



Partition of a mixture of chlorinated organic compounds in real contaminated soils between soil and aqueous phase using surfactants: Influence of pH and surfactant type

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ABSTRACT

The equilibrium between surfactant adsorption and contaminants desorption was studied. Two soil samples from a polluted site with residues from lindane production, compounded of a complex mixture of 28 chlorinated organic compounds (COCs) and different concentration of COCs in soil (2.27 and $34.69 \text{ mmol}_{\text{COCs}} \cdot \text{kg}_{\text{soil}}^{-1}$), were used. Soil was in contact with aqueous surfactant solutions ($1\text{--}15 \text{ g} \cdot \text{L}^{-1}$) of nonionic (E-Mulse® 3, and Tween® 80) and anionic (sodium dodecylsulfate) surfactants. Due to alkaline pH promoting the dehydrochlorination of COCs, neutral pH and strongly alkaline pH ($\text{pH} > 12$) were studied. It was found that the higher the COCs concentration adsorbed in soil, the higher the adsorption of the surfactants, finding an irreversible adsorption in the case of nonionic surfactants. The desorption of COCs increased with the surfactant concentration in the aqueous phase and was not selective towards any contaminant. Although at neutral pH, higher COC desorption was found with nonionic surfactants, at alkaline pH surfactant the anionic surfactant improved its COCs desorption capacity significantly. Finally, the adsorption of the surfactants was well adjusted to Langmuir, and the apparent partition coefficient predicted the partitioning of COCs between the soil and aqueous phases, which changes with the surfactant concentration in the aqueous solution.

1. Introduction

Contaminated soil and groundwater by non-aqueous phase liquids (NAPLs) is a vast and severe environmental problem. Free phases that are denser than water are called dense non-aqueous liquid phases (DNAPL), those formed by chlorinated organic compounds (COCs) [10] being persistent. DNAPL can migrate vertically due to gravity forces, forming DNAPL pools by encountering low permeability areas and leaving behind a plume of contamination that travels in the groundwater direction [13,23,40,46]. Furthermore, DNAPL is trapped in the soil pores, and this adsorption depends on factors related to the nature of the soil and the contaminants [2,6].

The low water solubility and slow dissolution kinetics of COCs are responsible for considerably lengthening remediation times [26,27,53], which makes some well-known technologies, such as pump-and-treat, inefficient [22,30]. The use of surfactants has been proposed to overcome these limitations, removing the subsoil contaminant mass in a shorter time. Surfactants can be injected into the soil as an aqueous solution to desorb the contamination using low pore volumes of water, and as the fluid is injected, recovered and treated on-site, this technology is called surfactant enhanced aquifer remediation (SEAR) [18,28,31,32]. SEAR moves the soil contamination into the aqueous phase but does not eliminate the contaminant in situ. Surfactant enhanced in-situ chemical oxidation (S-ISCO) is a promising technology that couples the use surfactants and oxidation processes with the effective in-situ

Abbreviations: B, Soil sample B; CB, Chlorobenzene; COCs, Chlorinated Organic Compounds Concentration; D, Soil sample D; DCBs, Isomers of dichlorobenzene; DNAPL, Dense non-aqueous liquid phase; E3, E-Mulse®3; ECD, Electron capture detector; FID, Flame ionization detector; GC, Gas chromatography; HCHs, Isomers alpha, beta, delta, gamma, epsilon of hexachlorocyclohexane; HeptaCHs, Isomers of heptachlorocyclohexane; HexaCXs, Isomers of hexachlorocyclohexene; HOC, Hydrophobic organic compound; ISTD, Internal standard; MeOH, Methanol; NAPL, Non-aqueous liquid phase; PCB, Pentachlorobenzene; PentaCXs, Isomers of pentachlorocyclohexene; PSA, persulfate activated by alkali; PTFE, Teflon; SDS, Sodium dodecylsulfate; SEAR, Surfactant enhanced aquifer remediation; S-ISCO, Surfactant enhanced in-situ chemical oxidation; SOM, Soil organic matter; T80, Tween 80; TCBs, Isomers of trichlorobenzene; TetraCBs, Isomers of tetrachlorobenzene.

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Nomenclature			
C_{xj}	Concentration of each COC in the aqueous phase with surfactant j, $\text{mmol}\cdot\text{L}^{-1}$	n_{COCs}	Total moles of COCs in the slurry, mmol
$C_{\text{COCs},j}^m$	Concentration of the sum of all COCs into the micelles of surfactant j in the aqueous phase, $\text{mmol of COCs}\cdot\text{g}^{-1}\text{ of surfactant j}$	q_{xj}	Concentration of each COCs in the soil phase using surfactant j, $\text{mmol}\cdot\text{kg}^{-1}$
$C'_{\text{COCs},j}$	Concentration of the sum of all COCs in the aqueous phase outside of the micelles of surfactant j, $\text{mmol of COCs}\cdot\text{L}^{-1}$	$q'_{\text{COCs},j}$	Concentration of the sum of all COCs in the solid of soil phase with surfactant j, $\text{mmol of COCs}\cdot\text{kg}^{-1}$
C_j	Surfactant concentration in aqueous phase, $\text{g}\cdot\text{L}^{-1}$	$q_{\text{COCs},j}^m$	Concentration of the sum of all COCs in the surfactant j adsorbed in soil phase, $\text{mmol of COCs}\cdot\text{g}^{-1}\text{ of surfactant j}$
CMC_j	Critical micellar concentration of surfactant j in milli-Q water, $\text{g}\cdot\text{L}^{-1}$	q_j	Surfactant concentration in soil phase, $\text{g}\cdot\text{kg}^{-1}$
IC	Inorganic carbon, %w of CaCO_3	r^2	Regression Coefficient.
K_d^*	Apparent partition coefficient of COCs with surfactant j, $\text{mmol of COCs in soil phase}\cdot\text{mmol}^{-1}\text{ of COCs in aqueous phase}\cdot\text{L}\cdot\text{kg}^{-1}$	TOC	Total organic carbon, $\text{mg}\cdot\text{kg}^{-1}$
$K_{L,j}$	Langmuir constant, $\text{g}\cdot\text{L}^{-1}$	V	Volume of the aqueous phase, L
$K_{ws,j}$	Partition coefficient of solute between surfactant j adsorbed in soil phase and its micelles in aqueous phase, <i>dimensionless</i>	W	Mass of the soil phase, kg
MSR_j	Molar solubilization ratio of surfactant j, $\text{mmol}\cdot\text{g}^{-1}$	Superscripts	
n_x	Total moles of each COC in the slurry, mmol	s	Saturation
		m	diluted in surfactant (micelles in the aqueous phase and surfactant adsorbed in the soil phase).
		Subscripts	
		0	Initial
		COCs	Sum of COCs
		j	Surfactants
		x	Individual COC

remediation of residual DNAPLs in soil [4,7,11]. In both technologies, SEAR, and S-ISCO, the interaction of the surfactant with the soil must be known. The partition equilibria of surfactant and COCs in the three possible phases (soil, sorbed DNAPL and aqueous phase) should be modelled to design the delivery of reagents and estimate the treatment time required.

The surfactant adsorption in the soil has been usually described in relation to sorption isotherms [33], depending on the surfactant nature and the mineral/organic composition of the soil. Adsorption of ionic surfactants is strongly affected by the soil surface charge, increasing when the solid surface and the ionic surfactant have opposite charges. This effect can be mitigated or intensified by the presence of electrolytes or by pH [34,36,43]. The presence of inorganic cations, as Ca^{2+} from carbonates, promotes the precipitation of anionic surfactants [19].

Nonionic surfactants are generally less affected by the presence of electrolytes or electrostatic charges [37]. If polyethoxylated nonionic surfactants are used, the adsorption is usually governed by the capacity to form hydrogen bonds between the metal oxides on the soil surface and the surfactant oxygen ethers [18,41]. As observed by several authors, the formation of these hydrogen bonds is favoured by the presence of strong Bronsted acids (SiO_2) compared to that produced by the presence of strong Lewis acids (Al_2O_3 and Fe_2O_3) [29,41]. The organic matter in the soil (SOM) or organic pollutants sorbed or trapped in the soil pores also promotes surfactant adsorption [36,47,55].

The isotherms for surfactant adsorption and COCs desorption can be linear or Langmuir [33,55]. The parameters of both isotherms could change with the surfactant concentration or COCs concentration, but this topic has been scarcely studied [19,55]. Usually, the works carried out in literature to model the partition equilibria have been accomplished with single pollutants spiked in soils, despite the real contaminated soils containing NAPLs with complex compositions. Moreover, the effect of alkaline pH on the partition equilibria has not been studied. Nevertheless, the study of the effect of the alkaline conditions on the partition equilibria is motivated by the use of NaOH in the design of S-ISCO technologies where the persulfate is activated by alkali (PSA). PS is a common oxidant in ISCO treatments due to its stability in soils and effectivity at a wide pH range. Among the PS activators, alkali addition is a well-known technology [4,44,57] being effective due to the high

oxidizing power of the radicals obtained (OH^\cdot and $\text{O}_2^{\cdot-}$). In addition, the effectiveness of this reagent to oxidize the COCs involved in this work was proved in a previous work [17]. Pilot runs have been carried out at field scale in the Bailin Landfill using PS activated by alkali (<http://www.lifediscovered.es/>).

This paper studies and models the partition of COCs and surfactants between soil and aqueous phases. Two different soil samples from a real polluted site in Sabinánigo (Spain) have been used. These soils were contaminated decades ago by a DNAPL composed of 28 COCs, many of which are not commercial compounds [39]. This contamination was caused by the dumping of chlorinated liquid wastes from lindane manufacture in a landfill in the nearby factory [13,38,39]. Different surfactants have been tested, all commercial and widely used: EMulse® 3 (E3), Tween® 80 (T80) and sodium dodecylsulfate (SDS).

E3, formulated with limonene (25%wt) as a cosolvent, has shown a high COCs solubilization capacity [15]. Besides, this surfactant was successfully applied in S-ISCO treatments with persulfate activated with NaOH in creosote and DNAPL remediation [4,12]. T80, without cosolvents, has been successfully applied to solubilize chlorinated organic compounds from polluted soils [1,7,35,54]. Moreover, SDS is commonly used in the remediation of polluted soil with hydrophobic organic compounds (HOCs) [5,25]. Besides, SDS was successfully used in the recovery of 4,40-dichlorobiphenyl in polluted soils [9].

The selectivity of the desorption of each surfactant was studied both at neutral pH and alkaline conditions ($\text{pH} > 12$). The partition equilibria of surfactant and COCs are obtained and modelled at both pHs considering the three-phase present: organic, soil and water. Hysteresis in the adsorption equilibrium of the surfactants is also studied. From our knowledge, information available in the literature about the partition equilibria of surfactants and COCs in real and complex polluted soils at the wide pH range used here is scarce and insufficient.

2. Experimental

2.1. Materials

In this work, three surfactants were used: two of them were polyethoxylated nonionic surfactants E-Mulse® 3 (E3) and Tween® 80

(T80), which are biodegradable and non-toxic agents [15,38], and an anionic surfactant, sodium dodecylsulfate (SDS), was also tested. The main properties of the three surfactants are shown in Table SM-1 of the Supplementary Material.

Soil samples, B and D, were obtained from two different wells in the alluvial of Sardas landfill (Sabiñánigo, Spain) described elsewhere [17, 26]. These samples correspond to a permeable gravel-sand layer with some clay interbedded, located at 13.75 and 13.5 m b.g.l, respectively. The soil was sieved using the fraction of size 0.25–0.02 mm for this study (45% of the total soil weight under 2 mm).

The quantification of COCs was accomplished using calibration curves prepared with standard samples of known concentration in methanol from commercial compounds (analytical quality, Sigma-Aldrich): 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 ($\alpha, \beta, \gamma, \delta$ and ϵ -HCH). Bicyclohexyl ($C_{12}H_{22}$, Sigma-Aldrich) and tetrachloroethane ($C_2H_2Cl_4$, Sigma-Aldrich) were used as internal standards (ISTD) for quantification by gas chromatography (GC).

2.2. Experimental procedure

Different variables on the partition equilibrium of surfactant and COCs in the aqueous and soil phases were investigated. Those variables were: the initial COCs concentration in soil ($B = 34.69 \text{ mmol}\cdot\text{kg}^{-1}$ and $D = 2.27 \text{ mmol}\cdot\text{kg}^{-1}$), the surfactant concentration ($1\text{--}15 \text{ g}\cdot\text{L}^{-1}$), the pH, $\text{pH} = 7$ (natural) and $\text{pH} > 12$ (obtained adding $7 \text{ g}\cdot\text{L}^{-1}$ NaOH), and the surfactant type, using E3, T80, and SDS.

The experiments were carried out in well-mixed vials (40 mL) of PTFE with PTFE screw caps. 0.03 L of aqueous phase (V) at the corresponding concentrations of surfactant and NaOH were put in contact with 0.003 kg of the soil sample (W) (W/V of $0.1 \text{ kg}\cdot\text{L}^{-1}$). Vials were agitated at 30 rpm at room temperature ($22^\circ\text{C} \pm 1$) in a Labolan rotatory agitator. The initial pH of soil samples was analysed following the EPA METHOD 9045D. The pH of both soil samples B and D was 8.9 ± 0.3 at $22^\circ\text{C} \pm 1$. The initial pH of aqueous surfactant solutions was about 5.8, but after these solutions were mixed with soil samples B and D, the pH was 7.0 ± 0.3 in all aqueous phases.

In those runs carried out at $\text{pH} > 12$, the soil samples were previously treated with a solution of $7 \text{ g}\cdot\text{L}^{-1}$ of NaOH, using the ratio W/V of $0.1 \text{ kg}\cdot\text{L}^{-1}$ during 24 h. After that, the supernatant was separated. The soil samples were rinsed with Milli-Q water and dried to be used in the experiments at $\text{pH} > 12$.

A vial was sacrificed at the desired time. Phases were separated by centrifugation (Meditronic-BL-S, J.P, Selecta® speed = 9000 rpm; time = 10 min), supernatants were taken and filtered (nylon / $0.45 \mu\text{m}$). The centrifugation effectively separated the soil and aqueous phases. Similar values of COCs and surfactant concentrations in the aqueous phase were obtained using centrifugation or separating both phases with sedimentation and filtering with $0.45 \mu\text{m}$.

The concentration of each COC by each surfactant j in the aqueous phase, $C_{x,j}$ ($\text{mmol}\cdot\text{L}^{-1}$) was analysed by GC. The COCs concentration in soil $q_{x,j}$ ($\text{mmol}\cdot\text{kg}^{-1}$) was determined by extraction using MeOH. Moles of each compound (n_x) and total moles of COCs in the slurry n_{COCs} were obtained from the mass balance:

$$n_x = VC_{x,j} + Wq_{x,j} \quad (1)$$

$$n_{\text{COCs}} = \sum n_x \quad (2)$$

V and W being the aqueous phase volume (L) and the soil phase mass (kg) used, respectively. As there is not a reaction in the media n_x and n_{COCs} should be equal to those initially in soil.

$$n_{x,0} = q_{x,0} \cdot W \quad (3)$$

The remanent surfactant concentration, G_j ($\text{mmol}\cdot\text{L}^{-1}$), in the aqueous phase was measured by TOC analysis after subtraction of the contribution to TOC of COCs.

2.2.1. Preliminary experiments

The first set of experiments is summarized in Table SM-2. Those runs were carried out to study the time required to achieve equilibrium conditions in surfactant adsorption and contaminant desorption. Experiments with 1 and $15 \text{ g}\cdot\text{L}^{-1}$ of initial surfactant concentration under neutral conditions and for both B and D soil samples were used. The analyses of COCs and surfactants were carried out at different times, up to 72 h.

2.2.2. Partition experiments

The second set of experiments was carried out in the conditions summarized in Table SM-3, following the experimental procedure explained above. In these runs, vials were sacrificed at 24 h when the equilibrium between soil and aqueous phase was achieved. These runs were carried out duplicated.

The pH effect on the surfactant partition has been studied in this work due to two reasons. First, the use of NaOH promotes the dehydrochlorination of HCH and HeptaCHs to TCB and TetraCBs, respectively, also in the presence of surfactant, these being less toxic compounds than the original pollutants (García-Cervilla, Romero et al., 2020). Secondly, persulfate activated by alkali is the oxidant applied in the remediation of this polluted soil [17,39]. As the COCs concentration in soil B is remarkably higher than in soil D, experiments were carried out with soil B at $\text{pH} = 7$ and $\text{pH} > 12$ to study the pH effect on the partitioning of COCs and surfactants between soil and aqueous phases.

2.2.3. Desorption

The desorption experiments were carried out using the soil phase from partitioning runs at neutral pH (see Table SM-3) after centrifugation and drying. An amount of 0.003 kg of this dried soil and 0.03 L of milliQ water were put in contact during 24 h. After this time, the remanent COCs and surfactant in soil and the aqueous phase concentration were analysed.

2.3. Analytical methods

The concentrations of COCs in soil samples were analysed following the method explained elsewhere [17]. 2 g of well-homogenized dried soil (using Na_2SO_4) were extracted with 30 mL of methanol in a Milestone Ethos One microwave following the EPA-3546 method. The liquid phase was filtered (nylon / $0.45 \mu\text{m}$) and analysed by gas chromatography coupled with a flame ionization detector and an electron capture detector (GC-FID/ECD), whose method conditions were described elsewhere [39]. Analysis of aqueous phases, separated by centrifugation, was carried out depending on the surfactant used. With E3 and T80, a volume of 0.1 mL of supernatant was diluted with 0.9 mL of MeOH containing the ISTD. If SDS was used, the surfactant was removed from the aqueous sample before COCs analysis by precipitation with NaCl. For this, 2.5 g of NaCl were added to 5 mL of the aqueous sample. Following, the supernatant was extracted with hexane (volume ratios water: hexane of 1) and the COCs analysed in the organic extract. Then the organic phases, methanol or hexane, were analysed by GC-FID/ECD.

The total carbon (TC) of the soil and aqueous phases was analysed with a Shimadzu TOC-V CSH analyser coupled with an SSM-5000A soil using synthetic air as a carrier gas and a furnace temperature of 900°C . Inorganic carbon (IC) of solid samples was analysed in the same equipment using synthetic air, but phosphoric acid was added, and the furnace temperature was reduced to 400°C . Total organic carbon (TOC) was calculated by a mass balance between TC and IC. The surfactant

concentration in the soil and aqueous phases was calculated by a mass balance between COCs and TOC analysis results.

Metal content was obtained by acid digestion according to the EPA-3051A method using a Milestone Ethos One microwave. The liquid extract was filtrated and subsequently analysed by an Agilent 4100 MP-AES. The positioning view and nebulizer pressure were previously optimized using a mixture of 50 mg·L⁻¹ of each analyte at the different weight length selected: Fe: 438 nm; Mg: 383 nm; Zn: 481 nm; Ca: 646; Cu: 510 nm; Mn: 403 nm; Na: 330 nm; Al: 308 nm and K: 769 nm.

2.4. Modelling

The partitioning of surfactant between polluted soil and the aqueous phase was modelled explained using a Langmuir isotherm [21] in Eq. (4).

$$q_j = \frac{K_{L,j} \cdot q_j^s \cdot C_j}{1 + K_{L,j} \cdot C_j}, \forall j \in \{E3, T80\} \quad (4)$$

where K_L and q_j^s are the Langmuir constant (g⁻¹·L) and the saturation concentration of j compound (surfactant) in soil. Values of q_j vs. C_j in Fig. 3 were used to fit the parameters in Eq. (4).

Since the chlorinated pollutants in soil were not selectively dissolved, a $((K_d^*)_{COCs,j})$ global distribution coefficient is defined in Eq. (5). It can be used for each surfactant and pH conditions tested, treating the mixture of COCs as a single compound.

$$(K_d^*)_{COCs,j} = \frac{K_{ws,j} \cdot q_j}{C_j}, j = E3, T80, SDS \quad (5)$$

The estimated values and statistical significance of parameters in Eq. (4) $K_{L,j}$ and q_j^s and $K_{ws,j}$ in Eq. (5) were fitted to the experimental data. $K_{ws,j}$ (Eq. (6)) means the partition equilibrium constant between COCs in the surfactant micelles in soil and COCs in the surfactant micelles in the aqueous phase.

$$K_{ws,j} = \frac{q_{COCs,j}^m}{C_{COCs,j}^m} \quad (6)$$

3. Results and discussions

3.1. Soil characterization

Table SM-4 shows the concentration of COCs in soil samples B and D in mg·kg⁻¹; the corresponding molar fractions are presented in Table SM-5. A low concentration of volatile compounds, such as chlorobenzene and dichlorobenzenes, was found, probably due to volatilization during soil transport, storage and drying of soil sample at room temperature. The contamination levels were significantly different between soil B and D (34.69 and 2.27 mmol of COCs·kg⁻¹ in B and D, respectively).

As explained before, HCHs and HeptaCHs in the soil (Table SM-4) can suffer alkaline hydrolysis producing different CBs and DCBs [39] with lower toxicity. Therefore, prior to studying the partition of surfactant and COCs at alkaline conditions, the soil was in contact with an aqueous alkali solution, as described in the experimental section. The composition of soil samples B and D after the alkali addition is also shown in Table SM-4 and Table SM-5. As can be seen in Table SM-5 the total concentration of COCs, in mmol of COCs·kg⁻¹, does not change after the alkali addition, but PentaCXs, HCHs, HexaCXs and HeptaCHs have disappeared due to transformation in TCBs or TetraCBs.

Total carbon (TC) and inorganic carbon (IC) (expressed as a mass percentage, %w, of CaCO₃) in solid samples were measured. Total organic carbon (TOC) values were calculated as the TC and IC difference, summarized in Table 1. TOC values obtained can be explained by the total concentration of COCs measured in both D and B samples. The difference can be attributed to experimental error or a small amount of

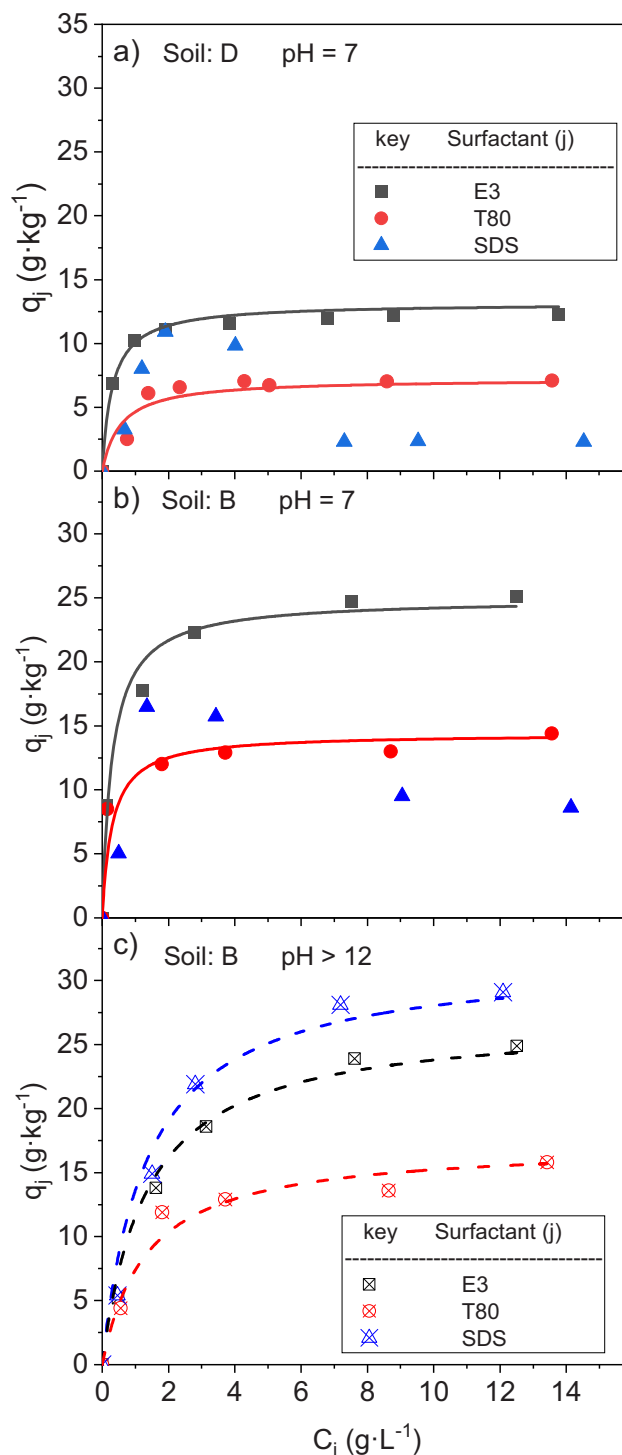


Fig. 1. Adsorption isotherms of E3, T80 and, SDS in contaminated soil: a) soil D at neutral pH, b) soil B at neutral pH and c) soil B at alkaline conditions (NaOH = 7g·L⁻¹). Experimental conditions are summarized in Table SM-3. Experimental results were depicted as symbols and predicted values of Langmuir isotherms as lines using Eq. (4) and parameters in Table 2.

organic matter which can be neglected.

Metal content in both soils is shown in Table 1. Ca²⁺ was the main cation found in the soil sample due to the high content of carbonates.

3.2. Preliminary runs

The time required to achieve the partition equilibrium of surfactant

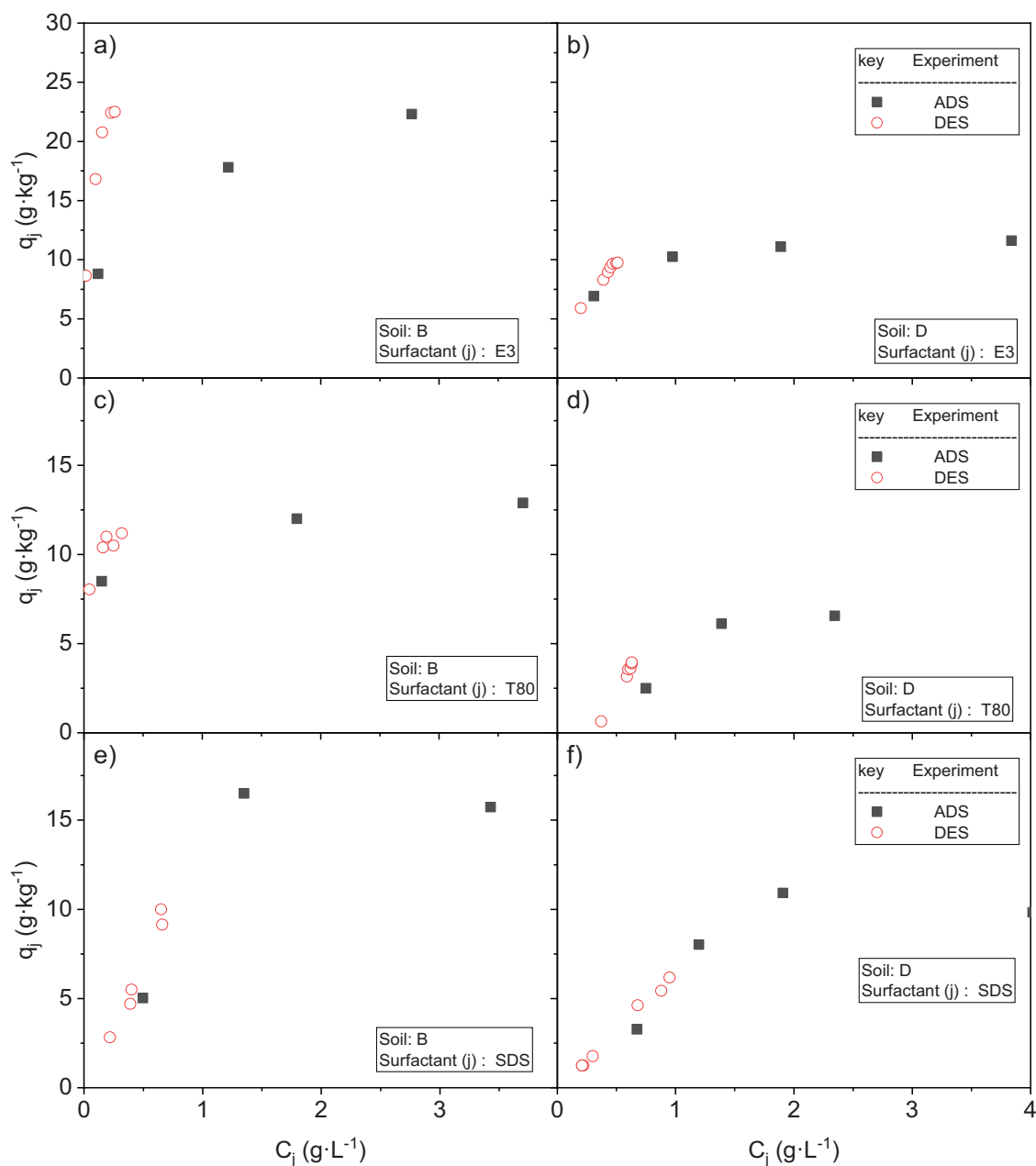


Fig. 2. Adsorption (solid symbols) and desorption (open symbols) of surfactants E3, T80 and SDS from soil samples a) B and b) D.

between soil and aqueous phases was studied with the preliminary runs summarized in Table SM-2. The experiments were carried out at two different concentrations of surfactants 1 and $15 \text{ g}\cdot\text{L}^{-1}$. Adsorbed surfactant values with shaking time (0–72 h) are shown in Fig. SM-1, for soil D (Fig. SM-1a) and soil B (Fig. SM-1b). The profile obtained yielded a fast adsorption of surfactant in the first 3 h. Afterwards, the adsorption rate became slower (3–5 h), reaching the equilibrium at approximately 5 h of contact time. This finding agrees with that reported in the literature [21,42,43]. Moreover, Ussawarujikulchai et al. found that 2 h was sufficient time to reach an equilibrium in the adsorption of the Triton X-100, a soil polluted with naphthalene and decane. Ussawarujikulchai et al. [45].

Simultaneously to the surfactant adsorption, the desorption of COCs from the soil to the aqueous phase took place. The time required to reach the partition equilibrium of COCs between soil and the aqueous phase was studied. Fig. SM-2 shows the concentration of COCs desorbed in the aqueous phase at different contact time between soil B and the aqueous

surfactant solution (experiments in Table SM-2). Fig. SM-2 shows that the COCs desorption profiles are similar to the surfactant adsorption kinetic given in Fig. SM-1, reaching equilibrium after 3 h. As expected, the surfactant adsorbed, and COCs desorbed were higher in those runs carried out at the highest initial surfactant concentration ($15 \text{ g}\cdot\text{L}^{-1}$). Other authors also found this time enough to reach the equilibrium of contaminant desorption into an aqueous surfactant phase [3,20].

3.3. Surfactant partition equilibrium

The surfactant partition equilibrium between soil and the aqueous phase was studied at the experimental conditions summarized in Table SM-3. The contact time was 24 h to ensure that the equilibrium was reached. The concentration of surfactant and COCs was measured in both phases under equilibrium conditions. Results are shown in Fig. 1.

The adsorption of surfactant in soil was first studied at neutral pH. The experimental results of surfactant concentration in the aqueous and

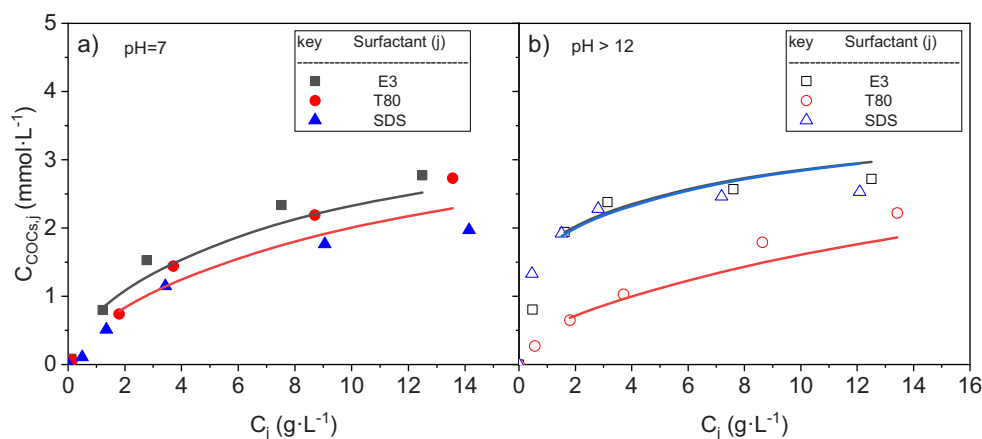


Fig. 3. COCs concentration in the aqueous phase vs. the surfactant concentration in the aqueous phase at equilibrium conditions, using B soil sample at a) neutral pH and b) alkaline conditions. Experimental data are depicted as symbols, and predicted data using Eq. (10) are depicted as lines using an initial concentration of COC adsorbed in the soil of $34.69 \text{ mmol} \cdot \text{kg}^{-1}$.

Table 1

Organic and inorganic characterization of soils B and D.

Soil sample	D	B
$q_{\text{COCs},0} (\text{mmol} \cdot \text{kg}^{-1} \text{ soil})$	2.27	34.69
$\text{TOC}_{\text{COCs}} (\text{mg}_{\text{organic C}} \cdot \text{kg}^{-1} \text{ soil})$	164	2498
$\text{TOC} (\text{mg}_{\text{organic C}} \cdot \text{kg}^{-1} \text{ soil})$	169	2506
$\text{TC} (\text{mg}_{\text{total C}} \cdot \text{kg}^{-1} \text{ soil})$	54,067	54,400
$\text{IC} (\text{mg}_{\text{inorganic C}} \cdot \text{kg}^{-1} \text{ soil})$	53,898	51,894
$\text{IC} (\text{as kg of CaCO}_3) \cdot \text{kg}^{-1} \text{ soil}$	0.45	0.43
Metal composition ($\text{mg} \cdot \text{kg}^{-1}$)		
Fe	35,209	31662
Mg	5551	6420
Zn	0	0
Ca	179,661	172,981
Cu	127	42
Mn	400	573
Na	1463	1645
Al	12,774	16,035
K	3385	3316

soil phases using soil D and soil B at $\text{pH} = 7$ are shown in Fig. 1a and Fig. 1b, respectively. As can be seen, at neutral pH, the adsorption of nonionic surfactant E3 was higher than the T80 adsorption in both soils B and D. Moreover, asymptotic values are of q_i vs C_j , which have been always obtained with nonionic surfactants.

SDS (anionic surfactant) presents a maximum value at neutral pH and for both types of soils close to the critical micellar concentration (CMC), of SDS ($\text{CMC}_{\text{SDS}} = 1.8 \text{ g} \cdot \text{L}^{-1}$), as is shown in Fig. 1a. SDS behaviour develops a maximum that can be explained by the precipitation of SDS for concentrations lower than its CMC due to the presence of cations such as Ca^{2+} or Mg^{2+} . For a concentration higher than CMC, the micelles can redissolve the precipitates due to the counterion binding of Ca^{2+} or Mg^{2+} into these micelles, which means a significant decrease in SDS loss at equilibrium concentrations above its CMC. This indicates that SDS loss was mainly attributed to precipitation [19,47,48,52].

The influence of the COCs adsorbed in soil on the surfactant adsorption at neutral pH is analysed by the comparison of results in Fig. 1a (soil D) and Fig. 1b (soil B), the latter with a significantly higher COCs concentration (as can be seen in Table SM-4). For the three surfactants tested, the concentrations of surfactant adsorbed in B soil at neutral pH are higher than those observed using the soil D, as shown in Fig. 1b. This fact is explained by the high content of hydrophobic organic material of soil B, which produced an increase in the amount of surfactant adsorbed [14,21,24,36,45]. [21] found a higher adsorption of

T80 with trichloroethylene polluted soil with a low soil organic matter $0.46\text{--}0.25 \text{ g} \cdot \text{kg}^{-1}$ [21] to that noticed in the absence of soil organic matter (trichloroethylene) due to oxidative treatment. Rodríguez-Cruz et al. studied the adsorption of SDS on soil with different amounts of trichloroethylene adsorbed in soil ($10\text{--}60 \text{ g} \cdot \text{kg}^{-1}$), finding the higher amount of organic matter, the higher SDS adsorption [36].

As explained before, the influence of pH on the equilibrium partition of surfactant and COCs was investigated due to the dehydrochlorination of HCHs to TCBs and HeptaCHs to TetraCBs [39], which occurs at strong alkaline conditions ($\text{pH} > 12$). This study has been carried out with soil B containing the highest COCs concentration. The composition of COCs in soil B at alkaline conditions was summarized in Table SM-4.

In Fig. 1c, the partition of surfactant at alkaline conditions ($7 \text{ g} \cdot \text{L}^{-1}$ of NaOH) using soil B has been plotted as open symbols. Comparing results at neutral pH (Fig. 1a) and alkaline conditions (Fig. 1c) reveals that at a low concentration of surfactant in the aqueous phase, the lower adsorption of nonionic surfactants was noticed at alkaline conditions. However, the same asymptotic value is reached when C_j increased to $8 \text{ g} \cdot \text{L}^{-1}$. The nonionic surfactant adsorption in the soil is usually poorly affected by electrolytic content in the aqueous phase [37]. However, the interaction between surfactant in solution and adsorbed COCs can be affected by the COCs concentration and type [21]. The use of NaOH modifies the COCs distribution in soil, as can be seen in Table SM-4; the initial COCs distribution was different at $\text{pH} > 12$. The distribution of COCs also affects the adsorption of surfactant. As was studied in a previous study, the absorption of E3 and T80 in a DNAPL phase similar to that present in soil studied was lower at alkaline pH [15].

On the other hand, the partition of SDS between aqueous and soil phases was seriously affected by alkaline conditions. Comparing results in Fig. 1a and c reveals that the adsorption and/or precipitation of SDS at $\text{pH} > 12$ is higher than neutral pH. Since SDS is an anionic surfactant, the electrolyte content in the medium can improve the SDS adsorption and/or precipitation in the soil phase [37,43]. At $\text{pH} > 12$, the maximum was not observed. The solubilization of divalent cations in aqueous phases is lower than neutral pH, and the loss of SDS can be attributed to adsorption instead of precipitation. Pavan et al. reported the SDS adsorption at $\text{pH} = 9$ over hydrotalcite-like compounds [34]. Besides, OH^- anions can modify the surface charge of the soil [34].

Finally, it was noticed in both soils B and D, and for all the surfactant tested, that linear isotherms cannot explain the equilibrium partition of surfactant between the soil and the aqueous phase.

3.4. Surfactant desorption

The desorption of the adsorbed surfactants in the soil samples was

studied as described in the experimental section.

In Fig. 2, the desorption isotherm is shown as open symbols. These values are compared with the adsorption isotherm obtained in the partitioning runs (shown in Fig. 1, and also depicted as solid symbols in Fig. 2).

The desorption experiments were carried out to determine the reversibility of the surfactant adsorption process and the behaviour with time of the adsorbed surfactant in the aquifer after the SEAR treatment. From the results in Fig. 2, the adsorption of nonionic surfactants tested (E3 and T80) was found irreversible in soil B. This finding can be explained by the strong retention of the adsorbed surfactant by the COCs in the soil sample. The lower COCs content of soil D can explain the higher reversibility obtained with this soil. A more remarkable hysteresis and higher adsorption was noticed with surfactant E3 than with T80 in soil B, explained by higher interaction of E3 with COCs. Therefore, surfactant E3 is also less desorbed than T80, with a more marked hysteresis between adsorption and desorption. In contrast, a negligible hysteresis between adsorption and desorption was found when SDS was used, for both soils tested.

3.5. COCs partition

The partition of COCs was studied with runs in Table SM-3. The contact time between phases was set at 24 h, to ensure enough time to reach the equilibrium. The concentration of COCs in the aqueous phase and the remaining COCs in the soil were measured; the mass balance was checked with Eqs. (1)–(3).

The experimental values of COCs concentration vs. surfactant concentration in the aqueous phase, at equilibrium conditions, using soil B and neutral and alkaline conditions, are plotted in Fig. 3. As can be seen, the addition of surfactants remarkably improved the desorption of COCs. The concentration of COCs in aqueous solution in contact with a soil polluted by similar COCs type and concentration was $0.15 \text{ mmol}\cdot\text{L}^{-1}$ and $0.05 \text{ mmol}\cdot\text{L}^{-1}$ at neutral and alkaline conditions, respectively [26]. Values of up to $3 \text{ mmol}\cdot\text{L}^{-1}$ were obtained with surfactant concentration about $13 \text{ g}\cdot\text{L}^{-1}$ in the aqueous solution, at both pHs.

As shown in Fig. 3, the higher the surfactant concentration in the aqueous phase, the higher the COCs in solution, as noticed by other authors [47,55]. However, asymptotic values are obtained when the surfactant concentration in the solution reached $8 \cdot \text{L}^{-1}$.

Fig. 3 shows that the order for COCs desorption at neutral pH was $\text{E3} > \text{T80} > \text{SDS}$. This trend was also reported elsewhere when the solubilization of a similar DNAPL to that used here was studied [15]. Yuan et al. [49] studied hexachlorobenzene desorption (HCB) from kaolin in the presence of T80, sodium dodecylbenzene sulfonic (SDBS), and myristyl pyridinium bromide (MPB). They reported a higher desorption of HCB from kaolin using T80 than with the other two ionic surfactants. A higher solubilization capacity of pure COC tetrachloroethylene, trichloroethylene, cis-chloroethylene) was also obtained with T80 than with SDS and SDBS in the study carried out by Zhang et al. [51].

The effect of alkaline conditions on COCs desorption from soil B is also shown in Fig. 3. E3 and SDS yield similar profiles at this pH. Moreover, alkali addition increases the COCs desorption at a low surfactant concentration in the aqueous phase with E3 and SDS compared to the values obtained at neutral pH. This finding is specially marked with SDS and the E3 behaviour can be related to a cosolvent (limonene) in this surfactant. However, when surfactant concentration in the aqueous phase increases, asymptotic values for COCs desorbed are reached with E3 and SDS. A similar value of the asymptote is obtained at both pHs with surfactant E3 while with surfactant SDS, the asymptotic value for COCs desorption is higher with alkali addition.

The increase noticed at the alkaline condition with SDS can be explained by reducing CMC of anionic surfactant by adding electrolytes [16,32,42]. It was experimentally proved elsewhere [16] that the CMC of SDS at alkaline conditions reaches a value of $0.4 \text{ g}\cdot\text{L}^{-1}$ using $7 \text{ g}\cdot\text{L}^{-1}$ of NaOH.

Moreover, soil composition changes at alkaline conditions (as shown in Table SM-4), the non-aromatic compounds disappearing (PentaCX, HCHs, HexaCX and HeptaHCH), transformed by alkaline dehydrochlorination to TCBs and TetraCBs. These chlorobenzenes are more polar and more soluble than the parent compounds, explaining the increase in solubility noticed in the first region in Fig. 3b. An inhibitory effect of the alkali addition on COCs desorption was noticed when T80 was used, this surfactant desorption capacity decreasing at $\text{pH} > 12$.

An essential point for figuring out is whether the surfactants promoted selective desorption of any COCs in the organic hydrophobic phase. In Fig. SM-3 of the Supplementary Material, the fingerprints of COCs in the soil and the aqueous phase (as molar percentages) are plotted. The COCs distribution in the aqueous phase after reaching equilibrium was similar to the COCs distribution obtained in soil B (shown in Table SM-4 at neutral pH and alkaline conditions). This fact allows considering the total sum of COCs present in the soil as a single compound to study its desorption with surfactant. This behaviour was also noticed using a mixture of DNAPL and an aqueous surfactant solution was put in contact in the absence of soil [15,50].

3.6. Partitioning model discrimination

In this section, the surfactant and COCs partition equilibrium between the aqueous and soil phases has been modelled.

From the results shown in Fig. 1, it can be deduced that a linear isotherm cannot describe the surfactant partition equilibrium adequately. Therefore, a Langmuir isotherm [21] in Eq. (4) has been proposed to model the adsorption of surfactants tested and both pH. In the case of SDS, the experimental results obtained under neutral pH were not fitted to the Langmuir isotherm because a maximum was obtained.

Experimental values of q_j vs. C_j in Fig. 3 were used to fit the parameters in Eq. (4). The values of $K_{L,j}$ and q_j^s are summarized in Table 2. The predicted values of q_j vs. C_j with Eq. (7) and the parameters in Table 2 are plotted as lines in Fig. 1, finding a good agreement between the experimental and predicted values.

The values of q_j^s in Table 2 confirm that the presence of COCs in the soil increases the maximum amount of surfactant adsorbed in soil, as shown in Fig. 1. This saturation value is slightly enhanced (about 20%) at alkaline conditions with E3 and T80. Besides, $K_{L,j}$ was constant for the different surfactant tested at the same pH conditions, a slight decrease being observed at alkaline conditions.

The modelling of the equilibrium partition of COCs between soil and aqueous phases should consider that the higher the concentration of surfactant in the aqueous phase, the higher the concentration of COCs in the aqueous phases, as was shown in Fig. 3. Different approaches can be found in the literature. Paria et al. proposed a linear relationship between the surfactant concentration in the aqueous phase and the solubilized COCs, using the molar solubilization ratio at equilibrium conditions (MSR) (Eq. SM-1) [32]. MSR values for each surfactant j were obtained and shown in Fig. SM-4 of the Supplementary Material. As can be seen, the MSR_j values decrease when the surfactant increases, achieving an asymptotic value at C_j values over $8 \text{ g}\cdot\text{L}^{-1}$. Therefore, the profiles of MSR_j in Fig. SM-4 discard a linear relationship between the surfactant in solution and COCs dissolved.

This fact agrees with the profile in Fig. 3, where the surfactant concentration in the aqueous phase higher than $8 \text{ g}\cdot\text{L}^{-1}$ does not enhance the solubilization of COCs in the aqueous phase. A similar finding was reported by Yuan et al. [49], studying the change in the effectiveness of the surfactant micelles to desorb COCs from the soil. They found a change in the slopes of MSR_j at C_j values lower than $3 \text{ g}\cdot\text{L}^{-1}$ and $7 \text{ g}\cdot\text{L}^{-1}$ for nonionic and anionic surfactants, respectively. This nonlinearity of the MSR can be explained by the effect of the soil phase on the COCs adsorption. On the contrary, a constant MSR value was obtained for each surfactant E3, T80 and SDS in a previous study where solubilization of a

Table 2

Parameters estimated by fitting experimental data in Fig. 1a,b to the Langmuir isotherm in Eq. (4).

SOIL D, pH = 7	$K_{L,j}, g^{-1} \cdot L$	$q_j^*, g \cdot kg^{-1}$	r^2
E3	2.45 ± 0.33	13.16 ± 0.30	0.99
T80	2.42 ± 0.52	7.23 ± 0.38	0.91
SDS	–	–	–
SOIL B, pH = 7	$K_{L,j}, g^{-1} \cdot L$	$q_j^*, g \cdot kg^{-1}$	r^2
E3	3.33 ± 0.64	24.93 ± 0.72	0.98
T80	3.29 ± 0.71	14.39 ± 0.91	0.90
SDS	–	–	–
SOIL B, pH > 12	$K_{L,j}, g^{-1} \cdot L$	$q_j^*, g \cdot kg^{-1}$	r^2
E3	0.78 ± 0.06	29.16 ± 0.71	0.997
T80	0.75 ± 0.13	17.25 ± 0.70	0.96
SDS	0.72 ± 0.07	31.78 ± 1.08	0.992

free DNAPL phase whose composition was similar to the present in the soil B was studied [16].

Therefore, the partition model of COCs in soil must consider the interaction between soil, COCs and surfactants. A global partition coefficient quantifying the distribution of each COC (x) between the soil and aqueous phase $(K_d)_{x,j}^*$ was proposed by Chiou et al. as shown in Eq. (7) [8].

$$(K_d)_{x,j}^* = \frac{q_{x,j}}{C_{x,j}} \quad (7)$$

$q_{x,j}$ and $C_{x,j}$ being the total concentration of a compound x in, respectively, the soil and the aqueous phases, which were experimentally obtained. The subscript j corresponds in this work to the different surfactant tested (j = E3, T80, SDS).

In Figure SM-5, the global partitioning coefficients $(K_d)_{x,j}^*$ for each surfactant and COC(x) at neutral pH (Figure SM-5a) and alkaline pH (Figure SM-5b) are plotted vs. the surfactant concentration in the aqueous phase. As can be seen, the higher the surfactant concentration, the lower $(K_d)_{x,j}^*$ confirming that the surfactant addition enhances the COCs desorption from the soil (shown Fig. 3). However, a surfactant concentration in aqueous phase higher than 8–10 g·L⁻¹ does not produce an appreciable enhancement in the COCs desorption (see Fig. 3). Moreover, negligible differences are obtained among $(K_d)_{x,j}^*$ for each individual compound x. This fact indicates that the chlorinated pollutants in soil were not selectively dissolved, in agreement with the molar distribution of COCs shown in Figure SM-3. Therefore, the mixture of COCs can be considered as a single compound in desorption studies. For this reason, a unique K_d^* in Eq. (8) was proposed for each surfactant and pH tested.

$$(K_d^*)_{COCs,j} = \frac{q_{COCs,j}}{C_{COCs,j}}, j = E3, T80, SDS \quad (8)$$

$q_{COCs,j}$ and $C_{COCs,j}$ being the total concentration of COCs in the soil and aqueous phase, respectively, when surfactant j is used. $(K_d^*)_{COCs,j}$ vs. C_j profiles are shown in Fig. 4.

In accordance with the results reported by Zhou et al., Zhu [55,56], $(K_d^*)_{COCs,j}$ is a function of the surfactant active concentration in the aqueous phase ($C_j - CMC_j$) at equilibrium conditions. It considers the partition equilibrium of COCs among three phases: the aqueous phase containing the surfactant micelles, the sorbed surfactant in soil, and the soil uncovered with surfactant, introducing the corresponding equilibrium partition constant using Eq. (9). The numerator is the total concentration of COCs in soil ($q_{COCs,j}$) and the denominator is the total COCs concentration in the aqueous phase ($C_{COCs,j}$).

$$(K_d^*)_{COCs,j} = \frac{q'_{COCs,j} + q''_{COCs,j} \cdot q_j}{C'_{COCs,j} + C''_{COCs,j} \cdot (C_j - CMC_j)}, j = E3, T80, SDS \quad (9)$$

where $q'_{COCs,j}$ (mmol_{COCs}·kg_{soil}⁻¹) is the concentrations of COCs adsorbed in the fraction of soil not covered by surfactant and $q''_{COCs,j}$ (mmol_{surf,soil}·kg_{surf}⁻¹ in soil) is the concentration of COCs contained in the surfactant adsorbed in the soil. $C'_{COCs,j}$ (mmol_{COCs}·L_{aq}⁻¹) is the concentration of COCs in the aqueous phase but not in the surfactant micelles and $C''_{COCs,j}$ (mmol_{surf,soil}·kg_{surf}⁻¹ in aq) is the concentration COCs inside the surfactant micelles in the aqueous phase.

However, in the experimental conditions tested in this work, $C_j > CMC_j$ and the following assumptions can be made:

- $C'_{COCs} \ll C''_{COCs,j}$ and $C_j - CMC_j \approx C_j$.
- the soil fraction not covered by surfactant is negligible:
 $q'_{COCs,j} \ll q''_{COCs,j} \cdot q_j$

With these hypotheses, the values of C'_{COCs} and $q'_{COCs,j}$ can be neglected and taking into account the definition of $K_{ws,j}$ in Eq. (6), Eq. (9) can be simplified to Eq. (5).

The data gathered in Fig. 4 and q_j calculated by Eq. (3) (parameters in Table 2) have been used to obtain the partition constant $K_{ws,j}$ (except for SDS at neutral pH). The estimated values and statistical significance of parameters $K_{ws,j}$ in Eq. (5) are summarized in Table 3. Predicted values of $(K_d^*)_{COCs,j}$ are depicted with lines in Fig. 4. As can be seen, a good agreement between the experimental and predicted $(K_d^*)_{COCs,j}$ values was obtained.

As shown in Table 3, the pH affects $K_{ws,j}$. For E3, $K_{ws,j}$ is lower at alkaline conditions favouring the migration of COCs to the aqueous solution, resulting in a lower $(K_d^*)_{COCs,j}$, and a higher desorption of COCs (see Fig. 3). This point could be related to the change in COC composition at alkaline pH due to dehydrochlorination reactions. The pH also affects the solubilization capacity of SDS [15]. The higher the pH, the higher the COC desorbed with SDS and the lower $(K_d^*)_{COCs,j}$. On the contrary, $K_{ws,j}$ of T80 increases with the pH.

The experimental profiles of $C_{COCs,j}$ vs. C_j in Fig. 3 can be predicted with the COCs and surfactant mass balances in Eq. (10) and Eq. (11), respectively.

$$q_{COCs,0} = q_{COCs,j} + C_{COCs,j} \cdot \frac{V}{W}, j = E3, T80, SDS \quad (10)$$

$$C_{j,0} = q_j \cdot \frac{W}{V} + C_j, j = E3, T80, SDS \quad (11)$$

$q_{COCs,0}$ being the initial concentration of COCs in soil and $C_{j,0}$ the initial concentration of surfactant in the aqueous phase. The partitioning of COCs and surfactant in aqueous and soil samples can be predicted by substituting Eq. (3), Eq. (5) and Eq. (6) in Eq. (10) and Eq. (11) using the parameters in Table 2 and Table 3. Predicted values of $C_{COCs,j}$ vs. C_j in soil B at the different surfactant concentrations used in runs in Table SM-3 are compared in Fig. 3 (lines) with the experimental values (symbols). As can be seen, a good agreement was obtained between the predicted values and the experimental ones.

4. Conclusions

The partition of surfactant and COCs between soil and aqueous phases has been studied using nonionic surfactants E3 and T80 and anionic surfactant SDS. The soil was polluted with aged contamination (more than two decades) composed of about 28 chlorinated compounds, from chlorobenzene to heptachlorocyclohexane, which was dumped, as was the dumping of dense liquid phase (DNAPL), from lindane production.

It was noticed that the presence of COCs in soil enhances the surfactant adsorption, this adsorption being described adequately by using Langmuir isotherms. The pH also had a remarkable effect on both the

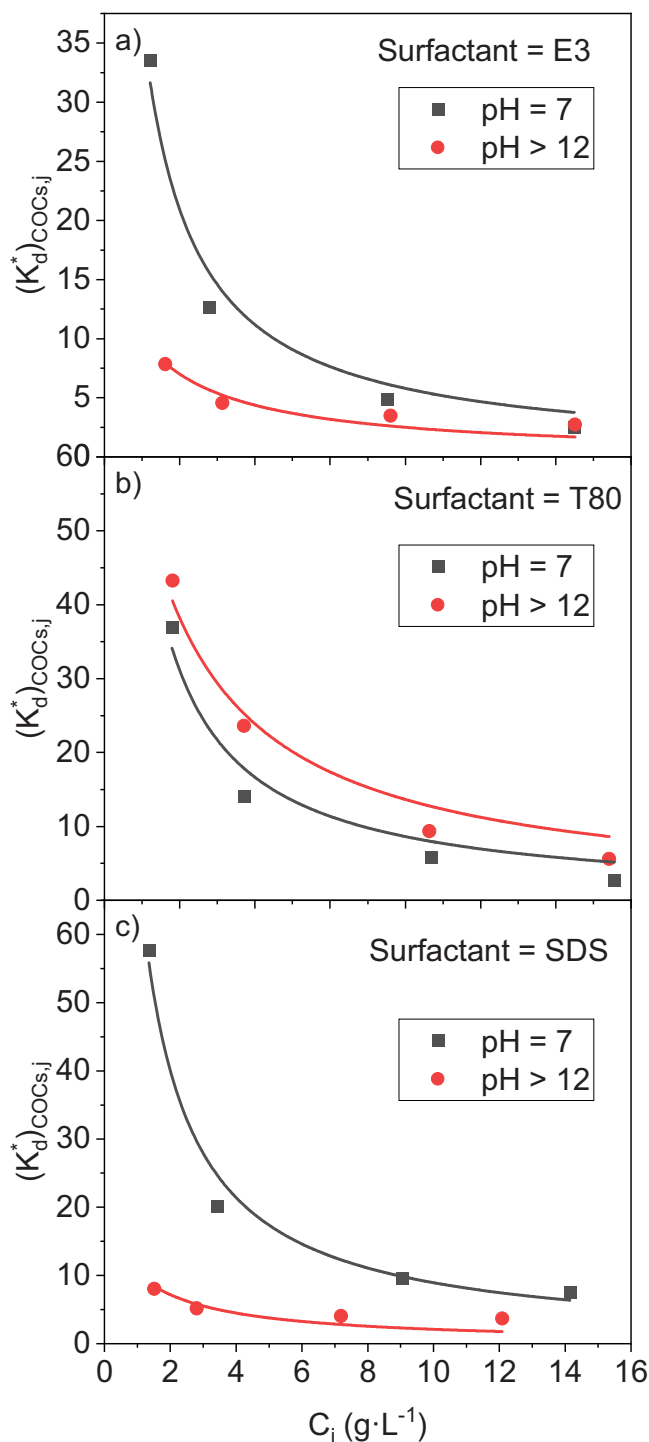


Fig. 4. $(K_d^*)_{COCs,j}$ ($\text{mmol}_{COCs,SOIL} \cdot \text{mmol}_{COCs,AQ}^{-1} \cdot \text{L} \cdot \text{kg}^{-1}$) values calculated by Eq. (7) for each surfactant (E3, T80 and SDS) vs. aqueous concentration of surfactant C_i at alkaline and neutral pH (runs in Table SM-3). Experimental values are given as symbols and predicted values using Eq. (9) and parameters in Table 3 are depicted as lines.

adsorption of surfactants and desorption of COCs. Neutral and alkaline pH was studied. It was found that alkaline conditions favour the most toxic compounds in soil (hexachlorocyclohexanes and heptachlorocyclohexanes) being completely dehydrochlorinated to trichlorobenzenes and tetrachlorobenzenes.

Among the two nonionic surfactants tested, E3 showed the maximum adsorption at neutral and alkaline pH and promoted higher COCs

Table 3

Parameters estimated by fitting experimental data in Fig. 4 to Eq. (9) to estimate the partitioning coefficient of COCs neutral pH and alkaline conditions.

SOIL B, pH = 7	CMC ^a , L·g ⁻¹	$K_{ws,j}$, L·g ⁻¹	r^2
E3	0.10	1.93 ± 0.12	0.98
T80	0.01	5.12 ± 0.54	0.97
SDS	1.8	–	–
SOIL B, pH > 12		$K_{ws,j}$, L·g ⁻¹	r^2
E3	0.10	0.77 ± 0.05	0.87
T80	0.01	7.69 ± 0.37	0.96
SDS	0.40	0.76 ± 0.08	0.80

^a CMC obtained from [16].

desorption at both pHs. This finding can be related to the presence of a cosolvent (limonene) in this surfactant. It was noticed that SDS precipitated at neutral conditions due to the presence of calcium cations in the aqueous phase. Alkaline conditions increase the SDS adsorption and COCs desorption.

The desorption selectivity of the surfactants used in COCs desorption was studied. It was found that the complex COCs mixture in soil behaves as a single compound. The COCs dissolved in the aqueous phase have the same distribution as the COCs present initially in soil. The desorption equilibrium of COCs from the soil phase to the aqueous phase in the presence of surfactants was well-modelled using a partition coefficient $(K_d^*)_{COCs,j}$ that takes into account the concentration of the surfactant in the aqueous phase and the equilibrium between the COCs in the surfactant micelles in both soil and aqueous phases.

From the results obtained here, soil washing or soil flushing with surfactants will allow the decontamination of this soil but several pore volumes of the surfactant solution will be needed. Moreover, the increase of COCs solubilization by the surfactant addition is of great interest for applying in situ treatment as S-ISCO (In Situ Chemical Oxidation enhanced by Surfactant addition).

CRedit authorship contribution statement

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

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.105908.

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