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Remediation of real soils polluted with pesticides by activated persulfate and surfactant addition

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ABSTRACT

The existence of soils contaminated with organochlorine pesticides represents a serious environmental problem. In this work, a real soil contaminated with hexachlorocyclohexanes ($\Sigma HCH = 373$ mg kg^{-1}), persistent organic pollutants included in the Stockholm Convention, was remediated. Surfactants were used to enhance the pollutants solubilization and activated persulfate (PS) oxidation to degrade the pollutants. Solubilization experiments were performed to evaluate the effect of surfactant (sodium dodecyl sulfate (SDS), Emulse-3® (E3) and Tween-80® (T80)), pH, reagents addition order and concentration ($C_{surfactant} = 0–10$ g L^{-1}, $C_{NaOH} = 0–13.5$ g L^{-1}). Surfactants selection was performed attending to their ability to solubilize chlorinated organic compounds (COCs). The use of surfactants improved COCs solubilization, especially at pH > 12; conditions at which HCHs hydrolyze to trichlorobenzenes (TCBs), with higher solubility. The higher the surfactant concentration, the higher the COCs concentration in the emulsion. COCs solubilization of 83 % and 89 % were achieved in three surfactant consecutive cycles at highly alkaline conditions using SDS and E3, respectively (T80 was unstable). The resulting emulsions were treated by PS activated by alkali and intensified by temperature. COCs conversion of 30 % and 96 % were achieved when treating E3 and SDS-emulsions (72 h), respectively, highlighting the suitability of SDS for the integrated process.

1. Introduction

In the last decades, industrial activities have generated vast quantities of soil polluted with hydrophobic organic compounds (HOCs), becoming a major environmental problem [1]. One of the most serious cases is the pollution caused by lindane wastes, the gamma isomer of hexachlorocyclohexane (γ-HCH), a polychlorinated pesticide globally used in the second half of the 20th [2]. The lindane manufacture generated large quantities of other HCH isomers (namely α-, β, ε-, and δ-HCH) without insecticidal properties, leading to large deposits of HCH wastes worldwide [3]. Three HCHs (α-, β-, and γ-HCH) have been included in the list of persistent organic pollutants (POPs) in the Stockholm Convention [4] because of their high refractoriness and adverse effects on the ecosystem and human beings. Thus, owing to its toxicity and health implications, the production and use of lindane have been banned in most European countries, the USA, and Canada. In this sense, feasible degradation technologies are required to remediate the sites polluted with these wastes and implement the abovementioned convention.

Advanced oxidation processes (AOPs) can be a feasible option for the remediation of HCHs-polluted soils. Among the AOPs tested (using H_2O_2 and persulfate (PS) as oxidants), PS-based treatments led to better results [5,6] due to the high stability, aqueous solubility, and low cost of this oxidant [7,8]. The degradation power of PS is usually increased activating this oxidant by metal cations, alkali (NaOH), heat, or other energy sources, such as ultrasound, ultraviolet, etc., generating different radicals species [9–15]. Among these systems, PS activated by temperature [5,16], NaOH [10,17], the combination of NaOH and temperature [10,17] and the intensification of NaOH with US [9] have recently been studied for the remediation of HCH-polluted soils. The main limitations found are the high HCHs adsorption onto the soil particles and their low solubility. Thus, their transfer into the aqueous phase, where the degradation process takes mainly place [17–19], is restricted. This limitation can be overcome by the use of surfactants, amphiphilic-nature substances able to reduce the surface tension of water [20], enhancing HOCs solubilization [21]. In this context, the use of surfactants [1,22] and the treatment of the resulting emulsions [23,24] for the remediation of soils contaminated with HOCs has received increasing attention in the

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last decade. The successful application of surfactants combined with oxidation treatments largely depends on the pollutant/surfactant/oxidant system. Thus, several factors should be considered in the surfactant-enhanced pollutants solubilization step, such as the type and surfactant concentration, soil and pollutants characteristics, pH conditions, and soil/water ratio, among others. Concerning the oxidation step, the surfactant should be relatively stable in the presence of the oxidant (due to the organic nature of surfactants, they can compete with the pollutants for the radical species), facilitating the selective oxidation of pollutants [24]. An excess of surfactant hinders the pollutants oxidation and increases the unproductive consumption of the oxidant [25–27]. Thus, the global treatment efficiency will be determined by the surfactant ability to solubilize the HOCs from the polluted soil and the oxidant ability to selectively degrade the emulsions' contaminants.

The remediation of soils contaminated with lindane-wastes by surfactant-enhanced solubilization has been recently reviewed [28]. Most of the papers focus on washing lindane-spiked soils [29–32] instead of real polluted soils and the treatment of the emulsions has been rarely studied. In this sense, deepening the application of the combined process (surfactant-enhanced pollutants solubilization + pollutants oxidation) for the remediation of real HCHs-polluted soils needs further investigation. In this work, real soil mainly contaminated with α-HCH and β-HCH, collected from the old Bailin landfill, close to Sabiñánigo, in the Aragonian Pyrenees (Spain), where the company INQUINOSA dumped lindane wastes from 1984 to 1992, has been remediated. Three commercial surfactants, an anionic surfactant, sodium dodecyl sulfate (SDS), and two non-ionic surfactants, Tween®-80 (T80) and Emulse®-3 (E3), widely used in remediation treatments [1,21,24,33,34], have been evaluated for the first time for this purpose. Firstly, the main variables of the pollutants solubilization step (surfactant, pH, reagents addition order, reagents concentration, liquid/soil ratio, number of solubilization cycles, etc.) were studied, providing valuable information before implementing the process on a full scale. Secondly, the resulting emulsions have been treated by PS activated with alkali and intensified with temperature.

2. Materials and methods

2.1. Polluted soil

The real polluted soil was collected by SARGA (*Sociedad Aragonesa de Gestión Agroambiental*) from the Bailín landfill (Sabiñanigo, Spain) at a depth of 0–0.3 m. The soil sample was crushed in the landfill facilities. The fraction with a particle diameter between 0.02 and 0.25 mm was selected to carry out the experiments [9,17]. HCHs in soil are present as white grains and adsorbed into the soil.

2.2. Chemicals

Three commercial surfactants were used, two nonionic: E-Mulse®-3 (E3) and Tween®-80 (T80, $C_{64}H_{124}O_{26}$), and one anionic, sodium dodecyl sulfate (SDS, $C_{12}H_{25}NaO_4S$). T80 and SDS were purchased from Sigma-Aldrich, and E3 from EthicalChem. N-hexane (C_6H_{14}) and methanol (CH_3OH), used for the extraction of pollutants from the aqueous and solid phases, were provided by Honeywell and Fisher, respectively. Sodium chloride (NaCl), used to break the SDS emulsion for the chromatographic analysis, was supplied by Sigma-Aldrich. Bicyclohexyl ($C_{12}H_{22}$) and tetrachloroethane ($C_2H_2Cl_4$), used as standard internal compounds (ISTD) for pollutant quantification, were provided by Sigma-Aldrich. The oxidant, sodium persulfate (PS, $Na_2S_2O_8$), was purchased by Sigma-Aldrich. Sodium hydroxide (NaOH), used to achieve alkaline conditions in solubilization and oxidation experiments, was supplied by Riedel-de Haën. Potassium iodide (KI) and sodium hydrogen carbonate ($NaHCO_3$) for PS quantification were provided by Fisher-Chemical and Panreac, respectively. Glucose ($C_6H_{12}O_6$), used for total organic carbon (TOC) calibration, was supplied by Riedel-de Haën. All the reagents used were of analytical grade. Solutions were prepared with ultra-pure water produced by a deionizing system (Millipore Direct-Q).

2.3. Pollutants solubilization by surfactant addition

Solubilization experiments (SE) were performed in 40 mL-PTFE batch reactors with PTFE screw caps. The reactors were filled with 15 g of polluted soil and 30 mL of the aqueous solution containing the desired concentration of reagents (surfactant and/or alkali). The reactors were shaken in an LBX RR80 rotatory agitator (80 rpm) at ambient temperature for 24 h (time enough to reach the pollutants equilibrium between the aqueous and solid phases [9,35]). At equilibrium conditions, the slurry systems were centrifuged (10 min at 9000 rpm, MEDTRONIC-BL-S, JP SELECTA®) to separate both phases: soil and polluted emulsion.

The operational conditions of SE are listed in Table 1. This table contains the objective for each set of experiments, the run number (SE1-SE24), the surfactant used (SDS, E3, or T80) and its concentration ($C_{surfactant}$), the alkali concentration (C_{NaOH}), the liquid/soil ratio (V_L/W_S), the number of solubilization cycles and its duration. The variable studied in each series of experiments has been highlighted in bold type. SE runs have been duplicated, with the standard deviation always below 10 % (error bars have been included in de figures).

Firstly, two experiments in the absence of surfactant, at neutral (SE1) and alkaline conditions (SE2), were performed to evaluate the effect of pH on chlorinated organic compounds (COCs) solubilization. These results were compared to those carried out with 10 g L^{-1} of surfactant (SDS, E3, and T80) at neutral (SE3-SE5) and alkaline conditions (SE6-SE8, $C_{NaOH} = 13.5$ g L^{-1}), respectively. Moreover, the reagents (NaOH and surfactant) addition order effect has been evaluated by adding them simultaneously (^{a}) and sequentially (^{b}). In the second case, NaOH was added ($C_{NaOH} = 27$ g L^{-1}, 15 mL), and the reactor stirred for 4 h, time enough to achieve the complete dehydrochlorination of α-HCH (the main soil pollutant) [17]. Afterwards, 15 mL of surfactant ($C_{surfactant} = 20$ g L^{-1}) was added and shaken for 20 h. The effect of alkali (C_{NaOH}, from 2.5 to 13.5 g L^{-1}, SE6-SE14) and surfactant concentration ($C_{surfactant}$, from 2 to 10 g L^{-1}, SE10, SE12, SE15-SE18) has also been evaluated (simultaneous addition of alkali and surfactant). The liquid/soil ratio (V_L/W_S) used in all these experiments was 2.

Finally, three successive solubilization cycles using SDS (SE16, SE19, and SE20) and E3 (SE18, SE22, and SE23) have been performed. The first cycle was carried out at alkaline conditions to favour COCs dehydrochlorination in soil, enhancing their solubility [9]. The second and third cycles were carried out without alkali addition to solubilize the remaining hydrolyzed COCs in the soil. Lower surfactant concentration was used in cycles 2 and 3 than in the first, as the COCs content in the soil also decreased with solubilization cycles. The results after the third solubilization cycle were compared with those obtained in a single step using the highest surfactant concentration applied in the three consecutive cycles (5 g L^{-1}) and an aqueous volume and time sum of that used in the three cycles ($V_L/W_S = 6$, t = 72 h). These experiments are named SE21 and SE24 for SDS and E3, respectively.

2.4. Oxidation of polluted emulsions

Polluted emulsions (PEs) were treated by the alkaline activation of PS intensified by temperature [17]. Oxidation runs were carried out in thermostatted closed cylindrical glass vials (10 mL) without head-space to minimize COCs volatilization. The solution was magnetically stirred (80 rpm) and heated (40 °C) using a TechRADLEYS heating stirrer plate. The oxidation experiments started once PS was added (40 g L^{-1}). A NaOH: PS molar ratio of 2 was used in all runs [9,10,18].

PEs were obtained from SE16 (SDS) and SE18 (E3) experiments, named PE-SDS-1 and PE-E3-1, respectively. Moreover, the emulsion resulting in the three successive solubilization cycles: PE-SDS-1,2,3 (sum of aqueous phases from SE16, SE19, and SE20 runs) and PE-E3-1,2,3

Table 1

Operational conditions of solubilization experiments (SE) ($C_{COCs,0} = 373$ mg kg^{-1}, $W_S = 15$ g).

Objective	SE number	Surfactant	$C_{surfactant}$ (g L^{-1})	C_{NaOH} (g L^{-1})	V_L/W_S	Number of solubilization cycles	Solubilization time (h)
Effect of surfactant and pH	SE1	**No surfactant**	0	**0**	2	1	24
	SE2	**No surfactant**	0	**13.5**	2	1	24
	SE3	**SDS**	10	**0**	2	1	24
	SE4	**E3**	10	**0**	2	1	24
	SE5	**T80**	10	**0**	2	1	24
	SE6[a,b]	**SDS**	10	**13.5**	2	1	24
	SE7[a,b]	**E3**	10	**13.5**	2	1	24
	SE8[a,b]	**T80**	10	**13.5**	2	1	24
Effect of alkali concentration	SE9	SDS	10	**2.5**	2	1	24
	SE10	SDS	10	**4**	2	1	24
	SE6	SDS	10	**13.5**	2	1	24
	SE11	E3	10	**2.5**	2	1	24
	SE12	E3	10	**4**	2	1	24
	SE7	E3	10	**13.5**	2	1	24
	SE13	T80	10	**2.5**	2	1	24
	SE14	T80	10	**4**	2	1	24
	SE8	T80	10	**13.5**	2	1	24
Effect of surfactant concentration	SE15	SDS	**2**	4	2	1	24
	SE16	SDS	**5**	4	2	1	24
	SE10	SDS	**10**	4	2	1	24
	SE17	E3	**2**	4	2	1	24
	SE18	E3	**5**	4	2	1	24
	SE12	E3	**10**	4	2	1	24
Successive solubilization cycles and V_L/W_S ratio	SE16	SDS	5	4	2	**1**	24
	SE19	SDS	2.5	0	2	**2**	24
	SE20	SDS	1.25	0	2	**3**	24
	SE21	SDS	5	4	**6**	**1**	**72**
	SE18	E3	5	4	2	**1**	24
	SE22	E3	2.5	4	2	**2**	24
	SE23	E3	1.25	0	2	**3**	24
	SE24	E3	5	0	**6**	**1**	**72**

[a] Simultaneous and [b] sequential reagents (NaOH and surfactant) addition order. When not specified, the addition of reagents has been carried out simultaneously. The variable studied in each set of experiments has been highlighted in bold type.

(sum of aqueous phases form coming from SE18, SE22 and SE23 experiments) have also been treated. The characteristics of these emulsions, including the PE name, the SE they come from, and the surfactant ($C_{surfactant}$) and pollutants concentration (C_{COCS}) (experimentally determined), have been included in the Supplementary Material (Table SM 1). Blank runs were also carried out to determine the COCs reduction by adsorption or volatilization in the absence of PS. Unproductive consumption of the oxidant was also studied in the absence of solubilized COCs. The objective of the experimental set (blank runs, COCs oxidation, and unproductive PS consumption) and the corresponding experimental conditions (PS concentration, NaOH:PS molar ratio, and reaction temperature) are included in Table SM 1. The ratio between the concentration of PS used and the stoichiometric amount required for COCs mineralization ($C_{PS}/C_{PS,stq}$) has also been included. $C_{PS,stq}$ has been calculated considering the $OH^{\bullet}$ generated in the alkaline activation of PS and the oxidation of the COCs (mainly TCBs) present in the PEs treated [17].

The evolution of each reaction was followed by preparing several vials and sacrificing one at each selected reaction time. The vials were refrigerated for 1 h using an ice bath, and the reaction media was immediately analyzed. PE oxidation experiments were carried out in triplicate, and a standard deviation of <10 % was found (error bars have been included in de figures).

2.5. Analytical techniques

The chemical characterization of the polluted soil, including total organic and inorganic carbon content (TOC and IC, respectively) and metal concentration, were determined in previous work [10].

COCs extraction from soil was accomplished by mixing 15 g of soil with 30 mL of methanol in 40 mL-PTFE vials at 45 °C and placed in an ultrasound bath (Power sonic 505) for 180 min [9,36]. After extraction, the sample was cooled and centrifugated for 10 min at 9000 rpm (MEDTRONIC-BL-S, JP SELECTA®). The organic and soil phases were separated by decantation, and the organic phase was analyzed by gas chromatography (GC).

COCs concentration in the aqueous phases was also analyzed by GC. Sample preparation before GC analysis depends on the presence and type of surfactant used. Aqueous phases without surfactants (those corresponding to experiments SE1 and SE2) were analyzed by liquid-liquid extraction (hexane-water 1/1 mass ratio). The biphasic mixture was vigorously agitated, and COCs concentration in the organic extract was analyzed by GC. In the case of emulsions, direct liquid-liquid extraction is not possible. When SDS was employed, due to its ionic nature, the surfactant was previously precipitated, and the emulsion was broken, adding salt (NaCl) [35]. After that, COCs in the aqueous phase were extracted with hexane (1/1 mass ratio) and subsequently analyzed. In the case of the nonionic surfactants E3 and T80, the aqueous emulsion was diluted with methanol (1/10 volume ratio) and analyzed by GC.

COCs identification in the organic phase was accomplished by gas chromatography (Agilent 6890) coupled with a mass spectrometry detector (GC-MSD), and their quantification was performed by GC coupled with flame ionization and electron capture detectors (GC-FID and GC-ECD, respectively). The column exit (HP-5-MS, 30 m × 0.25 mm i.d., 5 % phenol methyl siloxane) was split to both detectors and simultaneously measured. Additional information on the chromatographic method can be found elsewhere [10,18,37].

The initial and remanent surfactant concentration in the emulsions after SE was determined by TOC, considering the carbon content in SDS, E3, and T80 was respectively 0.50, 0.58, and 0.60 $g_C\, g_{surf}^{-1}$ [34] and subtracting the TOC contribution of COCs in the aqueous phase (previously quantified by GC-FID/ECD). TOC was measured by a Shimadzu TOC-V CSH analyzer coupled with an SSM-5000A using synthetic air as a carrier gas and a furnace temperature of 900 °C. TOC calibration was performed with glucose solutions (0.1–500 mg L^{-1}).

PS concentration in the aqueous phase was determined by a colorimetric method using a water/KI/$NaHCO_3$ solution [38]. The yellow iodine colour formed, proportional to PS concentration, was measured using a BOECO S-20 UV-VIS spectrophotometer at 352 nm. The pH of the aqueous phases in the different experiments (SE and oxidation of PE) was determined using a Basic 20-CRISON pH electrode.

3. Results and discussion

The molar concentration of each COC (i) in the soil ($q_{i,\ soil}$, μmol kg^{-1}) and aqueous ($C_{i,aq}$, μmol L^{-1}) phases were obtained from GC analysis. The moles of each compound (n_i, μmol) and total moles of COCs (n_{COCs}, μmol) in the slurry (sum of moles in soil and aqueous phases) were obtained from the mass balance (Eqs. (1) and (2)), where W and V are the soil phase mass (kg), and aqueous phase volume (L) used, respectively.

$$n_i = Wq_{i,soil} + VC_{i,aq} \tag{1}$$

$$n_{COCs} = \sum n_i \tag{2}$$

n_{COCs} should be closed to those measured in the initial polluted soil. The mass balance (Eqs. (1) and (2)) between both phases (data not showed) was accomplished in all SE (± 5 %).

3.1. Soil characterization

The polluted soil was characterized in a previous work [10]. Metals in a more significant proportion were calcium (168.8 g kg_{soil}^{-1}), iron (21.1 g kg_{soil}^{-1}), and aluminium (17.1 g kg_{soil}^{-1}). Lower sodium, magnesium, potassium, and manganese concentrations were also detected. Labile iron in the solution was low (< 2 mg L^{-1}). It presents a high carbonate content (>40 %), which gives it a strong buffer character, with a pH between 7.5 and 7.8.

The HCHs concentration in the polluted soil (d_p = 0.02–0.25 mm) was 373 mg kg_{soil}^{-1} ($q_{COCs,soil}$ = 1282 μmol kg_{soil}^{-1}). Therefore, 19.23 μmol of COCs are initially present in each reactor (15 g of soil), with around 80 % of α-HCH and 13 % of β-HCH. The remaining 7 % corresponds to other HCH isomers (γ-, δ-, and ε-HCH). Identified COCs represent only a small percentage (<1 %) of measured soil TOC. Thus, the rest of the soil organic matter can be associated with natural organic matter [10].

Fig. SM 1-a and b show the molar distribution of pollutants in soil (grey bar) and aqueous (blue bar) phases at equilibrium conditions (in the absence of surfactants) at neutral and alkaline pH, respectively. A distinction has been made between the majority compounds (α-HCH and β-HCH) and the minority ones (Σγ-, δ-, ε-HCH). In addition, it should be considered that at alkaline conditions (pH > 12), HCHs hydrolyze to trichlorobenzenes (TCBs) [10,17], according to Eq. (3). Therefore, the moles of TCBs and total COCs have been included in Fig. SM 1.

$$HCH + 3OH^- \rightarrow TCB + 3Cl^- + 3\ H_2O \tag{3}$$

The partition coefficient ($K_{d,COCs}$) represents the ratio between the COCs concentration in the soil ($q_{COCs,\ soil}$, mmol kg^{-1}) and aqueous ($C_{COCs,\ aq}$, mmol L^{-1}) phases at equilibrium conditions (Eq. (4)) [35]. Values of $K_{d,COCs}$ (L kg^{-1}) have been calculated and included in Fig. SM 1.

$$K_{d,COCs} = \frac{q_{COCs,soil}}{C_{COCs,aq}} \tag{4}$$

As shown in Fig. SM 1-a, HCHs are the only pollutants at neutral pH. Almost total dehydrochlorination of α-HCH to TCB was found at alkaline pH (Fig. SM 1-b), as previously reported [17]. The percentage of the different isomers of TCBs formed (data not included in the figure) agrees with that reported in previous works (1,2,4-TCB = 85 %, 1,2,3-TCB = 12 %, 1,3,5-TCB = 3 %) [10,17,39]. However, it should be highlighted that not all HCH isomers hydrolyze at the same rate [9,17]. α-, δ-, γ- and ε-HCH were completely dehydrochlorinated to TCBs after 24 h (considered equilibrium conditions), whereas at the same reaction time, the hydrolysis of β-HCH, the most refractory HCH isomer, was below 40 %.

As previously stated, the remediation of HCHs-polluted soils is mainly limited by the low aqueous solubility of the pollutants [9,16], with values in the range: α-HCH = 4.1–6.9 μmol L^{-1} and β-HCH = 0.5–2.4 μmol L^{-1} [39]. Thus, the moles of COCs in the aqueous phase in equilibrium with the soil at the conditions tested (15 g of soil and 30 mL of water) are low (0.6 μmol, Fig. SM 1-a). The moles of COCs solubilized in the aqueous phase highly increased at alkaline conditions (4.8 μmol, Fig. SM 1-b), decreasing the partition coefficient ($K_{d,COCs}$, from 69.2 to 5.8 L kg^{-1}). This fact is attributable to the higher aqueous solubility of TCBs (1,2,4-TCB = 170.8–270.0 μmol L^{-1}, 1,2,3-TCB = 89.8–99.2 μmol L^{-1} and 1,3,5-TCB = 33.1 μmol L^{-1}) than the parent pollutants [10,39].

3.2. Selection of solubilization conditions

The selection of the surfactant-enhanced solubilization step conditions (surfactant, pH, reagents addition order, reagents concentration, and the number of solubilization cycles) was performed by attending to the surfactant ability to solubilize the pollutants from the soil to the emulsion. Other important aspects, such as the adsorption of the surfactant in the soil, or the unproductive consumption of oxidant associated with the surfactant in the following oxidation stage, will be later considered.

3.2.1. Effect of surfactant and pH

To evaluate the surfactant capacity, the moles of COCs in the aqueous phase (blue bars) and the remaining COCs in the soil (grey bars) after SE were determined in the presence of surfactants at neutral (Fig. 1-a) and alkaline (Fig. 1-b) conditions. The final pH of the aqueous phase has been depicted as points (right axis). The results obtained without surfactants have also been included to facilitate comparison. The corresponding $K_{d,COCs}$ values (red bar, Eq. (4)) at neutral and alkaline pH have been represented in Fig. 1-c and Fig. 1-d, respectively. The lower the partition coefficient, the greater the pollutants solubilization in the aqueous phase and, therefore, the greater the solubilization capacity of the evaluated surfactant.

As shown in Fig. 1-a and c, adding surfactants (SDS, E3, and T80) at neutral pH improved COCs solubilization from the soil, significantly decreasing $K_{d,COCs}$ values. The order obtained was T80 ≈ SDS > E3. Different order for these surfactants (E3 > T80 > SDS) was reported in the literature when they were used for COCs solubilization from the dense non-aqueous liquid phase (DNAPL) composed by a mixture of 28 COCs [34,35]. This can be attributable to the different phases involved and different compositions of DNAPL and technical-HCH, highlighting the importance of studying the behaviour of each surfactant in the presence of different real contamination matrices. Carboneras et al. [30] reported a lindane recovery of about 40 % from spiked soil (1000 mg kg_{soil}^{-1}) when using 5 g L^{-1} of SDS and a V_L/W_S = 5 [30]. This value corresponds to $K_{d,COCs}$ = 7.5 L kg^{-1}, being similar to those obtained in this work at neutral pH but with higher surfactant concentration (10 g L^{-1}). This fact could be explained by: i) pollutants of the soil treated in the current work are mostly α- and β-HCH (isomers with lower water solubility than γ-HCH) and ii) it is a real polluted soil, with aged pollution (instead of a spiked soil). It is well known that the ageing process leads to contaminant sequestration by soil [40,41], hindering the subsequent solubilization. This point underlines the importance of studying aged polluted soils (real contamination) instead of spiked soils.

A significantly higher COCs solubilization was obtained at alkaline conditions (pH > 12) with E3 and SDS ($K_{d,COCs}$ = 1.8 L kg^{-1}) in

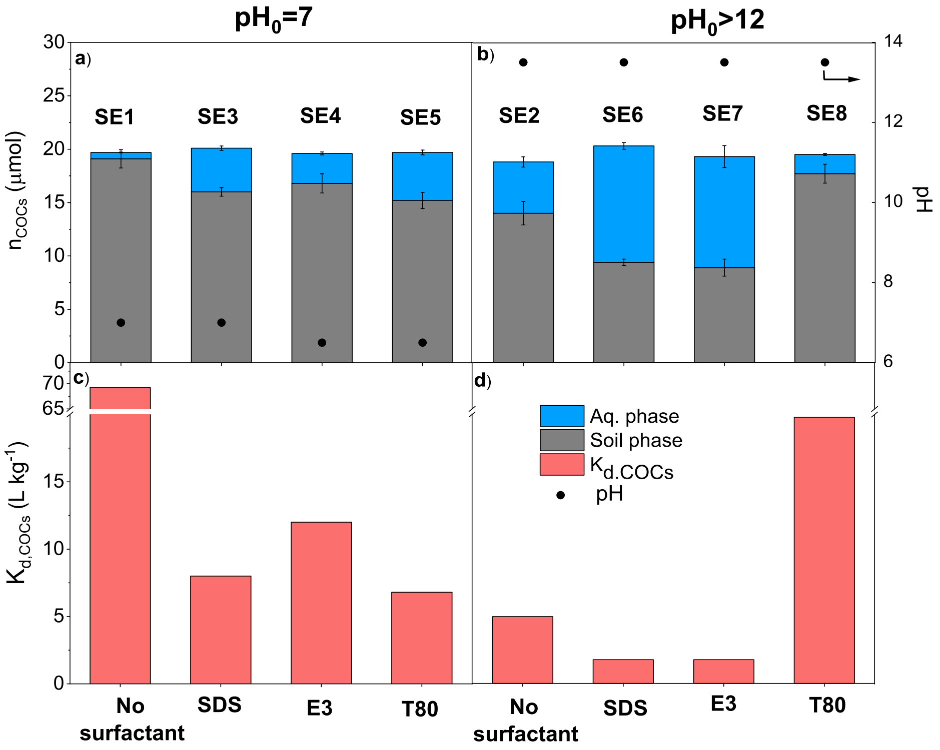

Fig. 1. Effect of surfactants on COCs solubilization and $K_{d,COCs}$ values calculated by Eq. (4) at pH = 7 (a and c) and pH > 12 (b and d, $C_{NaOH} = 13.5$ g L^{-1}). Final pH values (●). 15 g of soil and 30 g of the aqueous phase. $C_{surfactant} = 10$ g L^{-1}.

comparison with the values obtained at neutral pH ($K_{d,COCs} = 8.0$ and 12.0 L kg^{-1}, respectively) (Fig. 1-c and d). On the contrary, a lower $K_{d,COCs}$ at neutral pH ($K_{d,COCs} = 6.8$ L kg^{-1}) than at alkaline conditions ($K_{d,COCs} = 19.8$ L kg^{-1}) was obtained with the nonionic surfactant T80 (Fig. 1-c and d).

The different soil COCs composition with pH can explain differences in $K_{d,COCs}$ values at neutral and alkaline conditions. Dehydrochlorination of HCHs to TCBs at alkaline pH enhances the COCs solubilization. Moreover, the effect of pH on the surfactant properties must be considered. SDS critical micellar concentration (CMC) decreases when the pH increases [34,42], contributing to the higher COCs solubilization. The pH effect on E3 CMC at room temperature was negligible in previous works [34]. The results obtained suggest that T80 stability decreased with the pH increase, and surfactant precipitation was found using T80 at alkaline conditions (see Fig. SM 2, at pH > 12), explaining the decrease of COCs solubilization and the corresponding $K_{d,COCs}$ increase (Fig. 1-b and d, respectively). Iglesias et al. [43] tested the stability of this surfactant over the pH range 2–10, founding that a pH increase had a positive effect on the surface tension of T80 [43], which could be related to the better stability of fatty-acids-surfactant micelles in the presence of a base [43,44]. Thus, the poor results obtained for the T80 surfactant in the current work could be attributed to the extremely alkaline conditions here employed (pH > 12, $C_{NaOH} = 13.5$ g L^{-1}). In order to increase T80 stability, the effect of NaOH concentration and contacting time (maintaining pH > 12), have been further analyzed (Subsections 3.2.2 and 3.2.3).

The distribution of the pollutants (in μmol) in the soil and aqueous phases after the surfactant-enhanced solubilization step (runs SE3-SE8) for each surfactant and pH condition are shown in Fig. SM 3. Since there is no COCs transformation at neutral pH, HCHs isomers explain around 98 % of COCs in both phases. At alkaline pH, the HCHs hydrolysis (Eq. (3)) justifies that the predominant compounds are TCBs in both phases [10,17,39]. Regardless of the surfactant used, β-HCH was not completely dehydrochlorinated (Fig. SM 3-d, e, and f), emphasizing that β-HCH hydrolysis (to TCBs) is the limiting step for the solubilization process, as previously reported in bibliography [9,17].

3.2.2. *Reagents addition order (pH > 12)*

The sequential reagent adding produces HCHs dehydrochlorination to TCBs before the surfactant is added, and further addition of the surfactant facilitates the TCBs solubilization. In this way, the time that surfactant is kept at alkaline conditions in the pollutants solubilization step decreases, and its stability (in the case of T80) is expected to increase. The moles of COCs solubilized in the aqueous phase and those remaining in the soil are shown in Fig. 2-b (moles of COCs in the aqueous phase before and after the surfactant is added are also indicated). For the scope of comparison, the moles of COCs in both phases corresponding to the simultaneous addition of NaOH and surfactants have also been plotted (Fig. 2-a). Corresponding $K_{d,COCs}$ values (L kg^{-1}) are also shown in Fig. 2.

As shown in Fig. 2-b, the moles of COCs solubilized after NaOH addition (1.2 μmol, stage common for the three experiments SE6, SE7 and SE8) are significantly lower than those shown in Fig. SM 1 after soil alkalinization (4.8 μmol, SE2). The alkalinization step in SE6, SE7 and SE8 lasted 4 h, instead of the 24 h required in SE2 to reach equilibrium conditions. The short time used in SE6, SE7 and SE8 did not allow to reach the equilibrium (achieved in SE2) due to diffusional limitations in COCs solubilization (mainly TCBs) from the soil phase (where they are generated) to the aqueous phase [9,17].

Firstly, the negative effect of NaOH on T80 stability is confirmed with the lower values of $K_{d,COCs}$ obtained in the sequential treatment than the simultaneous one. $K_{d,COCs}$ with T80 at alkaline conditions in both experiments are remarkably higher than those obtained with SDS and E3. On the other hand, the sequential addition of reagents produced slightly higher solubilization of contaminants compared with the simultaneous addition of NaOH and surfactant for SDS and E3. Therefore, further experiments will be carried out by adding the reagents simultaneously. It should be noted that the reagents addition order did not influence the final pH of the pollutants solubilization step, maintaining a final pH value higher than 12 in both cases (data not shown).

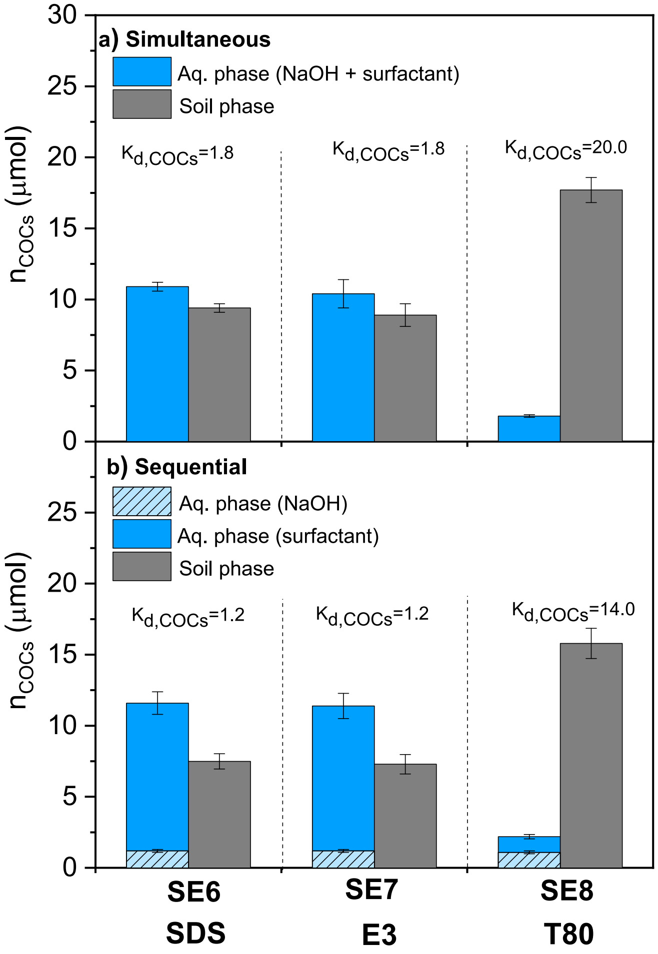

Fig. 2. Effect of reagents (NaOH and surfactant) addition order a) simultaneous and b) sequential on COCs solubilization and $K_{d,COCs}$ (L kg^{-1}) values (Eq. (4)) at pH > 12. 15 g of soil and 30 g of aqueous phase. $C_{surfactant} = 10$ g L^{-1} and $C_{NaOH} = 13.5$ g L^{-1}.

3.2.3. Effect of alkali concentration

As previously observed, the solubilization efficiency increased at alkaline conditions. Regrettably, the stability of one of the tested surfactants (T80) is compromised in these conditions. Experiments at lower NaOH concentrations (4 and 2.5 and g L^{-1}, $pH_0 > 12$ in all cases) with the three surfactants tested have been performed to increase surfactant stability and reduce subsequent soil alkalinity and the reagents cost. The distribution of COCs between the soil and the aqueous phase, the corresponding $K_{d,COCs}$ and final pH values have been plotted in Fig. 3 a-f. As shown, as NaOH concentration decreases, the pH of the resulting emulsion (24 h) decreases regardless of the surfactant used. Nevertheless, it remains above 12 at all the NaOH concentrations, ensuring the HCHs conversion to TCBs in all the scenarios tested.

The decrease of NaOH increases the solubilized moles of COCs when T80 is used, with the consequent decrease in the partition coefficient ($K_{d,COCs}$ was 19.8, 7.0, and 2.4 L kg^{-1} for $C_{NaOH} = 13.5$, 4.0, and 2.5 g L^{-1}, respectively). However, this value is higher than those obtained with the other two surfactants at the three concentrations of NaOH tested, so the use of T80 in subsequent tests is discarded.

Working with SDS and E3, the partition coefficient decreases when NaOH concentration decreases from 13.5 to 4 g L^{-1} but slightly increases at NaOH concentrations below 4 g L^{-1}. Therefore, a concentration of NaOH equal to 4 g L^{-1} has been selected for the pollutants solubilization step with these surfactants (SDS and E3).

3.2.4. Effect of surfactant concentration

The effect of surfactant concentration (2–10 g L^{-1}) was studied using C_{NaOH} of 4 g L^{-1} in the presence of SDS and E3. The results obtained for COCs distribution, final pH, and $K_{d,COCs}$ have been depicted in Fig. 4 a-d. The higher the surfactant concentration, the higher the COCs concentration in the emulsion, a conclusion previously reported in the literature [35,43,45–48]. Thus, $K_{d,COCs}$ decreased by increasing the surfactant concentration (Fig. 4-b and Fig. 4-d for SDS and E3, respectively), being more significant from 2 to 5 g L^{-1} than from 5 to 10 g L^{-1}. This fact may be due to the solubility of contaminants is likely to increase up to a given value and no improvement is obtained by working with higher concentrations [49,50], highlighting the need to study each particular case.

On the other hand, an excessive concentration of surfactant in the subsequent oxidation stage is undesirable because it decreases the efficiency of the process due to: i) surfactant micelles can act as a protective medium, significantly reducing the COCs availability towards radicals oxidation [23,27], and ii) the surfactant can compete with the contaminants for the radicals formed [25–27]. Thus, a concentration of surfactant of 5 g L^{-1} has been selected for the solubilization stage.

3.2.5. Effect of successive solubilization cycles

Three successive solubilization cycles were performed with SDS and E3 at the conditions previously selected. COCs removal percentage from polluted soil in these cycles ("solubilization rate") has been calculated following Eq. (5), in which $C_{COCs,aq}$ is the COCs concentration in the aqueous phase, $q_{COCs,soil}$ is the initial COCs concentration in the polluted soil, and V_L/W_S is the liquid/soil ratio used. The results obtained are depicted in Fig. 5. Additionally, the $K_{d,COCs}$ (L kg^{-1}) values (Eq. (4)) for each solubilization cycle have been included.

$$Solubilization\ rate\ (\%) = \frac{C_{COCs,aq}\cdot\frac{V_L}{W_S}}{q_{COCs,soil}}\cdot 100 \qquad (5)$$

According to Fig. 5, 58.4 %, 21.1 % and 3.0 % of the initial COCs in soil were solubilized to the aqueous phase after the first, second and third solubilization cycle with SDS (total removal: 82.5 %). Final COCs removal was slightly higher (88.8 %) with E3. $K_{d,COCs}$ values in the successive solubilization cycles increase in the case of SDS (Fig. 5-a) and slightly decrease in E3 (Fig. 5-b). In the first solubilization cycle with SDS, a higher amount of COCs in the soil is solubilized (compared to using E3). The remaining COCs in the soil after the first solubilization cycle seem less accessible to the surfactant due to stronger adsorption to the soil or a hindering effect of the adsorbed SDS. On the contrary, adding E3 allows desorbing COCs with the same effectiveness in successive solubilization cycles (similar $K_{d,COCs}$ values). COCs solubilized in runs SE21 (SDS) and SE24 (E3) were lower (72 %) despite the higher mass of surfactant used in these runs compared with the total surfactant added in the corresponding three successive solubilization runs.

3.3. Oxidation of polluted emulsions

The polluted emulsions (PEs) obtained in runs SE16 (SDS), SE18 (E3) and the liquid phase sum of emulsion from runs SE16, SE19, and SE20 (SDS) and runs SE18, SE22, and SE23 (E3) have been used for the study of COCs oxidation. These runs are named PE-SDS-1, PE-E3-1, PE-SDS-1,2,3 and PE-E3-1,2,3, respectively.

As a result of the solubilization step, part of the surfactant was adsorbed into the soil [35,51]. After the solubilization, the surfactant concentration (SDS and E3) was calculated from TOC measurements, and the results obtained are included in Table SM 1. The initial concentration of surfactants (SDS and E3) used in the SE16 and SE18 experiments was 5 g L^{-1} (Table 1). The equivalent initial surfactant concentration in runs SE16, SE19, and SE20 (SDS) and runs SE18, SE22 and SE23 (E3) was 2.9 g L^{-1} (average of three values employed of 5, 2.5 and 1.25 g L^{-1}). The measured concentration of SDS after soil washing was 4.1 and 2.6 g L $^{-1}$ for PE-SDS-1 and PE-SDS-1,2,3, respectively. The

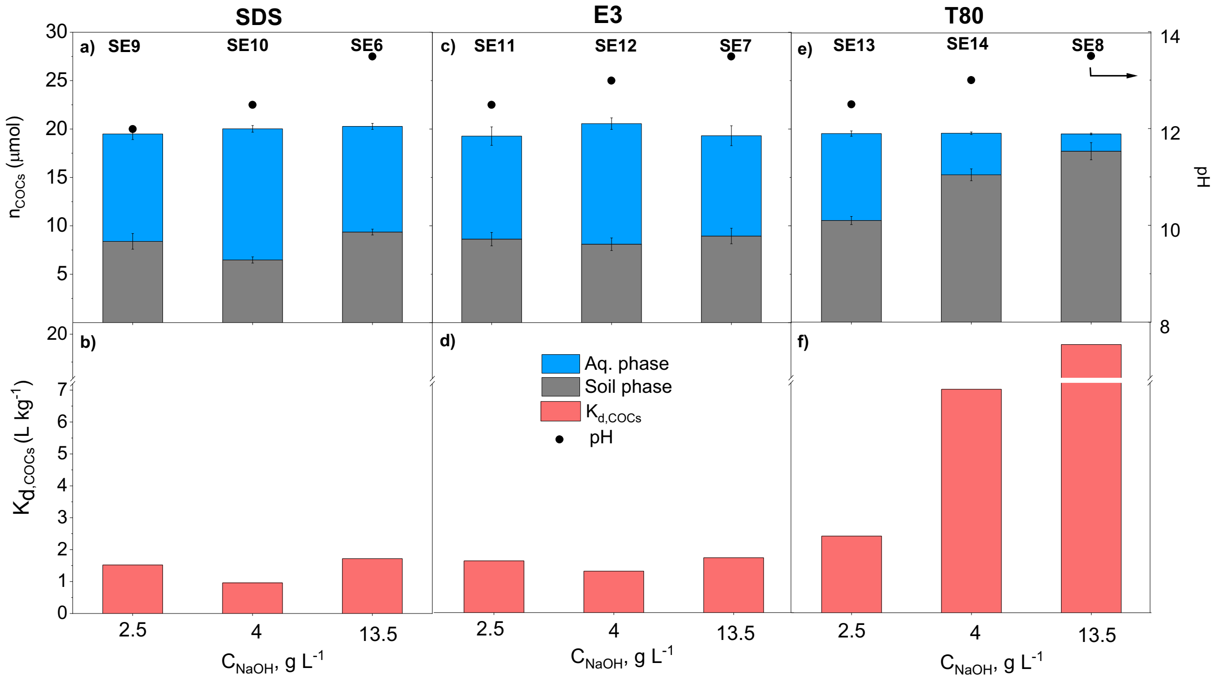

Fig. 3. Effect of alkali concentration on COCs solubilization and $K_{d,COCs}$ values calculated by Eq. (4) when using SDS (a-b), E3 (c-d), and T80 (e-f). Initial pH > 12 in all runs. Final pH values (●). $C_{surfactant} = 10$ g L^{-1}.

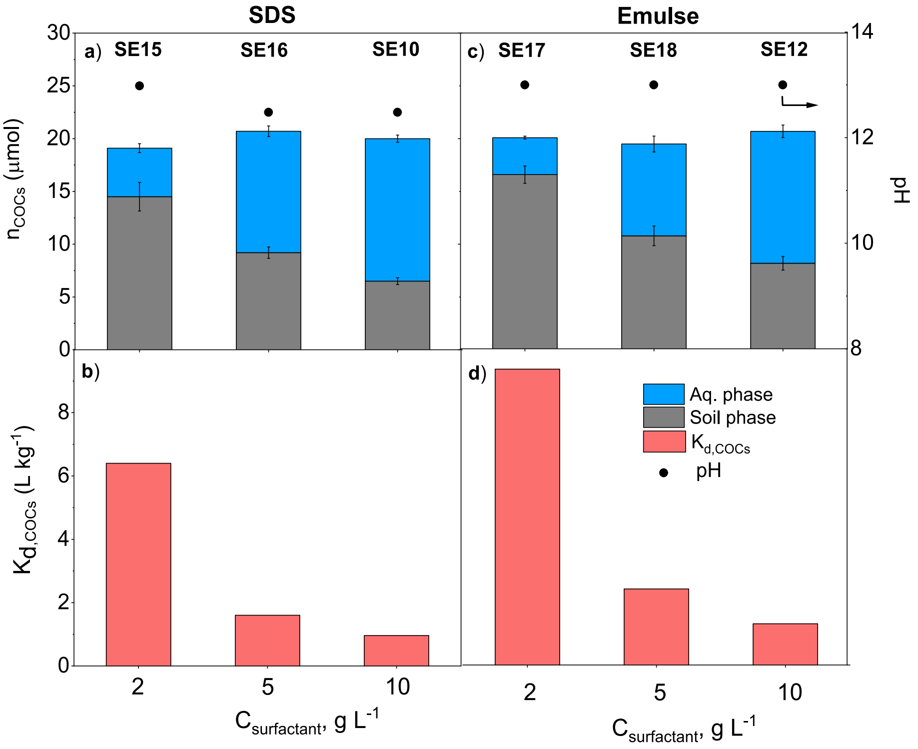

Fig. 4. Effect of surfactant concentration on COCs solubilization and $K_{d,COCs}$ values calculated by Eq. (4) when using SDS (a-b) and E3 (c-d). Final pH values (●). $C_{NaOH} = 4$ g L^{-1}.

measured concentration of E3 in the resulting PEs was 3.1 and 2.3 g L^{-1} for PE-E3-1 and PE-E3-1,2,3, respectively. From these results, it can be inferred that higher adsorption of E3 (3.8 g kg^{-1}_{soil}) than SDS (1.8 g kg^{-1}_{soil}) on the polluted soil was found at the conditions tested. Conversely, Garcia-Cervilla et al. [35] reported a slightly higher SDS adsorption than E3 into a highly polluted soil (COCs>10,000 mg kg^{-1}_{soil}), at alkaline conditions (pH > 12, $C_{NaOH} = 7$ g L^{-1}) [35]. These authors also reported that a higher COCs concentration in soil, resulted in higher surfactant adsorption [35]. Thus, the differences obtained with respect to the current work can be related to i) the significant difference in COCs concentration (10,000 mg kg^{-1} vs 373 mg kg^{-1}), and ii) the different nature of COCs (28 COCs vs only HCHs isomers). All this points to the

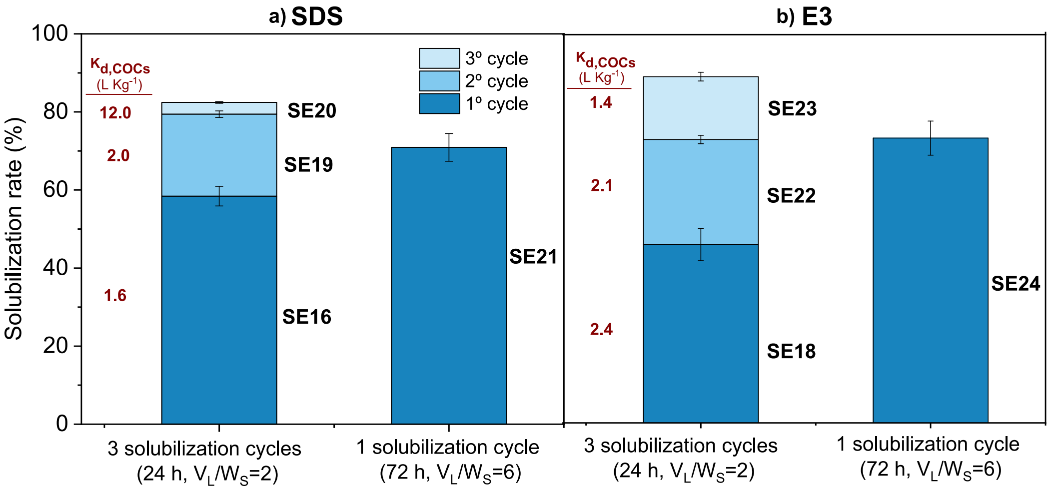

Fig. 5. Effect of successive solubilization cycles and V_L/W_S in the percentage of COCs removed from the soil with SDS (a) and E3 (b). $K_{d,COCs}$ values calculated by Eq. (4). Experimental conditions: Table 1.

need to study the behaviour of each surfactant in soils with different types of real pollution. Additionally, it should be higlighted that the remanent surfactant concentration adsorbed to soil (1.8 (SDS) - 3.8 (E3) g kg_{soil}^{-1}, both in the case of a single and 3 successive solubilization cycles) would not represent a problem, since the application of this technology is intended to treat a very delimited area of the landfill and the treated soil would not be used in any case for agricultural or livestock purposes but rather could be used as a building material.

Considering the alkaline pH obtained in the polluted emulsions, the oxidation system selected for the subsequent COCs abatement in the emulsion is PS activated by alkali. On the other hand, considering the promising results recently obtained when this process was intensified by temperature [5,10,17,52] a temperature of 40 °C was selected. The oxidizable organic matter in the reaction medium is comprised of solubilized COCs (in this case, mainly TCBs) and the surfactant. A relatively high oxidant dose was used to avoid the oxidant depletion by an unproductive reaction with the surfactant [1,23,53,54,57]. Therefore, a PS concentration of 40 g L^{-1} has been selected [10,17,52]. Finally, the molar NaOH/PS ratio was fixed at 2, a value commonly found in the literature which ensures a pH > 12 (necessary for alkaline activation of PS) during the reaction [9,10,18].

The time-evolution of COCs (X_{COCs}) and oxidant (X_{PS}) conversion under the selected operating conditions is shown in Fig. 6-a and b, respectively. Blank experiments (in the absence of PS) were undertaken to discard volatilization or adsorption of COCs (mainly TCBs) during PEs treatment at 40 °C (experimental conditions summarized in Table SM 1). The decrease of COCs concentration in blank runs was below 20 % in all cases (72 h, data not shown). Fig. SM 4 shows the colour evolution of the emulsions in the oxidation (ox.) and blank (blank) experiments. As can be seen, the colour remains unchanged in the blank experiments during the experimental time, indicating that no reaction took place. However, the colour becomes yellowish with time in the case of oxidation experiments, suggesting that COCs and surfactant oxidation occurred [23].

PS conversion was considerably higher when treating E3 (PE-E3-1, $X_{PS} > 50$ %, 6 h) than SDS (PE-SDS-1, $X_{PS} < 20$ %, 6 h) emulsions. Furthermore, the oxidant consumption was higher in the experiment carried out with a higher initial concentration of E3 (PE-E3-1,2,3), which can be associated with the unproductive consumption of PS with this surfactant (Fig. 6-b). In the case of SDS-emulsions, the differences in PS conversion in the tests with different concentrations of surfactant (PE-SDS-1 and PE-SDS-1,2,3, respectively) are less significant (Fig. 6-b).

The rapid decomposition of PS in the experiments with E3 emulsions generated a high concentration of hydrogen cations [17] which is associated with a considerable decrease in the pH of the reaction medium (Fig. 6-c). In these experiments, the pH decreased below the required value for the alkaline activation of PS (pH $\geq$ 12), and thus, hydroxyl radicals are no longer produced [17]. All this led to low contaminant conversion ($X_{COCs} < 30$ %, 72 h, Fig. 6-a).

It should be noted that COCs conversion was slightly higher when treating PE-E3-1,2,3 than PE-E3-1, with lower surfactant concentration (Table SM 1), which can be attributed to a protecting effect of surfactant micelles against pollutants oxidation. This behaviour was previously observed in the oxidation of a complex liquid mixture of COCs by using PS activated by alkali as an oxidant and E3 as a surfactant [57]. In that work, it was found that concentrations of E3 above 2.5 g L^{-1} caused only unproductive reactions, without COCs removal. This hindering effect was also noticed in the presence of other surfactants and PS activation methods [24,25,46]. Thus, considering this aspect, to improve the oxidation treatment, lower concentrations of E3 should have been used in the precedent solubilization process, which would limit the efficiency of this first stage.

When treating the SDS emulsions, higher COCs conversions were achieved, removing 96 % of the contaminants in 72 h of treatment (Fig. 6-a). At these conditions, no chlorinated intermediate compounds were detected, as previously observed in the treatment of this soil by PS/NaOH/T [17]. Comparing with the results obtained in that work, it should be underlined the higher COCs conversion (96 vs 80 %) achieved in the presence of surfactant at the same operating conditions ($C_{PS} = 40$ g L^{-1}, 40 °C, 72 h) [17], highlighting the beneficial role of the surfactant. Additionally, due to the low solubility of β-HCH (the most recalcitrant HCH isomer) and low hydrolysis rate (to TCBs), the conversion of this compound when no surfactant was used was below 70 % [17]. In the current work, the solubilization of β-HCH in the emulsion was almost 80 % (Fig. SM 3), confirming that the synergetic effect of NaOH and surfactant enhanced the dehydrochlorination of this refractory compound and subsequent solubilization of TCBs (which were further removed in the oxidation treatment).

Additional experiments in the absence of COCs and using the same concentration of PS (40 g L^{-1}) and surfactants (SDS and E3) were performed to know more about the unproductive consumption of the oxidant due to the presence of surfactant (experimental conditions in Table SM 1). The oxidant consumption was almost independent of the COCs presence (data not shown) for each surfactant. Therefore, PS was mostly consumed in an unproductive reaction with the surfactant at the temperature tested. The unproductive consumption of PS (40 g L^{-1}) at different temperatures in the absence of surfactant was studied in a previous work, obtaining significantly lower oxidant consumption: 7.5 % and 20 % at 35 °C and 45 °C, respectively (72 h) [5]. These results

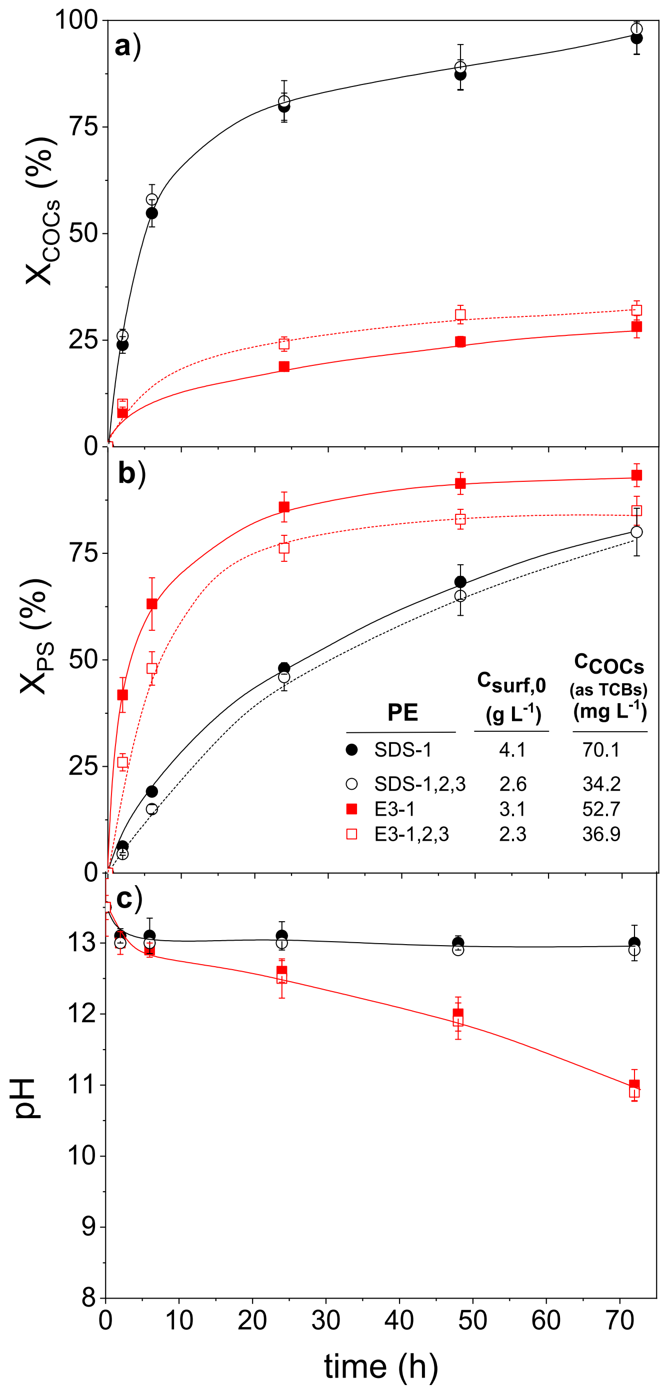

Fig. 6. Evolution of COCs (mainly TCBs) (a), PS (b) conversion, and pH (c) with reaction time when treating PEs (Table SM 1). $C_{PS} = 40$ g L^{-1}, NaOH:PS = 2, T = 40 °C.

demonstrate that the presence of surfactant (both SDS and E3) significantly increases the unproductive oxidant consumption ($X_{PS} > 70$ % in both cases). Additionally, as previously mentioned in the case of COCs presence (Fig. 6-b), the unproductive PS consumption in the presence of the non-ionic surfactant (E3) was considerably higher than using SDS (data not shown), in accordance with that previously reported in the literature [19,24,55,56]. Wang et al. [56] reported that the higher stability of SDS against PS was associated to the existence of repulsion forces between $SO_4^{\bullet -}$ radicals generated in the PS/T system and the sulfonate anions located at the exterior of the SDS micelle [56].

In conclusion, the lower unproductive consumption of PS with SDS and the higher COCs removal from the emulsion make SDS preferable for this treatment at the experimental conditions used.

4. Conclusions

The results obtained in the present work reveal that the combination of surfactant-aided solubilization and selective oxidation of pollutants by PS activated by alkali and intensified by temperature is a promising alternative for the remediation of real HCHs-polluted soils. The pH plays a fundamental role in the remediation process. At neutral pH, surfactant addition slightly increased the solubilized mass of COCs, decreasing the partition coefficients. At pH > 12, higher COCs solubility was achieved since HCHs hydrolyze to trichlorobenzenes, with significantly higher water solubility than the parent compounds. One of the surfactants tested, T80, was not stable at pH > 12 and the concentration of COCs solubilized decreased. NaOH and surfactant concentration remarkably affected the pollutants solubilization efficiency. The highest COCs solubilization was obtained at moderate NaOH concentration (4 g L^{-1}), finding the surfactant solubilization order: SDS ($K_{d,COCs} = 1.0$ L kg^{-1}) > E3 ($K_{d,COCs} = 1.3$ L kg^{-1}) > T80 ($K_{d,COCs} = 7.0$ L kg^{-1}). The higher the surfactant concentration, the lower the $K_{d,COCs}$ value, being this improvement lower as the surfactant concentration increases. More than 80 % of COCs were extracted from the soil using optimal solubilization conditions (SDS or E3 (5 g L^{-1}), pH > 12, simultaneous addition of reagents, $V_L/W_S = 2$ and 3 successive solubilization cycles of 24 h). The resulting emulsions (ΣCOCs = 34–70 mg L^{-1} (mainly as TCBs)) were subsequently treated by PS/NaOH/T ($C_{PS} = 40$ g L^{-1}, NaOH: PS = 2, and T = 40 °C). COCs conversions of 30 % and 96 % were achieved in 72 h when treating E3 and SDS-emulsions, respectively, highlighting the suitability of SDS for the integrated surfactant-enhanced solubilization and emulsion treatment process. This work provides practical information for the design of a future on-site remediation treatment of superficial real HCH-polluted soils. However, pilot studies using large-scale reactors need to be performed before field-scale implementation, considering the location and agitation type, the geometry of the reactors, the flow rates, and the energy consumption, among others.

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2023.103829.

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