



Simultaneous addition of surfactant and oxidant to remediate a polluted soil with chlorinated organic compounds: Slurry and column experiments

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ABSTRACT

The inadequate management of wastes associated with chlorinated organic compounds (COCs) has become a huge environmental problem. Surfactant Enhanced In-Situ Chemical Oxidation (S-ISCO) was studied as a successful technique to remediate polluted sites. This work investigated the reaction between an aqueous solution of nonionic surfactant (Emulse-3®) and an oxidant (sodium persulfate activated with NaOH) with a real polluted soil with a complex mixture of COCs from lindane liquid wastes. Two experimental setups were used. In the first one, the reactions were carried out in batch mode under slurry conditions using different surfactant concentrations (0–10 g·L⁻¹), 210 mM of persulfate and 420 mM of NaOH with an aqueous to soil ratio $V_L/W = 10$ L·kg⁻¹. The runs were carried using a column loaded with the soil in the second experimental setup. The solution of surfactant, oxidant and activator was put in contact with soil in four pore volumes with a ratio aqueous to soil ratio $V_L/W = 0.2$ L·kg⁻¹. Under these experimental conditions, the surfactant addition improved the reduction of COCs compared with the application carried out without surfactant, from 40.1% to values of conversion of 64.8–90.4%. However, an excess of surfactant hindered the COCs oxidation and increased the unproductive consumption of the oxidant, resulting in an optimal value of surfactant in the aqueous phase (1–2 g·L⁻¹). A remarkable drop in the surfactant concentration in the aqueous phase and COCs solubilized was noticed in column runs due to the surfactant adsorption.

1. Introduction

Hydrophobic organic compounds (HOCs) such as chlorinated pesticides or solvents has been widely produced worldwide. The inadequate management of the production wastes has become a huge environmental problem [20,27,36,39].

The remediation of polluted sites with mixtures of HOCs is a challenge attracting the researchers interest [38]. In situ chemical oxidation (ISCO) has been successfully applied [1,33–35]. However, ISCO only takes place in the aqueous phase. The low solubility in water of HOCs [39] limits the ISCO application [38], increasing the time needed to remove the contamination on soil heavily contaminated [4,6,37]. To overcome this disadvantage, the simultaneous application of surfactants and oxidants (S-ISCO) has recently gained attention [4,5,23,25]. The surfactant enhances the HOCs solubilization in the aqueous phase [29,31] and improves the abatement reaction rate [4,8].

The selection of surfactant and the dose used in the S-ISCO application is not a trivial task. The surfactant must be biodegradable and

have low toxicity and adequate capacity for solubilization [40]. Among the different types of surfactants, the nonionic ones have been tested successfully in the S-ISCO applications ([6,10,44], Wang et al., 2019a, 2019b).

Despite, the higher the surfactant concentration, the higher amount of pollutants solubilized in the aqueous phase [21], the dose of surfactant must be optimized because of the following aspects: i) the surfactant reacts with the oxidant [18,28,43]; ii) the increase of surfactant concentration promotes a hindering effect in the contaminants avoiding the direct attack of the oxidant [5,19]; iii) the use of a high concentration of surfactant can produce the dispersion of contaminants in the polluted sites.

The application of surfactant and oxidant in polluted soil has been studied at a laboratory scale using well-agitated reactors where the polluted soil and the aqueous solution were put in contact in slurry experiments, using high ratios of aqueous volume to the soil. Li et al. used a 5 L·kg⁻¹ of aqueous to soil ratio to study the simultaneous solubilization and oxidation of chlorinated organic compounds [22]; On the

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other hand, Wang et al. used a ratio of $200 \text{ L}\cdot\text{kg}^{-1}$ in the remediation of polyaromatic hydrocarbons from coal tar [43] with heat-activated persulfate and several anionic and nonionic surfactants. However, the S-ISCO technology at the field scale (in soils with effective porosity between 0.15 and 0.3) requires lower ratios between the injected aqueous phase and soil mass than those used in the literature.

Under these last conditions, where the ratio of aqueous phase to mass soil is low, the adsorption of surfactant injected on the polluted soil could significantly modify the partitioning of pollutants adsorbed and surfactant between soil and the aqueous phases [30,45]. The latter aspects even reduce the surfactant concentration in the aqueous phase, which means the surfactant capacity losses [16]. In addition, the oxidation reaction can contribute to the overall oxidation rate in soils with a high surface [17]. These aspects can be studied in a realistic way using column experiments. From our knowledge, the S-ISCO works in column experiments are very scarce [25,42]. These works were focused on determining the efficiency of pollutants removal without studying the surfactant adsorption, the HOCs oxidation in the soil surface and the consumption of oxidants by the adsorbed surfactants.

To fill this gap, this work studies the simultaneous addition of oxidant and surfactant in slurry and column ways to remediate heavily polluted soil. The selected soil was obtained from a polluted landfill where the liquid residue from lindane production was uncontrolled dumped [12,33,34]. This residue is composed of a mixture of chlorobenzenes (CB), hexachlorocyclohexanes (HCH) and hexachlorocyclohexanes (HeptaCH). These compounds have low solubilities in water and high adsorption in soil, forming a complex mixture adsorbed. The oxidant selected was sodium persulfate (PS) activated by alkali (PSA). PSA was successfully applied in a similar soil without surfactant [17]. In addition, NaOH promotes a quick dehydrochlorination of HCHs and HeptaCH to Trichlorobenzenes (TCB) and Tetrachlorobenzenes (TetraCBs), respectively, at $\text{pH} > 12$ [26].

From our knowledge, the S-ISCO applied to remediate real soil polluted by wastes of lindane production has not been carried out. The partition equilibrium and the oxidation of COCs and surfactants in both phases will be considered. Moreover, results obtained in slurry and column setups will be compared.

2. Material and methods

2.1. Materials

The soil used in this work was obtained from the Sardas landfill in Sabiñánigo (Spain), from a permeable layer heavily contaminated with the residues of the lindane production located at 13.5–14.0 m b.g.l. The subsoil of Sardas landfill is segmented into horizontal permeable and impermeable layers, being the soil used in the permeable layer (alluvium) where the groundwater flows. The alluvium contain gravel-sand with some clay interbedded [32]. Soil from the same well and depth was characterized elsewhere [15]. The characterization revealed a high carbonates content (higher than 43%w, expressed as CaCO_3). The total organic carbon in this soil was also determined, and the measured value was adequately explained by the COCs concentration in the soil. Therefore, the amount of other natural organic matter was considered negligible. Furthermore, different contamination levels were noticed in previous works depending on the soil size [15]. Therefore, the soil from the alluvium was sieved in two soil fractions: F ($< 0.25 \text{ mm}$) and G ($0.25\text{--}2 \text{ mm}$).

The surfactant used was E-Mulse® 3 (E3), a commercialized by EthicalChem. This surfactant was successfully applied in field remediation processes [11] applying S-ISCO in polluted sites with light and dense Non Aqueous Phase Liquids [4]. E3 is a non-toxic and biodegradable polyethoxylated nonionic surfactant. In addition, E3 was selected considering the results obtained from previous studies where different surfactants were tested [14,16,18]. The experimental results

showed that E3 presented a better solubilization ratio of COCs and compatibility with the PS activated with NaOH system than SDS, Tween 80 or Span 20.

Sodium persulfate (PS, Fisher Scientific) activated with alkali (NaOH, Fisher Scientific) was used as the oxidant agent. This oxidant system effectively eliminated COCs from the soil in the aqueous phase without surfactants [9,17]. The high amount of carbonates in the soil [16] make unbearable the use of the Fenton reagent with this soil due to the decomposition of H_2O_2 and Fe precipitation [9]. Regarding the activation methods of the PS, temperature, Fe or UV-light cannot be used since the contamination was found at depths higher than 15.

Commercial standards from Sigma-Aldrich were used for the identification of COCs from soil samples: chlorobenzene (CB), dichlorobenzene isomers (1,2-DCB; 1,3-DCB; 1,4-DCB), trichlorobenzene isomers (1,2,3-TCB; 1,2,4-TCB; 1,3,5-TCB), tetrachlorobenzene isomers (1,2,3,4-TeCB; 1,2,4,5-TeCB; 1,2,3,5-TeCB), pentachlorobenzene (PCB) and hexachlorocyclohexane isomers (α -HCH; β -HCH; γ -HCH; δ -HCH; ϵ -HCH). Standards of different solutions of DNAPLs in methanol (MeOH, Fisher Scientific) were used for the non-commercial isomers (pentachlorocyclohexenes, hexachlorocyclohexenes and heptachlorocyclohexanes), which were quantified elsewhere [33,34]. The COCs compositions in the soil fractions F and G, before any treatment, are summarized in the Table SM-1. As can be seen, a complex mixture of chlorinated compounds was identified. Most of the lighter chlorinated benzenes (chlorobenzene and dichlorobenzenes) were lost during soil transportation, storage, drying and milling.

Sodium sulfate (Fisher Scientific) was used to dry the soil samples. Hexane (Honeywell) and MeOH were used as extractants. Potassium iodide (Fisher Scientific), sodium hydrogen carbonate (Panreac), sodium thiosulfate pentahydrate (Sigma-Aldrich), and acetic acid (Sigma-Aldrich) were used in the analysis of oxidant concentration in the aqueous phases. Milli-Q water was used in all aqueous solutions.

2.2. Slurry experiments

Fraction F, with the highest COCs content ($35.04 \text{ mol}\cdot\text{kg}^{-1}$, $10063 \text{ mg}\cdot\text{kg}^{-1}$) has a low hydraulic permeability due to the small particle sizes and cannot be used in column experiments. Experiments using F fraction were carried out in slurry mode using well-mixed vials of PTFE. An amount of 2 g of soil (W) was put in contact with 0.02 L of a NaOH (V_L) solution ($100 \text{ mmol}\cdot\text{L}^{-1}$), to achieve the total dehydrochlorination of all non-aromatic COCs (Hexachlorocyclohexanes, HCH, and Heptachlorocyclohexanes, HeptaCHs) in the soil to TriChloroBenzenes and TetraChloroBenzenes, respectively [17].

After 24 h the samples were centrifugated and the supernatant was replaced by 0.019 L of a solution with the corresponding concentration of surfactant (E3). Once the equilibrium between the aqueous and the solid phases was reached ($< 24 \text{ h}$) [16], 0.001 L from an PS and NaOH concentrated solution with a molar ratio NaOH:SP = 2 was added. The experimental conditions of the runs carried out are summarized in Table 1. As can be seen, initial NaOH and PS concentrations in the vials in all the runs were $420 \text{ mmol}\cdot\text{L}^{-1}$ and $210 \text{ mmol}\cdot\text{L}^{-1}$. The surfactant concentration was $0 \text{ g}\cdot\text{L}^{-1}$ (run B0), $2.5 \text{ g}\cdot\text{L}^{-1}$ (run B2), $5 \text{ g}\cdot\text{L}^{-1}$ (run B5) and $10 \text{ g}\cdot\text{L}^{-1}$ (run B10). The water to soil (V_L/W) ratio was $10 \cdot\text{kg}^{-1}$.

Zero time was considered after the oxidant and alkali addition. Vials were agitated ($20\text{--}30 \text{ rpm}$) in a Labolan rotatory agitator. 5 vials were used for each experiment, and each vial was sacrificed at a reaction time.

Table 1
Experimental conditions of slurry runs. Aqueous to soil ratio $V_L/W = 10 \text{ L}\cdot\text{kg}^{-1}$.

Name	E3 ($\text{g}\cdot\text{L}^{-1}$)	PS ($\text{mmol}\cdot\text{L}^{-1}$)	NaOH ($\text{mmol}\cdot\text{L}^{-1}$)
B1	0	210	420
B2	2.5	210	420
B3	5	210	420
B4	10	210	420

All experiments were conducted in duplicate, finding discrepancies between the experimental results lower than 6%. Aqueous and soil phases were separated by centrifugation, being remaining COCs analyzed in each phase.

A schematic of slurry runs and procedure can be seen in Figure SM-1 a) of the [supplementary material](#).

2.3. Column experiments

The soil with a higher size (G) was placed in glass columns. Each column has a diameter of 0.03 m with a side-feed (0.03 m from the bottom end) and a side-outlet (0.03 m from the top end). The effective length of the column is 0.0475 m. The bottom end of the column was closed with a cap of flexible silicone with a folding skirt. The bottom was filled with glass spheres (0.25 mm of diameter), on which fibreglass was placed (completely covering the feed). After this, the polluted soil (fraction G, 10.83 mmol·kg⁻¹ of COCs) was added (0.05 kg). The column interior was completed by placing the fibreglass (covering the side-outlet), the glass spheres, and the cap (for the top end of the column). Finally, the side-feed was connected to a peristaltic pump (Spetec Perimax 12) to add the feed solutions from a glass bottle, and a tube was connected to the side outlet to collect the output solutions. A metallic mesh was always placed between the soil bed and the fibreglass. Figure SM-1 b) of the [supplementary material](#) shows a schematic of the column assembly.

Milli-Q water was injected in the glass column to reach pore water saturation as a previous treatment. Following, 100 mL of an aqueous solution 100 mmol·L⁻¹ in NaOH was injected at 0.3 mL·min⁻¹, being reposed in the columns during 24 h. These conditions were enough to convert non-aromatic COCs of soil into TCBs and TetraCBs [17]. It was confirmed that nor HCHs nor HeptaCHs were detected in the aqueous phase after this period. In this process, the total COCs removed from the soil to the aqueous phase were quantified being less than 1% of the initial COCs in soil.

After the alkaline treatment, an aqueous solution containing oxidant/activator and surfactant was injected into each column at 0.3 mL/min. The oxidant concentration at the column exit was monitored by finding a S profile, with an average retention time of 35 min. A 95% of the inlet oxidant concentration was measured in the outlet stream after 40 min of injection time (12 mL injected). In plug flow, the breakthrough curve for the oxidant concentration would correspond to a step profile after injecting the PV (10 mL) for 34 min at the flow rate employed (0.3 mL/min). Therefore, the small axial dispersion of the injected fluid can be inferred.

After 40 min, the flow stopped, and the aqueous solution injected remained the chosen reaction time in the column. Moreover, it should be noticed that the reaction time between injections was 70–170 times higher than the time required for injection of each PV.

After each reaction time selected, the aqueous phase in the columns was flushed by injecting another pore volume of an aqueous solution containing the same concentrations of reagents used in the previous pore volume injected. The aqueous phase flushed with each pore volume injection was collected and analyzed, and this procedure was repeated four times. Finally, a pore volume of Milli-Q water was injected to flush the last pore volume injected with the reagents, and the column was disassembled. Then, the remaining COCs in the soil were analyzed by triplicate. The soil was divided into three fractions: column bottom, center and top.

The conditions of column experiments are summarized in.

Table 2. As can be seen, in column C1 no surfactant was injected (ISCO run), while in columns C2 and C3 (S-ISCO), a concentration of 5 and 10 g·L⁻¹ of surfactant was injected, respectively, with each pore volume. Oxidant (PS) and activator (NaOH) at each pore volume injected were 210 and 420 mmol·L⁻¹, respectively. Injection flow rate was of each pore volume was 0.3 mL·min⁻¹.

Table 2

Experimental Conditions in column runs. COCs in soil G 10.94 mmol·kg⁻¹ PS= 210 mM,.

Parameters	C1	C2	C3
Soil height (m)	4.75·10 ⁻²	4.75·10 ⁻²	4.75·10 ⁻²
Soil mass (kg)	0.053	0.052	0.051
Pv (L)	1.12·10 ⁻²	1.09·10 ⁻²	1.08·10 ⁻²
C _{E3} injected (g·L ⁻¹)	0	5	10
C _{PS} injected (mM)	210	210	210
C _{NaOH} injected (mM)	420	420	420
reaction times (h): Pv1/Pv2/ Pv3 /Pv4	113/48/ 48/113 (all columns)		

2.4. Analytical methods

The soil was analysed at each reaction time in the slurry experiment or at the final time in column runs. The soil moisture was removed by adding anhydrous sodium sulfate, and 30 mL of MeOH was added to 2 g of soil and COCs were extracted by ETHOS ONE microwave (Milestone). This procedure was carried out following EPA 3546. The liquid phase obtained was filtered (0.45 µm, nylon), and the COCs were analyzed in Gas Chromatograph equipped with a flame ionization detector and electron capture detector (GC-FID/ECD). The chromatographic method was described elsewhere [15]. The soil before the treatments described above was dried at room temperature (23 ± 2 °C), however the extraction of COCs was carried out following the same methodology.

In the aqueous phases collected, pH COCs and PS concentrations were analyzed. In the absence of surfactant, the COCs were extracted from the aqueous phase using hexane in a volume ratio of 1:1, and GC-FID/ECD analyzed the organic phase. In the presence of E3, the COCs were analyzed directly from the aqueous phase after dilution of the sample with MeOH (volume ratio 1:10). The oxidant in the aqueous phase was analyzed by potentiometric titration (Metrohm, Tiamo 2.3) using a titrant solution of sodium thiosulfate. A Basic 20-CRISON pH electrode determined the pH.

3. Results and discussion

3.1. Alkaline pretreatment

The COCs composition in F and G soil fractions after the alkaline treatment is summarized in Table SM-1 in the [supplementary material](#). In slurry and column experiments, the alkaline treatment converted the non-aromatic cyclic chlorinated HCHs-PentaCXs and HexaCXs-HeptaCHs, respectively, in TCBs and TetraCBs. as described elsewhere [15,26]. These compounds were produced by the dehydrochlorination of the non-aromatic COCs in the alkaline pretreatment. As shown in Table SM-1, the COCs molar content in soils is similar before and after the alkaline treatment, but the average molecular weight of COCs in soils has been reduced due to reactions schematized in Figure SM-2.

Although the soil fractions F and G have different COCs content, the COCs distributions are similar, as shown in Figure SM-3. After alkaline treatment, COCs removed from the soil phase (in slurry and column experiments) were a small fraction (less than 2%) of the initial COCs in soil.

3.2. Slurry experiments

The amount of COCs (in mmol) in the aqueous and soil phases in the presence and absence of surfactant (runs B1, B2, B3 and B4) before the oxidant addition (zero time) are plotted in Fig. 1. As can be seen, the concentration of COCs in the aqueous phase remarkably increased by adding surfactant. The surfactant promotes the desorption of COCs from the soil [16], Wang et al., 2019a,2019b, [16,21]]. The solubilization of hydrophobic organic compounds is carried out by micelles formed by the surfactant molecules in the aqueous phase [21,31]. COCs solubilization in micelles is expected as the surfactant concentrations used here

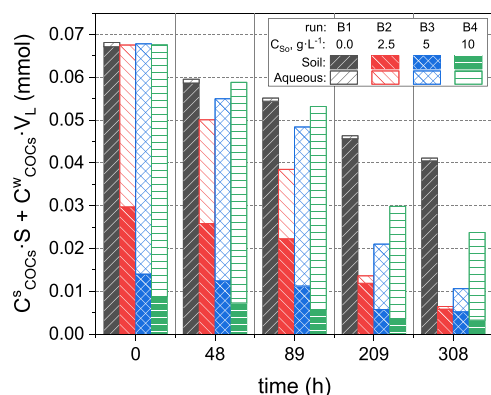


Fig. 1. Total amount of COCs (mmol) in soil (solid bars) and aqueous phases (lined bars) at different reactions times and initial surfactant concentration. $C_{PSO} = 210 \text{ mmol} \cdot \text{L}^{-1}$, $C_{NaOH} = 420 \text{ mmol} \cdot \text{L}^{-1}$ and $V_L/W = 10 \text{ L} \cdot \text{kg}^{-1} = 10$, with $V_L = 20 \text{ mL}$ $W = 2 \text{ g}$ and $(C_{COCs_{soil}})_0 = 33.8 \text{ mmol kg}^{-1}$.

were higher than CMC of E3 ($\text{CMC} = 80 \text{ mg} \cdot \text{L}^{-1}$) [13,45,46]. The higher the initial surfactant concentration, the higher the solubilization of COCs in the aqueous phase. However, the solubilization increases more slowly when the surfactant concentration increases, confirming the Langmuir type isotherm noticed elsewhere [16]. In the absence of surfactant (B1) solubilized COCs are less than 2% of the initial COCs in soil. Adding 2.5, 5, and $10 \text{ g} \cdot \text{L}^{-1}$ of surfactant, the solubilized COCs are 56%, 80% and 88% of the initial COCs in soil, respectively.

Moreover, surfactant adsorption should be considered. As was previously reported, the surfactant added in the aqueous phase is adsorbed in polluted soil, reducing the amount of active surfactant in the aqueous phase. After the surfactant addition, a new equilibrium of surfactant and COCs are reached between the aqueous and soil phases. Considering the results in previous works [16], surfactant concentrations in soil when equilibrium is reached (at zero time) are calculated, being approximately 11000, 20100, 23900, $\text{mg} \cdot \text{kg}^{-1}$ in runs B2, B3 and B4, respectively (zero time). Taking into account that $V_L/W = 10$, the surfactant adsorption only changes the active surfactant concentration significantly in the aqueous phase when the initial surfactant added was $2.5 \text{ g} \cdot \text{L}^{-1}$ (B2 run). In run B2 the surfactant concentration in the aqueous phase at equilibrium conditions was calculated as $1.4 \text{ g} \cdot \text{L}^{-1}$. In runs B3 and B4, negligible differences between the initial surfactant added and the active surfactant concentration in the aqueous phase were obtained when the equilibrium was reached (zero time). The active surfactant concentration was defined as the concentration of virgin surfactant with the same COCs solubilization capacity as that observed in the surfactant aqueous solutions after oxidation.

The partition equilibrium of COCs between the aqueous and soil phases is defined in Eq. (1) as:

$$K_D = \frac{C_{COCs_{soil}}}{C_{COCs_{aq}}} \quad (1)$$

Being $C_{COCs_{soil}}$, in (mmol kg^{-1}) , and $C_{COCs_{aq}}$, in $(\text{mmol} \cdot \text{L}^{-1})$, the COCs concentration in the soil and aqueous phases at the corresponding reaction times. In a previous work [16] the partition equilibrium of surfactant and COCs between the soil and the aqueous phase was studied in slurry experiments. It was found that the partitioning equilibrium between phases was achieved in less than 2–3 h [16], and this time is much shorter than reaction times required for COCs abatement. In that way, it can be considered that the equilibrium of COCs and surfactants between soil and aqueous phases is reached with the reaction progress. Corresponding K_D values are calculated and shown in Fig. 2. The partition coefficient remarkably decreases after the surfactant addition. This parameter is influenced by the active surfactant concentration in the aqueous phase, in agreement with previously reported results [16]. The active surfactant in the aqueous phase with at zero and 308 h were

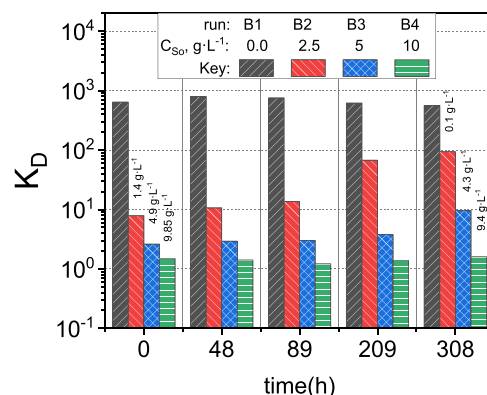


Fig. 2. Partitioning coefficient of surfactant between soil and aqueous phases in $\text{L} \cdot \text{kg}^{-1}$ calculated with Eq. (1) for runs in Table 1. Active surfactant concentration at zero time and after 308 h were measured and given as numbers above the bars.

measured following the procedure given elsewhere [18] by knowing the amount of COCs dissolved in the aqueous solution. These values are shown in Fig. 2 above the bars. As shown in Fig. 2, the active surfactant concentration in the aqueous phase decreases with time due to the unproductive consumption of the oxidant at $2.5 \text{ g} \cdot \text{L}^{-1}$, whilst this reduction was lower.

The molar distributions of COCs in both soil and aqueous phases at equilibrium conditions before the oxidant addition (zero time) are shown in Figures SM-4–6. Similar COCs distributions were obtained in the soil and the aqueous phases of runs B2, B3 and B4. On the contrary, in the absence of surfactant, the percentage of TCBs (in the total COCs) in the aqueous phase is higher than the TCB percentage in the soil phase. Therefore, the surfactant solubilizes the COCs mixture initially adsorbed on the soil as a single phase. On the contrary, in the absence of surfactant, the preferential solubilization of the lighter compounds (TCBs) was noticed, in agreement with previously reported [7,26].

Once the equilibrium between soil and aqueous phases was reached, PS and NaOH were added to the reaction medium. The concentration of COCs in the aqueous and soil phases was analyzed at different reaction times for runs B1 to B4 in Table 1. The total amount of COCs (in mmol) remaining in each phase at different reaction times are also plotted in Fig. 1. The conversion of COCs has been calculated from the sum of remaining COCs in both phases, according to Eq. (2).

$$X_{COCs_{batch}} = \frac{C_{COCs_{soil}} W + C_{COCs_{aq}} V_L}{(C_{COCs_{soil}})_0 W} \quad (2)$$

being $(C_{COCs_{soil}})_0$ the concentration of COCs in the soil before it was in

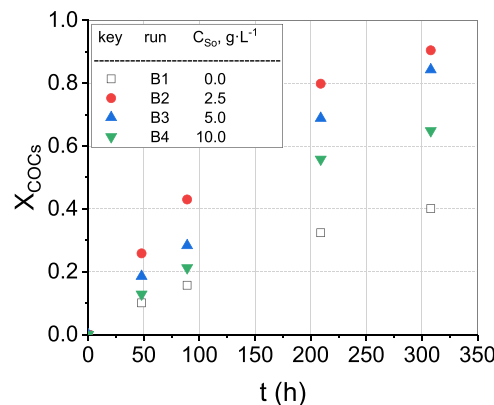


Fig. 3. COCs conversion in slurry runs with reaction time in runs summarized in Table 1.

contact with the aqueous phase. Values of $X_{COCs_{batch}}$ with time are shown in Fig. 3.

As shown in Fig. 1, the sum of COCs in both phases decreased as the reaction time increased. Accordingly, the COCs conversion increases with reaction progress (Fig. 3). When a surfactant is added, a significant decrease in the total COCs in the reaction media is noticed at the final time studied (308 h) compared to the decrease obtained in the absence of surfactant (run B1). The higher conversion observed using surfactant can be explained by the increase of COCs concentration in the aqueous phase. The solubilization capacity of the surfactant improved the availability of COCs to the oxidant in this phase [4,22,24]. Li, Liao et al. Li et al., [22] studied the oxidation of different hydrophobic organic compounds, initially adsorbed in soil samples, using several oxidants in the presence and absence of surfactant. They found that the combination of surfactant and oxidant enhanced the elimination of the contaminants compared with using only the oxidant.

However, an increase in the initial surfactant concentration above 2.5 g L^{-1} did not result in a higher conversion of COCs, as shown in Fig. 1 and Fig. 3. On the contrary, COCs conversion decreases when the initial surfactant concentration rises from 2.5 to 5 g L^{-1} . The X_{COCs} values at 380 min were 0.4, 0.9, 0.86 and 0.62 when initial surfactant concentration added was 0, 2.5, 5 and 10 g L^{-1} . This trend of COCs conversion with the surfactant concentration increase was also noticed in the aqueous phase in the absence of soil [5], Wang et al., 2019a,2019b). It can be related to higher surfactant concentrations that prevent COCs oxidation in the micelles. Moreover, higher surfactant concentration in the aqueous phase favours the unproductive consumption of PS to the COCs oxidation. The higher the surfactant concentration, the higher the COCs in solution, the higher the surfactant hindrance to COCs oxidation, and the higher unproductive PS consumption. Therefore, the solubilized COCs is more efficient at lower surfactant concentration because higher surfactant concentration hinders the oxidation of COCs in the micelles [5,41]. Therefore, the decrease in the COCs conversion with the increase of the surfactant concentration, Fig. 3, was due to the protective effect of the micelles on the COCs solubilized inside of the micelles [41]. However, the lower the surfactant in the aqueous phase, the lower the COCs solubilized. As a result, there is an optimal value of surfactant in the aqueous phase to increase the overall oxidation rate of COCs, in agreement with previously reported [2,3,5].

The PS conversion in runs in Table 1 is shown in Figure SM-5. The higher the initial surfactant concentration, the higher the PS conversion. In the absence of surfactant (run B1), the PS conversion increases gradually with time. On the contrary, the higher the initial surfactant concentration, the higher the initial consumption of PS. The initial fast consumption of PS could be related to the unproductive consumption of PS by reaction with the surfactant micelles in the aqueous phase. However, the increase in PS conversion is not linear with the surfactant concentration added, in agreement with previously reported in the soil absence [19].

With the results in Figure SM-5 and Fig. 3, it can be deduced that higher PS consumption does not imply higher COCs conversion. In fact, despite the lower PS consumed in B2, COCs conversion obtained in runs B3 and B4 are lower than that obtained in B2, confirming the relevance of unproductive PS consumption at higher surfactant dosages. The PS consumed per mol of COCs reacted (θ_{PS}) was calculated by Eq. (3):

$$\theta_{PS_{batch}} = \frac{V_L(C_{PS0} - C_{PS})}{[(C_{COCs})_0 W - C_{COCs_{soil}} W + C_{COCs_{aq}} V_L]} \quad (3)$$

where C_{PS0} and C_{PS} are the PS concentrations (mmol L^{-1}) in the aqueous phase at zero time and at the corresponding reaction time, respectively. The time profiles of θ_{PS} in runs B1 to B4 are plotted in Fig. 4.

It was noticed that higher $\theta_{PS_{batch}}$ are obtained when surfactant concentration increases, confirming the competitive reaction between surfactant and COCs for the oxidant in the aqueous phase. However, lower values of θ_{PS} are obtained in the presence of soil compared to those

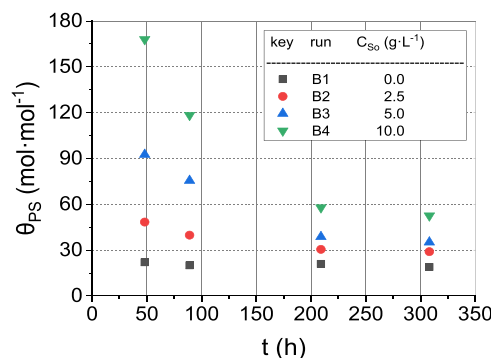


Fig. 4. Consumption of PS per sum of the total COCs consumed in slurry runs summarized in Table 1.

obtained previously in the soil absence [19]. This difference can be due to the contribution of the reaction between adsorbed COCs and PS to overall COCs conversion. The direct reaction of COCs adsorbed on the soil surface with the oxidant has been reported in the absence of surfactant [17]. Thus, it can be inferred that both dissolved COCs in the aqueous phase and adsorbed COCs react with the oxidant.

In the presence of surfactant, the partition coefficient increases with time, as shown in Fig. 2. This rise corresponds to a surfactant decrease in the aqueous phase with time. Two reasons can explain this drop. The first reason is the surfactant oxidation in the aqueous phase since PS can react with surfactant and COCs in a competitive reaction, as was reported in experiments performed in the absence of the soil [26]. The second reason is the oxidation of adsorbed COCs with time, causing a new equilibrium between soil and aqueous phases, resulting in continuous adsorption of surfactant micelles with COCs from the aqueous phase to the soil phase, and the corresponding decrease of the surfactant in the aqueous phase. Considering the initial surfactant concentration in the aqueous phase and the VL/W ratio used, the effect of surfactant adsorption on active surfactant concentration change in the aqueous phase is more relevant in B2 than in B3 and B4. This fact explains that the rise in K_D in Fig. 2 follows the trend $B2 > B3 > B4$. The higher the surfactant concentration added, the lower the K_D increase with the reaction time.

The molar distributions of COCs in both phases at 308 h of reaction time in runs B1, B2, B3, and B4 are shown in Figure SM-6 (aqueous phase) and Figure SM-7 (soil phase). These figures also provide the initial molar distribution of COCs in the initial soil (fraction F). Comparing the results in Figure SM-4 (zero time), Figure SM-6 and Figure SM-7, it is found that when a surfactant is added, similar COCs distributions were found in the initial soil, aqueous phase and soil phase with the reaction progress.

3.3. Column experiments

The column experiments were carried out with the soil fraction G (0.25–0.2 mm) with higher permeability than fraction F ($<0.25 \text{ mm}$), allowing experiments with water flow. As mentioned previously, soil fractions F and G have a similar distribution of COCs. The initial concentration of contaminants in the F fraction was higher than in the G fraction (Table SM-1).

In the column experiments, the surfactant (E3) concentrations tested were 0 (C1), 5 (C2) and 10 g L^{-1} (C3) maintaining the oxidant and activator concentration in the solution fed in 210 and 420 mmol L^{-1} , respectively. The experimental procedure has been described in the Experimental section, and the operating conditions are summarized in Table 2.

The mmol of COCs in each flushed pore volume (PV1 to 4, shown in Table 2) after remaining a specific time in the soil column is shown in Fig. 5a. The mmol of COCs flushed from the column with the injection of

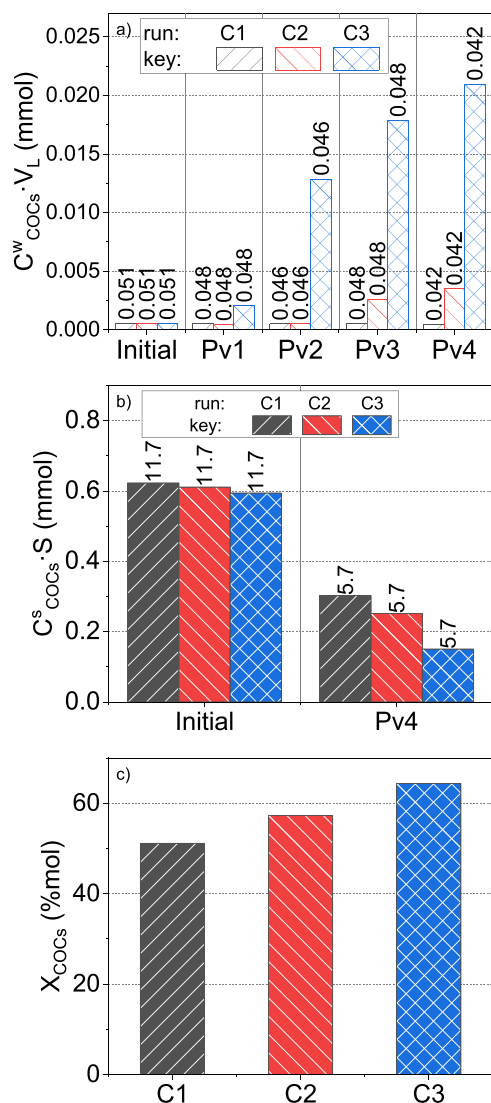


Fig. 5. (a) mmol of COCs in each Pore Volume flushed from the column (b) mmol of COCs in the initial soil in the column and in the soil after the column disassembling. (c) COCs conversion calculated by Eq. (4) after column disassembling. The concentration of COCs as $\text{mmol}\cdot\text{L}^{-1}$ (aqueous phase) or $\text{mmol}\cdot\text{kg}^{-1}$ (soil phase) are indicated at the top of the bars (experimental conditions in Table 2).

the first pore volume (named as initial) is also shown in Fig. 5a. The amount of COCs (mmol) in the initial soil placed in the column and the amount of COCs (mmol) remaining in the soil after the columns disassembling are shown in Fig. 5b. The COCs concentration ($\text{mmol}\cdot\text{L}^{-1}$) in the aqueous phase of each PV flushed and the COCs concentration in soil ($\text{mmol}\cdot\text{kg}^{-1}$) after the column disassembling are indicated at the top of the bars.

As shown in Fig. 5a, the surfactant injected into the column improved the solubilization of the COCs in the aqueous phase. The higher the surfactant concentration in the pore volume injected, the higher the solubilized COCs in the pore volume extracted. Moreover, as more pore volumes with a surfactant are injected, more COCs are solubilized in the Pore Volume extracted. This last observation can be mainly related to surfactant adsorption in soil. As more pore volumes with a surfactant are injected or higher surfactant concentrations are injected in the column, the partition equilibrium of surfactant between the soil and aqueous phases yields higher surfactant concentration and COCs dissolved in both phases. In the absence of surfactant injections (run C1) the COCs concentration in the four pore volumes flushed have

similar values.

The total conversion of COCs in each column after the column disassembling has been calculated considering the mmol remaining in the soil and the mmol of COCs eluted in the four-pore volume flushed, according to Eq. (4). The remanent amount of COCs in soil was measured at the bottom, centre and top, finding similar values between the different fractions (standard deviation lower than 5%).

$$X_{COCs} = \frac{((C_{COCs})_o - C_{COCs})W - \sum_{1}^{4VP} C_{COCsVP}VP}{(C_{COCs})_o W} \quad (4)$$

Overall COCs conversion after column disassembling is shown in Fig. 5c. As can be seen, the simultaneous injection of E3 and oxidant (experiments C2 and C3) promotes COCs oxidation. Accordingly, the higher the concentration of surfactant injected, the higher the total conversion obtained in the column experiments. There is a significant conversion of the COCs in C1 without surfactant. In a previous work [17], an ISCO treatment was applied to the same soil in slurry way, being noticed that reaction took place not only in the aqueous phase but also in the soil surface.

The COCs distributions in each PV flushed, and the COCs molar distribution in the soil after the column disassembling are plotted in Fig. 6. In run C1 (carried out in the absence of the surfactant, ISCO), there is lower solubilization of COCs in the aqueous phase, with similar values of solubilized COCs at all the pore volumes flushed. Moreover, in C1 the TCBs in soil are selectively dissolved to TetraCBs, as noticed in slurry runs in the absence of surfactant (Figure SM-6). This selectivity in the COCs solubilization was also observed in the first and second PV flushed from the column C2 ($5\text{ g}\cdot\text{L}^{-1}$ of surfactant was injected into the column). The amounts and distribution of COCs solubilized in these first two pore volumes in C2 are like the corresponding values found in C1 (in the absence of surfactant). On the other contrary, the molar distribution of COCs in flushed PV3 and PV4 (C2) was similar to that found in initial soil. When the surfactant concentration in the pore volume injected was $10\text{ g}\cdot\text{L}^{-1}$ (column C3), the molar distribution of COCs in all the PV flushed was always like the initial molar distribution of COCs in the soil placed in the column.

As shown in Fig. 5, the concentration of solubilized COCs increases with the number of PVs injected. Using $10\text{ g}\cdot\text{L}^{-1}$ of surfactant (C3), the highest solubilization of COCs in the aqueous phase was noticed (up to $2\text{ mol}\cdot\text{L}^{-1}$ in the four pore volume flushed). As a first approach, the surfactant remaining in the aqueous phase of each PV flushed can be calculated from the isotherms provided in previous work [16]. Taking into account the desorption isotherms in the Molar Solubilization Ratio in the aqueous phase is approximately linear in the range $0.2\text{--}2\text{ g}_{\text{surf}}\cdot\text{L}^{-1}$. A value of 2 mM of COCs in the aqueous phase (noticed in PV4, C3) can be approximately related to $2\text{ g}\cdot\text{L}^{-1}$ of surfactant in the aqueous phase if desorption equilibrium is faster than oxidation in the aqueous phase. From results in Fig. 5 and data previously reported [19] the surfactant in the aqueous phase in all the PV and columns have been estimated and values are shown in Figure SM-8. As can be seen, the maximum surfactant concentration in any of the PVs flushed in C2 and C3 was lower than $2\text{ g}\cdot\text{L}^{-1}$. The low solubilization of COCs in flushed PV1 and PV2 in C2, and the selective solubilization of TCBs suggest the absence of surfactant in the aqueous phase, explained by the surfactant adsorption.

The first and fourth pore volumes injected remains similar times in the column before being flushed. As can be seen in Fig. 5 and Figure SM-8, COCs solubilized and active surfactant concentration in flushed PV4 in C3 were higher than those found in VP1. The increase in solubilized COCs and surfactant concentrations in solution with successive PVs indicates that surfactant adsorption is the cause of these trends.

The column experiment also investigated the oxidant consumption in the absence (C1) and presence (C2, C3) of surfactant. The conversion of PS in each PV injected is shown in Fig. 7a. In C1, C2 and C3, the PS conversion in the flushed PV1 and PV4 is higher than in PV2 and PV3.

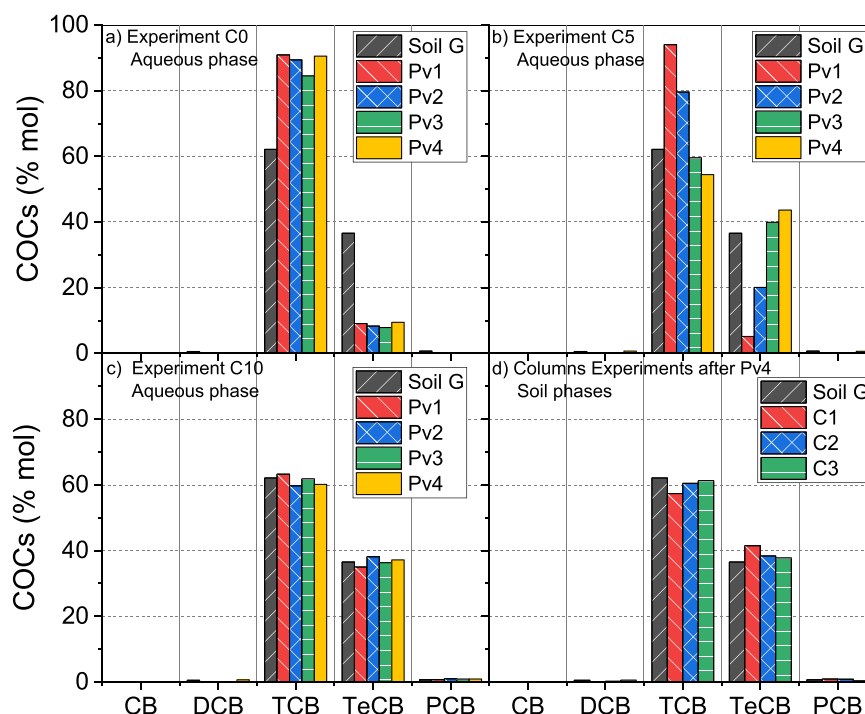


Fig. 6. Molar distribution (%) of COCs a) in the aqueous phase in column C0, b) in the aqueous phase in column C1, c) in the aqueous phase in column C2 d) in the soil after column disassembling. Black bars correspond to the soil placed in the column after alkaline treatment.

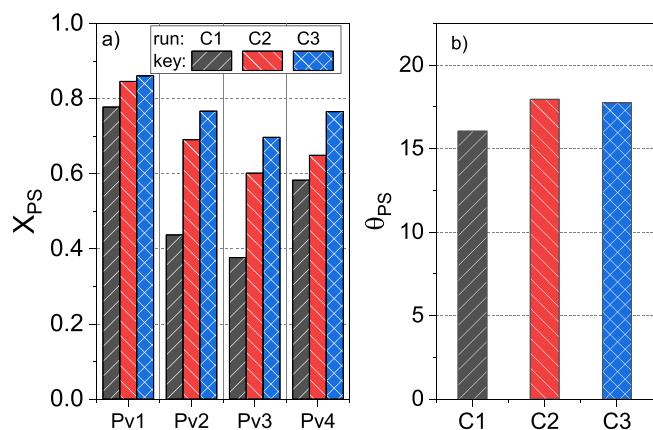


Fig. 7. (a) conversion of PS at each PV injected. (b) θ_{PS} coefficient (mmol of oxidant consumed per mmol of COCs by Eq. (5)).

This fact is explained considering that PV1 and PV4 remained in the column 113 h, more than double that of PV2 and PV3 (48 h). Moreover, the higher the surfactant concentration injected, the higher the PS conversion obtained at each PV. However, differences in PS conversion obtained in PV1 among C1, C2, and C3 are relatively low, relating to the low amount of surfactant in the column. The differences increase remarkably in PV2 and PV3.

On the other hand, PS conversion in PV1 is lower than PS conversion in PV4 in all the columns. Considering that injected PV1 and PV4 remained the same time in the column, the lower PS conversion obtained in PV4 could be due to the lower COCs concentration remaining in the soil when PV4 is injected. However, the surfactant adsorbed is higher in PV4 than in PV1, indicating that the surfactant adsorbed do not produce a substantial consumption in PS.

The ratio of PS consumed to COCs oxidized ($\theta_{PS, column}$) has been calculated according to Eq. (5), and those are shown in Fig. 7b.

$$\theta_{PS, column} = \frac{\sum_{VP} (C_{PS0} - C_{PS}) VP}{C_{COCs0} X_{COCs} W} \quad (5)$$

being C_{COCs0} the initial concentration of COCs adsorbed in soil, and X_{COCs} is the COCs conversion calculated with Eq. (4).

As can be seen in Fig. 7b, $\theta_{PS, column}$ in C2 and C3 are slightly higher than the observed in the run without surfactant C1. These differences can be explained by the competition between COCs and surfactants for the oxidant. However, the $\theta_{PS, column}$ values are much lower than noticed in slurry runs for the similar COCs conversion (Fig. 4). The ratio VP/W in the column is approximately 0.2 (Table 2), and VL/W in slurry runs (Table 1) was 10. Therefore, the higher values of $\theta_{PS, batch}$ can be explained by the higher contribution of the surfactant oxidation in the aqueous phase in the slurry runs. On the other hand, the slight differences noticed in $\theta_{PS, column}$ between C1, C2 and C3 suggest that the surfactant adsorbed has a small contribution on $\theta_{PS, column}$. The total amount of surfactant added in the four PVs per mass of soil was 0, 4 and 8 $g_{suf} kg_{soil}^{-1}$ in C1, C2 and C3, respectively. The active surfactant concentration in the aqueous phase was always lower than 2 $g \cdot L^{-1}$ (Fig. 5 and Figure SM-8). The differences between surfactant concentration values in injected PVs and flushed PVs are due mainly to surfactant adsorption.

4. Conclusions

This work studied the simultaneous addition of surfactant (E3) and oxidant (PS alkali activated) in the remediation of a real highly polluted soil from lindane wastes. The composition of the initial mixture of chlorinated compounds in soils changes after alkaline treatment, reducing the chlorinated non-aromatic compounds initially present in the soil to chlorobenzenes.

The simultaneous addition of surfactant and oxidant enhances the COCs reduction in both experiments (slurry and column). However, surfactant adsorption modifies the partition equilibrium of surfactant and COCs between soil and aqueous phases. It was noticed that there is an optimal value of surfactant concentration in the aqueous phase. If

surfactant concentration in the aqueous phase increases, the solubilization of COCs in the aqueous phase rises but the hindrance of the oxidation of COCs in the micelles also becomes more critical. Moreover, the reaction of PS with the COCs adsorbed in the soil have a remarkable contribution to the COCs abatement in the absence of surfactant. The high soil surface per mass of soil (due to interbedded clay) probably facilitates the reaction between COCs and PS on the soil surface. The surfactant adsorption in soil does not seem to hinder or decrease the COCs oxidation on the soil surface in the column runs.

The treatment of the Sardas landfill by S-ISCO treatment using E3 as surfactant and PS activated with NaOH seems to be an effective technology, and promising results have been obtained in this work. However, to optimize the S-ISCO process, further study is necessary. The surfactant concentration injected must be enough to increase the solubilization of the COCs but maintain the surfactant concentration under a selected value in the aqueous phase (in this work, about $1.5\text{--}2\text{ g}\cdot\text{L}^{-1}$) to avoid unproductive oxidant consumption. Therefore, the surfactant concentration and the strategy of PV injections will depend on the soil properties (surfactant adsorption isotherms, COCs desorption isotherms) and the COCs and surfactant properties. In general, a higher concentration of surfactant in the first injections can be recommended. Monitoring of surfactant and COCs concentration with time will be required for further injections.

CRedit authorship contribution statement

Raúl García-Cervilla: Methodology, Investigation, Writing – original draft. **Aurora Santos:** Funding acquisition, Resources, Conceptualization, Supervision. **Arturo Romero:** Funding acquisition, Resources. **David Lorenzo:** Conceptualization, Methodology, Supervision, Original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2022.107625](https://doi.org/10.1016/j.jece.2022.107625).

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