Contents lists available at ScienceDirect





Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Compatibility of nonionic and anionic surfactants with persulfate activated by alkali in the abatement of chlorinated organic compounds in aqueous phase



Raul García-Cervilla, Aurora Santos, Arturo Romero, David Lorenzo*

Chemical Engineering and Materials Department, University Complutense of Madrid, Spain

HIGHLIGHTS

GRAPHICAL ABSTRACT

- The oxidation of surfactant reduces the pollutant solubilization.
- Nonionic surfactants have higher MSR but are more easily oxidized by PSA.
- S-ISCO with nonionic surfactants reduces removal time of DNAPL with PSA.
- The S-ISCO treatment was more efficient with Emulse-3 than SDS.

ARTICLE INFO

Received in revised form 16 August 2020

Article history:

Editor: Jay Gan

Kevwords:

DNAPI

Received 10 June 2020

Accepted 17 August 2020

Available online 19 August 2020

Nonionic and anionic surfactants

Persulfate activated by alkali

Lindane wastes S-ISCO



ABSTRACT

Surfactant Enhanced In-Situ Chemical Oxidation (S-ISCO) is an emerging technology in the remediation of sites with residual Dense Non-Aqueous Phase Liquids (DNAPLs), a ubiquitous problem in the environment and a challenge to solve. In this work, three nonionic surfactants: *E*-Mulse3® (E3), Tween80 (T80), and a mixture of Tween80-Span80 (TS80), and an anionic surfactant: sodium dodecyl sulfate (SDS), combined with persulfate activated by alkali (PSA) as oxidant have been investigated to remove the DNAPL generated as liquid waste in lindane production, which is composed of 28 chlorinated organic compounds (COCs).

Because the compatibility between surfactants and oxidants is a key aspect in the S-ISCO effectiveness the unproductive consumption of PS by surfactants was investigated in batch (up to 864 h) varying the initial concentration of PS (84–42 mmol·L⁻¹) and surfactants (0–12 g·L⁻¹) and the NaOH:PS molar ratio (1 and 2). The solubilization capacity of a partially oxidized surfactant was analyzed by estimating its Equivalent Surfactant Capacity, ESC, (as $mmol_{COCS\ dissolved\ gsurf}$) and comparing it to the expected value for an unoxidized surfactant, ESC_o. Finally, the abatement of DNAPL with simultaneous addition of surfactant and PSA was studied.

At the conditions used, a negligible unproductive consumption of PS was found by SDS; meanwhile, PS consumption at 360 h ranged between 70 and 80% using the nonionic surfactants. The highest ratios of ESC/ESC_o were found with SDS and E3 and these surfactants were chosen for the S-ISCO treatment. When oxidant and surfactant were simultaneously applied for DNAPL abatement the COC conversion was more than three times higher with E3 (0.6 at 360 h) than SDS. Moreover, it was obtained that the time needed for the removal of a mass of DNAPL by PSA in the absence of surfactants was notably higher than the time required when a suitable surfactant was added.

© 2020 Elsevier B.V. All rights reserved.

* Corresponding author.

E-mail addresses: raugar05@ucm.es (R. García-Cervilla), aursan@quim.ucm.es (A. Santos), aromeros@quim.ucm.es (A. Romero), dlorenzo@ucm.es (D. Lorenzo).

1. Introduction

Petroleum hydrocarbons, pesticides, or chlorinated solvents are hydrophobic organic compounds (HOCs) that have been released in the environment. Do the low solubility in the aqueous phase of these compounds they form non-aqueous phase liquids (NAPLs) that pollute the soil and groundwater for decades (Interstate Technology Regulatory Council, 2000; Soga et al., 2004; Katsoyiannis and Samara, 2005; National Research Council, 2013; Wacławek et al., 2016). Moreover, many of these NAPLs are formed by complex mixtures rather than single compounds (Mobile et al., 2016; Tomlinson et al., 2017). This constitutes a ubiquitous problem in the environment and it is a challenge to solve, especially in the case of Dense NAPL while this phase percolated through the saturated zone.

To shorten the required time for the remediation of sites polluted with NAPLs, surfactants and cosolvents have been recently proposed and applied (Mulligan et al., 2001; Dugan et al., 2010; Mao et al., 2015; Trellu et al., 2016; Besha et al., 2018; Dominguez et al., 2019b; Santos et al., 2019). Surfactants reduce the interfacial tension between the organic phase (NAPL) and the aqueous phase (Paria, 2008; Dugan et al., 2010) due to their amphiphilic properties (Rosen and Kunjappu, 2012) and increase the solubility of HOCs in the aqueous phase. Moreover, a partition of the surfactant between the aqueous and organic phase occurs, decreasing the viscosity of the organic phase and facilitating its extraction (Paria, 2008; Kang et al., 2019).

The SEAR (Surfactant Enhancement Aquifer Remediation) treatment consists of injecting an aqueous solution of surfactant-cosolvent into the areas contaminated by HOCs, and subsequently extracting the injected fluid and treating it *on-site* (Londergan and Yeh, 2003; Dugan et al., 2010; Mao et al., 2015; Dahal et al., 2016; Besha et al., 2018). This technology has already been implemented, but it presents some concerns. The dispersion of contamination by the injection of the surfactant must be avoided, and *on-site* treatment of the extracted fluid is required since the contamination has only changed from the soil phase to the aqueous phase.

Surfactant Enhanced In-Situ Chemical Oxidation (S-ISCO) consists of the simultaneous injection of a surfactant solution and oxidants to increase the solubility of HOCs in the aqueous phase, where the oxidation takes place, and thus reduce the time required for the removal of the contaminant mass in the aquifer (Lanoue et al., 2011; Besha et al., 2018). S-ISCO treatment minimizes the inconvenience of the SEAR technology since a lower concentration of surfactant is used: the problem of contaminant dispersion is minimized, and the injected oxidant produces the destruction of the HOCs in-situ. Although this technology is emerging, studies in the literature on its application are scarce (Dugan et al., 2009; Dugan et al., 2010; Hoag and Collins, 2011; Wang et al., 2013; Lominchar et al., 2018a).

Hydrogen peroxide and persulfate have often been applied to remove the contaminants in the subsoil (Siegrist et al., 2011). Both oxidants can produce radicals under certain conditions. H_2O_2 catalyzed by iron salts (Fenton Reagent) generates hydroxyl radicals ($^{\circ}OH$) and persulfate (PS), activated by Fe(II), heat, or alkali, can produce sulfate (SO_4^{-}) and/or hydroxyl radicals, which both have high oxidation capacity (Baciocchi, 2013; Devi et al., 2016).

However, the Fenton process frequently exhibits significant limitations for in-situ applications due to the high unproductive consumption of this oxidant by the soil. Moreover, the optimal pH for the Fenton process is 2.8–3, and it not feasible to maintain these conditions in the subsoil. The optimal acidic conditions are quite difficult to obtain in the subsoil due to the high content of carbonates in the groundwater usually (Siegrist et al., 2011).

These disadvantages explain the increase in the use of activated PS as the oxidant in ISCO treatments in recent years. PS is highly stable in the subsoil, which means that it can be transported for long distances, is easy to handle and produces benign end-products (Sra et al., 2014; Ike et al., 2018). Among the activation methods of PS, the use of bases

(mainly NaOH) is gaining attention in recent years (Furman et al., 2010; Lominchar et al., 2018b). In the alkaline activation of PS, multiple reactive species are produced (Liang and Lei, 2015), according to Eqs. (1) and (2), making the process highly versatile against a wide variety of pollutants. Moreover, it does not require either heat or acidic conditions (such as activation by metals), which are both challenging to achieve in the subsoil.

$$2S_2O_8^{2-} + 2H_2O \xrightarrow{OH} 3SO_4^{2-} + SO_4^{--} + O_2^{--} + 4H^+$$
(1)

$$SO_4^{\bullet-} + OH^- \to SO_4^{2-} + {}^{\bullet}OH \tag{2}$$

In works elsewhere, it was found that in the presence of alkali some Chlorinated Organic Compounds (COCs) suffered dehydrochlorination reactions generating species of lower toxicity, which adds an advantage in the use of alkali as an activator (Santos et al., 2018b; García-Cervilla et al., 2020b; Lorenzo et al., 2020).

The success of the application of S-ISCO technology depends on the selection of the most suitable oxidizer-surfactant/pollutant system. The oxidant must be effective in abating the contaminants, and the surfactant must increase the solubility of these contaminants and be relatively stable with the oxidant. The oxidants can attack the surfactant and the pollutants because both are organic compounds. Therefore, the surfactant stability can be a crucial aspect in the design of an S-ISCO process. Another important aspect to consider is the possible loss of surfactant into the soil by adsorption, which depends on both the nature of the surfactant and the type of soil (Lee et al., 2000; Yang et al., 2006).

However, only a few works are available in the literature studying the oxidation of pollutants in the presence of surfactants, and few of them use PS as an oxidant. Moreover, most of these works are carried out in two steps. In the first step, the pollutant is solubilized by a surfactant in the aqueous emulsion. Usually, an artificially spiked soil with a single pollutant or a DNAPL of a pure pollutant is in contact with the aqueous surfactant emulsion. In the next step, the aqueous emulsion with the surfactant and the pollutant extracted is treated on-site using PS. Some works used PS activated by UV radiation (Long et al., 2013; Bai et al., 2019) with toluene and phenanthrene as pollutants and SDS or Tween 80 as surfactants. Another work studied the abatement of phenanthrene in the emulsion of three surfactants (SDS, lauryl betaine, and Neodil 25-7) by temperature (Bouzid et al., 2017). Zheng et al. (2016) and Tsai et al. (2009) studied the removal of tetrachloroethylene (in spiked sand) using Tween 80 as a surfactant and PS activated by Fe (II), respectively (Tsai et al., 2009; Zheng et al., 2016). Long et al. (2014) studied the selective abatement of toluene in an emulsion with SDS and iron as a PS activator (Long et al., 2014). In these last works, iron was used to maintain the pH acidic (Tsai et al., 2009) or was presumably adjusted to the acidic range while this variable was not controlled with the reaction progress (Long et al., 2014; Zheng et al., 2016). Even though methods cited above are effective in an on-site treatment of the pollutant-surfactant emulsion, they cannot be applied in the subsoil and are not, therefore, the most suitable for an in-situ S-ISCO treatment.

In this work, the simultaneous addition of biodegradable surfactants (nonionic and anionic) and PS activated by alkali (PSA) to remove a real DNAPL consisting of 28 COCs (Santos et al., 2018a) originated as a liquid waste in the lindane production process is studied. Stability of the surfactant with the oxidant and the surfactant capacity remaining after surfactant oxidation are firstly studied to choose the most suitable surfactants for the S-ISCO treatment. Influence of the initial surfactant concentration, initial concentration of PS and NaOH:PS molar ratio on the unproductive consumption of oxidant by the surfactant and the solubilization capacity of oxidized surfactants are analyzed. For the selected surfactants the time required for the abatement of a mass of DNAPL by PSA with and without simultaneous addition of surfactants

is determined, in order to assess the advantages of S-ISCO vs. ISCO process.

2. Materials and methods

2.1. Chemicals and DNAPL

In this work, four surfactants were tested: Sodium dodecyl sulfate (SDS), an anionic surfactant applied in soil washing treatments and three nonionic surfactants: *E*-Mulse®3 (E3), Tween®80 (T80), and a mixture of 35% of Tween®80 and 65% w: w of Span®80 (TS80). The first three are commercial surfactants, and the last one is a mixture of two commercial surfactants, which was successfully tested in a previous study (Corcho et al., 2015) using a Dense Non-Aqueous Phase Liquid (DNAPL) similar to the one employed in this work. In Table SM-1, the properties of these surfactants are summarized.

Persulfate (PS) was provided by Sigma-Aldrich and the activator (sodium hydroxide), by Riedel-de Haën. PS quantification was carried out using a titration method with potassium iodide (KI, Fisher Chemical), sodium hydrogen carbonate (NaHCO₃, Panreac), sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O, Sigma-Aldrich) and acetic acid (C₂H₄O₂, Sigma-Aldrich) as reactants. The aqueous solutions were prepared using Milli-Q water. Moreover, sodium bisulfite (NaHSO₃, Sigma-Aldrich) was used to quench PS in the reaction samples taken.

The DNAPL sample used was obtained at Bailin landfill (Sabiñanigo, Spain). This sample was characterized in a previous work finding that it was composed of 28 Chlorinated Organic Compounds COCs (Santos et al., 2018a). In Table SM-2, the composition of the DNAPL sample (CAS and acronym) is provided. Moreover, as the oxidation of surfactant and COCs was carried out in strong alkaline conditions, dehydrochlorination reactions of pentachlorocyclohexene (PentaCXs) and hexachlorocyclohexane (HCHs) isomers to trichlorobenzene isomers (TCBs), and hexachlorocyclohexane (HexaCXs) and heptachlorocyclohexane isomers (HeptaCHs) to tetrachlorobenzenes (TetraCBs) are expected in the aqueous phase (Lorenzo et al., 2020). For a mass of DNAPL completely solubilized in the aqueous phase, the molar fraction of each COC in alkaline conditions (pH > 12) is also shown in Table SM-2.

The quantification of COCs was accomplished using commercial compounds (analytical quality, Sigma-Aldrich) to prepare calibration curves: Chlorobenzene (CB), 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TetraCB), 1,2,3,5-tetrachlorobenzene (1,2,3,5-TetraCB), and 1,2,3,4-tetrachlorobenzene (1,2,3,4-TetraCB), HCHs (α , β , γ , δ and ε -HCH). The calibration samples were prepared, dissolving the COCs in methanol. Bicyclohexyl (C₁₂H₂₂, Sigma-Aldrich) and tetrachloroethane (C₂H₂Cl₄, Sigma-Aldrich) were used as internal standards (ISTD) for quantification in flame ionization detector (FID) and electron capture detector (ECD), respectively.

2.2. Experimental runs and procedures

Four sets of runs were carried out. In the first set, the influence of NaOH and NaCl concentration on the Critical Micellar Concentration (CMC) of the surfactants was determined. In set 2, the unproductive consumption of persulfate of each one of the tested surfactants was studied. Operating conditions similar to those used in an S-ISCO treatment were applied (Besha et al., 2018). In set 3, the surfactant capacity remaining after oxidation treatment was studied. In set 4, the removal of COCs from the surfactant emulsion was evaluated. The procedure is described below.

2.2.1. Set 1: effect of NaOH and NaCl concentration on CMC

The effect of salinity (NaCl concentration) and pH (NaOH) on the CMC value was studied for the four surfactants (SDS, E3, T80, and TS80). Aqueous solutions of $12 \text{ g} \cdot \text{L}^{-1}$ of the surfactant and NaOH or

NaCl concentration within the range 0–500 $mmol \cdot L^{-1}$ were prepared in closed glass vials of 20 mL. After magnetic agitation for 2 h and 24 h of rest at room conditions, the CMC of the surfactant solution was measured by the procedure described elsewhere (Dominguez et al., 2019b).

2.2.2. Set 2: unproductive consumption of oxidant by surfactants

In set 2, the consumption of PS due to the oxidation reaction of the surfactant was studied to determine the unproductive consumption of oxidant. In this set of experiments, 22 runs were carried out in the absence of DNAPL. The variables considered were the initial concentration of surfactant (within the range $3-12 \text{ g} \cdot L^{-1}$), the initial PS concentration ($42-84 \text{ mmol} \cdot L^{-1}$) and the NaOH:PS molar ratio (1:1 and 2:1). The experimental conditions are summarized in Table SM-3. In runs C1-C5, C6-C11, C12-C16, and C17-C22, SDS, E3, T80, and TS80 were used as surfactants, respectively. Moreover, four experiments were accomplished without surfactants as blank experiments.

This set of runs was carried out in well-mixed batch reactors, consisting of a 40 mL PTFE tube with PTFE screw caps. A volume of 35 mL of the aqueous solution with the corresponding concentrations of NaOH, PS, and surfactant was placed in the PTFE tube (time zero). The tubes were stirred using a Labolan rotary agitator (ref 51752) under controlled room conditions ($22 \degree C \pm 1$) up to 860 h. At different reaction times, a tube was sacrificed, and the remaining PS, pH, Surface Tension, and total organic carbon (TOC) were quantified. Furthermore, at 360 h of reaction, a sample of the oxidized solution was analyzed by GC–MS to identify the byproducts of surfactant oxidation. The experiments were carried out in triplicate finding a standard deviation of <10%. In the following section, an average of the measured values is used. All experimental conditions are shown in Table SM-3.

2.2.3. Set 3: study of solubilization capacity of the partially oxidized surfactant

The solubilization capacity that remains in the partially oxidized surfactant solution was checked by the dissolution of an amount of DNAPL. This amount was compared with the amount of DNAPL solubilized at time zero (before the partial oxidation of surfactant).

After 168 and 360 h of reaction time in runs C1, C5, C6, C10, C11, C15, C16, C20 in Table SM-3 samples of 20 mL were taken and quenched, adding 1.5 g of $Na_2S_2O_3 \cdot 5H_2O_1$ Then a mass of DNAPL was added. The mixtures were magnetically agitated for 6 h to ensure that the equilibrium between the organic and aqueous phase was achieved. After that, the emulsions settled for 24 h. The aqueous phase was analyzed by GC-FID/ECD to quantify the solubilized COCs. The experimental conditions of this set of runs are shown in Table SM-4.

2.2.4. Set 4: oxidation of COCs in emulsion

In these runs, the surfactant and the pollutant were in contact with the oxidant (PS) at the activator (NaOH) from time zero. The surfactants used were SDS and E3. Firstly, the emulsion with solubilized COCs was prepared by adding 1.85 mmol of DNAPL to 500 mL of an aqueous solution of $12 g \cdot L^{-1}$ of SDS or $3 g \cdot L^{-1}$ of E3 in alkaline conditions (84 *mmol* L^{-1} of NaOH). These solutions were stirred at 400 rpm for 6 h and settled for 24 h. Then, samples of 30 mL of each supernatant were taken, placed in PTFE tubes with PTFE screw caps and PS was added (time zero) to each tube to reach a concentration of 84 *mmol* L^{-1} . The experimental conditions are shown in Table SM-5. The PTFE tubes were agitated at 80 rpm in the rotatory agitator previously described. At different reaction times, a tube with SDS (run S1) or E3 (run S2) was sacrificed, and the remaining PS, COCs, TOC, and pH were measured.

2.3. Analysis

The CMC was determined with a Krüss tensiometer (Hamburg, Germany) by measuring the surface tension (ST) of a concentration series of samples of surfactant ($0.001-3 g \cdot L^{-1}$) in pure water and constant concentration of NaOH and NaCl in each experiment. The CMC

resulted from the intersection between the regression line of surfactant concentration vs. ST data (in the region where both variables are linearly dependent) and the straight line which passes through the plateau obtained above the CMC (in the region where the ST is independent of the concentration of surfactant).

The total organic carbon (TOC) concentration of the aqueous emulsion was measured with a Shimadzu TOC-V CSH analyzer (Kyoto, Japan) using an infrared detector.

The concentration of PS in aqueous solution was determined by iodometric titration using a potentiometric titration analyzer (Metrohm, Tiamo 2.3, Gallen, Switzerland). The pH was measured using a Basic 20-CRISON pH electrode (Barcelona, Spain).

COCs were identified in the aqueous phases by using a gas chromatograph (GC) coupled with a mass selective detector (Agilent MSD 5975B, Santa Clara, CA, USA). The quantification of COCs was carried out using a GC (Agilent 6890, Santa Clara, CA, USA) with a flame ionization detector (FID, Santa Clara, CA, USA) and electron capture detector (ECD, Santa Clara, CA, USA), simultaneously. The chromatographic method was described elsewhere (Santos et al., 2018a). The samples were taken at different reaction times. Due to the presence of a surfactant in the aqueous solution, the following procedure was performed for COC analysis. When SDS was used, a mass of salt (NaCl) was added to a volume of the emulsion until it broke. After that, hexane was added, and the mixture was vigorously shaken for 2 min. The hexane phase with the COCs extracted was injected in the GC.

When using the nonionic surfactants, it was not possible to break the emulsion with the addition of salt. In this case, 0.1 mL of the emulsion was added to 0.9 mL of methanol and injected in the GC.

Carboxylic acids were measured by ionic chromatography (Metrohm 761 Compact IC, Gallen, Switzerland) with anionic chemical suppression and a stationary-phase conductivity detector was a column from Metrosep (A SUPP5 5-250, which dimensions are 25 cm in length and 4 mm in diameter) and the mobile phase was a solution of NaHCO₃ (1 mM) and Na₂CO₃ (3.2 mM) in water at 0.7 mL · min⁻¹. The Results injection system (injection volume = 250 µL) was coupled with an online filtering system (0.45 µm).

3. Results

3.1. Effect of NaOH and NaCl concentration on the CMC of surfactants

The concentration of NaOH (activator of PS) in the medium could modify the capacity of the surfactant to generate micelles (Rosen and Kunjappu, 2012). Moreover, the groundwater in the polluted site is likely to present high concentrations of salt (conductivity of the groundwater in the landfill is higher than $3000 \ \mu S/cm$ (Santos et al., 2018b)) and these salts could also affect the surfactant properties. For this reason, NaCl was selected to study the effect of the ion concentration on the surfactant properties. The CMC values of surfactants selected were measured at different concentrations of NaOH and NaCl, as indicated in Sections 2.2.1 and 2.3. The results obtained are plotted in Fig. SM-1.

As can be seen in Fig. SM-1, both NaOH and NaCl concentration greatly affect the CMC of SDS (ionic surfactant). In contrast, the CMCs of the nonionic surfactants do not change in the range of NaOH or NaCl concentration tested. The observed effect of ions on the CMC of the anionic surfactant SDS coincides with that reported by Rosen (Rosen and Kunjappu, 2012). Moreover, for a given molar concentration of salt in the media, no differences were found with NaOH or NaCl.

As is plotted in Fig. SM-1a, the higher the concentration of NaOH or NaCl, the lower the CMC of SDS. The drop in the CMC value with SDS at high concentrations of salts can be attributed to the decrease in the electrostatic repulsions among the ionic head groups of the anionic surfactant, located at the micelle outside, in the presence of the additional electrolyte (Rosen and Kunjappu, 2012). Moreover, it should be expected that the lower the CMC value of SDS in the presence of an electrolyte, the higher the solubilization of DNAPL. An increase in the

molar solubility ratio (MSR) of COCs when the NaOH was added to the SDS solution was reported elsewhere ($MSR_{without NaOH} = 0.7$ $mmol_{COCs} \cdot g_{surf}^{-1}$ and $MSR_{with NaOH} = 1.32 \ mmol_{COCs} \cdot g_{surf}^{-1}$) (García-Cervilla et al., 2020a). Moreover, in that work it was also found that the solubility of DNAPL with the three nonionic surfactants studied here was not affected by the addition of alkali, in accordance with the constant CMC shown in Fig. SM-1b. For the nonionic surfactant here used an almost constant value $MSR = 4.33 \ mmol_{COCs} \cdot g_{surf}^{-1}$ was obtained. Therefore, it can be concluded that the CMC of the nonionic surfactants tested is not affected by the NaCl or NaOH addition in the whole range of concentration studied here. On the other hand, the electrolyte concentration in the medium has a remarkable influence on CMC of the anionic surfactant SDS, but this effect does change with the type of electrolyte used (NaOH or NaCl). The remediation treatment selected requires the addition of alkali to activate PS, but the addition of chloride is not needed. Although chloride is naturally present in the groundwater of the polluted site at a concentration in the range 11–28 mmol $\cdot L^{-1}$ (Santos et al., 2018b; Santos et al., 2019) this concentration did not modify the results obtained in the abatement of COCs by PS activated by alkali (Santos et al., 2018b).

3.2. Unproductive consumption of persulfate by the surfactants

In this section, a study of the main variables that can affect the rate of persulfate consumption in the presence of surfactants and absence of DNAPL is accomplished.

Firstly, some blank runs were carried out to evaluate the consumption of PS activated by alkali in the absence of surfactants, experiments (B1 to B4 in Table SM-3). After 864 h of reaction time, the consumption of persulfate was lower than 0.05 under the more powerful oxidant conditions tested ($C_{PS, 0} = 84 \text{ mmol} \cdot L^{-1} C_{NaOH, 0} = 186 \text{ mmol} \cdot L^{-1}$). For this reason, it was assumed that the consumption of PS in the absence of surfactants was negligible in the range of variables and time used here, in accordance with previous reports (Lominchar et al., 2018b; García-Cervilla et al., 2020b).

3.2.1. Effect of the initial surfactant concentration

The effect of the initial concentration of surfactant (3, 6 and 12 g · L^{-1}) on PS decomposition was studied at $C_{PS,0} = 84 \text{ mmol} \cdot L^{-1}$, the molar ratio of NaOH:PS = 1 and room temperature. The experimental conditions of the runs were summarized in Table SM-3. The remaining PS concentration at different reaction times and different initial concentrations of surfactants was measured, and results obtained are plotted in Fig. 1.

Fig. 1a shows the experimental values of the remaining PS when SDS was used. As can be seen, the fraction of the remaining persulfate was close to 0.9 in the different initial concentrations of SDS tested. Therefore, it can be considered that the anionic surfactant is stable against PS and did not produce a significant unproductive consumption of the oxidant.

The remaining concentration of PS when nonionic surfactants were used is shown in Fig. 1b, c, and d for E3, T80, and TS80, respectively. In contrast to the results obtained when employing SDS, the presence of nonionic surfactants enhanced the consumption of PS, in accordance with that previously reported in the literature (Wang et al., 2017; Lominchar et al., 2018a; Wang et al., 2020). Wang et al. (Wang et al., 2020) studied the consumption of PS by anionic and nonionic surfactants using thermally activated PS. They found higher consumption of PS by nonionic surfactant than by anionic surfactant. The higher stability of SDS against PS was already reported by Wang et al. (2020), using thermal activated PS. These authors reported the existence of repulsion forces between the anionic radicals (SO_4^- in that work) and the sulfonate anions located at the exterior of the SDS micelle (Wang et al., 2020). Using PSA, the repulsions are the consequence of the anionic radical $O_2^{\bullet-}$, according to Eq. (1) and the activator (OH^-). Moreover, Wang et al. (2020) considered that the hydroxyl radical can attack the C-H



Fig. 1. Remaining PS vs. reaction time at different initial surfactant concentrations (3, 6 and $12 g \cdot L^{-1}$) at $C_{PS, 0} = 84 \text{ mmol} \cdot L^{-1}$ and NaOH:PS = 1 mmol $\cdot \text{ mmol}^{-1}$. Runs in Table SM-3 (a) SDS, (b) E3, (c) T80, and (d) TS80. In run C20, NaOH was added twice (marked with circles) to keep pH over 12.

bond of the linear alkyl chain of SDS molecules in solution (by hydrogen abstraction). The alkyl radical formed can react with $(S_2O_8)^{2-}$ to cause persulfate decomposition and generate more radicals (in this work, hydroxyl and superoxide radicals). However, as these authors explain, the linear alkyl radical is relatively stable against PS and retards the PS decomposition. The fact that the linear alkyl chain of SDS is more refractory to oxidation than the polyethoxylated chains of nonionic surfactants (E3, T80 y TS80) has also been reported by Brand et al. (1998) and Pagano et al. (2008).

As can be seen in Fig. 1b to d, if nonionic surfactants are used, the higher the initial concentration of surfactant, the lower the remaining PS concentration. This behavior was also found by other authors (Wang et al., 2020) in the consumption of thermally activated PS using Brij 35, whose chemical structure is similar to some of the surfactants used here.

For the three nonionic surfactants used, the persulfate conversion was about 0.3 at t = 900 h when the initial surfactant concentration was 3 $g \cdot L^{-1}$ ($C_{PS, 0} = 84 \text{ mmol} \cdot L^{-1}$ and NaOH:PS = 1 mmol $\cdot \text{ mmol}^{-1}$). However, the consumption of PS was about 0.7 for E3 and TS80 and 0.8 for T80 when the initial concentration of surfactant was $12 g \cdot L^{-1}$. Therefore, the increase in surfactant concentration has a remarkable effect on PS consumption. Moreover, the unproductive consumption of PS by E3 or TS80 is slightly lower than that by T80 in the same conditions.

Runs in Table SM-3 were carried out at a pH close to 13. However, in run C20 (using $12 g \cdot L^{-1}$ of TS80) the pH dropped to 10 at reaction times of 168 h and 336 h. At each of these times, NaOH was added to raise the pH to 13. This drop of pH could indicate that the oxidation of TS80 produces byproducts with stronger acidity since this decrease was only detected using this surfactant and PS consumption obtained was similar with TS80, E3 and T80.

The mineralization of the surfactants was studied from results in runs C1 and C5 for SDS; C6 and C10 for E3; C11 and C15 using T80 and C16 and C20 for TS80. The remaining TOC was measured at 864 h of reaction time. The corresponding initial TOC was calculated with the fraction of C in the surfactant mass ($FR_{TOC, surf}$) in Table S1. Regardless of the type of surfactant and PS conversion, experimental data provided in Fig. SM-2, negligible surfactant mineralization was achieved at all of the initial surfactant concentrations tested (3 and 12 $g \cdot L^{-1}$). This finding has also been reported in the literature (Pagano et al., 2008; Mendez-Diaz et al., 2010).

3.2.2. Effect of the initial concentration of PS

The effect of the initial concentration of PS was studied for the four surfactants selected at a concentration of 3 $g \cdot L^{-1}$ and using two initial concentrations of PS (84 and 42 *mmol* $\cdot L^{-1}$). The results of the fractional remaining PS vs. reaction time are plotted in Fig. 2.

As can be seen in Fig. 2a, the consumption of PS by SDS was negligible at the two PS concentrations used, and their effect on PS conversion cannot be discerned. On the contrary, when nonionic surfactants were used a decrease in oxidant conversion was always observed when the initial concentration of PS decreases. For instance, at 864 h the degradation of PS were 0.2 and 0.4 when the initial PS concentration was 42 *mmol* \cdot L^{-1} , or 84 *mmol* \cdot L^{-1} , respectively. This fact agrees with the reported by Wang et al. (2020), considering that the reactions between surfactants and PS involved a radical-chain mechanism. The surfactant molecules react with the radicals, and these react with the PS anion to produce more radicals, increasing the PS consumption. In this way, the higher the initial concentration of PS used, the faster the initiation and propagation reactions are. This effect is more noticeable when nonionic surfactants are used due to the higher reactivity of the



Fig. 2. Fractional remaining PS at different initial concentrations of PS (42 and 84 *mmol* \cdot L^{-1}) for the surfactants (a) SDS, (b) E3, (c) T80 and (d) TS80. Runs in Table SM-3, $C_{Surf, 0} = 3 g \cdot L^{-1}$ NaOH:PS = 1 *mmol* \cdot *mmol*⁻¹.

radicals formed compared with the alkyl radicals produced with SDS (Wang et al., 2020).

The highest mineralization conversion (5% at 864 h) was obtained using TS80 and 84 *mmol* \cdot *L*⁻¹ of PS (run C18), in accordance with the data plotted in Fig. SM-2.

3.2.3. Effect of NaOH:PS molar ratio

When an alkali is used to activate PS, the molar ratio between the activator (NaOH) and the oxidant (PS) could influence the production of radicals. In Fig. 3, the fractional remaining PS vs. reaction time obtained with NaOH:PS molar ratios 1 and 2 are shown. In these runs, PS and surfactant concentrations were $84 \text{ mmol} \cdot L^{-1}$ and $3 \text{ g} \cdot L^{-1}$, respectively. As can be seen, small differences were found in PS conversion with both molar ratios tested. The pH change with time noticed in runs plotted in Fig. 3 was also monitored, and the pH profiles are shown in Fig. SM-3 of the Supplementary material. It was found that the pH was quite constant for 864 h, being slightly lower when the NaOH:PS ratio had a value of 1 (pH was higher than 12 in all cases). An almost negligible influence of this activator:oxidant ratio was found on the PS or pollutant conversion if pH was high enough (>12) in accordance with that reported in the literature (Santos et al., 2018b; Dominguez et al., 2019a; Dominguez et al., 2020; García-Cervilla et al., 2020b).

3.3. Effect of the oxidant on surfactant solubilization capacity

It is expected that the reaction between the oxidant and the surfactant modify the surfactant properties, among them, the solubilization capacity of the latter. The runs in Table SM-4 (set 3) were carried out to study the loss of solubilization capacity of the partially oxidized surfactant. This information and the unproductive consumption of PS obtained from runs in set 1 are used in the selection of the more appropriate surfactants in an S-ISCO application. As indicated in Section 2.2.3, the aqueous surfactant solutions were in contact with the oxidant under the experimental conditions in Table SM-3. After 360 h of reaction time, the reaction was quenched with sodium bisulfite, and an amount of DNAPL was added to the partially oxidized surfactant solution. After the agitation and settling of the resulting mixture for 24 h, the concentration of dissolved COCs was measured.

The molar solubilization ratios (MSR) of each surfactant for the DNAPL used here were experimentally found elsewhere (García-Cervilla et al., 2020a). The MSR in conditions of equilibrium is calculated using Eq. (3).

$$MSR = \frac{\left(\sum C_{jAQ}\right)_{eq}}{\left(C_{surf_{AQ}}\right)_{eq}} \tag{3}$$

where C_{jAQ} is the concentration of COC j in the aqueous phase $(mmol_{COC} \cdot L^{-1})$ and $C_{surf_{AQ}}$ the surfactant concentration in the aqueous phase $(g_{surf} \cdot L^{-1})$ after equilibrium was reached. The MSR values obtained elsewhere under strong alkaline conditions (García-Cervilla et al., 2020a) were 1.32 mmol_{COCs} $\cdot g_{surf}^{-1}$ with SDS and 4.33 mmol_{COCs} $\cdot g_{surf}^{-1}$ with the nonionic surfactants (E3, T80, and TS80) and DNAPL employed here.

The surfactant initially added has been partially oxidized after a period of contact with the oxidant. An equivalent surfactant concentration (ESC in $g_{surf} \cdot L^{-1}$) is defined as the concentration of virgin surfactant that would yield the solubilization the COCs found in runs in Table SM-4, carried out with partially oxidized surfactants. The value of ESC can be estimated according to Eq. (4), using the corresponding MSR for each surfactant and the sum of solubilized COCs obtained in runs in Table SM-4, after the addition of an amount of DNAPL to the partially oxidized surfactant solution.



Fig. 3. Fractional remaining PS vs. reaction time at initial molar ratios NaOH:PS 1 and 2. (a) SDS, (b) E3, (c) T80, and (d) TS80. Runs in Table SM-3 $C_{Surf, 0} = 3 g \cdot L^{-1}$ and $C_{PS, 0} = 84 \text{ mmol} \cdot L^{-1}$.

$$ESC = \frac{\sum COC_j (mmol \cdot L^{-1})}{MSR (mmol_{COC} \cdot g_{surf}^{-1})}$$
(4)

The ESC value obtained by Eq. (4) is compared with the ESC value

expected if the initial surfactant added were not oxidized, called ESCo.

The value of ESC_o is lower than $C_{surf, 0}$ while the partitioning of the surfactant between aqueous and organic phases should be considered. The

relation between ESC_o and $C_{surf, 0}$ is obtained by Eq. (5).

$$C_{surf,0} \cdot V_{aq} = \text{ESC}_{o} \cdot V_{aq} + (C_{surf_{ORG}})_{eq} \cdot W_{DNAPL}$$
(5)

where V_{aq} is the volume of the aqueous phase and w_{DNAPL} the mass of DNAPL added to this volume (experiments summarized in Table SM-4).

The distribution of the surfactant among organic (DNAPL) and aqueous phases was well predicted by a linear partitioning equilibrium as shown in Eq. (6).

$$\left(C_{surf_{ORG}}\right)_{eq} = K_L \cdot ESC_o \tag{6}$$



Fig. 4. Loss of surfactant solubilization capacity as ESC/ESC₀ after the surfactant solution and PS/NaOH were in contact for 168 and 360 h (a) $C_{surf, 0} = 3 \text{ g} \cdot L^{-1}$, (b) $C_{surf, 0} = 12 \text{ g} \cdot L^{-1}$. Experimental runs in Table SM-4.

A value of the linear partitioning coefficient $K_L = 0.02 g_{surf_{ORG}} \cdot L \cdot g_{surf}^{-1} \cdot g_{ORG}^{-1}$ was found elsewhere (García-Cervilla et al., 2020a) for all the surfactants and DNAPL used in this work at pH > 12 and using the DNAPL from Bailin landfill.

From Eqs. (5) and (6) the value of ESC_o can be obtained as:

$$ESC_{o} = \frac{C_{surf,0} \cdot V_{aq}}{V_{aq} + K_{L} \cdot w_{DNAPL}}$$
(7)

and the remaining solubilization capacity of the surfactant after its partial oxidation can be calculated by the ratio of *ESC/ESC*_o. This remaining ESC/ESCo value is a crucial point in the S-ISCO treatment.

The ratios *ESC/ESC*_o obtained at 168 and 360 h of contact between the surfactant and the oxidant are shown in Fig. 4. As can be seen, for a given surfactant, the higher the reaction time with the oxidant, the higher the loss of surfactant capacity. Moreover, the ESC/ESCo ratio depends on both the initial concentration of the surfactant and the surfactant studied. Some surfactants (T80 and TS80) show a quick loss of ESC in the early stages. This fact can be explained by the preferential chemical attacks of PS on the polyethoxylated functional groups (Wang et al., 2020). This oxidation can produce clouding/oiling in the solutions (Mukherjee et al., 2011) and a decrease in the ESC value. The remaining surfactant capacity could be attributed to the surfactant properties of the oxidation byproducts (Pagano et al., 2008).

The highest values of ESC/ESCo (close to unity) are obtained with SDS (anionic surfactant) in accordance with the lowest consumption of PS noticed using this surfactant (Fig. 1). The loss of solubilization capacity was higher with the nonionic surfactants; among these, the lowest decrease was obtained with E3.

The DNAPL used was composed of a total of 28 COCs, as detailed in Section 2.1, that can be gathered in compounds with the same number of chlorine atoms in the molecule. The COCs dissolved in the aqueous phase in runs in Table SM-4 were analyzed to figure out if the oxidized surfactant showed preference in solubilizing some type of COCs. Molar fraction (as a percentage) of COCs in solution when the surfactant was partially oxidized (at 168 and 360 h) is shown in Fig. SM-4 in the Supplementary material. The corresponding distribution of COCs in the original DNAPL phase in alkaline conditions (Lorenzo et al., 2020) was summarized in Table SM-2 and is also shown in Fig. SM-4. It can be seen that the distribution of COCs in the DNAPL (at alkaline conditions) is similar to that obtained for the solubilized COCs in the partially oxidized surfactant aqueous emulsion, independently of oxidation time. Differences are lower than 15%. This fact can be explained assuming that the organic phase is similarly trapped in the micelles formed by virgin molecules of partially oxidized surfactant.

3.4. Oxidation of COCs in aqueous surfactant emulsion by PS activated with alkali

Surfactants and oxidants are simultaneously injected in an S-ISCO treatment with the scope of enhancing the solubilization of hydrophobic organic pollutants. Consequently, a decrease in the time required for the removal of the NAPL mass from the site is expected. However, this time is not proportional to the increase in pollutant solubilization. The competition of surfactants and contaminants for the oxidant, and the protective effect of the surfactant against the oxidation of pollutants trapped in the micelles should also be considered.

The experiments in Table SM-5 were carried out, adding the oxidant (PS) and the activator (NaOH) to the aqueous emulsion containing the pollutant (DNAPL solubilized) and the surfactant, according to the procedure in Section 2.2.4. SDS and E3 were selected as the anionic and nonionic surfactants, respectively, for this study. As mentioned above, SDS presented lower MSR than nonionic surfactants but a negligible consumption of PS. On the other hand, E3 was the nonionic surfactant that yielded less PS consumption and a higher ESC/ESC₀ ratio.

Taking into account the MSR values ($MSR_{SDS} = 1.32 \text{ mmol } COCs \text{ } g_{DS}^{-1S}$ and $MSR_{E3} = 4.33 \text{ mmol } COCs \text{ } g_{E3}^{-1}$) the solubilization of the DNAPL added (3.7 mmol in 1 L of aqueous surfactant solution) was complete with the initial concentration used for SDS ($12 \text{ } g \cdot L^{-1}$) and E3 ($3 \text{ } g \cdot L^{-1}$). In both runs in Table SM-5, PS concentration and NaOH/PS molar ratio were 84 mmol $\cdot L^{-1}$ and 1, respectively.

At time zero (when PS was added), the concentration of COCs dissolved was 3.70 $mmol_{COCs} L^{-1}$. At different reaction times, a vial with SDS (run S1) or E3 (run S2) was sacrificed, and the remaining PS, COCs, TOC, and pH were measured. In this set of runs, the total reaction volume was diluted in MeOH (1:10 in volume) and analyzed. In this way, the total amount of COCs in the reaction media was quantified, regardless of the phases present in the vial. The PS and COCs profiles showing time are plotted in Fig. 5.

In Fig. 5a, the remaining fractional PS vs. time in runs S1 and S2 in Table SM-5 (simultaneous oxidation of COCs and surfactants from time zero) is plotted with crossed symbols. For the scope of comparison, the results obtained at the same oxidant, activator and surfactant concentrations but without dissolved COCs (runs C5 and C6 in Table SM-3) are also shown (plotted with solid symbols). It can be observed that similar PS consumption was obtained despite the presence or not of COCs in solution.



Fig. 5. Fractional remaining of a) PS and b) COC vs. time using SDS $(12 g \cdot L^{-1})$ and E3 $(3 g \cdot L^{-1})$ and $C_{PS,0} = 84 \text{ mmol} \cdot L^{-1}$, NaOH:PS molar ratio = 1. Solid symbols correspond to runs without COCs in solution (Runs C5, C6, Table SM-3) and data with initial solubilized DNAPL (3.709 mmol COCs L_{aq}^{-1} , runs S1 and S2 in Table SM-5) are plotted with crossed symbols.

The remaining fractional COCs with the reaction time in runs S1 and S2 (Table SM-5) are plotted in Fig. 5b. As can be seen, the conversion of COCs with time was much higher with E3 than with SDS, despite the higher unproductive PS consumption in the first case. At 679 h, the conversion of COCs dissolved in E3 (run S2) and SDS (run S1) was 0.65 and 0.21, respectively. As can be seen, the conversion of COCs with time was much higher with E3 than with SDS, despite the higher unproductive PS consumption in the first case. At 679 h, the conversion of COCs dissolved in E3 (run S2) and SDS (run S1) was 0.65 and 0.21, respectively. The inhibition of the potential oxidation of PS caused by SDS can be explained by the electrostatic repulsion forces between the oxidant $(S_2O_8^{2-})$ and activator (OH⁻) and the hydrophilic anionic groups of SDS. These repulsions result in lower unproductive consumption of PS and lower degradation of COCs when SDS is the surfactant used. The Coulomb forces hinder the accessibility of oxidant and activator to the inside of SDS micelle. Consequently, the production of radicals in the micelle inside decreases, resulting in lower oxidation of COC, and the organic compounds in the inside of the micelles staying isolated from the attack of the radicals (Trellu et al., 2017).

The role of hydroxyl radical in oxidation of chlorinated organics, including HCHs has been recently discussed by Wacławek et al. (2019).

On the contrary, these repulsion forces and inhibition effects are lower with nonionic surfactants. Moreover, some polar compounds, such as chlorobenzenes, can diffuse to the outside of the micelle, favoring contact between pollutants and oxidants (Rosen and Kunjappu, 2012). Therefore, despite the higher PS consumption obtained with E3, a higher conversion of COCs is obtained with this surfactant.

Moreover, the conversion of COCs with time in S-ISCO (runs S1 and S2, Table SM-5) can be compared with those calculated if the oxidation of the same mass of DNAPL took place in the absence of surfactant (ISCO). For this comparison, it is considered that an amount of 0.07 mmol of DNAPL is added to the aqueous volume ($V_{aq} = 0.02 L$) with an initial oxidant concentration $C_{PS, 0} = 84 \text{ mmol} \cdot L^{-1}$ and a NaOH:PS molar ratio = 1. To estimate the time required to remove this DNAPL amount in the absence of surfactant, the following assumptions have been made:

- The mass transfer resistance between the organic (DNAPL) and the aqueous phase has been neglected. Therefore, the concentration of COCs in the aqueous solution corresponds to the partitioning equilibrium with the organic phase.
- 2) 1,2,4 TCB is the most abundant compound in DNAPL in alkaline conditions –Table SM-2- and this compound also has the highest solubility in these conditions (0.17 mmol $\cdot L^{-1}$) among all TCBs and TetraCBs isomers. Therefore, the concentration of COCs in solution in the absence of surfactant is set to this value ($C_{COCS}^* \approx 0.17$ mmol $\cdot L^{-1} \lor time$)
- 3) The kinetics of the oxidation of chlorobenzenes in aqueous phase with PS and NaOH was obtained elsewhere (Santos et al., 2018b). The kinetic model is summarized in Eq. (8).

$$r_{j,aq} = k_{j,aq} \frac{C_{j,aq}}{M_j} C_{PS} C_{NaOH}^0 \left(mmol \ j \cdot L^{-1} \cdot h^{-1} \right)$$
(8)

where $k_{j, aq}$ is the kinetic constant of the oxidation of compound *j* in the aqueous phase (*j* = CB, DCB, TCB, TetraCB). A similar value of the kinetic constant $k_{j, aq}$ for all chlorobenzenes ($k_{j aq} = 3.9 \cdot 10^{-3} L \cdot mmol^{-1} \cdot day^{-1}$) was obtained elsewhere (Santos et al., 2018b).

Based on the above assumptions, the removal rate of the moles of COCs in DNAPL added can be seen in Eq. (9).

$$-\frac{dn_{COCS}}{dt} = r_{jaq} V_{aq} = k_1 C_{NaOH}^0 \cdot C_{PS} \cdot C_{COC}^{eq} \cdot V_{aq}$$
⁽⁹⁾

where k_1 is the kinetic constant (0.0039 $L \cdot mmol^{-1} \cdot day^{-1}$), C_{PS} the PS concentration in *mmol* $\cdot L^{-1}$, V_{aq} the volume of the aqueous phase and C_{COC}^{eq} the concentration of COCs in the aqueous phase. Under hypothesis

Table 1

Comparison of time required in the removal of 0.07 mmol of DNAPL in 0.020 L of the aqueous phase with surfactant (S-ISCO, Fig. 5) and without surfactant (ISCO), Eq. (11) surfactant $C_{PS,0} = 84 \text{ mmol} \cdot L^{-1}$, NaOH:PS molar ratio = 1.

X _{COCs}	ISCO, time (days) (Eq. (11))	Surfactant	S-ISCO, time (days) (Fig. 5)
0.2	>15 (>360 h)	SDS	11 (264 h)
	>15 (>360 h)	E3	2 (48 h)
0.65	>51 (<1224 h)	SDS	No data
	>51 (<1224 h)	E3	28 (672 h)

2, the latter is assumed to be a constant value with time ($C_{COC}^{eq} = 0.17$ mmol $\cdot L^{-1}$). Integrating Eq. (9) and taking into account the conversion of COC defined in Eq. (10), the relationship between time and COC conversion in the absence of surfactants is obtained by Eq. (11).

$$X_{\text{COCs}} = 1 - \frac{n_{\text{DNAPL}}}{n_{\text{DNAPL},0}} \tag{10}$$

$$t = n_{\text{COCS},0} \cdot \frac{X_{\text{COCS}}}{\left(k_1 \cdot C_{\text{PS}} \cdot C_{\text{TCB}}^{eq} \cdot V_{aq}\right)} \tag{11}$$

The reaction times needed to reach COC conversion values of 0.2 and 0.65 without a surfactant at $C_{PS, 0} = 84 \text{ mmol} \cdot L^{-1}$ and NaOH:PS molar ratio = 1, have been estimated with Eq. (11), and values are shown in Table 1. The reaction time values experimentally found to reach this conversion with SDS and E3, in the same oxidant conditions and mass of DNAPL added, are also summarized in Table 1 (values taken from Fig. 5). As can be seen, the time required to reach a certain COC conversion is remarkably lower with nonionic surfactant addition (E3) than without surfactant addition. The time needed without a surfactant, underestimated due to the equilibrium between phases, has been assumed. Moreover, the solubility of 1,2,4 TCB has been used as the concentration of dissolved COCs.

Neither non-chlorinated nor aromatic compounds were detected by GC–MS or GC-ECD-FID as oxidation byproducts of COCS in DNAPL, with or without surfactants.

4. Conclusions

The results obtained in the present work indicate that the selection of suitable surfactants for the application of an S-ISCO treatment is a complex task. It should take into account issues such as the compatibility of surfactants and oxidants, the solubilization capacity of virgin and partially oxidized surfactants, and the oxidation rate of COCs in the aqueous surfactant emulsion.

It was observed that the anionic surfactant studied (SDS) did not produce an appreciable consumption of PS in the conditions tested. However, this surfactant showed a lower molar solubility ratio (MSR) and a lower rate of COC oxidation in the emulsion. The low unproductive oxidant consumption and the low oxidation rate of COCs in the SDS micelles can be explained by the electrostatic repulsions between the reagents producing radicals (oxidant and activator) and the hydrophilic groups of SDS. The decrease in radical generation inside the micelles explains the lower oxidation rate of COCs in the micelles.

In contrast, higher PS conversions were found using the three nonionic surfactants studied (E3, T80 and TS80), where E3 showed slightly lower unproductive oxidant consumption. Of note is the increase of nonionic surfactant concentration, which increases the unproductive consumption of the oxidant.

Despite the higher unproductive PS consumption found with the nonionic surfactants, the conversion of DNAPL in the surfactant emulsion was higher, due to the absence of the electrostatic repulsions mentioned above. Moreover, some polar compounds, such as chlorobenzenes present in DNAPL, can diffuse to the outside of the micelle, favoring contact between pollutants and oxidants. Therefore, for the DNAPL and surfactants studied here, the higher the surfactant stability in relation to the oxidant, the higher the protective effect of surfactants against oxidant attack on the pollutants trapped in the core of the micelles.

The choice of optimal surfactant dosages should balance the higher solubilization of COCs, and the increase in unproductive consumption of the oxidant found when the surfactant concentration increased. Still, results obtained in this paper encourage further research on the simultaneous application of surfactants and oxidants in DNAPL removal in the environment.

CRediT authorship contribution statement

Raul 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.

Acknowledgments

This work was supported by the EU LIFE Program (LIFE17 ENV/ES/ 000260), the Regional Government of Madrid, through the CARESOIL project (S2018/EMT-4317), and the Spanish Ministry of Economy, Industry, and Competitiveness, through project CTM2016-77151-C2-1-R. Raúl García-Cervilla acknowledges the Spanish FPI grant (ref. BES-2017-081782). The authors thank the Department of Agriculture, Livestock and the Environment, Government of Aragon, Spain, as well as EMGRISA, for kindly supplying the DNAPL samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2020.141782.

References

- Baciocchi, R., 2013. Principles, developments and design criteria of in situ chemical oxidation. Water Air Soil Pollut. 224. https://doi.org/10.1007/s11270-013-1717-8.
- Bai, X., Wang, Y., Zheng, X., Zhu, K., Long, A., Wu, X., et al., 2019. Remediation of phenanthrene contaminated soil by coupling soil washing with Tween 80, oxidation using the UV/S2082- process and recycling of the surfactant. Chem. Eng. J. 369, 1014–1023. https://doi.org/10.1016/j.cej.2019.03.116.
- Besha, A.T., Bekele, D.N., Naidu, R., Chadalavada, S., 2018. Recent advances in surfactantenhanced in-situ chemical oxidation for the remediation of non-aqueous phase liquid contaminated soils and aquifers. Environ. Technol. Innov. 9, 303–322. https://doi.org/ 10.1016/j.eti.2017.08.004.
- Bouzid, I., Maire, J., Brunol, E., Caradec, S., Fatin-Rouge, N., 2017. Compatibility of surfactants with activated-persulfate for the selective oxidation of PAH in groundwater remediation. Journal of Environmental Chemical Engineering 5, 6098–6106. https://doi. org/10.1016/j.jece.2017.11.038.
- Brand, N., Mailhot, G., Bolte, M., 1998. Degradation photoinduced by Fe(III): method of alkylphenol ethoxylates removal in water. Environ. Sci. Technol. 32, 2715–2720. https://doi.org/10.1021/es980034v.
- Corcho, D., Fernández, J., Laperou, L., J., G., 2015. Laboratory evaluation of mixed surfactants solutions to mobilise hexachlorocyclohexane (DNAPL) from sardas landfill (Aragón, Spain). 13th HCH & Pesticides Forum 2015, Zaragoza, Spain.
- Dahal, G., Holcomb, J., Socci, D., 2016. Surfactant-oxidant co-application for soil and groundwater remediation. Remediation-the Journal of Environmental Cleanup Costs Technologies & Techniques 26, 101–108. https://doi.org/10.1002/rem.21461.
- Devi, P., Das, U., Dalai, A.K., 2016. In-situ chemical oxidation: principle and applications of peroxide and persulfate treatments in wastewater systems. Sci. Total Environ. 571, 643–657. https://doi.org/10.1016/j.scitotenv.2016.07.032.
- Dominguez, C.M., Rodriguez, V., Montero, E., Romero, A., Santos, A., 2019a. Methanolenhanced degradation of carbon tetrachloride by alkaline activation of persulfate: kinetic model. Sci. Total Environ. 666, 631–640.

- Dominguez, C.M., Romero, A., Santos, A., 2019b. Selective removal of chlorinated organic compounds from lindane wastes by combination of nonionic surfactant soil flushing and Fenton oxidation. Chem. Eng. J. 376. https://doi.org/10.1016/j.cej.2018.09.170.
- Dominguez, C.M., Rodriguez, V., Montero, E., Romero, A., Santos, A., 2020. Abatement of dichloromethane using persulfate activated by alkali: a kinetic study. Sep. Purif. Technol. 241, 116679.
- Dugan, P. J., Siegrist, R. L., Crimi, M. L. 2009. Method and Compositions for Treatment of Subsurface Contaminants. United State Patent US7553105-B1.
- Dugan, P.J., Siegrist, R.L., Crimi, M.L., 2010. Coupling surfactants/cosolvents with oxidants for enhanced DNAPL removal: a review. Remediation 20, 27–49. https://doi.org/ 10.1002/rem.20249.
- Furman, O.S., Teel, A.L., Watts, R.J., 2010. Mechanism of base activation of persulfate. Environ. Sci. Technol. 44, 6423–6428. https://doi.org/10.1021/es1013714.
- García-Cervilla, R., Romero, A., Santos, A., Lorenzo, D., 2020a. Surfactant-enhanced solubilization of chlorinated organic compounds contained in DNAPL from lindane waste: effect of surfactant type and pH. Int. J. Environ. Res. Public Health 17, 4494. https:// doi.org/10.3390/ijerph17124494.
- García-Cervilla, R., Santos, A., Romero, A., Lorenzo, D., 2020b. Remediation of soil contaminated by lindane wastes using alkaline activated persulfate: kinetic model. Chem. Eng. J. 393. https://doi.org/10.1016/j.cej.2020.124646.
- Hoag, G. E., Collins, J. 2011. Soil remediation method and composition. United State patent US7976241.
- Ike, I.A., Linden, K.G., Orbell, J.D., Duke, M., 2018. Critical review of the science and sustainability of persulphate advanced oxidation processes. Chem. Eng. J. 338, 651–669. https://doi.org/10.1016/j.cej.2018.01.034.
- Interstate Technology Regulatory Council, 2000. Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies.
- Kang, S., Lim, H.S., Gao, Y., Kang, J., Jeong, H.Y., 2019. Evaluation of ethoxylated nonionic surfactants for solubilization of chlorinated organic phases: effects of partitioning loss and macroemulsion formation. J. Contam. Hydrol. 223. https://doi.org/10.1016/ j.jconhyd.2019.03.007.
- Katsoyiannis, A., Samara, C., 2005. Persistent organic pollutants (POPS) in the conventional activated sludge treatment process: fate and mass balance. Environ. Res. 97, 245–257. https://doi.org/10.1016/j.envres.2004.09.001.
- Lanoue, M., Kessell, L., Athayde, G., 2011. Surfactant-Enhanced In Situ Chemical Oxidation (S-ISCO®). Águas Subterrâneas.
- Lee, J.F., Liao, P.M., Kuo, C.C., Yang, H.T., Chiou, C.T., 2000. Influence of a nonionic surfactant (Triton X-100) on contaminant distribution between water and several soil solids. J. Colloid Interface Sci. 229, 445–452. https://doi.org/10.1006/jcis.2000.7039.
- Liang, C.J., Lei, J.H., 2015. Identification of active radical species in alkaline persulfate oxidation. Water Environ. Res. 87, 656–659. https://doi.org/10.2175/ 106143015x14338845154986.
- Lominchar, M.A., Lorenzo, D., Romero, A., Santos, A., 2018a. Remediation of soil contaminated by PAHs and TPH using alkaline activated persulfate enhanced by surfactant addition at flow conditions. J. Chem. Technol. Biotechnol. 93, 1270–1278. https:// doi.org/10.1002/jctb.5485.
- Lominchar, M.A., Santos, A., de Miguel, E., Romero, A., 2018b. Remediation of aged diesel contaminated soil by alkaline activated persulfate. Sci. Total Environ. 622, 41–48. https://doi.org/10.1016/j.scitotenv.2017.11.263.
- Londergan, J., Yeh, L., 2003. Surfactant-Enhanced Aquifer Remediation (SEAR) Implementation Manual. No. NFESC, Technical Report: TR-2219-ENV, INTERA INC AUSTIN TX.
- Long, A., Zhang, H., Lei, Y., 2013. Surfactant flushing remediation of toluene contaminated soil: optimization with response surface methodology and surfactant recovery by selective oxidation with sulfate radicals. Sep. Purif. Technol. 118, 612–619. https://doi. org/10.1016/j.seppur.2013.08.001.
- Long, A., Lei, Y., Zhang, H., 2014. Degradation of toluene by a selective ferrous ion activated persulfate oxidation process. Ind. Eng. Chem. Res. 53, 1033–1039. https://doi. org/10.1021/ie402633n.
- Lorenzo, D., Garcia-Cervilla, R., Romero, A., Santos, A., 2020. Partitioning of chlorinated organic compounds from dense non-aqueous phase liquids and contaminated soils from lindane production wastes to the aqueous phase. Chemosphere 239. https:// doi.org/10.1016/j.chemosphere.2019.124798.
- Mao, X., Jiang, R., Xiao, W., Yu, J., 2015. Use of surfactants for the remediation of contaminated soils: a review. J. Hazard. Mater. 285, 419–435.
- Mendez-Diaz, J., Sanchez-Polo, M., Rivera-Utrilla, J., Canonica, S., von Gunten, U., 2010. Advanced oxidation of the surfactant SDBS by means of hydroxyl and sulphate radicals. Chem. Eng. J. 163, 300–306. https://doi.org/10.1016/j.cej.2010.08.002.
- Mobile, M., Widdowson, M., Stewart, L., Nyman, J., Deeb, R., Kavanaugh, M., et al., 2016. Insitu determination of field-scale NAPL mass transfer coefficients: performance, simulation and analysis. J. Contam. Hydrol. 187, 31–46. https://doi.org/10.1016/j. jconhyd.2016.01.010.
- Mukherjee, P., Padhan, S.K., Dash, S., Patel, S., Mishra, B.K., 2011. Clouding behaviour in surfactant systems. Adv. Colloid Interf. Sci. 162, 59–79. https://doi.org/10.1016/j. cis.2010.12.005.
- Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. Surfactant-enhanced remediation of contaminated soil: a review. Eng. Geol. 60, 371–380. https://doi.org/10.1016/s0013-7952 (00)00117-4.
- National Research Council, 2013. Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites. The National Academies, Washington, DC.
- Pagano, M., Lopez, A., Volpe, A., Mascolo, G., Ciannarella, R., 2008. Oxidation of nonionic surfactants by Fenton and H2O2/UV processes. Environ. Technol. 29, 423–433. https://doi.org/10.1080/09593330801983862.
- Paria, S., 2008. Surfactant-enhanced remediation of organic contaminated soil and water. Apr. 138, 24–58. https://doi.org/10.1016/j.cis.2007.11.001.
- Rosen, M.J., Kunjappu, J.T., 2012. Surfactants and Interfacial Phenomena. John Wiley & Sons.

- Santos, A., Fernandez, J., Guadano, J., Lorenzo, D., Romero, A., 2018a. Chlorinated organic compounds in liquid wastes (DNAPL) from lindane production dumped in landfills in Sabinanigo (Spain). Environ. Pollut. 242, 1616–1624. https://doi.org/10.1016/j. envpol.2018.07.117.
- Santos, A., Fernandez, J., Rodriguez, S., Dominguez, C.M., Lominchar, M.A., Lorenzo, D., et al., 2018b. Abatement of chlorinated compounds in groundwater contaminated by HCH wastes using ISCO with alkali activated persulfate. Sci. Total Environ. 615, 1070–1077. https://doi.org/10.1016/j.scitotenv.2017.09.224.
- Santos, A., Dominguez, C.M., Lorenzo, D., Garcia-Cervilla, R., Lominchar, M.A., Fernandez, J., et al., 2019. Soil flushing pilot test in a landfill polluted with liquid organic wastes from lindane production. Heliyon 5. https://doi.org/10.1016/j.heliyon.2019.e02875. Siegrist, R.L., Crimi, M., Simpkin, T.J., 2011. In Situ Chemical Oxidation for Groundwater
- Remediation. Springer-Verlag New York, New York.
- Soga, K., Page, J.W., Illangasekare, T.H., 2004. A review of NAPL source zone remediation efficiency and the mass flux approach. J. Hazard. Mater. 110, 13–27. https://doi.org/ 10.1016/j.jhazmat.2004.02.034.
- Sra, K.S., Thomson, N.R., Barker, J.F., 2014. Stability of activated persulfate in the presence of aquifer solids. Soil Sediment Contam. 23, 820–837. https://doi.org/10.1080/ 15320383.2013.722142.
- Tomlinson, D.W., Rivett, M.O., Wealthall, G.P., Sweeney, R.E.H., 2017. Understanding complex LNAPL sites: illustrated handbook of LNAPL transport and fate in the subsurface. J. Environ. Manag. 204, 748–756. https://doi.org/10.1016/j.jenvman.2017.08.015.
- Trellu, C., Mousset, E., Pechaud, Y., Huguenot, D., van Hullebusch, E.D., Esposito, G., et al., 2016. Removal of hydrophobic organic pollutants from soil washing/flushing solutions: a critical review. J. Hazard. Mater. 306, 149–174. https://doi.org/10.1016/j. ihazmat.2015.12.008.
- Trellu, C., Oturan, N., Pechaud, Y., van Hullebusch, E.D., Esposito, G., Oturan, M.A., 2017. Anodic oxidation of surfactants and organic compounds entrapped in micelles -

selective degradation mechanisms and soil washing solution reuse. Water Res. 118, 1–11. https://doi.org/10.1016/j.watres.2017.04.013.

- Tsai, T., Kao, C., Hong, A., 2009. Treatment of tetrachloroethylene-contaminated groundwater by surfactant-enhanced persulfate/BOF slag oxidation—a laboratory feasibility study. J. Hazard. Mater. 171, 571–576.
- Wacławek, S., Antoš, V., Hrabák, P., Černík, M., 2016. Remediation of hexachlorocyclohexanes by cobalt-mediated activation of peroxymonosulfate. Desalin. Water Treat. 57, 26274–26279. https://doi.org/10.1080/19443994.2015.1119757.
- Wacławek, S., Silvestri, D., Hrabák, P., Padil, V.V.T., Torres-Mendieta, R., Wacławek, M., et al., 2019. Chemical oxidation and reduction of hexachlorocyclohexanes: a review. Water Res. 162, 302–319. https://doi.org/10.1016/j.watres.2019.06.072.
- Wang, W.H., Hoag, G.E., Collins, J.B., Naidu, R., 2013. Evaluation of Surfactant-enhanced In Situ Chemical Oxidation (S-ISCO) in contaminated soil. Water Air Soil Pollut. 224, 1713. https://doi.org/10.1007/s11270-013-1713-z https://ARTN.
- Wang, L., Peng, L., Xie, L., Deng, P., Deng, D., 2017. Compatibility of surfactants. And thermally activated persulfate for enhanced subsurface remediation. Environ. Sci. Technol. 51, 7055–7064. https://doi.org/10.1021/acs.est.6b05477.
- Wang, L., Wu, H., Deng, D., 2020. Role of surfactants in accelerating or retarding persulfate decomposition. Chem. Eng. J. 384. https://doi.org/10.1016/j.cej.2019.123303.
- Yang, K., Zhu, L., Xing, B., 2006. Enhanced soil washing of phenanthrene by mixed solutions of TX100 and SDBS. Environ. Sci. Technol. 40, 4274–4280. https://doi.org/ 10.1021/es060122c.
- Zheng, F., Gao, B., Sun, Y., Shi, X., Xu, H., Wu, J., et al., 2016. Removal of tetrachloroethylene from homogeneous and heterogeneous porous media: combined effects of surfactant solubilization and oxidant degradation. Chem. Eng. J. 283, 595–603.