplage ozone/ultraviolet (O_3/UV)

Le couplage avec peroxyde/ultraviolet est basé sur la formation des radicaux hydroxyles suite à la photolyse du peroxyde d'hydrogène présent en solution. Les études récentes sont plus focalisées vers le couplage des radiations UV avec des oxydants puissants tels que l'ozone et le peroxyde d'hydrogène (UV/H_2O_2, UV/O_3). L'irradiation à des longueurs d'ondes comprises entre 200 nm et 300 nm provoque une coupure homolytique de la liaison O-O de la molécule de H_2O_2 et conduit à la formation de radiaux hydroxyles (Benitez et al., 2004; Kim et al., 2008). La vitesse de production des radicaux libres dépend de plusieurs facteurs dont le pH, la dose du H_2O_2 ainsi que les caractéristiques des lampes UV. En particulier, Vogna et al. (2004a) en appliquant la technique du couplage peroxyde/ultraviolet à des eaux synthétique contenant le CBZ obtiennent des taux d'élimination de CBZ de 100% et de 35% de COT après 4 min de traitement (lampe à 254nm, 5mmol H_2O_2 L^{-1}, pH 5). Une autre étude effectuée par le même auteur a également permis de démontrer les performances épuratoires (100% de dégradation) sur le diclofénac en imposant un pH7, une concentration de 0,1 à 1,0 mmol H_2O_2 L^{-1} en présence d'UV (254nm, 17W) (Vogna et al., 2004b).

Il y a aussi un grand intérêt dans l'utilisation de couplage avec l'ozone pour traiter des effluents médicamenteux de type pharmaceutique. Par comparaison à d'autres espèces oxydantes (H_2O_2, HClO, etc), l'ozone est un oxydant très puissant (E° = 2.07 V) qui a été largement utilisé pour la désinfection des eaux potables mais son application dans les filières de traitement des eaux usées reste très limitée du au coût énergétique très élevé (Benitez et al., 2004). En solution, l'ozone est capable d'oxyder les polluants par voie directe et indirecte. Le couplage de l'ozone avec les radiations UV (O_3/UV) conduit à la production de radicaux libres qui sont des espèces oxydantes très réactives et efficaces pour éliminer les polluants organiques réfractaires (Meunier et al., 2006). L'application d'un procédé d'ozonation (10 mg O_3 L^{-1}) en couplage avec les radiations UV (238-366 nm) a assuré également une dégradation totale de sulfaméthoxazole (10^{-4} mol L^{-1}) après 10 min de traitement (Beltran et al., 2009).

Couplage réactif de Fenton/ultraviolet (Fe^{2+}/H_2O_2/UV)

Le procédé photo-Fenton est un POA hybride qui utilise une source de radiation (généralement l'UV) pour augmenter le taux de production de radicaux hydroxyles en stimulant la réduction du Fe^{3+} en Fe^{2+} (Schrank et al., 2005). La combinaison entre le procédé Fenton (H_2O_2/Fe^{2+}) et les radiations UV permet de décomposer par photolyse le peroxyde d'hydrogène pour former des radicaux hydroxyles mais aussi d'augmenter l'activité catalytique du fer (De la Cruz et al., 2012). Néanmoins, la dose du fer et du peroxyde d'hydrogène utilisée dans la réaction photo-Fenton est un paramètre important qui détermine l'efficacité du procédé. Il faut également tenir compte des caractéristiques spectrales et de la puissance des lampes utilisées, de leur encrassement, de la turbidité des effluents limitant le parcours des rayonnements ainsi que des coûts d'installation et de fonctionnement supplémentaires (Kumar, 2011; De la Cruz et al., 2012). Le procédé photo-Fenton a été efficacement utilisé par Shemer et al. (2006) pour le traitement de la Métronidazole (6.0 µg L^{-1}) présent dans une eau dé-ionisée. Des taux de dégradation se situant entre 36 et 94% ont été enregistrés en utilisant le système UV/H_2O_2/Fe^{2+}, alors que des taux compris entre 43 et 76% ont été obtenus avec le système H_2O_2/Fe^{2+}.

Procédé photocatalytique

L'application de la photocatalyse hétérogène pour le traitement des effluents contaminés des polluants organiques émergents reçoit un intérêt grandissant. Cette technologie est basée sur l'irradiation d'un catalyseur, en général un semi-conducteur (ex.TiO_2, ZnO) qui peut être photo-excité pour former des sites électro-donneurs et des sites électro-accepteurs et ainsi induire des réactions d'oxydoréduction (Lin et al., 2012). Sous irradiations UV, si les photons absorbés possèdent une énergie supérieure au gap d'énergie (> 3.2 eV pour le TiO_2) entre la bande de valence (BV) et la bande de conduction (BC) de TiO_2, des pairs électrons-trous se créent dans le semi-conducteur. Les électrons photo-générés dans la BC favorisent la réduction de l'oxygène en radicaux superoxydes, alors que les trous photo générés dans la BV peuvent oxyder directement le contaminant adsorbé ou alors oxyder les groupes hydroxyles à la surface de TiO_2 pour former des radicaux hydroxyles (Adeli et al., 2013). La dégradation de polluants contenus dans les eaux usées peut ainsi s'effectuer directement à la surface du semi-conducteur ou indirectement en interagissant avec des radicaux hydroxyles (Lin et al., 2012). Par exemple, le procédé photochimique utilisant une lampe de xénon de 150W a été testé pour la dégradation de la CBZ à pH 7 pendant 90min. Un taux de dégradation de 20% a été enregistré avec une eau synthétique artificiellement contaminée à la CBZ (C_0= 1 mg L^{-1}), alors qu'un pourcentage de dégradation de 35% a été enregistré pour une eau de surface contaminée par la CBZ (C_0= 1 mg L^{-1}) (Avisar et al., 2013). Une autre étude portant sur le traitement photo-catalytique d'une eau usée contaminée par la CBZ (C_0= 5 mg L^{-1}) a été effectuée par Chong et al. (2011b). Une concentration de catalyseur de TiO_2 de 1g L^{-1} en présence d'une lampe UVC a été utilisée pendant un temps de traitement de 60 min. Un taux d'abattement de CBZ jusqu'à 61 % a été enregistré, alors que 70% du TOC a été éliminé.

Le tableau 1.4 suivant présent quelque performances des procédés pour la dégradation des POEs.

Tableau 1. 4 Performances de quelques procédés pour la dégradation de POEs de type pharmaceutique

Procédés	Type de Matrice	Polluant	Conditions opératoires	Résultats et commentaires	Références
Nano filtration	Eau portable	Carbamazepine, CBZ ($0.025\ \mu g\ L^{-1}$) Diclofenac, DIC ($0.05\ \mu g\ L^{-1}$) Ibuprofen, IBU ($0.1\ \mu g\ L^{-1}$)	Nano filtre membranaire type FM NP010, pression de 12 bars, le débit est 3 L min^{-1} à 25^oC.	Taux d'éliminer varies entre 31 - 39% pour CBZ et 55-61% pour DIC et IBU	(Vergili, 2013)
Photo dégradation, verre de TiO_2 revêtu dopé à l'azote	Solution synthétique et eau de surface	Carbamazepine, CBZ ($1.0\ mg\ L^{-1}$)	pH=7 (buffer Na_2HPO_4/NaH_2PO_4); irradiation par une lampe à xénon 150W) pour 90 min.	Taux de réduction est de 20% pour eau synthétique et 35% pour eau de surface	(Avisar et al., 2013)
Hydrodynamic acoustique cavitation	Solution synthétique	Carbamazepine, CBZ ($5\ \mu g\ L^{-1}$)	Plaque à orifice de 12mm, fréquence 24KHz, amplitude de fréquence 125µm, 180 min de traitement.	Taux de dégradation de CBZ est de 96% (15 min). Taux de minéralisation (TOC) est de 20% (180min)	(Braeutigam et al., 2012a)
Sonochimie combiné avec Fenton procédé	Solution synthétique	Carbamazepine, CBZ ($10\ mg\ L^{-1}$)	Ultrason à fréquence 24KHz, pH = 3-9, Fe^o additive (0,44-3,57 mM)	100% CBZ éliminé à pH 3 après 30 min. 90% CBZ éliminé à pH5 après 60 min.	(Ghauch et al., 2011)

Photo degradation	Eau usée	Carbamazepine, CBZ (5 mg L^{-1})	Mélangé avec TiO$_2$ catalytique (1g L^{-1}) pendant 30 min, irradiation par une lampe à UVC pour 60 min	70% DOC réduction après 10,5 h de traitement pour un volume de 7L.	Chong et al., 2011
Electrochimie	Solution synthétique	Carbamazepine, CBZ (50 mg L^{-1})	BDD électrode, curent intensité appliqué de 0-320 mA cm^{-2}, Na$_2$SO$_4$ électrolyte (0,48 M)	100% CBZ éliminé à pH9, 190mA cm^{-2}, débit de 1,25 cm^3 min^{-1}.	Dominguez et al., 2010)
Sonochimie	Eau usée	Diclofenac (2,5mg L^{-1}) CBZ (2,5, 5 et 10 mg L^{-1}) Amoxicilline (2,5 et 5 mg L^{-1})	Puissance ultrason de 25-100W. Température 24°C. pH 7,5.	Taux d'élimination de TOC est 11% après 30 min. Taux d'élimination de DC0 =19% (60 min). BOD5 augmenté de 5 à 10 mg L^{-1}	(Naddeo et al., 2009c)
Electrochimie	Eau synthétique	Paracetamol (N-(4-hydroxyphenyl)acetamide, 1g L^{-1})	pH 2 – pH 12 curent intensité de 100-450 mA. anode BDD, cathode graphite.	À 300 mA, complète minelisation après 120, 150 et 240 min pour une concentration initiale de 78, 157 et 315 mg L^{-1}, respectivement.	(Brillas et al., 2005)
Biologique traitément	Eau usée	Estrone (E1), 17β-estradiol (E2),	Concentration de biomasse (40 g L^{-1}).	Après 4 mois d'opération, 62,2% de E1, 68% de E2,	(Balest et al., 2008)

		biphenyl A (BPA), 4-tert-octylphenol (4t-OP)	Rétention temps de 6 mois.	91.8% de BPA et 77.9% de 4t-OP sont été éliminé.	
Biologique membrane réacteur	Eau du robinet	17a-ethinylestradiol (EE2) (83 ng EE2 L^{-1})	Nitrifier enrichment culture, débit: 6,9 Lm^{-2} h^{-1}. Opimal NH_4 concentration 1,0 mg L^{-1}.	Taux d'élimination de EE2 est 99% avec taux de charger 208 ng L^{-1} j^{-1}.	(De Gusseme et al., 2009)
Charbon activé	Eau usée	17a-ethinyl estradiol (EE2) 5-fluorouracil (5-Fu) Cytarabine (CytR)	Granule charbon active, mix avec eau contaminé pendant 16h à $20^{o}C$ puis filtré.	Pour enlever 90% de polluant EE2, 5-Fu et CytR, 18, 70, and 87 mg L^{-1} de GCA a besoin, respective.	(Kovalova et al., 2013)
Électrochimie	Eau synthétique	17a-ethinylestradiol (EE2) (0,5 à 10 mg EE2 L^{-1})	$TiSnO_2$ électrode 20x30mm, électrolyte Na_2SO_4 0,2 M, intensité de courant 10 mA cm L^{-1}, temp= $20^{o}C$,	Taux d'élimination de EE2 est de 0,019 min^{-1} à 0,112 min^{-1}. Taux de réduction de COT est de 78% après 8h de traitement.	(Feng et al., 2010)
Sonochimie	Eau synthétique	Ibuprofen	Acoustique puissance 20-80W Fréquence 300 kHz Température $20^{o}C$ Temps 30 min.	Taux d'élimination de 1,35 et 6,1 mmol $L^{-1}min^{-1}$ initiale concentration de 9,7 mmol L^{-1} et 101 mmol L^{-1}.	(Mendez-Arriaga et al., 2008b)

1.4 OXYDATION SONO-ÉLECTROCHIMIQUE DE POLLUANTS ORGANIQUES ÉMERGENTS DE TYPE PHARMACEUTIQUE.

L'application des procédés sono-électrochimiques visant à la protection de l'environnement a déjà montré son efficacité dans l'élimination de polluants organiques (Leite et al., 1999; Abdelsalam et al., 2002; Walton et al., 2003; Esclapez et al., 2010; Saez et al., 2011; de Vidales et al., 2013). Cette partie décrit le principe de fonctionnement du procédé en s'appuyant sur le mécanisme et les facteurs affectant l'oxydation sono-électrochimique.

1.4.1 Spécificité des techniques d'oxydation électrochimique

L'intérêt des techniques électrochimiques réside dans leur aspect non polluant, leur facilité d'automatisation qu'elle apporte ainsi que leur capacité d'action à deux niveaux sur les polluants cibles, laquelle capacité leur confère à priori un avantage par rapport aux procédés conventionnels d'oxydation chimique. En effet, l'oxydation électrochimique de composés organiques peut s'effectuer soit exclusivement sur l'électrode (*effet direct*) et/ou par génération *in situ* d'un oxydant en solution (*effet indirect*) (Chaplin, 2014). Il est aujourd'hui admis que l'action directe d'oxydation anodique des produit organiques s'effectue en deux étapes (Comninellis, 1994). Premièrement, une décharge anodique de la molécule d'eau est obtenue avec formation du radical hydroxyle (OH°) adsorbé sur des sites actifs de l'électrode M suivant la réaction **Eq. 01:**

$$H_2O + M \rightarrow M[OH^\circ] + H^+ + e- \qquad \textbf{Équation 1}$$

Par la suite, le polluant organique R est oxydé par les radicaux libres adsorbés suivant la réaction **Eq. 02**:

$$R + M[OH^\circ] \rightarrow M + RO + H^+ + e- \qquad \textbf{Équation 2}$$

où RO représente le produit organique oxydé qui peut être davantage oxydé par les radicaux hydroxyles qui sont continuellement formés par la décharge anodique de l'eau. Les radicaux libres sont des espèces capables d'oxyder plusieurs molécules organiques complexes, non oxydables chimiquement ou difficilement oxydables (Pulgarin et al., 1994), telles que les composés organiques émergents (Alsheyab et al., 2009). Il s’agit d’espèces hautement actives susceptibles de réagir avec la quasi-totalité des molécules biologiques. Ces radicaux libres réagissent avec les doubles liaisons -C=C- et attaquent les noyaux aromatiques, composants majeurs des hydrocarbures aromatiques poly-insaturés (Comninellis, 1994; Pulgarin et al., 1994). Ainsi, l’oxydation anodique peut conduire à l’oxydation totale des polluants organiques (dégagement de CO_2 et formation de H_2O) ou à la formation de composés plus simples, non toxiques et biodégradables (Comninellis, 1992). En revanche, des réactions anodiques compétitives (réactions parasites) peuvent se dérouler et limiter la formation de ces radicaux libres, telle que la réaction de formation de l’oxygène moléculaire.

$H_2O + M[OH^\circ] \rightarrow M + O_2 + 3H^+ + 3e-$ **Équation 3**

L’action indirecte de l’électrolyse est également intéressante pour oxyder des composés organiques réfractaires. En effet, en présence d’ions sulfates et d’ions chlorures, ceux-ci peuvent être oxydés à l’anode et formés respectivement en solution l’acide persulfurique ($H_2S_2O_8$) et l’acide hypochloreux (HClO), des oxydant puissants capables d’oxyder ou de modifier la structure des molécules organiques réfractaires (Canizares et al., 2002) et conduire ainsi à la formation de composés plus oxydés.

$2SO_4^{2-} + 2H^+ \rightarrow H_2S_2O_8 + 2e-$ **Équation 4**

$Cl^- + 2H_2O \rightarrow HClO + H_3O^+ + 2e-$ **Équation 5**

Aussi, lors de l’électrolyse, il est possibles de générer *in situ* le peroxyde d’hydrogène (H_2O_2) par réduction cathodique de l’oxygène dissous (Drogui et al., 2007) :

$O_{2(dissous)} + 2H^+ + 2e- \rightarrow H_2O_2$ **Équation 6**

La production *in situ* d’oxydant en solution lors de l’électrolyse ainsi que la formation de radicaux libres sur des sites actifs de l’électrode n’est pas observée dans toutes les cellules électrolytiques. Ces réactions dépendent de plusieurs paramètres dont le type et la structure des électrodes sont proposés dans les sections suivantes, des critères globaux de mesure d’efficacité épuratoire et quelques paramètres opératoires pouvant grandement influencer l’élimination des polluants organiques émergeant.

1.4.2 Spécificité des techniques d'oxydation sonochimique

Les ultrasons sont de plus en plus utilisés en milieu industriel pour notamment accélérer ou activer un mécanisme réactionnel. L'intérêt des ultrasons réside dans leur aspect non polluant et leur facilité d'automatisation. En milieu aqueux, les ultrasons peuvent agir suivant deux modes d'action, soit par action chimique (indirecte) ou encore par une action physique (directe). L'action indirecte, souvent obtenue à hautes fréquences (100-1000 kHz) (Fig. 1-1), conduit à la génération de radicaux libres ($HO\cdot$, $HO_2\cdot$ et $O\cdot$) induite par rupture homolytique de la molécule d'eau ou d'oxygène (Gogate, 2007; Leong et al., 2011; Pang et al., 2011). Aussi, à hautes fréquences, les ultrasons peuvent provoquer la formation de peroxydes dans l'eau. Les radicaux libres sont des espèces hautement actives susceptibles de réagir avec la quasi-totalité des molécules biologiques (Naffrechoux et al., 2000; Rooze et al., 2011).

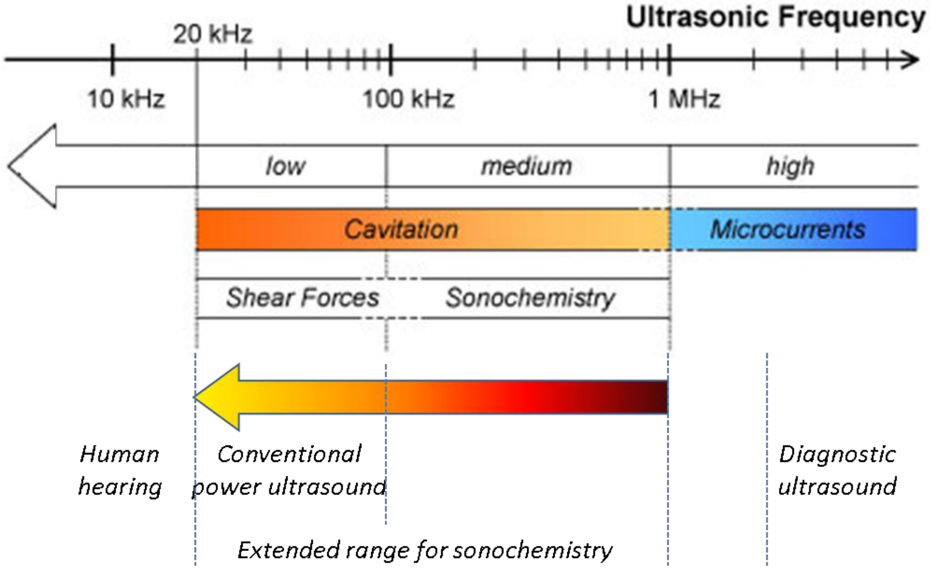


Figure 1. 1 **Schéma des fréquences sonores (Leong et al., 2011)**

De plus, ils réagissent avec les doubles liaisons -C=C-, composants majeurs des POE. Ainsi, les ultrasons peuvent s'appliquer à l'élimination des composés organiques réfractaires présents dans les eaux (Naffrechoux et al., 2000). L'action directe induite par les ultrasons est également intéressante pour le traitement des eaux. Aussi, les ultrasons peuvent avoir dans l'eau des effets biocides induits par ces phénomènes de cavitation qui brisent les cellules bactériennes (Gonze et al., 1999).

À haute fréquence, les ultrasons peuvent provoquer la formation de peroxydes dans l’eau. L’action directe induite par les ultrasons est également intéressante pour le traitement d’effluents industriels. En effet, les ultrasons génèrent des bulles de cavitation, créant ainsi des micro-jets de liquide et des forces de cisaillement très puissantes lors de leur implosion, lesquelles sont favorables à une meilleure homogénéisation du milieu réactionnel (Sinisterra, 1992; Gonze et al., 1999). Aussi, les ultrasons peuvent avoir dans l’eau des effets biocides induits par ces phénomènes de cavitation qui brisent les cellules bactériennes. Lorsqu’une bulle de cavitation s’effondre (implosion), cela entraîne une élévation locale de température de plusieurs milliers de degrés (2 000 à 5 000 °C) et une pression de plusieurs centaines d’atmosphère (500 atm) (Fig. 1-2). Dans ces conditions extrêmes, des radicaux issus de la sonolyse de l’eau sont alors éjectés dans le milieu où ils vont réagir avec les composés en solution.

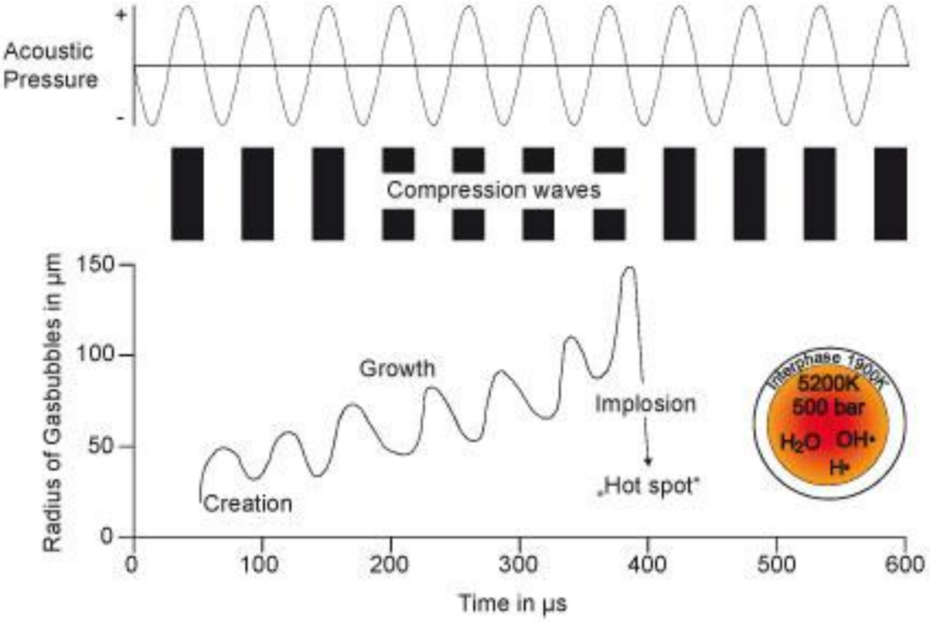


Figure 1. 2 **La formation, la croissance, et l'implosion d'une bulle de cavitation (Leong et al., 2011)**

Les bulles de cavitation agissent alors comme des microréacteurs. Les mécanismes contrôlant la destruction dépendent de la nature du polluant, mais aussi de l’intensité de la cavitation, soumise elle-même aux conditions opératoires du réacteur sonochimique. Le processus de cavitation utilisé en traitement des eaux est réalisé en utilisant des ondes sonores de fréquences variant entre 16 kHz et 3 MHz (Chowdhury et al., 2009).

Le processus de cavitation dépend de plusieurs paramètres tels que la fréquence ultrasonore, l'intensité, la composition de l'effluent et le type de réacteur. Le phénomène de cavitation repose sur deux composantes essentielles, le milieu liquide et la source de vibrations de haute énergie (Sinisterra, 1992; Tudela et al., 2014). Le milieu liquide est nécessaire car la sonochimie est dirigée par la cavitation acoustique se produisant uniquement dans un liquide. La fréquence et l'amplitude des ondes ultrasonores générées par l'émetteur (sonde ultrasonore) sont des paramètres déterminants pour l'efficacité de dégradation des polluants. Les valeurs optimales de fréquence et d'amplitude, afin d'avoir la meilleure efficacité de traitement, dépendent des caractéristiques de l'effluent à traiter (type de polluants, concentration, etc.) ainsi que des conditions opératoires (volume du réacteur, temps de traitement, etc.) (Asakura et al., 2008; de La Rochebrochard et al., 2012; Tudela et al., 2014). L'objectif, dans le cas du traitement des eaux usées contenant des composés persistants, est de produire un maximum de radicaux libres. Des études récentes ont montré qu'à fréquence peu élevée (de 20 à 100kHz), l'intensité de la cavitation augmente impliquant alors une plus grande formation de radicaux libres et donc une meilleure efficacité de dégradation des composés à l'intérieur de la bulle de cavitation (Asakura et al., 2008; de La Rochebrochard et al., 2012). La durée de vie des bulles de cavitation augmente et donc une certaine proportion des radicaux libres formés se recombinent pour former de l'eau et n'ont donc pas le temps d'être efficaces. Les propriétés physicochimiques de l'effluent (pression de vapeur, tension superficielle, viscosité, présence d'impuretés/gaz, etc.) affectent de manière importante les performances du processus sonochimique (Chowdhury and Viraraghavan, 2009). En effet, la taille et le nombre des bulles de cavitation produites dépendent des propriétés du liquide. L'idéal est de minimiser la puissance nécessaire au déclenchement du phénomène de cavitation (en modifiant les propriétés physico-chimiques) pour que l'énergie nécessaire à la croissance et à l'effondrement des bulles de cavitation soit maximale, ce qui induirait une augmentation de la pression d'implosion. En outre, la dégradation sonochimique des polluants est plus efficace à faible concentration. De nombreuses études ont montré l'efficacité des procédés d'oxydation sonochimique pour dégrader certains composés organiques présents dans les eaux usées (Sinisterra, 1992; Pulgarin et al., 1994; Gonze et al., 1999; Chowdhury and Viraraghavan, 2009).

1.4.3 Les intérêts du couplage sonochimie et électrochimie

Dans le but de minimiser les dépenses énergétiques, les procédés oxydation avancée peuvent être utilisés en synergie avec des procédés sonochimiques. Les ultrasons sont capables de modifier la structure des molécules et des matières particulaires présentes dans les eaux. Sachant que certains polluants organiques peuvent être solidement liés à ces particules, l'action directe des ultrasons (formation de bulles de cavitation) peut contribuer à briser ces liaisons et faciliter ainsi la mise en solution de ces polluants de type organique lors du traitement d'oxydation avancée. Aussi, certains métaux toxiques peuvent former avec des composés organiques, des molécules très complexes (complexes organométalliques) (Petronio et al., 1993), lesquels peuvent être à l'origine de faibles rendements d'oxydation des polluants organiques dans les eaux résiduaires (Drogui et al., 2007). L'action indirecte des ultrasons (génération de radicaux libres), permettrait d'oxyder efficacement ces molécules réfractaires et de libérer ainsi les métaux initialement piégés. Ils permettent de désolidariser les bactéries des solides ou des agglomérats bactériens, lesquels assurent leur protection.

Walton et al. (1995) ont étudié l'effet synergique des ultrasons et de l'électrolyse par voltamétrie cyclique à l'aide d'un Potentiostat/Galvanostat (Fig. 1-3). L'intensité de courant a été majoré de deux à trois fois lorsque des fréquences de 25 et 800kHz sont respectivement appliquées.

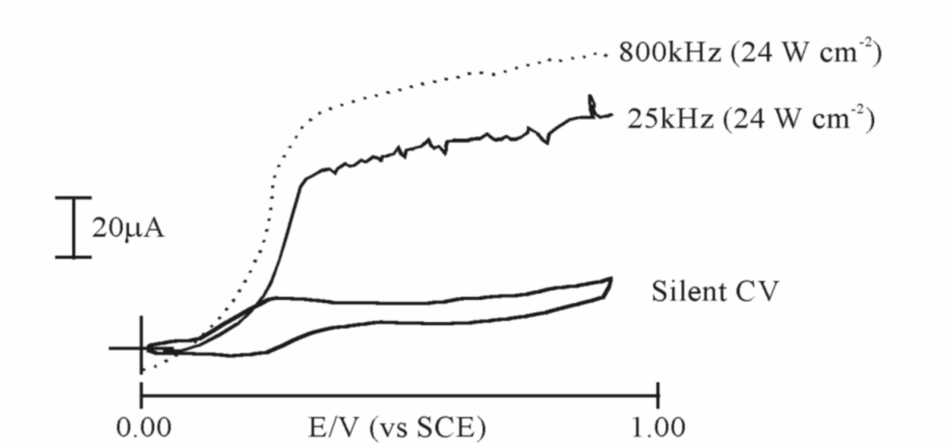


Figure 1. 3 Effet de la fréquence des ultrasons sur le ferricyanure.

En particulier, couplés avec les techniques électrolytiques, les ultrasons devraient contribuer à améliorer le transfert de matière électrode –électrolyte. Ils devraient également contribuer à éliminer simultanément des débris fixés à la surface des électrodes ainsi à réduire la chute ohmique et minimiser la consommation énergétique (Hardcastle et al., 2000; Esclapez et al., 2010; Ren et al., 2013a).

1.5 HYPOTHÈSES - OBJECTIFS DE RECHERCHE ET DÉMARCHE EXPÉRIMENTALE

1.5.1 Hypothèse

Dans l'optique de protéger le milieu récepteur, il est nécessaire d'intégrer dans la filière de traitement de ces eaux usées une étape supplémentaire visant à dégrader ces -POE. De ce point de vue, les techniques combinaisons d'oxydation électrochimique et d'oxydation sonochimique avancés sont particulièrement intéressantes. Au cours de l'électrolyse, il est fréquent d'observer une baisse des performances d'épuration due à la fixation de sous-produits d'oxydation sur la surface des électrodes (réduction de la surface active) (Compton et al., 1994; Zhao et al., 1997; Vuorema et al., 2008). La combinaison des ultrasons aux procédés électrolytiques devrait permettre de limiter ce phénomène et de majorer les performances épuratoires des eaux résiduaires contaminées par des POE et autres polluants inorganiques et microbiens. Les ultrasons peuvent agir suivant deux modes d'action, soit par action chimique (indirecte) ou encore par une action physique (directe). L'action indirecte, souvent obtenue à hautes fréquences, conduit à la génération de radicaux libres ($HO\cdot$, $HO_2\cdot$ et $O\cdot$) induite par rupture homolytique de la molécule d'eau ou d'oxygène (Chowdhury and Viraraghavan, 2009; Bremner et al., 2011; Mason, 2012). Les radicaux libres sont des espèces hautement actives capables de réagir avec les doubles liaisons -C=C- et d'attaquer les noyaux aromatiques, composants majeurs des POE (Mahamuni et al., 2010; Mason, 2011).

1.5.2 Objectifs

Objectif global

L'objectif général de cette étude consiste à concevoir, tester et optimiser un procédé de traitement d'oxydation sono-électrochimique US-EO (combinaison de procédés d'ultrason (US) et d'électro-oxydation (EO)) à l'échelle du banc d'essai en laboratoire pour le traitement des eaux et effluents résiduaires contenant des polluants organiques émergents (POE) de type pharmaceutique tels que la carbamazépine (CBZ), l'Ibuprofène (IBU) et la Chlorotétracycline (CTC).

Objectifs spécifiques

Les objectifs spécifiques de cette thèse sont les suivantes :

- Évaluer la capacité d'une cellule US-EO à produire *in situ* des oxydants radicalaires (ex. OH°, etc.) pour le traitement des eaux usées contaminées par des résidus médicamenteux.
- Évaluer une méthodologie statistique de plan d'expériences permettant d'évaluer le comportement épuratoire du procédé US-EO et d'optimiser les conditions de fonctionnement pour la dégradation des POEs de type pharmaceutique.
- Démontrer par une batterie de tests, l'effet synergique des procédés US-EO contribuant à minimiser le dépôt de films polymériques sur la surface des électrodes.
- Identifier les sous-produits d'oxydation et proposer un mécanisme réactionnel de dégradation par voie sonoélectrochimique.
- Valider les performances épuratoires du procédé US-EO sur un effluent réel de type municipal artificiellement contaminé par la CBZ, IBU et CTC.

1.5.3 Originalité de l'étude

L'originalité de ce projet de recherche se situe à plusieurs niveaux. Si les procédés d'oxydation électrolytiques (EO) et sono-chimique (US) ont été séparément étudiés par plusieurs auteurs, la combinaison des deux procédés dans un même réacteur (procédés US-EO) n'a pas encore été amplement explorée et constitue l'intérêt principal de ce projet de recherche. L'intérêt de développer des techniques hybrides profitant de la synergie des mécanismes sono-électrochimique réside dans leur aspect non polluant, leur facilité d'automatisation ainsi que leur capacité d'action à deux niveaux sur les polluants (action directe et indirecte). Bien que des études récentes ont exploité les procédés d'oxydation sono-électrochimique pour la dégradation des polluants organiques réfractaires tels que le phénol, 4-chlorophénol, per-chloroéthylene, alkyl benzène sulfonâtes, etc., cette technique n'a pas été appliquée pour le traitement des effluents contaminés par des POEs de type pharmaceutique comme CBZ, IBU ou CTC. Ce travail contribuera donc à élargir les applications des procédés US-EO, une technologie propre et pouvant être économiquement rentable dans l'industrie des technologies environnementales. En somme, l’originalité de la thèse consiste à *développer un procédé hybride US-EO innovant pour la dégradation des contaminants d’intérêt émergents de type pharmaceutique*.

1.5.4 Démarche méthodologique

Les premiers travaux ont consisté en la conception et au montage de la cellule du procédé US-EO. La partie subséquente portait sur l’évaluation et la caractérisation de la cellule US-EO en termes de sa capacité de production des oxydantes radicalaires (notamment HO·, etc.). Par la suite, la performance du procédé US-EO a été évaluée sur une solution synthétique artificiellement contaminée par la CBZ. Les performances épuratoires du procédé hybride US-EO ont été comparées avec les procédés d’ultrasons (US) et d’électro-oxydation (EO) utilisés séparément. Par la suite, l’optimisation du système US-EO pour la dégradation du CBZ a été effectuée grâce à une stratégie expérimentale basée sur une étude quantitative des facteurs (matrice factorielle), suivie du plan de surface de réponse (plan central composite). Subséquemment, le procédé US-EO a été testé pour la dégradation de la CBZ dans un effluent réel de type municipal. Finalement, dans l’optique d’étendre son spectre d’activité, le procédé US-EO a été testé pour la dégradation de deux autres polluants de type pharmaceutique, l’Ibuprofène (IBU) et la chlortétracycline (CTC) couramment rencontrés dans les eaux usées résiduaires. Une description schématique de la démarche méthodologique est présentée à la Fig. 1.4.

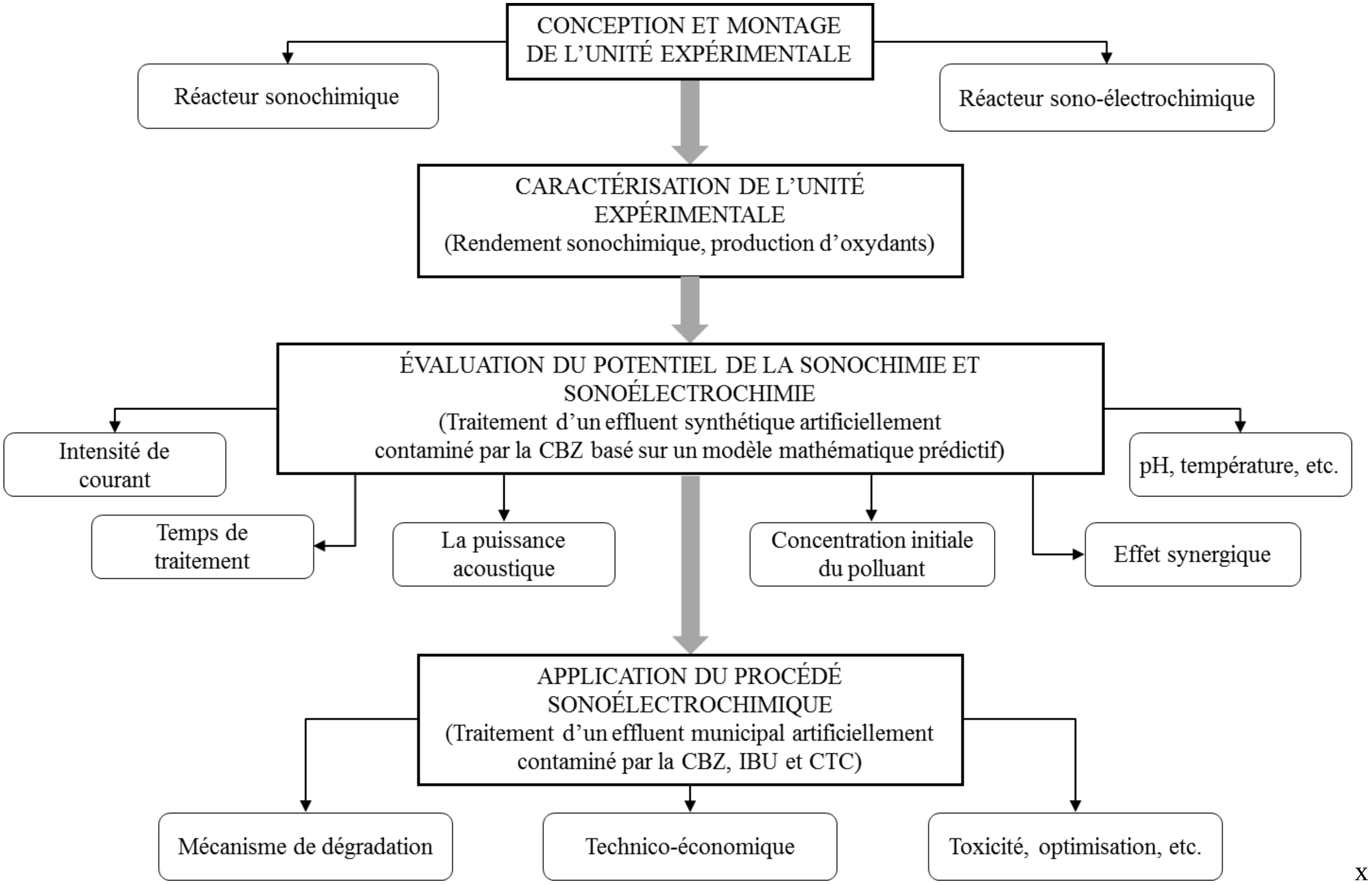


Figure 1. 4 **Description schématique de la démarche méthodologique suivie**

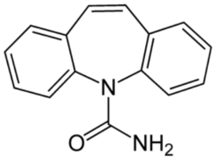
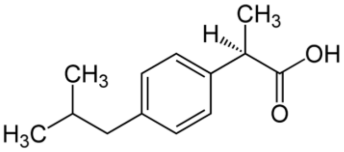
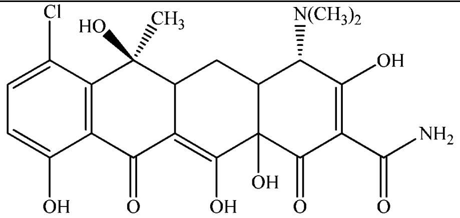
1.5.4.1 Polluants ciblés

La CBZ est un antidépressif utilisé principalement pour soigner l’épilepsie, pour contrôler les douleurs chroniques ainsi que pour traiter les différents troubles et maladies mentales (Andreozzi et al., 2002; Chong et al., 2011a). Une fois que la CBZ est administrée, son absorption dans le corps est lente avec environ 2 à 3% de la dose appliquée est excrétée à travers l’urine. Approximativement, 72% de la dose de CBZ administrée par voie orale est absorbée, alors que 28% reste inchangée et est excrétée à travers les selles (Metcalfe et al., 2003; Miao et al., 2005a). La CBZ ne peut être traité efficacement par les filières de traitement classique des eaux et se retrouve ainsi dans les eaux de surface, les eaux souterraines et même dans l’eau potable à des concentrations allant de 60 ng L^{-1} jusqu’à 800 ng L^{-1} (Ternes et al., 2002; Miao et al., 2005a).

L’ibuprofène est un anti-inflammatoire non stéroïdien. L’ibuprofène est recommandé pour traiter les douleurs et les inflammations modérées, comme la douleur musculaire, le mal de dos, la douleur articulaire, ou les douleurs de tension telle que la polyarthrite rhumatoïde. Dans un rapport concernant des pharmaceutiques et de soins personnels ainsi que des hormones dans des eaux usées, de l’eau de surface et de l’eau potable au Québec, 87% d’eaux usées a détecté l’ibuprofène avec une concentration maximal mesurée est de 5900 ng L^{-1}. La concentration maximale d’ibuprofène était de 240 ng L^{-1} ont été détectées à au moins une occasion dans plus de 60 % des stations de production d’eau potable échantillonnées.

La chlortétracycline est un antibiotique bactériostatique de la famille des tétracyclines. Son activité antibactérienne s'exerce par inhibition de la synthèse protéique (Zaviska et al., 2011). Le rejet d’antibiotiques dans l’environnement représente un sujet de préoccupation en raison de leur impact potentiel sur les êtres vivants. Seulement une faible proportion des antibiotiques ingérés sont métabolisés, la majorité est ainsi excrétée à travers les urines et les excréments des animaux sous forme inchangée. Les résidus des composés pharmaceutiques, telle que la chlorotétracycline rejetés par le ruissellement agricole ou par les stations d’épuration des eaux usées sont fréquemment détectés dans les eaux de surface, les eaux souterraines et même dans l’eau potable. Les tétracyclines sont des molécules amphotères et possèdent de multiples groupements fonctionnels chargés (phénol, amine, alcool, etc.). De ce fait, divers interactions peuvent exister entre les multiples fonctionnalités et peuvent fortement influencer leur enlèvement dans les eaux usées.

Tableau 1. 5 Propriétés physico-chimique des polluants à étudier.

Polluant	Formule moléculaire	Structure chimique	Poids moléculaire (g.mol^{-1})	Solubilité (mg.L^{-1})	Log K_{OW}
Carbamazépine (CBZ)	$C_{15}H_{12}N_2O$		236,26	112	2,45
Ibuprofène (IBU)	$C_{13}H_{18}O_2$		206,28	4,3	4,91
Chlortétracycline (CTC)	$C_{22}H_{23}ClN_2O_2$		478,88		1,41

1.5.4.2 Préparation de solutions synthétiques

Les solutions synthétiques ont été préparées individuellement à partir d'eau distillée et de composés organiques de grade analytique. Une conductivité minimale de la solution synthétique est nécessaire afin que le processus d'électrolyse puisse avoir lieu (transfert du courant électrique par conductivité ionique). Du sulfate de sodium est ajouté à cette solution dans une gamme de concentration allant de 0.1 mol.L^{-1}.

1.5.4.3 Échantillonnage et caractérisation des eaux réelles

Dans l'optique d'évaluer l'efficacité du procédé de sono-électro oxydation sur des effluents réels contenant des polluants organiques, des échantillons d'eaux usées ont été prélevés et artificiellement contaminés par du contaminant (CBZ ou IBU ou CTC). Ces effluents proviennent de la station municipale d'eaux usées de la ville de St-Nicolas (Levis, QC). La filière de traitement de cette station se compose d'un prétraitement comprenant un dégrillage et dessablage, d'un traitement primaire caractérisé par une décantation gravitaire, suivi d'un traitement secondaire par biologique et enfin d'un traitement de désinfection aux ultraviolets fonctionnant exclusivement en période estivale. La filière de traitement des eaux usées de la station municipale de la ville de St-Nicolas a été décrite dans la Fig. 1-5.

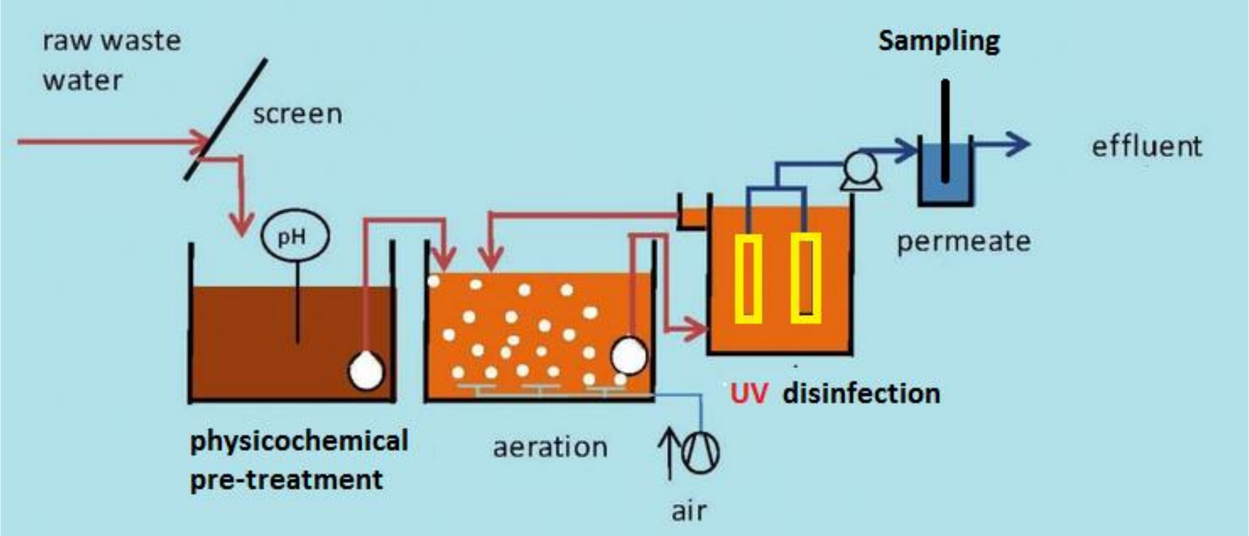


Figure 1. 5 **Filière de traitement des eaux usées de la station d'épuration de la ville de Saint Nicolas.**

Les effluents utilisés dans le cadre de cette étude ont été prélevés après désinfection, à la sortie de la station. Les échantillons ont été collectés et stockés dans des bouteilles en polypropylène et conservés à 4°C.

1.5.4.4 Montage des réacteurs et fonctionnement de l'unité expérimentale

- *Réacteur d'oxydation sonochimique US (Cellule C1)*

Le réacteur sonolytique utilisé lors de cette étude est fait en verre avec double couche et possède une capacité de 4 L (80 cm de hauteur et 8 cm d'interne diamètre). Les ultrasonores ont été introduits à partir du bas du réacteur par d'un transducteur céramique (un disque piézo-électrique ayant un diamètre de 4 cm). La figure 1-6 montre un dessin schématique de la configuration du réacteur à ultrasons utilisé pour cette étude.

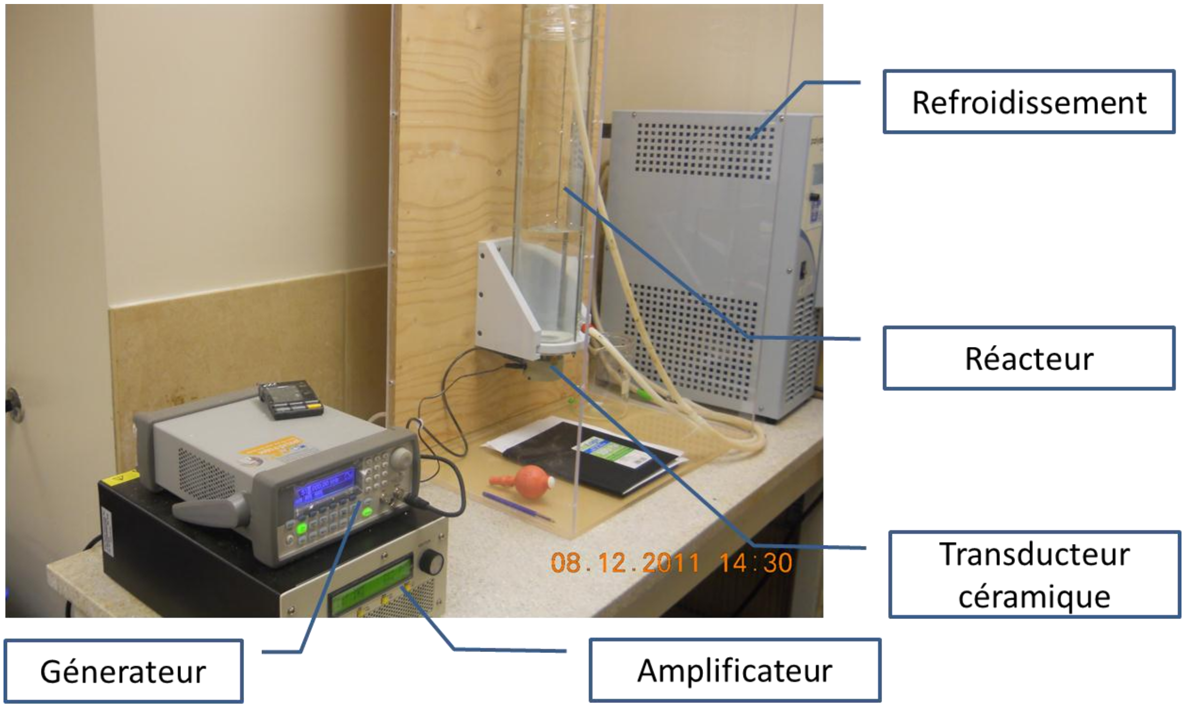


Figure 1. 6 **Photo de réacteur sonolytique (cellule C1) et de l'unité expérimentale**

L'unité expérimentale décrite schématiquement en **Erreur ! Source du renvoi introuvable.** fonctionne en mode batch. Une fréquence de 520 kHz et une puissance variant entre 10 et 40 W ont été imposées grâce à un générateur de courant (Agilent 33210A, Agilent Technologies Canada Inc.) équipé d'un amplificateur à fréquence (de l'AG 1016, T & C Power Conversion Inc.). La température du réacteur a été maintenue constante à 20 °C en utilisant un système de refroidissement Polystat (Cole-Parmer Canada Inc.).

- *Réacteur d'oxydation sono-électrochimique US-EO (Cellule C2)*

Le réacteur de sono-électrochimique a été faite en Plexiglas (caractérisé par un vérin à double couche) avec une dimension interne de 20 cm (hauteur) x 14,5 cm (diamètre). La cathode cylindrique (16 cm de hauteur x 12 cm de diamètre x 0,2 cm d'épaisseur) a été réalisée en titane (Ti) ayant une aire de surface solide de 420 cm^2 et une zone de vide de 180 cm^2. L'anode cylindrique (16 cm de hauteur x 8,0 cm de diamètre x 0,2 cm d'épaisseur) était titane recouvert d'oxyde de plomb (Ti/PbO_2) ayant une aire de surface solide de 280 cm^2 et une zone de vide de 120 cm^2. La distance entre des électrodes dans la cellule est de 2,0 cm. L'anode est placée au centre de la cellule et la cathode a été fixée à la périphérie. Les électrodes ont été mécaniquement attachées et disposées pour assurer une distribution correcte de l'eau dans la cellule.

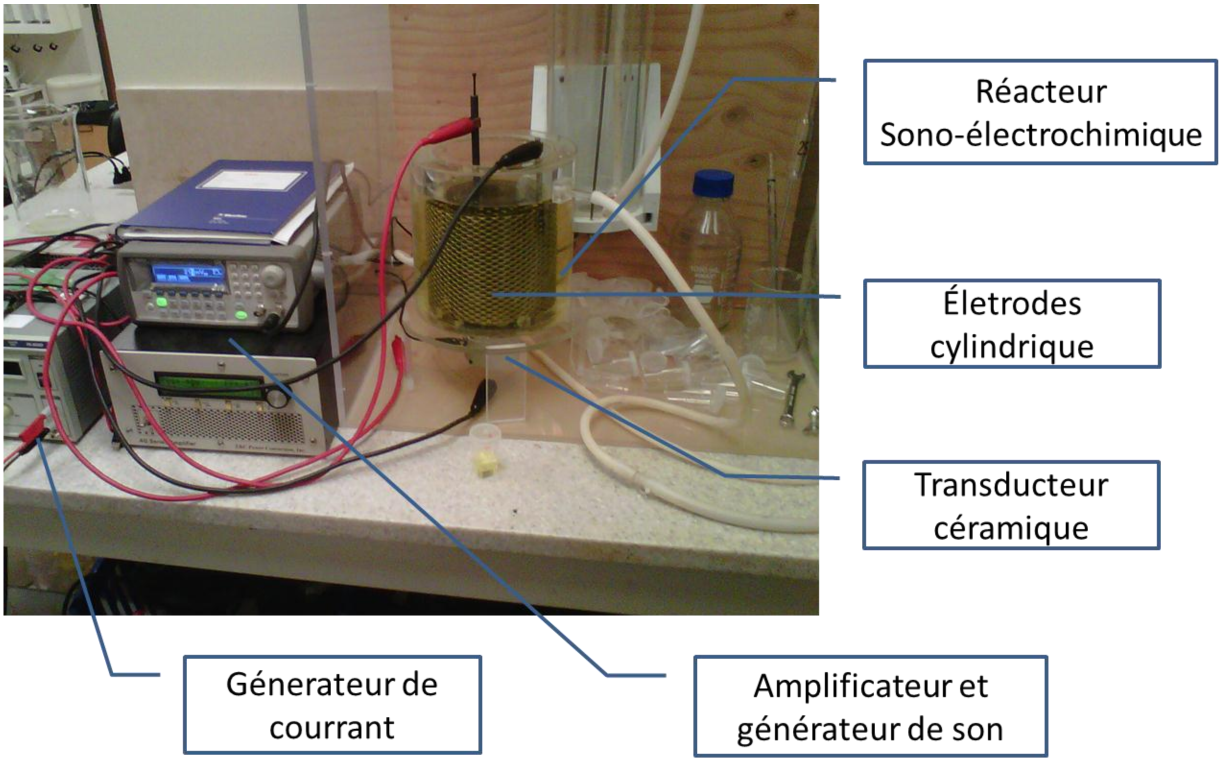


Figure 1. 7 **Photo de réacteur sono-électrolytique (cellule C2) et de l'unité expérimentale**

L'unité expérimentale décrite schématiquement en Figure 1-7 fonctionne en circuit fermé. Le courant électrique (de 1 à 5A) a été appliqué à l'aide d'un générateur de courant XFR 40-70 (Xantrex Technology , Burnaby , Colombie-Britannique , Canada) avec un courant nominal maximal de 70 A à un potentiel de 40 V. Les ultrasons (520 kHz) ont été introduits par le bas du réacteur par l'intermédiaire d'un transducteur céramique. Le mélange dans le réacteur a été réalisé en faisant recirculer l'eau à travers la cellule au moyen d'une pompe péristaltique fonctionnant à un débit constante de 100 ml min^{-1}. Le bac de recirculation (1,0 L de capacité) a été réalisée dans le même matériau que la cellule d'électrolyse.

1.5.4.5 Méthodologie de plan d'expérience

- *Plan factoriel*

Le plan factoriel (PF) est l'un des plans expérimentaux les plus courants. C'est un outil de décision qui permet de mettre en évidence très rapidement l'existence d'interaction entre les facteurs. L'hypothèse de base est d'assigner pour chaque facteur sa valeur la plus basse (-1) et sa valeur la plus haute (+1). Ainsi, pour k facteurs, il est possible de construire une matrice d'expérience de 2^k valeurs possibles permettant de planifier les différents essais expérimentaux à réaliser. Le PF est basé sur le critère d'orthogonalité, c'est-à-dire que les niveaux de chaque paramètre (-1 et +1) sont combinés les uns avec les autres. Le PF est un outil de décision qui permet d'obtenir le maximum d'informations sur les effets et interactions des différents facteurs influençant la réponse. Néanmoins, il ne peut être utilisé exclusivement pour optimiser un processus.

- *Plan central composite*

Le plan central composite (PCC) est un plan qui permet de déterminer les conditions opératoires optimales. Le PCC s'avère très intéressant d'un point de vue expérimental car celui-ci est basé sur un PF (2^k) complété par un plan en « étoile » ou chaque facteur varie un à un à une distance ± α du centre (les autres facteurs sont au centre du domaine). Il permet ainsi à partir d'un PF d'évoluer progressivement vers un plan de surface réponse (PSR).

1.5.4.6 Méthodes analytiques

- *Mesures des paramètres opératoires*

Lors de différentes expérimentations, des mesures de pH et de la conductivité ont été effectuées afin de suivre le bon fonctionnement du processus d'oxydation US-EO, de comprendre les différents mécanismes mis en jeu et d'établir certaines conclusions en terme d'efficacité. Les mesures du pH ont été effectuées en utilisant un pH-mètre (Fisher Acumet, modèle 915) équipé d'une électrode Cole-Palmer à double jonction (référence Ag/AgCl). Un conductimètre (Oakton, modèle 510) a été également utilisé afin de déterminer la conductivité électrique de l'effluent traité et non-traité.

- *Mesure des contaminants organiques, inorganiques et microbiens*

La DCO se caractérise par la consommation en oxygène induite lors de l'oxydation de substances organiques et minérales dans l'eau. Cette mesure permet d'évaluer la quantité de matière organique en solution et par conséquent d'évaluer l'efficacité de dégradation US-EO. L'analyse de la DCO a été effectuée selon la méthode prescrite par le ministère du Développement durable de l'Environnement et des Parcs du Québec (Méthode d'analyse-MA.315-DCO 1.1) (CEAEQ, 2012) en utilisant un spectrophotomètre de type Varian UV 0811 M136 (Australie). Pour évaluer le degré de minéralisation du polluant, des mesures du COT ont été effectuées. Les mesures du COT ont été effectuées grâce à un appareil TOC-5000A Shimadzu (Corporation Shimadzu, Japon). L'analyse des CF présents dans les eaux usées municipales (SM-9222D) a été effectuée en duplicata par le laboratoire Bodycote (Québec, Qc, Canada).

- *Mesure de la couleur*

La coloration d'une eau peut être d'origine naturelle (éléments métalliques, matières humiques, etc.) ou soit associée à sa pollution (composés organiques colorés synonymes de la présence de composés dissous). La couleur des eaux usées domestiques peut être en particulier affectée par les colorants dissous, la teinture, qui malheureusement n'arrivent pas à être éliminer totalement par les procédés de traitement usuels. Aussi la couleur indique des rapports directs avec la plupart des autres paramètres de qualité de l'eau. La mesure de la couleur dans l'eau a été effectuée selon la méthode d'analyse MA. 103 – Col. 2 (CEAAQ, 2008). La coloration de l'eau peut être causée par la présence de minéraux naturels comme le fer, le manganèse, par les composés organiques et inorganiques. La mesure de la couleur est effectuée d'après l'échelle platino-cobalt en comparant la couleur de l'échantillon à celle d'une série de solutions étalons. La solution étalon mère de couleur vraie de 500 unités a été préparée avec 1.246 g de chloroplatinate de potassium, K_2PtCl_6 (CAS no 16921-30-5) et 1 g de chlorure de cobalt, $CoCl_2.6H_2O$ (CAS no 7791-13-1) dissous dans 1 L d'eau déminéralisée. La droite d'étalonnage de couleur vraie a été préparée à partir de la solution étalon mère à différente concentrations:5, 10, 20, 50, 75 et 100 unités. La mesure de l'absorbance de chacun des étalons de la courbe d'étalonnage et des échantillons à été réalisés à l'aide de spectrophotomètre UV-visible (Carry 50 MPR microplate reader, Varian) à 400 nm. La concentration en couleur vraie d'un échantillon est obtenue à l'aide d'une régression linéaire passant par zéro des concentrations par rapport à l’absorbance des étalons. La courbe d’étalonnage et le calcul des concentrations sont exprimés en UCV (Unité de couleur vraie).

- *Mesure de la CBZ au spectrophotomètre UV*

La spectrométrie UV-visible est une technique analytique basée sur la loi de Beer-Lambert qui consiste à mesurer l’absorbance ou la densité optique d’une solution contenant des espèces capables d’absorber certains rayonnements UV ou visibles. La concentration d’une espèce est déterminée par analogie entre la mesure de la densité optique et la droite d’étalonnage effectuée préalablement au maximum d’absorbance de ce composé (λ_{max}). La CBZ a été analysé par spectrophotométrie UV-visible. Le spectromètre utilisé est un modèle Varian UV 0811 M136 (Australie). La concentration résiduelle de CBZ a été évaluée à 286 nm par la mesure de l’absorbance relative. L’absorbance relative ($Abs_R = H\text{-}H_o$) permet de déterminier la hauteur du pic d’adsorption en fonction des points isobéstique. Une courbe de calibration a ainsi été réalisée à cette longueur d’onde pour évaluer la concentration résiduelle de la CBZ.

Dans la deuxième partie, l'absorption intégrée (basée sur l'aire de la surface du spectre, plutôt que la hauteur du pic) de CBZ mesurée dans la plage de 200 nm à 400 nm a été choisie afin d'évaluer les concentrations résiduelles de CBZ. L’absorbance intégrée ($Abs_I = A\text{-}A_0$) permet de déterminer la surface du pic d’adsorption en fonction des points isométriques. La figure ci-dessous permet de distinguer l’absorbance relative (hauteur de pic) et l’absorbance intégrée (aire de surface du spectre).

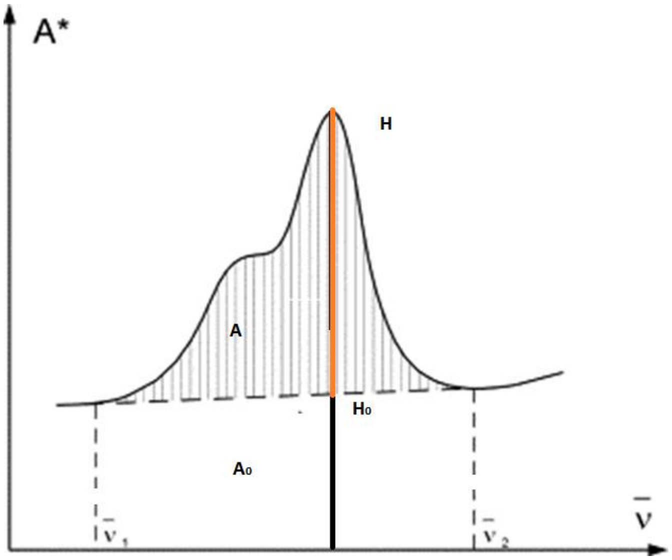
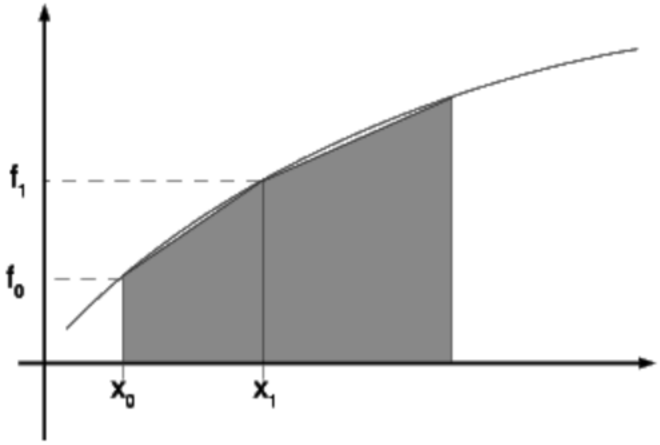


Figure 1. 8 **L’absorbance intégré et l’absorbance relative**

La surface du pic est moins sensible par rapport la hauteur du pic. Ces effets de dispersion entraînent le raccourcissement des pics spectraux, mais ont peu d'effet sur la superficie totale sous le pic. La surface du pic reste proportionnelle à la quantité totale de contaminants et ses sous-produits.

Cette méthode a été choisie afin de préserver la mise en évidence de sous-produits non connus qui sont formés au cours de l'expérience et donc d'éviter de perdre des informations pouvant fausser nos résultats illustrant la dégradation des polluants ciblés. De plus, on note la présence de pics d'absorbance pour différentes longueur d'onde avec des points isobestiques différents alors que la superficie peut rester constante, donc la surface est plus reproductibles que la valeur maximale du pic. On note aussi que lorsque le pic d'intérêt est très faible, il est possible d'utiliser la surface pour les calculs, afin de limiter la marge d'erreur contrairement au cas d'application de la méthode d'absorbance relative.

Cette méthode est basée sur le principe des intégrales des trapèzes. Elle consiste à déterminer la surface sous une courbe en sommant l'ensemble des surfaces des trapèzes compris dans cette surface. Ce qui signifie qu'elle est basée sur la technique de fractionnement de l'intégrale de la courbe d'absorbance en un grand nombre de trapèzes, qui sont ensuite "sommés" pour fournir une estimation de l'aire totale sous la courbe d'absorbance. L'étude se fera à partir d'une mesure du signal cumulé en absorbance en fonction du temps. La plupart du temps ces deux points correspondent aux points isobestiques du pic d'étude. Le principe de cette méthode est similaire à celui de l'intégration par la méthode des rectangles, mais implique une meilleure précision au niveau des calculs effectués. Pour une courbe f(x) sur un intervalle n+1 points, on va définir l'intégrale sur l'intervalle [X_0,X_1].



L’intégration va alors se faire en sommant l’aire des trapèzes, on obtient :

$$I = \sum_{i=0}^{n-1} \frac{f_{i+1} + f_i}{2} \times (x_{i+1} - x_i)$$

Chaque intervalle définissant chaque trapèze appelé pas d’étude, est défini. Ici 1 nm. Application de la formule des trapèzes pour un point i, on obtient alors la surface de courbe moyenne pour cet intervalle.

$$\boldsymbol{I = \frac{A_{i+1} + A_i}{2} \times (l_{i+1} - l_i)}$$

Sommation de toutes ces surfaces de trapèzes pour estimer la surface totale située sous la courbe pour un intervalle défini.

$$\boldsymbol{I = \sum_{i=0}^{n-1} \frac{A_{i+1} + A_i}{2} \times (l_{i+1} - l_i)}$$

Rejoindre cette surface totale à une concentration de contaminant avec l’utilisation de l’équation de droite d’étalonnage fait auparavant. Une courbe d'étalonnage de concentration connue CBZ, CTC ou IBU (0,0 à 15,0 mg L^{-1}) en fonction de la valeur d'absorbance intégré a été utilisé pour calculer la concentration résiduelle contaminants et pour estimer l'efficacité.

- *Mesure du CBZ au LC-MS/MS*

Le suivi de la dégradation PEC du CBZ et de ses sous-produits (acridine et l’acide anthranilique) a été réalisé par analyse au LC-MS/MS (Thermo TSQ Quantum Access). Les analyses au LC ont été réalisées en utilisant une colonne chromatographique Hypersil Gold C18 (100 * 2.1 mm * 3 µm). Un flux isocratic de 200 µL min^{-1} d’éluant constitué de A : 50% d’eau et 0.1% d’acide formique et B: 50% d’acétonitrile et 0.1% d’acide formique a été appliqué. La détection a été conduite par un système MS/MS utilisant une interface electrospray (ESI) en mode ionisation positive. L’analyse quantitative du CBZ ainsi que de ces sous-produits (acridine et l’acide anthranilique) a été déterminée en utilisant le sulfamethazine C_{13} comme standard interne.

- *Mesure de la concentration des oxydants radicalaires*

La durée de vie des oxydants radicalaires est extrêmement courte (n’excédant pas le dixième de microseconde). Donc la méthode très répandue de nos jours, mais est également très coûteuse.

La méthode permettant leur analyse directe est la Résonnance de Spin Électronique (RSE) lorsque les radicaux libres sont produits en quantités relativement élevées. En outre, elle présente des inconvénients comme, par exemple, le fait de devoir effectuer les analyses in situ. Cependant, une autre méthode indirecte de détection des radicaux peut être utilisée. Le principe consiste à piéger le radical étudié par une substance susceptible (ex : p-nitrosodiméthylaniline ou potassium d'iodure) de former un adduit stable, lequel sera par la suite isolé et ensuite analysé par une autre technique. Dans cette étude, les spécimens oxydants (en termes de radicaux hydroxyles) ont été estimés en utilisant la réaction Weissler, qui est composée de l'oxydation des ions iodure en iode. Un volume de 3,0 ml d'échantillon a été prélevé à partir du réacteur toutes les 2,5 min pendant une période de 25 min d'oxydation. Le tri-iodure a été analysé par des mesures d'absorbance (λ_{I}^{3-} = 26303 L mol $^{-1}$ cm $^{-1}$) à l'aide d'un spectrophotomètre (Cary UV 50 , Varian Inc. , Mississauga , ON , Canada) à 352 nm.

- *Tests de toxicité*

Des tests de toxicité de l'effluent traité versus l'effluent non traité ont été réalisés par le laboratoire Exova. Une série d'essais de létalité aiguë sur *Daphnia magna* (Environnement Canada, 2000) a été effectuée. Ces essais consistent à déterminer la concentration létale à 50% (CL$_{50}$) d'un échantillon ou d'un produit, après une exposition de 48 h, du crustacé (*Daphnia magna*) en conditions contrôlées. Une série de dilutions de l'échantillon a été effectuée (au moins 5 concentrations et 1 contrôle). Une deuxième série d'essais de toxicité sur une bactérie luminescente a parallèlement été effectuée. Ces essais consistaient à déterminer la concentration d'inhibition de bioluminescence à 50% (CI$_{50}$) d'un échantillon ou d'un produit après une exposition de 5, 15 ou 30 min, de la bactérie luminescente (*Vibrio fischeri*) en conditions contrôlées (Environnement Canada, 1992). Une série de dilutions de l'échantillon a été effectuée (au moins 6 concentrations et 1 contrôle).

1.6 PRINCIPAUX RÉSULTATS

1.6.1. Caractérisation de l'unité expérimentale

Rendement sonochimique

L'objectif de cette partie de l'étude consiste à évaluer l'efficacité sonochimique du transducteur piézoélectrique. Au cours de la formation des bulles de cavitation, il y a dissipation de l'énergie sonochimique sous forme de chaleur. L'énergie sonochimique peut être assimilée à une énergie calorimétrique due à l'augmentation de la température dans un volume d'eau et pour un temps de traitement donné. La puissance de consommation ultrasonique (puissance acoustique ou puissance calorimétique, P_{US}) peut être écrite comme suit :

$$P_{US} = P_{cal} = \left(\frac{dT}{dt}\right)_{t_{US}} .C_P.M_{eau}$$ **Équation 7**

Dans cette expression $\left(\frac{dT}{dt}\right)$ représente l'augmentation de la température de l'eau ($K\ s^{-1}$), Cp est la capacité calorifique de l'eau ($4.18 J.g^{-1}K^{-1}$), M est la masse de l'eau (g) soumise au traitement et t_{US} le temps de sonolyse (s). La puissance électrique (P_{Elec}) imposée tout au long de ce test était comprise entre 10 et 40W et correspond à la puissance consommée par le générateur de courant de l'amplificateur et du transducteur. L'augmentation de température enregistrée lors du traitement sonochimique d'une eau ultra pure de 250 mL pour une période de 12 min, induisait une puissance calorimétrique variant entre 10 et 40 W. La figure 1-9 montre l'évolution de a température au cours du temps (au cours de la sonolyse et après sonolyse). Les températures ont été enregistrées toutes les 30 secondes lors de la sonolyse et lors du refroidissement (perte calorifique du système). L'équation suivante permet par la suite de calculer le rendement sonocchimique (η).

$$\eta = \frac{P_{us}}{P_{Élec}}$$ **Équation 8**

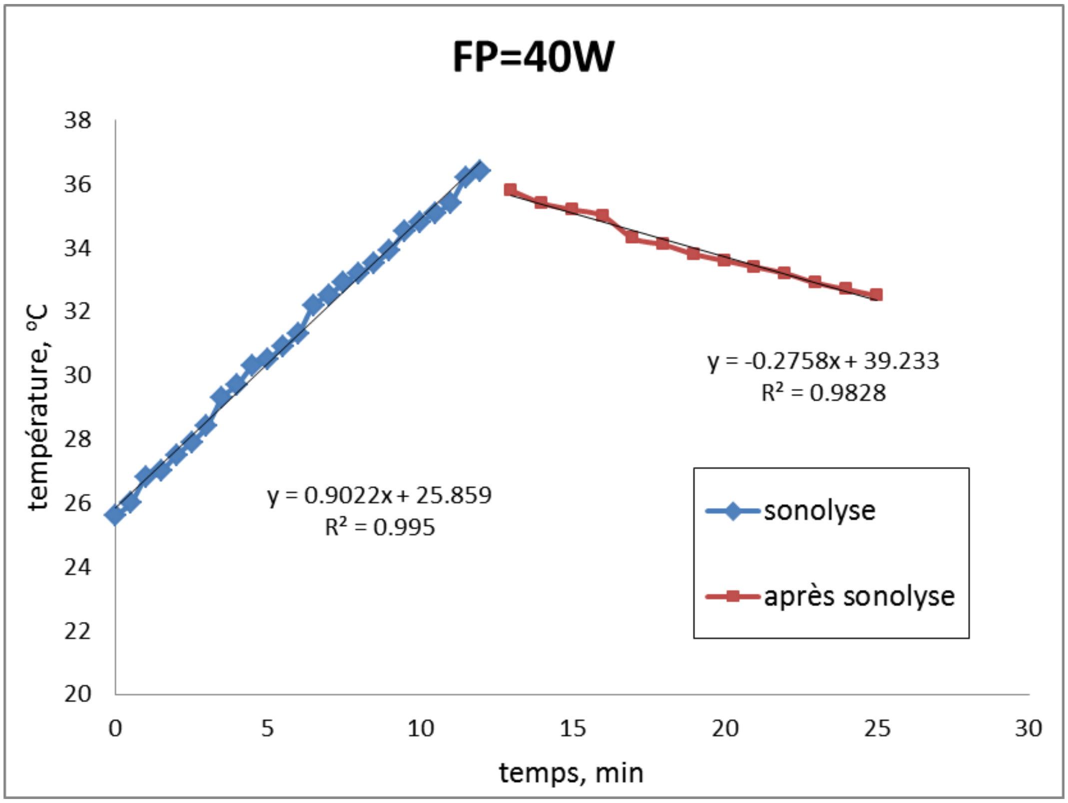


Figure 1. 9 **Enregistrement de la température toutes les 30sec lors de la sonolyse de 250ml d'eau distillée pendant 12min ainsi que lors de refroidissement (perte calorifique du système).**

L'influence de différentes puissances telles que 10W, 20W, 30W et 40W ont été étudiés et les résultats sont présentées dans le Tableau 1.6.

Tableau 1. 6 **Rendement sonochimique du transducteur piézoélectrique pour différentes puissances**

Power électrique (P_{Elec})	*10W*	*20W*	*30W*	*40W*
Puissance acoustique (P_{US})	3.52W	9.98W	15.6	20.62
Rendement sonochimique (η)	35.2 %	49.9 %	52.1 %	51.5 %

Les résultats de cette partie démontrent que le rendement sonochimique de notre transducteur piézoélectrique varie entre 35,2% et 52,1%. Ces résultats sont relativement plus élevés que ceux obtenu par Bussemaker et al. (2014). Bussemaker and Zhang (2014) ont étudié les efficacités sonochimiques à différentes fréquences et de puissances. En imposant différentes fréquences (40, 376, 995 et 1179 kHz) à une puissance de 240W, ils obtinrent une puissance acoustique variant entre 50W à 92W (ce qui correspond à un rendement se situant entre 20.8% et 38.3%). Cette différence peut s'expliquer par la configuration du réacteur. Bussemaker and Zhang (2014) ont utilisé un agitateur mécanique qui permet d'augmenter la transfert de masse dans la solution; mais cela contribue à une perte d'efficacité calorifique du système pendant la sonolyse.

Production d'espèces oxygénées réactives (EORs)

Plusieurs espèces oxygénées réactives (EORs : ·OH, H_2O_2, O_3, etc.) peuvent être générées lors de l'application du procédé US-EO. En particulier, les radicaux hydroxyles (·OH) peuvent être générés par décharge anodique de la molécule d'eau sur des électrodes catalytiques dites à forte surtension d'oxygène (Pt, Ti/IrO_2, Ti/RuO_2, Ti/SnO_2, PbO_2, Gr, etc.) (Cantrell et *al.*, 1995; Gandini *et al.,* 1998; Rajkumar et Palanivelu, 2003). Les radicaux libres peuvent également être générés en solution lors de l'implosion des bulles de cavitation. Ainsi le radical hydroxyle a été mis en évidence par la méthode indirecte de Spin trapping qui consiste à "piéger" le radical par la p-nitrosodiméthylaniline (RNO). La quantité de RNO dégradée correspond à la quantité de radicaux hydroxyles formés, car une mole de RNO réagit avec une mole de radical hydroxyle. L'attaque électrophile du radical °OH sur la RNO est susceptible de conduire à la formation d'un adduit très stable pouvant être mesuré par spectrophotométrie UV-Visible (λ_{max} = 440 nm) (Muff *et al.,* 2011). Il est cependant important de noter que, la molécule de RNO réagit de manière sélective avec les radicaux hydroxyles (réaction sélective entre RNO et °OH) et ne réagit pas avec l'oxygène singulet ($^1O_2$), l'anion superoxyde (O_2^-) et d'autres espèces peroxygénées (Simonsen *et al.,* 2010; Muff *et al.,* 2011). Cependant, l'ozone (O_3), l'acide hypochloreux (HClO) et l'ion hypochlorite (ClO^-) sont d'autres oxydants chimiques puissants pouvant réagir avec le RNO (Simonsen *et al.,* 2010). Dans nos conditions opératoires, HClO et ClO^- ne peuvent être présents dans l'eau dans la mesure où le seul électrolyte utilisé est le sulfate de sodium (Na_2SO_4, 0.1 M). L'ozone est pratiquement le seul oxydant pouvant être conjointement produit lors de l'électrolyse (et la sonolyse) et pouvant simultanément réagir avec le RNO. Une courbe de calibration a été obtenue (ANNEX B), laquelle établit une corrélation entre la concentration de RNO et l'absorbance à $\lambda_{max} = 440$ nm. Des solutions standard de RNO de concentrations variant entre 0,0 mg L^{-1} à 6,0 mg L^{-1} ont été utilisées. Comme prévu par la loi de Beer-Lambert, l'absorbance varie linéairement avec la concentration de RNO. La solution de RNO est re-circulée (en boucle) dans l'unité expérimentale pendant une période de 180 min. Des échantillons ont été prélevés en moyenne toutes les 30 min et analysés immédiatement par spectrophotométrie UV-Visible. La vitesse de production des EORs (incluant principalement HO° et possiblement O_3) est égale à la vitesse de disparition du RNO selon l'Équation 9 :

$$V_{(EOR)} = \frac{d[RNO]}{dt} = -k_R.[RNO]$$

Équation 9

La Figure 1-10 présente de la concentration d'oxydant (EORS) en fonction du temps pour les procédés US, EO et US-EO. La puissance d'ultrason appliquée est de 40W (pour US et EO-US procédés). Le courant électrique appliqué est de 1A (pour EO et EO-US procédés).

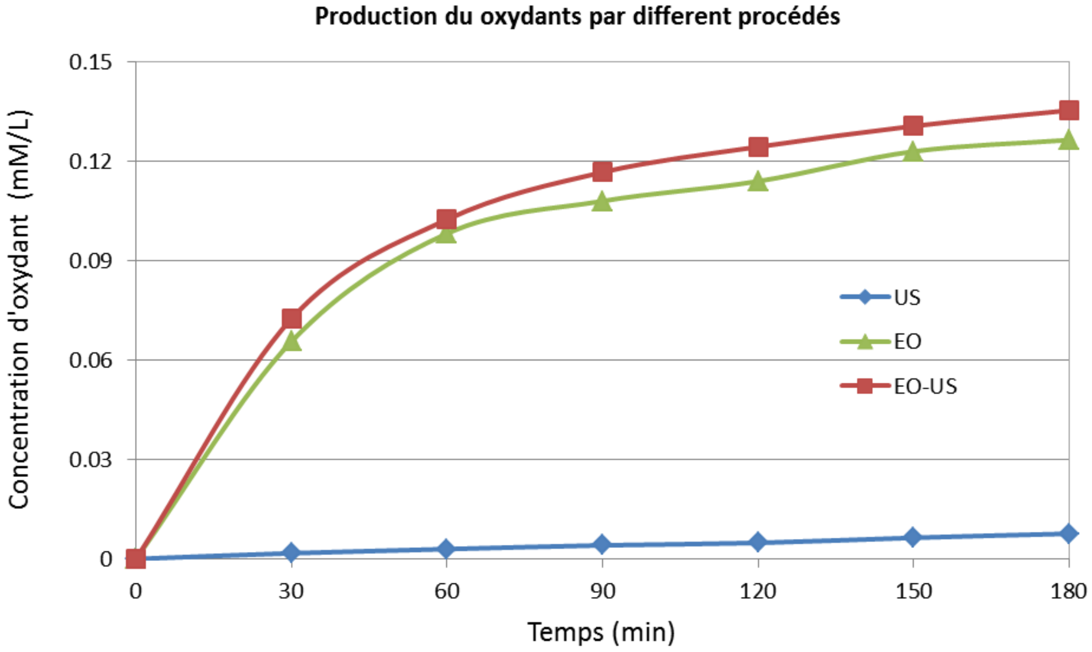


Figure 1. 10 **Production du oxydants par différent procédés**

Un taux de dégradation relativement élevé de RNO a été enregistré comparativement aux valeurs mesurées lors de l'application des procédés conventionnels d'oxydation électrochimique (EO), de sonochimique (US) et de couplage (EO-US). Le procédé EO-US utilisant Ti/PbO_2 comme anode et le Ti à la cathode et fonctionnant à une intensité de courant de 1A pendant 180 min en présence d'une puissance ultrason à 40A a permis de générer une quantité d'oxydant (EORs) de 0,135 mM L^{-1}. La constante cinétique de production des EORs est estimée à 0.00095 min^{-1}. Par comparaison, les constantes cinétiques de 0.00089 min^{-1} et 0.00004 min^{-1} ont respectivement été enregistrées lors les procédés EO et US sont utilisée. Ceci démontre que la vitesse de production des espèces oxydantes par notre procédé couplage EO-US est 1,1 et 23 fois plus rapide que pour les procédés conventionnels EO et US, respectivement.

1.6.2 Dégradation de polluants organiques émergents de type carbamazepine par sonochimie (Dégradation sono-chimique de la carbamazépine)

Un des l'objectifs de ce travail était d'évaluer le potentiel d'oxydation sonochimique de la CBZ. Pour cela, des eaux usées synthétiques ont été artificiellement contaminées par du CBZ puis soumises au traitement d'oxydation sono-chimique. Plusieurs facteurs incluant la puissance électrique, le temps du traitement, le pH et la concentration initiale de CBZ ont été étudiés. L'utilisation d'une matrice factorielle 2^4 a permis d'atteindre la meilleure performance de dégradation de la CBZ (90,1% d'élimination) en imposant une puissance électrique de 40 W, 120 minutes de traitement, un pH initial de 10,0 avec une solution de 6.0 mg.L^{-1} de CBZ. Le temps de traitement et la puissance calorimétrique étaient les paramètres les plus influents sur le taux dégradation de CBZ. Par la suite, les paramètres expérimentaux optimaux pour la dégradation CBZ ont été étudiés en utilisant le plan central composite. À ces conditions optimales (puissance électrique de 43W et 116min de traitement), 86% d'enlèvement de CBZ a été enregistré lorsqu'une concentration initiale de 5,62 mg CBZ L^{-1} a été imposée. Dans le cas d'une concentration initiale plus faible de 8,05 µg CBZ L^{-1}, un taux d'enlèvement de 90% a été enregistré. Pendant le processus sono-chimique, l'analyse par LC-MS a confirmé que la CBZ a été principalement transformée en acide anthranilique et acridine. Les résultats de cette partie des travaux ont fait l'objet d'un article publié dans la revue de calibre international *Journal of Environmental Management*.

1.6.3 Oxydation sono-électrolytique de la carbamazépine dans l'eau : optimisation par la méthodologie des surfaces de réponses.

L'objectif de ce travail était d'évaluer le potentiel d'un processus d'oxydation combinant la sono-chimie et l'électrochimie pour la dégradation de la CBZ. La décomposition de la carbamazépine (CBZ) en solution dans l'effluent synthétique et municipal a été étudiée en utilisant un réacteur sono-électrochimique. La sono-électrolyse a été réalisée en utilisant deux électrodes concentriques installées dans un réacteur cylindrique contenant un transducteur céramique. La concentration initiale de CBZ (Co = 10 mgL^{-1}) a diminué de façon optimale jusqu'à 90% en appliquant une intensité de courant de 4.86 A, un temps de traitement de 177 min et une puissance énergétique de 38,29 W. Les conditions optimales ont été ensuite appliquées pour le traitement tertiaire d'effluents d'eaux usées municipales contaminées avec 10 µg CBZ.L^{-1}. Les rendements d'élimination signalés de CBZ, COT, COD et de la couleur étaient 93%, 60%, 93% et 86%, respectivement. De même, la toxicité de l'effluent d'eaux usées municipales a été complètement enlevée (bactérie *Vibrio fisheri*) (> 96%). Les avantages du couplage des ultrasons avec l'électrooxydation (US-EO) pour le traitement de la CBZ ont été démontrés. Une méthodologie de conception expérimentale basée sur la méthodologie des surface de réponses a été appliquée pour déterminer les conditions expérimentales optimales en termes de coût / efficacité de l'élimination. Un article, portant sur les résultats originaux de cette étude a été publié dans la revue internationale *Journal of Chemical Technology and Biotechnology*.

1.6.4 Effets synergiques des ultrasons sur l'oxydation électrochimique de la carbamazépine.

Les effets synergiques ont été évalués lors de l'oxydation de la carbamazépine par le procédé procédé sono-électrochimiques. La sono-électrolyse a été réalisée en utilisant deux électrodes concentriques installées dans un réacteur cylindrique contenant un transducteur céramique. La concentration initiale de CBZ était 10 mgL^{-1} (solution synthétique). Plusieurs paramètres opératoires ont été étudiés, incluant la puissance des ultrasons, l'intensité du courant et le temps de traitement. Les éffets synergétiques augmentent lorsque l'intensité de courant diminue et quand la puissance ultrasonore augmente. Les plus fortes valeurs de degrée de synergie (33%)

ont été enregistrées pour les valeurs d'intensité de courant la plus faible (1.0 A) et de puissance ultrasonique la plus élevée (40 W). En outre, les effets bénéfiques des ultrasons ont étré observés lorsque la CBZ est traité sur une longue période de traitement (pendant 30 jours d'expérience sans interruption). Un taux de dégradation relativement important de 99.5 % a été enregistré (I=1 A, P=40 W) lors de la dégradation sono-électrochimique de la CBZ, comparativement au pourcentage de dégradation de 91% enregistré lors de l'électrolyse seule (I=1 A, P=0 W). Aussi, les observations réalisées au microscope électronique à balayage (MEB) et les mesures d'impédance spectoscopique électrochmique ont revélé l'absence d'impuretés déposées à la surface des électrodes et ce, lorsque les ultrasons sont simultanément appliqués. Un article, portant sur nos résultats originaux de l'effet synergique des ultrasons sur l'oxydation électrochimique de la CBZ, été publié dans la revue internationale *Ultrasonics Sonochemistry*.

1.6.5 Optimisation de l'oxydation de l'ibuprofene dans les eaux usées par sono-électrochimie

Dans l'optique d'élargir le spectre d'activité d'oxydation du procédé EO-US à d'autres types de polluants pharmaceutiques, des travaux additionnels ont été entrepris afin de vérifier les performances du procédé pour la dégradation de l'ibuprofène (IBU). La décomposition de l'ibuprofène en solution synthétique (10 mg/L) et dans les effluents municipaux a été étudiée en utilisant un réacteur électro-sonochimique. Une étude préliminaire a permis de comparer la dégradation du CBZ en utilisant différents procédés (EO, US et EO-US) dans l'optique de sélectionner le procédé le plus efficace. Le succès du couplage des ultrasons avec l'électro-oxydation (EO-US) pour éliminer l'ibuprofène a été démontré. Le degré de synergie enregistré était de de 5,26%. Une dégradation de CBZ allant jusqu'à 84,7% a été enregistrée en utilisant le procédé EO-US à une intensité de courant de 4 A en imposantes la puissance d'ultrason de 30W durant 120 min. Dans l'optique de décrire et optimiser le processus de dégradation EO-US du CBZ, plusieurs facteurs tels que l'intensité du courant, la puissance des ultrasons et le temps de traitement ont été étudiés. Une matrice factorielle (suivie du plan de surface de réponse) a été utilisée pour déterminer les paramètres influents sur la dégradation de l'ibuprofène. Le temps de traitement et l'intensité de courant ont été les principaux paramètres influents sur l'efficacité de dégradation de la CBZ. La meilleure performance de la dégradation de l'ibuprofène (77%

d'élimination) a été obtenue par utilisation d'une matrice factorielle 2^3 en sélectionnant 40 W de puissance ultrasonore avec une intensité de courant de 5,0 A et un temps de 120 minutes de traitement. Subséquemment, les paramètres expérimentaux optimaux pour la dégradation de l'ibuprofène ont été études grâce à une méthodologie centrale composite. Dans ces conditions optimales déterminées par cette méthode, EO-US peuvent être appliqués pour oxyder l'ibuprofène dans les effluents municipaux (jusqu'à 90% d'élimination) en utilisant une intensité de courant de 4,09 A pour une durée de 110 min et en appliquant les 20 W des ultrasons de puissance. Finalement, dans l'optique d'évaluer l'efficacité du procédé d'oxydation EO-US sur des effluents réels contenant des micropolluants organiques, le procédé EO-US a été testé pour la dégradation de l'IBU dans les eaux usées municipales issues de station d'épuration de la ville de Levis (QC). Les résultats expérimentaux déterminés en utilisant une chromatographie liquide spectrométrie de masse (LC / MS / MS) ont montré que l'élimination des IBU variait entre 83,7 ± 3,11 % à 90,0 ± 2,67 %. Cette étude a permis de mettre en évidence l'intérêt de l'application du procédé EO-US en tant que traitement tertiaire des eaux usées pour l'élimination des polluants organiques réfractaires (tels que l'IBU) tout en assurant une désinfection des eaux. Dans ces conditions, un coût de traitement du procédé EO-US de \$3,39 par m^3 a été enregistré. Un article, portant sur les résultats originaux de cette étude a été publié dans le *Journal of Environmental Chemical Engineering*.

1.6.6 Procédé hybride d'électro-oxydation – ultrasons (EO-US) pour le traitement de la chlortétracycline.

L'oxydation électrochimique utilisant une anode de Ti/PbO_2 sous irradiations ultrasoniques (10-40W) a été évaluée pour la dégradation de la CTC. Pour ce faire, des eaux usées de type municipal ont été artificiellement contaminées par du CTC (10 mg/L) puis soumises au traitement d'oxydation EO-US. Une étude préliminaire a permis de comparer l'influence de divers paramètres tels que le courant électrique appliqué, la puissance des ultrasons et le temps de traitement. Afin de décrire et d'optimiser le processus de dégradation EO-US de la CTC, l'optimisation a été étudié en utilisant le plan central composite (PCC). Les résultats ont indiqué que le taux de dégradation de la chlortétracycline a été fortement influencé par le courant électrique et le temps de traitement. Une intensité de courant de 3,92 A sous irradiation ultrasonore de 20 W (à 500 kHz) pendant 95 minutes ont été les meilleures conditions pour l'oxydation de la chlortétracycline. La concentration initiale (10 mg/L) peut être réduite de façon optimale de 73,3%. Dans ces conditions, une minéralisation relativement élevée de la chlortétracycline (61,4% d'élimination de carbone organique total) a été enregistré. Ensuite, les conditions optimales ont été appliquées sur des effluents d'eaux usées municipales (échantillonnées après traitement secondaire) et artificiellement contaminés avec 10 µg/L, 100 µg/L et 10 mg/L de CTC, respectivement. Le traitement a été plus efficace avec l'effluent municipal (la chlortétracycline peut être oxydée jusqu'à 98%) en raison de la présence d'ions chlorures qui pourraient être transformés en chlore actif. La chlortetracycline peut être oxydée à la fois par oxydation directe à l'anode (au moyen des radicaux $^{\bullet}OH^{\cdot}$) et par oxydation indirecte par l'intermédiaire de médiateurs, tels que l'acide hypochloreux produit dans la solution suite à l'oxydation des ions chlorures. Un article, portant sur les résultats originaux de cette étude a été publié dans le *Journal of Environmental Engineering*.

1.7 CONCLUSIONS GÉNÉRALES

Ce travail est une contribution au développement d'un procédé de dégradation de polluants organiques émergents de type pharmaceutique en combinant une technique d'electro-oxydation/ultrasons. Cette étude a permis d'obtenir quelques résultats que nous rappelons succinctement.

Des réacteurs sono-chimiques constitués d'une pièce céramique piézoélectrique (transducteur) ont été conçus et caractérisés en terme de leur capacité de production d'oxydants radicalaires (radical hydroxyle, peroxyde d'hydrogène, ozone etc.). La possibilité de générer simultanément des espèces oxydantes a été mise en évidence par la réaction de Weissler en présence de la molécule de KI. Deux types de réacteurs comprenant des électrodes catalytiques (Ti/PbO_2) et un transducteur sono chimique ont été conçus. Après avoir établi les caractéristiques des réacteurs sono-chimiques, ces réacteurs ont été par la suite testés en termes de leur capacité de dégradation des composés organiques émergents de type pharmaceutiques (CBZ, IBU, CTC) et pour le traitement tertiaire des eaux usées de type municipal.

Plus spécifiquement, l'étude menée sur la CBZ (résidus médicamenteux de type antiépileptique) a fait ressortir les points suivants:

- Les meilleurs résultats en terme de coût-efficacité (90% d'élimination des CBZ) ont été obtenus à l'aide du réacteur sono-électrochimique constitué d'un transducteur et d'électrodes (anode : Ti/PbO_2 ; cathode Ti) opéré à une intensité de courant de 4,86 A pendant un temps de traitement de 177 min avec une puissance ultrasonique de 38.3 W. Des taux de dégradation du COT et du COD relativement élevés (une élimination de 60% et 93% de carbone organique total et de COD, respectivement) ont été également enregistrés.
- L'étude de la toxicité sur des espèces aquatiques telle que la vibrio fisheri, montre une diminution de la toxicité dans l'effluent traité par comparaison à l'effluent non-traité.
- Les analyses complémentaires effectuées par spectroscopie d'impédance électrochimique (SIE) et par micoscopie électronique à balayage (MEB) ont démontré les effets synergiques et bénéfiques de la combinaison des procédés US et EO. Cette combinaison contribue à minimiser le dépôt de films polymériques sur la surface des électrodes. Dans ces conditions, le taux de dégradation le plus élevé a été obtenu avec le procédé sono-électrochimique (2A, 40W) après 30 jours (99,5%) comparé à l'électrolyse sans ultrasons dont le taux d'abattement était de 91 %. De plus, aucune impureté (sous-produits d'oxydation) n'a été observée sur la surface des électrodes en présence d'ultrasons.
- Les coûts de traitement incluant uniquement les coûts énergétiques se situent aux alentours de 0,61 US$ par gramme de CBZ traitée.

L'étude menée sur la CTC (résidus médicamenteux de type antibiotique) a fait ressortir les points suivants:

- La méthodologie des plans d'expérience a permis de décrire le processus de dégradation de la CTC. Les conditions optimales de dégradation de la CTC ont été identifiées. L'utilisation des ultrasons à une puissance de 20W, une intensité de courant de 3,92 A pendant 95 min et en imposant une concentration initiale en CTC de 10 $mg.L^{-1}$ a été retenue comme conditions optimales en terme de coût et d'efficacité.

- Dans ces conditions, un taux d'abattement allant jusqu'à 73,3% de CTC a été enregistré. De plus, une minéralisation partielle de la CTC (61,4% d'élimination du COT) a été enregistrée dans les conditions optimales.

L'étude menée sur l'IBU a fait ressortir les points suivants:

- L'application du procédé EO-US sur le composé IBU a permis d'enregistrer une dégradation de 90% en imposant une intensité de courant de 4,09 A pendant 110 min de traitement et en présence d'ultrasons fonctionnant à une puissance de 20W.
- La voie de dégradation principale de l'IBU conduit à la formation du l'ibuprofène carboxylique acide, 1-hydroxy ibuprofène et 2-hydroxy ibuprofène. En outre, l'oxydation de l'IBU dans les conditions optimales conduit à une réduction du COT de 84%.
- Dans ces conditions, un coût total de 3,39 US\$.m^{-3} a été enregistré incluant seulement les coûts d'énergie et d'électrolyte.

1.8 RECOMMANDATION

Cette étude a permis de montrer l'efficacité du procédé EO-US pour le traitement des polluants organiques émergents de type pharmaceutique. Cependant, ce n'est qu'une première approche et il serait très important d'effectuer des travaux supplémentaires plus poussés dans le but d'optimiser l'efficacité de ce procédé:

- Tester le procédé EO-US sur d'autres matrices principalement contaminées par les résidus médicamenteux, tels que les effluents résiduaires issus d'établissements hospitaliers.
- Rechercher de nouveaux types d'ultrasons pour favoriser à la fois l'effet de cavitation de la sono-lyse lors de la dégradation des POE.
- Tester à l'échelle préindustrielle le procédé complet afin de développer son domaine d'application. Cette étude de pilotage préindustriel permettrait d'évaluer sa performance globale et de montrer l'intérêt économique et environnemental du procédé EO-US.

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PARTIE II ARTICLES SCIENTIFIQUES

CHAPITRE 2

Sonochemical techniques to degrade pharmaceutical organic pollutants

Le Chapitre 2 est constitué de l'article de revue suivant:

Tran, N., Drogui, P., Brar, S.K. (2015), *Sonochemical techniques to degrade pharmaceutical organic pollutants*, Environmental Chemistry Letters, DOI: 10.1007/s10311-015-0512-8.

2.1 Abstract

Pharmaceuticals are one of the chemical groups largely used in health care, diagnosis aids, cure, treatment, and prevention of disease. Increasing production and use of pharmaceutical products has led to the entry of these products into the environment and eventual pollution. Several processes have been studied including the use of ultrasound for the removal of these pollutants from the aquatic environment. This review summarizes recent research advances dealing with the development of sonochemical technologies for the degradation of pharmaceutical organic pollutants. The review also includes the mechanism of sonochemical processes, the characteristics of irradiation sources, and the types of reactors used. Moreover, the important factors affecting the sonochemical oxidation efficiency are discussed, including the electrical power, frequency, and temperature. Finally, this paper discusses the recent applications of sonochemical processes on the degradation of pharmaceutical organic pollutants and suggests new research directions for the development of this promising technology.

2.2 Introduction

Pharmaceuticals belong to a group of compounds used by humans or administrated to animals to enhance growth or health of livestock. Depending on the medication, up to 90 % of these products pass through a human body unchanged and are rejected in the environment (Boxall et al. 2012; Fram and Belitz 2011; Gadipelly et al. 2014). Scientists demonstrated that organic pollutants, such as pharmaceuticals, may enter the receiving water source through excretion, improper disposal of pharmaceutical waste, and excess quantities used by human and animal (Heberer et al. 2002; Roberts and Thomas 2006). This results in a substantial amount of anthropogenic compounds being directly or indirectly released into the aquatic environment which is present in relatively low concentrations of the range of ng L-1 to lg L-1 (Andreozzi et al. 2003; Heberer et al. 2002). The recent development of new analytical techniques has allowed detection of these low concentrations in the environment (Siddiqui et al. 2013). This type of concentration of some pollutants has been detected in surface water in many countries, such as USA, Canada, UK, and several other countries in Europe. Table 1 illustrates several pharmaceuticals found in water and wastewater. Although they are often present in low concentration, various studies on effects on quality and ecological functioning of water systems show that these chemicals form a potential new problem (Langenhoff et al. 2013). Their estrogenic and carcinogenic toxicity will impact the quality of ecological life and possibly affect human life (Leal et al. 2010). The toxicological studies have reported that the exposure of fish and other aquatic organisms to pharmaceuticals causes adverse reproductive effects, such as reduced viability of eggs, endocrine disruption, and changes in sperm density (Belgiorno et al. 2007). A considerable effort has been spent on understanding the removal and the degradation efficiencies of pharmaceuticals in water resources and wastewater discharges. Conventional wastewater treatment plant typically possess biological degradation using the activated sludge process, whereas advanced plants may have tertiary treatment processes, such as UV disinfection, reverse osmosis, ozonation, and other advanced oxidation process. Several works have been reported on the fact that pharmaceuticals are difficult to be completely removed using conventional biological/physicochemical treatment processes (Ferrey 2011; Fram and Belitz 2011). Some pharmaceutical discharges are degraded within the sewage treatment plants, but low removal rate was recorded depending on these physical and chemical characteristics (White et al. 2006). The majority of pharmaceuticals are relatively hydrophobic and therefore less effectively removed by sorption to sludge (Vieno et al. 2007). Wu et al. (2008) found a removal rate typical of 12–80 % for chlortetracycline (CTC) using conventional biological/physicochemical treatment processes, while others found even lower than 10 % for CBZ (Bound and Voulvoulis 2006).

Table 2-1 Concentrations of selected pharmaceuticals in the aquatic environment.

Compound	**Source**	**Concentration**	**Country**	**References**
Diclofenac	Wastewater	0.31-0.93 µg L^{-1}	Switzerland	(Buser et al., 1998)
	Wastewater	0.25-5.45 µg L^{-1}	France, Italy and Greece	(Andreozzi et al., 2003)
	Lake	1- 7 ng L^{-1}	Switzerland	(Buser et al., 1998)
	Lake	5 - 35 ng L^{-1}	Germany	(Heberer et al., 2002)
Carbamazepine	Wastewater	3.8 µg L^{-1}	Germany	(Heberer et al., 2002)
	Wastewater	< 6.3 µg L^{-1}	Germany	(Ternes, 1998)
	Wastewater	1.5 ng L^{-1}	USA	(Ferrey, 2011)
	River	< 1.1 µg L^{-1}	Germany	(Ternes, 1998)
	Ground water	0.42 µg L^{-1}	USA	(Fram et al., 2011)
	Surface water	0.4 ng L^{-1}	USA	(Ferrey, 2011)
Ibuprofen	Raw water	0.90- 2.11 µg L^{-1}	USA	(Richardson, 2007)
	Drinking water	1.35 µg L^{-1}	USA	(Richardson, 2007)
	River water	144-2370 ng L^{-1}	UK	(Roberts et al., 2006)
	Wastewater	13.95-8771 ng L^{-1}	UK	(Roberts and Thomas, 2006)
	River water	2-38.8 ng L^{-1}	UK	(Boxall et al., 2012)
Erythromycin	Wastewater	6.0 µg L^{-1}	Germany	(Hirsch et al., 1999)
	Wastewater	110-199 ng L^{-1}	Swiss	(McArdell et al., 2003)
	Surface water	1.7 µg L^{-1}	Germany	(Hirsch et al., 1999)

Advanced oxidation process is chemical oxidation with hydroxyl radicals, which are very reactive and short-lived oxidants (Illes et al. 2013; Riesz and Christman 1986). The radicals need to be produced on site, in a reactor where the radicals can contact the organics contaminant in the wastewater (Mahamuni and Adewuyi 2010). Hydroxyl radicals may be produced in systems using: ultraviolet radiation/hydrogen peroxide, ozone/hydrogen peroxide, ultraviolet radiation/ozone, and through other means. Advanced oxidation treatment processes (AOP), such as ozonation, electrochemical oxidation, can generally achieve higher removal rates for pharmaceuticals compared with conventional processes (Mahamuni and Adewuyi 2010). Ultrasound is one example of AOPs that transform or destroy organic contaminants (Bremner et al. 2011; Leong et al. 2011). When water is exposed to ultrasound, acoustic pressure waves are produced and lead to the formation of bubbles. When the sound intensity is greater than the cavitation threshold, within several cycles of growing and shrinking, bubbles will exponentially and eventually collapse. The collapse of bubbles causes extremely high temperatures and pressures within a microenvironment in the liquid leading to the breakdown of gaseous water molecules in the bubbles to form hydroxyl radicals. This radical is capable of oxidizing and removing great variety of organic contaminants from water (Gogate et al. 2001; Leong et al. 2011; Mason 2011, 2012). Recently, the use of ultrasound alone or combining with other process is contributed important role in all technical field and also for water treatment (Abdelsalam and Birkin 2002; Agranonik Ia et al. 1990). Ultrasound comprises unique advantages compared to other technologies, including no addition of chemicals, ease of use or automation, and high efficiency (Birkin et al. 2001; Bremner et al. 2011). However, according to the knowledge of the authors, a review of recent advances in the sonochemical techniques for the degradation of pharmaceutical organic pollutants was never published. This review presents the mechanisms and principal parameters for the degradation of pharmaceutical pollutants and its future prospects.

2.3 Mechanism of the sonochemical process

Ultrasound-induced cavitation is an extremely useful and versatile tool to carry out chemical reactions. Sonochemistry refers to the area of chemistry where chemical reactions are induced by sound (Mason 2012; Rooze et al. 2013). The extreme temperature conditions generated by a collapsing bubble can also lead to the formation of radical chemical species. Sonochemistry normally uses frequencies between 20 and 100 kHz as this is the range employed in common laboratory equipment (Klima 2011; Leong et al. 2011). However, since acoustic cavitation in liquids can be generated well above these frequencies, recent research into sonochemistry uses wide range up to 1 MHz (Bremner et al. 2011). Ultrasound consists of cycles of compression and rarefaction. When ultrasound is introduced into liquid, it creates oscillating regions; compression cycles exert a positive pressure, while rarefaction cycles exert negative pressure (Bremner et al. 2011; Klima 2011). Correspondingly, the liquid molecules experience periodic compression and expansion cycles. When the pressure amplitude exceeds the tensile strength of liquid during the rarefaction of ultrasonic waves, cavitational bubbles are formed as microbubbles; they absorb energy from ultrasound waves and grow. However, it will reach a stage of unstable size where it can no longer efficiently absorb energy (Bringas et al. 2011; Gallego-Juarez 2010). Fig. 2-1 presents the formation, growth, and implosion of a cavitation bubble with various reaction sites in a bubble. Without the energy input, the cavity can no longer sustain itself and implodes during the compression cycle of ultrasonic wave. It is this implosion of the cavity that creates an unusual environment for chemical reactions (Gogate 2007; Rooze et al. 2013). Localized hot spots are formed, which reach temperatures and pressures around 5000 K and 500 atm, respectively, depending on factors, such as ultrasonic power, frequency, hydrostatic pressure, temperature, solvent property, and dissolved gas (Gogate 2007; Gogate et al. 2001, 2003). Some authors (Mason 2012; Rooze et al. 2013; Sinisterra 1992) have reported that sonochemical reactions can occur at internal site or interface of a bubble. The first one is the bubble’s interior gas phase, and it is suggested as the dominant site for sonochemical reaction due to the intense temperatures attained during collapse (*5000 K) (Leong et al.). In this site, the typical reaction can be decomposed of water with the formation of radical species and the production of oxygen gas. The second one is the liquid–gas interface surrounding the bubble, which can reach temperatures of up to 1900 K (Leong et al. 2011). This region is represented by intermediate temperature/pressure. When the bubble collapses, the generation of shock waves/microstreamers/microjets in this region will lead to increased turbulence and shear forces which can facilitate mass transport (Leong et al. 2011; Mason and Lorimer 2003d). In addition to these two primary reaction sites on the bubble, solutes in bulk solution beyond the bubble itself can react with the radicals formed inside or on the surface of the collapsing bubble (Marken et al. 1998; Mason 2011). Any species dissolved in the solution is clearly going to be subject to chemical reaction in theses site. As a result of such processes, chemical reactions, by-products formation/ degradation or cleavage and radical generation from small molecules, can result. In a typical treatment, organic contaminants may degrade by decomposition (by heat produced in the gas and interfacial regions of the cavitation bubbles) and degrade by oxidation (react with hydroxyl radical in the gas, interface, and bulk region of the cavitation bubbles) (Leong et al. 2011; Xiao et al. 2014b). The degradation pathway of each organic contaminant is strongly dependent on its physical/chemical properties. For example, the major degradation site for volatile contaminants is in the gas region; hydrophobic pollutants in the interface site; and hydrophilic contaminants in bulk site. It is worth noting that the hydroxyl radicals generated during cavitation can be used for the oxidative degradation of organic pollutants in an aqueous system. The heat produced in the cavitation process can be used to remove volatile pollutants by pyrolytic decomposition (Leong et al. 2011). Generally, the production of hydroxyl radical, oxygen gas, and hydrogen peroxide is followed the reaction (Mason and Lorimer 2003d):

$H2O \rightarrow H\cdot^{+} + \cdot OH^{-}$

$2OH^{-} \rightarrow H_2O_2$

The hydronium and hydroxyl radical formed in this reaction are highly reactive and rapidly interact with other radical or chemical species in solution. H· are highly reducing in nature, and ·OH radicals are highly oxidizing (Gogate 2007; Mason and Lorimer 2003d). A common product of this reaction in water is hydrogen peroxide (Birkin et al. 2001; Mark et al. 1998). The generation of H and OH radicals, commonly referred to as primary radicals, has been confirmed and quantified by a number of experimental techniques.

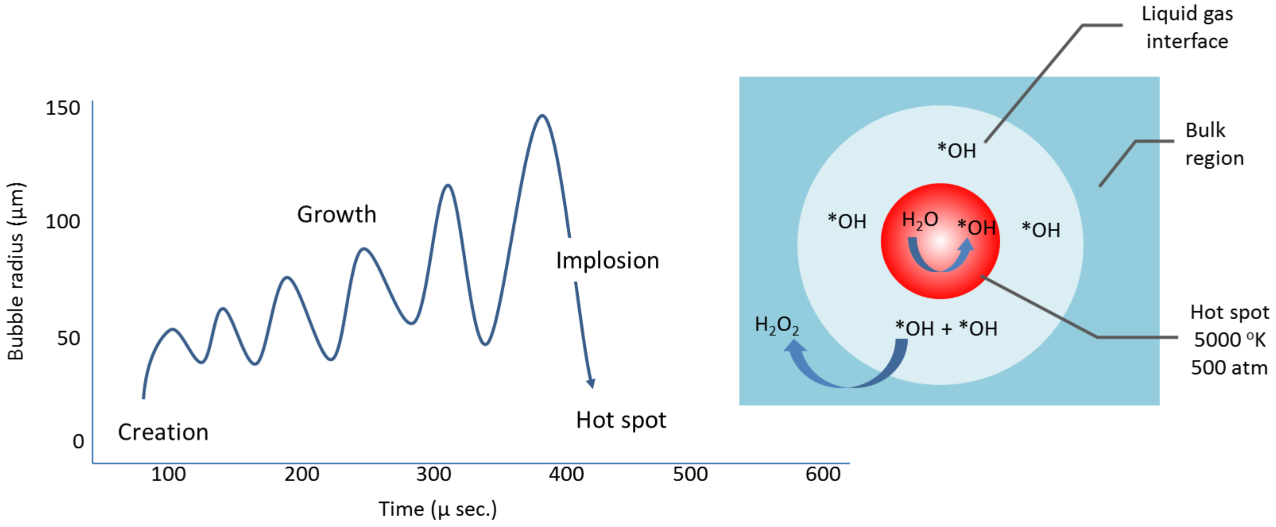

Fig. 2-1 Formation, growth, implosion and various reaction sites in a cavitation bubble.

Several methods of monitoring the sonochemical efficiency are available including the use of electron spin resonance (ESR) spin traps or the reaction with chemicals, such as terephthalic acid. In an alkaline aqueous solution, terephthalic acid produces terephthalate anions that react with hydroxyl radicals to generate highly fluorescent 2-hydroxyterephthalate ions which can be assayed using spectroscopy (Mark et al. 1998; Riesz and Christman 1986). In another dosimeter method, Fricke dosimetry, Fe^{2+} is oxidized by OH radicals and hydrogen peroxide to form Fe^{3+}, and Fe^{3+} is determined photometrically (Iida et al. 2005). One of the most simple methods used to quantify the amount of OH radicals formed in water is based on ‘‘Weissler’’ method. This method involves the oxidation of iodide ions (Birkin et al. 2001; Gogate et al. 2001; Leong et al. 2011). In this technique, iodine is added to water which is then sonicated and reacts with the hydrogen peroxide, and the reaction scheme for this method is:

$H_2O_2 + 2I^- \rightarrow 2OH^- + I_2$

$I_2 + I^- \rightarrow I_3^-$

The absorbance of I^{3-} at 355 nm with the molar absorptivity e = 26,300 dm3 mol^{-1} cm^{-1} can be measured with the spectrophotometer. The dosimeters based on photometry, such as Weissler method, produced reliable and reproducible results, but the sensitivity is not enough for special applications, for example chemical monitoring of single-bubble cavitation (Iida et al. 2005).

2.4 Sonochemical reactors

2.4.1 Ultrasonic transducers

Ultrasonic transducers are designed to convert either mechanical or electrical energy into high-frequency sound, and there are three main types: gas driven, liquid driven and electromechanical (Leong et al. 2011; Tudela et al. 2011). The most readily available experimental setup for carrying out sonochemical reactions is the electromechanical transducers, which is currently used not only at laboratory level but also on a larger scale (Compton et al. 1997). The two main types of electromechanical transducers are based on either the piezoelectric or the magnetostrictive effect. Magentostrictive transducer is based on ferromagnetic materials which change dimension when a magnetic field is applied. Rapid on/off application leads to vibrations and sound energy

(Mason and Lorimer 2003a). These are devices which use an effect found in some materials, e.g., nickel which reduces in size when placed in a magnetic field and returns to normal dimensions when the field is removed. When the magnetic field is applied as a series of short pulses to a magnetostrictive material, it vibrates at the same frequency (Mason and Lorimer 2003b). The most commonly used ones are piezoelectric transducers generally employed to power the bath- and probe-type sonicator systems (Mason and Lorimer 2003e). Piezoelectric transducer is the most common piezoelectric effect-instantaneous generation of electric charge between opposite faces of certain materials when a sudden pressure is applied across them; transducers use opposite of this effect by either expansion or contraction when an electric charge is applied (Gonzalez-Garcia et al. 2010b; Mason and Lorimer 2003e). Usually an alternating charge at 20 kHz is applied. Piezoelectric materials are ceramics dispersed with $BaTiO_3$, $PbNb_2O_6$, and lead zirconate titanate (PZT). Although more expensive than mechanical transducers, still electromechanical transducers are by far the most versatile (Compton et al. 1997; Margulis 1985). The most common form is a disk with or without a central hole. Another form is the piezoelectric transducer within the converter, where it is changed to mechanical vibrations (Mason and Peters 2002). The vibrations from the converter are intensified by the horn (probe), creating pressure waves in the liquid. Normally, piezoelectric devices must be cooled if they are to be used for longer periods at high temperatures because the ceramic material will degrade under these conditions (Mason and Peters 2002). Such transducers are highly efficient (>95 %), and depending on dimensions, they can be used over the whole range of ultrasonic frequencies from 20 kHz to several MHz (Leong et al. 2011; Mason and Lorimer 2003c; Rooze et al. 2013).

2.4.2 Ultrasonic reactors

The reactor design plays an important role for the efficacy of sonochemical reaction. Table 2 presents typical sonochemical transducers system used for degradation of pharmaceuticals. Ultrasonic baths were mostly manufactured for cleaning purposes. Typical baths usually have the transducers (pieces of piezoelectric in form of disk or plate) attached to the bottom, although the transducers can be submersed in a conventional tank to obtain similar effects (Gogate 2007; Gogate et al. 2011). For this type of transducer, the size (or diameter) of immersion transducer relative to the reactor size is one of the most important parameters. This ratio mainly affects the level of turbulent dissipation of energy and the intensity of the ultrasound and hence would be more essential where the physical effects are needed (Gogate et al. 2011). Bath systems are widely used in sonochemical research because they are readily available and relatively inexpensive. The reaction vessel is typically immersed in the fluid contained in the bath (indirect sonication) (Grcic et al. 2012; Reisse et al. 1994). In addition, obtaining reproducible results may be difficult because the amount of power reaching the reaction mixture is highly dependent upon the placement of the sample in the bath (Gogate et al. 2011; Klima 2011). When indirect sonication is used, the ultrasonic power which reaches the reaction vessel is relatively low as compared to other ultrasonic systems, such as a probe (Andaluri et al. 2012; Gogate 2007). The probe systems, also called horn systems, in which the transducers can be submersed in the fluid contained in the reactor, are more frequently used for sonochemical research in the laboratory due to the fact that this type of system is capable of delivering large amounts of power directly to the reaction mixture which can be regulated by varying the amplitude delivered to the transducer (Grcic et al. 2012; Siddique et al. 2011). The position of immersion probe in an ultrasonic horn is an important parameter which may affect the extent of reflection of the incident sound waves from the liquid surface as well as the reactors walls (Gogate et al. 2011). A few novel reactor configurations based on continuous operation have been developed for food processing and other application (Gogate and Pandit 2015; Graff 2015). However, in the laboratory scale, the batch operation approach is commonly used due to the size and possibility of successful application at small operation.

Table 2-2: Typical sonochemical transducer system used for degradation of pharmaceuticals

Application	**Type of reactor**	**Position of transducers**	**Process mode**	**Power**	**Frequency**	**References**
Degradation of fluoxetin	Piezoelectric disk	Exterior, Bottom	Batch	20-60W	600 kHz	(Serna-Galvis et al., 2015)
Oxidation of ibuprofen	Piezoelectric disk	Exterior, Bottom	Batch	100W	35, 300, 500 and 1000 kHz	(Thokchom et al., 2015)
Degradation of dicloxacillin	Piezoelectric disk	Exterior, Bottom	Batch	20-60W	600 kHz	(Villegas-Guzman et al., 2015)
Degradation of Cetirizine dihydrochloride	Ultrasonic bath	Exterior, Bottom	Batch	30-150W	20 and 40 kHz	(Sutar et al., 2015)
Degradation of ciprofloxacin and ibuprofen	Probe	Interior, Immersion	Batch	20W / 50W	20 and 620 kHz	(Xiao et al., 2014b)
Tinidazole removal	Ultrasonic bath	Exterior, Bottom	Batch	750W	40 – 160 kHz	(Rahmani et al., 2014)
Degradation of atenolol	Plate type piezoelectric	N/A	Batch	20-80W	200- 1000 kHz	(Nejumal et al., 2014)
Decomposition of diclofenac	Plate type piezoelectric and horn type piezoelectric	N/A	Batch	115W / 28.5W	577 – 1145 kHz 20 kHz	(Ziylan et al., 2013)

Treatment of pharmaceutical effluent	Ultrasonic bath	Exterior, Bottom	Batch	N/A	30 kHz	(Nachiappan et al., 2013)
Mineralization of antipyrine	Horn sonicator	Interior, Immersion	Batch	200W	24 kHz	(Duran et al., 2013)
Degradation of naproxen	Ultrasonic bath	N/A	Batch	Up to 500W	59 kHz	(Lan et al., 2012)
Degradation of carbamazepine	Probe	Interior, Immersion	Batch	200W	24 kHz	(Braeutigam et al., 2012a)
Degradation of ofloxacin	Horn sonicator	Interior, Immersion	Batch	130-600W	20 kHz	(Hapeshi et al., 2010)
Degradation of cephalexin	Horn sonicator	Interior, Immersion	Batch	200W	24 kHz	(Guo et al., 2010)
Sonolysis of paracetamol	Piezoelectric disk	Exterior, Bottom	Batch	9-32 W	574, 860 and 1134 kHz	(Isariebel et al., 2009)
Degradation of ibuprofen	Piezoelectric disk	Exterior, Bottom	Batch	20-80W	300 kHz	(Mendez-Arriaga et al., 2008b)

2.5 Parameters affecting the sonochemical process

2.5.1 Influence of the ultrasonic power

The power of ultrasound is the power delivered to the liquid divided by the surface area of the ultrasonic transducer (Gallego-Juárez and Graff 2015). The power can be characterized by two parameters: ultrasonic intensity, defined as the ratio between the power inputs to the irradiated medium to the transmitting area, or the power density, defined as the ratio between the power inputs to the irradiated medium to the sonication volume (Andaluri et al. 2012; Gallego-Juarez 2010). Higher acoustic pressure (amplitude of vibration), greater amounts of cavitational events, and more violent cavitational collapse happen at elevated power intensity of ultrasound. The relationship between the ultrasonic power intensity and the acoustic pressure may be expressed as Eq. 5 (Mason et al. 1990):

$$I = \frac{P_0^2}{2\rho C}$$

where I is the power intensity of a sound wave (W), P_0 is the acoustic pressure (Pa), ρ is the density of the liquid (kg m^{-3}), C is the sound speed in the liquid (m s^{-1}).

There exists a threshold value of intensity at which the beneficial effects of cavitation start to occur. Some authors have demonstrated that the increase in the yield with the power input is weak and reaches saturation, and attribute this effect to the coalescence of the bubbles, which would increase their size, leading to lower pressure pulses at the end of the collapse (Gallego-Juarez 2010; Pang et al. 2011). This saturation has been observed in several systems. Isariebel et al. (2009) investigates the influence of ultrasonic power on levodopa and paracetamol degradation carried out at the frequency of 574 kHz, and ultrasonic powers of 9, 17, 22 and 32 W were found that above a threshold power of about 9 W, the initial degradation rates increase linearly with the actual power for both products (with correlation coefficients of 0.9939 for levodopa and 0.9967 for paracetamol). This result is expected because by increasing the magnitude of power dissipation of the horn, there will be an increase in the number of cavities generated, and hence, the cumulative pressure pulse (number of cavities multiplied by the collapse pressure due to a single cavity) will also increase. After investigating the sonophotolytic degradation of synthetic pharmaceutical wastewater (composition of 4-aminophenol, paracetamol, phenol, chloramphenicol, benzoic acid, salicylic acid, diclofenac sodium, and nitrobenzene), Ghafoori et al. (2015) have found that by increasing the ultrasound power, higher TOC percent removal was achieved. The TOC removal was 60.22 % at 20 W compared to 75.26 % with power of 140 W. The elevated ultrasound power causes the higher rate of the breakage of H2O2 molecules in aqueous solution; consequently, the concentration of hydroxyl radicals was increased, and the produced radicals attack the organic matters. Furthermore, an increase in the ultrasonic power contributed to enhance mixing intensity due to the turbulence and microstreaming which is generated during the cavitational microbubble collapse (Ghafoori et al. 2015). Other authors have pointed out that lower intensities are more effective than higher intensities at the same total power, not only in experiments on water sonolysis but also in the degradation of organic compounds. Increasing intensity will raise the acoustic amplitude, resulting in a more violent cavitation bubble collapse. A study by Memarian and Farhadi (2008) to investigate the oxidation of dihydropyrimidinones by sonothermal process has shown that by increasing the ultrasound intensity, a decrease in the time of reaction is observed. The time of disappearance of dihydropyrimidinones was lowest (11 min) at highest power (460 W), due to the formation of oxidant compounds brought about by the sonochemical process. Similar phenomena have been observed by other authors (Mendez-Arriaga et al. 2008; Naddeo et al. 2009; Suri et al. 2007; Villegas-Guzman et al. 2015), while sonochemical process for degradation of estrogen hormones, ibuprofen, diclofenac, and dicloxacillin was applied; the degradation rates increased linearly with the power. This was confirmed when the hydrogen peroxide and hydroxyl radical formation is increased when ultrasound power increased (Villegas-Guzman et al. 2015). Lan et al. (2012) also observed that the extent of degradation increased with an increase in the ultrasonic power. The degradation efficiency of naproxen by combination of Fenton reagent and ultrasound irradiation after 33 min was only 66 % with power amplitude at 40 %.When power amplitude was set at 90 %, the degradation efficiency increased to almost 100 %. In the study of Thokchom et al. (2015) for the ultrasonically electrochemical oxidation of ibuprofen, the rate constants of ibuprofen were increased linearly with increasing ultrasonic power density. The degradation trend followed: 100 W L^{-1} > 80 W L^{-1} > 60 W L^{-1} > 40 W L^{-1}. The number of active cavitation bubbles increases with an increase in the acoustic power leading to an increase in the corresponding amount of OH radicals generated. However, in another study the degradation of the antibiotic cephalexin in aqueous solution, Guo et al. (2010)

have obtained that the optimal ultrasound power for cephalexin degradation in the system was 200 W (when compared to other ultrasonic powers 100, 300, 400, and 500 W). At higher power output, a large number of gas bubbles exist in the solution, which scatter the sound waves to the walls of the vessel or back to the transducer. Thus, less energy is dissipated in the liquid due to cavitational activity, although the vessel is exposed to higher power. Bubble cloud formation may occur at the surface of the horn or transducer if the power is too high, resulting in attenuation of the sound wave (Guo et al. 2010). Also, due to the higher number of cavities per unit volume of liquid, there is a coalescence of the cavities resulting in the formation of a larger cavity (the collapse pressure is inversely proportional to the size of the cavity). Sutar and Rathod (2015) also reported this phenomenon using ultrasound assisted enzyme catalyzed degradation of cetirizine dihydrochloride. Effect of irradiation power on degradation was investigated by varying the power in the range of 30–150 W and keeping constant frequency of 25 kHz. The degradation was less at lower irradiation power of 30 and 50 W (~50 %), as compared to higher irradiation power (~90 % at 100 W and ~80 % at 150 W). At highest power, more bubbles were formed with further increase in irradiation power, hampering the propagation of shock waves so that degradation gets decreased. Also at higher irradiation power, the bubbles coalesce to form bigger bubbles causing weak implosion so that degradation was reduced (Sutar and Rathod 2015). It is interesting that some of the authors have argued that the trend in energy consumption and its efficiency, higher power gave the best efficiency from the view point of degradation; however, the application of lower power is recommended for scale-up purposes (Gogate and Pandit 2015; Mason 2012; Thokchom et al. 2015). Summary of effect of the ultrasonic power on the degradation of pharmaceutical compounds is presented in Table 3.

Table 2-3 Removal of different types of organic pollutants in solutions using sonochemical processes: effect of power

Matrix	Type of pollutant	Operating conditions	Results and comments	References
Millipore water	Ibuprofen	Initial conc. = 21 mgL^{-1}; pH=3; Frequency =300 kHz; pH = 3; Temp = 25^{o}C; Treatment time = 30 min; Power= 20, 40, 60 and 80W.	Degradation rate (µmol L^{-1}min^{-1}) at different power was: P_{20W} = 1.18; P_{40W} = 2.44; P_{60W} = 3.51; P_{80W} = 6.1; Degradation efficiency = 25% (20W), 40% (40W), 90% (60W) and > 95% (80W)	(Mendez-Arriaga et al., 2008b)
Ultrapure water	Levodopa	Initial Conc. = 25 mg L^{-1}; Treatment time = 240 min; Frequency = 574 kHz; Volume = 300 mL; Temp. = 20^{o}C; Temp. = 20^{o}C; Power = 9, 17, 22 and 32W.	Degradation rate (mg L^{-1} min^{-1}): 0.001 (9W); 0.05 (17W); 0.1 (22W) and 0.16 (32W).	(Isariebel et al., 2009)
Ultrapure water	Paracetamol	Initial Conc. = 25 mg L^{-1}; Treatment time = 240 min; Frequency = 574 kHz; Volume = 300 mL; Temp. = 20^{o}C; Temp. = 20^{o}C; Power = 9, 17, 22 and 32W.	Degradation rate (mg L^{-1} min^{-1}): 0.001 (9W); 0.11 (17W); 0.22 (22W) and 0.3 (32W).	(Isariebel et al., 2009)
Millipore water	Diclofenac	Initial conc. = 80 mgL^{-1}; Frequency 20 kHz; Treatment time = 60min; Temp. = 20^{o}C; Volume = 150mL; Power densities = 200 and 400 W L^{-1}.	The degradation efficiency: 55% (400 WL^{-1}); and 35% (200 WL^{-1})	(Naddeo et al., 2009a)

Millipore water	Cephalexin	Initial Conc. = 20 mg L^{-1}; treatment time = 60 min; Frequency =24 kHz; Ultrasonic power = 100, 200, 300 and 400W; Volume = 100mL; Temp. = 25°C; pH = 6.5;	The degradation rates: 26% (100W); 52% (200W); 35% (400W) and 28% (500W).	(Guo et al., 2010)
Millipore water	Naproxen	Initial Conc = 10 mg L^{-1}; Treatment time = 33min; Frequency= 59 kHz; Volume = 50 mL; Temp. = 28–33°C; Fe^{2+} = 2.43 mg L^{-1}; H_2O_2 =1.76 mmol L^{-1}; pH =3.0; Ultrasonic power = 450W, 300W and 200W.	Degradation efficiency: 40% (200W); 90% (300W); 100% (450W).	(Lan et al., 2012)
Ultrapure water	Carbamazepine (CBZ)	Initial conc. = 10 mg L^{-1}; Treatment time = 120min; Volume = 350 mL; Temp. = 25°C; Power = 130, 260, 390, 510, 640 W L^{-1}.	The CBZ conversion rate: 3 to 50% with power density from 130 to 640 W L^{-1}; DOC removal was around 21% for 640 W L^{-1}.	(Jelic et al., 2013)
Synthetic wastewater	4- Aminophenol, Paracetamol, Phenol, Chloramphenicol, Benzoic acid, Salicylic acid, Diclofenac	Initial TOC conc. = 10-30 mg L^{-1}; Treatment time = 120min; Volume = 7.0 L; Power = 20-140W.	The TOC removal rate: 60.22% to 75.26% with power from 20 to 140 W.	(Ghafoori et al., 2015)

	sodium,			
Deionized water	Ibuprofen	Initial Conc. = 2.0 mg L^{-1}; Frequency = 1000 kHz; Temp. = 25^{o}C; Time = 60 min; Volume = 1000mL; Power = 100, 80, 60 and 40 W L^{-1}.	Degradation rate (mg L^{-1} min^{-1}): 0.034 (100W); 0.03 (80W); 0.027 (60W) and 0.026 (40W).	(Thokchom et al., 2015)
Millipore water	Dicloxacillin	Initial Conc. = 0.21 mM; Frequency = 600 kHz; Temp. = 20^{o}C; Time = 60 min; Volume = 500mL; Power = 20, 40 and 60 W.	Degradation rate (mol L^{-1} s^{-1}): 1.96 10^{-8} (20W); 3.11 10^{-8} (40W); and 4.36 10^{-8} (60W).	(Villegas-Guzman et al., 2015)
Deionized water	Cetirizine dihydrochloride	Initial Conc. = 5.0 mg L^{-1}; Frequency = 25 kHz; Time = up to 7h; Volume = 20mL; Power = 30W, 50W, 100W and 150 W.	Efficiency of degradation: ~ 50% (30 and 50W); ~ 80% (150 W) and ~90% (100W).	(Sutar and Rathod, 2015)

2.5.2 Influence of the frequency

Frequency is the number of occurrences of a repeating event per unit time. The frequency is one of the most important operational variables in a sonochemical process. The frequency of ultrasound directly affects the generation, oscillation, resonant size, and final collapse of cavitational bubbles in terms of the amount of collapse and the violence of collapse. At lower frequency, more violent cavitation will be produced, resulting in higher localized temperature and pressure. High frequency will reduce cavitational effect because the negative pressure produced by rarefaction cycle is insufficient in duration and/or intensity to initiate cavitation, or compression cycle occurs faster than the time for microbubbles to collapse (Gonzalez-Garcia et al. 2010a; Leong et al. 2011). Figure 2-2 shows the frequencies range diagram and its effects on sonochemistry.

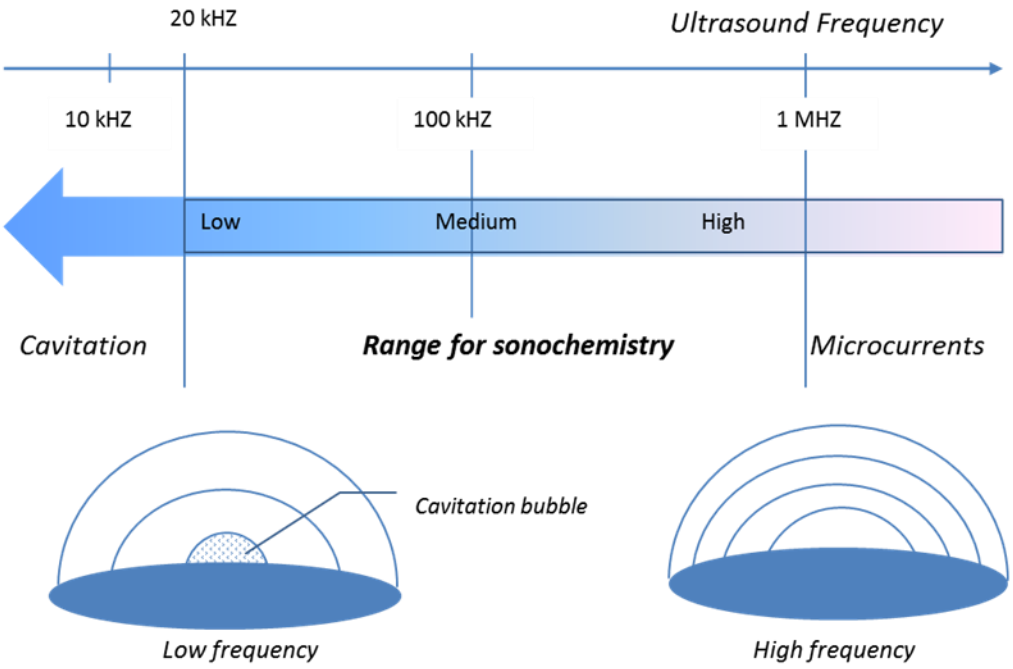

Fig. 2-2 Frequency range diagram and its effect on sonochemistry.

Generally, at low frequency, ultrasound has stronger sonophysical effects, and at high frequency, it increases the production of hydroxyl radicals (Chen et al. 2011; Mason et al. 1990). Thokchom et al. (2015) have reported that high frequencies in the range of a few hundred to thousand kilohertz are recommended for the efficient degradation of contaminants pollutants in wastewater treatment, and lower frequencies are more typically employed in biotechnological applications, textile processing, solid–liquid extractions. At very high frequencies, the cavitation activity is reduced because either the rarefaction cycle of the sound wave produces a negative pressure which is insufficient in its duration and intensity to initiate cavitation or the compression cycle occurs faster than the time required for the bubbles to collapse (Gonzalez-Garcia et al. 2010a; Mason 2011). For example, at 20 kHz, 20,000 implosions per second could occur, whereas at 300 kHz, approximately 100,000 cavitational events occur per second (Chen et al. 2011). In a study by Rahmani et al. (2014), the application of the frequencies over 120 kHz does not have a noticeable effect on efficiency removal of tinidazole from aqueous solution by sonolysis in the presence of hydrogen peroxide. The efficiency degradation was about 40 % at 40 kHz and 60 % at 80 kHz. At higher frequencies, the efficiency was 74 % at 120 kHz and 75 % at 180 kHz. The author argued that by increasing the frequency, the number of acoustic cycles and bubble collapse increased. The resulting bubbles released less energy than the low-frequency ones for one single pulsation. Thus, applying higher frequency may compensate for the lower energy released in the single-bubble explosion. In the study of sonoelectrochemical oxidation of ibuprofen (IBP), Thokchom et al. (2015) have found that the kinetic rate constants for frequencies from 35 to 1000 kHz were found to increase from 0.014 min^{-1} (~19 % IBP removal) to 0.027 min^{-1} (~58 % IBP removal) and 1000 kHz shown to be the best for the oxidation of IBP. Author suggested that increased frequency decreases the lifetime of bubbles, thereby increasing bubble collapse per unit time producing more OH radicals, which in turn facilitates the transport activities across the interface (Thokchom et al. 2015). Besides, at a higher frequency, a shorter lifetime and quick collapse favor the ejection of hydroxyl radicals before they are able to recombine (Vajnhandl and Le Marechal 2007). For relatively low frequency, the number of cavitational events is increased, and bubbles have relatively more time to grow and collapse, which results in maximum size and violent collapse. However, for relatively high frequency, a large number of oscillations (the pulsation and collapse of the bubble occurs more quickly) might still be attributed to a larger fraction of hydroxyl radical escaped from the bubbles and lead to a higher frequency resulting in increase in the number of free radicals in the system. These results were confirmed by Im et al. (2013) during degradation of acetaminophen and naproxen by using ultrasound in the presence of single-walled carbon nanotubes. The authors found that the efficiency degradation of acetaminophen was 27.1 % at 28 kHz and 86.1 % at 1000 kHz. Similar results have also been reported in the case of naproxen, and the degradation efficiency was 52.5 % at 28 kHz and more than 99 % at 1000 kHz. After applying ultrasound assisted enzyme catalyzed degradation of cetirizine dihydrochloride, Sutar and Rathod (2015) showed higher degradation at 25 kHz (~80 %) than 40 kHz (~30 %). At higher frequency, the cavitation decreases because smaller and less energetic bubbles are formed which lead to decreased cavitation zone violence. Also it has been observed that at same energy dissipation in the reactor: less scattering and attenuation of sound waves as well as easy cavitation at lower frequency (Sutar and Rathod 2015). The optimal frequency for the degradation of an organic compound also depends on its properties, such as low or high solubility, volatility. For the low volatility (similar to properties of most of the pharmaceutical products), the degradation rate was better at the frequency at which the formation of hydroxyl radical or hydrogen peroxide was higher. Isariebel et al. (2009) showed that the degradation efficiency of the levodopa and the paracetamol in aqueous solution by the ultrasound at various frequencies (574, 860, and 1134 kHz) is maximum at 574 kHz, which was strongly linked to the reaction, whereby hydroxyl radicals and hydrogen peroxide were formed. Guyer and Ince (2011) indicated that a relatively high degradation rate was achieved at a frequency of 861 kHz during degradation of diclofenac in water by sonolysis. After 60 min of treatment, maximum rates were attained at 861 kHz due to a larger number of active bubbles and oscillations and ultimately efficiency of hydroxyl radical release into the bulk solution. Some other authors (Nejumal et al. 2014; Xiao et al. 2014a) have reported the same phenomena that faster degradation of pharmaceutical organic compounds at frequencies ranging from 350 to 600 kHz. The summary effect of the various frequencies on the sonochemical degradation of pharmaceutical organic compounds is shown in Table 4.

Table 2-4 Removal of different types of organic pollutants in solutions using sonochemical processes – effect of frequency

Matrix	Type of pollutant	Operating conditions	Results and comments	References
Deionized water	Levodopa	Initial Conc. = 25 mg L^{-1}; Treatment time = 240 min; Power = 32 W; Volume = 300 mL; Temp. = 20^oC; Frequency = 574 kHz, 860 kHz and 1134 kHz.	Efficiency of degradation: 91% (574 kHz); 90% (860 kHz) and 66% (1134 kHz).	(Isariebel et al., 2009)
Deionized water	Paracetamol	Initial Conc. = 25 mg L^{-1}; Power = 32W; Temp. = 20^oC; Treatment time = 240 min; Volume = 300 mL; Frequency = 574 kHz, 860 kHz and 1134 kHz.	Efficiency of degradation: 95% (574 kHz); 92% (860 kHz) and 67% (1134 kHz).	(Isariebel et al., 2009)
Millipore water	Diclofenac	Initial Conc. = 30 µM; Power = 108 W; Temp. = 25^oC; Treatment time = 60 min; Volume = 500 mL; Frequency = 577 kHz, 861 kHz and 1145 kHz.	Efficiency of degradation: ~ 19% (577 kHz), ~ 21% (861 kHz), ~ 14% (1145 kHz)	(Guyer et al., 2011)
Deionized water	Acetaminophen	Initial Conc. = 5 µM; Power = 180 W; Temp. = 25^oC; Treatment time = 60 min; Volume = 1000 mL; Frequency = 28 kHz and 1000 kHz	Efficiency of degradation: 27.1% (28 kHz); 86.1% (1000 kHz).	(Im et al., 2013)
Deionized water	Naproxen	Initial Conc. = 5 µM; Power = 180 W; Temp. = 25^oC; Treatment time = 60 min; Volume = 1000 mL; Frequency = 28 kHz and 1000 kHz	Efficiency of degradation: 52.5% (28 kHz); > 99% (1000 kHz).	(Im et al., 2013)
Ultrapure water	Atenolol	Initial Conc. = 10^{-5} mol L^{-1}; Power = 50 W; Treatment time = 60 min; Temp. = 25^oC; Frequency = 200, 350, 620 kHz and 1 MHz.	Efficiency of degradation: ~ 16% (200 kHz), ~ 43% (350 kHz), ~ 36% (620 kHz) and	(Nejumal et al., 2014)

			~ 36% (620 kHz).	
Ultrapure water	Tinidazole	Initial Conc. = 80 mg L^{-1}; Power = 750W; Temp. = $25^{o}C$; Treatment time = 150 min; Volume = 100mL; pH = 3; C_{H2O2} = 333 mM L^{-1}; Frequency = 40 kHz, 80 kHz, 120 kHz and 180 kHz.	Efficiency of degradation: ~ 40% (40 kHz); ~ 60% (80 kHz); ~ 74% (120 kHz) and ~ 75% (180 kHz).	(Rahmani et al., 2014)
Millipore water	Ciprofloxacin	Initial Conc. = 100 µM; Power density = 400 WL^{-1}; Temp. = $20^{o}C$; Time = 150 min; Volume = 125mL; pH = 8.5; Frequency = 20 kHz and 620 kHz.	Efficiency of degradation: ~ 26% (20 kHz); ~ 98% (620 kHz).	(Xiao et al., 2014a)
Millipore water	Ibuprofen	Initial Conc. = 100 µM; Power density = 400 WL^{-1}; Temp. = $20^{o}C$; Time = 150 min; Volume = 125mL; pH = 8.5; Frequency = 20 kHz and 620 kHz.	Efficiency of degradation: ~ 49% (20 kHz); ~ 99% (620 kHz).	(Xiao et al., 2014a)
Deionized water	Ibuprofen	Initial Conc. = 2.0 mg L^{-1}; Power density = 100 WL^{-1}; Temp. = $25^{o}C$; Time = 60 min; Volume = 1000mL; Frequency = 35 kHz, 300, 500 and 1000 kHz.	Efficiency of degradation: ~ 19% (35 kHz); ~ 34% (300 kHz), ~46% (500 kHz); ~ 58% (1000 kHz).	(Thokchom *et al.*,2015)
Deionized water	Cetirizine dihydrochloride	Initial Conc. = 5.0 mg L^{-1}; Power density = 32 W; Time = up to 7h; Volume = 20mL; Frequency = 25 kHz and 40 kHz.	Efficiency of degradation: ~ 30% (40 kHz); ~ 80% (25 kHz).	(Sutar and Rathod, 2015)

2.5.3 Influence of the temperature

It is known from the literature that cavitation-induced reactions are optimal with respect to operating temperature (Mason 2012; Rooze et al. 2013). Most of the ultrasonic experiments were carried out in temperature-controlled system to ensure that the isothermal conditions are maintained (Mason and Lorimer 2003c). With increasing temperature, the vapor pressure of water increased leading to an easier generation of cavitation bubbles and decreasing temperatures and pressures during the collapse-phase (collapse intensity) (Leong et al. 2011; Margulis and Margulis 2002). With the increasing vapor pressure, more cavitation bubbles are generated, collapsing with lower temperatures resulting in decreased hydroxyl radical concentration and therefore observed decrease in contaminant degradation. Thokchom et al. (2015) mentioned that the degradation trend followed: 40 °C > 30 °C > 20 °C > 10 °C when applied ultrasound to enhanced electrochemical oxidation of ibuprofen. An increase in temperature leads to the increased diffusion rate caused by the decreased viscosity of the medium with increasing temperature. Furthermore, less dissolved gas is present at higher temperatures and higher intensities, and more cavitation bubbles may be formed. Braeutigam et al. (2012), while investigating the degradation of carbamazepine in water by hydrodynamic-acoustic-cavitation, have found that the rate constant depends on the reaction temperature, and thus, an increase in temperature should lead to increased conversion. Reactions below the value of 25 °C resulted in lower formation of cavitation bubbles, lower bubble density, higher collapse intensity, and lower rate constants. For carbamazepine, an optimal temperature of 25 °C was detected which showed 90 % degradation of CBZ. With low solubility of the organic compound, the solubility was improved at higher temperature of the test samples from a heated stock solution (40 °C), as shown by Ziylan et al. (2013), and degradation of diclofenac at pH 3.0 by ultrasound contributed to higher degradation rate. However, an increase in solution temperature was shown to have a negative effect on the formation of cavitation, leading to a linear decrease in the collapse pressure. High temperatures during sonication likely facilitate bubble formation by increasing the equilibrium vapor pressure, and bubbles contain more vapors that cushion bubble implosion and decrease the temperature which was achieved upon bubble collapse, reducing the cavitation effects (Manousaki et al. 2004). Moreover, high temperatures can cause degassing of the liquid phase reducing the number of microsite available for cavitation. The degradation rate of organic compounds was shown to be directly proportional to temperature as organic molecules migrated from the bulk solution to the gas–liquid interface region where the temperature and hydroxyl radical concentration are high (Gallego-Juárez and Graff 2015; Neis 2015; Pétrier 2015). This phenomenon was observed by Im et al. (2013) while investigating ultrasound degradation of acetaminophen and naproxen in the presence of single-walled carbon nanotubes. The degradation rates of the acetaminophen increased gradually from 15 °C to 25 °C or 35 °C; however, temperatures higher than 35◦C resulted in a slight decrease in acetaminophen degradation at 1000 kHz. Similar results clearly show that the increase in temperature is not responsible for a faster mineralization of antipyrine in aqueous solution by sonophotocatalytic (Duran et al. 2013). Another report of Sutar and Rathod (2015) for the degradation of cetirizine dihydrochloride also shows that at lower temperature (30–50 °C), the extent of degradation is lower as compared to higher temperature range (60–70 °C). With an increase in reaction temperature from 40 to 50 °C, the degradation obtained after 7 h was increased from 58 to 84 %. The cavitation effect starts decreasing as the temperature was further increased higher, and only ~70 % of cetirizine dihydrochloride was removed at 60 °C and even lower at 70 °C (~20 %). Table 5 summarizes the effect of temperature on removal of different types of pharmaceutical organic pollutants in solution using sonochemical processes.

Table 2-5 Removal of different types of organic pollutants in solutions using sonochemical processes – effect of temperature

Matrix	Type of pollutant	Operating conditions	Results and comments	References
Millipore water	Carbamazepine	Initial Conc. = 43.9 µg L^{-1}; Time = 15 min; Volume = 1.0 L; pH = 8.5; Frequency = 24 kHz; Temp. = 15-35^{o}C;	The CBZ conversion rate was highest at 25^{o}C (aprox. 90%).	(Braeutigam et al., 2012a)
Millipore water	Antipyrine	Initial Conc. = 50 ppm; C_{H2O2} = 1500 ppm; $C_{Fe(II)}$ = 12 ppm; $UV_{190\text{-}280nm}$ = 150W; Frequency = 24 kHz; Frequency amplitude = 100%; Pulse length (cycles) = 0.3 during 15min; pH = 2.7; Volume = 400 mL; Temp = 30^{o}C.	The increase in temperature is not the responsible for a faster mineralization of antipyrine.	(Duran et al., 2013)
Deionized water	Acetaminophen	Initial Conc. = 5 µM; Power = 180 W; Treatment time = 60min; Volume = 1000 mL; Frequency = 28 kHz; Temp. = 15-55^{o}C.	Efficiency of degradation: 13.2% (15^{o}C); 14.5% (25^{o}C); 12.8% (35^{o}C); 7.7% (55^{o}C).	(Im et al., 2013)
Deionized water	Naproxen	Initial Conc. = 5 µM; Power = 180 W; Treatment time = 60min; Volume = 1000 mL; Frequency = 1000 kHz; Temp. = 15-55^{o}C.	Efficiency of degradation: 83.1% (15^{o}C); 89.9% (25^{o}C); 94.5% (35^{o}C); 93.2% (55^{o}C).	(Im et al., 2013)
Ultrapure water	Diclofenac	Initial Conc. = 30 µM L^{-1}; Frequency = 861 kHz; Time = 50 min; Power = 9W, 14.5W and 57.5W; Volume = 250mL; Temp. = 22^{o}C and 40^{o}C	The Diclofenac fraction in the solution: 0.75 (22^{o}C), 0.86 (40^{o}C).	(Ziylan et al., 2013)

Deionized water	Ibuprofen	Initial Conc. = 2.0 mg L^{-1}; Power density = 100 WL^{-1}; Time = 60 min; Volume = 1000mL; Frequency = 1000 kHz; Temp. = 10^{o}C; 20^{o}C; 30^{o}C; 40^{o}C.	Efficiency of degradation: ~ 15% (10^{o}C); ~ 18% (20^{o}C), ~20% (30^{o}C); ~ 27% (40^{o}C).	(Thokchom *et al*.,2015)
Deionized water	Cetirizine dihydrochloride	Initial Conc. = 5.0 mg L^{-1}; Power = 50 W; Time = 7h; Volume = 20mL; Frequency = 25 kHz. Temp. = 40^{o}C; 50^{o}C; 60^{o}C; and 70 ^{o}C.	Efficiency of degradation: ~ 58% (40^{o}C); ~ 84% (50^{o}C), ~ 70% (60^{o}C), ~ 20% (70^{o}C), .	(Sutar and Rathod, 2015)

2.6 Sonochemical degradation of contaminants in association with different methods

The sonochemical processes for the oxidation of organic compounds have been developed as a powerful tool for treatment of effluents (Compton et al. 1997; Gogate and Pandit 2004; Mason 2012). Thus, Fenton reaction is well known in the degradation of organic material by extra generation of hydroxyl radicals. Hydrogen peroxide generated through cavitation action (ultrasound) of molecular oxygen is highly active toward the destruction of an organic species. Fenton reagent system can be applied to circumvent this problem that enabled the maximum amount of free radicals (specifically hydroxyl radicals) to be generated. This was achieved by the addition of Fe2+ to the solution that is known to catalyze the destruction of organic material through the generation of extra hydroxyl radicals, according to a Fenton-type mechanism. Lan et al. (2012) presented a method for degradation of naproxen by combination of Fenton reagent and ultrasound irradiation. Optimum dosage of Fenton reagent for naproxen removal comprised hydrogen peroxide at 9.98 mmol L−1, ferrous ion at 4.83 mg L−1 while naproxen at 20 mg L−1. The degradation of naproxen by ultrasound alone was very slight (only 30 %); however, when combined with Fenton, a degradation efficiency of 100 % was achieved within 10 min under sonolysis (Lan et al. 2012). In the Fenton process, Fe3+ reacted with H2O2 and produced a complex intermediate (Fe–O2H2+). Under ultrasound irradiation, the decomposition rate of Fe–O2H2 + could be greatly enhanced. Once the Fe2+ was isolated, it reacted with H2O2 and produced ·OH again, and then, a cycle mechanism was established (Sun et al. 2007) following the reaction:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot H + H_2O \qquad (6)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}O_2H^{2+} + H^+ \qquad (7)$$

$$Fe\text{-}O_2H^{2+} \rightarrow Fe^{2+} + \cdot OOH \qquad (8)$$

Due to that, more ·OH can be formed rapidly in the process of US/Fenton, and so, the best degradation result of naproxen was achieved. On the other hand, there are other methods associated with sonochemical processes, such as in the presence of ozone or hydrogen peroxide and in conjunction with photocatalysis. Duran et al. (2013) reported the degradation of antipyrine in aqueous solution using an innovative homogeneous sono-photocatalytic oxidation process. At the selected operation conditions [H_2O_2] = 1500 ppm, [Fe^{2+}] = 12 ppm, pH = 2.7, ultrasound amplitude = 100 %, pulse length (cycles) = 0.3 for 15 min and later 1 min, 92 % of TOC was removed after 50 min resulting in an aqueous solution containing 50 ppm of antipyrine. An important synergistic effect between sonolysis and photoFenton (UV/H_2O_2/Fe) of 45.4 % was quantified using the first-order rate constants for TOC (Duran et al. 2013). Ghafoori et al. (2015) have investigated the use of ultrasound to enhance degradation of synthetic pharmaceutical wastewater (a mixture of 4-aminophenol, paracetamol, phenol, chloramphenicol, benzoic acid, salicylic acid, diclofenac sodium, and nitrobenzene) by applying different processes including sonolysis (US alone), photolysis (UV alone), and combination of both UV and US. Total organic carbon (TOC) measurements were used to determine the effectiveness of oxidation process. After 120 min treatment time, it was found that removal of TOC from US is only about 3.1 % higher with photolytic (8 % reduction in the TOC was observed). However, combining UV and US did not enhance the degradation. The TOC reduction in the US/UV process was 4 % which is lower than that of the single process alone. The lower in reported results could be explained by considering the nature of components being studied which is a multicomponent wastewater more complicated than that of single component. Also, the output power of the US instrument and the power of the UV light could be influential in the degradation efficiency (Ghafoori et al. 2015). In another study, Naddeo et al. (2009) reported a method for the removal of diclofenac in aqueous solutions using ultrasound treatment with ozone addition. Under the conditions applied (31 g h^{-1} O3 flow, at 400 W L^{-1} ultrasonic power density), ozone, ultrasound, and combination of both proved effective in inducing diclofenac oxidation, leading to 22 % of mineralization for O_3 and 36 % for US after 40 min of treatment. The synergy observed in the combined schemes, mainly due to the effects of US in enhancing the O_3 decomposition, led to higher mineralization (about 39 %) for 40 min treatment and to a significantly higher mineralization level for shorter treatment duration. The molecular ozone in aqueous solutions is one of the most active oxidizing agents. It also can interact with water, giving oxygen, hydroxyl ion, and radical. Unlike the ozone, Rahmani et al. (2014) used hydrogen peroxide and ultrasonics assisted in enhancement of the degradation efficiency for the tinidazole removal from aqueous solution. The maximum removal efficiency of 75 % was achieved under the optimum operating conditions (pH 3, 120 kHz frequency, 333 mM L^{-1} of H_2O_2 and 150 min of operating time). It has been confirmed that the ultrasound waves improve agitation and also play a significant role in increasing the reaction rate, which could be due to the enhancement of the contact area between the hydroxyl radicals and the pollutants. The results also revealed that no harmful intermediate compounds were observed. Another approach to the combination, Secondes et al. (2014) have investigated the removal of emerging contaminants (diclofenac, carbamazepine, and amoxicillin) by simultaneous application of membrane ultrafiltration (Me), activated carbon adsorption (A), and ultrasound (US). It is interesting that the addition of ultrasound in the membrane filtration increased removal rate from an average of 92 % in the A–Me process to over 99 % in the US–A–Me process. This enhancement is a result of a fluid flow effect called microstreaming, and intense shear stress is produced as the flow velocities change which allows the contaminants to penetrate the porous structure. Biological is an alternative method for treatment of organic contaminant and has now been investigated along with ultrasound irradiation (Serna-Galvis et al. 2015). This technique uses aerobic microorganisms, and ultrasound was found to be able to remove the pharmaceutical fluoxetine. Biological degradation test of the sonicated and nonsonicated effluents has shown ~70 % of TOC removal within 360 min of sonication compared to ~10 % of TOC removal without sonication. The improvement was due to the transformation of the fluoxetine into more biodegradable substances under ultrasound irradiation (the BOD_5/COD ratio changes from 0.05 to 0.41), and therefore, they could be more easily eliminated in a biological process (Serna-Galvis et al. 2015). The use of enzyme catalyzed in conjunction with ultrasound for degradation of cetirizine dihydrochloride has been also shown to be more effective as compared to conventional enzymatic degradation technique (Sutar and Rathod 2015). Using enzyme catalyzed alone, cetirizine dihydrochloride was degraded less about 13 % only in 24 h. On the combination, the maximum degradation of 91 % has been achieved at optimized experimental parameters (0.02 % enzyme loading (w v^{-1}), 50 °C, power 100 W, frequency 25 kHz and 50 % duty cycle with agitation speed of 200 rpm). It is observed that enzymatic degradation of cetirizine dihydrochloride under the influence of ultrasound irradiation not only enhances the degradation but also reduces the time of degradation. This is due to the fact that more interaction between enzyme and substrate particles enhances the degradation percentage. Recently, the study of using ultrasound, along with electrochemical, has increased considerably for degradation of pharmaceutics contaminants (Thokchom et al. 2015; Tran et al. 2015). The beneficial results from exposing electrochemical cells to the effects of power ultrasound include the enhancement of mass transport, the increase in current efficiencies, and the continuous activation of the electrode surface (Birkin and Silva-Martinez 1997). These effects can be ascribed to the rapid generation and collapse of microbubbles within the electrolyte medium or nearby the electrode surface. This cleaning effect has been reported to improve electron exchanges by peeling out passivation films on surface electrode or piercing them by microholes (Compton et al. 1997). Tran et al. (2015) have described the sonolytic degradation of pharmaceutics pollutants and found that the carbamazepine concentration (10 mg L^{-1}) could be optimally diminished up to 90 % by applying a current intensity of 4.86 A for a 177-min reaction period and by imposing an ultrasound power of 38.29 W. The optimal conditions were subsequently applied for tertiary treatment of municipal wastewater effluent contaminated with 10 µg CBZ L^{-1}. The removal efficiencies of CBZ, TOC, COD, and color recorded were 93, 60, 93, and 86 %, respectively. Likewise, the toxicity was completely removed (bacterium Vibrio fischeri) from municipal wastewater effluent. The synergistic effect is defined as an effect arising between two or more agents, entities, factors, and substances that produce an effect greater than the sum of their individual effects. The degree of synergy, S, which can be calculated via kinetics constant k by the equation:

$$S = \frac{k_{EO-US}-(k_{EO}+k_{US})}{k_{EO-US}} x100 \qquad (9)$$

From this equation, the author calculated the degree of synergy was 11.11 % indicating that the CBZ removal is higher when both processes, ultrasound and electrochemical, are present than individually. In this combination, ultrasounds enhance the mass transfer between the electrolyte and the electrodes (Tran et al. 2015). Other studies performed by Thokchom et al. (2015) on the sonoelectrochemical degradation of Ibuprofen reported that among the methods examined (US, EC, and US/EC), the hybrid method US/EC resulted 89.32, 81.85, and 88.7 % degradations using NaOH, H_2SO_4, and deionized water, respectively, with a constant electrical voltage of 30 V, an ultrasound frequency of 1000 kHz, and a power density of 100 W L^{-1} at 25 °C in 1h treatment time. When compared to single process alone, only 73.81 % (NaOH), 50.54 % (H2SO4), and 21.46 % (deionized water) removals of IBP were achieved by electrolysis. The positive synergic process may be attributed to various mechanisms such as acoustic streaming induced by the ultrasonic transducer, enhancing mass transport to the electrode, electrode surface activation by hindering passive layer formation due to cavitational collapse at the solid–liquid interface; a highly reactive ·OH radicals produced by violent collapse of ultrasonic cavitation (Thokchom et al. 2015). Table 6 summarizes the removal of different types of pharmaceutical organic pollutants in solution using sonochemical combination process.

Table 2-6 Removal of different types of organic pollutants in solutions– sonochemical in association with different methods

Association methods	**Contaminants**	**Operating conditions**	**Results and comments**	**References**
Sono-Ozonation	Diclofenac	Initial Conc = 40 mg L^{-1}; Treatment time = 40min; Frequency= 20 kHz; Volume = 150 mL; Temp. = 20^{o}C; O_3 = 31 g h^{-1}; pH =3-4; US power = 400 W L^{-1}.	Efficiency of degradation (TOC removal): US = 36%, O_3 = 22% and US+O_3= 39%.	Naddeo et al. (2009)
Sono-Fenton	Naproxen	Initial Conc = 10 mg L^{-1}; Treatment time = 33min; Frequency= 59 kHz; Volume = 50 mL; Temp. = 28–33^{o}C; Fe^{2+} = 2.43 mg L^{-1}; H_2O_2 =1.76 mmol L^{-1}; pH =3.0; Ultrasonic power = 450W.	Degradation efficiency: US = ~30%, Fenton = ~50% and US/Fenton = 100%.	(Lan et al., 2012)
Sonophotocatalytic	Antipyrine	Initial Conc. = 50 ppm; C_{H2O2} = 1500 ppm; $C_{Fe(II)}$ = 12 ppm; Frequency = 24 kHz; Frequency amplitude = 100%; Pulse length (cycles) = 0.3 during 15min; pH = 2.7; Volume = 400 mL; Temp = 28-50^{o}C	Synergistic degree: UV/H_2O_2/Fe/US = 45.4%.	(Duran et al., 2013)
Sono-ultrafiltration	Diclofenac, carbamazepine, and amoxicillin	Initial Conc. = 50 ppm; Membrane ultrafiltration (AME) 6.6 cm^2, Permeate flux= 150 L m^2 h; US frequency = 35 kHz. Time = 240min.	Efficiency of degradation: AME= 92%; US/AME > 99%.	(Secondes et al., 2014)

Sono-Biological	Fluoxetin	Initial Conc. = 16.0 mg TOC L^{-1}; Volume = 300 mL; Power = 60W; Frequency = 60 kHz; Temp. = 20^{o}C; Biological process= aerobic microorganisms (aerated in 5 days, 37 °C and 2% v/v of microorganisms.)	~70% of TOC removal with 360 min of sonication compare with ~10% of TOC removal without sonication	(Serna-Galvis et al. 2015)
Ultrasound assisted enzyme catalyzed	Cetirizine dihydrochloride	Initial Conc. = 5.0 mg L^{-1}; Power = 100 W; Time = 7h; Volume = 20mL; Frequency = 25 kHz. Temp. = 50^{o}C.	Efficiency of degradation: With sonication = 91%; without sonication = 13%.	(Sutar and Rathod 2015)
Sonophotolytic	Synthetic pharmaceutical wastewater	Initial TOC conc. = 20 mg L^{-1}; Treatment time = 120min; Volume = 7.0 L; Power = 80W, UV_{253nm} = 13W, pH=3.9, air flow rate = 2 L min^{-1}.	Efficiency of degradation (TOC removal): UV = 8%, UV/US = 4%.	(Ghafoori et al., 2015)
Sono-Electrochemical	Carbamazepine	Initial conc. = 10.0 mg L-1; time = 120 min; volume = 4.0 L; electric current = 2A, US power = 40 W, frequency = 500 kHz, temp. = 25oC;	Efficiency of degradation: EO= 48%; US= 8%; EO-US=58%. Synergistic degree = 11.11%.	(Tran et al. 2015)
Sono-Electrochemical	Ibuprofen	Initial conc. = 2.0 mg L-1; time = 60 min; volume = 1000mL; electric voltage = 30 V, US power = 100 W L-1, frequency = 1000 kHz, temp. = 25oC; Electrolyte = NaOH.	Efficiency of degradation: EC= 73.81%; US= 70.7%; EC-US=89.32%.	(Thokchom et al. 2015)

2.7 Current, future prospects and challenges of sonochemical processes

Ultrasound-induced cavitation is an effective tool for application of sonochemistry in the field of wastewater treatment. This tool has been recently exploited rapidly due to the availability of industrial transducers and ultrasonic reactors. The hydroxyl radicals generated during cavitation can be used for the oxidative degradation of organic pollutants in an aqueous system. Recently reported studies have shown that sonochemical degradation of various pharmaceutical organic pollutants could be achieved by both oxidative and pyrolysis mechanisms. Ultrasound has shown that they have been often used in conjunction with conventional techniques, such as ultra-filtration, biological, UV, Fenton, ozonation, electrochemical, that can increase effectiveness and also demanded lower requirements for chemical or energy usage. In combination with ozone or hydrogen peroxide, ultrasound can be used to add excessive oxidizing power which provides faster degradation rates. Ultrasound can also combine with ultraviolet light for the destruction of chemical pollutants. The improvement is the result of mechanical effects of ultrasound to increase mass transport in the system. However, effect of ultrasound on the synergistic effect (lower or higher efficiency), mass transport (increase or decrease in the transport of species in the bulk), especially effect of ultrasound on the cleaning electrodes surfaces (in sono-electrochemical or sono-photo-electrochemical), is still not cleared and is under development. More over many of these techniques based on ultrasound are frequently unclear because by-products have been unidentified or even more persistent and toxic than original contaminants. It is well known that the beneficial effect of ultrasound for cleaning is widely used, and during the electrochemical treatment, the organic compounds and/or sample constituents have usually strong interactions with the surface of electrodes thus inhibiting their usage in practical. The future study should be focus on the association of ultrasound with other methods and the synergistic phenomena. The energy consumption, efficiency, and another important factor such as reactor design, scale-up also need to be considered. The reactor design in terms of the energy requirement, the size of the transducer, ratio of the transducer to the reactor diameter, also size of reactor, and position of the transducers should be considered as to play an important role in the specific application. Electrochemical processes can be a powerful tool for the degradation of contaminant, since the ultrasound is responsible for the increase in mass transport, activation of electrodes surfaces using the electrochemical direct/indirect oxidized contaminants. Ultrasound is particularly effective due to its cavitational effect, and it can reach electrode surface or mixing the system which is not easily reached by conventional methods. The main drawback of sonochemical processes is its energy cost and its application at large scale. The important scale-up consideration is to set up the optimum parameters for the treatment in terms of the operating cost/design/efficiency factor that influence cavitation. However, the application of ultrasound on an electrolytic solution is beneficial so that it reduces the resistant, activation electrode surface, thereby allowing discharge at lower applied voltage, which could contribute to lower consumption of energy for total system. Also, the design and produced materials should be planned to overcome application on large scale to provide economically viable treatments.

2.8 Conclusion

Ultrasonic cavitation, which is an AOP, has been proposed as an attractive alternative method for the treatment of pharmaceutical contaminants due to its advantages of being nonselective and without generating secondary pollutants. Different theories are usually used to explain sonochemical effect, but hot-spot theory is usually used to explain the process, in which microbubbles are produced to generate heat and different reactive species. Ultrasonic cavitation is known to generate reactive species which are able to oxidize toxic contaminants present in the environment. The mechanisms of ultrasound make it unique when compared with other AOPs. Ultrasound can effectively decompose pharmaceutical compounds in aqueous solution, and the extent of degradation depends strongly on the operating conditions, such as ultrasound power, ultrasound frequency, and temperature of the medium. However, the degradation rate is slow if only the ultrasonic treatment is used. Therefore, some efforts have been made to increase the degradation efficiency by applying hybrid techniques, such as sonobiological, sonofiltration, sonoelectrochemical, sonophotocatalytic, sono/Fenton/ozonation. The combination has shown that the effectiveness of this application can be increased. This proves that sonochemical processes is an advanced technology and is gaining importance for the purification of contaminated water, especially for pharmaceutical pollutants.

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CHAPITRE 3 Sonochemical degradation of the persistent pharmaceutical carbamazepine

Ce chapitre est constitué dès l'article suivant:

Tran, N., Drogui, P., Zaviska, F., Brar, S.K. Sonochemical degradation of the persistent pharmaceutical carbamazepine (2013) *Journal of Environmental Management*, 131, pp. 25-32. (DOI: 10.1016/j.jenvman.2013.09.027).

3.1 ABSTRACT

The objective of this work was to evaluate the potential of a sonochemical oxidation process for the degradation of carbamazepine (CBZ). Several factors, such as electrical power, treatment time, pH and initial concentration of CBZ were investigated. Using a 2^4 factorial matrix, the best performance for CBZ degradation (90.1 % of removal) was obtained with an electrical power of 40 W, a treatment time of 120 min and an initial pH of 10.0 imposed in the presence of 6.0 mg L^{-1} of CBZ. The treatment time and the calorimetric power were the most influential parameters on the degradation rate of CBZ. Subsequently, the optimal experimental parameters for CBZ degradation were investigated using central composite design. The sonochemical oxidation process, applied under optimal operating conditions (at an electrical power of 43 W for 116 min), oxidized 86 and 90 % of the initial CBZ concentration of 5.62 mg L^{-1} and 8.05 µg L^{-1}, respectively. During the sonochemical process, CBZ was primarily transformed into anthranilic acid and acridine.

3.2 INTRODUCTION

The increasing production and intensive use of pharmaceutical products has led to the entry of these products into the environment and to the eventual pollution of soil, ground and surface water. The pharmaceutical residues have been identified and quantified in sewage treatment plant effluents, surface waters, ground water and drinking water (Sires and Brillas, 2012). The presence of these residues poses a potentially serious risk to both the environment and to human health due to direct or indirect exposure to the residues in food and drinking water (Cleuvers, 2004). Carbamazepine (CBZ) is a prescription drug used for the treatment of epilepsy as well as for various psychotherapeutic applications. In Canada, approximately 28 tons of prescription CBZ was sold in 2001 (Miao et al., 2005). Some pharmaceutical discharges are degraded within the sewage treatment plants, but a removal rate below 10 % for CBZ was recorded (Bound et al., 2006). CBZ appears to be more persistent than other pharmaceuticals in the aquatic environment. Due to it's high persistence, it is resistant to biodegradation at low concentrations and conventional physicochemical, biological treatment of effluents are often not significantly decomposed or removed. Due to that CBZ was used as an anthropogenic marker in the environment by which standards could be set regarding the fate of many pharmaceuticals and healthcare products in the environment (Scheurer et al., 2011; Vernouillet et al., 2010). Therefore, a need exists for efficient treatment technology for the removal of this pollutant from the aquatic environment.

Advanced oxidation processes (AOPs) have been proposed as alternative methods for the removal of many toxic and bio-recalcitrant compounds in wastewater (Chong et al., 2011). AOPs are characterized by the generation of the hydroxyl radical species (·OH). These radicals are short-lived, highly reactive and able to selectively oxidize organic pollutants. A chemical oxidation process using UV/H_2O_2 has been investigated by Vogna et al. (2004) to degrade CBZ. Other advanced treatment technologies, such as ozonation, UV irradiation were effective in removing CBZ (Ternes et al., 2002). These methods achieve effective oxidation of CBZ, but the large chemical consumption of H_2O_2 or O_3 and the relatively high treatment costs constitute major barriers for large-scale applications (Martinez-Huitle and Ferro, 2006).

The ultrasonication process has been identified as a successful alternative for the destruction and mineralization of some recalcitrant organic compounds in water and does not require the addition of chemicals (Gogate, 2007; Naffrechoux et al., 2000). Since 1990, the ultrasound process has received considerable interest for the destruction of organic pollutants that are present in wastewater (Gogate, 2008). Acoustic cavitation, derived from the high calorimetric power of a liquid, can provide unusual and unique reaction sites as a result of the extremely transient and small cavitation bubbles that are created with high temperatures and high pressures. Ghauch et al. (2011) investigated the suitability of CBZ oxidation by an improved Fenton's process based on ultrasonic technique. Another study conducted by Naddeo et al. (2009) reported the ultrasound treatment of CBZ with gas sparging to enhance the sonochemical activity. A recent study using the combination of sonochemical-hydrodynamic (ultrasound and utilization of hydrodynamic phenomena) was carried out by Braeutigam et al. (2012). Most of the studies cited in the literature combine sonochemical oxidation processes with other processes (chemical or physical processes) to remove CBZ from water.

To the best of our knowledge, this is the first time that, complementary Factorial Design (FD) and Central Composite Design (CDD) experimental methodologies have been instrumental to identify the optimal operating set of conditions for the efficient degradation of CBZ using sonication alone. The aim of the present study is to evaluate the performance of an ultrasonication process for the efficient treatment of water contaminated by CBZ. Thus, an experimental design methodology was used to investigate the influence of the principal experimental parameters (electrical power, treatment time, pH and pollutant concentration) on the efficiency of the ultrasonication process for CBZ degradation. A second objective of this study was to use a statistical method for the rational analysis of the combination of operational factors that led to the best treatment process. In addition, the specific objectives of the present work were to propose a mechanism (reaction pathway) for CBZ degradation based on the identified by-products and to verify the quality of treated effluent (versus untreated effluents) in terms of its toxicological effect.

3.3 EXPERIMENTAL

3.3.1 Ultrasonic reactor setup

Ultrasonic irradiation of the aqueous samples was performed in a batch sonolysis reactor. The reactor unit was made of Pyrex glass and characterized by a double layer cylinder; it possessed a 4.0 L capacity with dimensions of 80 cm (height) x 8.0 cm (diameter). Ultrasonic waves were introduced from the bottom of the reactor via a ceramic transducer (a piezoelectric disk having a diameter of 4 cm). The frequency (520 kHz) and power (from 10 to 40W) of the piezoelectric disk were supplied and controlled by an external waveform generator (Agilent 33210A, Agilent Technologies Canada Inc.) equipped with a low frequency amplifier (AG 1016, T&C Power

Conversion Inc.). The reactor temperature was held constant at 20oC using a Polystat cooling/heating recirculator (Cole-Parmer Canada Inc.). Figure 3-1 shows a schematic drawing of the ultrasonic reactor setup used for this study.

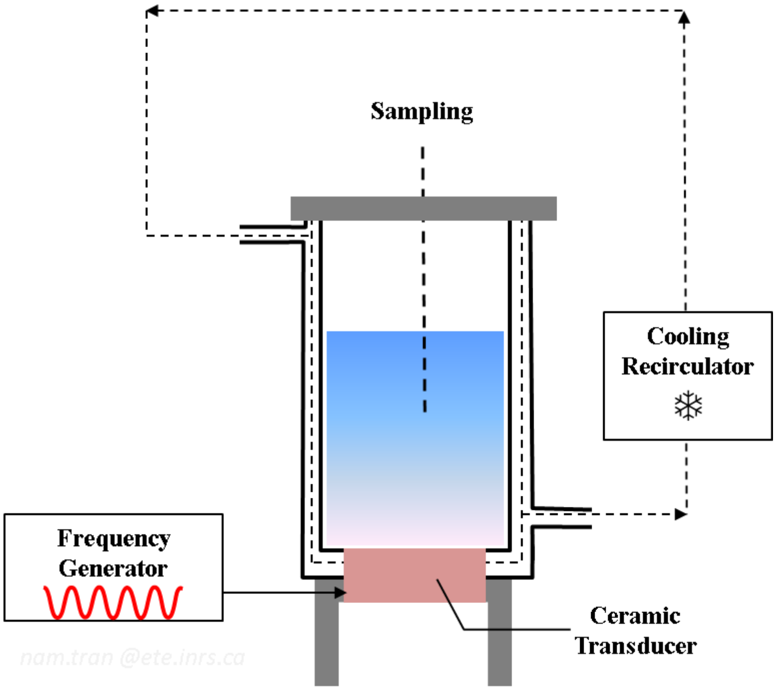

Figure 3-1 Schematic diagram of the experimental setup.

3.3.2 Preparation of the synthetic solution

CBZ analytical grade reagent (99 %) was obtained from Acros Organics BVBA (Belgium). Synthetic solutions of CBZ were prepared in glass beakers containing 3.5 L of demineralized water and 21 to 42 mg of CBZ. The CBZ was solubilized using a magnetic stirrer (500 rpm) at an ambient temperature (25°C) for 24 h. The resulting mixtures constituted the CBZ solutions (final concentrations in the range of 6.0 - 12 mg L^{-1}). All CBZ degradation experiments were performed with a volume of 1.0 L.

3.3.3 Ultrasound reactor characterization

Calorimetric tests

The objective of the calorimetric tests was to determine the sonochemical efficiency of the transducer. The methodology used for the estimation of the sonochemical efficiency of the system is mentioned elsewhere (Gogate et al., 2001). In our experimental conditions, the sonochemical energy can be assimilated to a calorimetric energy owing to the increase of the temperature in a volume of 250 mL of water and for a time period of treatment. The sonochemical efficiency (η) can be expressed as the ratio of the calorimetric power (P_{Cal}) and the electrical power consumption (P_{Elec}).

The acoustic power can be estimated using the following equation:

$$P_{US} = P_{cal} = \left(\frac{dT}{dt}\right)_{t_{US}} .C_P.M_{eau}$$ **Équation 10**

In this expression, $\left(\frac{dT}{dt}\right)$ represents the increase of the temperature of water (C s^{-1}), C_p is the calorific capacity of the liquid (4.2 J. $g^{-1}C^{-1}$), M is the water weight (g) subjected to treatment and t_{US} represents the sonication time (s). The sonochemical efficiency η can be expressed as the ratio of the acoustic power P_{us} and the electric power consumption P_L (corresponded to the power consumed by the generator of frequency).

$$\eta = \frac{P_{us}}{P_L}$$ **Équation 11**

Calorimetric experiments were performed for different PElec (10 W, 20 W, 30 W and 40 W) in a volume of 250 mL of deionized water at a frequency of 520 kHz, which is in the proven high efficiency range (de La Rochebrochard et al., 2012). The increase in temperature per unit of sonication time (K s^{-1}) was recorded every 30 s during the sonolysis process (12.5 min) and the cooling process (12.5 min).

Oxidizing species measurements

It has been reported that when an aqueous solution is irradiated by an ultrasonic wave, water is decomposed and oxidant species are generated (Rooze et al., 2013). Hydroxyl radicals are considered to be the primary oxidizing species generated during the sonication (Birkin et al., 2001). The understanding of the generation rates of hydroxyl radicals is essential to the estimation of the performance of a sonochemical reactor. In this experiment, the total oxidizing species (in terms of hydroxyl radicals) was estimated using the Weissler reaction, which consisted of the oxidation of iodide ions into iodine (Weissler et al., 1950). The sonolysis was performed using different electrical powers (10 W, 20 W, 30 W and 40 W) at 20.0 ± 1.0°C. A volume of 3.0 mL of sample was taken from the reactor every 2.5 min for a period of 25 min of sonication. Tri-iodide was analyzed by absorbance measurements (λ_{I}^{3-} = 26303 L mol^{-1} cm^{-1}) using a spectrophotometer (Cary UV 50, Varian Inc., Mississauga, ON, Canada) at 352 nm.

3.3.4 Experimental design

Optimization of the process conditions for the sonochemical degradation of CBZ was conducted using response surface methodology (RSM). First, a FD was employed to investigate the effects of the main factors and their eventual interaction on the degradation of CBZ. Subsequently, CCD was employed to describe and optimize the CBZ treatment using a sonolysis process. Four independent variables were used in this study: the electric power (X_1), sonication time (X_2), initial CBZ concentration (X_3) and pH of solution (X_4). A four-factorial design (at two-levels) completed by a central composite design, with six replicates at the center of the experimental region for each categorical factor, led to a total number of forty experiments employed for response surface modeling.

The experimental response associated with a 2^4 factorial design (four variables) is represented by a linear polynomial model with the interaction.:

$$\begin{aligned} Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + \\ b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \end{aligned} \qquad \textbf{Équation 12}$$

where Y represents the response (CBZ degradation efficiency) and b_1, b_2, b_3 and b_4 represent the estimation of the principal effect of the independent variables, X_1, X_2, X_3 and X_4, respectively. The interaction coefficients are represented by b_{12}, b_{13}, b_{14}, b_{23}, b_{24} and b_{34}.

The CBZ degradation efficiency (Y) was considered to be a dependent variable (the experimental response). Each independent variable was coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\Delta_x}$$ **Équation 13**

where x_i is the coded value of the independent variable, X_i is the actual value of the independent variable, X_0 is the actual value of the independent variable at the center point, and Δ_X represents the step of the variation. For the evaluation of experimental data, the response (degradation efficiency) was described by a second-order model in the form of the quadratic polynomial equation given below:

$$Y = b_0 + \sum_{i=1}^{k} b_i.X_i + \sum_{i=1}^{k} b_{ii}.X^2{}_i + \sum_{j} \sum_{i=2}^{k} b_{ij}.X_i X_j$$ **Équation 14**

where

Y is the experimental response

b_0 is the average of the experimental response

b_i is the estimation of the principal effect of the factor j for the response Y

b_{ii} is the estimation of the second effect of the factor i for the response Y

b_{ij} is the estimation of the interaction effect between factors i and j for the response Y.

This design is made up of uniformly distributed points within the space of the coded variable (Xi). Advantages of CCD are the possibility of exploring the whole of the experimental region and the usefulness of interpolating the response. The coefficients of this model are calculated in the experimental region using the least squares method

$$B = \left(X^T X\right)^{-1} X^T Y$$ **Équation 15**

where B is the vector of estimates of the coefficients, X is the model matrix, and Y is the vector of the experimental results. The CCD matrix allows for the description of a region around an optimal response and is comprised of a factorial matrix (described above) and twelve additional experiments. The twelve additional assays consisted of six runs, required at the center of the experimental region investigated, plus six axial runs. For the axial runs matrix, α has been chosen to have an iso-variance property by using rotation, with $\alpha = (N_f)^{1/4} = 1.682$ (N_f represents the number of points required for the factorial matrix).

The experimental range and levels of independent variables investigated for CBZ degradation with the coded values are shown in Table 1. The values of the variables and their variation limits were selected based on previous literature (Braeutigam et al., 2012; Ghauch et al., 2011; Hamdaoui and Naffrechoux, 2008; Naffrechoux et al., 2000).

Table 3-1 Experimental range and levels of independent variables.

Coded variables (x_i)	**Factor (u_i)**	**Description**	**Experimental field**		**$U_{i,0}$**	**ΔU_i**
			Min value (−1)	Max value (+1)		
X_1	U_1	Power (W)	20	40	30	10
X_2	U_2	Time (min)	60	120	90	30
X_3	U_3	CBZ conc. (mg L^{-1})	6	12	9	3
X_4	U_4	pH	7	10	–	–

3.3.5 Analytical details

CBZ measurements

The concentration of CBZ in the solution was determined by the mean of the absorption spectral measurements for ease of analysis during optimization. The maximum absorption of CBZ measured at 286 nm was chosen to evaluate the residual CBZ concentration. A calibration curve of known CBZ concentration (0.0-15.0 mg L^{-1}) versus relative absorbance was used to calculate the residual CBZ concentration and to define the efficiency. Once the appropriate values of the optimal parameters were determined, the optimal conditions were repeated in triplicate to verify the reproducibility. During this series of experiments, the residual concentration of CBZ and the by-products were analyzed by liquid chromatography/mass spectrometry (LC-MS/MS). The chromatographic column used was the Hypersil Gold C18 (Thermo Hypersil Ltd., Runcorn, UK) with a particle size of 3.0 µm and a 2.1 x 100 mm inner diameter. The isocratic mobile phase was A: water and B: acetonitrile at a flow rate of 200 µL min^{-1}. Mass spectral data shown in this study were acquired using LCQ Duo ion trap tandem mass spectrometry (Thermo Finnigan, USA) equipped with an electrospray ionization (ESI) source operated in the positive ion mode. Qualitative analysis of CBZ was determined using the standard addition method (SAM). SAM is based on the addition of small known quantities of a standard to the sample. Calibration solutions were prepared by serial dilution of the stock solutions in methanol, at concentrations of 2.0 µg L^{-1} – 1.5 mg L^{-1}. A certified control was prepared at a concentration of 5.0 mg L^{-1} in the center of the curve. The recovery percentage of the analysis was 83 %, and the limit of detection was 0.4 µg L^{-1}.

Other parameter measurements

The pH and temperature were measured using a pH/conductivity meter (Oakton model 510) equipped with a pH and temperature probe. Total organic carbon (TOC) was measured using a Shimadzu TOC 5000A analyzer (Shimadzu Scientific Instruments, Kyoto, Japan). The quality of the treated solution (versus untreated solution) was evaluated using a biotest battery to gain information about its toxic effect. Microtox bioassay tests were performed, which included a standardized toxicity test using the luminescent marine bacterium, Vibrio fisheri (Software MTX6, version 6.0, Microbics Corporation). This test consisted of one control and six serial dilutions of each sample (1.5, 3.0, 6.25, 12.5, 25.0 and 50 % v v^{-1}). The endpoint of the Microtox test is the measurement of bioluminescence reduction. The bioluminescence emitted by V. fisheri was first measured after 10 min of incubation using a control assay that did not contain any sample. Then, the synthetic solution (treated or untreated) was added to the bacterial suspension. The bioluminescence reduction measurements were determined after a 5, 15 and 30 min exposure to the contaminant. The toxicity was determined by measuring the EC50, which is the concentration of the test sample at which there is 50 % reduction in bacterial light production.

3.3.6 Data processing and analysis

Experimental data were obtained from the average of three to five treatment replicates. Uncertainties were removed and calculated with a significance level of $p \leq 0.05$. The analysis of variance (ANOVA) and other statistical results were calculated and generated using the Design Expert Software version 7.1 (Stat-Ease Inc., USA).

3.4 RESULTS AND DISCUSSION

3.4.1 Characterization of the ultrasonic reactor

Sonochemical efficiency

The acoustic efficiency was calculated using a calorimetric method based on the above equation (Eq. 1). The results are summarized in Table 3-2.

Table 3-2 Variation of the sonochemical efficiencies at 520 kHz.

Parameters	**Unit**	**Electric Power (W)**			
		10	20	30	40
Water volume	mL	250	250	250	250
Sonolysis time	min	12.5	12.5	12.5	12.5
Acoustic power	W	4.19	11.6	17.5	23.5
Acoustic efficiency	%	41.9	58.2	58.5	58.7

The calorimetric power calculated by this method varied from 4.19 W to 23.47 W, whereas the imposed electrical power varied from 10 to 40 W. The total sonochemical efficiencies were 41.9 %, 58.2 %, 58.5 % and 58.7 % for 10, 20, 30 and 40 W, respectively. The sonochemical efficiencies recorded for 20 W, 30 W and 40 W were very similar and higher than that measured for 10 W. As the calorimetric power increases, the transmittance of ultrasonic energy into the reactor increases. Due to this energy, the pulsation and collapse of bubbles occur at a faster rate, resulting in a larger number of cavitation bubbles. The effect of power (amplitude) is that the higher power increases the number of bubbles undergoing cavitation (Neppolian et al., 2009). These results are consistent with those obtained by Hamdaoui et al. (2008) while treating 4-chlorophenol (0.78 mM solution) using a sonochemical oxidation process. After 10 min of treatment, the sonochemical degradation rate of 4-chlorophenol was increased from 5 to 10 µM min^{-1} when ultrasonic power increased from 15.2 to 38.3W.

Generation of oxidant species

Fig. 3-2 shows the variation in the residual concentrations of oxidant species as a function of time for different electrical powers.

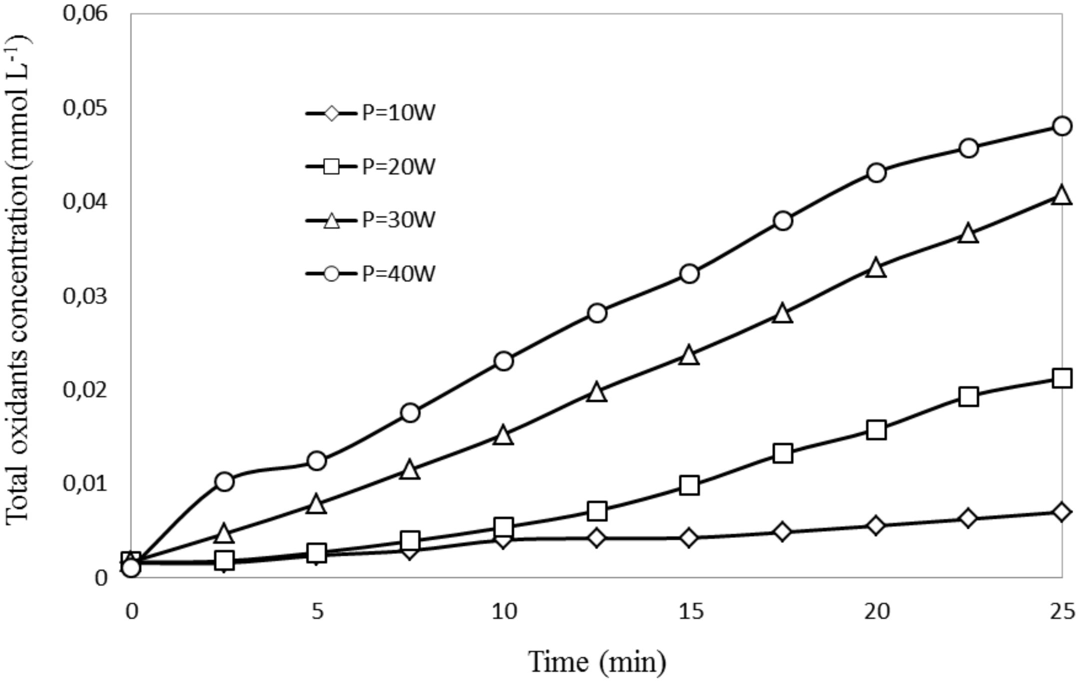

Figure 3-2 Variation of the total oxidants concentration versus sonolysis time.

The figure shows that the oxidant species concentrations (in terms of the hydroxyl radical) increased linearly with the sonication time. From 0 to 25 min, the ●OH concentration increased slowly, with the application of a relatively low electrical power (such as 10 W or 20 W). The hydroxyl radical concentrations varied from 0.0 to 0.02 mM for 20 W and from 0.0 to 0.005 mM for 10 W. In comparison, when an electrical power of 30 W or 40 W was used, the residual ●OH concentrations were two to ten times higher than those recorded using either 10 or 20 W after 25 min of sonolysis. These results are consistent with those recorded by Henglein and Gutierrez (1990) while evaluationg the amount oxidant species during a sonochemical process. They observed that the amount of oxidant species (oxidation of KI) linearly increases till a power dissipation of 50 W, marginally increases with a further increase till 100W and then decreases sharply. In fact, the effect of ultrasonic power and oxidant species are mainly influence by the bubble dynamics. Bubble dynamics studies indicated that the bubble distribution in terms of size, number of bubbles, maximum life time and collapse pressure are complex function of power dissipation rate (Gogate et al., 2011). Similar results have also been reported by Gogate et al. (2011). As power dissipation rate increases, the number of bubbles formed around the transducer surface increases significantly and results in a cloud formation due to coalescence effects. These bubble clouds can absorb or scatter the incident sound waves resulting in decrease transfer of energy and the concentration of oxidant species can decrease.

3.4.2 Effect of the experimental parameters on CBZ degradation

The influence of four main factors on the CBZ degradation was investigated including electrical power (U1), sonolysis time (U2), initial concentration (U3) and pH (U4) using the FD methodology by means of a factorial matrix (2k). The experimental factorial matrix and results are summarized in Table 3-3.

Table 3-3 Experimental factorial matrix and degradation efficiency.

Run	**Experiment design**				**Experiment plan**				Degradation efficiency (%)
	X_1	X_2	X_3	X_4	U_1	U_2	U_3	U_4	
1	−1	−1	−1	−1	20	60	6	pH 7	37.93
2	−1	+1	−1	−1	20	120	6	pH 7	41.63
3	−1	−1	+1	−1	20	60	12	pH 7	27.97
4	−1	+1	+1	−1	20	120	12	pH 7	39.61
5	+1	−1	−1	−1	40	60	6	pH 7	55.89
6	+1	+1	−1	−1	40	120	6	pH 7	87.12
7	+1	−1	+1	−1	40	60	12	pH 7	45.98
8	+1	+1	+1	−1	40	120	12	pH 7	78.52
9	−1	−1	−1	+1	20	60	6	pH 10	36.43
10	−1	+1	−1	+1	20	120	6	pH 10	39.47
11	−1	−1	+1	+1	20	60	12	pH 10	32.15
12	−1	+1	+1	+1	20	120	12	pH 10	43.17
13	+1	−1	−1	+1	40	60	6	pH 10	60.92
14	+1	+1	−1	+1	40	120	6	pH 10	90.06
15	+1	−1	+1	+1	40	60	12	pH 10	46.05
16	+1	+1	+1	+1	40	120	12	pH 10	80.02

The coefficients of the model were calculated using the half-difference between the arithmetic average of the response values when the associated coded variable is at a level (+1) and the arithmetic average of the response values when the associated coded variable is at level (-1). An approximate function of the degradation efficiency based on the experimental response associated with a 24 factorial design (four variables) is represented below:

$$Y = 52.69 + 15.39X_1 + 9.76X_2 - 3.50X_3 + 0.85X_4 + 6.09X_1X_2 - 1.93X_1X_3 + 1.38X_2X_3 \quad \textbf{Éq. 16}$$

The analysis of variance for the model is summarized in Table 3-4.

Table 3-4 Analysis of variance for selected factorial model.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	6207.15	7	886.74	231.76	< 0.0001
X_1-Power	3791.17	1	3791.17	990.86	< 0.0001
X_2-Time	1524.71	1	1524.71	398.5	< 0.0001
X_3-CBZ conc.	196.49	1	196.49	51.35	0.0018
X_4-pH	11.44	1	11.44	2.99	0.2051
X_1X_2	592.80	1	592.80	154.93	0.0001
X_1X_3	59.87	1	59.87	15.65	0.0207
X_2X_3	30.66	1	30.66	8.01	0.0628
Residual	30.61	8	3.83		
Cor Total	6237.75	15			
Std. Dev.	1.96		R-Squared		0.9951
Mean	52.69		Adj R-Squared		0.9908
C.V. %	3.71		Pred R-Squared		0.9804
PRESS	122.44		Adeq Precision		42.664

The F value (231.76) and the low probability value (Pr > F = 0.0001) indicate that the model is statistically significant for CBZ degradation. The value of the correlation coefficient (R squared) indicates that only 0.01 % of the total variation could not be explained by the empirical model. According to Henika (1982), R-squared should be at least 0.75-0.80 for a good model fit. The R-squared value (0.9951) obtained in the present study indicated that the linear polynomial model described by Eq. (7) explained the reaction well. Calculations using Eq. (7) revealed that the electrical power (b1 = +15.39) greatly influenced the rate of CBZ oxidation. The average rate of CBZ oxidation increased 30.78 % (2 x 15.39) when the electrical power increased from 20 to 40 W. The second most important factor on CBZ oxidation was the sonolysis time, which had a positive effect (b2 = +9.76). The increase in treatment time contributed to an increased rate of CBZ degradation. The average rate of CBZ oxidation increased 19.5 % (2 x 9.76) when the treatment time increased from 60 to 120 min. However, the pollutant concentration had a negative effect (b3 = -3.50) on CBZ oxidation. The increase in the CBZ concentration contributed to a decreased rate of CBZ degradation. The average rate of CBZ oxidation decreased 7.0 % (2 x 3.50) when the pollutant concentration increased from 6.0 to 12 mg L^{-1}. The effect of pH (b4= + 0.85) on CBZ oxidation was relatively weak. The contribution (Pi) of each factor on the response can be calculated according to the following relation:

$$P_i = \left(\frac{b_i^2}{\sum b_i^2} \right) * 100 \quad (i \neq 0)$$ **Équation 17**

where bi represents the estimation of the principal effects on the factor i. Thus, the contribution of the electrical power and the treatment time on CBZ removal is approximately 61.0 % and 24.5 %, respectively, whereas the contribution of pH and initial CBZ concentration account for only 0.19 % and 3.16 %, respectively. The interaction effect of X1X2 on CBZ degradation accounts for 9.6 %, whereas the other interaction effects (X1X3 and X2X3) represent only 0.96 % and 0.49 %, respectively (see Fig. 3-3).

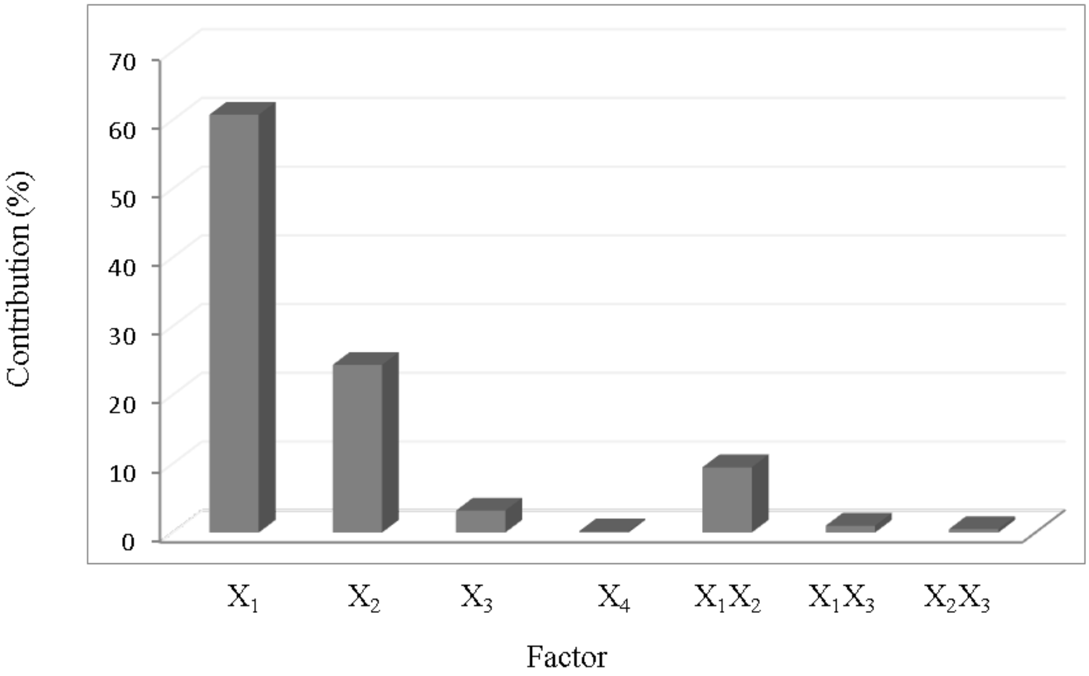

Figure 3-3 Pareto chart standardized effects of single and interaction factors on the degradation of CBZ (X_1:Power; X_2: Time; X_3: Initial CBZ concentration; X_4: pH).

The interpretation of the interaction effect of X_1X_2 on CBZ degradation can be seen in Fig. 3-4.

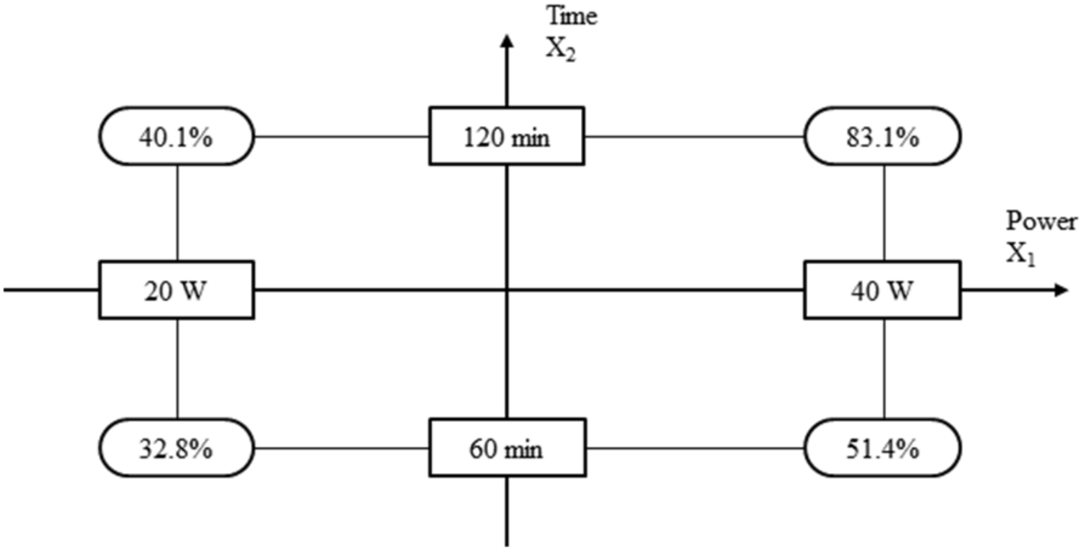

Figure 3-4 Interaction between power applied and sonolysis time.

This figure is obtained as follows: each summit of the square represents a combination of the level of the two factors: electrical power and treatment time. One of the most important factors is the electrical power. As the electrical power increases, the number of cavitational activity increases. According to the results obtained by Koda et al. (2003) the cavitation activity linearly increased with energy input (the electrical power is linked to the calorimetric power). The increase of cavitation activity improves the hydroxyl radical production and consequently, enhances the pollutant degradation. This is one of the main reason for which the electrical power has a significant influence on the removal of CBZ (see Figure 3-3). When the treatment time (variable X2) is fixed at the highest level (120 min), the electrical power (X1) had a relatively large influence on the response. The average rate of CBZ degradation changed from 40.1 % to 83.1 % (a reduction gain of 37.0 units) when the electrical power passed from 20W to 40W. However, if the treatment time is fixed at the lowest level (60 min), the electrical power had a relatively low effect on the response. The average rate of CBZ degradation changed from 32.8 % to 51.1 % (a reduction gain of only 18.6 units). Madhavan et al. (2010) reported similar results while studying the oxidation of diclofenac pollutant using a sonochemical process. The degradation rate of diclofenac increased with an increase in the ultrasound power. Likewise, our results are consistent with those recorded by Somayajula et al. (2012) while they studied the decolorization of Reactive Red 195 by increasing the power density of the sonochemical reactor.

The treatment time is also one of the most important parameter during a sonochemical oxidation process. This effect is due to the increase in the exposure time of CBZ in solution in the presence of acoustic cavitations, leading to higher oxidation rates and the possible mineralization of organic matter (Gogate et al., 2003). When the treatment time increases, the hydroxyl radicals (generated by acoustic cavitations) have more opportunities to participate in degradation of CBZ pollutant. As it can be seen from Figure 3-4, the average rate of CBZ degradation changed from 51.4% to 83.1% (a reduction gain of 31.7 units) when the treatment time passed from 60 min to 120 min for an electrical power fixed at the highest level (40 W). However, if the the electrical power is fixed at the lowest level (20 W), the treatment time had a relatively small effect on the response. The average rate of CBZ degradation changed from 32.8% to 40.1% (a reduction gain of only 7.3 units). Consequently, the electrical power is a major factor that influenced the rate of CBZ oxidation, but it directly depends on the treatment time.

3.4.3 Optimization of CBZ degradation

A two-level central composite experimental design with six replicates at the center point leading to a total number of forty experiments was used for response surface modeling Table 3-5.

Table 3-5 Central composite matrix and experimental results.

Run	**Experimental design**			**Experimental plan**			**Degradation efficiency**
	X_1	X_2	X_3	U_1	U_2	U_3	(%)
For pH 7							
17	−1.68	0	0	13.18	90	9	24.99
18	1.68	0	0	46.82	90	9	74.64
19	0	−1.68	0	30	39.55	9	29.58
20	0	1.68	0	30	140.45	9	74.9
21	0	0	−1.68	30	90	3.95	74.68
22	0	0	1.68	30	90	14.05	35.42
23	0	0	0	30	90	9	61.62
24	0	0	0	30	90	9	57.85
25	0	0	0	30	90	9	55.6
26	0	0	0	30	90	9	59.81
27	0	0	0	30	90	9	53.24
28	0	0	0	30	90	9	54.67
For pH 10							
29	−1.68	0	0	13.18	90	9	22.38
30	1.68	0	0	46.82	90	9	77.23
31	0	−1.68	0	30	39.55	9	28.79
32	0	1.68	0	30	140.45	9	82.71
33	0	0	−1.68	30	90	3.95	70.3
34	0	0	1.68	30	90	14.05	37.38
35	0	0	0	30	90	9	57.77
36	0	0	0	30	90	9	59.79

37	0	0	0	30	90	9	58.95
38	0	0	0	30	90	9	58.9
39	0	0	0	30	90	9	60.03
40	0	0	0	30	90	9	60.8

Thus, the regression model in terms of coded variables has been expressed by the following equation:

$$Y = 57.00 + 13.83X_1 + 13.14X_2 - 5.01X_3 + 0.68X_4 + 3.93X_1X_2 - 4.54X_1X_3 + 3.77X_2X_3 - 2.19X_1^2$$

Équation 18

From the analysis of variance in Table 3-6, the model F-value of 40.08 and the low probability value (Pr>F = 0.0001) indicate that the model is statistically significant for CBZ degradation.

Table 3-6 Analysis of variance for selected central composite model.

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	11586.48	7	1448.31	40.08	< 0.0001
X_1-Power	5222.57	1	5222.57	144.54	< 0.0001
X_2-Time	4716.47	1	4716.47	130.53	< 0.0001
X_3-CBZ conc.	684.28	1	684.28	18.94	0.0001
X_1X_2	246.65	1	246.65	6.83	0.0137
X_1X_3	329.42	1	329.42	9.12	0.0050
X_2X_3	227.41	1	227.41	6.29	0.0176
X_1^2	140.93	1	140.93	0.06	0.0572
Residual	1120.11	31	36.13		
Cor Total	12706.59	39			
Std. Dev.	6.01		R-Squared		0.9118
Mean	55.51		Adj R-Squared		0.8891
C.V. %	10.83		Pred R-Squared		0.8358
PRESS	2085.94		Adeq Precision		22.908

The value of the correlation coefficient (R^2 = 0.912) indicates that only 8.88 % of the total variation could not be explained by the empirical model. The R2 value recorded in the present study for CBZ removal was higher than 0.80, indicating that the regression model explained the reaction well. The predicted contour plots (curves of constant response) and the three-dimensional representation of the same plots is given in Fig. 3-5. The effect of treatment time and electrical power on CBZ removal efficiency is illustrated in Fig. 3-5 for an initial pH value of approximately 7.0.

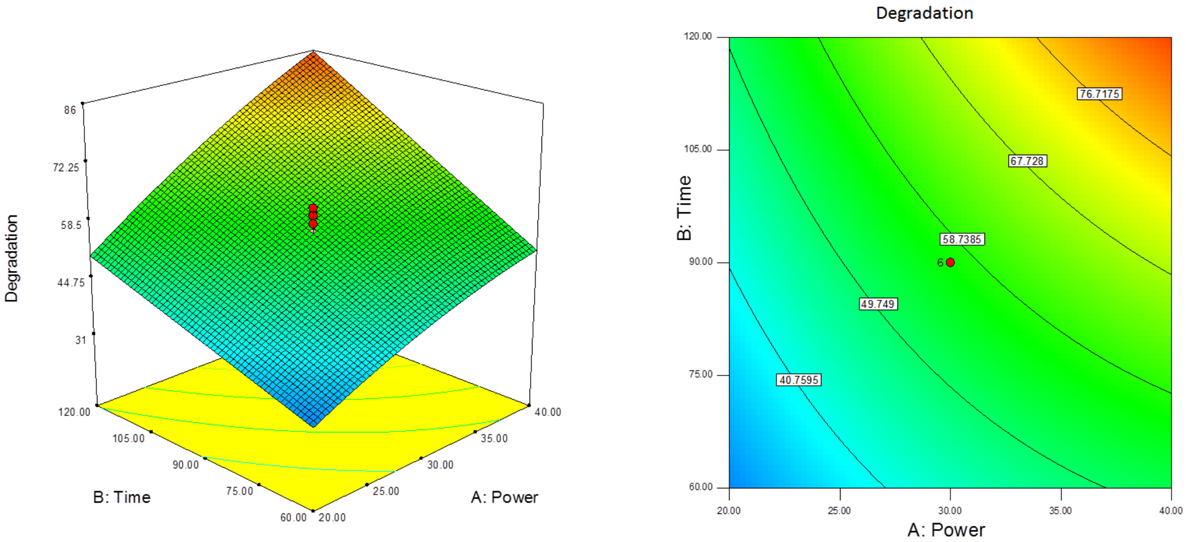

Figure 3-5 The effect of power applied (W) and sonication time (min) on CBZ degradation (%) at pH 7, initial concentration of CBZ 9.0 mg L^{-1}.

When the CBZ concentration at the center of the experimental region investigated was kept constant at 9.0 mg L^{-1}, the CBZ removal efficiency increased with increasing treatment time and was maintained at all electrical powers. As seen from the contour plot, more than 76 % of CBZ removal could be recorded at a concentration of 9.0 mg L^{-1} with the electrical powers set higher than 35 W and the treatment times longer than 100 min. To achieve a high level of removal efficiencies (> 60 %) and to reduce the treatment time, electrical power values become relatively important. For example, for a relatively low electrical power of 28 W, a treatment time longer than 120 min is required to achieve CBZ removal efficiencies higher than 60 %, whereas only 90 min was required when the electrical power increases to 40 W. In terms of optimization, the treatment time has a more significant impact on CBZ removal efficiency than electrical power. To determine the optimal conditions for CBZ degradation in terms of cost-effectiveness, the energy consumption during sonolysis and the degradation efficiency needed to be evaluated. The criteria selected for the optimization condition for CBZ degradation were the following: the degradation percentage of CBZ must be maximized with the highest importance (5/5 weighting factor), and the energy consumption must be minimized with a lower importance (3/5 weighting factor) to reduce the treatment cost. The treatment cost includes energy (power applied) and treatment time. The treatment time and initial CBZ concentration were set in the range from 60-120 min and 6.0 – 12 mg L^{-1}, respectively. Based on these criteria, the Design Expert Program Software proposed an interesting solution to obtain a high degradation of CBZ. The optimal conditions for CBZ degradation in terms of effectiveness/energy consumption were found after 116 min of treatment using a concentration of 6.23 mg L^{-1} of CBZ and the maximum power applied of 43 W. Under these conditions, the degradation of CBZ should be nearly 95 %. These optimal conditions were applied and the experiments were repeated in triplicate to verify the effectiveness and reproducibility of the sonochemical process performance in treating CBZ Table 3-7.

Table 3-7 Optimum operating conditions and experimental results.

Parameter	**Optimal value and results**
Operating condition	
Power applied, W	43
Treatment time, min	116
Pollutant concentration, mg L^{-1}	6.23
pH	7
Theoretical response, %	94.9
Experimental results	
Influent (before treatment)	
Carbamazepine, mg L^{-1}	5.62 ± 0.13
Acridine, mg L^{-1}	< 0.008
Anthranilic acid, mg L^{-1}	< 0.008
Total organic carbon, mg L^{-1}	4.90 ± 0.10
Effluent (after treatment)	

Carbamazepine, mg L^{-1}	0.73 ± 0.08
Acridine, mg L^{-1}	< 0.008
Anthranilic acid, mg L^{-1}	0.027 ± 0.0004
Total organic carbon, mg L^{-1}	4.80 ± 0.05
Experimental response, %	86.9 ± 1.88

An average CBZ degradation of 86.9 ± 1.88 % was recorded at the end of these experiments, a value that was 8.0 % lower than that proposed by the model (94.9 % of CBZ degradation). This result was consistent with the correlation coefficient value ($R^2 = 0.912$) indicating that only 8.88 % of the total variation could not be explained by the empirical model. Likewise, residual TOC concentrations were measured. The residual concentration recorded at the end of the sonochemical oxidation process was 4.80 ± 0.05 mg TOC L^{-1}. By comparison, 4.90 ± 0.1 mg TOC L^{-1} was measured in the initial solution. These results indicated that the CBZ was only transformed into smaller molecules, such as anthranilic acid and acridine; CBZ was not completely oxidized into water and carbon dioxide. Therefore, the pollutant was transformed into by-products.

3.4.4 Economical aspect and validity of CBZ degradation

The economic study included the consideration of energy consumption. The electric cost was estimated to be approximately US$0.06 per kWh. The optimal conditions involved a total cost of US$5.16 per cubic meter of treated effluent (or US$0.83 per gram of CBZ removed).

Low concentrations of CBZ (varying from 0.7 to 50 µg L^{-1}) were reported in wastewater samples (Metcalfe et al., 2003; Vernouillet et al., 2010), and the validity of the optimization procedure in the presence of a low initial concentration of CBZ (8.05 ± 0.16 µg L^{-1}) in the synthetic solution was of interest. These conditions were repeated in triplicate, and the residual concentrations of CBZ were analyzed using LC/MS/MS rather than UV-visible spectroscopic analysis. A residual concentration of 0.80 ± 0.07 µg L^{-1} was measured in the treated effluent (compared with 8.05 ± 0.16 µg L^{-1} recorded in the untreated effluent), which corresponded to 90.1 ± 2.27 % of CBZ removal. These results confirmed that the process can be effective in the removal of very low concentrations of CBZ by applying the optimal conditions determined using the Design Expert

Program Software. Concerning toxicity, Microtox tests performed under optimal conditions showed that the treated effluent remained acutely toxic (EC_{50} > 50). According to the literature, the lethal dosage (LD_{50}) of orally administered CBZ is approximately 1100 - 2000 mg kg^{-1} (Almgren et al., 2008). By comparison, the lethal dosages of by-products (anthranilic acid and acridine) resulting from CBZ oxidation are estimated at 5410 mg kg^{-1} and 2000 – 2400 mg kg^{-1}, respectively (Ayer and Jones, 1979). These values show that one of the by-products, acridine, can have toxic effects similar to the initial pollutant (CBZ). Thus, the treated effluent remained toxic.

In some cases, the by-products can be as toxic as or more toxic than the initial pollutant. To circumvent this drawback, by-products must be further oxidized into water and carbon dioxide. To enhance CBZ removal and to avoid the possible toxicity of the treated effluent, an electrolytic cell could be integrated inside the sonolysis reactor (sono-electrochemical process). The integrated electrolytic cell could be comprised of a boron–doped diamond (BDD) electrode (anode) and a vitreous carbon electrode (cathode). The boron–doped diamond anode has a much greater oxygen overvoltage and is capable of producing a larger quantity of the hydroxyl radical than other anodes in water oxidation, thus, yielding a faster oxidation of organics (Brillas et al., 2005; Nasr et al., 2005; Polcaro et al., 2004). Using a vitreous carbon electrode, hydrogen peroxide (H2O2) can be electrochemically generated by cathodic reduction of dissolved oxygen (Xie and Li, 2006). Under ultrasonic irradiation, hydrogen peroxide can be decomposed into the hydroxyl radical, which should enhance the degradation of CBZ and its by-products. Likewise, the combination of ultrasounds with the electrolytic processes should limit the deposition of polymeric films that reduce the electrode's active surface.

3.4.5 Proposed mechanism of CBZ degradation

During LC/MS/MS analysis, two CBZ by-products (anthranilic acid and acridine) were confirmed and compared with authentic standards. The proposed mechanism of CBZ degradation by the sonochemical process is depicted in Fig. 3-6. Hydroxyl radicals produced in the sonolysis reactor electrophilically attack the CBZ aromatic ring, which leads to the formation of a monohydroxy derivative of CBZ (10-hydroxy-carbamazepine).

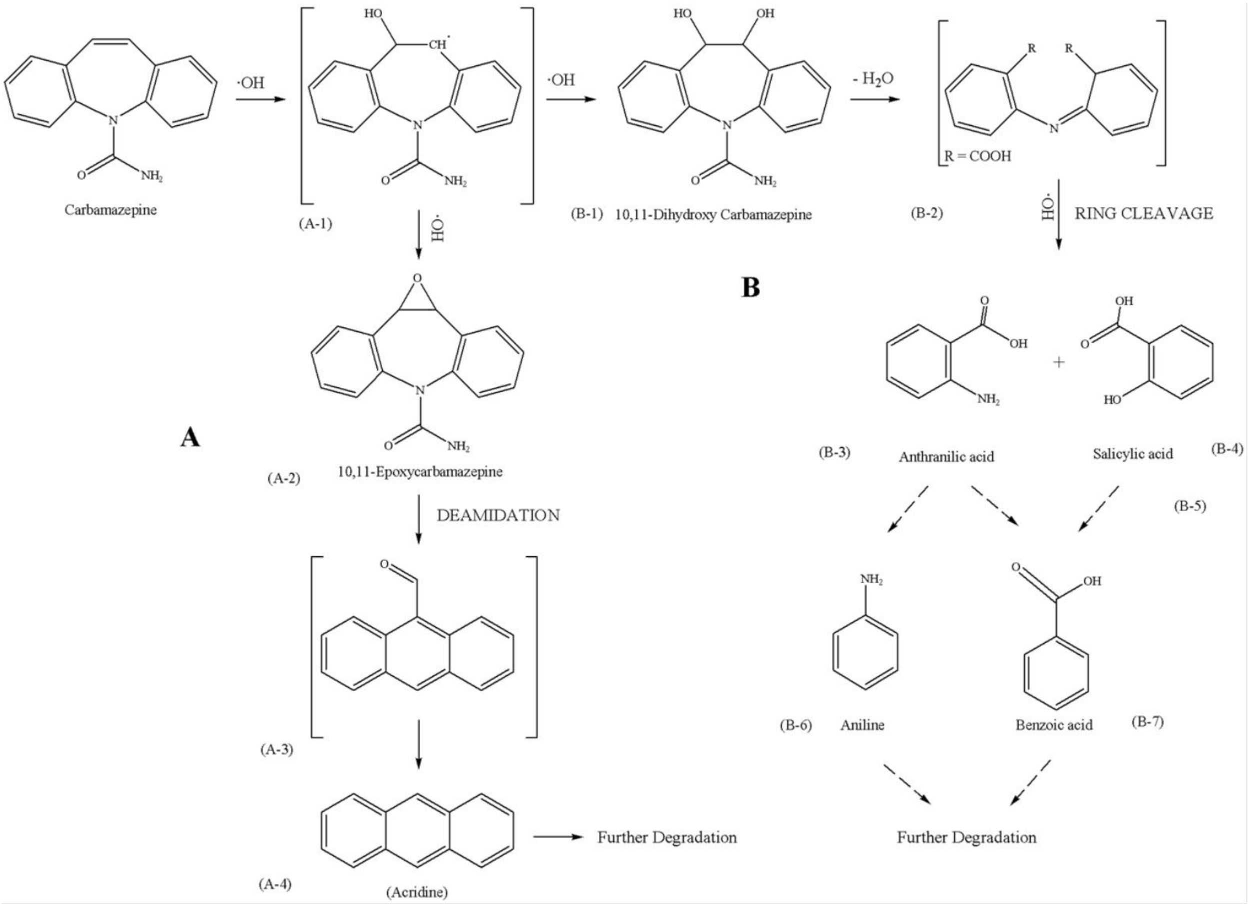

Figure 3-6 Proposed reaction mechanism for the degradation of CBZ by ultrasound.

This compound could be attacked by hydroxyl radicals and transformed into further intermediates, leading to the formation of 10, 11-epoxy CBZ (A) and 10, 11-dihyroxy CBZ (B) by two different pathways (Vogna et al., 2004). In the first pathway, 10, 11-epoxy CBZ is oxidized by hydroxyl radicals and then forms acridine through a deamination reaction. Various intermediates or mineralization products may be formed in this pathway (Chiron et al., 2006; Li et al., 2011). In the second pathway, 10, 11-dihyroxy CBZ is oxidized by a hydroxyl radical and forms anthranilic acid and salicylic acid following ring cleavage reactions. The subsequent irradiation of these acids leads to the formation of aniline and benzoic acid. Strong oxidation of these compounds may result in fully oxidized reaction products and lead to the formation of carbon dioxide and water. According to Braeutigam et al. (2012), the conversion of CBZ and the appearance of the primary degradation products follow pseudo-first order kinetics.

3.5 CONCLUSION

The degradation of CBZ in an aqueous solution by ultrasound using a sonochemical process was studied. The sonolysis reactor was characterized, and the generation of the oxidant species was evaluated. The reactor achieved the highest efficiency at the applied electrical power of 40 W, producing 0.048 mM of oxidant species. By investigating the sonochemical process for CBZ degradation in aqueous solution, the treatment time and the electrical power were found to be the most influential parameters. The contribution of the electrical power and treatment time on CBZ degradation were 61.0 % and 24.5 %, respectively. The sonochemical process applied under optimal conditions (at an electrical power of 43 W during 116 min) was able to oxidize 86.9 ± 1.88 % and 90 ± 2.27 % of an initial CBZ concentration of 5.62 mg L^{-1} and 8.05 µg L^{-1}, respectively. The analysis using LC/MS/MS showed that acridine and anthranilic acid are the two main by-products resulting from CBZ oxidation. The majority of the pollutant was transformed into by-products.

However, in view of enhancing CBZ removal and to avoid possible toxicity of treated-effluent, additional experiments using different volume or higher power should be considered; more over with the aim of apply to the pilot scale which is potential for the treatment of drinking water, industrial, agricultural and municipal wastewaters.

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CHAPITRE 4 Sonoelectrochemical oxidation of carbamazepine in waters: optimization using response surface methodology

Ce chapitre est constitué de l'article suivant:

Tran, N., Drogui, P., Brar, S.K. Sonoelectrochemical oxidation of carbamazepine in waters: optimization using response surface methodology. Journal of Chemical Technology & Biotechnology (DOI: 10.1002/jctb.4399)

4.1 ABSTRACT

BACKGROUND: The decomposition of carbamazepine (CBZ) in synthetic solution and in municipal effluent was investigated using a sono-electrochemical reactor. Sono-electrolysis was conducted using two concentrically electrodes installed in a cylindrical reactor containing a ceramic transducer.

RESULTS: The CBZ concentration (C0= 10 mg L^{-1}) could be optimally diminished by up to 90% by applying a current intensity of 4.86 A for a 177 min reaction period and by imposing an ultrasound power applied of 38.29 W. The optimal conditions were subsequently applied for tertiary treatment of municipal wastewater effluent contaminated with 10 µg CBZ L^{-1}. The removal efficiencies of CBZ, TOC, COD and colour recorded were 93%, 60%, 93% and 86%, respectively. Likewise, the toxicity was completely removed (bacterium *Vibrio fisheri*) from municipal wastewater effluent.

CONCLUSIONS: The interest of coupling ultrasonication and electrooxidation (US-EO) treatment for CBZ removal was demonstrated. An experimental design methodology base on response surface methodology was applied to determine the optimal experimental conditions in terms of cost/effectiveness.

4.2 INTRODUCTION

The increasing production and intensive use of pharmaceutical products has led to the entry of these products into the environment and to the eventual pollution of soil, ground and surface water. The pharmaceutical residues have been identified and quantified in sewage treatment plant effluents, surface waters, ground water and drinking water [1, 2]. Carbamazepine (CBZ) is one of the most common pharmaceutical residue often found in groundwater sources and drinking water supplies [3-5]. It has been classified as emerging organic pollutants (EOPs) due to resistance to natural degradation processes and its ability to remain in the environment for a long period. Several researchers have been reported some negative effects on human and animal health caused by CBZ contamination [1, 3, 6]. Therefore, a need exists for efficient treatment technology for the removal of this pollutant from the aquatic environment.

Advanced oxidation processes (AOPs) have been proposed as alternative methods to remove many toxic and bio-recalcitrant compounds in wastewater [7]. Chemical oxidation process using UV/H_2O_2 has been investigated by Vogna, et al. [8] to oxidize CBZ. In spite of the good oxidation of CBZ, the high chemical consumption of H2O2 and the relatively high treatment costs constitute the major barriers for large scale applications [9]. The ultrasonication process has been identified as a successful alternative for the destruction and mineralization of some recalcitrant organic compounds in water and does not require the addition of chemicals [10-12]. Since 1990, the ultrasound process has received considerable interest for the destruction of organic pollutants that are present in wastewater [10, 13, 14]. Acoustic cavitation, derived from the high calorimetric power of a liquid, can provide unusual and unique reaction sites as a result of the extremely transient and small cavitation bubbles that are created with high temperatures and high pressures. Ghauch, et al. [15] investigated the suitability of CBZ oxidation by an improved Fenton’s process based on ultrasonic technique.

In the present study, we plan to combine ultrasonication (US) with electrooxidation (EO) to remove CBZ from water. The destruction and mineralization of organic pollutants in waters by using US-EO process has been reported in the literatures [16-19]. However, to the best of our knowledge, this is a first time that ultrasonication and electrooxidation have been synergistically put together to tackle the challenging problem of efficient degradation of CBZ. The specific objectives of this study are the followings: a) evaluate the interest of coupling ultrasonication and electrooxidation processes for CBZ removal from water; b) use a statistical methodology for a rational analysis of the combination of operational factors that led to the best treatment ; c) verify the quality of treated effluent (versus untreated effluents) in terms of its toxicological effects and in terms of simultaneously removal CBZ, colour, COD and TOC while treating real municipal wastewater effluent contaminated by CBZ.

4.3 MATERIALS AND METHODS

4.3.1 Preparation of the synthetic effluent (SE)

The water samples used in this study were prepared synthetically by dissolving CBZ in de-ionized water. CBZ analytical grade reagent (99 %) was obtained from Acros Organics BVBA (Belgium). SE solutions of CBZ were prepared in a glass beaker containing 3.0 L of water and 30 mg of CBZ. The CBZ was solubilized using a magnetic stirrer (500 rpm) at room temperature (25°C) for 24 h. The resulting mixtures constituted the CBZ solutions of 10 mg L^{-1} in which a sodium salt (Na2SO4 0.01 mol L^{-1}) was added to increase electrical conductivity.

4.3.2 Wastewater CBZ-spiking

In view of testing the US-EO process on real effluent containing refractory organic pollutants and to simulate CBZ contamination, wastewater samples were enriched with CBZ at a concentration of 10 μg L^{-1} without the addition of supporting electrolyte. The real effluents were sampled at Levis Urban Community wastewater treatment plant (WTP, Levis, Canada). This is a conventional WTP with a physicochemical pre-treatment and a sequential biological treatment system followed by a disinfection process using ultraviolet light. Samples were collected at the outlet of treatment plant (after the disinfection system) and stored in polypropylene bottles and kept at 4°C until use.

4.3.3 Sono-electrochemical reactor setup

The assays were carried out in a closed loop, depicted schematically (Fig. 4-1). The sono-electrochemical reactor was made of Plexiglas material (characterized by a double layer cylinder) with an internal dimension of 20 cm (height) x 14.5 cm (diameter) and both electrodes (anode and cathode) were used in the form of expanded metal. The cylindrical cathode electrode (16 cm height × 12 cm diameter x 0.2 cm thick) was made of titanium (Ti) having a solid surface area of 420 cm^2 and a void area of 180 cm^2. The cylindrical anode electrode (16 cm height x 8.0 cm diameter x 0.2 cm thick) was titanium coated with lead oxide (Ti/PbO_2) having a solid surface area of 280 cm^2 and a void area of 120 cm^2. The inter-electrode gap was 2.0 cm in the electrolytic cell. The anode was placed at the center of the cell and the cathode was fixed at the periphery.

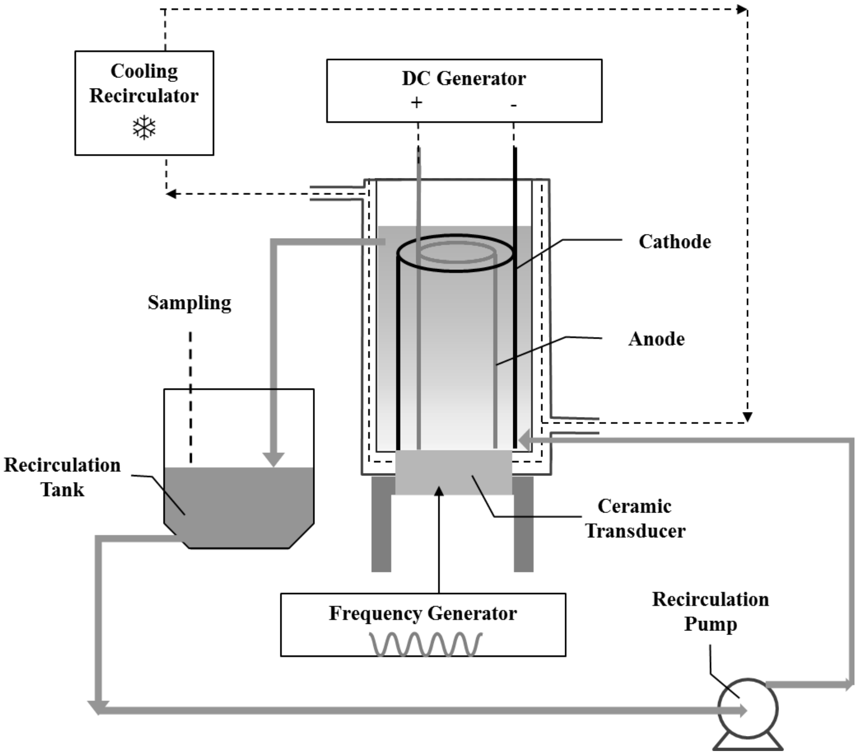

Figure 4-1 Schematic diagram of the experimental setup.

The electrodes had been mechanically attached and arranged to ensure the proper water distribution in the electrolytic cell. The electrical current was applied using a digital DC power supply XFR 40–70 (Xantrex Technology, Burnaby, British Columbia, Canada) with a maximum current rating of 70 A at an open circuit potential of 40 V. Ultrasonic waves were introduced from the bottom of the reactor via a ceramic transducer (a piezoelectric disk having a diameter of 4 cm). The frequency (520 kHz) and electrical power (from 10 to 40W) of the piezoelectric disk were controlled by an external waveform generator (Agilent 33210A, Agilent Technologies Canada Inc.) equipped with a low frequency amplifier (AG 1016, T&C Power Conversion Inc.). The reactor temperature was held constant at 20^{o}C using a Polystat cooling/heating recirculator (Cole-Parmer Canada Inc.). Mixing in the reactor was achieved by recirculating water through the cell by means of a peristaltic pump operated at a constant speed of 100 mL min^{-1}. The recirculation tank (1.0 L of capacity) was made of the same material as the electrolytic cell. In all tests, a total volume of 3.0 L of contaminated water was used. The working volume of the electrolytic cell was 2.5 L, whereas 0.5 L was required for the recirculation tank.

4.4 EXPERIMENTAL PROCEDURE

4.4.1 Preliminary experiments

The first set of experiments was was conducted to compare the removal efficiencies of CBZ using ultrasonication alone (US), electrooxidation alone (EO) and the combination of ultrasonication/electrooxidation (US-EO) processes. During these tests, only the residual CBZ concentration was measured. An electric power of 40 W of ultrasound at a frequency of 520 kHz was imposed. The treatment time was 120 min and the current intensity was fixed at 2.0A (anodic current density of 7.14 mA cm^{-2}).

4.4.2 Experimental design

The removal of CBZ by sono-electrochemical was optimization using response surface methodology (RSM). A factorial design (FD) was firstly employed to investigate the effects of the main factors and their eventual interaction. Then, a central composite design (CCD) methodology was employed to describe and optimize the CBZ treatment using the US-EO process. Three independent variables were used in this study: the electric power of ultrasound, treatment time and current intensity. A three-factorial design (at two-levels) completed by a central composite design, with five replicates at the center of the experimental region for each numeric factor, led to a total number of twenty experiments employed for response surface modeling. The experimental range and levels of independent variables investigated for CBZ degradation with the coded values are shown in Table 4-1. The values of the variables and their variation limits were selected based on preliminary experiments and our previous studied [20, 21].

Table 4-1 Experimental range and levels of independent variables.

Coded variables	**Factors**	**Description**	**Experimental field**		**$U_{i,0}$**	**ΔU_i**
			Min value	Max value		
X_1	U_1	Current intensity (A)	2	5	3.5	3
X_2	U_2	Time of treatment (min)	90	180	135	90
X_3	U_3	Power of ultrasound (W)	20	40	30	20

During these assays, the effectiveness of the process was evaluated by measuring the residual CBZ, total organic carbon (TOC) and chemical oxygen demand (COD). Experimental data were obtained from the average of at least of three treatment replicates. Uncertainties were removed and calculated with a significance level of $p \leq 0.05$. The analysis of variance (ANOVA) and other statistical results were calculated and generated using the Design Expert Software version 7.1 (Stat-Ease Inc., USA).

4.4.3 Analytic detail

CBZ measurements

The concentration of CBZ in the solution was determined by the mean of the absorption spectral measurements for ease of analysis during preliminary and optimization step. The integrated absorption (basis on peak area rather than peak height) of CBZ measured in the range of 200 nm to 400 nm was chosen to evaluate the residual CBZ concentrations. The peak area is less sensitive to the influence of peak broadening (dispersion) mechanisms and often found to be more reliable than peak height measurement [22]. These dispersion effects, which arise from many sources, cause spectral peaks to become shorter, broader, and more unsymmetrical, but have little effect on the total area under the peak. The peak area remains proportional to the total quantity of CBZ and its residual substance passing into the detector. A calibration curve of known CBZ concentration (0.0-15.0 mg L^{-1}) versus integrated absorbance value was used to calculate the residual CBZ concentration and to define the efficiency. However, when the optimal conditions were determined and repeated in triplicate to verify the effectiveness and the reproducibility of the US-EO process, the residual concentration of CBZ and the by-products were analyzed by liquid chromatography/mass spectrometry (LC-MS/MS) rather than UV-visible spectroscopic analysis. The chromatographic column used was the Hypersil Gold C18 (Thermo Hypersil Ltd., Runcorn, UK) with a particle size of 3.0 µm and a 2.1 x 100 mm inner diameter. The isocratic mobile phase was A: water and B: acetonitrile at a flow rate of 200 µL min^{-1}. Mass spectral data shown in this study were acquired using LCQ Duo ion trap tandem mass spectrometry (Thermo Finnigan, USA) equipped with an electrospray ionization source operated in the positive ion mode. Calibration solutions were prepared by serial dilution of the stock solutions in methanol, at concentrations of 2.0 µg L^{-1} – 1.5 mg L^{-1}. The recovery percentage of the analysis was 83 %, and the limit of detection was 0.4 µg L^{-1}.

Other parameter measurements

The pH and conductivity were measured using a pH/conductivity meter (Oakton model 510) equipped with a pH and conductivity probe. COD determination was measured based on standard method 5220D 23 and using a spectrophotometer Carry UV 50 (Varian Canada Inc.). TOC was measured using a Shimadzu TOC 5000A analyzer (Shimadzu Scientific Instruments, Kyoto, Japan). Residual colour concentrations were determined in conformity with the standard method MA.103-Col 2.0 24 and using a spectrophotometer. Likewise, biotests (Microtox) were carried out to have information about the toxicity of the initial and treated solution under optimum experimental conditions. Microtox analysis is a standardized toxicity test using the luminescent marine 25, Vibrio fisheri (Software MTX6, version 6.0, Microbics Corporation). The toxicity effects were monitored as the average percentage of light emission inhibition compared to the control assay and the toxicity units (TU) were calculated according to the equation below:

$TU=100/EC_{50}$ **Équation 19**

Where EC_{50} are the concentration of the test sample where there is 50 % reduction in bacterial light production.

4.5 RESULT AND DISCUSSION

4.5.1 Preliminary investigation of CBZ degradation

Experiments using ultrasonication (US), electro-oxidation (EO) and sono-electrooxidation (US-EO) processes were carried out in order to compare the CBZ degradation efficiencies. The treatment time was 120min. The US process consisted in treating the effluent using only ultrasonication at an electrical power of 40 W. The EO process was applied to treat the effluent using Ti/PbO_2 anode and Ti cathode electrodes operated at a current intensity of 2.0 A without ultrasounds. In the US-EO process, a current intensity of 2.0 A and ultrasounds (P=40W) were simultaneously imposed. Fig. 4-2 shows the degradation rate of CBZ by these different processes employed.

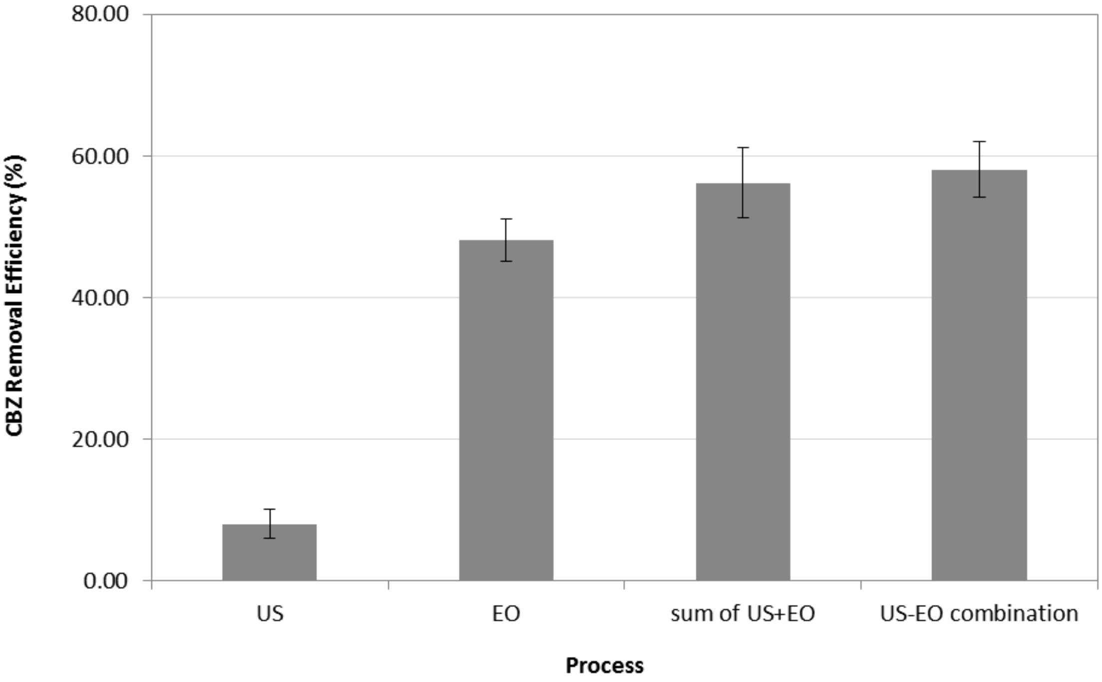

Figure 4-2 The efficiency of CBZ degradation by different processes.

As a single process, 8.0% degradation of CBZ was recorded during the US process, whereas 48% of CBZ was removed using the EO process. By comparison, 58% of CBZ was removed using the combined process (US-EO). From these results, it is evident that the combination of processes shows a more effective degradation of CBZ owing to the synergistic effects. The synergistic effect is defined as an effect arising between two or more agents, entities, factors or substances that produce an effect greater than the sum of their individual effects. In this combination, ultrasounds enhance the mass transfer between the electrolyte and the electrodes 16. These results are consistent with those obtained by Ren, et al. [16] while treating an effluent containing phenol by using a process combining sonication (US) and electrochemical (EC) methods. The electrolysis cell was comprised of stainless steel as anode and stainless steel as cathode. A potential of 10 V and an electrical ultrasound power of 170 W imposed during a period of treatment of 1.0 h. The synergistic effects of US and EC allowed recording 70 % of phenol degradation, compared to 48% obtained while the sum of the processes was used. The authors observed a passive layer on the anode surface after the electrochemical reaction that inhibits the reaction. However, this layer was not observed in the combined system. The mechanical effects of cavitation cleaned the electrode surface and prevented any such passive layer forming. These results indicate the advantage of the ultrasound-electrochemical combination compared to ultrasonication or electrooxidation process applied alone. Therefore, additional experiments were carried out to optimize the sonoelectrochemical technique for the treatment of water contaminated by CBZ.

4.5.2 Effect of the experimental parameters on the CBZ degradation using factorial design methodology

The influence of different variables: current intensity (U_1), treatment time (U_2) and ultrasound power (U_3) on the CBZ removal was investigated using factorial matrix (2^k, k being the number of factors; k = 3). The experiment region investigated for CBZ degradation and the code values are shown in Table S1. The experimental results are presented in Table 1. With this design it was possible to calculate the principle effect of each factor and the interaction between them. The experimental response associated to a 23 factorial design (three variables) is represented by a linear polynomial model with interaction, as follows:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 \quad \textbf{Équation 20}$$

Where Y represents the experimental response (CBZ degradation); b0 represents the average value of the responses of the 8 assays; Xi the coded variable (-1 or +1); bi represents the principal effect of each factor i on the response and bij represents the interaction effect between factor i and factor j on the response. The coefficients of the model were calculated using the half-difference between the arithmetic average of the response values when the associated coded variable is at a level (+1) and the arithmetic average of the response values when the associated coded variable is at level (-1). Design-Expert ® Program Software (Design Expert 7, Stat-Ease Inc., Minneapolis) was used to calculate the coefficient of the polynomial model.

$$\text{Degradation} = +51.34 + 15.06 * X_1 + 16.87 * X_2 + 1.53 * X_3 + 2.04 * X_1 * X_2 - 0.28 * X_1 * X_3 + 0.18 * X_2 * X_3 \quad \textbf{Équation 21}$$

The analysis of variance is used for validating the model and statistical tests (Table 4-2).

Table 4-2 ANOVA for selected factorial model

Sum of	**Mean**	**F**	**p-value Square**	**Value**	**Prob > F**	
Source	**Squares**	**df**				
Model	4144.22	6	690.70	11949.88	0.0070	significant
X_1-Current	1815.03	1	1815.03	31401.92	0.0036	
X_2-Time	2276.10	1	2276.10	39378.90	0.0032	
X_3-Power	18.73	1	18.73	324.00	0.0353	
X_1X_2	33.46	1	33.46	578.83	0.0264	
X_1X_3	0.64	1	0.64	11.05	0.1861	
X_2X_3	0.27	1	0.27	4.61	0.2775	
Residual	0.058	1	0.058			
Cor Total	4144.28	7				

Std. Dev.	0.24	**R-Squared**	1.0000
Mean	51.34	**Adj R-Squared**	0.9999
C.V. %	0.47	**Pred R-Squared**	0.9991
PRESS	3.70	**Adeq Precision**	297.569

The value of the regression coefficient R^2 was 0.9991 indicating that the linear polynomial model described by Equation (21) explained the reaction well; only 0.01 % of the total variation could not be explained by the empirical model. The values of "Prob > F" less than 0.0500 indicate model terms are significant. This analysis of variance for the model is indicated that the model is statistically significant for CBZ removal. The coefficient b0 = 51.34 represents the average value of the response of 8 assays. According to Equation (21), it can also be seen that current intensity (b_1 = +15.06) and treatment time (b_2 = + 16.87) have a positive effect on CBZ degradation and these effects were higher than that of ultrasound power (b_3 = +1.53). The interaction effects were globally weaker than the main effects. The half-normal plot of the absolute values of various effects (Fig. 4-3) where the response variables are decrease in CBZ concentration is used for isolating the main effects. The contributions of the principal effects (X_1, X_2, and X_3) on the percentage of CBZ degradation are 43.79 %, 54.92 % and 0.45 %, respectively.

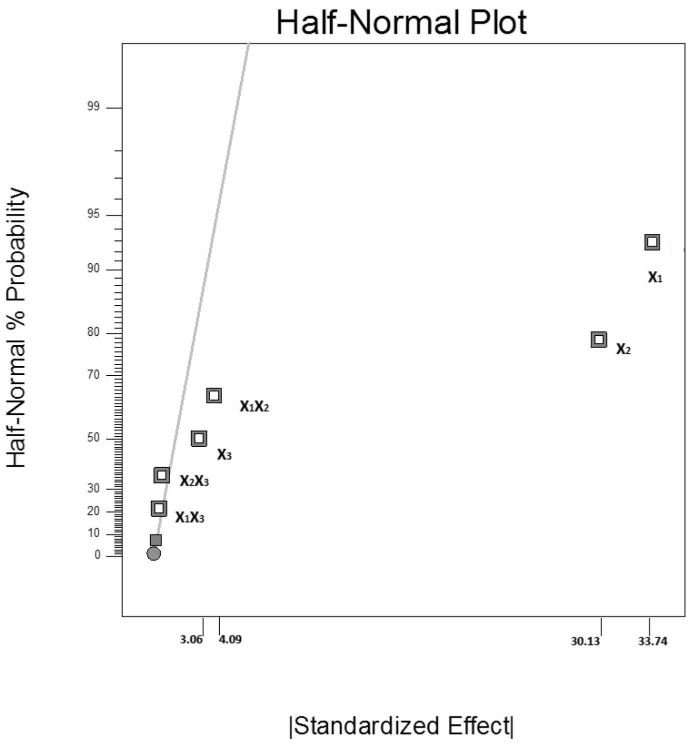

Figure 4-3 Half-normal plot of decrease in CBZ concentration by sonoelectrochemical

With the exception of the interactions X_1X_2 (current intensity and treatment time), the other interactions have a negligible effect. The interaction effect of X_1X_2 on CBZ degradation is presented in Figure 3. Each point represents the combination between two factors: current intensity and treatment time. At current intensity of 5.0 A and 180 min of treatment time, an average reduction of 85.3% was recorded (assays 3 and 8). When the treatment time (X_2) is fixed at the highest level (180 min), current intensity has a significant influence on the removal of CBZ. The degradation rate passed from 51.1% to 85.3% (a reduction gain of 34.2 units). When the treatment time is fixed at the lowest level (90min), the degradation rate passed from 21.5% to 47.5% (a reduction gain of 26 units). Consequently, current intensity is a major factor that influences degradation rate of CBZ, but it directly depends on the treatment time. In the Sono-electrochemical process, current intensity is a key factor that influences pollutant degradation efficiency. This can be explained by the fact that in the solution, the organic contaminants must be transported toward the anode electrode surface to be oxidized there. The organic contaminant degradation may be subjected either to current control or mass transfer control. Both of these parameters are greatly influenced by the exposure time of CBZ to the synergistic effect of ultrasounds and electrolysis. On the other hand, when the treatment time increases, the hydroxyl radical concentrations generated at the surface of anode electrode and generated by acoustic cavitations increase. The hydroxyl radicals have more opportunities to participate in degradation of CBZ and leading to higher oxidation rates and the possible mineralization of organic matter [11]. These results are consistent with those obtained by Siddique, et al. [17] while studying the decomposition of reactive blue-19 dye in a ultrasound assisted electrochemical reactor. At pH 8, the percentage of dye goes from 50% to 67.68% when the reaction time goes from 60 to 120 min. The reaction order and the apparent rate constant of CBZ removal can be determined by plotting Ln (C/C_0) against time (t) (Fig. 4-4).

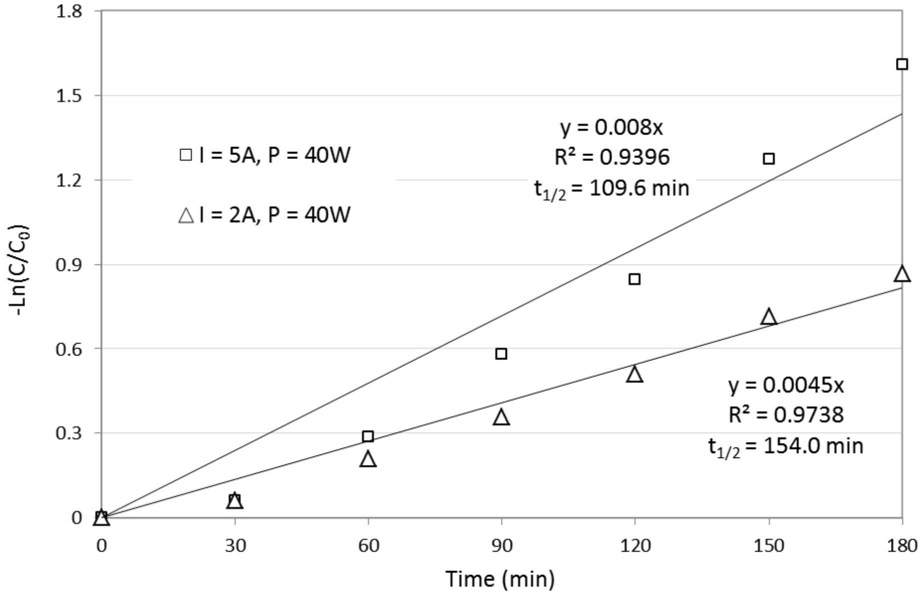

Figure 4-4 The reaction order and apparent reaction rate constant for CBZ removal (Operating condition: P=40W, t= 180 min, I= 2A and 5A).

The experimental data are well fitted to first-order kinetics (with correlation coefficients ranging from 0.94 to 0.97) predicting a linear variation with elapsed time (t) of the –Ln (C/C_0):

$$-Ln\left(\frac{C}{C_0}\right) = k.t$$ **Équation 22**

Where "C_0" and "C" represent respectively the initial and residual CBZ concentration in the bulk solution and "k" is the first-order rate coefficient. The first-order reaction rate apparent constants of CBZ degradation reaction were measured for two current intensities (2.0 and 5.0A) at an ultrasound power of 40 W and initial CBZ concentration of 10 mg L^{-1}. As shown in Figure , the reaction rate apparent constant for CBZ degradation (0.008 min^{-1}) at a current intensity of 5.0A was almost two times higher than that recorded (0.0045 min^{-1}) at a current intensity of 2.0A. These results are consistent with the discussion mentioned above while studying the interaction between current applied and treatment time Fig. 4-5.

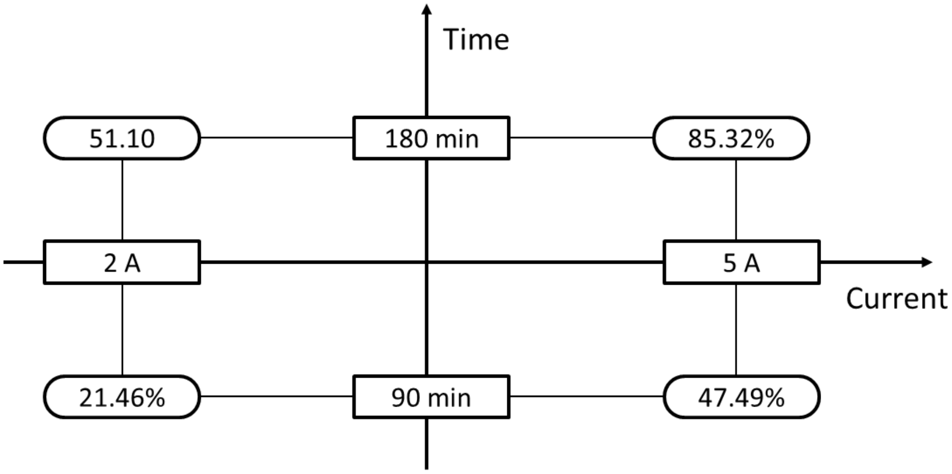

Figure 4-5 Interaction between current applied and treatment time.

To further understand the behavior of the sono-electrochemical process, the degradation progress of CBZ in solution was monitored by absorbance measurements (evolution of absorption peaks) using a spectrophotometer. The UV-visible absorption spectrum of CBZ solution is shown in Fig. 4-6 (initial curve, solid line). This spectrum is characterized by two main peaks located in the ultraviolet region at 225 nm and 285 nm, respectively.

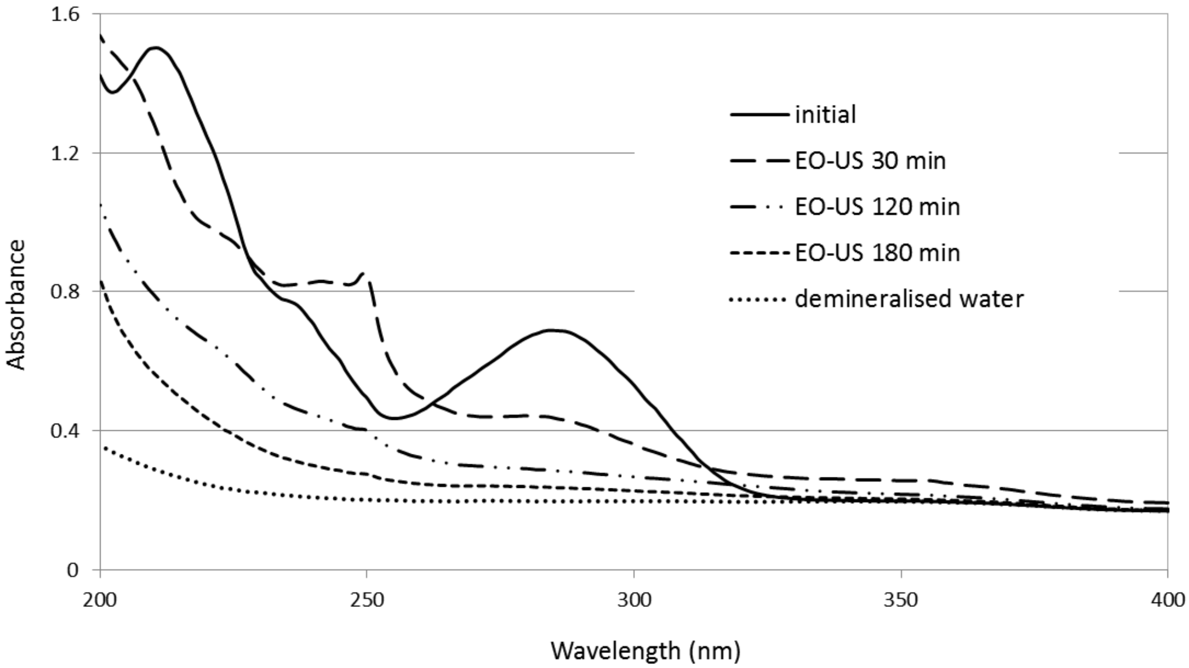

Figure 4-6 UV Spectra of CBZ at different time of sono-electrochemical oxidation (Operating condition: I= 5A, P=40W).

After 30 min of period of treatment, a new peak appeared around 250 nm, whereas the initial peaks (located at 225 and 285 nm, respectively) decreased indicating the destruction of CBZ. The disappearance of the initial peaks after a period of 30 min was due to the fragmentation of CBZ by the oxidants species produced (namely, hydroxyl radicals) during the sono-electrochemical process. The appearance of the new peak (around 250 nm) was considered as an evidence of by-products formation in the solution. It is can be assumed that the decomposition of the CBZ take place on such an anodic electrode (Ti/PbO$_2$) and enhanced by the sonolysis process due to the electrophilic attack of oxidizing species, including hydroxyl radicals, which are generated sono-electrochemically. When the treatment pursued (after 120 et 180 min), the initial peaks (located at 225 and 285 nm) and the new peak (around 250 nm) completely disappeared. In particular, the absorbance spectrum measured at 180 min was quite similar to that recorded using demineralized water. The complete decrease in absorbance peaks was mainly attributed to degradation of CBZ and its by-products. Several authors argued that the generated species at anode react favorably with the double bonds (-C=C-) and attack the aromatic nucleus 26-28, which are the major components of CBZ. CBZ were simultaneously destroyed at the anode surface (direct anodic oxidation by hydroxyl radical) and in solution via hydroxyl radical production (indirect oxidation). Hydroxyl radical was electrochemically generated by water oxidation at the anode and sono-chemically generated in solution by the bubble cavitation. These reactions can be summarized as follows:

$H2O \rightarrow HO\cdot + H+ + 1e-$ **Équation 23**

$HO\cdot + CBZ \rightleftharpoons$ Intermediates **Équation 24**

$HO\cdot$ + Intermediates $\rightarrow CO_2 + H2O$ **Équation 25**

Firstly, hydroxyl radical reacts with CBZ and leads to the formation of intermediates. Intermediates compounds are consecutively transformed via next attacks of hydroxyl radical into further intermediates, including ring-opened structures. The subsequent oxidation of the ring-opened structure may results in fully oxidized reaction products and leads to the formation of carbon dioxide (CO_2). This hypothesized of CO_2 formation is based on the results recorded while measuring the residual concentrations of TOC. The change in TOC in the synthetic solution during the treatment (Table 4-3) shows that more than 80% of TOC can be removed after 180 min. The relatively high yield of TOC removal indicated that only the majority of CBZ and its by-products were completely oxidized into water and carbon dioxide. These results are consistent with those recorded by absorbance measurements.

Table 4-3. CBZ and TOC concentration at different time of treatment (Operating condition: I= 5A, P=40W)

Treatment time (min)	CBZ concentration (mg L^{-1})	Total organic compounds (mg L^{-1})	Efficiency of CBZ degradation (%)	Efficiency of mineralization (%)
0	11.41 ± 0.74	10.20 ± 0.45	0	0
60	7.24 ± 0.25	6.71 ± 0.14	36.55	34.22
90	5.88 ± 0.33	5.70 ± 0.14	48.47	44.12
120	4.10 ± 0.18	4.19 ± 0.12	64.07	58.92

180	1.50 ± 0.15	1.98 ± 0.10	86.85	80.59

Finally, the factorial plan design was useful for determining the interactions affecting the response and indicates if the lowest or the highest levels of the factors are favorable or not. The conclusions of the results are reliable based on the tendency of the response, which is greatly influenced by the factors having a significant effect. However, this type of model cannot be used to predict or to determine the optimization conditions. In a second step, a surface response methodology should be used to determine the optimal operating condition for CBZ degradation using the sono-electrochemical oxidation process.

4.5.3 Optimization conditions for CBZ degradation using central composite design methodology

Central composite matrix 29 was used to represent the response of the three numeric factors in the all experimental field. Indeed, the central composite matrix presents a number of advantages such as: i) the ability to explore the whole of the experimental region; ii) the possibility to determine the coefficient of a mathematical model fitting with a second-order polynomial equation; iii) the usefulness of interpolating the response. There are three quantitative factors (U1, U2 and U3) that might potentially affect the degradation efficiency of CBZ. The CCD matrix is comprised of three sets: factorial matrix (assays 1 to 8), a set of point at the centre of the experimental domain (assays 15 to 20) and star matrix (assays 9 to 14). A total of twenty experiments were required for response surface modeling (Table 4-4).

Table 4-4 Central composite matrix and experimental results.

Run	**Experimental design**			**Experimental plan**			**Degradation efficiency**
	X_1	X_2	X_3	U_1	U_2	U_3	(%)
9	−1.68	0	0	0.98	135	30	26.52
10	1.68	0	0	6.02	135	30	83.45
11	0	−1.68	0	3.5	59.32	30	27.61
12	0	1.68	0	3.5	210.68	30	81.66

13	0	0	−1.68	3.5	135	13.18	61.42
14	0	0	1.68	3.5	135	46.82	62.36
15	0	0	0	3.5	135	30	59.26
16	0	0	0	3.5	135	30	61.19
17	0	0	0	3.5	135	30	58.57
18	0	0	0	3.5	135	30	56.22
19	0	0	0	3.5	135	30	62.2
20	0	0	0	3.5	135	30	60.2

The response can be described by a second order model for predicting the response in all experimental regions from the following equation:

$$\text{Degradation} = 59.79 + 15.85*X_1 + 16.56*X_2 + 1.03*X_3 + 2.01*X_1*X_2 - 2.84*X_1^2 - 2.96*X_2^2 - 0.40*X_3^2$$

Équation 26

The analysis of variance of the predicted response surface quadratic model was shown in the Table 4-5. As it can be seen from this table, the regression model explained the sono-electrochemical process well.

Table 4-5 ANOVA for Response Surface Reduced Quadratic Model

Sum of Source	**Mean Squares**	**F df**	**p-value Square**	**Value**	**Prob > F**	
Model	7444.30	7	1063.47	87.09	< 0.0001	significant
X_1-Current	*3432.60*	*1*	*3432.60*	*281.11*	*< 0.0001*	
X_2-Time	*3743.62*	*1*	*3743.62*	*306.58*	*< 0.0001*	
X_3-Power	*14.54*	*1*	*14.54*	*1.19*	*0.2966*	
X_1X_2	*32.36*	*1*	*32.36*	*2.65*	*0.1295*	
X_1^2	*116.25*	*1*	*116.25*	*9.52*	*0.0094*	
X_2^2	*126.60*	*1*	*126.60*	*10.37*	*0.0074*	
X_3^2	*2.29*	*1*	*2.29*	*0.19*	*0.6724*	

Residual	146.53	12	12.21
Cor Total	7590.83	19	

Std. Dev.	3.49	**R-Squared**	0.9807
Mean	55.56	**Adj R-Squared**	0.9694
C.V. %	6.29	**Pred R-Squared**	0.9132
PRESS	659.24	**Adeq Precision**	30.264

To rigorously determine the optimal condition for CBZ degradation in terms of cost and effectiveness, the energy consumption during the sono-electrochemical process has to be taken into account. The criteria selected for the optimization condition for CBZ degradation are the following: i) treatment time and current intensity have to be minimized with a relatively high importance (3/5 weighting factor) in order to reduce the treatment cost (including the energy cost); ii) The power of ultrasound having a low impact must be minimized with the highest importance (1/5 weighting factor); iii) the percentage of CBZ degradation must be maximized with the highest importance (5/5 weighting factor). The treatment costs include energy for ultrasonication and electrolysis. Based on these criteria, the Design Expert Program Software proposed several interesting solutions to obtain a high degradation of CBZ (Table 4-6). The optimal conditions for CBZ degradation in terms of cost/effectiveness were established as follows: 177 min of treatment using a current intensity of 4.86 A and an ultrasound power applied of 38.29 W.

Table 4-6 Optimal condition for removal of CBZ

Constraints Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Current	is in range	2	5	1	1	3/5
Time	is in range	90	180	1	1	3/5

Power	is in range	20	40	1	1	1/5
Degradation	maximize	19.47	86.83	1	1	5/5

The desirability function value was 1.00 for these optimum conditions. It means that the degradation is very close from what we expected and the software has done only few compromises to satisfy the imposed criteria. The theoretical response proposed for CBZ degradation was 87.1 %. To confirm the model adequacy and the validity of the optimization procedure, additional experiments were performed under optimal operating conditions. The average value of the experimental response (experiments repeated in triplicate) was 89.6 ± 2.9 %. This CBZ degradation rate of ~90 % was recorded at the end of this experiment, and is found to be close to the value proposed by the model. This result was consistent with the correlation coefficient value (R2 = 0.9694) indicating that only 4.06 % of the total variation could not be explained by the model. These optimal conditions involved a total energy cost of US$0.61 per gram of CBZ removed (or US$5.41 per cubic meter of treated effluent).

4.5.4 Application to wastewater treatment contaminated by CBZ

The effectiveness of the US-EO in treating wastewater effluent contaminated by CBZ (around 7.0 to 10 µg L $^{-1}$) was evaluated at a current intensity of 4.86A and a retention time of 177 min in the presence an ultrasound power of 38W (optimal conditions determined above using the Design-Expert Program Software). The objective was to test the effectiveness of the US-EO process as tertiary treatment to remove emerging pollutants such as CBZ. It was important to determine whether the results of these tests are reproducible or not. To that end, the experiments were repeated in triplicate to verify the effectiveness and reproducibility of the US-EO process performance in treating municipal wastewater effluent (MWE) contaminated by CBZ in the presence of other types of organic, inorganic and microbial pollutants (Table 4). These results are compared with those recorded in synthetic effluent prepared with distilled water contaminated by CBZ (10 µg L $^{-1}$). Table 4-7 compares the untreated effluents (control samples) and the treated effluents using the US-EO process.

Table 4-7 Treated-effluent versus untreated effluent artificially contaminated by CBZ: Application to the treatment of municipal wastewater effluent (MWE) and synthetic effluent (SE)

Parameters	**Unity**	**MWE (with CBZ spiked)**		**Synthetic effluent (SE) (with CBZ spiked)**	
		Untreated	Treated	Untreated	Treated
pH		6.5 ± 0.5	6.4 ± 0.3	6.9 ± 0.2	6.9 ± 0.2
Conductivity	µS cm^{-1}	410 ± 25	399 ± 15	220 ± 12	215 ± 15
Residual $_{[TOC]}$	mg L^{-1}	7.83 ± 0.09	3.13 ± 0.24	1.79 ± 0.07	0.60 ± 0.05
Residual $_{[COD]}$	mg L^{-1}	58 ± 13	< LD	-	-
Residual $_{[Colour]}$	TCU	21.3 ± 0.5	3.0 ± 0.3	-	-
Residual $_{[CBZ]}$	µg L^{-1}	10.7 ± 0.3	0.80 ± 0.2	7.2 ± 0.5	< LD
Toxicity	TU	45.5	< 2	16.9	< 2
CBZ removal	%		92.6		> 94.4
TOC removal	%		60.00		67.54
COD removal	%		> 93		-
Colour removal	%		86.0		-
Toxicity removal	%		> 96		> 88

LD: Limit detection, LD_{CBZ} = 0.4 µg L^{-1}, LD_{TOC} = 50 µg L^{-1}, LD_{COD} = 4.0 mg L^{-1}.

The untreated effluent consisted only of agitating the samples contaminated by CBZ in the reactor without imposing any current intensity and any ultrasound power. The removal rates of CBZ, TOC, COD and toxicity were determined by subtracting the residual concentrations from the initial values recorded in effluents, and the resulting value was divided by the same initial concentrations. A concentration of 10.7 ± 0.3 µg CBZ L^{-1} was measured in the initial MWE (untreated effluent). A concentration of 0.80 ± 0.2 µg CBZ L^{-1} was recorded in the treated effluent, which corresponded to an abatement of 93%. Likewise, more than 93% of COD, 86% of colour and 60% of TOC could be simultaneously removed from MWE. Besides, a relatively high toxicity of 45.5 TU was measured for luminescent bacterium Vibrio fisheri in the untreated effluent. By comparison, a value of toxicity unit below the detection limit (i.e., < 2 TU) was recorded after treatment of MWE. These results recorded on MWE can be compared with those obtained while treating synthetic effluent (SE) contaminated only with CBZ. More than 94% of CBZ can be removed, the residual concentration of CBZ (after treatment of SE) being below the detection limit (i.e., 0.4 μgL^{-1}), whereas a residual concentration of 0.80 ± 0.2 μg CBZ L^{-1} was recorded in the treated effluent of MWE. Indeed, the relatively high initial values of COD (58 ± 13mg L^{-1}) and colour (21.3 ± 0.5 mgL^{-1}) recorded in MWE can be in competition with CBZ removal in the real effluent.

4.6 CONCLUSION

This study investigated the treatment of water contaminated by CBZ in a batch recirculation mode using a sono-electrochemical reactor. The first part of these works was performed in synthetic media in order to demonstrate the interest of coupling ultrasonication and electrooxidation (US-EO) treatment for CBZ removal. An experimental design methodology has been subsequently applied to determine the optimal experimental conditions in synthetic effluent. The factorial design (FD) demonstrated that the current intensity and treatment time are the most influent parameters for the sono-electrochemical oxidation of CBZ. The effect of these two main factors is around 98.7 % on the investigated response, whereas the effect of ultrasound power represents only 0.45 %. Moreover, a central composite design (CCD) was employed to define the optimal operating conditions for CBZ degradation. The sono-electrochemical reactor operated at a current intensity of 4.86 A during 177 min of treatment time in the presence of an ultrasound power of 38.29 W was found to be the optimal conditions in terms of cost/effectiveness (89.6 ± 2.9 % of CBZ degradation for a total cost of US$0.61 per gram of CBZ removed). The total cost included only the energy consumption required for both electrolysis and ultrasonication processes. These optimal conditions were then applied for the treatment of real municipal wastewater effluent (MWE) contaminated by CBZ. The removal efficiencies of CBZ, TOC, COD and colour recorded were 93%, 60%, 93% and 86%, respectively. The US-EO process was also effective to completely remove the toxicity (bacterium Vibrio fisheri) of the MWE. The US-EO process is a promising technology that can be used as tertiary treatment to remove emerging pollutants, as well as COD, TOC and colour from MWE.

Acknowledgements

Sincere thanks are extended to the National Sciences and Engineering Research Council of Canada for their financial contribution to this study.

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CHAPITRE 5 Synergistic effects of ultrasounds in the sonoelectrochemical oxidation of pharmaceutical carbamazepine pollutant

Ce chapitre est constitué de l'article suivant:
Nam Tran, Patrick Drogui, Satinder K. Brar, De Coninck Arnaud, Synergistic effects of ultrasounds in sonoelectrochemical oxidation of pharmaceutical carbamazepine pollutant. Article soumis à *Ultrasonics Sonochemistry*, Avril 2016.

5.1 Abstract

The synergistic effects were evaluated during the oxidation of carbamazepine using a sono-electrochemical process. The sono-electrochemical oxidation was performed using two types of experimental units (having 1 L and 100 L of working volume, respectively) and containing one anode (Ti/PbO2) and one cathode (Ti). Different operating parameters, including power of ultrasounds, current intensity and reaction time were investigated. The degree of synergy increased when the current intensity decreased, whereas it increased with the power of ultrasounds imposed. The highest value of the synergy degree (33 %) was recorded for the lowest current intensity (1.0 A) and the highest power of ultrasounds (40 W). Likewise, the benefits of ultrasound were observed during a long-term period of treatment of CBZ (30 days of experiments without interruption). A relatively high degradation rate was recorded using the sono-electrochemical process (99.5 %) (at I=1 A, P=40 W), compared to a percentage of CBZ degradation of 91 % recorded during electrolysis alone (at I=1 A, P=0 W). Likewise, the scanning electron microscopy views and the measurements of the electrochemical impedance spectroscopy (EIS) revealed that there are not impurities deposited on the surface of electrode in the present of ultrasounds.

5.2 Introduction

Nowadays, the wide application and intensive use of pharmaceuticals in human and veterinary medicine have led to a great concern regarding the environmental pollution. In many countries, the pharmaceutical residues have been identified and quantified in treated sewage, municipal effluent, industrial effluent, and even in drinking water. The presence of these residues poses a potentially serious risk to both the environment and human health due to direct or indirect exposure to the residues in food and drinking water [1]. Carbamazepine (CBZ) is one of the most popular pharmaceutical used for the treatment of epilepsy as well as for various psychotherapeutic applications. CBZ is produced and consumed in great quantities, in Canada, approximately 28 tons of prescription CBZ was sold in 2001 [2]. This drug extremely resistant to biological degradation processes and presented in the aquatic environment due to its continuous input in the environment. Conventional physicochemical, biological treatment of effluents are often not significantly decomposed or removed of CBZ. Due to that CBZ was used as an anthropogenic marker in the environment by which standards could be set regarding the fate of many pharmaceuticals and healthcare products in the environment [3, 4].

A variety of advanced treatments methods like electrochemical have been extensively used for degradation of effluents containing toxic organic chemicals since these technologies present some advantages: versatility, environmental compatibility and potential cost effectiveness. An electrochemical oxidation process using Ti/BDD has been investigated by Dominguez, et al. [5] to degrade CBZ. The author has found an optimum carbamazepine degradation of 100 % at pH 9, flow rate of 1.25 cm^3 min^{-1}, and current density of 190 mA cm^{-2} using a supporting electrolyte concentration of 0.48 mol L^{-1} [5]. Likewise, an electrochemical oxidation process using Ti/PbO_2 circular anode electrode was effective in removing CBZ while a current intensity of 1.37 A was imposed for a period of treatment time of 101 min [6]. However, a loss in the efficiency of many electrochemical processes was observed owing to the formation of organic substances on the electrode surface that reduces its electrode active surface. This aspect constitutes a major barrier for large-scale applications [7,8]. Consequently, the electrochemical processes have been explored in conjunction with the ultrasounds for the destruction and mineralization of some recalcitrant organic compounds in water [9, 10]. Ultrasonic methods were introduced as effective process with the collapse and formation of tiny bubble under locally high temperatures and high pressures. This phenomenon could enhance the reaction rate and produce a new reaction [11]. Ultrasounds have been found beneficial effects on mass transport, on cleaning of the electrode surface and on the generation of hydroxyl radicals. The ultrasounds have been proposed to overcome the passivation of electrodes due to their ability for cleaning the electrode surface. The ultrasounds combined with other processes have been finding increased use for the destruction of organic pollutants from wastewaters. Ghauch, et al. [12] investigated the suitability of CBZ oxidation by an improved Fenton's process based on ultrasonic technique. Another study conducted by Naddeo, et al. [13] reported the ultrasound treatment of CBZ with gas sparging to enhance the sonochemical activity. A recent study using the combination of sonochemical-hydrodynamic (ultrasound and utilization of hydrodynamic phenomena) was carried out by Braeutigam, et al. [14]. The electrochemical oxidation can be enhanced in the presence of ultrasounds capable of modifying the polymeric film deposited on the electrode surface. Thus, sono-electrochemical process can combine the advantages of both sonochemical and electrochemical oxidation. However, some researchers argued that under certain conditions the US effects can be negligible or can have a negative effect on EO process [9, 15-17]. Therefore, the investigation on the synergistic effect is needed. To the best of our knowledge, this is the first time that, synergistic effects of ultrasound on the sono-electrochemical oxidation have been investigated to tackle the challenging problem of efficient degradation of pharmaceutical pollutant such as carbamazepine (CBZ). Thus, the synergistic degree was used to study the influence of the principal experimental parameters (electric current, power of ultrasound, treatment time) on CBZ degradation. A second objective of this study was to monitor the efficiency of the sono-electrochemical process during long-term period of treatment of CBZ. The third objective consisted to determine the mechanism/contribution of ultrasounds during the degradation of CBZ.

5.3 Materials and methods

5.3.1 Preparation of the synthetic effluent (SE)

The water samples used in this study were synthetically prepared by dissolving CBZ in tap water. The characteristic of tap water sample is shown in Table 5-1. CBZ analytical grade reagent (99 %) was obtained from Acros Organics BVBA (Belgium). SE solutions of CBZ were prepared in a glass beaker containing 3.0 L of water and 30 mg of CBZ. The CBZ was solubilized using a magnetic stirrer (500 rpm) at room temperature (25°C) for 24 h. The resulting mixtures constituted CBZ solution of 10 mg L^{-1} in which sodium salt (Na_2SO_4 0.01 mol L^{-1}) was also added to increase electrical conductivity.

Table 5-1 Characteristic of tap water sample

Parameter	**Units**	**Minimum**	**Maximum**
Conductivity	µS cm^{-1}	140	240
pH	pH	6.9	7.4
Total suspended solid	mg L^{-1}	20	50
Calcium	mg L^{-1}	16.5	29.1
Magnesium	mg L^{-1}	3.3	6.0
Sodium	mg L^{-1}	2	10
Potassium	mg L^{-1}	1	3
Chloride	mg L^{-1}	5	15
Iron	mg L^{-1}	< 1	< 1
Manganese	mg L^{-1}	< 1	< 1
Total organic carbon	mg L^{-1}	1.5	2.5
Chemical oxygen demand	mg L^{-1}	< 4	< 4

5.3.2 Electrochemical-sonochemical experimental units

Two types of experimental units (R1 and R2) having different capacities were used to evaluate the synergistic effects of the EO-US process for CBZ degradation. Fig. 5-1 shows a schematic drawing of the set-up used for the sono-electrochmical tests for CBZ oxidation. The first one (R1) had a working volume of 1.0 L (without recirculation tank), whereas the unit R2 had a total working volume of 101 L (including the experimental unit R1 (1.0 L) and a recirculation tank having a volume of 100 L). Both electrodes (anode and cathode) were used in the form of expanded metal plate. The rectangular cathode (110 cm height × 100 mm width x 2 mm thick) was made of titanium (Ti) having a solid area of 700 mm^2 and void area of 400 mm^2. The rectangular anode (110 mm height x 100 mm width x 4 mm thick) was titanium coated with lead oxide (Ti/PbO_2) having a working surface area of 1100 mm^2 and void area of 120 cm^2. The inter-electrode gap in both reactors was kept at 20 mm. The anode was placed at the center of the cell and the cathode was fixed at the periphery. The electrodes had been mechanically attached and arranged to ensure the proper water distribution in the electrolytic cell. The electrical current was applied using a digital DC power supply XFR 40–70 (Xantrex Technology, Burnaby, British Columbia, Canada) with a maximum current rating of 70 A at an open circuit potential of 40 V. Ultrasonic waves were introduced from the bottom of the reactor via a ceramic transducer (a piezoelectric disk having a diameter of 4 cm). The frequency (520 kHz) and electrical power (from 10 to 40W) of the piezoelectric disk was controlled by an external waveform generator (Agilent 33210A, Agilent Technologies Canada Inc.) equipped with a low frequency amplifier (AG 1016, T&C Power Conversion Inc.). The reactor temperature was held constant at 20oC using a Polystat cooling/heating recirculator (Cole-Parmer Canada Inc.). Mixing in the reactor was achieved by recirculating water through the cell by means of a peristaltic pump operated at a constant speed of 200 mL min^{-1}.

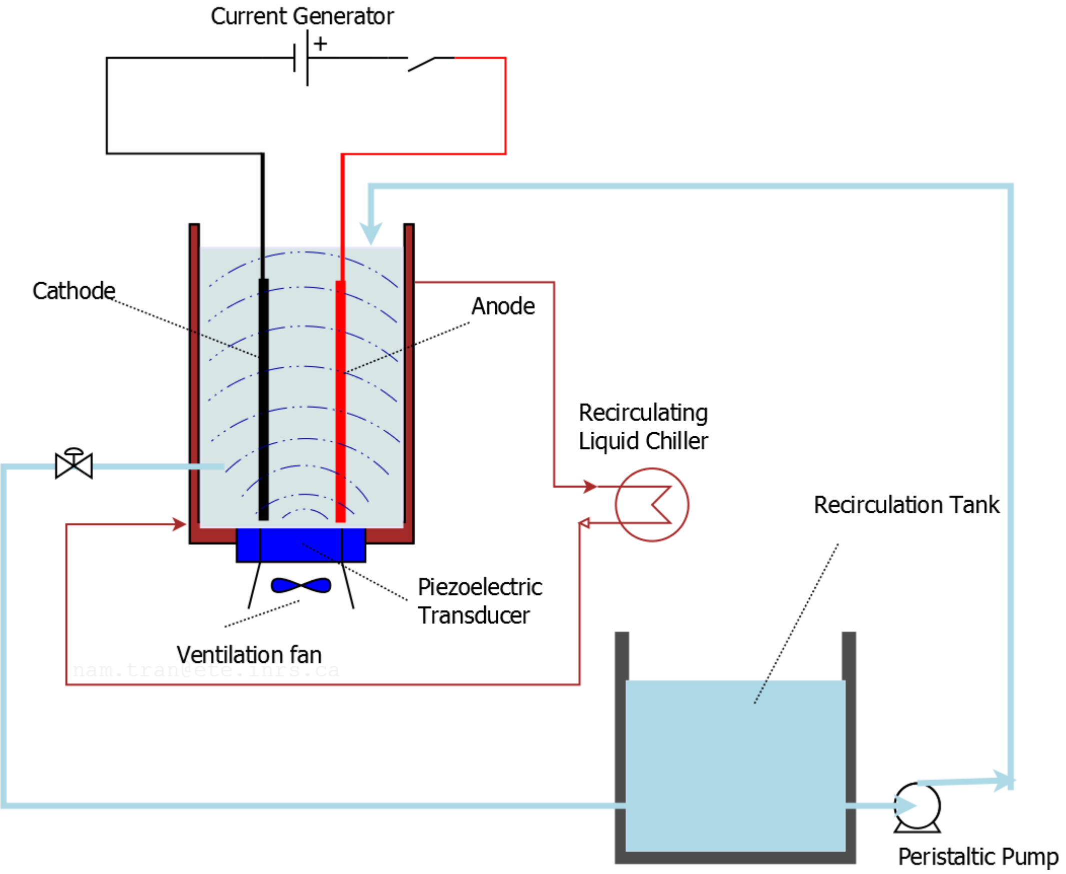


Fig. 5-1 Schematic diagram of the experimental setup for the CBZ degradation

5.4 Experimental

5.4.1 Effects of the operating condition

The unit R1 was used to determine the influence of operating conditions on the synergistic effects of ultrasounds in sonoelectrochemical oxidation of CBZ. The current applied varied from 1 to 15 A. The treatment times of 90-180 min were tested. Likewise, different electrical powers of ultrasounds were studied, including 20W, 30W and 40W. Samples were taken regularly from unit (R1) and monitored for residual CBZ concentrations. The reaction order and the apparent reaction rate constant of CBZ degradation can be determined by plotting Ln (C/C_0) against time.

$$-Ln\left(\frac{C}{C_0}\right) = k.t \qquad (1)$$

where "C_0" and "C" represent the initial and residual CBZ concentrations, respectively in the bulk solution, and "k" is the first-order rate coefficient. The degree of synergy (S) can be calculated by using the following equation [15]:

$$S = \frac{k_{EO-US} - (k_{EO} + k_{US})}{k_{EO-US}} x100 \qquad (2)$$

In this equation, $k_{EO\text{-}US}$ represents the reaction rate apparent constant recorded when the sono-electrooxidation (US-EO) process was used, whereas k_{EO} and k_{US} represent the rate apparent constants when ultrasonication (US) and electro-oxidation (EO) were respectively applied for the degradation of CBZ.

5.4.2 Long-term efficacy of US-EO process during the treatment of CBZ

The unit R2 was used during this set of experiment. The use of unit R2 required a high volume of water when compared to unit R1. Thus, an effluent was prepared using tap water in order to simulate real treatment conditions (100 L of water containing 10 mg/L of CBZ). Samples were taken daily from the recirculation tank and monitored for the residual CBZ concentration. The potential and current values were recorded for the estimation of treatment cost (in terms of energy consumption). During these tests, the electrodes were withdrawn every week and examined by scanning electronic microscopy (SEM) observations to monitor the surface state of electrodes. Electrode samples were mounted on a 5-axes motorized compucentric specimen stage and were observed without metal coating on the surface as they are conductive. The Carl Zeiss EVO® 50 SEM is equipped with a wide range of imaging detectors including an Everhart-Thornley Secondary Electron Detector for topographic images. Backscattered electron (BSE) images were obtained using a 4-Quadrant Backscattered electron Detector (QBSD) which allows the viewing of images in chemical contrast, depending of the mean atomic number of the specimen. Elemental analyses of the nanoparticles present on the surface were enabled by an X-ray Energy Dispersive Spectroscopy (EDS) microanalysis system (INCAx-sight EDS detector, Oxford Instruments). This EDS is a Lithium Drifted Silicon Si (Li) detectors, it has a resolution of 133 eV and can detect elements from beryllium (Z=4) to uranium (Z=92) for concentrations over 1000 ppm. This detector was operated close to liquid nitrogen temperatures. The used accelerating voltage was 20 kV and working distance was 8.5 mm. Likewise, the measurements of the electrochemical impedance spectroscopy (EIS) were carried out in order to evaluate the adherent nature, the compactness and the character more or less electrochemically isolated of the polymeric film deposited on the surface of electrodes. The impedance measurements were performed by using a potentiostat/galvanostat with a three-electrode cell, with a frequency range between 0.1-10^5 Hz at -1.2 V vs Ag/AgCl.

5.5 Analytic detail

5.5.1 CBZ measurements

The residual concentrations of CBZ in solution were monitored by absorbance measurements (absorption peak previously determined) by using a spectrophotometer Carry UV 50 (Varian Canada Inc.). The *integrated absorption* (basis on peak area rather than peak height) of CBZ was measured in the range of 200 nm to 400 nm to evaluate the residual CBZ concentrations (Fig S1, Supplementary data). The peak area was proportional to the total quantity of CBZ and by-products generated during sonoelectrochemical oxidation. A calibration curve (integrated absorbance versus concentration) was used to calculate the residual CBZ concentration and to define the efficiency.

5.5.2 Other parameter measurements

The pH and conductivity were measured using a pH/conductivity meter (Oakton model 510) equipped with a pH and conductivity probe. TOC was measured using a Shimadzu TOC 5000A analyzer (Shimadzu Scientific Instruments, Kyoto, Japan). Experimental data were obtained from the average of at least of three treatment replicates. Uncertainties were removed and calculated with a significance level of $p \leq 0.05$.

5.6 Results and discussion

5.6.1 The ultrasounds effect

The primary objective of this study was to examine the effect of ultrasounds in CBZ degradation by the measurements of synergistic effects (see equation 2). The experimental unit R1 was used. Ultrasonication (US), electrooxidation (EO) and sono-electrochemical (US-EO) processes were respectively applied for a 180 min period of treatment time. The US process consisted to treat the effluent using an electrical power of ultrasounds ranging between 20 W and 40 W. The EO process was applied (without ultrasounds) to treat the effluent by imposing a current intensity of 1.0 A. In the US-EO process, a current intensity of 1.0 A and ultrasounds (P = 20 W, 30 W and 40 W) were simultaneously imposed. The data of CBZ degradation were fitted to the first order kinetics (Table 5-2).

Table 5-2. Effect of ultrasounds on the apparent degradation rate constant (I=1 A, t=180min; P= 20 – 40W)

Parameters	**Power of ultrasound**			
	0W	**20W**	**30W**	40W
k_{EO}, min^{-1}	2.1×10^{-3}	**-**	**-**	**-**
k_{US}, min^{-1}	-	2.4×10^{-4}	3.0×10^{-4}	3.6×10^{-4}
k_{EO-US}, min^{-1}	-	2.4×10^{-3}	2.7×10^{-3}	3.3×10^{-3}

As a single process, the corresponding kinetic constants were calculated and a value of 2.1×10^{-3} min^{-1} was recorded for EO process, whereas 3.6×10^{-4} min^{-1}, 3.0×10^{-4} min^{-1} and 2.4×10^{-4} min^{-1} was obtained using US process at various power ultrasounds (40 W, 30 W and 20 W, respectively). By comparison, the combined process (EO-US) gave the best kinetic rate constant of 3.3×10^{-3} min^{-1} (40 W), 2.7×10^{-3} min^{-1} (30 W) and 2.4×10^{-3} min^{-1} (20 W). The reaction rate apparent constants allow calculating the synergy degree (Eq. 2). The results are presented in Fig 5-2.

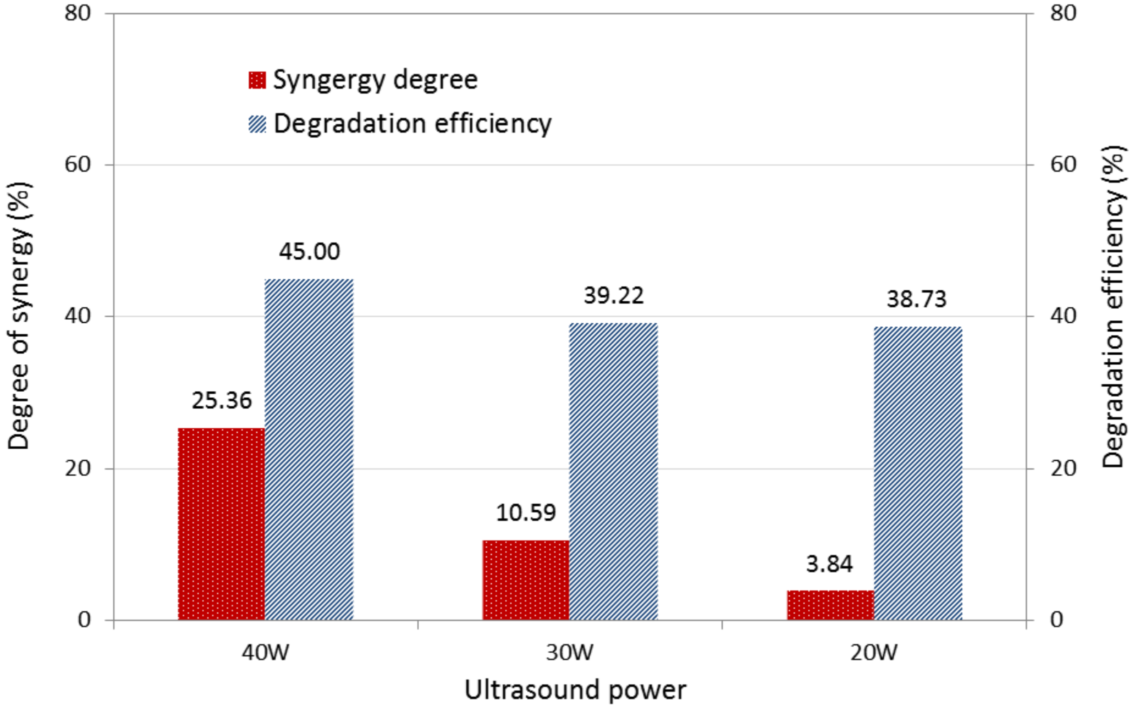


Fig. 5-2 Effect of ultrasound power on the synergistic effects and degradation efficiency (Unit R1 =1.0L, I = 1A, t=180min, P=20, 30 and 40W)

The synergy degree increased when the power of ultrasounds increased. For instance, a synergy degree of 25.4 % was measured for a power of ultrasound of 40 W, whereas 10.6 % and 3.84 % were recorded when 30 W and 20 W were respectively imposed. Likewise, the percentage of CBZ degradation at 40 W was higher (45.00 %) indicating that the contribution of ultrasounds on CBZ degradation was higher while increasing the electrical power of ultrasounds. The power of ultrasounds has a significant influence on CBZ degradation and on the synergy degree. As the power increases, the number of cavitational activity increases. According to the results obtained by Koda et al. (2003), the cavitation activity linearly increased with energy input (the electrical power is linked to the calorimetric power). The increase of cavitation activity improves the hydroxyl radical production and consequently, enhances the pollutant degradation. An electrical power of ultrasounds of 40 W was found to be the most effective for CBZ degradation and to record the relatively high value of synergy degree. This value (40 W) was selected for the next step of experiments.

5.6.2 The current intensity effect

The effects of the current intensities (1.0, 2.0, 3.0, 5.0, 10 and 15 A) on the degradation rates of CBZ were studied using US-EO processes. The results are presented in Fig. 5-3.

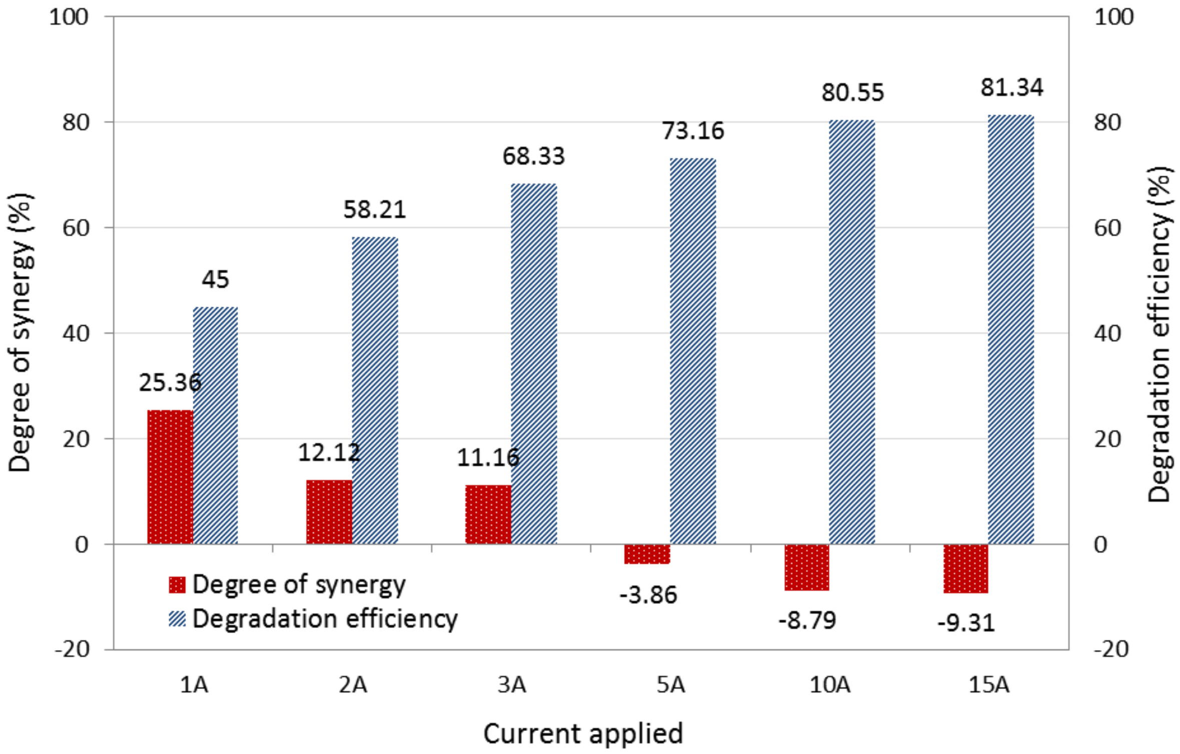


Fig. 5-3 Effect of current on the synergistic effects and degradation efficiency

(Unit R1 = 1.0L, I = 1-15A, t=180min, P= 40W)

In order to evaluate the synergy degree of the process EO-US, the first-order kinetic reaction rate constants were calculated in function of current intensity imposed (Table 5-3).

Table 5-3. Effect of current intensity on the apparent degradation rate constant (I=1-15 A, t=180min; P= 40W)

Current intensity, A	Parameters		
	k_{US}, min^{-1}	k_{EO}, min^{-1}	$k_{EO\text{-}US}$, min^{-1}
0	3.6×10^{-4}	-	-
1	-	2.1×10^{-3}	3.3×10^{-3}
2	-	3.6×10^{-3}	4.5×10^{-3}
3	-	5.4×10^{-3}	6.5×10^{-3}
5	-	7.2×10^{-3}	7.3×10^{-3}
10	-	8.3×10^{-3}	8.0×10^{-3}
15	-	1.35×10^{-2}	1.27×10^{-2}

According to the calculated values, the order of CBZ degradation rate apparent constants can be presented as follows: k_{15A} (1.27×10^{-2} min^{-1}) > k_{10A} (8.0×10^{-3} min^{-1}) > k_{5A} (7.3×10^{-3} min^{-1}) > k_{3A} (6.5 $\times10^{-3}$ min^{-1}) > k_{2A} (4.5×10^{-3} min^{-1}) > k_{1A} (3.3×10^{-3} min^{-1}). The synergy degree was calculated based on the reaction rate apparent constants. As seen in Fig. 5-3, the most pronounced synergistic effects (S) are recorded at low current intensities. Negative (S) values were recorded when the current intensity was greater than 5.0 A. After 180 min of treatment, the synergy degree decreased when the current intensity increased. However, as the current intensity increased, the depurative efficiency increased. The highest value of the synergy degree (S_{1A} = 25.36 %) was recorded at the lowest current intensity, whereas the lowest synergy degree (S_{15A} = -9.31 %) was obtained at the highest current intensity (S_{15A} = -9.31 %). The degradation rate of CBZ increased, when the current intensity increased; the degradation efficiency varied from 45.0 % to 81.3 %. The synergistic effect EO-US was positive for the current intensities ranging between 1.0 A and 3.0 A, whereas the synergistic effect became negative for the current intensity varying from 5 A to 15 A. The positive synergistic effect means the sum of the individually process (EO + US) reached lower degradation rate than the combined process under the same parameter operations. The highest degree of synergy calculated (S_{1A} = 25.36 %) indicating that the CBZ degradation was higher when both processes (EO and US) were simultaneously used compared to EO and US individually and successively applied. This phenomenon can be explained by the fact that during EO process using non-active electrode (such as Ti/PbO_2); hydroxyl radical can be formed at the surface of electrode. Hydroxyl radical can participate in degradation of organic pollutants. Then, the use of US could contribute to increase the power of these oxidants by increasing the mass transfer between electrode and pollutants. In the solution, the organic contaminants must be transported toward the anode electrode surface to be oxidized there. The organic contaminant degradation may be subjected either to current control or mass transfer control. Both parameters were greatly influenced by the current applied to the synergistic effect of US and EO.

To further understand the behavior behind this phenomenon, additional investigations were carried out by cyclic voltammetry measurement using a potentiostat/galvanostat (PGZ402, Radiometer analytical) with three electrodes in unit R1. The reference electrode was a saturated Ag/AgCl/KCl electrode, while the auxiliary electrode was Ti and working electrode was Ti/PbO2. Cyclic voltammetry measurements were performed in potentiostatic mode (scan rate = 20 mV s-1, from 0 to 4.0 V vs Ag/AgCl). Electrolyte solution was Na_2SO_4 (0.01 mol L^{-1}) with the presence of CBZ 10 mg L^{-1}. The linear voltammetry curve of CBZ at Ti/PbO_2 electrode in the absence of ultrasound (EO) and presence of ultrasound (EO-US) is shown Fig. 5-4. It was shown that the current intensity increased with the potential imposed, that mean the higher the current density, the more effective the process was for CBZ oxidation. From 0 to 3.5 V vs. Ag/AgCl, at the same potential value; the higher the current density has been recorded for the EO-US process when compare to EO process. In the presence of ultrasound in solution, it is easier to transfer more electrons between the electrodes. However from 3.5 to 4.0 V vs. Ag/AgCl, there are small different between the current of EO and the current EO-US.

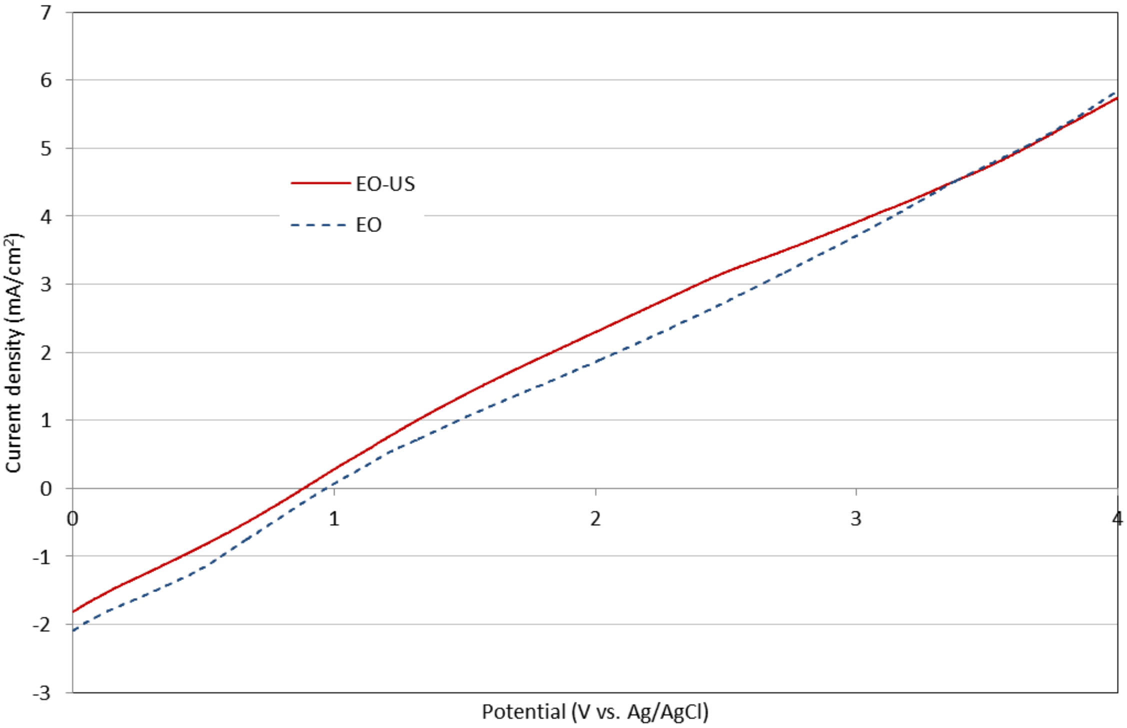


Fig. 5-4 Linear voltammetry curve of CBZ at Ti/PbO_2 electrode in the absence of ultrasound (EO) and presence of ultrasound (EO-US), (Na_2SO_4 = 0.01 mol L^{-1}, CBZ = 10 mg L^{-1}, Scan rate = 20 mV s^{-1}).

This is the reason why the contribution of ultrasound for CBZ oxidation is higher at lower potential while both effects (oxidation by US and EO) occur simultaneously. This result leading to higher degradation rate of CBZ at high current intensity but the contribution of sonication is not significant. Consequently, current intensity was a major factor that influenced on degradation rate of CBZ, but was negative effect on synergy degree at high current value.

5.6.3 The treatment time effect

The treatment time is also one of the most important parameter during a sono-electrochemical oxidation process. When the treatment time increases, the hydroxyl radicals (generated by EO or US) have more opportunities to participate in degradation of CBZ pollutant leading to higher oxidation rates and possible mineralization of organic matter. Fig. 5-5 compares the results of the synergy degree and degradation efficiency at different interval 90, 120, 150 and 180 min of treatment for the current intensity imposed of 1.0 A.

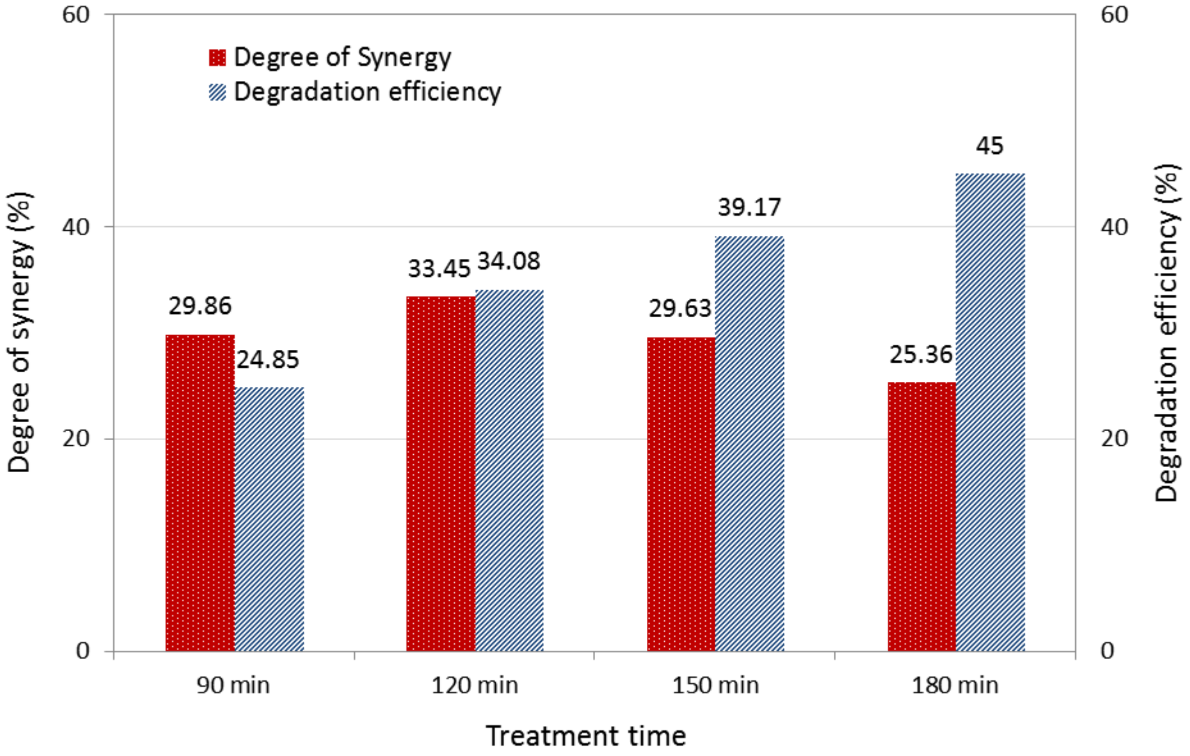


Fig. 5-5 Effect of treatment time on the synergistic effects and degradation efficiency

(Unit R1 = 1.0L, I = 1A, t=90-180min, P= 40W)

It can be seen that after 120 min of treatment, a synergy degree of 33.45 % was the highest value recorded. As treatment time increased from 90 to 120min, the degradation efficiency rapidly increased within 30 min (9.23 units) and then showed smaller change after 120 min (5.09 unit from 120-150 min and 5.83 units from 150-180 min). As mentioned above, the association of ultrasound with electrochemical oxidation can be a powerful technique for the degradation of pollutants, since the ultrasound is responsible for the increase of mass transport, activation of electrodes surfaces and generation of active hydroxyl radicals. When the treatment time increases, the hydroxyl radicals (generated by acoustic cavitation) have more opportunities to contribute to CBZ degradation leading to higher oxidation rates.

5.6.4 Comparison between EO and EO-US processes during long-term period of treatment of CBZ

The unit R2 was used during this set of experiment. The current intensity imposed during the treatment using EO process was 1.0 A without ultrasounds. For the EO-US process, the same current intensity of 1.0 A was applied and an electric power of 40 W was imposed. The changes in CBZ concentrations of the synthetic effluent during the treatment are presented in Fig. 5-6. Two main regions could be distinguished in the residual CBZ concentration vs. time plane (Fig. 5-6). In fact, from 0 to 15 days of period of treatment, residual CBZ concentrations decreased rapidly with a high slope for both processes (EO and EO-US). The two curves were quite similar for this period of treatment. There is no significant different between EO and EO-US process in term of CBZ degradation efficacy. In the second region (from 15 to 30 days of period of treatment); residual CBZ concentrations decreased slowly with a relatively low slope and remained steady beyond the 20th day.

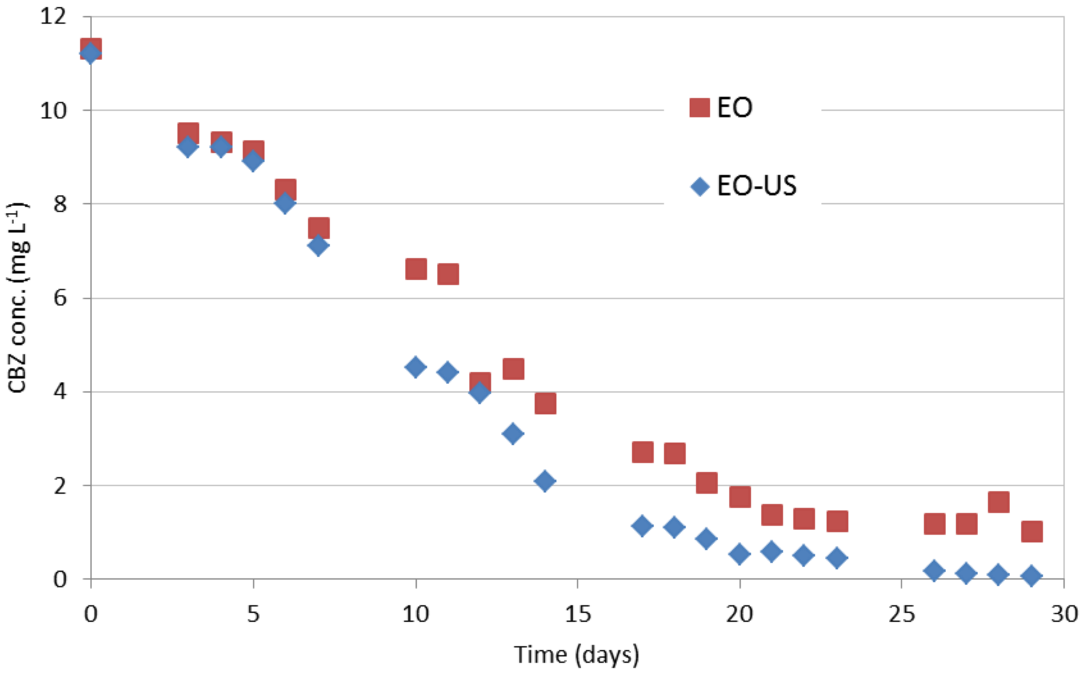
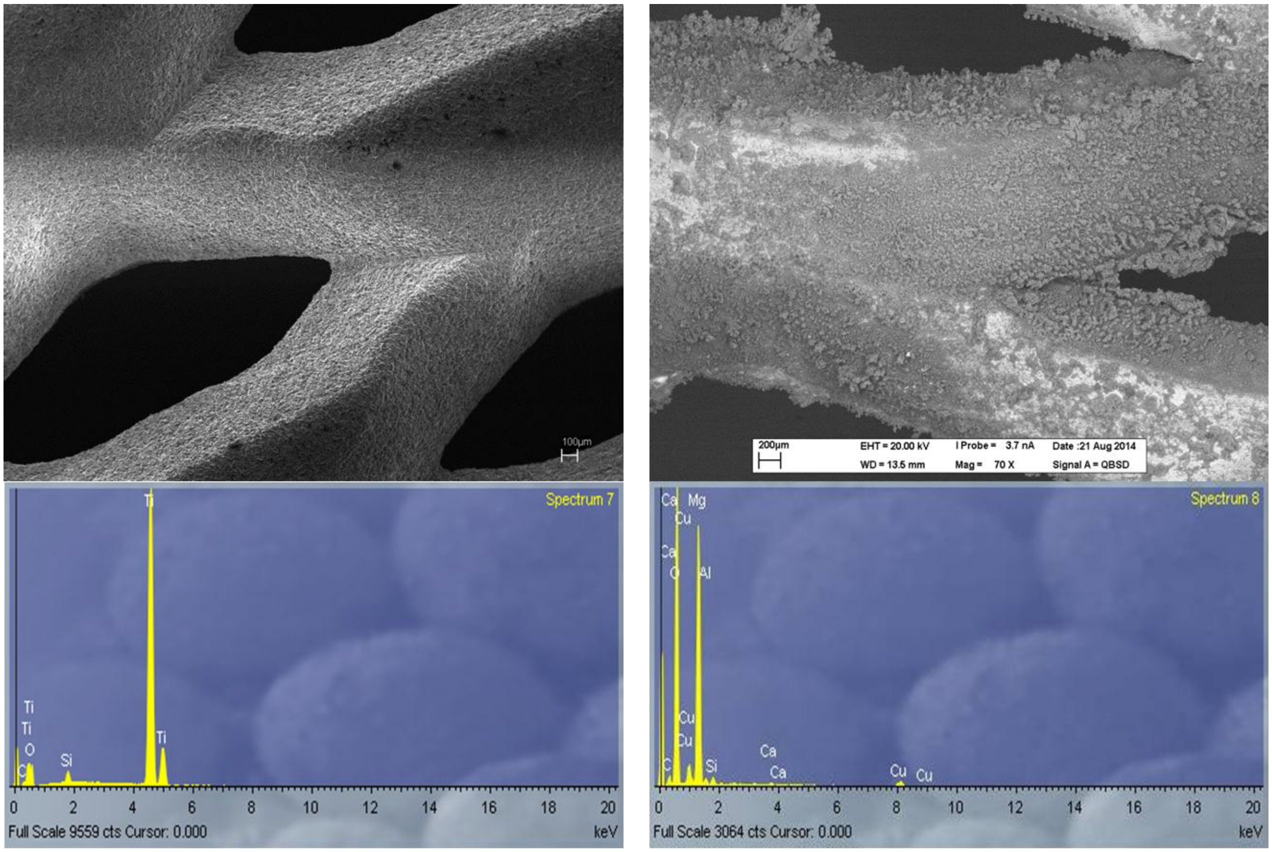


Fig. 5-6 Time profile of residual CBZ concentration during EO and EO-US process (Unit R2 = 100L, I = 1.0A, P= 40W)

At the end of the treatment, the residual CBZ concentrations recorded were 1.02 and 0.06 mg L^{-1} for the EO and EO-US, respectively. These values corresponded to the degradation efficiency of 91.0 % and 99.5 % for the EO and EO-US, respectively. These results indicated that the combined processes of EO and US can perform better than EO alone for a long-term period of treatment of CBZ.

To understand the mechanism behind CBZ degradation using EO-US process, additional investigation was carried out by scanning electron microscope (SEM) surface of electrode. Fig. 5-7 shows SEM images and elemental analyses of the surface cathode withdrawn at the end of treatment (30 days of period of treatment) for the EO-US (Fig. 5-7a) and EO (Fig. 5-7b).



a (EO-US)

b (EO)

Fig. 5-7 SEM image and EDS micro analysis of Ti cathode.

The SEM images of the titanium cathode can be clearly seen that the surface were uniformly on the whole electrode while the EO-US was applied (Fig. 7a). The substrate of the cathode withdrawn from EO process was covered by a layer of isolated particles which was multiform.

For the element measurement, the EDS microanalysis for the cathode withdrawn after EO-US process shows all of the peaks can be assigned to Ti, except small peaks for the Si, O and C. In the case of cathode withdrawn from EO process, the principal peak was detected is attributed to the Ca, Mg, Cu, Al and O which shown the impurities (byproducts) forming during EO process. Since the Ti element has been covered by impurities, it was no additional peak of Ti to be detected. These impurities formed could be explained by the reaction of electrolysis of water containing mineral elements, some chemical reactions may occur as follow:

Anodic reaction (oxidation of water):

$2H2O - 4e^{-} \rightarrow O_2 + 4H^{+}$

Cathodic reaction (reduction of water):

$4H_2O + 4e^{-} \rightarrow 2H_2 + 4OH^{-}$

In water containing mineral ions, a secondary reaction occurs at the electrodes:

(Anode) $H+ + HCO_3^{-} + H_2CO_3 \rightarrow CO_2 + H_2O$

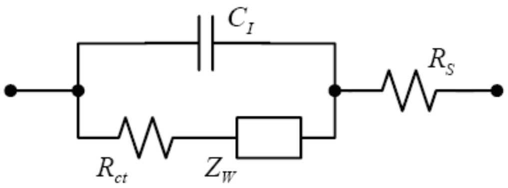
(Cathode) $OH^{-} + HCO_3^{-} \rightarrow CO_3^{2-} + H_2O$

(Cathode) $Me^{2+} + CO_3^{2-} \rightarrow MeCO_3\downarrow$

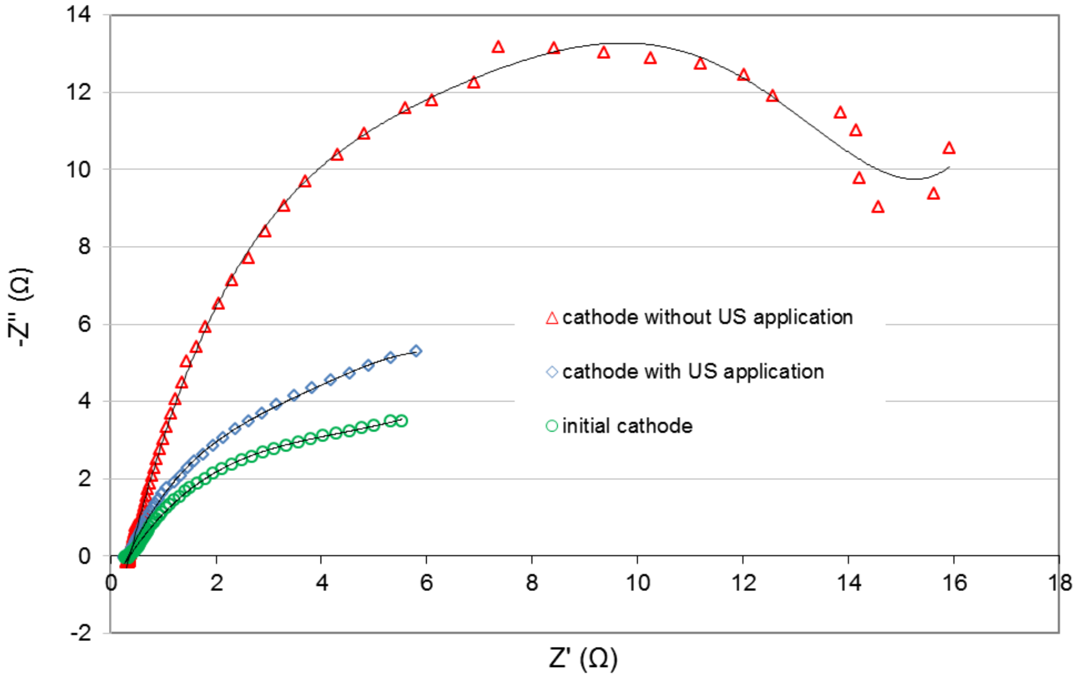
Where are Me^{2+} is metallic element like Ca, Mg, Fe. The fact is deposition of mineral scales ($CaCO_3$, $CaSO_4$, etc.) is a serious practical problem in many electrochemical processes [18].

The interface properties of electrodes were also investigated by EIS which is an effective tool for detecting the changes associated with the transfer of electrons. Electrochemical transformations occurring at the electrode/electrolyte interface can be modeled by using components of an equivalent electrical circuit. The circuit (Fig. 8a) was employed to fit the EIS experimental data contains the solution resistance (R_s), the charge transfer resistance (R_{ct}), the Warburg impedance (Z_W), and the double layer capacitance (C_I). It is important to emphasize that both C_I and R_{ct} depend on the insulating properties of electrode/electrolyte interface, while R_s and Z_W are related to the bulk properties of the electrolyte solution and the diffusion features of the redox probe in solution, respectively [19]. In an EIS measurement, the typical impedance spectra includes a semicircle at high frequencies which corresponds to the electron transfer limited process and a linear part at low frequencies representing the diffusion limited process.

Fig. 8b presents the Nyquist plot of the initial Ti cathode, Ti cathode with US application and Ti cathode without US application, respectively.



(8a)



(8b)

Fig. 5-8 Equivalent electrical circuit for electrode solution interface (a) and Nyquist plot obtained with Ti cathode (initial electrode, electrode with and without US application) at an applied potential of -1.4 V vs Ag/AgCl (b).

It was observed that the curves recorded with the electrode without US application has a single semicircle (high-medium frequency range) followed by a straight line at an angle of 45^o, in the low frequency range. The diameter of high-frequency semicircle is equal to the charge transfer resistance (R_{ct}). A high R_{ct} value indicates that the transfer of electrons takes place with difficulties, while a small R_{ct} value means a fast transfer of electrons. The EIS spectra of initial electrode and electrode with US application are characterized by no semicircle and only linear part which can be attributed to a very fast transfer of electrons. These results shows that with the application of US, higher electrons transfer could contribute to increase the number of CBZ molecules that can be oxidized at the electrode surface when compare to the electrode without US exposure. When the cathode is covered by a polymeric film, it modifies the surface state of the electrode and the conductivity of electrode decreases (owing to the increase of the electrical resistance). However, for anode surface, we did not find any important changes during electrolysis. Literatures [20] shown that ultrasound can improve the electrochemical degradation of pollutants by physical and chemical mechanisms. The propagation of acoustic waves in a liquid medium induces cavitation and even their violent collapse. These collapses are the high rates of micro mixing, the cleaning of the electrodes surfaces by dissolving or pitting the inhibiting layers [21, 22]. These effects result mainly in an enhancement of the solid-liquid mass transfer between the electrodes and the solution [23, 24]. The ultrasounds, when applied directly to an electrode surface, can provide a severe degradation of the surface by erosion of the electrode material [22], as well as it induces the activation and enhancement in the performance due to the electrode cleaning [22, 23]. Therefore, lower degradation rate has been observed for the electrochemical process without ultrasounds imposed. In our experiment, the SEM, EDS analysis and EIS measurement confirm that the surface of the ultrasonicated electrode does not exhibit any impurities or by products deposition. It is assuming that the applied of ultrasounds increases the degradation efficiency by removing or cleaning the film deposited at the surface of cathode.

5.7 Conclusions

This study investigated the synergistic effects for the treatment of water contaminated by CBZ using a sono-electrochemical process. The first part of these works in the sono-electrochemical reactor R1 demonstrated that the ultrasound power has a significant influence on the synergistic effects of the EO-US process for CBZ degradation. Under ultrasound irradiation for 120 min of treatment time at high power (P=40 W) and relatively low current intensity (I=1A), the highest synergy degree of 33.45 % was achieved. The positive value of synergy degree indicated that the CBZ degradation was higher when both processes (EO and US) were simultaneously used compared to the treatment of CBZ using the EO and US processes individually or successively applied. The EO-US process operated during a long-term period of treatment of CBZ was more effective than EO used alone. A percentage of CBZ degradation of 99.50 % was recorded using EO-US, compared to 91.00 % obtained using EO alone. In addition, SEM and EIS analyses confirmed that the used of ultrasounds removed impurities product formed at surface cathode during electrolysis. This study shows a promising technology that can be appliqued as tertiary treatment to degrade pharmaceutical residues from wastewater.

5.8 References

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CHAPITRE 6 OPTIMIZATION OF SONO-ELECTROCHEMICAL OXIDATION OF IBUPROFEN IN WASTEWATER

Ce chapitre est constitué de l'article suivant:

Nam Tran, Patrick Drogui, Laurent Nguyen, Satinder K. Brar, Optimization of sono-electrochemical oxidation of ibuprofen in wastewater, Journal of Environmental Chemical Engineering, http://dx.doi.org/10.1016/j.jece.2015.05.001.

6.1 Abstract

The decomposition of Ibuprofen in synthetic solution and in municipal wastewater effluent was investigated using an electro-sonochemical reactor. The concept of coupling ultrasonication and electrooxidation (EO-US) treatment for Ibuprofen removal was demonstrated. The degree of synergy was 5.26 %. Several factors such as current intensity, ultrasound power, treatment time were investigated. A factorial experimental design was used for determining the influent parameters on the ibuprofen degradation. The current intensity and treatment time were the main influent parameters on the degradation rate. Using a 2^3 factorial matrix, the best performance of ibuprofen degradation (77% of removal) was obtained by selecting 40W of ultrasound power, a current intensity of 5.0A and a treatment time of 120 min. Subsequently, the optimal experimental parameters for ibuprofen degradation have been investigated by using a Central Composite methodology. Under these, optimal conditions determined by this method, EO-US can be applied to oxidize ibuprofen in municipal wastewater effluent (up to 90% of degradation) while using a current intensity of 4.09 A for a period of 110 min and by applying 20W of ultrasound power.

6.2 Introduction

The increasing production and intensive use of pharmaceutical products has led to the entry of these products into the environment and to eventual pollutions of soil, ground and surface waters. The pharmaceutical residues are rejected into surface waters, ground water and may enter into drinking water sources (Matamoros et al., 2009; Brozinski et al., 2013). Ibuprofen (IBU) is an anti-inflammatory, analgesic and antipyretic in the human treatment of fever and pain often found in several water sources (Matamoros et al., 2009; Ambuludi et al., 2013). IBU have been found, among other pharmaceutical residues, in sewage wastewaters and surface waters (Ciriaco et al., 2009; Matamoros et al., 2009; Ambuludi et al., 2013; Brozinski et al., 2013). A typical concentration of IBU between 2 ng L^{-1} and 8.77 μgL^{-1} has been detected in US (Richardson, 2007) and UK surface waters (Roberts and Thomas, 2006). Several researchers have been reported that drugs found in aquatic systems may present a potential hazard for human health, especially where no advanced wastewater treatments are used (Stamatelatou et al., 2003; Miao et al., 2005a; Chiron et al., 2006). The removal of IBUs from water is a difficult task due to their low concentration and refractory properties (Ciriaco et al., 2009). Conventional methods frequently used in water treatment, such as biological and physicochemical treatments have been reported to be sometimes ineffective to remove emerging organic pollutants (EOPs) such as IBU. Therefore, a need exists for efficient treatment technology for the removal of this pollutant from the aquatic environment.

Advanced oxidation processes (AOPs) have been proposed as alternative methods to remove many toxic and bio-recalcitrant compounds in wastewater. Recent studied show that IBU degradation can be achieved through some other AOPs treatment such as electrochemical oxidation. For instance, pharmaceutical IBU was removed from water using an electrochemical oxidation process by means of carbon nanotubes electrodes (Motoc et al., 2013). After 116 min of electrooxidation, a relatively high degradation rate of 78% and a high mineralization rate of 60.84% were recorded at a potential of +1.25 V vs. Ag/AgCl in the presence of 10 mg L^{-1} of IBU. Ambuludi et al. (2013) have also studied IBU (C_0 = 0.2 mM) oxidation using an electrochemical advanced oxidation process in the presence of boron-doped diamond (BDD) anode electrode. After 8 h of electrolysis, total organic carbon (TOC) removal ranged from 91% to 96% by applying a current intensity in the range of 50–500 mA. Likewise, Ciriaco et al. (2009) studied IBU oxidation by using a Ti/Pt/PbO_2/BDD anode electrode. Different current densities were applied (10, 20 and 30 mA cm^{-2}) in the presence of initial concentrations of IBU ranging from 0.22 to 1.75mM. The COD removal ranged from 60 and 95%, whereas TOC removal varied from 48 to 92%.

In spite of good oxidation rates of IBU, many of electrochemical processes are inefficient to subsequently oxidize by-products formed during electrolysis (Klima et al., 1995; Compton et al., 1997). Indeed, during electrolysis, the electrode surface can be covered with organic substances that are formed during the treatment of organic-containing effluent. The formation of organic substances on the electrode surface reduces its electrode active surface. Since 1990, the ultrasound process has received considerable interest for the destruction of organic pollutants that are present in wastewater (Henglein et al., 1990; Leite et al., 1999; Gogate, 2007). The ultrasonication process has been identified as a successful alternative for the destruction and mineralization of some recalcitrant organic compounds in water and does not require the addition of chemicals (Gogate et al., 2003; Gogate, 2007; Oztekin et al., 2013). Acoustic cavitation, derived from the high calorimetric power of a liquid, can provide unusual and unique reaction sites as a result of the extremely transient and small cavitation bubbles that are created with high temperatures and high pressures (Birkin et al., 1997; Compton et al., 1997). The beneficial results from exposing electrochemical cells to the effects of power ultrasound include the enhancement of mass transport, the increase of current efficiencies and the continuous activation of the electrode surface (Klima et al., 1995; Birkin and SilvaMartinez, 1997). These effects can be ascribed to the rapid generation and collapse of micro bubbles within the electrolyte medium or nearby the electrode surface. This cleaning effect has been reported to improve electron exchanges by peeling out passivation films on surface electrode or piercing them by micro holes (Klima et al., 1995; Compton et al., 1997; Macounova et al., 1998).

The general objective of this study is to investigate the combination of ultrasonication (US) with electrooxidation (EO) to remove IBU from water. The specific objectives of this study are the followings: ***i***) Evaluate the interest of coupling ultrasonication and electrooxidation processes for IBU removal from water; ***ii***) Study the influence of the principal experimental parameters (electrical current, ultrasound power, treatment time, temperature) on the efficiency of the process for IBU degradation; ***iii***) Use a statistical methodology for a rational analysis of the combination of operational factors that led to the best conditions for IBU degradation and; ***iv***) verify the quality of treated effluent (versus untreated effluent) while treating real municipal wastewater contaminated by IBU.

6.3 Materials and methods

6.3.1 Preparation of the synthetic effluent (SE)

The water samples used in the first step study were prepared synthetically by dissolving IBU in de-ionized water. IBU analytical grade reagent (99 %) was obtained from Sigma Aldrich (Canada). Stock solutions of IBU were prepared in a beaker containing 100m L of methanol and 1.0 g of IBU. To eliminate the effect of methanol on IBU removal, the SE solution of IBU was solubilized by dilute small amount of stock solution (3.5 mL) in the de-ionized water (a beaker volume of 3.5 L) using a magnetic stirrer (500 rpm) at room temperature (25°C). The resulting mixtures constituted the IBU solutions of 10 mg L^{-1} in which a sodium salt (Na_2SO_4 0.01 mol L^{-1}) was added to increase electrical conductivity.

6.3.2 Wastewater IBU-spiking

In view of testing the sono-electrochemical process on real effluent containing refractory organic pollutants and to simulate IBU contamination, wastewater samples were enriched with IBU (10 µg L^{-1}, 100 µg L^{-1} and 10 mg L^{-1}, respectively) without addition of supporting electrolyte. The real effluents were sampled at Levis Urban Community wastewater treatment plant (WTP, Levis, Canada). This is a conventional WTP with a physicochemical pre-treatment and a sequential biological treatment system followed by a disinfection process using ultraviolet light. The sample had an initial content of COD = 30 ± 12 mg L^{-1}, DBO_5 = 4.4 ± 0.4 mg L^{-1}, TOC = 7.5 ± 2.2 mg L^{-1}, TSS = 6.7 ± 4.9 mg L^{-1}, N_{NH4} = 3.7 ± 3.1 mg L^{-1}, P_{tot} = 0.3± 0.1 mg L^{-1}, Cl^- = 2.5 ± 0.3 mg L^{-1}, pH = 6.6 ± 0.2 and conductivity = 450 ± 30 µS cm^{-1}. The effluents were sampled at the outlet of treatment plant (before the disinfection system) and stored in polypropylene bottles and kept at 4°C until use.

6.3.3 Electro-sonochemical reactor setup

The assays were carried out in a closed loop depicted schematically in Fig. 6-1. The sono-electrochemical reactor was made of Plexiglas material (characterized by a double layer cylinder) with an internal dimension of 20 cm (height) x 14.5 cm (diameter) and both electrodes (anode and cathode) were used in the form of expanded metal. The cylindrical cathode electrode (16 cm height × 12 cm diameter x 0.2 cm thick) was made of titanium (Ti) having a solid surface area of 420 cm^2 and a void area of 180 cm^2. The cylindrical anode electrode (16 cm height x 8.0 cm diameter x 0.2 cm thick) was titanium coated with lead oxide (Ti/PbO_2) having a solid surface area of 280 cm^2 and a void area of 120 cm^2. The inter-electrode gap was 2.0 cm in the electrolytic cell.

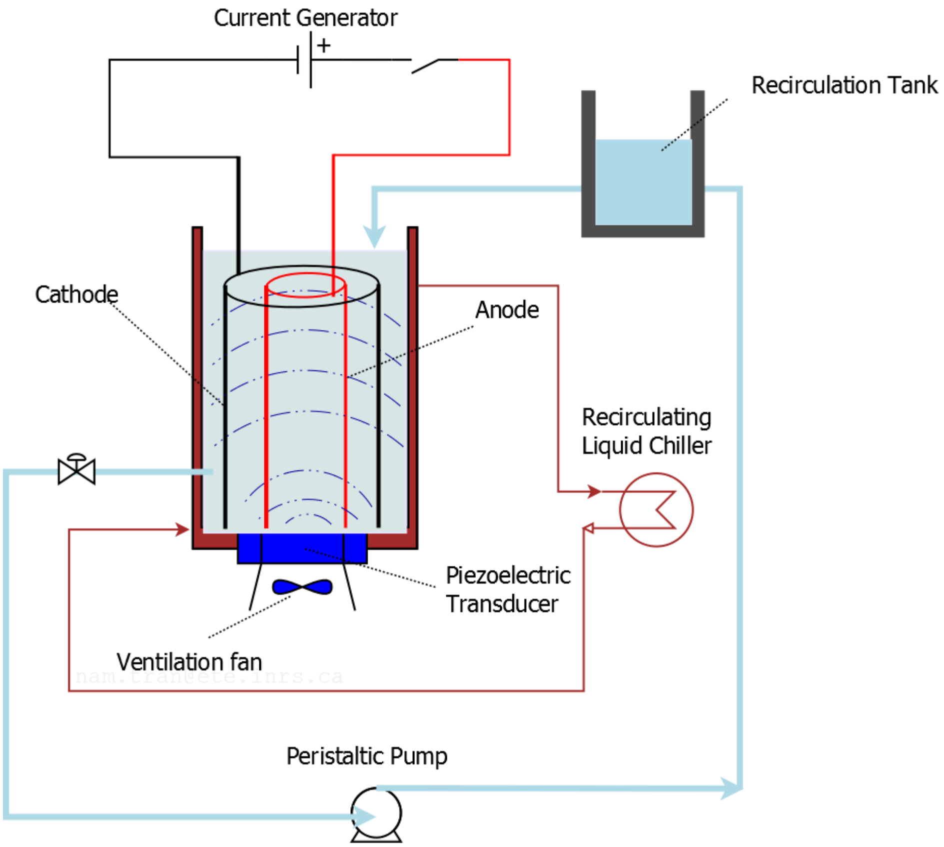

Fig. 6-1. Schematic view of the sonoelectrooxidation reactor with recirculation loop.

The anode was placed at the center of the cell and the cathode was fixed at the periphery. The electrodes had been mechanically attached and arranged to ensure the proper water distribution in the electrolytic cell. The electrical current was applied using a digital DC power supply XFR 40–70 (Xantrex Technology, Burnaby, British Columbia, Canada) with a maximum current rating of 70 A at an open circuit potential of 40 V. Ultrasonic waves were introduced from the bottom of the cell via a piezoelectric transducer (a ceramic disk having a diameter of 4 cm). The frequency (520 kHz) and electrical power (from 10 to 40W) of the piezoelectric disk were controlled by an external waveform generator (Agilent 33210A, Agilent Technologies Canada Inc.) equipped with a low frequency amplifier (AG 1016, T&C Power Conversion Inc.). The reactor temperature was held constant at 20^{o}C using a Polystat cooling/heating recirculator (Cole-Parmer Canada Inc.). Mixing in the reactor was achieved by recirculating water through the cell by means of a peristaltic pump operated at a constant speed of 100 mL min^{-1}. The recirculation tank (1.0 L of capacity) was made of the same material as the electrolytic cell. In all tests, a total volume of 3.0 L of contaminated water was used. The working volume of the electrolytic cell was 2.5 L, whereas 0.5 L was required for the recirculation tank.

6.3.4 Sonoelectrochemical treatment of the IBU containing SE

The sonoelectrochemical experiments was used to carry out different tests to determine the effect of operating conditions in treating water contaminated by IBU. The current densities varied from 3.6 to 35.7 mA cm^{-2} (current intensity from 1.0 to 10.0 A). The treatment times of 30-180 min were tested. Different electric power of ultrasound was studied, including 5W, 10W, 20W, 30W and 40W. Likewise, the effect of temperature (5^{o}C, 10^{o}C, 20^{o}, 30^{o}C and 40^{o}C) was studied.

6.3.5 Experimental design procedure

The removal of IBU by sono-electrochemical was optimized using response surface methodology (RSM). Experimental design of the sonoelectrooxidation process for IBU removal was carried out by using successively factorial design (FD) and central composite design (CCD) methodology. The FD was employed to firstly investigate the main and interaction effects of the factors on the percentage of degradation for IBU. Subsequently, the CCD was used for the optimization of sonoelectrooxidation process for IBU degradation.

6.4 Result and discussion

6.4.1 Evaluation of the synergistic effect between US and EO for IBU degradation

The first set of experiments was conducted to compare the removal efficiencies of IBU using ultrasonication (US) alone, electro-oxidation (EO) alone and sono-electrooxidation (EO-US) processes. During these tests, only the residual IBU concentration was measured. An electric power of 30 W of ultrasound at a frequency of 520 kHz was imposed. The treatment time was 180 min and the current intensity was fixed at 4.0A (anodic current density of 14.29 mA cm^{-2}). The US process consisted in treating the effluent using only ultrasonication at an electrical power of 30 W. The EO process was applied to treat the effluent using Ti/PbO_2 anode and Ti cathode electrodes operated at a current intensity of 4.0 A without ultrasounds. In the EO-US process, a current intensity of 4.0 A and ultrasounds (P=30W) were simultaneously imposed. Fig. 6-2 shows the kinetic rate constant of degradation IBU by these different processes employed. As a single process, the corresponding kinetic constants were calculated and a value of 0.0011 min^{-1} was recorded for US process, whereas 0.0079 min^{-1} was obtained using EO process. By comparison, the combined process (EO-US) gave the best kinetic rate constant of 0.0095 min^{-1} (corresponding to 84.74% of IBU removed). The comparison of these processes (EO, US, EO-US) shows that the lowest degradation efficiency was recorded for US technique. The EO-US process showed synergistic effects, whereas the sum of the individually process (EO + US) reached lower degradation rate than the combined process under the same parameter operations.

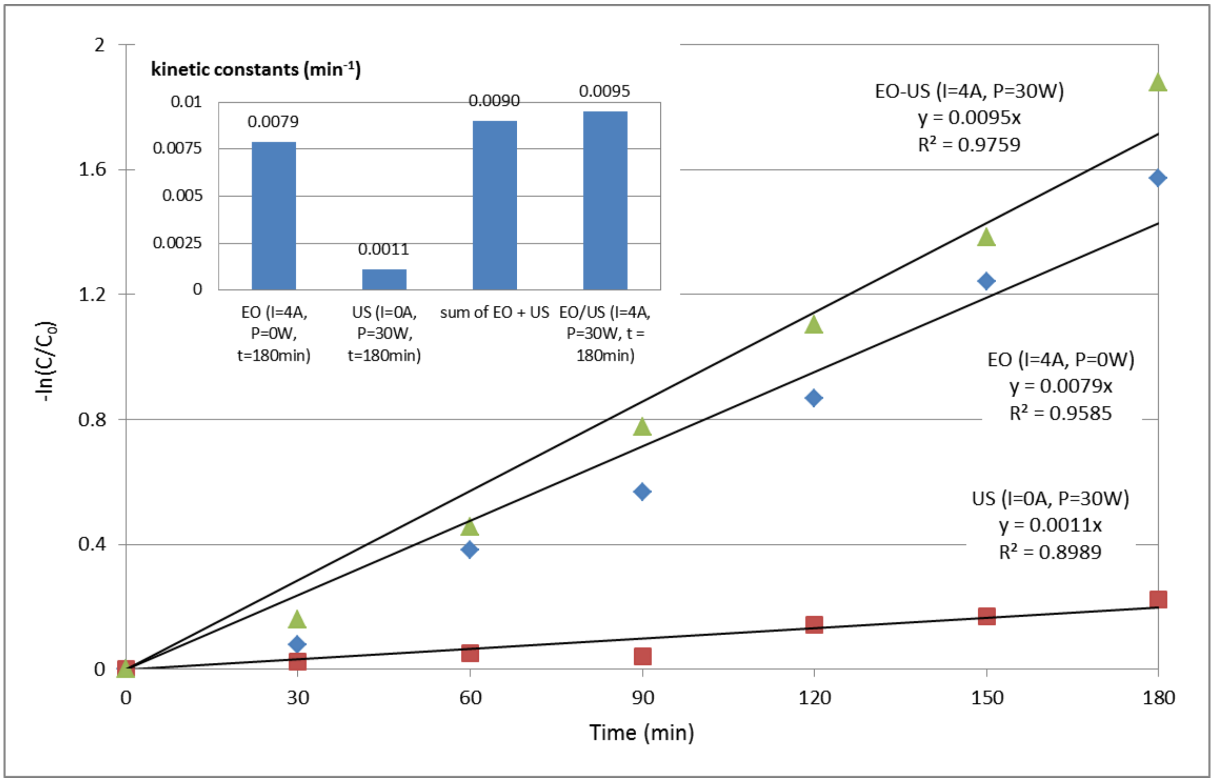

Fig. 6-2 The kinetic rate constant of IBU degradation by EO, US and combination of EO/US process, respectively.

The degree of synergy can be calculated as follows (Frontistis et al., 2012):

$$S = \frac{k_{EO-US} - (k_{EO} + k_{US})}{k_{EO-US}} x100 \qquad (1)$$

In the equation Eq. 1, $k_{EO\text{-}US}$ represents the reaction rate apparent constant recorded when the sono-electrooxidation (US-EO) process was used, whereas k_{EO} and k_{US} represent the rate apparent constants when ultrasonication (US) and electro-oxidation (EO) were respectively applied for the degradation of IBU. The degree of synergy calculated was 5.26 % indicating that the IBU removal was higher when both processes (EO and US) were simultaneously used compared to the treatment of IBU using the sum of EO and US processes (EO and US individually and successively applied). During EO process using non-active electrode (such as Ti/PbO$_2$), hydroxyl radical can be formed at the surface of electrode. Hydroxyl radical can participate to degradation of organic pollutants. Then, the use of US could contribute to increase the power of these oxidants by increasing the mass transfer between electrode and pollutants (Sires et al., 2014). The positive effects of cavitation bubbles (electrode activation, mass transfer, increase of current efficiencies) on the electrochemical degradation process were reported by several authors (Macounova et al., 1998; Braeutigam et al., 2012a; Ren et al., 2014). It can be observed that the synergistic effect determined in the present study were lower than those measured by Ren et al. (2013b) while treating an effluent containing phenol (1.0 mmol L^{-1}) by using a process combining sonication (US) and electrochemical (EC) methods. The electrolysis cell was comprised of stainless steel used as anode and cathode in a volume of 400 mL. A potential of 10 V and an electrical ultrasound power of 170 W was imposed for 1.0 h. The synergistic effects of US and EC allowed 75 % of phenol degradation, compared to 48% obtained while the sum of the US + EC processes was used. The degree of the synergistic effect calculated by Ren et al. (2013b) was around 60%. This value is 11.4 times higher than that measured in the present study. This discrepancy can be attributed to two major factors. Firstly, in the present study a power of 30 W was imposed in a working volume of 3.5L and in the presence of 10 mg L^{-1} of IBU, which corresponded to a specific power of 244 W per gram of IBU. By comparison, Ren et al. (2013b) imposed a power of 170 W in 400 mL of working volume and in the presence of 94.1 mg L^{-1} of phenol (4521 W per gram of phenol). The specific power imposed by Ren et al. (2013b) was 18 times higher than that imposed in the present study. Secondly, the IBU structure is more complex and more difficult to oxidise than phenol.

6.4.2 The current intensity effect

The current intensity effect on the sono-electrooxidation of IBU was evaluated by comparing the rates of IBU removal (by measuring the residual IBU concentration) at current intensities of 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 A (anodic current density of 3.6, 7.2, 10.7, 14.3, 17.9, 25 and 35.7 mA cm^{-2}). The electric power of ultrasound was fixed at 30 W. Fig. 6-3 shows time course changes in the normalized concentration of IBU.

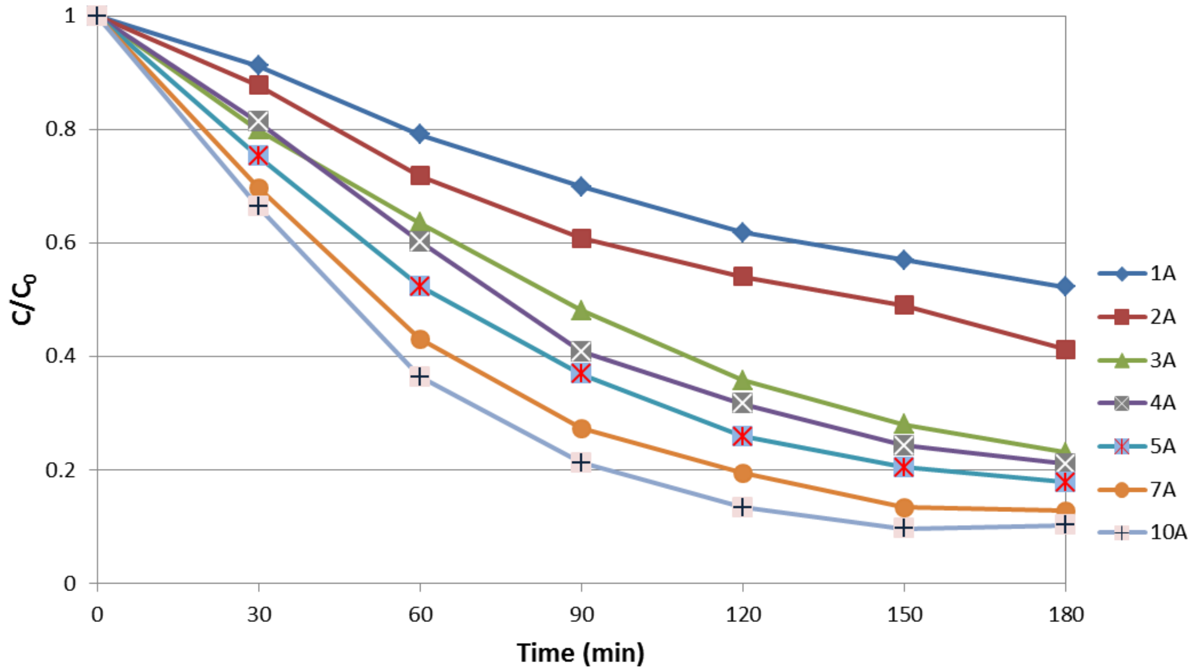

Fig. 6-3 Effect of the current applied versus IBU removal efficiency (I= 1-10A, P= 30W, t= 0-180min, temp. = 20°C)

The initial IBU concentration imposed during these tests was 10 mg L^{-1} and a temperature of 20°C was imposed. The degradation efficiency calculated at the end of the treatment varied from 47.80 % to 89.74 %. The residual IBU concentration decreased with the current intensity imposed. More than 89% of IBU was removed for a current intensity applied of 10A. As the current density increased, the depurative efficiency also increased. The removal of IBU can be due to the hydroxyl radicals reaction on the carboxylic group in solution and some intermediates can be generated (Vazquez-Gomez et al., 2012). However another way of the decomposition of the IBU occurs on such an anodic electrode due to the electrophilic attack of oxidizing species, including hydroxyl radicals, which are generated electrochemically. It is well known that those generated species react favorably with the double bonds (-C=C-) and attack the aromatic nucleus, which are the major component of IBU. Similar results have been recorded by Tran et al. (2009a) while studying electrochemical degradation of polycyclic aromatic hydrocarbons (PAHs) in creosote solution using ruthenium oxide on titanium expanded mesh anode. The PAHs removals efficiency varied from 59 to 69% with current intensities varying from 1.0A to 4.0A (anodic current density of 3.08 mA cm^{-2} to 12.3 $mAcm^{-2}$), respectively. During the sono-electrooxidation of IBU, the energy consumption (including electrolysis and sonolysis) linearly varied between 1.0A and 10A, from 1.43 to 85.7 $kWh.m^{-3}$.

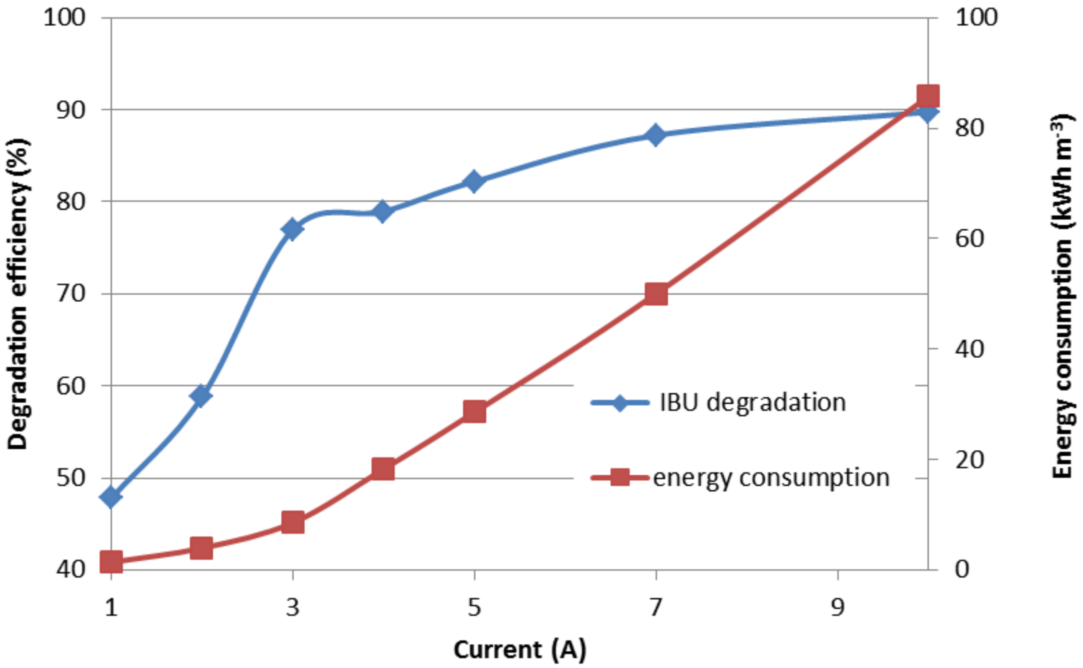

Fig 6-4. The comparison between the energy consumption and IBU degradation efficiency (I = 1-10A, P=30W, t = 180 min, temp.=20°C, C_{IBU}=10mg L^{-1})

The comparison between the energy consumption and the percentage of degradation showed that IBU could be optimally removed by selecting a current intensity around 5.0A (Fig. 6-4). Therefore, the current density of 5A was selected for the next step of the experiments.

6.4.3 The ultrasound power effect

The effect of the ultrasound power on the sono-electrooxidation of IBU was evaluated at various ultrasound powers ranging from 5W to 40W at a current intensity of 5.0 A (17.9 mA cm^{-2}) for a treatment time of 180 min and an initial IBU concentration of 10 mg L^{-1}. A temperature of 20°C was imposed. As shown in Fig. 6-5, the rate of IBU degradation increased (from 78.7% to 84.2) over this range (5W to 40W). As the ultrasound power increases, the number of cavitation activity increases.

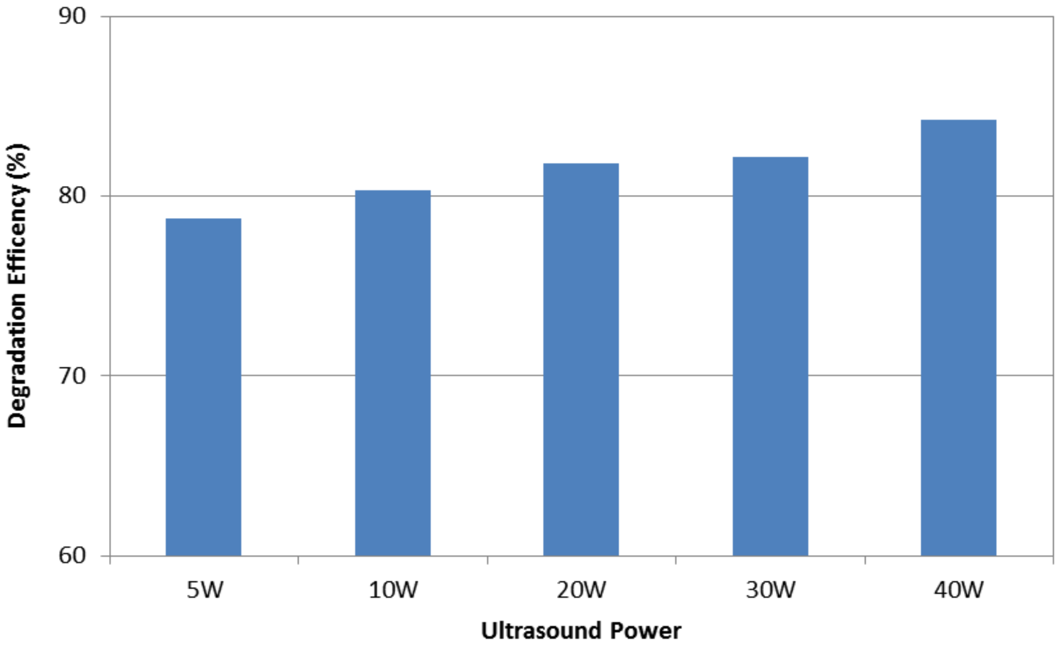

Fig. 6-5 Effect of ultrasonic power on the IBU degradation. (IBU=10 mg L^{-1}, I = 5A, time = 180min, temp. = 20°C).

The increase of cavitation activity improves the hydroxyl radical production and also the mass transfer of reactants into the electrodes consequently, enhances the pollutant degradation (Tran et al., 2013). According to the results obtained by Villaroel et al. (2014) while investigate the ultrasonic degradation of acetaminophen in water , the degradation rate rises four times with the increase in the acoustic power from 20 to 60W (acetaminophen concentration = 82.69 µmol L^{-1}, frequency = 600 kHz, pH =5.6, volume= 300 mL, temperature: 20 ± 1 °C). Madhavan et al. (2010) has been reported similar results while studying the oxidation of diclofenac pollutant using a sonochemical process. The degradation rate of diclofenac increased from 0.8 $x10^{-7}$ $Mmin^{-1}$ to 26.3 $x10^{-7}$ $Mmin^{-1}$ with an increase in the ultrasound power from 16 mW ml^{-1} to 55 mW ml^{-1}.

6.4.4 The temperature effect

It has been established that the treatment efficiency is greatly affected by the operating conditions such as the temperature (Braeutigam et al., 2012a; Villaroel et al., 2014). The effects of temperature on sonoelectrochemical oxidation of IBU are shown in Fig. 6-6.

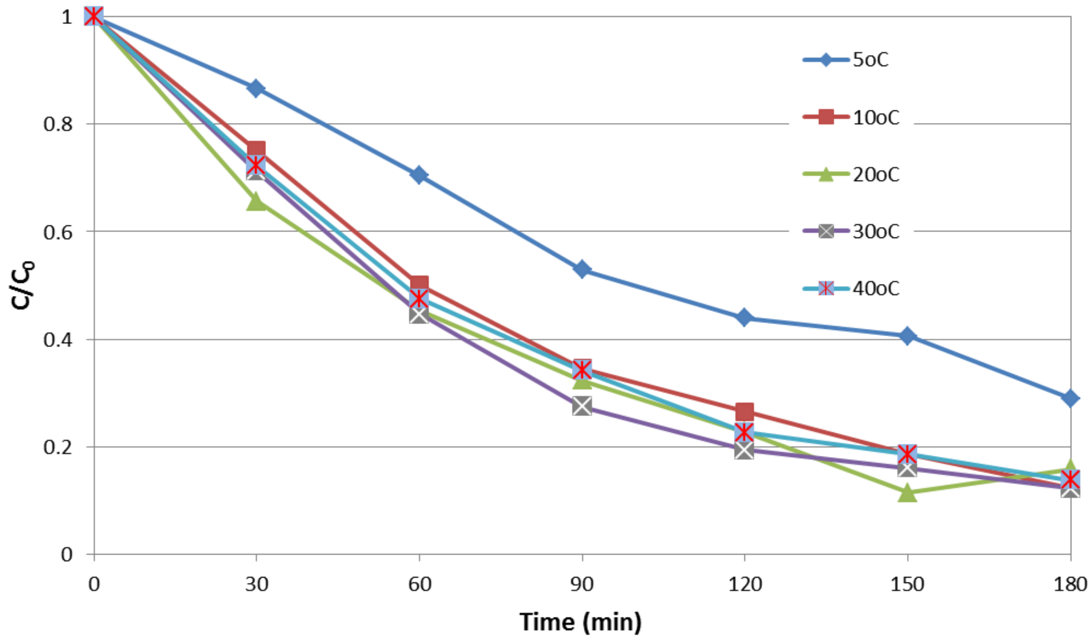

Fig. 6-6 Effect of temperature on the IBU degradation. (IBU=10 mg L^{-1}, I = 5A, t = 180min, P = 30W).

The temperature varied from 5.0^0C to 40^0C at the conditions the current intensity of 5.0A (17.9 mA cm^{-2}), 30 W of electric power of ultrasound and 10 mgL^{-1} of IBU concentration. With the exception of temperature of 5.0^0C, more than 80% degradation of IBU was reached for all temperatures imposed. Normally, with increasing temperature, the vapor pressure of water may increases leading to an easier generation of cavitation bubbles. Likewise, the solubility of IBU can be improved at higher temperatures, so that the degradation rate can be improved. However, there are no significant differences between the removal rates in the temperature range from 10 to 40^oC. By increasing the temperature (from 5.0^oC to 10^oC), the solubility of IBU in solution increase and the reaction rate constant improves. This was proven by the Van't Hoff-Arrhenius equation (Richards, 1925), where the rate constant k is linearly proportional to exp(-1/T).

$$Ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (2)$$

Where, k_1 (0.0039 min^{-1}) and k_2 (0.0048 min^{-1}) are the apparent constants rate for temperature T_1 (5^oC) and T_2 (10^oC), respectively; E_a is the energy activation; and where R is the universal gas constant. However, the apparent rate constant (k) did not significantly change when the temperature ranged between 10 °C and 40°C, probably due to the fact that the solubility was not greatly affected by this range of temperature (Garzon et al., 2004). So, in our experimental conditions, it is believed that from a certain level of temperature, the rate of IBU degradation did not change. The same trend has been observed by Ren et al. (2013b) while using a sonoelectrochemical process for phenol degradation in aqueous solution. At electric voltage of 10 V, ultrasound power of 170 W and reaction time of 60 min, the author concluded that only 2% of difference of degradation degree was recorded between the lowest (15 °C) and the highest (35°C) temperature imposed. On the other hand, low temperatures (for instance 5 °C) result in less efficient formation of cavitation bubbles, smaller hydroxyl radical concentrations and therefore decrease the rate of pollutant degradation.

6.4.5 Factorial design

The influence of different principal variables: current intensity (X_1), ultrasound power (X_2) and treatment time (X_3) on the IBU removal was investigated using factorial matrix (2^k, k being the number of factors; k = 3). The coefficients of the model were calculated using the half difference between the arithmetic average of the response values when the associated coded variable is at a level (+1) and the arithmetic average of the response values when the associated coded variable is at level (-1).

Table 6-1 Experimental range and levels of independent variables.

Coded variables (x_i)	**Factor (u_i)**	**Description**	**Experimental field**		**$U_{i,0}$**	**Δ_{Ui}**
			Min value (−1)	Max value (+1)		
X_1	U_1	Current (A)	2	5	3.5	3
X_2	U_2	Power (W)	20	40	30	10
X_3	U_3	Time (min)	60	120	90	30

Table 6-2 Experimental factorial matrix and degradation efficiency.

Assay	**Experiment design**			**Experiment plan**			**IBU Degradation efficiency (%)**
	X_1	*X_2*	*X_3*	*Current (A)*	*Power (W)*	*Time (min)*	
1	-1	-1	-1	2	20	60	29.51
2	+1	-1	-1	5	20	60	45.32

3	+1	+1	-1	5	40	60	54.05
4	-1	+1	-1	2	40	60	28.45
5	+1	-1	+1	5	20	120	71.51
6	-1	+1	+1	2	40	120	50.35
7	-1	-1	+1	2	20	120	45.84
8	+1	+1	+1	5	40	120	77.19

The experimental region investigated for IBU degradation and the code values are shown in Table 6-1. The experimental results are presented in Table 6-2. The experimental response associated to a 2^3 factorial design (three variables) is represented by a linear polynomial model with interaction, as follows:

$$Y = 50.28 + 11.74X_1 + 1.1X_2 + 10.95X_3 + 2.5X_1X_2 + 1.39X_1X_3 - 0.81X_2X_3 \quad (3)$$

The contribution (P_i) of each factor on the response can be calculated according to the following relation:

$$P_i = \left(\frac{b_i^2}{\sum b_i^2}\right) \; i \neq 0 \qquad (4)$$

where b_i represents the estimation of the principal effects on the factor i. With this design it was possible to calculate the principle effects of each factor and the interaction between them. Thus, the contribution of each factor can be seen in Fig 6.

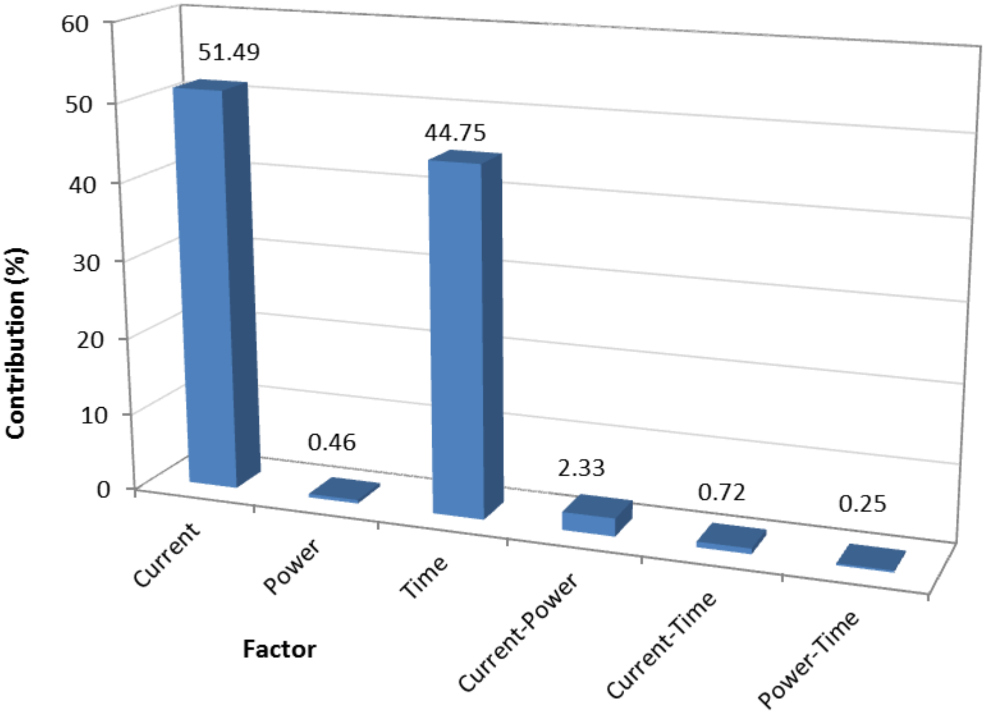

Fig. 6-7 Pareto graphic analysis of the effect of current, power, treatment time on IBU degradation.

It can be seen that the current intensity (X_1) and the treatment time (X_3) are the most determining factors on the degradation of IBU; their effect is 51.5% (for current intensity) and 44.7% (for treatment time) on the investigated response. However, the ultrasound power and the others interactions effects represent only 6% on the investigated response (IBU degradation rate). The current intensity is a major factor that influenced the rate of IBU oxidation, but it directly depended on the treatment time.

6.4.6 Central composite design

Central composite matrix was employed to optimize the sono-electrochemical process in IBU degradation. A two-level central composite experimental design, with six replicates at the center point leading to a total number of twenty experiments was used for response surface modeling (Table 6-3).

Table 6-3 Central composite matrix and experimental results

Assay	Experimental design			Experimental plan			Degradation (%)
	X_1	X_2	X_3	U_1	U_2	U_3	
9	+1.68	0	0	6.02 A	30 W	90 min	62.98
10	0	+1.68	0	3.5 A	46.82 W	90 min	60.39
11	0	0	+1.68	3.5 A	30 W	140 min	73.44
12	-1.68	0	0	0.98 A	30 W	90 min	35.89
13	0	-1.68	0	3.5 A	13.18 W	90 min	53.27
14	0	0	−1.68	3.5 A	30 W	40 min	23.34
15	0	0	0	3.5 A	30 W	90 min	55.03
16	0	0	0	3.5 A	30 W	90 min	55.05
17	0	0	0	3.5 A	30 W	90 min	58.43
18	0	0	0	3.5 A	30 W	90 min	58.15
19	0	0	0	3.5 A	30 W	90 min	51
20	0	0	0	3.5 A	30 W	90 min	54.77

The CCD matrix is comprised of three parts: factorial matrix (assays 1 to 8), a star matrix (assays 9 to 14) and a set of points at the center of the experimental region (assays 15 to 20). The response was described by a second-order model in the form of quadratic polynomial equation given below:

$$Y = b_0 + \sum_{i=1}^{k} b_i.X_i + \sum_{i=1}^{k} b_{ii}.X_i^2 + \sum_j \sum_{i=2}^{k} b_{ij}.X_i X_j + e_i \qquad (5)$$

where Y is the experimental response; X_i and X_j are the independent variables; b_0 is the average of the experimental response; b_i is the estimation of the principal effect of the factor j on the response Y; b_{ii} is the estimation of the second effect of the factor i on the response Y; b_{ij} is the estimation of the interaction effect between i and j on the response Y and e_i represents the error on the response Y. All coefficients are calculated using the least square method (Myers et al., 1995):

$$B = \left(X^T X\right)^{-1} X^T Y \qquad (6)$$

Where, B represents the vector of estimates of the coefficients; X is the model matrix, and Y is the vector of the experiment results. The variables (X_i) are coded according to the following equation:

$$X_i = \frac{U_i - U_{i,0}}{\Delta U_i} \qquad (7)$$

where $U_{i,0} = (U_{i,max} + U_{i,min})/2$, represents the value of U_i at the center of the experimental field; and $\Delta U_i = (U_{i,max} - U_{i,min})/2$, represents the step of the variation; and $U_{i,max}$ and $U_{i,min}$ are the maximum and minimum values of the effective variable U_i, respectively. The coefficients of the polynomial model (quadratic model) were calculated using the Design-Expert ® Program Software:

$$Y = 55.44 + 10.21X_1 + 1.52X_2 + 12.58X_3 + 2.0X_1X_2 + 1.39X_1X_3 - 0.81X_2X_3 - 2.33X_{12} + 0.28X_{22} - 2.7X_{32} \qquad (8)$$

The analysis of variance of the predicted response surface quadratic model show that F-value of 30.59 and a low probability value ($P_r > F = 0.0001$) indicate that the model is significant for IBU removal. The value of the correlation coefficient ($R^2 = 0.9649$) indicates that only 3.51% of the total variation could not be explained by the empirical model. The agreement between actual and predicted values of IBU removal is satisfactory and consistent with the statistical significance of the quadratic model. To rigorously determine the optimal conditions for IBU degradation in terms of cost and effectiveness, the energy consumption during the sono-electrochemical process has to be taken into account. The criteria selected for the optimization condition for IBU degradation are the following: *i*) treatment time and current intensity have to be minimized with a relatively high importance (3/5 weighting factor) in order to reduce the treatment cost (including the energy cost); *ii*) The power of ultrasound having a low impact must be minimized with the lowest importance (1/5 weighting factor); *iii*) the percentage of IBU degradation must be maximized with the highest importance (5/5 weighting factor). Based on these criteria, the Design Expert Program Software proposed several interesting solutions to obtain a high degradation of IBU. The optimal conditions for IBU degradation in terms of cost/effectiveness were established as follows: 110 min of treatment using a current intensity of 4.09 A and an ultrasound power applied of 20.00 W and the theoretical response proposed for IBU degradation was 65.22 %. To confirm the model adequacy and validity of the optimization procedure, additional experiments were performed under optimal operating conditions. The average value of the experimental response (experiments repeated in triplicate) was 66.9 ± 3.7 %. This degradation efficiency is found to be close to the value proposed by the model and was consistent with the correlation coefficient value ($R^2 = 0.9649$).

6.4.7 By product formation and proposed mechanism of IBU degradation

In order to follow the formation of byproducts and possibly identify chemical structures while treating synthetic solutions containing IBU, samples were collected at various time intervals. The sono-electrolysis cell was operated at a current intensity of 4.09A for 110 min of treatment and by imposing 20 W of electric power of ultrasounds (optimal conditions determined using the Design-Expert ®Program Software). The initial IBU concentration was fixed at 10 mg L^{-1} to be able to analyze the intermediates using LC-MS/MS. IBU and various reaction intermediates present in the sono-electrolyzed solution after 110 min is shown in Fig. 6-8.

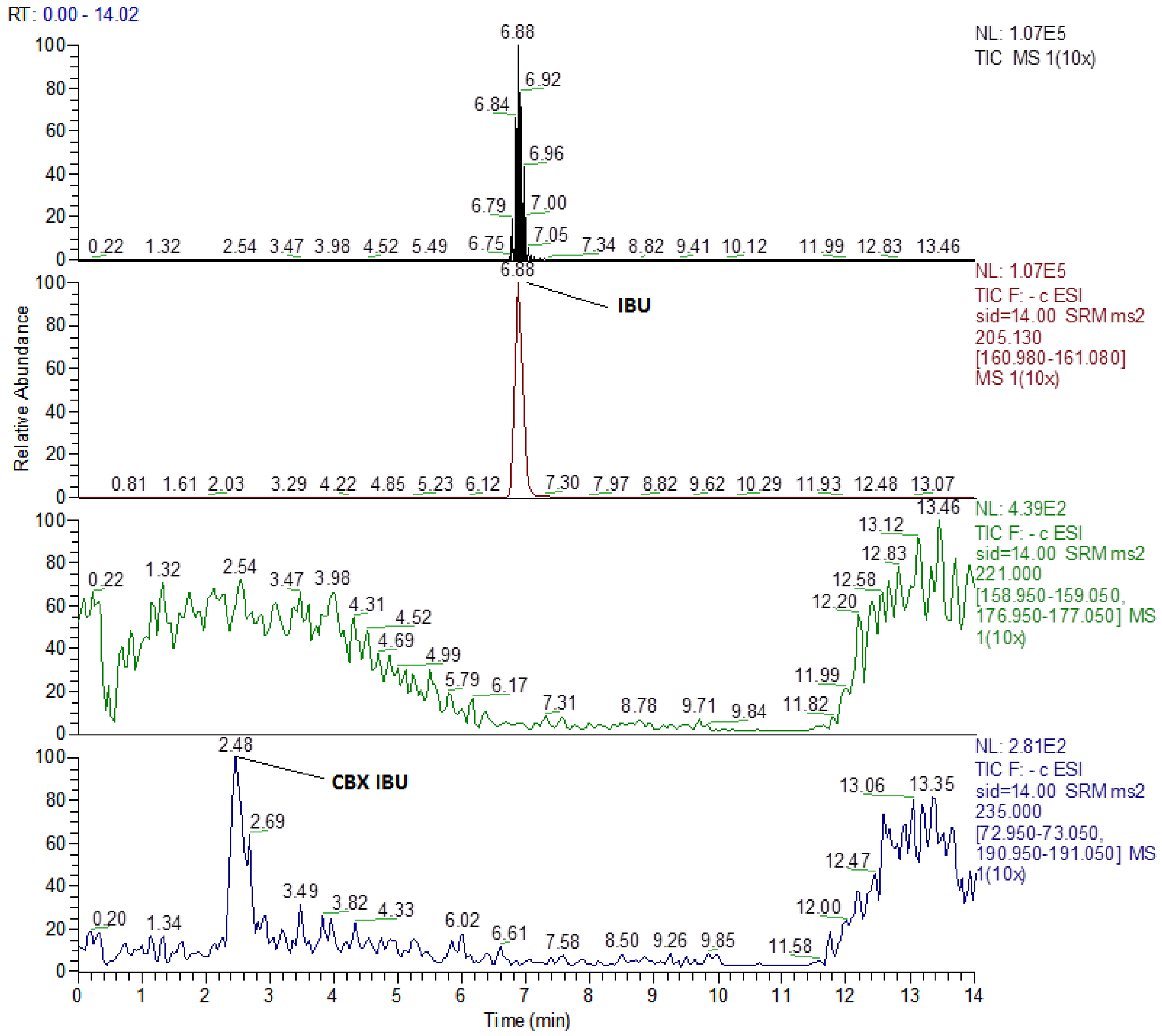

Fig. 6-8 LC/MS/MS chromatogram presented with individual MS spectra of possible by-products of IBU by EO-US process.

Among the peaks observed, a comparison was done in each case to identify the intermediates. Under the used instrumental conditions, tentative structural identification of all intermediates and its fragmentation pattern was compared against authentic standards whenever possible. Under this experimental condition with LC/MS/MS analysis, only one IBU by-products was identified on the basis of their mass spectra (Table S5, Supplementary data). However, other by-products could exist. Electro-sonolysis of IBU resulted in the degradation of IBU which was evidenced from the peak intensity corresponding to IBU parent (m/z 205, t_R = 6.88 min) (Fig S3, Supplementary data). The peaks that appear at t_R =2.48 min show the formation Ibuprofen carboxylic acid (m/z 235). This compound could be attacked by hydroxyl radicals and transformed into further intermediates with smaller m/z values. Mendez-Arriaga et al. (2008a) studied the photocatalytic degradation of IBU in presence of TiO_2 and reported the formation of 1-hydroxy ibuprofen or 2-hydroxy ibuprofen products (not detectable in this experiment) and argued that the hydroxylation process can be the first step of the degradation, followed by a second step of demethylation or decarboxylation. This pathway can lead to the formation of hydroquinone and benzoquinone (not detectable in this experiment), which can be furthermore oxidized to form small molecules of carboxylic acids (Bielicka-Daszkiewicz et al., 2012). In addition to IBU measurements, the total organic carbon (TOC) was also measured during the treatment. An average TOC concentration of 13.9 ± 0.2 mg L^{-1} was measured in untreated water. By comparison, the application of EO-US treatment reduced the TOC to an average value of 2.3 ± 0.5 mg L^{-1}. A removal rate of 84% of TOC was recorded. The relatively high removal rate of TOC indicated that the majority fraction of organic compounds (IBU) was oxidized into water and carbon dioxide, with the minority of the pollutants being transformed into small molecules that would difficult to detect in the treated solution. In fact, the electrolytic cell broke the double bonds producing smaller molecules. It is worth noting that, during electrolysis, organic pollutants can be subjected to two different paths in anodic oxidation: electrochemical conversion or electrochemical combustion (Martinez-Huitle et al., 2006b). Electrochemical conversion only transforms the non-biodegradable organic pollutants into biodegradable compounds, whereas electrochemical combustion yields water and carbon dioxide and no further treatment is then required. Based on the identified intermediates and literatures (Mendez-Arriaga et al., 2008a; Bielicka-Daszkiewicz et al., 2012), a proposed mechanism of IBU degradation during sono-electrochemical treatment is presented in Fig. 6-9.

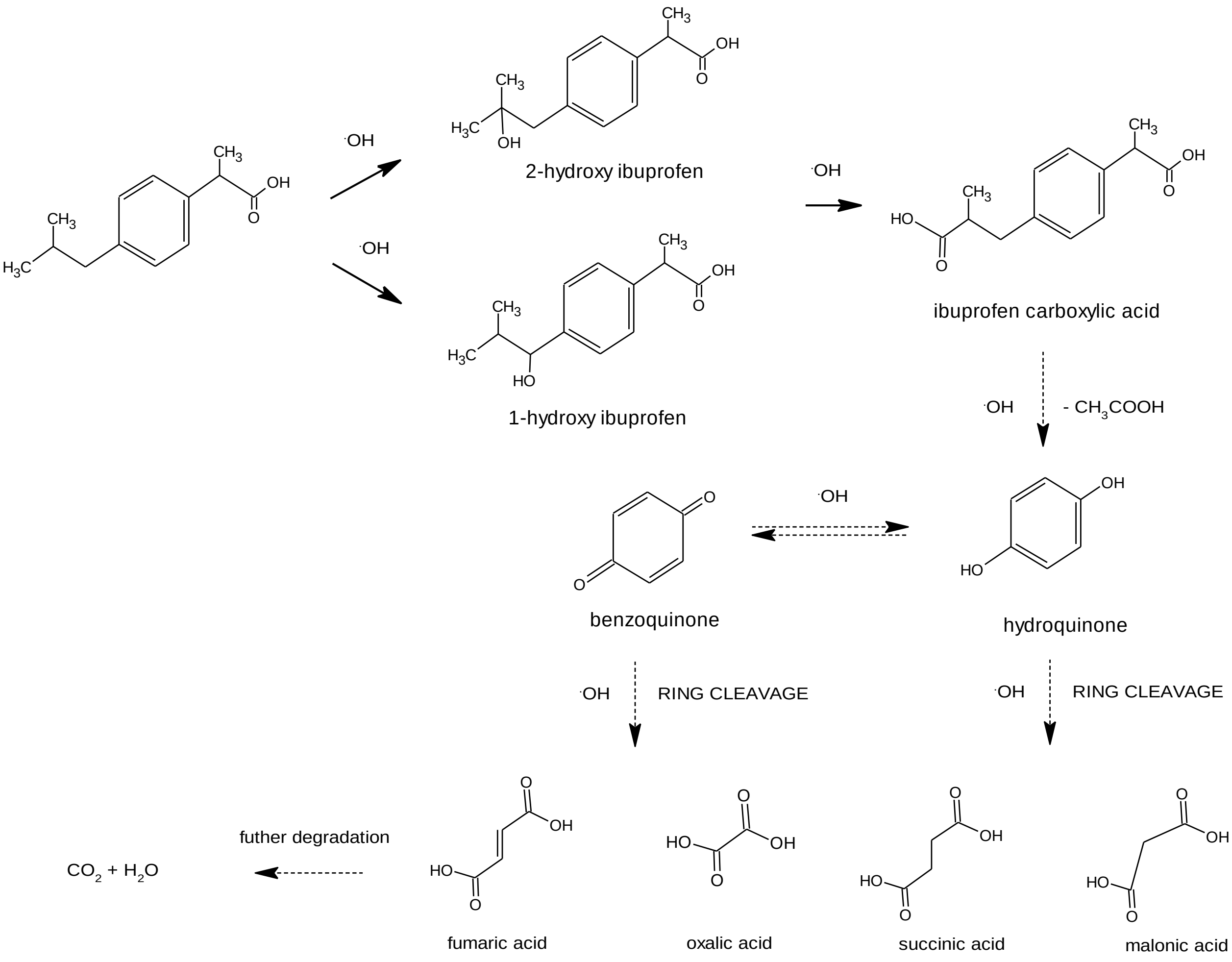

Fig. 6-9 The proposed reaction pathway for the EO-US degradation of IBU.

6.4.8 Application to wastewater treatment contaminated by IBU

The effectiveness of the sono-electrolytic cell in treating wastewater effluent contaminated by IBU was evaluated at a current intensity of 4.09A and a retention time of 110 min in the presence an ultrasound power of 20W (optimal conditions determined above using the Design-Expert® Program Software). The objective was to test the effectiveness of the sono-electrochemical process as tertiary treatment to remove IBU in the presence of other types of organic, inorganic and microbial pollutants. It was important to determine whether the results of these tests are reproducible or not. To that end, the experiments were repeated in triplicate to verify the effectiveness and reproducibility of the EO-US process performance in treating municipal wastewater effluent (MWE) contaminated by IBU (Table 4). The chromatographic analysis of this MWE showed that this effluent did not initially contained IBU. Before treatment, the MWE was artificially contaminated by IBU (initial IBU concentration of 20 µg L^{-1}, 100 µg L^{-1} and 10 mg L^{-1}, respectively). The experimental results determined using liquid chromatography mass spectrometer (LC/MS/MS) shows that the removal of IBU varied from 83.7± 3.11% to 90.0± 2.67%, compared to the predicted value (65.22% of IBU removal) proposed by the model in the optimal conditions. This discrepancy can be attributed to the two main factors. Firstly, it is worth noting that, during the optimization procedure carried out in SE, UV-visible absorption analytical method was used to evaluate the performance of the process. UV-visible absorption is an indirect analytical method. According to Beer-Lambert law, the measure of the concentration of species can be determined from the measured absorbance. The presence of interfering substance can influence the absorption spectrum and consequently can modify the results. By comparison, LC/MS/MS technique which combines simultaneously a powerful physical separation technique and a powerful technique of analysis and mass detection has a very high sensitivity and selectivity towards several pharmaceutical compounds (Hernandez et al., 2007).

Table 6-4 Application EO-US process for the removal of IBU in municipal wastewater.

	Control (raw wastewater)	**High concentration**		**Medium concentration**		**Low concentration**	
		Initial	*Final*	*Initial*	*Final*	*Initial*	*Final*
IBU (*µg L^{-1}*)	< 1	10950 ± 150	1410 ± 60	112.3 ± 8.89	18.67 ± 4.22	27.33 ± 2.22	2.73 ± 0.56
Removal rate IBU (%)		87.5 ± 0.5		83.67 ± 3.11		90.0 ± 2.67	
TOC (*mg L^{-1}*)	9.5	14 ± 2	11.3 ± 2	10.9 ± 1.4	8.5 ± 1.2	9.7 ± 1	7.5 ± 1
Removal rate TOC (%)		13.1 ± 2		22.0 ± 1.2		22.7 ± 1	

Secondly, this discrepancy may be attributed to the initial characteristic of MWE. Indeed, this type of municipal effluent can contain chloride ions, which facilitated the passage of electrical current intensity (Zaviska et al., 2012). Besides, these ions can favour hypochlorous acid (HClO) production and can improve IBU oxidation. Thus, under these experimental conditions using MWE, IBU can be oxidized by means of $^{\cdot}$OH and indirect electrochemical oxidation via mediators, such as hypochlorous acid generated by chloride oxidation. Both actions (*OH and indirect oxidation with HClO) lead to the formation of powerful oxidizing agents capable of rapidly oxidizing the IBU. The combination of both effects accelerates IBU degradation. Similar results have been recorded by Zaviska et al. (2012) while treating municipal wastewater contaminated by bisphenol-A (BPA) by combining direct and indirect electro-oxidation. The municipal effluent initially contained 465 ± 20 mg L^{-1} of chloride ion. Electrolysis was conducted using a cylindrical electrolytic cell containing two circular anodes (Ti/PbO_2) and two circular cathode electrodes (stainless steel). A period of 30 min of electrolysis was sufficient to reach complete BPA degradation in municipal effluent, compared to 100 min required for synthetic effluent prepared with distilled water in which Na_2SO_4 was added at a concentration varied from 150 to 250 mg L^{-1}. The initial TOC concentration of MWE contaminated by IBU varied from 9.7 ± 1 mg L^{-1} to 14 ± 2 mg L^{-1}. The residual TOC concentrations recorded at the end of the treatment ranged between 7.5 ± 1 mgL^{-1} and 11.3 ± 2 mg L^{-1}. The reductions in TOC varied from 13.1 ± 2% to 22.7 ± 1%. The relatively low yield of TOC removal (13 to 22%) indicated that only a small fraction of organic compounds (comprised of IBU and other refractory organic matter) was completely oxidised into water and carbon dioxide, with the majority of the pollutants being transformed into small molecules that would reduce the oxygen demand in the treated MWE. The removal rate of TOC in MWE is lower when compared with previous result (TOC removal of 84%) in synthetic effluent (SE) prepared with de-ionized water contaminated by IBU (10 mg L^{-1}). The untreated SE is consisted only IBU and electrolyte in the effluent without any other organic compounds; where in the MWE, the TOC were not only due to the presence of IBU, but it could be also attributed to the presence of natural organic matter or refractory organic matter in waters. Indeed, the relatively high present of other contaminants in MWE could be in competition with TOC removal in the real effluent.

Under these conditions, the energy consumption recorded was 56.57 kWh m^{-3}. The total treatment cost (including only energy consumption for sonolysis and electrolysis) was estimated to 3.39 \$ m^{-3}. This energy consumed was estimated at a cost of US\$ 0.06 per kWh, which corresponded to the cost in the province of Québec (Canada).

6.5 Conclusions

This study investigated the treatment of water contaminated by IBU in a batch recirculation mode using a sono-electrochemical reactor. The first part of these works was performed in synthetic media in order to demonstrate the concept of coupling ultrasonication and electrooxidation (EO-US) treatment for IBU removal. The degree of synergy calculated was 5.26 % indicating that the IBU removal was higher when both processes (EO and US) were simultaneously used compared to the treatment of IBU using the sum of EO and US processes (EO and US individually and successively applied). The factorial design demonstrated that the current intensity and treatment time are the most influent parameters for the sono-electrochemical oxidation of IBU. These two main factors contributed to 96.24 % on the investigated response, whereas the effect of ultrasound power represents only 0.46 %. A central composite design has been subsequently applied to define the optimal operating conditions for IBU degradation. The sono-electrochemical reactor operated at 110 min of treatment using a current intensity of 4.09 A and an ultrasound power applied of 20.00 W was found to be the optimal conditions in terms of energy consumption/effectiveness. The relatively high of TOC removal (84 %) confirmed that only a small fraction of organic compounds being transformed into small molecules, the majority of the pollutants was completely oxidized into water and carbon dioxide. These optimal conditions were then applied for the treatment of real MWE contaminated by IBU at various range. The removal efficiencies of IBU at 20 μg L^{-1}, 100 μg L^{-1} and 10 mg L^{-1} recorded were 87.5 %, 83.67 % and 90.0 %, respectively. The total treatment cost was estimated to 3.39 \$ m^{-3} which show promising technology that can be used as tertiary treatment to remove emerging pollutants from MWE.

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CHAPITRE 7 Hybrid process, electrooxidation-ultrasonication, for antibiotic chlortetracycline treatment

Ce chapitre est constitué de l'article suivant:
Tran, N., Drogui, P., Nguyen, L., and Brar, S. (2016). Electrooxidation–ultrasonication hybrid process for antibiotic chlortetracycline treatment. Journal of Environemental Engineering, 10.1061/(ASCE)EE.1943-7870.0001088 , 04016011.

7.1 Abstract

This study investigated the electrochemical oxidation of chlortetracycline in aqueous solution using a Ti/PbO$_2$ anode under ultrasound irradiations. The influence of various parameters such as electric current applied, power of ultrasound, and treatment time were evaluated and optimization process was investigated by using factorial design and central composite design methodology. The results indicated that the chlortetracycline degradation rate was greatly influenced by the current and the treatment time. A current intensity of 3.92 A under ultrasound irradiation of 20 W (at 500 kHz) for a period of treatment of 95 min were found to be the best conditions for chlortetracycline oxidation in term of cost-effectiveness. The initial concentration (10 mg/L) could be optimally diminished up to 73.3% while using a Ti/PbO$_2$ anode. Under these conditions, a relatively high mineralization of chlortetracycline (61.4% of total organic carbon removal) was recorded. Then, the optimal conditions were applied on a municipal wastewater effluent (sampled after secondary treatment) and artificially contaminated with 10 μg/L, 100 μg/L, and 10 mg/L, respectively. The treatment was more effective with the municipal effluent (chlortetracycline could be oxidized up to 98%) because of the presence of chloride ions that could easily be transformed into active chlorine. Chlortetracycline could be oxidized by both direct anodic electrochemical oxidation (by means of hydroxyl radicals) and indirect electrochemical oxidation via mediators, such as hypochlorous acid generated by chloride oxidation.

7.2 Introduction

Due to the global consumption of antibiotics in recent years, the discharge of antibiotics into the environment is one of the major and global public-health issues that need urgent action (Van Boeckel et al. 2014; Zaviska et al. 2013). Indirect measurements suggest that 40 - 90% of administered antibiotics are eliminated from animal body via feces or urine excreted either as the parent compound (Ray et al. 2014), with only small fractions being metabolized (Kemper 2008). Chlortetracycline (CTC), a member of tetracycline family, is the second most widely used antimicrobial in both production and usage, worldwide, with applications in human therapy and in the livestock industry (Bansal 2012; Kolpin et al. 2002). CTC may lead to the development of antibiotic resistance and other potential adverse effects are unknown (Davis et al. 2006; Mcgowan 1983). CTC can be used to prevent, control, and treat animal health problems as well as enhance growth rates of animals (Bansal 2012; Davis et al. 2006; Van Boeckel et al. 2014). Residues of veterinary pharmaceuticals, including CTC discharged from municipal wastewater treatment plants and agricultural runoff, are frequently detected in surface water, ground water, and even drinking water (Arikan 2008; Bansal 2012; Kolpin et al. 2002). CTC is not often detected in water sources, however they have been found, among other pharmaceutical residues, in sewage waters and effluents and also in surface waters. A study of Kolpin et al. (2002) has been detected CTC at a concentration of 0.69 μg/L in samples from streams in the U.S. using a LC/MS-ESI method. Several researchers have been reported that drugs are reaching the aquatic system, although in very low concentrations, and they may present a potential hazard for human health, especially where no advanced wastewater treatments are used (Karthikeyan and Meyer 2006; Kolpin et al. 2002; Van Boeckel et al. 2014). The removal of CTC from water is a difficult task due to their low concentration and refractory properties (Karthikeyan and Meyer 2006; Zaviska et al. 2013). Conventional methods frequently used in water treatment, such as biological and physicochemical treatments have been reported to be sometimes ineffective to remove emerging organic pollutants such as CTC. Therefore, a need exists for efficient treatment technology for the removal of this pollutant from the aquatic environment. Advanced oxidation processes (AOPs) have proven to be the methods of choice for the removal of emerging organic pollutants from wastewater. Recent studied show that organic compounds in group of tetracycline can be degraded through some other AOPs treatment such as electrochemical oxidation. Tetracyclines belong to a group of natural and semisynthetic products characterized by four rings structure with a carboxylamide functional group (Brinzila et al. 2013). A complete mineralization up to 100% can be recorded using boron doped diamond electrode inside an up-flow reactor operating in batch mode (Brinzila et al. 2013). Another recent study of Zaviska et al. (2013) has been demonstrated that electrooxidation can be applied to oxidize 96% of CTC. The performance of the electrolytic cell resulted from its capability of reacting on pollutants by using both effects of electrolysis where hydroxyl radicals are generated (direct effect), and they can be simultaneously oxidized in solution by means of active chlorine (indirect effect). In spite of the good oxidation of organic compounds, many of electrochemical techniques are frequently inefficient long term cause of by-products have been found during electro-oxidation (Compton et al. 1997; Klima et al. 1995). Since 1990, the ultrasound process has received considerable interest for the destruction of organic pollutants that are present in wastewater (Gogate 2007; Henglein and Gutierrez 1990; Leite et al. 1999). The ultrasonication process has been identified as a successful alternative for the destruction and mineralization of some recalcitrant organic compounds in water and does not require the addition of chemicals (Gogate 2007; Gogate et al. 2003). Acoustic cavitation, derived from the high calorimetric power of a liquid, can provide unusual and unique reaction sites as a result of the extremely transient and small cavitation bubbles that are created with high temperatures and high pressures (Birkin and SilvaMartinez 1997; Compton et al. 1997). The beneficial results from exposing electrochemical cells to the effects of power ultrasound include the enhancement of mass transport, the increase of current efficiencies, and the continuous activation of the electrode surface (Birkin and SilvaMartinez 1997; Klima et al. 1995). These effects can be ascribed to the rapid generation and collapse of micro bubbles within the electrolyte medium or nearby the electrode surface. This cleaning effect has been reported to improve electron exchanges by peeling out passivation films on surface electrode or piercing them by micro holes (Compton et al. 1997; Klima et al. 1995; Macounova et al. 1998).

In the present study, we plan to combine ultrasonication (US) with electrooxidation (EO) to remove CTC from water. The specific objectives of this study are the followings: a) evaluate the interest of coupling ultrasonication and electrooxidation processes for CTC removal from water; b) investigate the influence of the principal experimental parameters (electrical current, ultrasound power, treatment time) on the efficiency of the process for CTC degradation; c) use a statistical methodology for a rational analysis of the combination of operational factors that lead to the best treatment and; d) verify the quality of treated effluent (versus untreated effluent) while treating real municipal wastewater contaminated by CTC.

7.3 Materials and methods

7.3.1 **Preparation of the synthetic effluent (SE)**

The water samples used in the first step study were prepared synthetically by dissolving CTC in de-ionized water. The synthetic effluent (SE) of CTC (HPLC grade reagent, purity > 80 %, obtained from Fisher Scientific, Canada) was prepared in a 4.0 L glass tank containing 3.5 L of de-ionized water in which 3.5 mg of CTC was added. Mixing was achieved by a magnetic stirrer (500 rpm) at room temperature (25°C) during at least 30 min. The resulting mixtures constituted the CTC solutions of 10 mg/L in which a sodium salt (Na2SO4 0.01 mol/L) was added to increase electrical conductivity. In view of testing the sono-electrochemical process on real effluent containing refractory organic pollutants and to simulate CTC contamination, wastewater samples were enriched with CTC (10 µg/L, 100 µg/L and 10 mg/L, respectively) without addition of supporting electrolyte.

7.3.2 Wastewater CTC-spiking

The real effluents were sampled at Levis Urban Community wastewater treatment plant (WTP, Levis, Canada). This is a conventional WTP with a physicochemical pre-treatment and a sequential biological treatment system followed by a disinfection process using ultraviolet light. The sample had an initial content of COD = 30 ± 12 mg/L, DBO_5 = 4.4 ± 0.4 mg/L, TOC = 7.5 ± 2.2 mg/L, TSS = 6.7 ± 4.9 mg/L, N_{NH4} = 3.7 ± 3.1 mg/L, P_{tot} = 0.3± 0.1 mg/L, pH = 6.6 ± 0.2 and conductivity = 450 ± 30 µS/cm. Samples were collected at the outlet of treatment plant (before wastewater disinfection) and stored in polypropylene bottles and kept at 4°C until use.

7.3.3 Experimental reactor setup

The assays were carried out in a closed loop with the sono-electrochemical reactor (Figure 7-1) was made of Plexiglas material (characterized by a double layer cylinder).

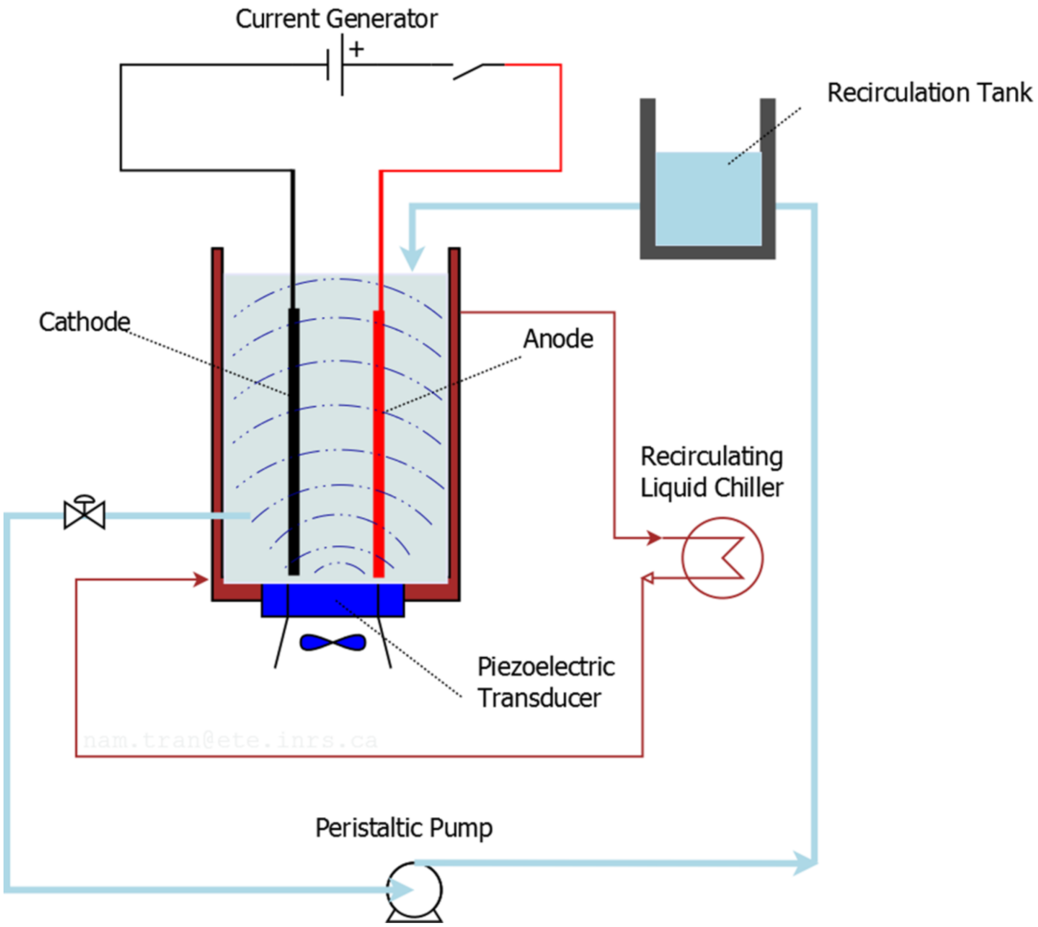

Fig. 7-1 Schematic view of sonoelectrooxidation reactor with recirculation loop.

An internal dimension of 20 cm (height) x 14.5 cm (diameter) and both electrodes (anode and cathode) were used in the form of expanded metal. The cylindrical cathode electrode (16 cm height × 12 cm diameter x 0.2 cm thick) was made of titanium (Ti) having a solid surface area of 420 cm2 and a void area of 180 cm2. The cylindrical anode electrode (16 cm height x 8.0 cm diameter x 0.2 cm thick) was titanium coated with lead oxide (Ti/PbO2) having a solid surface area of 280 cm2 and a void area of 120 cm2. The inter-electrode gap was 2.0 cm in the electrolytic cell. The anode was placed at the center of the cell and the cathode was fixed at the periphery. The electrodes had been mechanically attached and arranged to ensure the proper water distribution in the electrolytic cell. The electrical current was applied using a digital DC power supply XFR 40–70 (Xantrex Technology, Burnaby, British Columbia, Canada) with a maximum current rating of 70 A at an open circuit potential of 40 V. Ultrasonic waves were introduced from the bottom of the reactor via a ceramic transducer (a piezoelectric disk having a diameter of 4 cm). The frequency (520 kHz) and electrical power (from 10 to 40W) of the piezoelectric disk were controlled by an external waveform generator (Agilent 33210A, Agilent Technologies Canada Inc.) equipped with a low frequency amplifier (AG 1016, T&C Power Conversion Inc.). The reactor temperature was held constant at 20oC using a Polystat cooling/heating recirculator (Cole-Parmer Canada Inc.). Mixing in the reactor was achieved by recirculating water through the cell by means of a peristaltic pump operated at a constant speed of 100 mL/min. The recirculation tank (1.0 L of capacity) was made of the same material as the electrolytic cell. In all tests, a total volume of 3.0 L of contaminated water was used. The working volume of the electrolytic cell was 2.5 L, whereas 0.5 L was required for the recirculation tank.

7.3.4 Experimental procedure

Preliminary experiments

The first set of experiments was conducted to compare the removal efficiencies of CTC using US alone, EO alone and the combination of EO-US processes. During these tests, only the residual CTC concentration was measured. An electric power of 30 W of ultrasound at a frequency of 520 kHz was imposed. The treatment time was 180 min and the current intensity was fixed at 4.0A (anodic current density of 14.29 mA/cm2).

Coupling ultrasonication with electrochemical oxidation for the treatment of CTC

Electrochemical oxidation combined with ultrasonication was used to remove CTC from water. The current densities varied from 3.6 to 35.7 mA cm^{-2} (current intensity from 1.0 to 10.0 A). The treatment times ranging between 30 and 180 min were tested. Different electric powers of ultrasound were studied, including 5 W, 10 W, 20 W, 30 W and 40 W.

7.3.5 Analytical details

CTC measurements

The concentration of CTC in the solution in solution was firstly monitored by absorbance measurements by using a spectrophotometer Carry UV 50 (Varian Canada Inc.). The UV-VIS absorption spectrum of CTC solution is shown in Fig. 7-2.

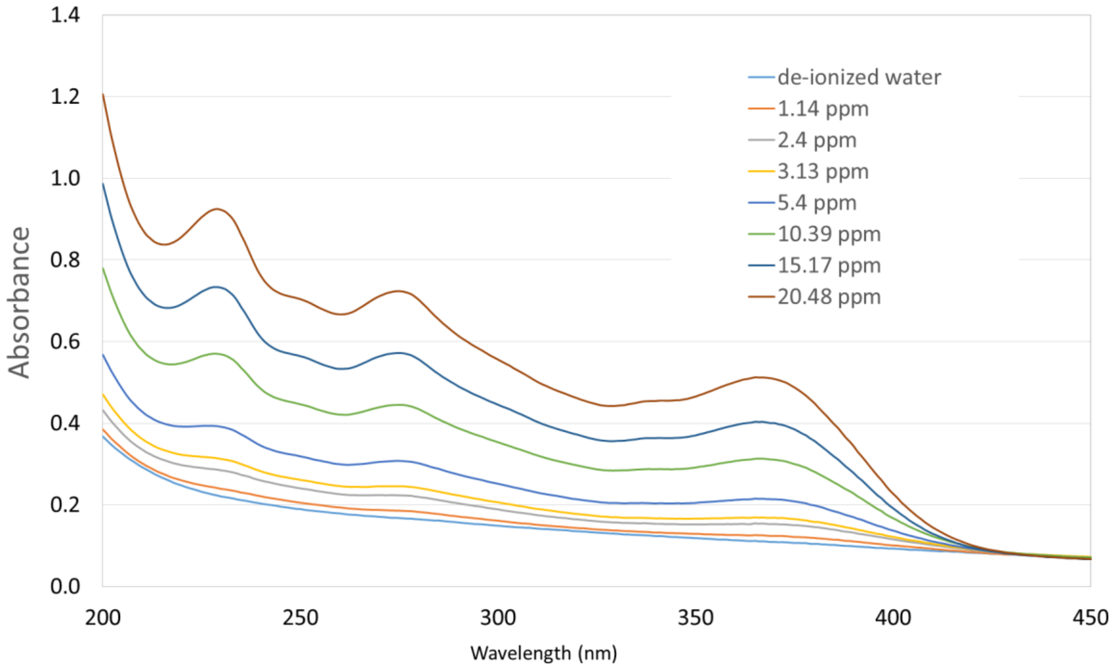

Fig. 7-2 UV-visible absorption spectrum of CTC in water (C_{CTC}=0-21 mg L^{-1})

This spectrum is characterized by three main peaks located in the ultraviolet region at 229, 276, and 370 nm, respectively. The *integrated absorption* (basis on total peak area rather than peak height) of CTC measured in the range of 210 nm to 420 nm was chosen to evaluate the residual CTC concentrations because at this range there was less interference and the peak area remains proportional to the total quantity of CTC and its residual substance passing into the detector. A calibration curve of known CTC concentration from 0.0 to 21.0 mg/L versus integrated absorbance value was used to calculate the residual CTC concentration and to define the efficiency (Fig. 7-3).

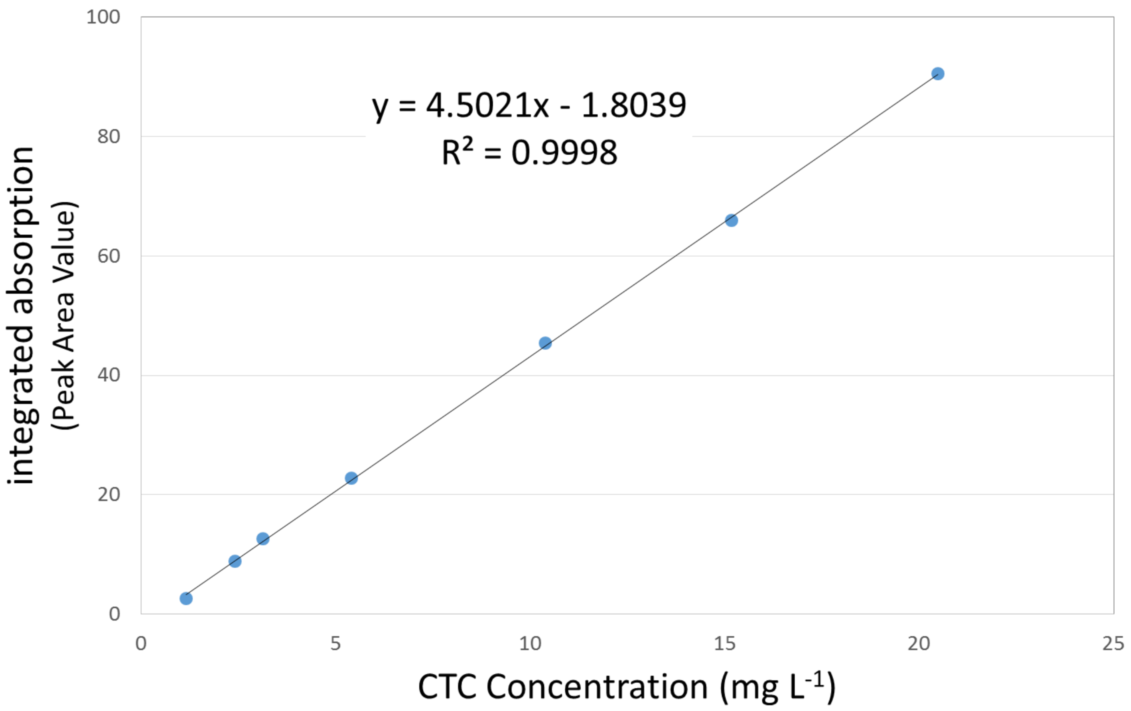

Fig. 7-3 Calibration curve of known CTC concentration (0-21 mgL^{-1}) versus absorbance integrated (total peak area value in range of 210-420 nm).

However, when the optimal conditions were determined and repeated in triplicate to verify the effectiveness and the reproducibility of the EO-US process, the residual concentration of CTC and by-products were analyzed by liquid chromatography/mass spectrometry (LC-MS/MS) rather than UV-VIS spectroscopic analysis. The chromatographic column used was a BetaBasic 18 (Thermo Scientific, USA) with 2.1 mm internal diameter, 10 cm length, and 3 µm particle size. Two mobile phases (A and B) were used during analysis: 0.1% formic acid in water (Phase A) and 0.1% formic acid in acetonitrile (Phase B). The injection of the two mobile phases was gradient programmed as follows: 90% (Phase A) and 10% (Phase B) for 2 min, 30% (Phase A) and 70% Phase (B) for 10 min, 90% (Phase A) and 10% (Phase B) for 5 min. The injection flow rate was 0.2 ml/min. The formation of reaction intermediates was monitored by using TSQ Quantum Access mass spectrometry (Thermo Scientific, USA) equipped with an electrospray ionization source operated in the positive ion mode. Analysis was performed in Selected Reaction Monitoring (SRM) mode. Nitrogen was used as a sheath and auxiliary gas. Working conditions were as followed: spray voltage was 5000 V and capillary temperature was 345^{o}C.

Calibration solutions were prepared by serial dilution of the intermediate (1 ppm) solutions in water at concentrations of 2µg/L - 100 µg/L with sulfamethazine C_{13} was used as internal standard. The limit of detection was 1.0 µg/L.

Other parameter measurements

The pH and conductivity were measured using a pH/conductivity meter (Oakton model 510) equipped with a pH and conductivity probe. Total organic carbon (TOC) was measured using a Shimadzu TOC 5000A analyzer (Shimadzu Scientific Instruments, Kyoto, Japan). Experimental data were obtained from the average of at least of three treatment replicates. Uncertainties were removed and calculated with a significance level of $p \leq 0.05$. The analysis of variance (ANOVA) and other statistical results were calculated and generated using the Design Expert Software version 7.1 (Stat-Ease Inc., USA).

7.4 Results and discussion

7.4.1 Preliminary investigation of CTC degradation

Comparison between US, EO and US-EO processes for CTC removal

Experiments using US, EO and US-EO processes were conducted to compare the CTC degradation efficiency. The treatment time was 180 min. The US process consisted in treating the effluent using only ultrasonication at a power of 30 W. The EO process was applied to treat the effluent using Ti/PbO2 anode and Ti cathode electrodes operated at a current intensity of 4.0 A without ultrasounds. In the US-EO process, a current intensity of 4.0 A and ultrasounds (P=30W) were simultaneously imposed. Figure 7-4 shows time course changes in the normalized concentration of CTC for different types of processes (US, EO and US-EO).

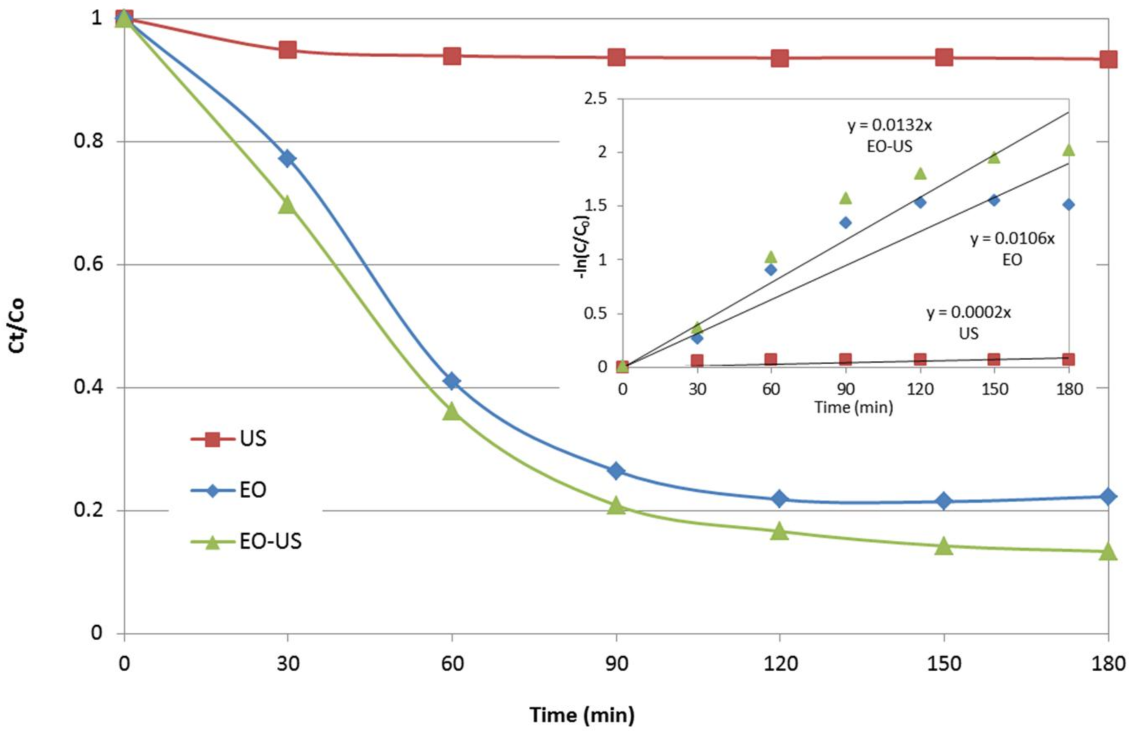

Fig. 7-4 Comparison between ultrasound (US), electrochemical oxidation (EO) and sono-electrochemical (EO-US) on the CTC degradation (I= 4A, t = 0-180 min, P = 40W).

As a single process after 180 min of treatment, 6.6% degradation of CTC was recorded during the application of US process, whereas 77.7% of CTC was removed using the EO process. By comparison, 86.7% of CTC was removed using the combined process (US-EO). The experimental data are well fitted to first-order kinetics (with correlation coefficients ranging from 0.823 to 0.904) predicting a linear variation with elapsed time (t) of the –Ln (C/C_0) according to Eq. 1:

$$-Ln\left(\frac{C}{C_0}\right) = k.t \qquad (1)$$

where C is the concentration of CTC at time t, k is the pseudo-first-order degradation rate constant. The reaction rate apparent constants were the followings: US (0.0002 min^{-1}), EO (0.0106 min^{-1}) and EO-US (0.0132 min^{-1}). The greater value of k indicated that the use of ultrasonic irradiation promoted the degradation reaction of CTC. The degree of synergy (S) of combination processes can be calculated as follows (Frontistis et al. 2012):

$$S = \frac{k_{EO-US} - (k_{EO} + k_{US})}{k_{EO-US}} x100 \qquad (2)$$

In the equation Eq. 2, $k_{EO\text{-}US}$ represents the reaction rate apparent constant recorded when the sono-electrooxidation process was used, whereas k_{EO} and k_{US} represent the rate apparent constants when ultrasonication and electro-oxidation were respectively applied for CTC degradation. The degree of synergy calculated was 18.2 % indicating that the CTC removal was higher when both processes (EO and US) were simultaneously used compared to the treatment of CTC using the sum of EO and US processes (EO and US individually and successively applied). In this combination, ultrasound enhances the mass transfer between the electrolyte and the electrodes. CTC can be oxidized at the electrode surface where hydroxyl radicals (·OH) are generated by direct effect (Brinzila et al. 2013; Zaviska et al. 2013) and mass transfer rate of organic pollutants to the surface electrode is a principal parameter to the process. These results are consistent with those obtained by Ren et al. (2014) while treating an effluent containing triclosan by using a process combining sonication and electrochemical methods. The electrolysis cell was comprised of diamond coated niobium electrode with ultrasound generator at 850 kHz. A potential of 10 V and an electrical ultrasound power of 170 W was imposed for 15 min. The synergistic effects of US and EO allowed 67 % of triclosan degradation, compared to 62% obtained while the sum of the processes was used which contribute to positive synergistic effects of 8%. These results indicated the advantage of the ultrasound-electrochemical combination compared to ultrasonication or electrooxidation process applied alone. Therefore, additional experiments were carried out to investigate the EO-US technique for the treatment of water contaminated with CTC.

7.4.2 The effect of current intensity on the US-EO process

The current intensity effect on the sono-electrooxidation of CTC was evaluated by comparing the rates of CTC removal at current intensities of 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 A. The electric power of ultrasound was fixed at 30 W.

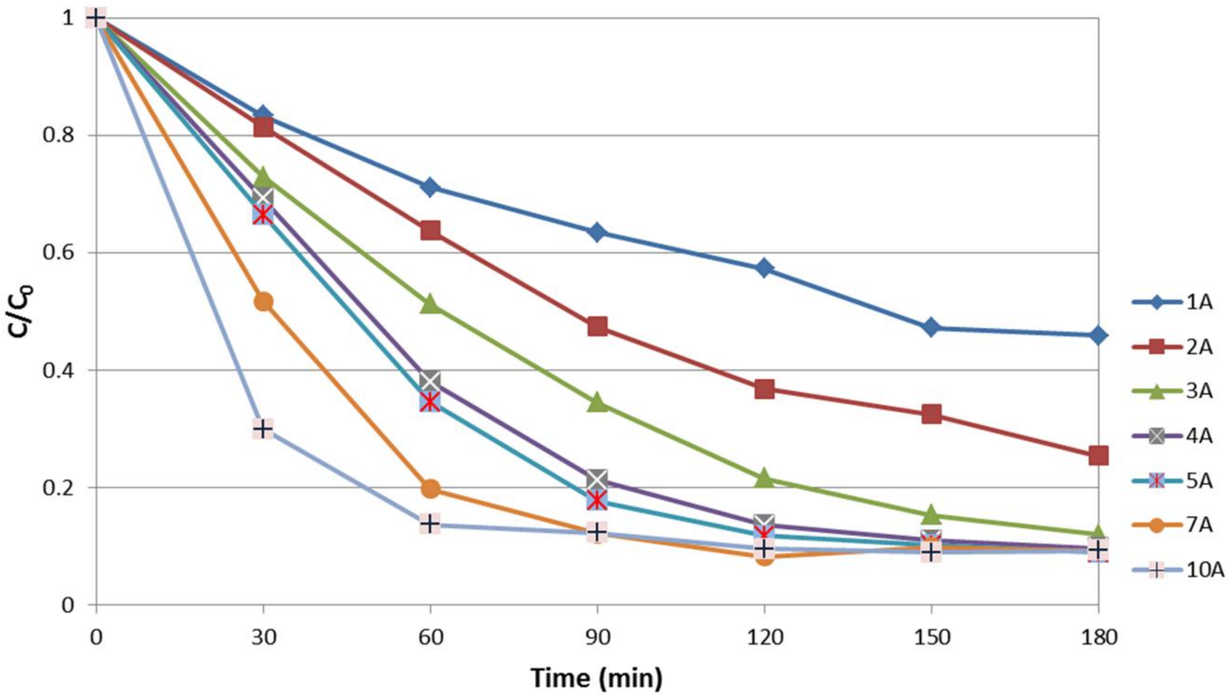

Fig. 7-5 Effect of the current applied and the time versus CTC removal efficiency (I= 1-10A, P= 30W, t= 0-180min, temp. = 20^{o}C)

Figure 3 shows time course changes in the normalized concentration of CTC. The initial CTC concentration imposed during these tests was 10 mg/L and a temperature of 20°C was imposed. The degradation efficiency calculated at the end of the treatment varied from 54.08 % to 90.78 %. The residual CTC concentration decreased with the current intensity imposed. More than 90% of CTC was removed for a current applied ranging between 7.0-10A at 180 min. As show in Figure 3, the current density increased, the depurative efficiency also increased. The higher the current density, the more effective is the oxidation of CTC. However the removal rate of CTC increased with current intensity until 3.0 A and then remained quite stable from 4.0 to 10 A. It has been found that the electrochemical oxidation is carried out using two steps. The first step is the anodic oxidation of water molecule leading to form hydroxyl radicals on the electrode surface “M”:

$$H_2O + M \rightarrow M[\cdot OH] + H^+ + e^- \quad (3)$$

Subsequently, the oxidation of organics “R” is mediated by adsorbed hydroxyl radicals and results in by-product molecule “RO” and may fully mineralization by hydroxyl radical while it is continuously produced at anode electrodes:

$$R + M[\cdot OH] \rightarrow M + RO + H^+ + e^- \qquad (4)$$

$$RO + M[\cdot OH] \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \qquad (5)$$

The accumulation of ·OH radicals favors the oxidation reaction. The hydroxyl radicals are species capable of oxidizing numerous complex organics, non-chemically oxidizable or difficulty oxidizable; during direct anodic oxidation of organic pollutant, competitive reactions (parasitic reactions) can take place and limit hydroxyl radical formation, such as molecular oxygen formation:

$$H_2O + M[\cdot OH] \rightarrow M + O_2 + 3H^+ + 3e^- \qquad (6)$$

Similar phenomena have been recorded by Tran et al. (2009) while studying electrochemical oxidation of polycyclic aromatic hydrocarbons (PAHs) in creosote solution using Ti/RuO_2 and Ti/SnO_2 mesh anode. The PAHs removals efficiency varied from 17% to 34% with current densities varying from 4.0 mA/cm^2 to 23 mA/cm^2, respectively. The largest PAHs oxidation was observed at 15.0 mA/cm^2; the increase of current intensity above 15.0 mA/cm^2 further induced parasitic reactions and does not show efficient to the oxidation of PAHs.

7.4.3 The effect of treatment time on the US-EO process

Beside the current intensity, the treatment time is also one of the most important parameter during a sono-electrochemical oxidation process. This effect is due to the increase in the exposure time of contaminant in solution in the presence of acoustic cavitations, leading to higher oxidation rates and the possible oxidizing of contaminants. When the treatment time increases, the hydroxyl radicals (generated by acoustic cavitations) have more opportunities to participate in degradation of organic pollutant. As it can be seen from Figure 3, the removal rate of CTC degradation changed dramatically when the treatment time passed from 0 min to 60 min. After 120 min of treatment, the average rate of CTC degradation changed slowly suggesting that it was not necessary to further increase the treatment time. It is well known that both processes (US and EO) had the capacity to generate hydroxyl radicals (·OH). In electrochemical oxidation process, the removal rate of pollutants is greatly linked to the limit of diffusion current of electro-actives-species (here the CTC) subjected to electrooxidation. During electrolysis, the residual concentration of pollutant decreases, and the limit of diffusion current required for pollutant oxidation becomes inferior to the current applied so that secondary reactions take place (such as water oxidation into oxygen) and the rate of oxidation of pollutant decreases or reach a steady state. It is a reason for which the CTC removal rate was quite negligible after 120 min of treatment.

7.4.4 Optimization pathway for CTC removal from solution using US-EO process

Effect of experimental parameters on CTC degradation using FC methodology

The influence of different variables including current intensity (X_1), treatment time (X_2) and ultrasound power (X_3) on the CTC removal was investigated using factorial matrix 2^3. The experiment region investigated for CTC removal is presented in Table 7-1 and the experimental results are presented in Table 7-2.

Table 7-1 Experimental region, experimental factorial matrix and degradation efficiency

Coded variables	**Factors**	**Description**	**Experimental field**		**$U_{i,0}$**	**ΔU_i**
			Min	Max		
X_1	U_1	Current intensity (A)	2	5	3.5	3
X_2	U_2	Time of treatment (min)	60	120	90	60
X_3	U_3	Power of ultrasound (W)	20	40	30	20

Table 7-2 Experimental factorial matrix and degradation efficiency

Run	**Experiment design**			**Experiment plan**			**Degradation efficiency (%)**
	X_1	X_2	X_3	U_1	U_2	U_3	
1	-1	-1	-1	2	60	20	29.90
2	+1	-1	-1	5	60	20	68.97
3	+1	+1	-1	5	120	20	86.97
4	-1	+1	-1	2	120	20	54.76
5	+1	-1	+1	5	60	40	72.66
6	-1	+1	+1	2	120	40	65.81
7	-1	-1	+1	2	60	40	35.24
8	+1	+1	+1	5	120	40	87.43

Design-Expert ® Program Software (Design Expert 7, Stat-Ease Inc., Minneapolis) was used to calculate the coefficient of the polynomial model:

$$Y = 62.72 + 16.29X_1 + 11.03X_2 + 1.64X_3 - 2.83X_1X_2 - 2.45X_1X_3 + 1.23X_2X_3 \qquad (7)$$

The analysis of variance is used for validating the model and statistical tests (Table S3, Supplementary file). The value of the regression coefficient R^2 was 0.9940 indicating that the linear polynomial model described by Eq.7 explained the reaction well; only 0.06 % of the total variation could not be explained by the empirical model. The values of "Prob > F" less than 0.0500 indicated model terms are significant. This analysis of variance indicated that the model was statistically significant for CTC removal. The coefficient b_0 = 62.72 represents the average value of the response of 8 assays. According to Eq. 7, it can also be seen that current intensity (b_1

= +16.29) and treatment time (b_2 = + 11.03) have a positive effect on CTC degradation and these effects were higher than that of ultrasound power (b_3 = +1.64). The interaction effects were weaker than the two main effects. Figure.7-6 (Supplementary data) represents the Pareto graphic analysis. The current intensity (X_1) and treatment time (X_2) are the most determining factors on the degradation of CTC (65.49 %, 30.00 %, respectively).

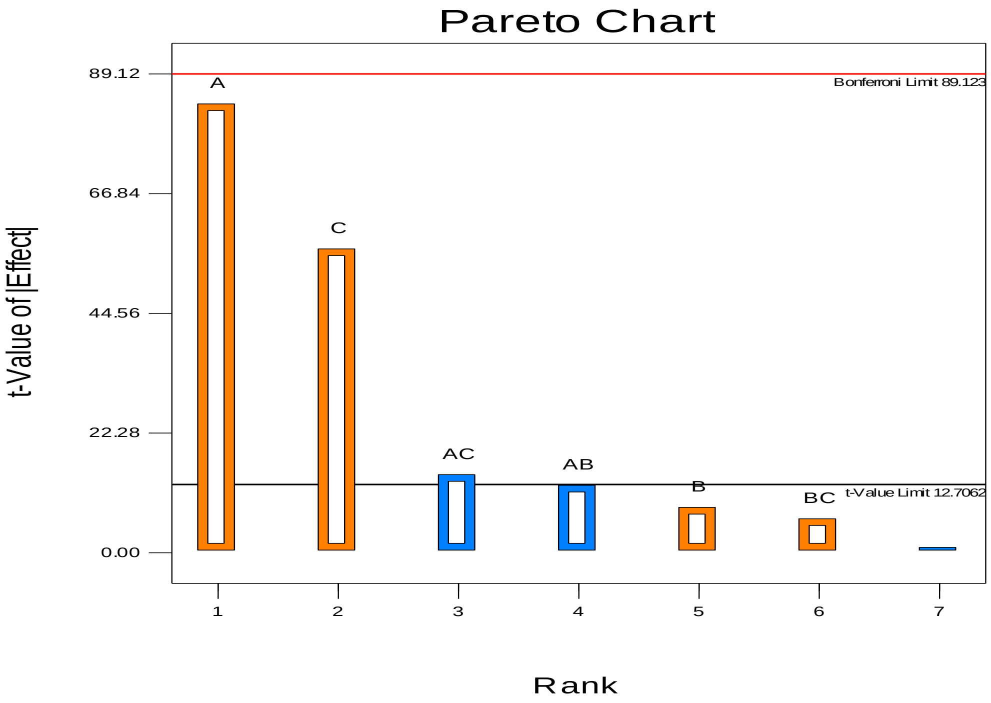

Figure 7-6. The contribution of various effects (A: Current, B: Power, C: Treatment time) and their interaction on the degradation of CTC.

The interaction effect of ultrasound power (X_3) with two other main factors (X_1 and X_2) on CTC degradation is presented in Figure 4. Each point represents the combination between two factors: power with current intensity and power with treatment time. With the interaction between power ultrasound and current applied (Fig. 7-7A), at current intensity of 5.0 A and power of 40W; an average reduction of 80.05% was recorded (assays 5 and 8). When the current (X_1) was fixed at highest level (5A), power had a negligible influence on the removal of CTC. The average degradation efficiency was passed from 79.82% to 80.05% (a reduction gain of 0.23 units).

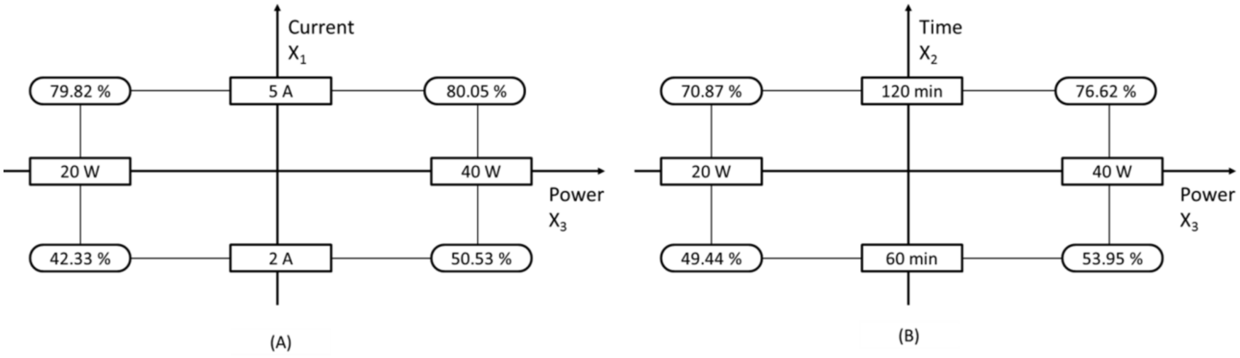

Fig. 7-7 Interaction between power ultrasound with current applied (A) and power ultrasound with treatment time (B).

By comparison, when the current was fixed at the lowest level (2 A), the average degradation rate passed from 42.33% to 50.53% (a reduction gain of 8.2 units). In the case of the interaction between power ultrasound and treatment time (Fig. 7-7B), when the treatment time (X_1) was fixed at highest level (120 min), power had a small influence on the removal of CTC. The average degradation efficiency passed from 70.87% to 76.82% (a reduction gain of 5.95 units). When the current was fixed at the lowest level (60 min), the average degradation rate passed from 49.44% to 53.95% (a reduction gain of 4.51 units). Consequently, with the increasing of power, dissipation of ultrasonic energy into the reactor increases resulted in an increase of CTC degradation. The ultrasound power had higher impact on degradation efficiency at low value of current intensity when compare to high current intensity; this can be explained by the fact that in the solution, the organic contaminants has been oxidized both by the electrochemical process and also by sonochemical process. The organic contaminant degradation may be controlled either by current or power ultrasound. However, the current intensity influenced greatly US-EO process compared to the power of ultrasound. Factorial plan design was thus useful for determining the interactions affecting the response and indicated if the lowest or the highest levels of the factors ware favourable or not. However, this type of model cannot be used to predict or to determine the optimization conditions. Thus, a surface response methodology should be used to determine the optimal operating condition for CTC degradation using the sono-electrochemical oxidation process.

Central composite design (CCD)

In this section, a two-level central composite experimental design with six replicates at the center point leading to a total number of twenty experiments was used for response surface modeling. The CCD matrix is comprised of three sets: factorial matrix (assays 1 to 8), a star matrix (assays 9 to 14) and a set of point at the center of the experimental domain (assays 15 to 20) (Table 7-3).

Table 7-3 Central composite matrix and experimental results

Run	**Experimental design**			**Experimental plan**			**Degradation (%)**
	X_1	X_2	X_3	U_1	U_2	U_3	
9	+1.68	0	0	6.02 A	30 W	90 min	82.78
10	0	+1.68	0	3.5 A	46.82 W	90 min	73.88
11	0	0	+1.68	3.5 A	30 W	140 min	87.89
12	-1.68	0	0	0.98 A	30 W	90 min	41.14
13	0	-1.68	0	3.5 A	13.18 W	90 min	66.61
14	0	0	−1.68	3.5 A	30 W	40 min	42.99
15	0	0	0	3.5 A	30 W	90 min	73.92
16	0	0	0	3.5 A	30 W	90 min	64.43
17	0	0	0	3.5 A	30 W	90 min	63.60
18	0	0	0	3.5 A	30 W	90 min	74.79
19	0	0	0	3.5 A	30 W	90 min	69.24
20	0	0	0	3.5 A	30 W	90 min	70.94

The response was described by a second-order model in the form of quadratic polynomial equation given in the Eq. 8:

$$Y = b_0 + \sum_{i=1}^{k} b_i . X_i + \sum_{i=1}^{k} b_{ii} . X_i^2 + \sum_j \sum_{i=2}^{k} b_{ij} . X_i X_j + e_i \qquad (8)$$

where Y is the experimental response; X_i and X_j are the independent variables; b_0 is the average of the experimental response; bi is the estimation of the principal effect of the factor j on the response Y; b_{ii} is the estimation of the second effect of the factor i on the response Y; b_{ij} is the estimation of the interaction effect between i and j on the response Y and e_i represents the error on the response Y. All coefficients are calculated using the least square method (Myers and Montgomery 1995):

$$B = \left(X^T X\right)^{-1} X^T Y \qquad (9)$$

Where, B represents the vector of estimates of the coefficients; X is the model matrix, and Y is the vector of the experiment results. The variables (X_i) are coded according to the following equation (Eq.10):

$$X_i = \frac{U_i - U_{i,0}}{\Delta U_i} \qquad (10)$$

where $U_{i,0} = (U_{i,max} + U_{i,min})/2$, represents the value of U_i at the center of the experimental field; and $\Delta U_i = (U_{i,max} - U_{i,min})/2$, represents the step of the variation; and $U_{i,max}$ and $U_{i,min}$ are the maximum and minimum values of the effective variable U_i, respectively. The coefficients of the polynomial model (quadratic model) were calculated using the Design-Expert ® Program Software:

$$\begin{aligned} Y &= 69.58 + 14.67X_1 + 1.80X_2 + 11.99X_3 - 2.45X_1X_2 - 2.83X_1X_3 + 1.23X_2X_3 \\ &\quad - 3.26X_1^2 - 0.42X_2^2 - 2.03X_3^2 \end{aligned} \qquad (11)$$

The analysis of variance of the predicted response surface quadratic model show that F-value of 28.47 and a low probability value (Pr > F = 0.0001) indicate that the model is significant for CTC removal. The value of the correlation coefficient ($R^2 = 0.9286$) indicates that only 7.14% of the total variation could not be explained by the empirical model. The agreement between actual and predicted values of CTC removal is satisfactory and consistent with the statistical significance of the quadratic model. To rigorously determine the optimal conditions for CTC degradation in terms of cost and effectiveness, the energy consumption during the sono-electrochemical process has to be taken into account. The criteria selected for the optimization conditions for CTC degradation are the following: *i*) treatment time and current intensity have to be minimized with a relatively high importance (3/5 weighting factor) in order to reduce the treatment cost (including the energy cost); *ii*) The power of ultrasound having a low impact must be minimized with the lowest importance (1/5 weighting factor); *iii*) the percentage of CTC degradation must be maximized with the highest importance (5/5 weighting factor). Based on these criteria, the Design Expert Program Software proposed several interesting solutions to obtain a high degradation of CTC. The optimal conditions for CTC degradation in terms of cost/effectiveness were established as follows: 95 min of treatment using a current intensity of 3.92 A and an ultrasound power applied of 20 W and the theoretical response proposed for CTC degradation was 73.34 %. By comparison, the average value of the CTC removal measured using UV–VIS absorption spectrophotometer is 78.8% ± 0.9%. This result was recorded at the end of this experiment and it is found to be very close to the value proposed by the model. In order to follow the formation of byproducts and possibly identify chemical structures while treating synthetic solutions containing CTC, samples were collected at various time intervals to be able to analyze the intermediates using LC-MS/MS. Under our experimental conditions with LC/MS/MS analysis, none of any by-products was identified on the basis of their mass spectra. However, other by-products could exist. In addition to CTC measurements, the TOC related to the organic compounds were also measured during the treatment. An average TOC concentration of 8.3 ± 0.3 mg/L was measured in untreated water. By comparison, the application of EO-US treatment reduced the TOC to an average value of 3.2 ± 0.2 mg/L. A removal rate of 61.45% of TOC was recorded. The relatively high removal rate of TOC indicated that the majority fraction of organic compounds (CTC) was oxidized into water and carbon dioxide with the other fraction being transformed into small molecules that could be difficult to detect in the treated solution.

7.4.5 Application to municipal wastewater treatment contaminated by CTC

The effectiveness of the sono-electrolytic cell in treating real wastewater effluent contaminated by CTC was evaluated at a current intensity of 3.92A and a retention time of 95 min in the presence an ultrasound power of 20W (optimal conditions determined above using the Design-Expert® Program Software). The objective was to test the effectiveness of the sono-electrochemical process as tertiary treatment to remove CTC in the presence of other types of organic, inorganic and microbial pollutants. It was important to determine whether the results of these tests are reproducible or not. To that end, the experiments were repeated in triplicate to verify the effectiveness and reproducibility of the EO-US process performance in treating municipal wastewater effluent (MWE) contaminated by CTC (Table 4).

Table 7-4 Application EO-US process for the removal of CTC in municipal wastewater effluent (MWE).

Parameters	**Raw MWE**	**Test 1**		**Test 2**		**Test 3**	
		Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
CTC ($\mu g\ L^{-1}$)	< 1	11733 ± 195	217 ± 4.4	120 ± 0.5	2.0 ± 0.1	12.5 ± 0.5	1.0 ± 0.2
TOC (mg L^{-1})	8.4 ± 0.2	14.03 ± 0.22	8.8 ± 0.13	12.37 ± 0.62	8.3 ± 0.2	8.5 ± 0.22	8.03 ± 0.3
CTC removal, (%)	-	98.08 ± 0.4		98.33 ± 0.1		92.0 ± 0.3	
TOC removal (%)	-	37.3 ± 2		32.4 ± 4.8		5.8 ± 1.7	

The chromatographic analysis of this MWE showed that this effluent did not initially contained CTC. Before treatment, the MWE was artificially and respectively contaminated by CTC: *i*) initial CTC concentration around 10 µg/L (**test 3**); *ii*) initial CTC concentration around 100 µg/L (**test 2**) and; *iii*) initial CTC concentration around 1000 µ g/L (**test 1)**. The experimental results determined using liquid chromatography mass spectrometer (LC/MS/MS) shows that the removal of CTC varied from 92.0± 0.3% to 98.33± 0.1%, compared to the predicted value (73.34% of CTC removal) proposed by the model in the optimal conditions. This discrepancy can be attributed to the two main factors. Firstly, it is worth noting that, during the optimization procedure carried out in synthetic solution (SE), UV-visible absorption analytical method was used to evaluate the performance of the process. UV-visible absorption is an indirect analytical method. According to Beer-Lambert law, the measure of the concentration of species can be determined from the measured absorbance. The presence of interfering substance can influence the absorption spectrum and consequently can modify the results. By comparison, LC/MS/MS technique which combines simultaneously a powerful physical separation technique and a powerful technique of analysis and mass detection has a very high sensitivity and selectivity towards several pharmaceutical compounds (Hernandez et al. 2007). Secondly, this discrepancy can be attributed to the initial characteristic of MWE. Indeed, this type of municipal effluent can contain chloride ions, which facilitated the passage of electrical current (Zaviska et al. 2012). Besides, these ions can favour hypochlorous acid (HClO) production and can improve CTC oxidation. Thus, under our experimental conditions using MWE, CTC can be oxidized by means of ·OH and indirect electrochemical oxidation via mediators, such as hypochlorous acid generated by chloride oxidation. Both actions (·OH and indirect oxidation with HClO) lead to the formation of powerful oxidizing agents which has capable rapidly oxidizing the CTC. The combination of both effects accelerates CTC degradation. Similar results have been recorded by Zaviska et al. (2012) while treating municipal wastewater contaminated by bisphenol-A (BPA) by combining direct and indirect electro-oxidation. The municipal effluent initially contained 465 ± 20 mg/L of chloride ion. Electrolysis was conducted using a cylindrical electrolytic cell containing two circular anodes (Ti/PbO_2) and two circular cathode electrodes (stainless steel). A period of 30 min of electrolysis was sufficient to reach complete BPA degradation in municipal effluent, compared to 100 min required for synthetic effluent prepared with distilled water in which Na_2SO_4 was added at a concentration varied from 150 to 250 mg/L.

The initial TOC concentration of MWE contaminated by CTC varied from 8.5 ± 0.22 mg/L to 14.03 ± 0.22 mg/L. The residual TOC concentrations recorded at the end of the treatment ranged between 8.3 ± 0.2 mg/L and 8.8 ± 0.13 mg/L. The reductions in TOC varied from 5.8 ± 1.7% to 37.2 ± 2%. The relatively low yield of TOC removal indicated that only a small fraction of organic compounds (comprised of CTC and other refractory organic matter) was completely oxidised into water and carbon dioxide, with the majority of the pollutants being transformed into small molecules that would reduce the oxygen demand in the treated MWE. The removal rate of TOC in MWE is lower when compared with previous result (TOC removal of 61.45%) in synthetic effluent (SE) prepared with de-ionized water contaminated by CTC (10 mg/L). The untreated SE is only comprised of CTC and Na_2SO_4 used as supporting electrolyte in the effluent without any other organic compounds, whereas in the MWE, the TOC were not only due to the presence of CTC, but it could be also attributed to the presence of natural organic matter or refractory organic matter in waters. Indeed, the relatively high present of other contaminants in MWE could be in competition with TOC removal in the real effluent.

7.4.6 Comparison with other degradation methods

In order to validate the sonoelectrochemical reaction system a comparison with other reported degradation methods was carried out. Electric energy per order (E_{EO}) is the electric energy in kilowatt hours required to degrade a contaminant C by one order of magnitude in a unit volume of contaminated water (Bolton et al. 2001). This is a powerful scale-up parameter and a measure of electric cost when different energy doses are applied for degradation of a pollutant in a fixed volume. This parameter was usually used to compare the different AOPs with the slopes of the energy dose vs. log C_0/C_t curves used as the principle for the comparisons. In a batch operation, the E_{EO} can be calculated as follow (Bolton et al. 2001; Kim et al. 2012):

$$E_{EO} = \frac{P\ .\ t\ .1000}{V\ .60\ .\ \log(\frac{C_O}{C_t})} \qquad (12)$$

where E_{EO} is the electric energy in kWh required to degrade a contaminant by one order of magnitude in a unit volume, P is the rated power of the AOP system (kW), t is the treatment time (min), V is the volume of water treated in time t (L), C_o is the initial concentration of contaminant (mg/L), and C_t is the concentration of contaminant at the time t (mg/L). The calculated CTC removal efficiency and electrical energy consumption were taken into account and are shown in Table 7-5.

Table 7-5. Comparison the electric energy per order of different process for the CTC degradation.

Process	**Initial CTC conc. (mg L^{-1})**	**Removal efficiency (%)**	**$E_{E/O}$ (kWh m^{-3})**	**References**
EO (Ti/PbO_2)	10	96	2.91	(Zaviska et al., 2013)
$O_3/UV_{254}/TiO_2$	239	> 98	N/A	(Khan et al., 2013)
PECO	50	97%	19.48	(Daghrir et al., 2012)
UVC	10	~60%	15.5	(Kim et al., 2012)
EO-US	10	98%	7.90	This work

EO = Electrochemical Oxidation; PECO = Photoelectrocatalytic; UVC = Ultraviolet 254nm; EO-US = sono-electrochemical.

The radiation processes (electron beam) using gamma ray process shows the best degradation degrees (~100%) and electric energy per order (0.19 kWh) in this comparison. However, it is needed to consider other cost such as construction, and maintenance along with this method is higher cause of gamma ray may damage at a cellular level (radiation sickness, DNA damage, cell death due to damaged DNA, increasing incidence of cancer). The photolysis process show promise technologies to decomposition of CTC with high degradation degree (60-98%) however the electric energy consumption per order is still high. The use of electrochemical has shown potential in the work of (Zaviska et al. 2013); however in this study the solution contain chloride ions, which favor the passage of electrical current and improve CTC oxidation. This is probably due to the generation of active chlorine, which is a powerful oxidizing species. During electrolysis of an effluent containing chloride ions, chlorine can be produced at the anode however chlorination can be inappropriate, notably from the associated risk of forming toxic by-products (e.g., organochlorinated compounds). Under our optimized conditions, the sonoelectrochemical method, studied in this work shows a moderate rate electric energy per order (7.90 kWh) and high degradation degree (98% with real wastewater). The oxidizing agent is generated in situ without any addition of external additives and secondary pollution. Thus, there is no need of any pre- or post-process treatments like mixing, pH-control, separation or (re)activation of catalysts so this method is shown promising technology that can be used as tertiary treatment to remove emerging pollutants from MWE.

Conclusion

This study investigated recirculating batch treatment of effluent containing CTC using Ti/PbO_2 anode materials with ultrasound enhanced. The investigation of the combination ultrasound-electrochemical oxidation process on the CTC degradation by factorial design shows that the current applied, treatment time and ultrasound power influence the treatment efficiency of degradation. A central composite design has been applied to determine the optimal experimental conditions. The sonoelectrochemical treatment of CTC using Ti/PbO_2 as anode at 3.92 A of current intensity under US irradiations (20W) during 95min ensures a higher oxidation (up to 98.0 %) when applied to real wastewater effluent. This laboratory study demonstrated that the combined sonochemical and electrochemical processes is effective in removing CTC from MWE. This process shows different major advantages for industrial application concerning secondary pollution, easy control and adaption to different contaminant concentrations and pre- or post-process treatments. However, a complementary study (using a pilot plant) should be carried out to critically and sharply demonstrate the economic advantage of such a hybrid process.

7.5 References

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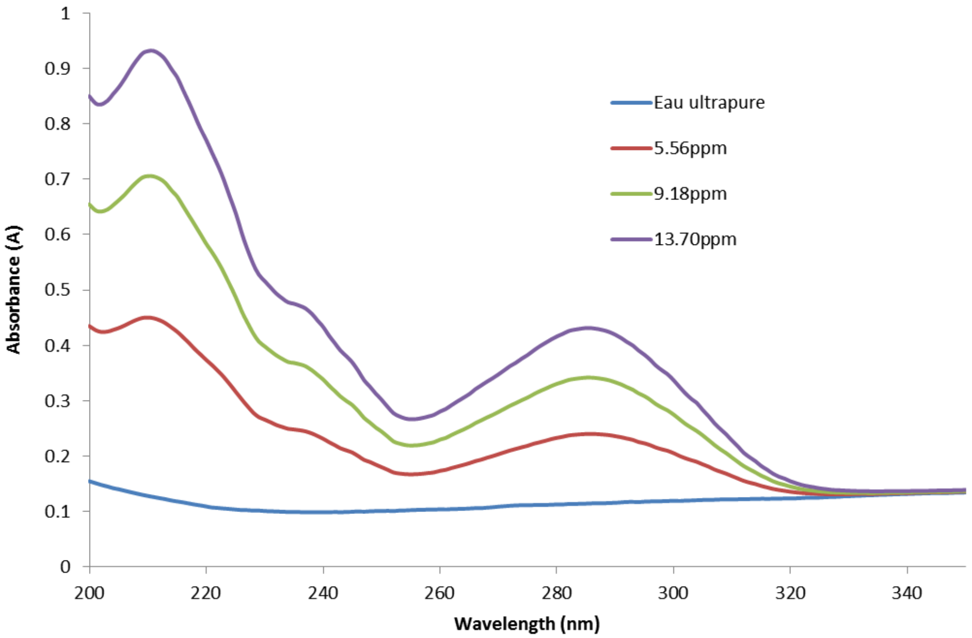
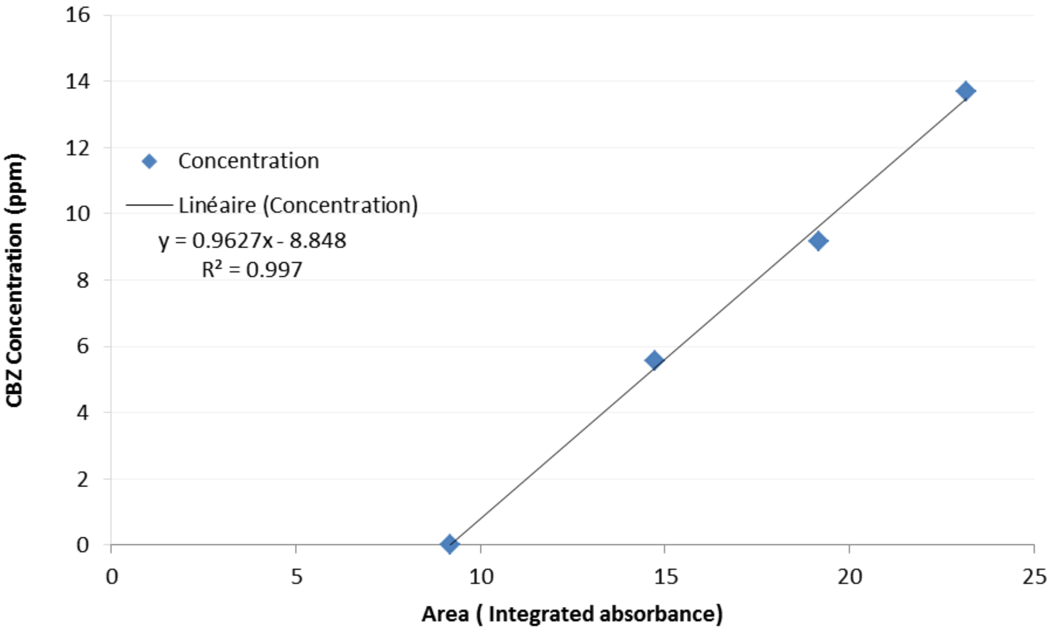
ANNEXES

ANNEX A: **Le spectre et la droite d'étalonnage pour CBZ analyse**





ANNEX B: **Le spectre et la droite d'étalonnage pour RNO analyse**