



Abatement of chlorobenzenes in aqueous phase by persulfate activated by alkali enhanced by surfactant addition

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ABSTRACT

Sites polluted by dense non-aqueous phases (DNAPLs) constitute an environmental concern. In situ chemical oxidation (ISCO) application is limited since oxidation often occurs in the aqueous phase and contaminants are usually hydrophobic. In this work, ISCO enhanced by the surfactant addition (S-ISCO) was studied for a complex liquid mixture of chlorinated organic compounds (COCs) using persulfate (PS) activated by alkali (PSA) as oxidant and Emulse-3® as a commercial non-ionic surfactant. The reaction between E3 and PSA was investigated in the absence and presence of solubilized COCs in the following concentration ranges: COCs 1.2–50 mM, PS 84–336 mM, NaOH:PS molar ratio of 2, and surfactant concentration 1–10 g·L⁻¹.

In the experiments carried out in the absence of COCs, the unproductive consumption of PS was studied. The higher the surfactant concentration, the lower the ratio PS consumed to the initial surfactant concentration due to more complex micelle structures hindering the oxidation of surfactant molecules. This hindering effect was also noticed in the oxidation of solubilized COCs. The reduction of chlorobenzenes by PSA was negligible at surfactant concentrations above 2.5 g·L⁻¹, independently of the COCs concentration solubilized. Instead, a surfactant concentration of about 1 and PS concentration of 168 mM yielded a significant decrease in the time required to abate a mass of DNAPL, compared with an ISCO process, with a bearable increase in the unproductive consumption of PS.

1. Introduction

Sites polluted by organic compounds are an environmental issue, contaminating soil and groundwater (van Liedekerke et al., 2014). In many cases, this contamination originated from spills of organic compounds from storage tanks (fuels, solvents) or from dumping in unsafe conditions (Interstate Technology Regulatory Council, 2000; Mobile et al., 2016; Soga et al., 2004; Tomlinson et al., 2017). On the other hand, the low water solubility of organic compounds present in spills and/or releases can originate their presence in the subsurface, as non-aqueous phase liquids (NAPLs) (Brusseau, 2013; CLU-IN, 1991; Tomlinson et al., 2017).

In situ chemical oxidation (ISCO) is one of the technologies that have been successfully applied in the remediation of groundwater contamination with organic compounds (Bacocchi et al., 2014; Siegrist et al., 2011). In the ISCO treatment, the oxidants are injected into the subsurface, reacting with the contaminants dissolved in the aqueous phase (Albergaria and Nouws, 2016). Therefore, the solubility of the organic compounds and the contact between the aqueous and organic phases are

critical factors for the ISCO process to be time- and cost-effective. However, this contact is often hindered because the organic phase is a residue trapped tightly in subsurface pores or fractures (Schaefer et al., 2009, 2016). Groundwater in contact with this phase generates a contamination plume that will persist until the removal of the organic phase, the contamination enduring for decades (Stroo et al., 2012).

A recently evaluated technology is the simultaneous injection of oxidants and surfactants into the subsurface (S-ISCO) (Besha et al., 2018; Lanoue et al., 2011). The surfactant increases the solubility of the organic compound in the aqueous phase and improves its oxidation rate. Thereby, S-ISCO decreases the time required to remove the residual organic phase trapped in the soil (Dahal et al., 2016). However, surfactants are organic molecules, which may compete with the contaminant for the oxidant (Bouid et al., 2017; Wang et al., 2017). The unproductive consumption of oxidants by the surfactant also generates a loss of surfactant that decreases the solubility of the organic compound in the aqueous phase (García-Cervilla et al., 2021).

The higher the surfactant concentration, the more complex the micelle aggregation structures are expected (Acharya et al., 1997; Lin

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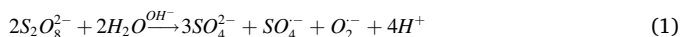
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et al., 2011; Rosen and Kunjappu, 2012). These structures could affect the reactivity of surfactants and solubilized contaminants against the oxidant. Besides, the selective oxidation of solubilized organic compounds in the micelle structure will also depend on the relative reactivity of both compounds (contaminant and surfactant) to the oxidant.

The oxidizing system and the characteristics of the organic compounds and surfactants will influence the efficiency of the process. In the still-limited studies in the literature on S-ISCO tests, oxidants such as persulfate (PS) and hydrogen peroxide or permanganate have been analysed in the removal of polyaromatic hydrocarbons (PAHs) (Bai et al., 2019; Bouzid et al., 2017; Li et al., 2019; Petitgirard et al., 2009; Qiu et al., 2019; Wang et al., 2017), total petroleum hydrocarbons (TPHs) (Lominchar et al., 2018; Wang et al., 2013) or organic phases formed by single compounds: toluene, (Long et al., 2014), tetrachloroethylene (Zheng et al., 2016), trichloroethylene (Li, 2004; Tsai et al., 2009). Most of these works generally focus on contaminant removal, paying less attention to unproductive oxidant consumption and loss of surfactant capacity.

The effect of surfactant and oxidant concentration on the selective COCs oxidation, unproductive consumption of oxidants and loss of surfactant capacity has not been previously studied in literature. However, the proper design of S-ISCO for a field application strongly depends on the interaction between surfactants, contaminants, and oxidants in the reaction media. Surfactant and organic pollutants in the aqueous phase compete for the oxidant, causing unproductive consumption of the oxidant and the loss of the surfactant capacity.

In this work, PS was selected as an oxidant since it is stable in the soil, allowing the transport of the injected fluid. PS can be activated by iron, heat or alkali. However, there is a lack of studies with alkali-activated persulfate (PSA) as an oxidizing system when surfactants are used. The alkali used as an activator (NaOH) generates a pull of radicals (Eq. (1) and (2)), being hydroxyl, OH^\bullet and superoxide, O_2^- , the prominent radicals at $pH > 12$ (Furman et al., 2010). Hydroxyl radicals produced in PSA are non-selective and strong oxidants (Gligorovski et al., 2015). Superoxide radicals play a non-negligible role in abating chlorinated pollutants (Checa-Fernandez et al., 2021; Dominguez et al., 2019).



PSA can be applied in soils with a neutral or alkaline pH. On the contrary, the addition of iron as an activator would require, in these cases, the addition of chelating agents (Pardo et al., 2015b; Rodrigo and Dos Santos, 2021). Chelating agents are organic compounds that can also compete with the pollutant for the oxidant (Pardo et al., 2015a) decreasing the efficiency of the process. On the other hand, other PS activations such as light (Bai et al., 2019) or temperature (Wang et al., 2017) cannot be applied in the subsoil.

The selected surfactant, Emulse 3 (E3), is a non-ionic and biodegradable commercial surfactant with a lower CMC and higher molar solubility ratio than anionic surfactants, such as SDS (García-Cervilla et al., 2020a). In addition, it was found that SDS blocks the oxidation of the dissolved COCs. Electrostatic repulsions among the sulfate groups of the surfactant and hydroxide and PS anions hinder the transport of PS and OH^- into the micelle and, consequently, the formation of radicals that attack the contaminants (García-Cervilla et al., 2021).

This work analyses the influence of the oxidant, surfactant, and contaminant concentration on removing an organic phase formed by different chlorinated organic compounds (COCs) through the simultaneous addition of PSA and surfactant. In this case, chlorobenzenes (chlorobenzene, dichlorobenzene, trichlorobenzene, tetrachlorobenzene) have been used as the Dense NAPL phase (DNAPL). This organic phase composition has been chosen to include compounds that frequently appear in spills or leaks (Wang and Jones, 1994) (Boutonnet et al., 2004; Djohan et al., 2005; Lecloux, 2003; Santos et al., 2018a; van

Wijk et al., 2006; Van Wijk et al., 2004). Moreover, these compounds have different solubility in the aqueous phase (Lorenzo et al., 2020).

The results obtained by S-ISCO are analysed and compared with those obtained in the absence of surfactant (ISCO). For this purpose, an instantaneous equilibrium between the aqueous and organic phases was assumed in the ISCO treatment. This hypothesis overestimates the effectiveness of the ISCO treatment since this equilibrium is not reached quickly under subsurface conditions.

2. Material and methods

2.1. Chemicals

The DNAPL used was formulated from commercial compounds. The COCs selected were purchased from Sigma-Aldrich with analytical quality: Chlorobenzene (CB), 1,2-dichlorobenzene (1,2-DCB), 1,2,3-trichlorobenzene (1,3,5-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), 1,2,3,5-tetrachlorobenzene (1,2,3,5-TeCB). The purity of all commercial COCs used was higher than 99.9%.

The DNAPL was prepared by mixing the selected COCs in a 20-mL glass vial with a PTFE screw cap. The molar (x_j) and mass (w_j) fractions of each j COC in DNAPL were summarized in Table 1. Five vials were performed in total.

Bicyclohexyl (C12H22, Sigma-Aldrich) and tetrachloroethane (C2H2Cl4, Sigma-Aldrich) were used as internal standards (ISTD) in GC/FID/ECD analysis.

The surfactant selected was E-Mulse 3® (E3), supplied by EthicalChem®. This biodegradable polyethoxylated surfactant was successfully applied in the laboratory and full-scale remediation runs with S-ISCO (EthicalChem, 2016n; García-Cervilla et al., 2020a). This surfactant is formulated with limonene as a co-solvent (15–25%).

Sodium Persulfate (PS, Sigma-Aldrich) was used as an oxidant and sodium hydroxide (NaOH, Fisher Scientific) was the activator selected; this system being successfully (PSA) applied in previous studies for chlorobenzenes (García-Cervilla et al., 2020b; Santos et al., 2018b). Potassium iodide (KI, Fisher Chemical), sodium hydrogen carbonate (NaHCO3, Panreac), sodium thiosulfate pentahydrate (Na2S2O3·5H2O, Sigma-Aldrich), and acetic acid (C2H4O2, Sigma-Aldrich) were used for PS quantification. All aqueous solutions were carried out with Milli-Q water.

2.2. COCs solubility with surfactant

The solubilisation of the DNAPL mixture of chlorobenzenes with E3 at basic pH was carried out in 20-mL glass vials with PTFE screw caps. Five aqueous solutions were prepared with different concentrations of E3 (0, 2.5, 5, 10 and 15 $g \cdot L^{-1}$). The alkaline conditions were achieved by adding NaOH (168 mM). An 18-mL volume of this alkaline aqueous solution was added to the corresponded vials. Then, a mass of DNAPL, was added to each vial. Vials were shaken, with a magnetic stirrer, for 5 h. Once the aqueous phase was homogenized, the agitation was stopped for 24 h, which was enough to reach the equilibrium between the aqueous and DNAPL phases (García-Cervilla et al., 2020a). Experiments

Table 1

Molar fraction x_j , and mass fractions, w_j , (as a percentage) of chlorobenzenes in formulated DNAPL. The average molar weight was $165.5 \text{ g} \cdot \text{mol}^{-1}$.

COCs	$x_j \cdot 100$	$w_j \cdot 100$	MW
CB	27.25	18.5	112.5
1,2-DCB	14.03	12.4	147.0
1,2,3-TCB	5.15	34.4	181.5
1,2,4-TCB	31.40	5.6	181.5
1,2,4,5-TeCB	7.91	10.4	216.0
1,2,3,4-TeCB	14.25	18.6	216.0

were carried out in triplicate, and the standard deviation was lower than 5%.

Once the equilibrium was reached, the aqueous phase in those vials without a surfactant addition was extracted with hexane, at a volume ratio of 4 (water):1 (hexane). In those vials with an added surfactant, the aqueous phase was diluted with MeOH (1:10 in volume). GC-FID/ECD was used to analyse these samples.

2.3. Oxidation runs

2.3.1. Unproductive consumption of PS by the surfactant

The unproductive consumption of PS by E3 was studied in wide oxidant and surfactant concentration ranges. The experiments were carried out in 20-mL glass vials with PTFE screw caps simulating as a stirred batch reactor. Vials were shaken intermittently, 2–5 min per day, with a magnetic stirrer to simulate the behaviour of the groundwater in the subsoil with low spatial velocity. An 18-mL volume of an alkaline aqueous solution containing the surfactant was added to the vials. Then, the PS was added as a pure solid (zero time). The concentrations of E3, NaOH and PS tested are summarized in Table S1. At each reaction time, a vial was sacrificed, the pH measured, and the oxidant concentration remaining determined.

2.3.2. Experiments regarding the oxidation of aqueous emulsions (COCs-E3)

Two sets of experiments were carried out to study the influence of surfactant, oxidant, and solubilized COCs in the S-ISCO treatment.

In the first set, 250 mL of alkaline aqueous solutions of E3 surfactant (5 or 10 g·L⁻¹) were saturated with DNAPL. The mass of DNAPL added was slightly higher than that required for total saturation to minimize the amount of non-dissolved organic phase. The mixtures were gently shaken with a magnetic stirrer for 24 h. Oxidation runs were carried out in vials with PTFE screw caps containing 18 mL of these saturated solutions. The reaction started after adding PS as a pure solid to the vials. Different concentrations of PS were tested using a NaOH:PS molar ratio of 2. Experimental conditions are summarized in Table 2. Vials were intermittently shaken with a magnetic stirrer (2–5 min per day). At different reaction times, solubilized and total COCs in vials were analysed by GC-FID/ECD. The solubilized COCs in the aqueous phase were measured by taking an aliquot of 0.1 mL of the supernatant (after 5 h of settling). The total concentration of COCs (dissolved and precipitated) was measured by taking a sample of the well-homogenized emulsion after vigorous stirring and diluting this volume in MeOH (volume ratio 1:10). The oxidant concentration and pH were also determined at each reaction time. Two replicates were carried out for each reaction time, and differences were lower than 10%.

The second set of experiments was carried with non-saturated emulsions in COCs. An 18-mL volume of the corresponding aqueous solution with the appropriate concentrations of E3 and NaOH was added to 20-mL glass vials with PTFE screw caps. Then, to obtain the desired concentration of COCs, the corresponding mass of DNAPL was added to each vial. Vials were strongly agitated with a magnetic stirrer. Once the COCs were entirely solubilized in the aqueous phase, PS was added as a pure solid (zero time). Several reaction times were used for each run, a vial being sacrificed at each reaction time. Vials were intermittently stirred (2–5 min per day) with a magnetic stirrer. Experimental conditions are summarized in Table 2. The solubilized and total COCs and PS concentrations were determined at different reaction times, and the pH of the emulsion was measured. Two replicates at each reaction time were performed, and differences were lower than 10%. Besides, two experiments were carried out without surfactant (ISCO treatment) using 168 mM of PS and 2.4 and 3.6 mM of initial COCs. The later concentrations were not completely solubilized in water, forming an organic phase. The reactions were carried out in 20 mL sealed-glass vials, and the reaction mixture in the vial was dissolved in MeOH (1:10) at each reaction time.

Table 2

Experimental conditions of the oxidation runs with COCs concentrations using a NaOH:PS of 2 mol·mol⁻¹.

Emulsion.	C _{so} (g·L ⁻¹)	COCs (mM)	CPS _o (mM)	reaction time (h)
S-ISCO: Saturated	5	24.9	84	0–450
			168	
			336	
	10	59.5	84	0–450
			168	
			336	
S-ISCO: Non Saturated	1	1.2	84	0–144
			168	
			252	
		2.4	84	
			168	
			252	
	2.5	1.2	84	0–144
			168	
			252	
		2.4	84	
			168	
			252	
5	1.2	84	0–144	
		168		
		252		
	2.4	84		
		168		
		252		
10	1.2	84	0–144	
		168		
		252		
	2.4	84		
		168		
		252		
ISCO	0	2.4	0–256	
		3.6		

2.4. Analysis

The aqueous phase, with or without surfactant, was diluted at 1:10 in MeOH or extracted with 1:4 n-hexane (volume ratios), respectively. COCs in MeOH or hexane were quantified by Gas chromatography coupled with a Flame Ionization Detector and an Electron Capture Detector (GC-FID/ECD). The chromatographic method is described elsewhere (García-Cervilla et al., 2020b; Santos et al., 2018a).

Moreover, gas chromatography coupled with a mass spectrometer detector (GC-MSD) was used to identify some intermediates in the oxidation of the surfactant. The GC/MS data were processed using Software MassHunter B08 (Agilent Technologies), and the identification of the compound was carried out by comparing the mass spectra with the NIST library records (Babushok et al., 2007) (NIST011 version).

PS in aqueous phases was measured by Iodometric titration with sodium thiosulfate. A potentiometric titration analyser (Metrohm, Tiamo 2.3) was used. A basic 20-CRISON pH electrode measured the pH. Micrographs of the emulsions were taken with an electron microscope equipped with a Gatan liquid nitrogen specimen holder for cryo-EM (see Supplementary Material). The hydrodynamic diameter was measured with a Nano Zetasizer (Malvern).

3. Results and discussions

3.1. Solubility of COCs

The solubilisation of COCs in pure alkaline water or alkaline surfactant solutions was investigated. The concentration of solubilized COCs (sum of chlorobenzenes) in the aqueous phase (C_{COCs}) vs the initial surfactant concentration used is plotted in Figure S1. The amount of DNAPL added was the minimum to ensure the saturation of the aqueous solution. Therefore, the surfactant absorbed in the non-solubilized organic phase at equilibrium conditions can be neglected, considering the equilibrium surfactant concentration as the initial surfactant concentration. The solubility of the sum of COCs in pure water without surfactant addition was 0.52 mM. In the presence of surfactant, the higher C_{So} , the higher the COCs concentration (C_{COCs}) dissolved in the aqueous phase, as can be seen in Figure S1. A linear relationship was found between C_{COCs} and C_{So} , under the experimental conditions tested. Solubilisation capacity of the surfactant (SCS), defined as the ratio between the solubilized COCs in the aqueous surfactant emulsion and the amount of E3, can be calculated as the slope of the trend in Figure S1, yielding a value of $5.7 \text{ mmol}_{COCs} \cdot \text{g}_{So}^{-1}$. This value was similar to that obtained with a real DNAPL of chlorinated compounds, including chlorobenzenes and hexachlorocyclohexanes (García-Cervilla et al., 2020a) at neutral and alkaline pHs ($4.33 \text{ mmol}_{COCs} \cdot \text{g}_{So}^{-1}$ in both cases).

The molar distribution of solubilized COCs in the presence or absence of surfactant is compared in Figure S2 with the molar distribution of the COC mixture in DNAPL. As can be seen, in the absence of surfactant, CB was selectively solubilized in the aqueous phase. This finding can be explained by the higher solubility of this CB in water (Lorenzo et al., 2020). The solubility of each chlorobenzene, j , in the alkaline aqueous phase without surfactant can be calculated with Eq. (3).

$$S_j \gamma_j = \frac{C_{j, aq}}{x_j} \quad (3)$$

$S_j \gamma_j$, x_j , $C_{j, aq}$ being the solubility, activity coefficient, molar fraction of j in DNAPL and concentration in the aqueous phase, respectively, of a

compound j . Values of $S_j \gamma_j$ at alkaline conditions are summarized in Table S2. By comparison of the results at alkaline pH (>12) with those obtained elsewhere at neutral pH (Lorenzo et al., 2020), it can be seen that $S_j \gamma_j$ is lower at alkaline conditions. The solubility of COC_j at pH 12 is about half of that obtained at pH = 7.

Using E3 a similar molar distribution of solubilized chlorobenzenes and chlorobenzenes in DNAPL was obtained regardless of surfactant concentration. This effect can be explained by assuming that the surfactant solubilizes DNAPL as a single pseudo-compound (García-Cervilla et al., 2020a; García-Cervilla et al., 2021). As the oxidation occurs in the aqueous phase, the heavier and less soluble chlorobenzenes could be removed in much shorter times if surfactant is added.

3.2. COCs oxidation with PSA in the presence of surfactant

Surfactants and pollutants compete for the oxidant (Bouزيد et al., 2017; Cheng et al., 2017; García-Cervilla et al., 2021; Mendez-Diaz et al., 2010; Olmez-Hanci et al., 2014). Therefore, an appropriate dosage of surfactant and oxidant is required to minimize the unproductive consumption of the oxidant and surfactant but reducing the time needed to remove a certain mass of DNAPL.

3.2.1. Unproductive consumption of the oxidant

This section analyses the results obtained under the experimental conditions of runs summarized in Table 2. The consumption of PS (as mM) and the ratio $R_{\Delta PS/S_o}$ at different times, initial surfactant and oxidant concentrations are plotted in Fig. 1. The $R_{\Delta PS/S_o}$ value is calculated as shown in Eq (4).

$$R_{\Delta PS/S_o} = \frac{C_{PS_o} - C_{PS}}{C_{S_o}} \quad (4)$$

As shown in Fig. 1, the PS consumption is almost negligible at times of up to 450 h (conversion of less than 7%) in the absence of surfactant. As can be seen in Eqs. (1) and (2), the alkaline activation of PS promotes the formation of SO_4^- , O_2^- and OH^- , these radicals react with the surfactant and COCs. In experiments carried out without surfactant and

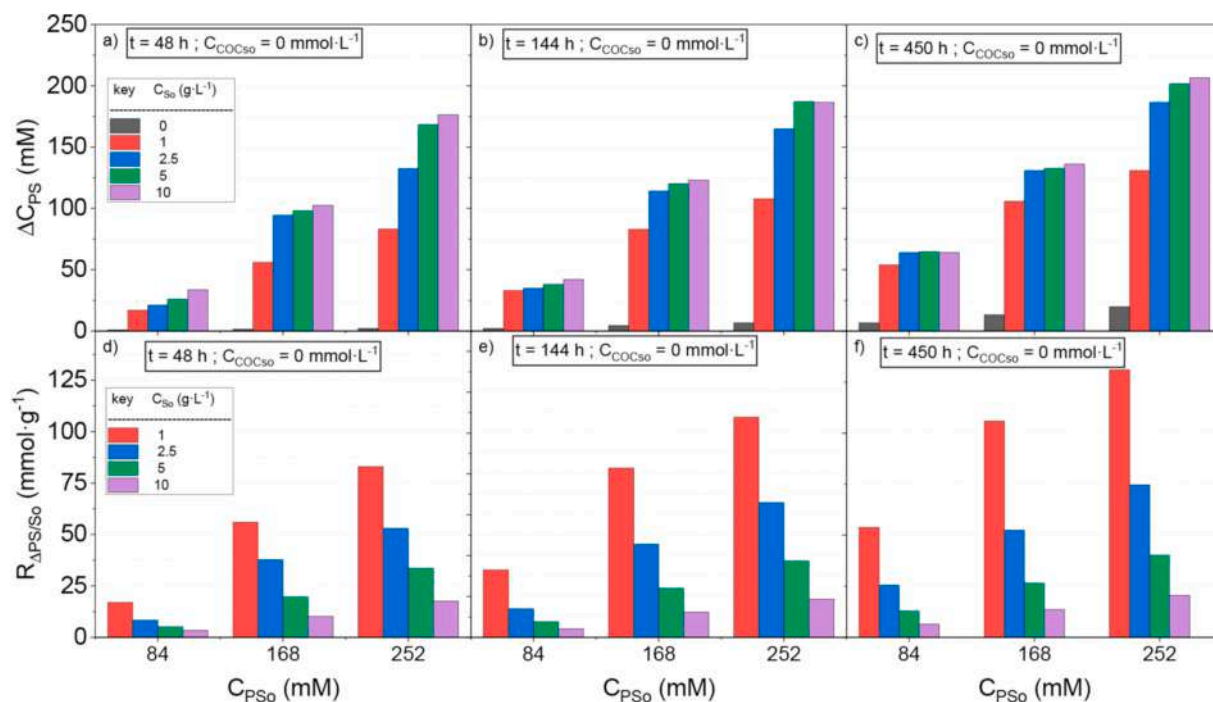


Fig. 1. PS consumption (a) 48 h and (b) 144 h (c) 450 h and $R_{\Delta PS/S_o}$ (d) 48 h and (e) 144 h (f) 450 h values at different oxidation times. Experimental conditions are shown in Table S1. The molar ratio NaOH:PS was 2 in all experiments.

COCs, these radicals were slowly consumed in unproductive reactions with PS and persulfate concentration remains almost constant with time. The consumption on version of PS in the absence of COCs and surfactant using 252 mM of PS and a molar ratio NaOH:PS 2:1 was lower than 15% after 21 days, as shown in Fig. 1. On the other hand, PS consumption remarkably increases when the surfactant is added.

At C_{S_0} constant, the higher the oxidant concentration, the higher the oxidant consumed, as shown in Fig. 1. However, for a given value of C_{PS_0} , the consumption of oxidant slightly increases while the initial surfactant concentration increases and the $R_{\Delta PS/S_0}$ value decreases.

The critical micellar concentration of surfactant E3 is about 80 mg L^{-1} (García-Cervilla et al., 2020a). The micelles are formed when the surfactant concentration is higher than this CMC value.

However, the shape and size of micelles change when surfactant concentration increases. It can be assumed that more complex micelle structures are formed at higher surfactant concentrations, lowering the external surface of micelles per mass of surfactant (Kosswig, 2000). The size of micelles was investigated by dynamic light scattering (DLS), using a Malvern Nano Zetasizer. With this technique, the hydrodynamic diameter (DH) of the micelles was measured for different surfactant concentrations within the range 1–100 $g \cdot L^{-1}$. It was observed that the higher the surfactant concentration, the lower the DH micelles (within the range of 13–9 nm for the surfactant concentration tested). Besides, using Cryo-EM was observed (see Figure S3 of the Supplementary Material) the amount of micelles was not appreciable increased between 5 and 10 $g \cdot L^{-1}$, this inferred the number of monomers per micell increased hindering the surfactant against oxidation.

The oxidation mechanism for the non-ionic surfactant was proposed by Brand et al. (1998) and Olmez-Hanci et al. (2014). The polyethoxylated chains in E3 are susceptible to radical oxidation (Brand et al., 1998; Olmez-Hanci et al., 2014; Wang et al., 2020). The main oxidation by-products are shortened ethoxylate chains, polyethylene glycols, aldehyde ethoxylates, carboxylated polyethylene glycols and carboxylated acids (Brand et al., 1998; Castillo et al., 2001; Olmez-Hanci et al., 2014). Some of the E3 oxidation by-products were identified by GC-MS analysis of the aqueous phases, as shown in Figures S4 and S5 of the Supporting Information. These by-products are more refractory to oxidation than the parent surfactant molecule, and the PS consumption rate slows down with time, as noticed in Fig. 1. The mineralization achieved for the surfactant was lower than 20%, in agreement with results elsewhere (Lominchar et al., 2018). Besides, E3 is formulated with limonene as a co-solvent. Limonene oxidation explains the by-products summarized in Figs. S6 and S7 of the Supporting Information.

3.2.2. Oxidation of COCs in saturated aqueous emulsions at a moderate-high surfactant concentration

Firstly, the selective oxidation of COCs in the aqueous emulsion with

a relatively high surfactant concentration and emulsified COCs were studied (runs in Table 2). The concentrations of solubilized COCs were 24.9 and 59.5 mM when the surfactant concentration was 5 and 10 $g \cdot L^{-1}$, respectively (saturation conditions). As can be seen in Table 2, three concentrations of NaOH were tested. No effect of the alkali concentration on initial solubilized COCs was found at the alkali concentration range studied.

The fraction of solubilized and total COCs remaining in the vial with reaction time was measured. Differences between solubilized and total COCs correspond to the precipitated COCs in the vial. Results using 5 and 10 $g \cdot L^{-1}$ of surfactant concentration at different PS concentrations are shown in Fig. 2.

As can be seen in Fig. 2a, COCs oxidation did not occur at 84 mM and no differences between total and solubilized COCs were noticed at this C_{PS_0} value during the time interval studied. However, a significant consumption of PS was noticed under the same conditions as shown in (Fig. 3a). This fact can be explained by taking into account the reaction between PS and the surfactant. The first surfactant oxidation by-products kept the initial surfactant capacity since the precipitation of COCs in the saturated solution did not occur.

On the contrary, at higher PS concentrations (Fig. 2b and c), the total and solubilized COCs concentrations in the vial become more different with time. After an initial period, precipitation of COCs takes place due to the progressive surfactant capacity lost. This initial period depends on the surfactant and PS concentrations. Using 168 mM of C_{PS_0} (Figs. 2b) and 5 $g \cdot L^{-1}$ of surfactant, the concentration of solubilized COCs dropped from 24.9 to 0.27 mM after 300 h in contact with PSA. However, at the same conditions of PS but using $C_{S_0} = 10 g \cdot L^{-1}$ precipitation of COCs did not occur, keeping the concentration of solubilized COCs at 59.5 mM. At 336 mM C_{PS_0} (Fig. 2c), the almost complete precipitation of COCs was noticed at 24 h and 400 h using 5 and 10 $g \cdot L^{-1}$ of C_{S_0} , respectively. This loss of surfactant capacity is due to surfactant oxidation by PSA and the corresponding PS consumed is shown in Fig. 3.

Therefore, the surfactant oxidation can be explained by two consecutive reactions. In the first reaction, the initial surfactant oxidation by-products (lumped as SOX_1 in Eq. (5)) maintain the surfactant capacity while initial solubilized COCs in the vial does not precipitated despite PS being consumed (Figs. 2a and 3a). The oxidation of first surfactant by-products (SOX_1) occurs as shorter times as PS concentration increases. The formed SOX_2 (Eq. (6)) must have a lower surfactant capacity explaining the precipitation of COCs noticed in Fig. 2b and c. The production of by-products with different surfactant capacity have been reported in the literature (Castillo et al., 2001; Olmez-Hanci et al., 2014; Wang et al., 2020). Moreover, no mineralization of the surfactant was noticed using PSA at the conditions tested.

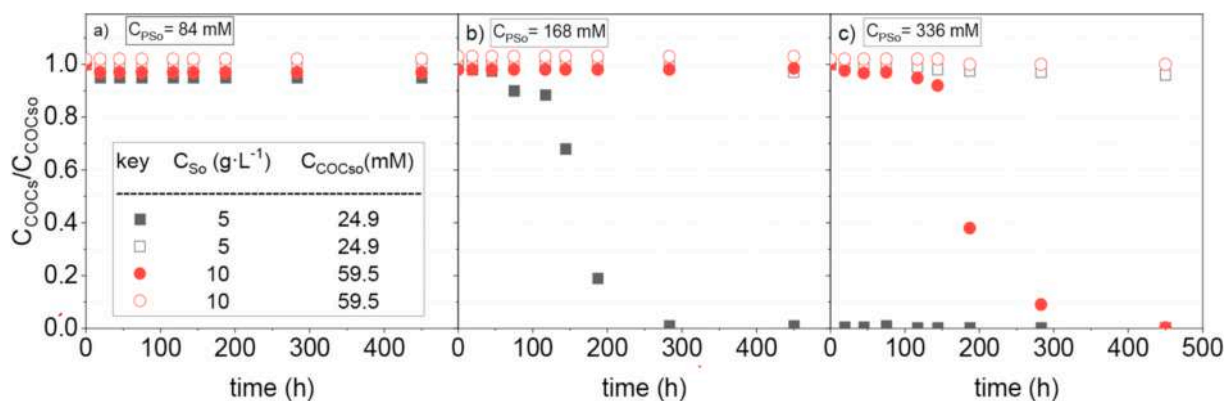


Fig. 2. Fraction of solubilized (solid symbols) and total (open symbols) COCs with time at two initial concentrations of surfactant (5 and 10 $g \cdot L^{-1}$) and solubilized COCs (24.9 and 59.5 mM). PS concentrations: a) $C_{PS_0} = 84$ mM; b) $C_{PS_0} = 168$ mM; c) $C_{PS_0} = 336$ mM. Molar ratio NaOH:PS was 2 in all experiments. Experimental Conditions in Table 2.

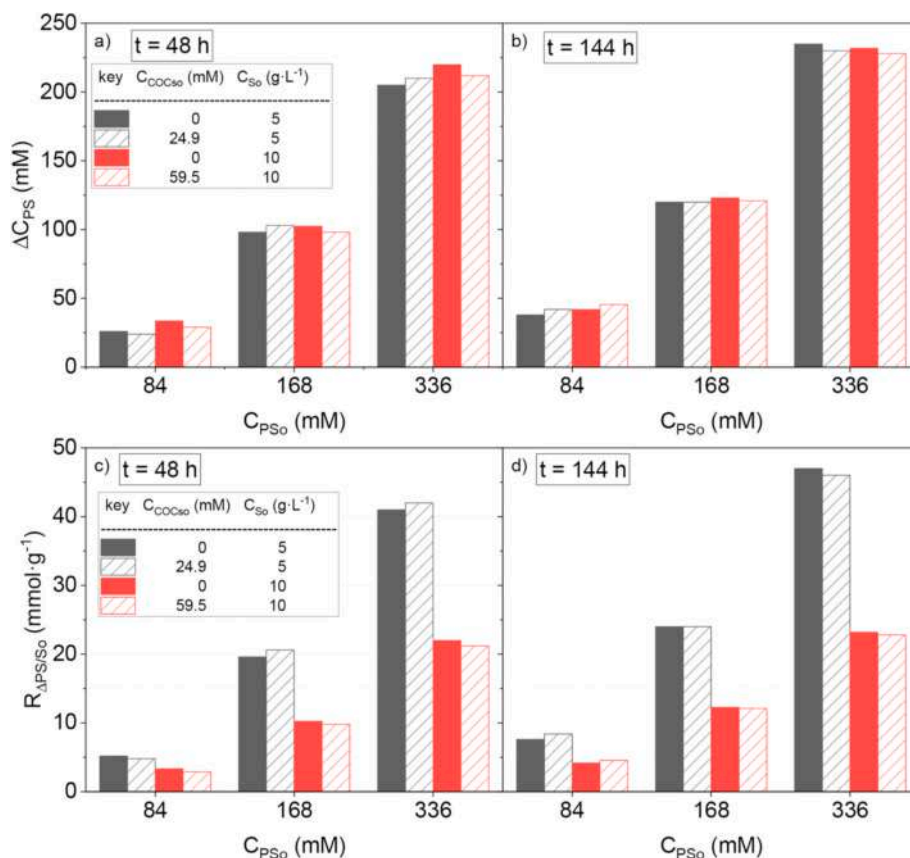


Fig. 3. PS consumption (a) 48 h and b) 144 h and $R_{\Delta PS/S_0}$ (c) 48 h and d) 144 h values at different oxidation times in runs in Table 2 at two initial concentrations of surfactant ($C_{S_0} = 5$ and 10 g·L⁻¹) and solubilized COCs ($C_{COCS_0} = 24.9$ and 59.5 mM). The molar ratio NaOH:PS was 2 in all runs.



It is worth highlighting that COCs are not oxidized under any conditions or during any runs in Table 2. Therefore, in these runs, the PS was mainly consumed by the surfactant. A similar consumption of PS in the absence (Table S1) and presence (Table 2) of COCs is noticeable by comparing results in Figs. 1 and 3.

At high enough surfactant and COCs concentration, macro-emulsions can be formed (Gupta and Mohanty, 2001; Kang et al., 2019; Okuda et al., 1996; Pennell et al., 1997; Zhou and Rhue, 2000). Macro-emulsions can contain a large amount of DNAPL as an organic phase in the micelle core (Pennell et al., 1997; Rosen and Kunjappu, 2012). (Okuda et al., 1996; Shiau et al., 1994). In Figure S8 of supplementary material, the visual aspect of the emulsion saturated with DNAPLs presented a milky phase characteristic of macro-emulsions (Kang et al., 2019; Pennell et al., 1997; Rosen and Kunjappu, 2012). The aspect of the corresponding surfactant solution in the absence of emulsified COCs is shown in Figure S9 of Supplementary Material.

On the other hand, the increase of initial surfactant concentration in Fig. 3 results only in a slight PS consumption increase. As cited in section 3.2.1, this finding can be explained by the formation of larger micelle structures as the surfactant concentration increases. These structures hinder the oxidation of surfactant and COCs molecules at the inside of the micelles. The higher the surfactant concentration, the higher the blocking of surfactant for both COCs and surfactant oxidation by PSA.

The initial concentration of surfactant in the runs in Table 2 using saturated emulsions seems to avoid the oxidation of COCs in the core of the micelle structure, hindering the contact between the oxidant, and the organic phase. Thus, the conditions tested in Table 2 are not

appropriate to apply an S-ISCO treatment with this reaction media (PSA, E3 non-ionic surfactant).

3.2.3. Oxidation of COCs in aqueous non-saturated emulsions

As deduced from previous sections, surfactant, COCs, and PS concentrations are critical parameters in the efficient application of S-ISCO. The experimental conditions for studying the oxidation of chlorobenzenes with a concentration lower than the saturation condition were summarized in Table 2.

Total COCs and solubilized COCs remaining in the vial are measured with time. Profiles are shown in Figure S10 of the supplementary information. The fraction of initial COCs that remain solubilized or precipitated with time is shown in Fig. 4. No aromatic or chlorinated by-products were detected in the oxidation of the chlorobenzenes mixture in the aqueous phase. The aspect of the solution at 3.6 mM is shown in Figure S11 of Supplementary Material.

As shown in Fig. 4 a, b, c, the higher the surfactant concentration, the lower the COCs removed (at constant initial COCs and PS concentration). This finding confirms the hindering of surfactant to COCs oxidation when the surfactant concentration increases. This fact agrees with that reported by Bouzid et al. (2017). The authors observed that the kinetic constant of phenanthrene oxidation using PS activated by temperature using Lauryl Betaine (LB) as surfactant decreased sharply with the increase of surfactant concentration.

At surfactant concentration of 1 g·L⁻¹ a remarkable decrease of total remaining COCs as the reaction time increased was noticed, achieving values of a remaining fraction of initial COCs between 0.19 and 0.3 at $C_{PS_0} = 252$ mM and 144 h of reaction time.

The ratio of the total oxidized COCs ($C_{COCS_0} - C_{COCS}$), which are shown in Figure S12a-c, and the corresponding PS consumed ($C_{PS_0} - C_{PS}$), which are shown in Figure S12d-f, defined as $R_{\Delta PS/S_0}$ in Eq. (7), is

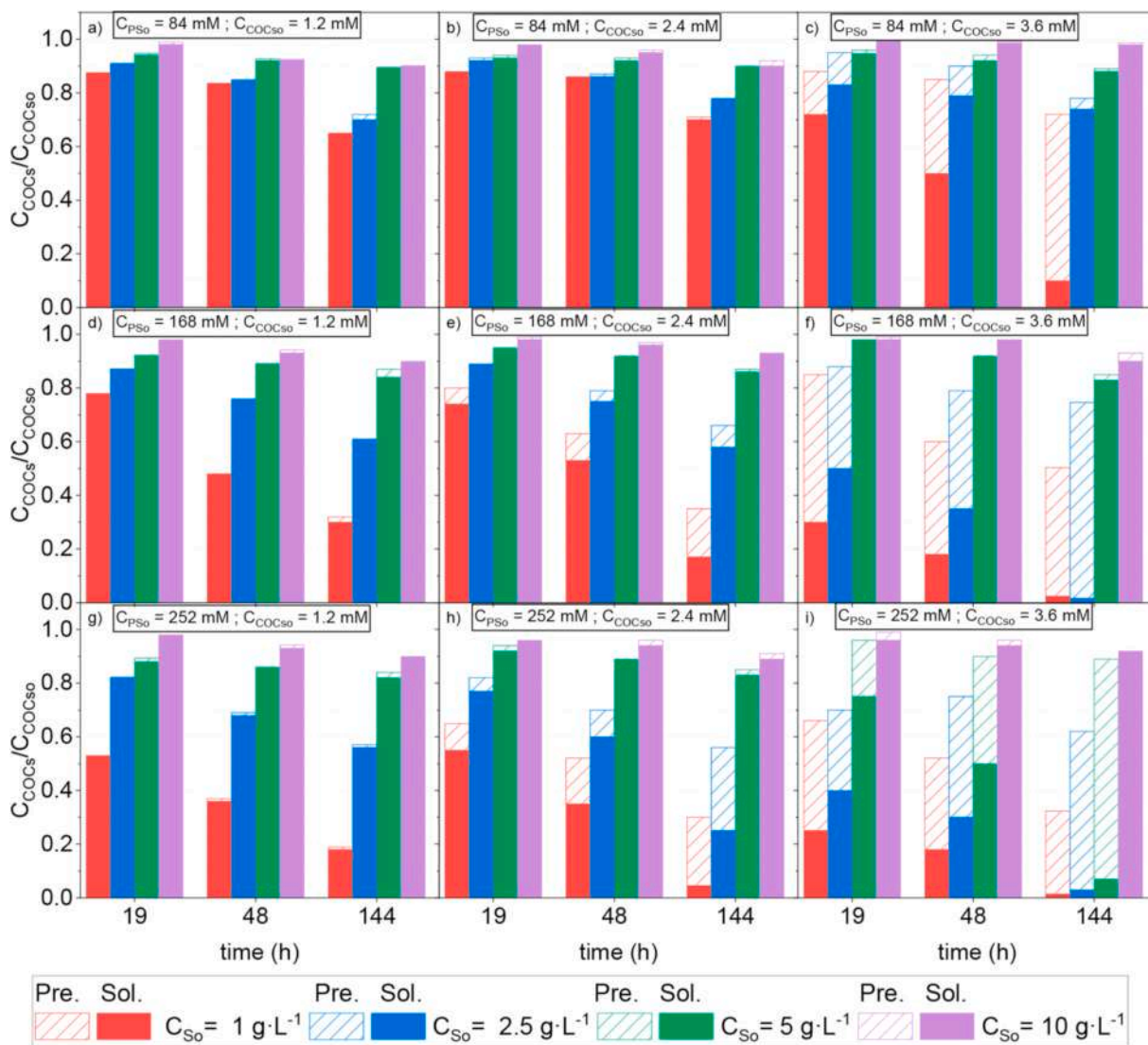


Fig. 4. Fractional remaining COCs in runs in Table 2, as the sum of solubilized COCs (Sol., filled bars) and precipitated COCs (Pre., patterned bars). Initial COCs solubilized: 1.2, 2.4 and 3.6 mM, PS concentration: 84, 168 and 252 mM and surfactant concentrations: 1, 2.5, 5 and 10 g/L. The molar ratio NaOH:PS was 2 in all runs.

shown in Fig. 5 for 144 h of reaction time. The PS consumption at different oxidation times (48 and 144 h) is shown in Figure S13 of the Supplementary Material.

$$R_{\frac{\Delta PS}{\Delta COCs}} = \frac{C_{PS0} - C_{PS}}{\Delta COCs - C_{COCs}} \quad (7)$$

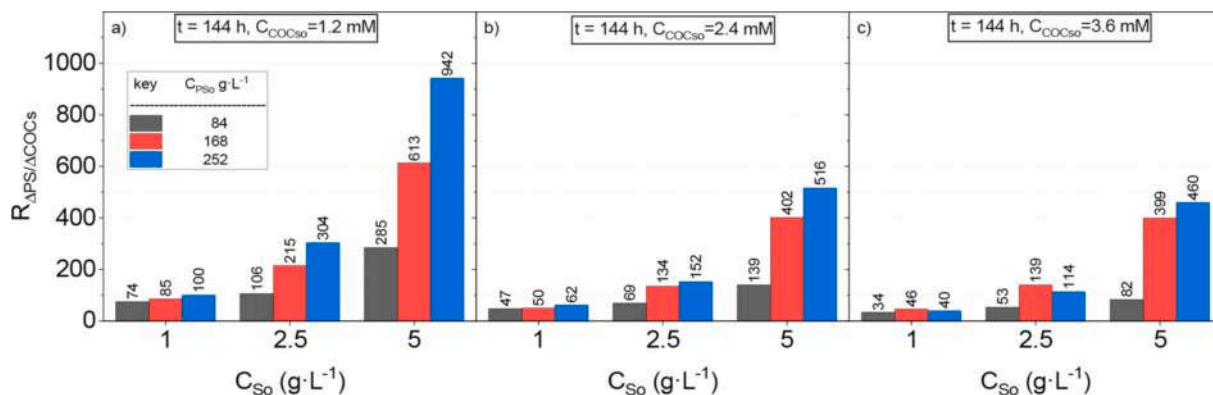


Fig. 5. Ratio $R_{\frac{\Delta PS}{\Delta COCs}}$ as a function of initial surfactant, PS and sum of chlorobenzene (COCs) concentrations calculated from results shown in Figure S12 (runs in Table 2). Initial COCs solubilized: a) 1.2, b) 2.4 and c) 3.6 mM and 144 h. The molar ratio NaOH:PS was 2 in all runs.

Higher efficiency of the oxidant in COCs abatement requires lower values of the ratio $R_{\Delta_{PS}/\Delta_{COCs}}$. In this way, better efficiencies were achieved at lower surfactant concentrations, as shown in Fig. 5. Moreover, for a given value of C_{S_0} , the higher the initial COCs solubilized, the lower the $R_{\Delta_{PS}/\Delta_{COCs}}$ value. However, if C_{S_0} decreases, the maximum amount of COCs that can be solubilized also decreases. Therefore, the surfactant dosage must be high enough to solubilize COCs at a concentration remarkably higher than the solubility achieved in the absence of surfactants but low enough to avoid the hindering of COCs to oxidation and promote a prohibited PS consumption.

A surfactant concentration of about 1 g L^{-1} has been chosen as the best value with PSA for the DNAPL mixture and surfactant used and tested reaction condition. With $C_{S_0} = 1 \text{ g L}^{-1}$, the maximum concentration of COCs that could be solubilized, according to Figure S1, is 5.2 mM. This value is about 10 times the solubilized COCs in the absence of surfactant if an equilibrium between the organic and aqueous phase is achieved.

On the other hand, the increase of initial PS concentration improves the oxidation of COCs, thus reducing the time required. However, the PS consumed per mol of removed chlorobenzenes, $R_{\Delta_{PS}/\Delta_{COCs}}$, also increases as PS concentration increases (Fig. 5). Consequently, the best value for PS initial concentration should consider both factors: the time required for COCs abatement and the unproductive PS consumption (associated with the loss of surfactant capacity and COCs precipitation). At the condition tested, a value of 168 mM can be chosen for S-ISCO runs. In addition, at a concentration of PS of 252 mM, fast precipitation of COCs occurs, as noticed in Fig. 4. However, the precipitation of COCs does not modify the COCs distribution in the aqueous phase, as shown in Figure S14 in the supplementary information.

3.2.4. ISCO vs S-ISCO

The time required in the presence (S-ISCO) or absence (ISCO) of surfactant to remove a mass of DNAPL contained in a liquid phase volume is compared in this section. Values selected for total DNAPL concentration in the vials (mass of DNAPL in a liquid volume) were 3.6 and 2.4 mM.

Selected conditions for S-ISCO in the previous section were $C_{PS_0} = 168 \text{ mM}$ and $C_{S_0} = 1 \text{ g L}^{-1}$. Moreover, with $C_{S_0} = 1 \text{ g L}^{-1}$ the maximum concentration of COCs that can be solubilized is 5.2 mM. Therefore, concentrations of 3.6 mM and 2.4 mM will be completely solubilized at zero time.

In the absence of surfactant, ISCO, the maximum concentration of solubilized COCs is 0.52 mM. The difference from this value to 2.4 or 3.6 mM will remain as an organic phase at zero time, and a partition of the DNAPL mass between aqueous and organic phases must be considered.

The time required to oxidize by PSA the COCs in a mass of DNAPL contained in a liquid volume, in the absence of surfactant, can be calculated, assuming that.

- The mass of DNAPL in the volume of the liquid phase is named as C_{DNAPL}
- C_{DNAPL} is the sum of solubilized DNAPL $C_{DNAPL_{aq}}$ and DNAPL remaining as an organic phase ($C_{DNAPL_{or}}$) (all concentrations in mM).

$$C_{DNAPL} = C_{DNAPL_{or}} + C_{DNAPL_{aq}} \quad (8)$$

- An equilibrium between organic and aqueous phases is assumed. Therefore, the aqueous concentration of compound j , j being each chlorinated compound in DNAPL, is calculated by Eq (3)
- The sum of solubilized Chlorobenzenes can be calculated as Eq (9)

$$C_{DNAPL_{aq}} = \sum S_j \gamma_j x_j \quad (9)$$

And the sum of Chlorobenzenes remaining as an organic phase can be

calculated as the difference between C_{DNAPL} and $C_{DNAPL_{aq}}$

- The oxidation of each chlorinated compound j occurs in the aqueous phase. Therefore, the removal of each j compound is calculated by Eq (10).

$$-\frac{dC_j}{dt} = k_{PS} C_{PS} C_{j_{aq}} = k_{PS} C_{PS} S_j \gamma_j x_j \quad (10)$$

C_{PS} being the concentration of PS (mM), k_{PS} the kinetic constant of reaction between PS and each chlorobenzene in the aqueous phase reported elsewhere (Santos et al., 2018b) ($k_{PS} = 1.31 \cdot 10^{-4} \frac{\text{L}}{\text{mmol h}}$) and C_j the concentration of j , sum of remaining j in the organic ($C_{j_{or}}$) and aqueous phases ($C_{j_{aq}}$)

$$C_j = C_{j_{aq}} + C_{j_{or}} \quad (11)$$

The sum of C_j being the remaining DNAPL in the media, C_{DNAPL} and the sum of $C_{j_{or}}$ the remaining DNAPL as an organic phase, $C_{DNAPL_{or}}$, both calculated by Eqs (12) and (13), respectively.

$$C_{DNAPL} = \sum C_j \quad (12)$$

$$C_{DNAPL_{or}} = \sum C_{j_{or}} \quad (13)$$

The removal of chlorobenzenes by PSA under the conditions of initial $C_{DNAPL} = 2, 4$ and 3.6 mM and $C_{PS} = 168 \text{ mM}$ has been predicted using Eqs (8)–(13). C_{PS} was considered constant with reaction time. $S_j \gamma_j$ values at $\text{pH} > 12$ and initial values of x_j for each j compound are shown in Table S2 of the supplementary information. The predicted values are compared with those obtained in the experiments carried out in absence of surfactant (ISCO experiment in Table 2). As can be seen in Fig. 6, a good agreement between the predicted and experimental values was found.

The partition of a mass of DNAPL between aqueous and organic phases when equilibrium is reached is named $R_{Aq/or}$, according to Eq. (14).

$$R_{Aq/or} = \frac{C_{DNAPL_{aq}}}{C_{DNAPL_{or}}} \quad (14)$$

The values of remaining fractional COCs with time in ISCO and S-ISCO and the profile of $R_{Aq/or}$ in ISCO are shown in Fig. 6.

As shown in Fig. 6, the time required to eliminate the COCs in the DNAPL mass in the liquid phase was remarkably reduced in S-ISCO compared with the value needed in ISCO. This fact is explained by the higher concentration of COCs in solution in S-ISCO. The ratio of DNAPL solubilized in the aqueous phase to that remaining as an organic phase, $R_{Aq/or}$, is of about 0.2 in ISCO (dotted lines in Fig. 6). If the oxidation occurs in the aqueous phase, the time required to remove a mass of DNAPL would be lower in S-ISCO.

In the absence of unproductive consumption of PS, the stoichiometric ratio for COCs mineralization is about 28 mM of PS per mM of chlorobenzenes (Dominguez et al., 2021). The consumption of PS is higher (about 40) under S-ISCO conditions (Fig. 4), but the time required for COCs abatement is remarkably lower.

On the other hand, the ISCO profiles in Fig. 6 have been calculated assuming a constant PS concentration value with time. Therefore, the DNAPL abatement simulated in ISCO has been slightly overestimated under this hypothesis. Moreover, an equilibrium between the organic and aqueous phases has been assumed. However, mass transfer between phases is usually limited under natural subsurface conditions, where DNAPL is trapped in soil fractures or low permeability zones. Therefore, the concentration of j in the aqueous phase will be lower than that considered in the ISCO simulation, and the DNAPL abatement achieved at a time by ISCO has been overestimated. Consequently, the improvement of S-ISCO has been underestimated.

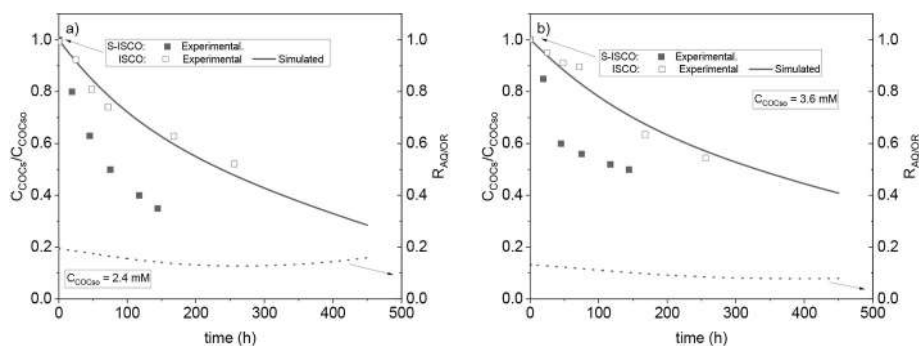


Fig. 6. Comparison of remaining fractional chlorobenzenes by S-ISCO (symbols, $C_{s0} = 1 \text{ g L}^{-1}$) and ISCO (solid lines). $C_{PS0} = 168 \text{ mM}$. Total COCs a) 2.4 mM and b) 3.6 mM. The dotted lines correspond to the fraction $C_{DNAPL_{aq}} / C_{DNAPL_{OR}}$ with time.

4. Conclusions

The simultaneous addition of PSA and surfactant decreases the time required to eliminate a mass of DNAPL in certain conditions. The optimal PS and surfactant concentration should consider the unproductive PS consumption, the solubilized COCs and the relative reactivity of surfactant and COCs with the oxidant.

The surfactant concentration increase slightly increases the PS consumption but produces a remarkable hindering of the COCs abatement. The formation of more complex micelle structures at higher surfactant concentrations could explain this phenomenon. The abatement of COCs was negligible due to a hindering effect of the surfactant. Using Emulse 3® as surfactant and a mixture of CB, DCB, TCB and TetraCBs as DNAPL, it was noticed that a surfactant concentration higher than 2.5 g/L caused only unproductive reactions without COCs removal.

The use of surfactant improved the solubility of COCs in water, solubilizing the DNAPL as a single pseudo-compound. The increase of surfactant concentration will increase the COCs solubilisation but hinder the COCs oxidation. Therefore, the surfactant concentration selected to eliminate this COCS with PSA was 1 g L^{-1} , considering affordable cost and time application. Besides, the increase of initial PS concentration improves the oxidation of COCs reducing the time required. However, the PS consumed per mol of removed chlorobenzenes increases with the initial PS concentration used. The PS concentration selected here was 168 mM. In general, the optimal value of these variables will depend on the nature of the COCs and surfactant and their relative reactivity against the oxidant. Each case requires laboratory studies before application to pilot or full scale to improve the efficiency of the treatment at a lower cost. Understanding the behaviour of oxidants, organic pollutants, and surfactants in the aqueous phase is critical to optimizing the operating conditions. However, the reactions taking place in the aqueous phase should be combined with the interaction between the specific soil and the aqueous phase for the design of each real case. The presence of soil can introduce adsorption phenomena that can be studied in each particular case.

Two reactions in series can explain the surfactant oxidation. The generation of the first surfactant by-products consumes PS, but the surfactant capacity is maintained. These by-products are further oxidized with an associate loss of the initial surfactant capacity promoting the COCs precipitation. Surfactant mineralization can be considered negligible.

Credit author 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, Writing – 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 Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2022.114475>.

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