Counter-current attrition process (CCAP) to remove metals, pentachlorophenol (PCP), dioxins and furans (PCDDF) from the 1-4-mm fraction of contaminated soil

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Abstract

The objective of this study was to evaluate the potential of a counter-current attrition process (CCAP) over 15 cycles for removing metals, pentachlorophenol (PCP) and polychlorinated dibenzo-p-dioxins and -furans (PCDDF) from contaminated soil. The CCAP, applied to the 1-4-mm fraction of a contaminated soil, included five attrition steps (pulp density (PD) = 40% (w w^{-1}), surfactant [BW] = 2% (w w^{-1}), t = 20 min, T = 20°C) followed by one rinsing step. The water emerging from the first attrition step was treated using flocculation in the presence of 0.04 g CMX 123 (commercial flocculent) L^{-1} before being reintroduced into the CCAP. The CCAP including the treatment of attrition wastewater (ATW) by flocculation achieved a removal of 44 ± 5% As, 26 ± 6% Cr, 24 ± 5% Cu, 49 ± 4% PCP and 45 ± 3% PCDDF. Moreover, the CCAP enabled a significant reduction (78%) in the amount of water required (around 14.5 m^3 of water per ton of the 1-4-mm soil fraction). The high removal yields obtained after 15 attrition cycles of the CCAP for PCP and PCDDF and the significant reduction of water consumption confirm that this CCAP can be considered for industrial applications.

Keywords: Attrition • Counter-current • Contaminated soil • Pentachlorophenol • Polychloro-dibenzodioxins and furans • Metals

1 Introduction

Soil contamination is a global concern and is considered a serious environmental problem that affects the health of humans and the ecosystem. Soil contamination is the result of industrial activities or inadequate waste disposal (Han et al., 2002; Wuana et al., 2011; Pohren et al., 2012; Coronas et al., 2016). This contamination leads to an increase in the concentration of inorganic (e.g., As, Cd, Cr, Cu, Ni, Pb, Se, and Zn) and organic compounds (e.g., polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol (PCP), polychlorinated dibenzo-*p*-dioxins and -furans (PCDDF)) present in soils. Chlorophenol compounds are known as one of the most important precursors leading to the formation of PCDDF (Holt et al., 2009).

Several efforts are being made across the world to develop technologies that can efficiently rehabilitate sites contaminated by both inorganic and organic compounds and that currently require a series of complex decontamination processes (USEPA, 2004). Destructive techniques, including incineration or dechlorination methods, are effective for the removal of organic contaminants such as PCP and PCDDF. However, these solutions are very expensive (Metahni, 2013) and are not effective at removing metals. Among the separative methods, thermal desorption seems to be the only method that can be used for the removal of PCP and PCDDF from contaminated soils (Young et al., 2000; Thuan and Chang, 2012; Thuan et al., 2013; Li et al., 2014). Presently, this technology is used at the industrial scale for the removal of organic compounds present in contaminated soils, despite the high costs (Dai et al., 2013; Lundin et al., 2013; Zhao et al., 2013; Tritz et al., 2014). However, at temperatures lower than 400°C, the application of thermal desorption to soils contaminated with chlorinated compounds may result in the formation of highly toxic compounds such as 2,3,7,8-tetra-CDD (Speir et al., 1997;). In addition, an inadequate retention time may lead to increased toxicity of the PCDDF compounds present in soils due to their incomplete destruction (Hung et al., 2016). Bioremediation methods have been used to remediate contaminated soils (Liu et al., 2014; Tu et al., 2014; Zhen et al., 2014), but they are not effective at removing toxic compounds such as PCDDF and inorganic contaminants when they are present in high concentrations.

Over the past several decades, several authors have studied physical and chemical decontamination processes to evaluate their ability to simultaneously remove inorganic and organic compounds from solid matrices, including soils (Riveiro-Huguet and Marshall, 2011; Bisone et al., 2013a; Reynier et al., 2013a, b; Guemiza et al., 2016; Metahni et al., 2016). The attrition uses high-intensity agitation to remove films around soil particles and/or to detach fine particles from the surface of coarse particles, resulting in the release of contaminants. Among the physical treatments (aqueous-based separation) developed, the attrition process is the most commonly used technology to remove both organic and inorganic contaminants from contaminated soils. The attrition process is governed by the physical contact between the contaminated particles themselves, the contact between the contaminated particles and the liquid phase, and the walls and the impellers present in the mixing reactor, which favor the removal of the fine particles that contain the contaminants. As most of the contaminants present in soil usually have low water solubility, such additives as acids, alkaline agents, surfactants and/or chelating agents are often added into the attrition pulp to improve the removal of both inorganic (e.g., As, Cr, Cu, Pb, and Zn) and organic compounds (e.g., PAHs, PCP, and PCDDFs) (Riveiro-Huguet and Marshall, 2011; Bisone et al., 2013a; Reynier et al., 2013b; Guemiza et al., 2016; Metahni et al., 2016). Surfactants are compounds that contain both hydrophilic and hydrophobic parts in their molecular structure. The use of surfactants during attrition washing seems to be a highly efficient method for the simultaneous removal of inorganic and organic contaminants.

Attrition processes may be used with or without a surfactant to remove organic compounds (e.g., PCP and PCDDF) from contaminated soils. The attrition process performed by Bisone et al. (2013a) that used a surfactant ([cocamidopropyl hydroxysultaine, CAS] = 0.2 g L^{-1}) achieved a removal of more than 90% of PAHs from contaminated soil. The decontamination process developed by Veetil et al. (2014) consisted of froth flotation (fractions < 250 µm), a Wilfley table (0.250-2 mm) and a physical separation column preceded by an attrition step as pre-treatment (> 2 mm). This process achieved a removal of 71% to 80% of PAHs, 61% to 65% of Cu, 27% to 33% of Zn and 36% to 40% of Pb. Organic compounds with high molecular weights (e.g., mineral oils, such as Catenex S341) present in contaminated soils seemed to be successfully extracted using an attrition process (Bayley and Biggs, 2005). According to Jobin et al. (2015), the effectiveness of attrition was positively correlated with the size of soil particles. Recently, Jobin et al. (2016) applied one attrition step (PD = 30%, t = 10 min, T = 25°C) as a pre-treatment to the physical technique of separation (gravity separation, elutriation column) to treat the 0.250-4-mm fraction of a soil contaminated by both organic and inorganic compounds. This sequence of decontamination processes allowed for the removal of 50% Cu, 64% Pb, and 40% PAHs. Metahni et al. (2016) studied the use of an attrition process without any surfactant to treat the coarse fractions (> 125 µm) of soils contaminated by As, Cr, Cu, PCP and PCDDF. The removal yields obtained ranged from 22 to 43% for As, from 0 to 13% for Cr, from 23 to 46% for Cu, from 0 to 85% of PCP and from 17 to 64% for PCDDF. These results showed that the nature of the soil and the type and initial level of the contaminants can influence the efficiency of the attrition process. Recently, Guemiza et al. (2016) showed that an attrition process (five attrition steps, 1-4-mm soil fraction, PD = 40%, T = 25°C, surfactant concentration [cocamidopropylbetaine: BW] = 2%, t = 20 min) achieved a removal of 56%, 55%, 50%, 67% and 62% of As, Cr, Cu, PCP and PCDDF, respectively, from a contaminated soil.

This research project aims to study the possibility of recirculating water into a multi-step attrition process using a counter-current attrition process (CCAP) without influencing the performance of this process in terms of removing both inorganic and organic compounds from the 1-4-mm soil fraction. A coagulation-flocculation process using organic polymers was also studied to reduce the suspended organic matter content in the attrition wastewaters, so that it could be recycled into the attrition process without impacting the decontamination performance.

2 Materials and Methods

2.1 Soil sampling and characterization

In this study, contaminated soil located in an industrial area in Canada was sampled at a depth of 0 to 15 cm and called J3. The soil samples were collected within the first 15 cm because several researchers highlighted that both inorganic (As, Cr and Cu) and organic contaminants (PCP and PCDD/F) are mainly immobilized in the top soil, between 0 and 15 cm (Chirenje et al., 2013; Lespagnol, 2003; Isosaari, 2004). The soil was preserved in 25-L high-density polyethylene (HDPE) containers and stored at room temperature. Next, the soil was sieved using a mechanical Sweco^{TM} and different sieves (12 mm; 4 mm; 1 mm and 0.250 mm) to get different soil fractions. Previous experiments have been done to characterize the contamination of the different soil fractions; highlighting that the 1-4 mm soil fractions represented 28% of the entire soil and its contamination was representative of the coarse fractions (> 0.25 mm). Therefore, the 1-4-mm soil fraction was kept and dried at 60°C overnight before being used for the counter-current attrition process (CCAP) experiments.

2.2 Counter-current attrition process

During this study, the attrition steps were conducted in a 10-L stainless reactor equipped with internal baffles with 2 kg of the 1-4-mm J3 soil fraction. Five attrition steps were performed under the optimized operating conditions defined by Guemiza et al. (2016): tap water, pulp density (PD) = 40% (w.w^{-1}), [BW] = 2% (w w^{-1}), t = 20 min, T = 20°C, mixing speed = 1,700 rpm. The pulp was shaken using a mechanical stirrer (Light EV1 P25, AXFLOW, New York, NY, USA) equipped with a stainless steel axial propeller (6 cm diameter) at 1,700 rpm. After each attrition step, the soil was sieved through a 0.5-mm sieve and washed with 4 L of tap water before being returned to the process until a total of five attrition steps (AT 1, AT 2, AT 3, AT 4 and AT 5) were achieved. After the 5th stage of attrition, the 1-4-mm soil fraction was washed with 4 L of water in a 20-L HDPE container using a Karcher (Karcher, electric sprayer, 2000 lb.po^{-2}, Quebec, QC, Canada) before being sieved through a 0.5-mm sieve. Then, the attrited soil was washed with 2 L of tap water.

Fifteen attrition cycles (loop 1 to loop 15) were conducted throughout this experiment, as shown in Fig. 1. The first series of five attrition steps (loop 1) was conducted using fresh water, and the attrition wastewaters were reused in the following cycles (loop 2 to loop 15). For example, the effluent emerging from the fifth attrition step (ATT 5) of loop 1 has been used to perform the fifth attrition step (ATT 5) of loop 2 while the effluents emerging from the second (ATT 2), the third (ATT 3) and the fourth (ATT 4) attrition steps of loop 1 have been used to perform the first (ATT 1), the second (ATT 2) and the third (ATT 3) of loop 2, respectively. The effluent emerging from the first attrition step (ATT 1) of loop was treated by flocculation before to be used to perform the fourth attrition step (ATT 4) of loop 2. At the end of each attrition cycle (five attrition steps), the remaining soil was collected and dried at 60°C in an oven, and the remaining concentrations of PCP, PCDDF and metals were measured to evaluate the performance of the treatment.

2.3 Removal of contaminants from attrition wastewaters by coagulation-flocculation

In the first series of experiments, the removal of organic contaminants from the attrition wastewater (ATW) was studied using chemical coagulation-flocculation. This ATW emerged from the first attrition step (ATW1) carried out on the 1-4-mm J3 soil fraction using the following operating conditions defined by Guemiza et al. (2016): tap water, pulp density (PD) = 40% (w w^{-1}), cocamidopropylbetaine concentration [BW] = 2% (w w^{-1}), t = 20 min, T = 20°C, mixing speed = 1,700 rpm. Coagulation-flocculation experiments were conducted in the presence of various polymers (8 polymers: Magnafloc 1011, Magnafloc 919, Magnafloc 10, AMX 232, CTE 176, Percol 9511, Zetag 7654 and CMX 123) (Ciba Specialty Chemicals Canada, Mississauga, ON, Canada). These flocculants have different cationic or anionic functional groups and are most commonly used to treat municipal and industrial wastewaters. An aqueous solution of 1 g L^{-1} of polymer was prepared for each polymer studied by diluting 1 g of polymer into one liter of tap water in a 2-L beaker and mixing the solution vigorously for 20 min with a magnetic stirrer. These polymers were later used at different concentrations, and the settling time was fixed at 1 h. For some experiments, a solution of ferric chloride (Chemco Inc., Saint-Augustin-de-Desmaures, QC, Canada, 11% of iron (w w^{-1})) was used. The effectiveness of the coagulation-flocculation was determined visually (formation and size of the flocs, clarity of the supernatant) and by measuring the total suspended solids (TSS) in the liquid phase (Method, MA. 115- S.S. 1.2).

The coagulation-flocculation experiments were performed with two different volumes of ATW1: 500 mL and 1 L. The first series of tests was conducted in 500-mL Erlenmeyer flasks to determine the best combination of coagulant/flocculent that should be used, whereas the second series of experiments was performed in 1-L Imhoff cones to validate the observations made in the small scale tests. The concentrations of As, Cr, Cu, PCP and PCDDF were determined in the ATW before and after coagulation and in the coagulation sludge, which was recovered after 1 h of settling.

2.4 Analytical methods

The pH was determined according to the method described by the Quebec Expertise Center for Environmental Analysis (MA. 100 - pH 1.1) (CEAEQ, 2014a) using a pH-meter (Accumet Research AR25 Dual Channel pH/Ion meter, Fischer Scientific Ltd., Nepean, ON, Canada) equipped with a double junction Cole-Parmer electrode with a Ag/AgCl reference cell. The total suspended solids were measured according to the CEAEQ method (MA.115 - S.S. 1.2) (CEAEQ, 2015). The total carbon (C) and organic carbon were analyzed according to the method CSNH 412.1 (Hedges and Stern 1984) using a CHNS Leco analyzer (LECO TruSpec® Micro CHNS 932, Michigan, USA).

Metals and metalloid contents were measured in the 1-4-mm fraction of each soil sample (dry basis) using an ICP-AES (inductively coupled plasma - atomic emission spectroscopy, Vista Ax CCO simultaneous ICP-AES from Varian, Mississauga, ON, Canada) after the digestion of 0.5 g of each soil sample according to the Method MA. 200 – Mét-P ass. 1.0 (CEAEQ, 2014b) using different acids (HNO_3 and HCl). Analytical quality control was performed by analyzing certified standard solutions (Multi-elements Standard 900-Q30-100, SCP Science, Lasalle, QC, Canada) and certified soil samples (SQC 001-Lot 011233). PCP analysis was performed using gas chromatography coupled with mass spectrometry (GC–MS) (Perkin Elmer, model Clarus 500, column type RXi-17, 30 m × 0.25 mm × 0.25 µm) according to the CEAEQ method MA. 400-

Phe. 1.0 (CEAEQ, 2013). The analysis of the 17 PCDDF congeners was performed using a GC-MS (Thermo Scientific, model Trace 1310 Gas Chromatograph coupled with a mass spectrometer detector ISQ, column type ZB Semi-volatile, 60 m × 0.25 mm × 0.25 µm) according to the CEAEQ method MA. 400-D.F. 1.1 (CEAEQ, 2015). The PCDDF value was established by ng TEQ kg^{-1} (toxic equivalence) based on the toxicity equivalency factors (TEF) and concentrations of 17 PCDDF congeners analyzed (NATO 1988).

3 Results and Discussion

3.1 Soil characterization

Table 1 presents a few basic parameters of the 1-4-mm J3 soil fraction and the initial concentrations of both inorganic and organic contaminants. The pH value of this soil was quite neutral (pH = 7.15). The organic content in this fraction was relatively low, with a total organic carbon concentration of 0.38%, whereas the inorganic carbon content only represented 0.22%. The elemental analysis of this soil fraction revealed relatively low phosphorus, calcium, iron, magnesium and potassium contents with values reaching 79, 3,452, 2,775, 2,447 and 49 mg kg^{-1}, respectively. This 1-4-mm soil fraction initially contained 15 mg As kg^{-1}, 23 mg Cr kg^{-1}, 52 mg Cu kg^{-1}, 9.5 mg PCP kg^{-1} and 3,860 ng TEQ PCDDF kg^{-1}. As this soil fraction contained high concentrations of organic contaminants, an attrition process was applied to simultaneously remove the inorganic and organic contaminants.

3.2 Counter-current attrition process

3.2.1 Changes in the performance of the attrition process with the reuse of ATW

The performances of an attrition process, consisting of five attrition steps and one rinsing step and including the recycling of attrition effluents to reduce the consumption of water into the decontamination process, have been evaluated in the present study to determine if the effluents can be recycled without any loss of the attrition process. During this study, the attrition wastewater (ATW) was reused in the attrition process applied to the 1-4-mm J3 soil fraction over 15 loops (Fig. 1). The performances of both inorganic and organic contaminants removals have been followed.

According to our results (values not shown), the metal removal yields obtained during 15 loops of the CCAP including the treatment of ATW 1 by flocculation varied between 32 and 52% for As, between 17 and 37% for Cr and between 15 and 37% for Cu. These results showed that low metal removal yields were obtained during the treatment of the 1-4-mm soil fraction by attrition, which was due to the initial metal concentrations in the soil to be treated by CCAP being very low: 15 mg As kg^{-1}, 23 mg Cr kg^{-1} and 52 mg Cu kg^{-1}. Furthermore, the attrition was performed at pH = 7 and the dissolution of metals is not favored at neutral pH (Djedidi et al., 2009a, b). The final metal concentrations measured in the treated soil over the 15 loops ranged from 7 to 10 mg As kg^{-1}, from 14 to 19 mg Cr kg^{-1} and from 33 to 44 mg Cu kg^{-1}. However, even if the attrition process showed low As, Cr and Cu removal efficiencies from the 1-4-mm soil fraction, the final concentrations of these metals in the soil fractions were very low, allowing the rehabilitation of contaminated sites. However, these contaminants can become more problematic in the next few years due to the potential increase of initial metals levels in soils due to some industrial activities, it seemed important to follow the performances of this attrition process to ensure that the sites can be efficiently rehabilitated.

Fig. 2 presents the final concentrations and the corresponding removal yields of PCP (Fig. 2a) and PCDDF (Fig. 2b) measured in the 1-4-mm soil fraction obtained during the 15 loops of the CCAP that included the treatment of ATW 1 by flocculation. According to the results presented in Fig. 2a, the removal yields obtained for the PCP ranged from 41 to 57% with an average value of 49 ± 4%. During the attrition process, PCP removal slightly decreased during loops 2 to 4 followed by an increase and then a stabilization of the PCP removal after loop 5. The PCP concentrations measured in the final 1-4-mm soil fraction varied between 4.1 and 5.7 mg kg^{-1} in the 15 loops of the CCAP. At the end of the CCAP, the average concentration of PCP measured in the treated 1-4-mm soil fraction was approximately 4.8 ± 0.4 mg kg^{-1}, indicating that the attrition process was quite efficient at removing this contaminant. These results support the conclusion that the recirculation of the attrition wastewater does not reduce the removal efficiency of PCP from the 1-4-mm soil fraction during the attrition process, as no loss of efficiency was observed after 15 loops.

As shown in Fig. 2b, the PCDDF removal yields obtained during the CCAP varied between 41 and 50% during the 15 loops with an average value of 45 ± 3%. The residual concentrations of PCDDF measured in the 1-4-mm soil fractions remained stable during loops 1 to 6 and then decreased slightly during loops 6 to 14. The attrition process resulted in a decrease in concentration of PCDDF in the 1-4-mm soil fraction from 3,900 ng TEQ kg^{-1} to an average of 2,100 ± 100 ng TEQ kg^{-1} over 15 loops. According to these results, no loss of removal efficiency of organic contaminants was observed after 15 loops of attrition wastewater recirculation. Therefore, the recirculation of the effluents into the attrition process could be performed without any loss of efficiency. Along the CCAP, a gradual increase in the amount of flocculation sludge from 4.8 to 6.9 g L^{-1} (14 to 23 g kg^{-1} of the 1-4-mm soil fraction) was observed during the treatment of ATW 1 by flocculation-decantation. These results confirm that this treatment was highly efficient at removing suspended matter from ATW 1, preventing the accumulation of organic matter in attrition wastewater, which could have reduced the performance of the attrition process. According to all the results obtained, this CCAP can efficiently remove both organic and inorganic contaminants from the 1-4-mm soil fraction, allowing the reduction of water consumption.

3.2.2 Water consumption and mass balance

The CCAP including the treatment of ATW 1 by flocculation is estimated to use 4.1 m^3 of water for the treatment of 1 metric ton of the 1-4-mm J3 soil fraction. Without recycling of the attrition effluents, this process would require 18.5 m^3 of water to treat 1 ton of the 1-4-mm J3 soil fraction. Therefore, the recycling of the attrition effluents resulted in a consumption of 4.1 $m^3\ t^{-1}$ and saves 14.5 $m^3\ t^{-1}$, leading to a reduction of 78% in water consumption, which results in a great economic advantage for the CCAP. These results are comparable to those obtained in previous works (Bisone et al., 2013 a, b; Lafond et al., 2013, 2014; Guemiza et al., 2014) that showed the reduction of water consumption when recycling the effluents in a counter-current leaching process and treating the leachates compared to a conventional process without the recovery and recycling of effluents.

Table 2 shows the mass balance of the 15th loop of the CCAP including the attrition process (five attrition steps and one rinsing step) and the treatment of ATW 1 by flocculation. According to our results, the output/input ratio (O/I) related to the dry 1-4-mm soil fraction was estimated to be 0.91. This indicated that 9% of the soil fraction was recovered as attrition sludge and flocculation sludge after the five attrition steps. For the water, the O/I ratio was approximately 1.06, indicating that no water was lost during the process. The surfactant (BW) O/I ratio was only 0.58, indicating that 42% of the BW was not present in the attrition effluent (liquid phases) but may be present in one of the solid phases including the remediated soil, attrition sludge and/or flocculation sludge (cannot be quantified). For the metals, the O/I ratios were approximately 0.94, 0.90 and 0.87 for As, Cr and Cu, respectively. The O/I ratios for PCP and PCDDF were approximately 1.06 and 0.91, respectively. These results showed good recoveries of both inorganic and organic contaminants in both liquid and solid phases all along the CCAP.

3.3 Optimization of removal of contaminants from attrition water

The use of an attrition process to decontaminate the 1-4-mm soil fraction led to an increase in the concentration of suspended organic matter and contaminants present in the attrition water (ATW); this required treatment before being reused in the decontamination process. The attrition water recovered from the first attrition step (ATW 1) following the solid/liquid separation performed to remove the attrition sludge (1 h settling) was treated by chemical flocculation using solutions of different organic polymers (Magnafloc 10, Magnafloc 1011, Magnafloc 919, AMX 232, Zetag 7654, CTE 176, CMX 123, Percol 9511).

Table 3 presents the concentrations of suspended solids present in the effluent before (control) and after treatment by flocculation using the same concentration (0.02 g L^{-1}) of different cationic or anionic polymers. According to the results, the addition of cationic polymers is more efficient for the removal of suspended organic matter present in the ATW compared to the use of anionic polymers. Indeed, the use of cationic flocculants (Zetag 7654, CTE 176, CMX 123 and Percol 9511) achieved a removal of 91% – 93% of the TSS, whereas inorganic polymers only removed 27% – 59% of TSS.

Additional experiments were carried out to evaluate the influence of the amount of cationic flocculent added and the presence of a coagulant (chloride ferric) on the removal of TSS from ATW 1. Table 4 presents the concentrations of TSS present in the supernatants after the treatment of ATW 1 by coagulation/flocculation using different concentrations of cationic polymers in the presence or absence of a coagulant (ferric chloride). These results show that an increase in the concentration of the flocculent from 0.02 to 0.04 g L^{-1} of ATW 1 led to increased removal of suspended matter for all the flocculants studied. Indeed, up to 93, 96, 96, and 97% of TSS were removed in the presence of 0.04 g L^{-1} of Percol 9511, CTE 176, Zetag 7654 and CMX 123, respectively, compared to 92, 91, 91 and 93% in the presence of 0.02 g L^{-1}. Moreover, the sludge obtained had solid contents varying from 5 to 7% for the assays performed in the presence of Zetag 7654, CTE 176 and Percol 9511, whereas it reached approximately 15% in the presence of CMX 123. According to these results, the flocculation-decantation of suspended matter present in ATW 1 is more favorable in the presence of 0.04 g CMX 123 L^{-1} compared to other flocculants. The experiments performed in the presence and absence of a coagulant show that the addition of a coagulant ($FeCl_3$) did not improve the removal of TSS present in ATW 1. Indeed, an increase in the content of suspended matter was observed for the experiments conducted in the presence of a coagulant (0.93-0.99 g L^{-1} in the presence of $FeCl_3$ versus 0.05-0.12 g L^{-1} in the absence of $FeCl_3$).

Three additional assays were carried out on 1 L of ATW 1, using the best conditions (0.04 g L^{-1} of CMX 123, with no $FeCl_3$ added). Tables 5 and 6 present the concentrations of TSS, both inorganic and organic contaminants, and the concentrations of each PCDDF congener measured in ATW 1 before and after flocculation, respectively. According to these results, the concentration of TSS was reduced from 2.77 g L^{-1} to 0.09 ± 0.01 g L^{-1}, which corresponded to a removal of 97%. These results also show low As, Cr and Cu removal yields (< 45%), which can be explained by the low metal contents initially measured in ATW 1. The concentrations of PCP and PCDDF measured in ATW 1 decreased from 0.85 to 0.33 mg L^{-1} and from 195 to 12 ng TEQ L^{-1} after flocculation, respectively. The results presented in Table 6 show that 12 of the 17 congeners considered to be toxic were initially present in ATW 1. The removal yields obtained for the hexa-chlorinated, hepta-chlorinated and octa-chlorinated dioxins and furans were very high, varying between 79% and 100%, except for the 1,2,3,4,7,8-hexa-CDD (only 39%). For the 1,2,3,7,8-penta-CDD, only 9% was removed from ATW 1 using flocculation. The final concentrations of both organic and inorganic contaminants didn't exceed 0.02 mg L^{-1} of As and Cr, 0.23 mg L^{-1} of Cu, 0.33 mg L^{-1} of PCP and 12 ng TEQ L^{-1} of PCDD/F; indicating that the effluent can be recycled into the attrition process without any loss of process performances. This treatment was quite efficient, achieving a removal of 97% of suspended matter, 61% of PCP and 94% of PCDDF. Therefore, the treatment of ATW 1 using flocculation seemed to be advantageous for reducing the concentrations of contaminants and for allowing the reuse of the wastewater in the attrition process.

4 Conclusions

The objective of this work was to remove the metals, PCP and PCDDF from a contaminated 1-4-mm soil fraction using a counter-current attrition process (CCAP), including the treatment of ATW 1 by flocculation. The treatment of the attrition water (ATW 1) by flocculation in the presence of a cationic polymer CMX 123 at 0.04 g L^{-1} seemed to be highly efficient for reducing the concentrations of PCP (61%) and PCDDF (94%), with residual concentrations of approximately 0.85 mg PCP L^{-1} and 195 ng TEQ PCDDF L^{-1}. The results confirm that the CCAP composed of five attrition steps (with conditions of tap water, PD = 40% (w w^{-1}), [BW] = 2% (w w^{-1}), t = 20 min, T = 20°C) followed by one rinsing step can be successfully used without affecting the performance of the attrition process in terms of the removal of metals, PCP and PCDDF. Indeed, after 15 loops, the entire attrition process achieved an average removal of 44 ± 5 of As, 26 ± 6 of Cr, 24 ± 5 of Cu, 49 ± 4 of PCP and 45 ± 3% of PCDDF. Moreover, compared to the conventional attrition process, the CCAP allowed for a reduction in the water consumption by approximately 14.5 m^3 per metric ton of the 1-4-mm soil fraction. Due to these encouraging results, it can be concluded that this CCAP can be considered for industrial application.

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Figure Caption List

Fig. 1 Schematic representation of the counter-current attrition process (CCAP) including five attrition steps, a rinsing step and the treatment of the attrition water by flocculation performed on the 1-4-mm J3 soil fraction ($[As]_0$ = 15 mg kg^{-1}, $[Cr]_0$ = 23 mg kg^{-1}, $[Cu]_0$ = 52 mg kg^{-1}, $[PCP]_0$ = 9.5 mg kg^{-1}, $[PCDDF]_0$ = 3,860 ng TEQ kg^{-1})

Fig. 2 PCP and PCDDF concentrations and the corresponding removal yields obtained during 15 loops of the counter-current attrition process (CCAP) on the 1-4-mm soil fraction, including the treatment of the attrition effluent by coagulation/flocculation (five attrition steps, PD = 40% (w w^{-1}), $[As]_0$ = 15 mg kg^{-1}, $[Cr]_0$ = 23 mg kg^{-1}, $[Cu]_0$ = 52 mg kg^{-1}, $[PCP]_0$ = 9.5 mg kg^{-1}, $[PCDDF]_0$ = 3,860 ng TEQ kg^{-1})

Table Caption list

Table 1 Soil parameters and contaminant contents measured in the 1-4 mm J3 soil fraction

Table 2 Mass balance of the fifteenth cycle of counter current attrition process (CCLP) with attrition’s effluent treatment including five attrition steps and one rinsing step

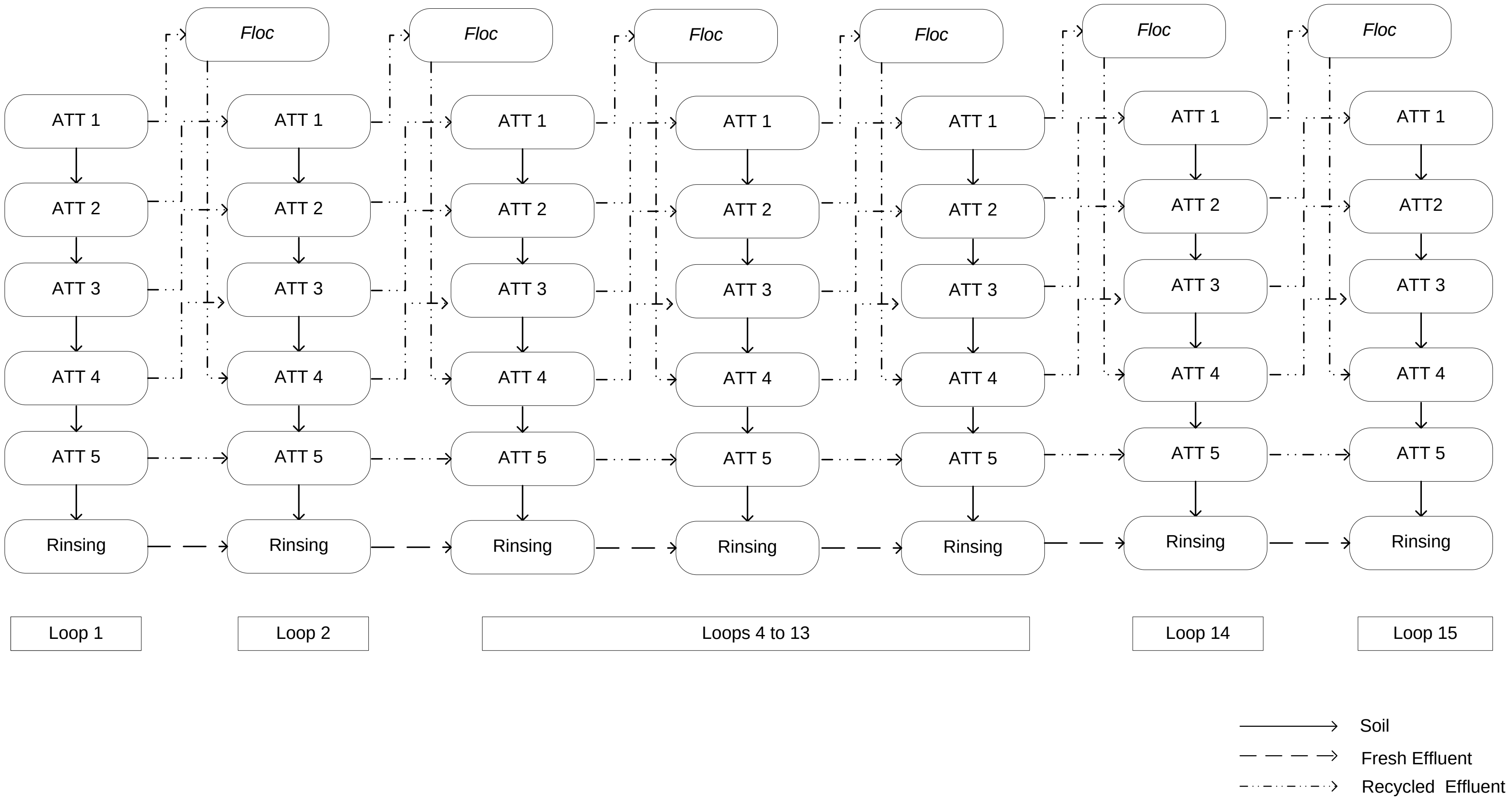
Table 3 Total suspended solids (TSS) concentrations (g L^{-1}) measured in the supernatant emerging from the treatment of the attrition wastewater step 1 (ATW 1) performed in the presence of different flocculants at a concentration of 0.02 g L^{-1}

(ATW 1 produced during the first step of attrition treatment performed using tap water, PD = 40% (w w^{-1}), [BW] = 2% (w w^{-1}), t = 20 min, T = 20°C, fraction 1-4 mm of the soil J3)

Table 4 Residual concentration of suspended matter present in the effluent after treatment of attrition wastewater step 1 (ATW 1) by coagulation/flocculation using different amounts of cationic polymers in the presence or the absence of coagulant ($FeCl_3$)

Table 5 Concentrations of total suspended solids (TSS), metals, PCP and PCDDF present in the attrition wastewater step 1 (ATW 1) before and after treatment by flocculation in the presence of 0.04 g L^{-1} of a cationic polymer CMX 123

Table 6 Toxicity equivalency factor (TEF), concentrations (ng TEQ L^{-1}), and removal yields (%) obtained for each dioxin or furan congener present in attrition wastewater step 1 (ATW 1) before and after treatment by flocculation in the presence of a cationic polymer ([CMX 123] = 0.04 g L^{-1})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Rinsing
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Rinsing
Rinsing
Loop 1
Loop 2
Loops 4 to 13
Loop 14
Loop 15
Soil
Fresh Effluent
Recycled Effluent

Figure 1

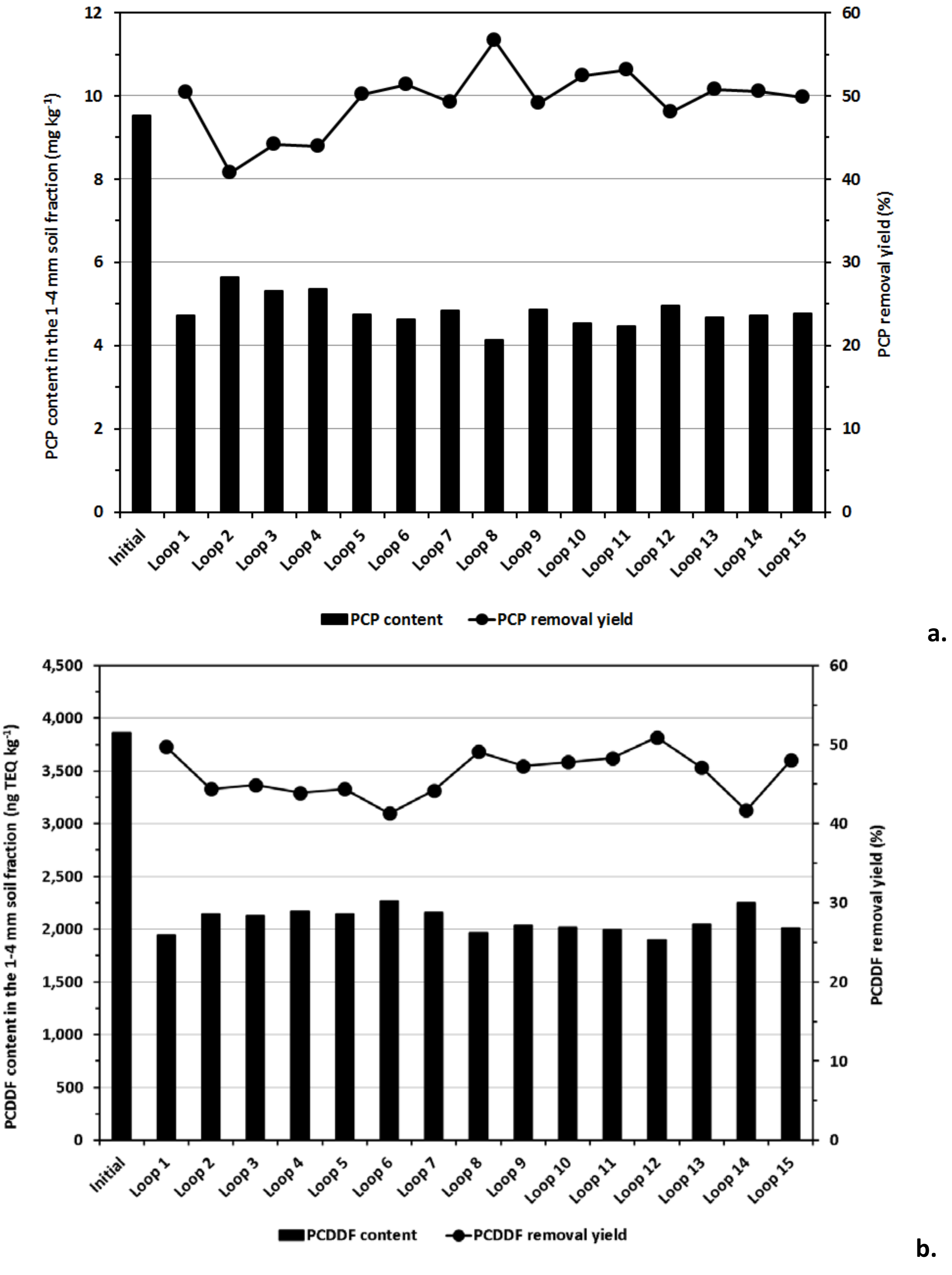
PCP content in the 1-4 mm soil fraction (mg kg-1)
PCP removal yield (%)
12
10
8
6
4
2
0
60
50
40
30
20
10
0
Initial
Loop 1
Loop 2
Loop 3
Loop 4
Loop 5
Loop 6
Loop 7
Loop 8
Loop 9
Loop 10
Loop 11
Loop 12
Loop 13
Loop 14
Loop 15
PCP content
PCP removal yield
a.
PCDDF content in the 1-4 mm soil fraction (ng TEQ kg-1)
PCDDF removal yield (%)
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
60
50
40
30
20
10
0
Initial
Loop 1
Loop 2
Loop 3
Loop 4
Loop 5
Loop 6
Loop 7
Loop 8
Loop 9
Loop 10
Loop 11
Loop 12
Loop 13
Loop 14
Loop 15
PCDDF content
PCDDF removal yield
b.

Figure 2

Table 1 **Soil parameters and contaminant contents measured in the 1-4 mm J3 soil fraction**

Soil	Values
Parameters	
pH in water at 25°C	7.15
Total organic carbon (%)	0.38
Inorganic carbon (%)	0.22
Elements (mg kg^{-1})	
Ca	3,452
Fe	2,775
K	49
Mg	2,447
P	79
Contaminants (mg kg^{-1})	
As	15
Cr	23
Cu	52
PCP	9.5
PCDDF (ng TEQ kg^{-1})	3,860

Table 2 **Mass balance of the fifteenth cycle of counter current attrition process (CCLP) with attrition's effluent treatment including five attrition steps and one rinsing step**

	Description	Dry soil (kg)	ATW (L)	BW (kg)	Quantity (mg)				
					As	Cr	Cu	PCP	PCDDF (ng TEQ)
Input (I)	Soil	2.00			29.0	46.0	104	19.1	7,727
	Water		37.31	0.502	2.93	2.96	41.4	15.9	5,478
Output (O)	Soil	1.82	0.20		15.2	34.4	74.1	8.70	3,659
	Water		37.88	0.291	3.25	2.66	39.1	11.0	2,684
	Attrition sludge		1.35		8.94	4.59	9.21	15.9	5,362
	Flocculation sludge		0.35		2.54	2.34	4.24	1.54	364
O/I		**0.91**	**1.06**	**0.58**	**0.94**	**0.90**	**0.87**	**1.06**	**0.91**

Table 3 **Total suspended solids (TSS) concentrations (g L^{-1}) measured in the supernatant emerging from the treatment of the attrition wastewater step 1 (ATW 1) performed in the presence of different flocculants at a concentration of 0.02 g L^{-1} (ATW 1 produced during the first step of attrition treatment performed using tap water, PD = 40% (w w^{-1}), [BW] = 2% (w w^{-1}), t = 20 min, T = 20°C, fraction 1-4 mm of the soil J3)**

Assays	**Flocculent**	**Type**	**TSS (g L^{-1})**
Control	-	-	1.61
2	Magnafloc 1011	Anionic	1.17
3	Magnafloc 919	Highly anionic	0.66
4	Magnafloc 10	Anionic	0.95
5	AMX 232	Anionic	1.39
6	CTE 176	Cationic	0.14
7	Percol 9511	Highly cationic	0.13
8	Zetag 7654	Cationic	0.15
9	CMX 123	Cationic	0.12

Table 4 **Residual concentration of suspended matter present in the effluent after treatment of attrition wastewater step 1 (ATW 1) by coagulation/flocculation using different amounts of cationic polymers in the presence or the absence of coagulant ($FeCl_3$)**

Assays	**Flocculent**	**Flocculent added ($g\ L^{-1}$ of ATW 1)**	**Coagulant ($FeCl_3$) ($g\ L^{-1}$ of ATW 1)**	**TSS ($g\ L^{-1}$)**
Control	-	-	-	1.62
2	Zetag 7654	0.02	-	0.15
3	Zetag 7654	0.04	-	0.06
4	Percol 9511	0.02	-	0.13
5	Percol 9511	0.04	-	0.11
6	CTE 176	0.02	-	0.14
7	CTE 176	0.04	-	0.07
8	CMX 123	0.02	-	0.12
9	CMX 123	0.04	-	0.05
10	CMX 123	0.06	-	0.06
11	CMX 123	0.02	0.5	0.99
12	CMX 123	0.04	0.5	0.93
13	CMX 123	0.06	0.5	0.99

Table 5 **Concentrations of total suspended solids (TSS), metals, PCP and PCDDF present in the attrition wastewater step 1 (ATW 1) before and after treatment by flocculation in the presence of 0.04 g L^{-1} of a cationic polymer CMX 123**

	TSS **(g L^{-1})**	**As** **(mg L^{-1})**	**Cr** **(mg L^{-1})**	**Cu** **(mg L^{-1})**	**PCP** **(mg L^{-1})**	**PCDDF** **(ng TEQ L^{-1})**
Before	2.77	0.03 ± 0.02	0.04 ± 0.01	0.28 ± 0.01	0.85	195
After	0.09 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.27 ± 0.01	0.33 ± 0.01	12.2 ± 0.1
Removal (%)	97 ± 1	26 ± 3	45 ± 4	3.4 ± 0.4	61 ± 2	94 ± 1

Table 6 **Toxicity equivalency factor (TEF), concentrations (ng TEQ L^{-1}), and removal yields (%) obtained for each dioxin or furan congener present in attrition wastewater step 1 (ATW 1) before and after treatment by flocculation in the presence of a cationic polymer ([CMX 123] = 0.04 g L^{-1})**

Dioxin or furan congener	**Toxicity Equivalency Factor (NATO 1988)**	**Before (ng TEQ L^{-1})**	**After (ng TEQ L^{-1})**	**Removal yield (%)**
2,3,7,8 Tetra-CDF	0.10	< 0.05	< 0.05	n.a*
2,3,7,8 Tetra-CDD	1.00	< 1.62	< 1.60	n.a
1,2,3,7,8 Penta-CDF	0.05	< 0.06	< 0.06	n.a
2,3,4,7,8 Penta-CDF	0.50	< 0.50	< 0.50	n.a
1,2,3,7,8 Penta-CDD	0.50	6.9	6.3	8.8
1,2,3,4,7,8 Hexa-CDF	0.10	2.7	< 0.50	100
1,2,3,6,7,8 Hexa-CDF	0.10	< 0.20	< 0.20	<0.2
1,2,3,7,8,9 Hexa-CDF	0.10	1.7	< 0.31	100
1,2,3,4,7,8 Hexa-CDD	0.10	0.6	0.4	39
1,2,3,6,7,8 Hexa-CDD	0.10	8.1	< 0.50	100
1,2,3,7,8,9 Hexa-CDD	0.10	3.7	< 0.50	100
2,3,4,6,7,8 Hexa-CDF	0.10	0.5	0.1	79
1,2,3,4,6,7,8 Hepta-CDF	0.01	9.0	0.6	94
1,2,3,4,6,7,8 Hepta-CDD	0.01	74	2.8	96
1,2,3,4,7,8,9 Hepta-CDF	0.01	1.0	0.1	89
Octa-CDD	0.001	82	1.7	98
Octa-CDF	0.001	5.1	0.3	95
Total (ng TEQ.L^{-1})	**-**	**195**	**12**	**94**

** n.a: not applicable.*