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Removal of alkylphenols from polluted sites using surfactant-assisted soil washing and photocatalysis

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Abstract

Background and Purpose Surfactant-assisted soil washing and photocatalysis are well known remediation processes of environmental concern. The application of photocatalysis to treat soil washing extracts containing 4-methylphenol, 4-ethylphenol and 4-tert-butylphenol in the presence of nonionic (C₁₂E₈ and C₁₂E₂₃) and anionic (SDS) surfactants and some of their binary mixtures was investigated in this work by studying the pollutants degradation in the presence of TiO₂ dispersions irradiated with simulated solar light.

Materials and methods Clean soil samples were spiked with the investigated alkylphenols. Aqueous solutions of the chosen surfactants were placed in contact for some hours with the spiked soil samples in a rotatory mixer. The pollutants recoveries were evaluated via HPLC analysis. Photocatalytic experiments were performed in solarbox on aqueous solutions and on aqueous surfactant solutions containing the pollutants.

Results The pollutants removal from the soil was proven effective using the examined surfactant solutions. The photocatalytic treatment of the wastes was faster using Brij 35, but also SDS and C₁₂E₈-SDS mixtures can be applied. After 2-5 hours the complete pollutants abatement was obtained, depending on the surfactant chosen and on the amount of TiO₂ employed. On the contrary, the treatment of wastes containing C₁₂E₈ was an extremely slow process.

Conclusions The photocatalytic approach can be applied to remove the examined aromatic pollutants from the washing wastes, confirming the viable coupling between this advanced oxidation method and the surfactant-based soil remediation treatments. Surfactant adsorption onto TiO₂ and micelles concentration play a dominant role.

Keywords Soil washing, surfactants, alkylphenols, photocatalytic degradation

1 Background and purpose

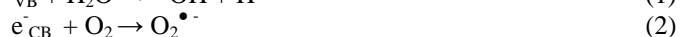
The selection of suitable surfactants to be employed in soil washing is a very important task in view of their application for soil remediation purposes (Deshpande et al.1999; Lee et al.2004). Relevant solubilization of organic compounds by surfactants occurs when the critical micellar concentration (cmc) is reached and becomes proportional to the surfactant concentration above the cmc. Nonionic surfactants are often preferred because of their lower cmc as compared to ionic surfactants and constant properties in the presence of salts. Moreover, these surfactants also show a lower tendency to precipitate fine soil particles and usually exhibit high solubilization capabilities towards most hydrophobic organic compounds (Santanu and Pak 2007).

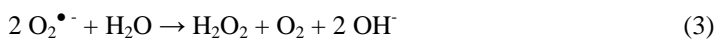
Also other aspects, such as the environmental impact, must be considered since residual surfactants adsorbed on the soil act themselves as pollutants. For practical purposes, an ideal surfactant should have high solubilizing ability towards the pollutant and low adsorption on soil. Although various studies have been reported, there are still different opinions about the surfactant adsorption mechanisms (Laha et al. 2009). Adsorption of ionic surfactants is generally correlated with electrostatic forces (Paria and Khilar 2004), whereas hydrogen bonding is considered the main force operating in nonionic surfactants adsorption.

After the soil washing, a crucial point becomes the disposal and/or treatment of the corresponding wastes before their discharge or reuse (Chu et al. 1998). In this direction, semiconductor-based photocatalysis can be proposed as an effective remediation treatment, essentially based on irradiation of the aqueous effluents with natural or simulated solar light in the presence semiconductor suspensions. Metal oxides, such as TiO₂, ZnO, SnO₂, WO₃, etc., were successfully employed, leading to the degradation and mineralization of most organic pollutants without the semiconductor alteration (Behnajady et al. 2007, Sleiman et al. 2007). The immobilization of such catalysts on proper solid supports allows also to operate under flow conditions (He et al. 2010; Lizama et al. 2005).

The mechanism of photocatalysis has been extensively investigated (Serpone and Pelizzetti 1989; Ollis and Al-Ekabi 1993; Hoffmann et al. 1995; Malato et al. 2002). Basically the photocatalytic reactions are founded on the generation of electron-hole pairs on the semiconductor surface when the photocatalyst is illuminated by light having energy higher than its band gap. The electron/hole pair can separately interact with electron donors and acceptors, giving rise in particular to the formation of strong oxidizing species which attack and decompose most organic compounds, leading to the formation of non toxic or less toxic end products (Legrini et al. 1993).

The following reactions give rise to the formation of the hydroxyl radical, considered the main oxidizing agent:





In addition to the oxidation paths, reduction processes involving the electrons in the conduction band can also be present (Muneer and Bahnemann 2002).

The main goal of the present work was to evaluate the extraction capabilities of three surfactants and their mixtures towards alkylphenols of tuned hydrophobicity present in soil, looking not only to the solubilization power of their aqueous solutions, but also to the feasible application of photocatalysis to treat the soil washing extracts. In this light the kinetics of the pollutants abatement in wastes was examined in detail, looking at the effects that soil components can exert on this treatment and investigating the possible correlations between the observed degradation rates and the pollutants partitioning equilibria existing in the investigated heterogeneous system.

2 Materials and methods

2.1 Soil Samples

A clean sandy clay loam having an organic carbon content of ca. 2.5% was sampled near Alba (Cuneo, Italy). Samples of such soil, taken from the 0-15 cm horizon, were dried at room temperature, then grinded in a mortar and sieved to < 2 mm to remove the bigger particles. The soil was further homogenized, transferred to closed vessels and kept in refrigerator.

2.2 Instruments

The following instruments were used: HPLC Merck-Hitachi, equipped with L-6000 and L-6200 pumps and a UV-VIS L-4200 detector; a microwave digestion system MARSX (from CEM Corporation). Surface tension measurements were performed with a digital tensiometer (K10, Krüss). UV-VIS spectra were obtained with a double beam spectrophotometer CARY 100 SCAN (Varian). All the irradiation experiments were carried out in Solarbox (CO.FO. MEGRA, Milan), where stirred cylindrical closed cells (40 mm i.d.; 25 mm high, made of Pyrex glass) were placed. A 1500 W Xenon lamp source, equipped with a 340 nm cut-off filter, was used to simulate the AM1 solar irradiation. The temperature within the cells was ca. 55°C.

2.3 Reagents

TiO₂ Degussa P25 (composed of ca. 80% anatase and 20% rutile) was employed to perform all the photodegradation tests. In order to remove any organic impurity this oxide was washed with water and irradiated in solarbox for about 12 hours. The washed semiconductor was then dried in the oven at 80°C. The TiO₂ dispersions were sonicated in water immediately before use. Acetonitrile (Lichrosolv, Merck) was used as eluent. The surfactants C₁₂E₈ (Nikkol), Brij 35 (Aldrich) and SDS (Merck), were used to prepare the soil washing solutions. Acetone and n-hexane (from Aldrich) were used for the microwave-assisted exhaustive extraction (MAE) of the soil samples. Pure water was produced using a Milli-Q™ system (Millipore). Pure standards of 4-methylphenol (Carlo Erba), 4-ethylphenol and 4-tert-butylphenol (Aldrich) were used in soil spiking experiments, calibration runs and photocatalytic tests.

2.4 Experimental methods

2.4.1 Soil Spiking Procedure

According to a reported soil spiking protocol (Prosen et al. 1998), 50 g of soil were treated with 50 mL of solutions containing a known concentration of the organic pollutants dissolved in acetone. The slurry was strongly stirred for one hour, then allowed to stand at room temperature under hood for ca. 24 hours to obtain the complete evaporation of the organic solvent.

2.4.2 Soil Washing Experiments

The soil washing tests were performed on relatively fresh (one week) spiked soil samples. The effect of ageing was not considered in this work.

Prior to the soil washing the spiked samples were analyzed following a standard exhaustive procedure (EPA method n° 3546): ca. 10 g of soil were weighed in the teflon microwave vessel and 25 mL of acetone/hexane (50:50, v/v) were added. The samples were micro-waved at 110°C and 100 psi for 20 min. The liners were cooled to 25°C and the suspensions were filtered through 0.45 µm Millex-LCR filters (Millipore). Acetone was finally replaced by acetonitrile before the HPLC analysis.

Soil washing experiments were performed in a rotatory mixer (rotation speed: ca. 10 rpm) on 2 g of soil to which were added 12.5 mL of the surfactant solutions. The contact time was 5 hours. After centrifugation at 5000 rpm for 10 min, aliquots of the supernatant solutions were filtered through a 0.45 µm Millex-LCR hydrophilic PTFE membrane (Millipore).

The HPLC determination of each analyte was performed on the filtered solutions, using different acetonitrile/water mixtures as eluents: 30:70 v/v for 4-methylphenol, 40:60 v/v for 4-ethylphenol and 50:50 v/v for 4-tert-butylphenol,

respectively. A 100 RP-C18 column (Lichrospher, 4 mm i.d x 125 mm long, 5 μ m particle size) was used. Isocratic elutions were performed at a flow rate of 1 mL/min; the detector wavelength was 220 nm.

2.4.3 Photodegradation tests

A series of preliminary experiments were carried out on 5 mL of aqueous micellar solutions containing 10 mg/L of each individual pollutant and 100 mg/L of TiO₂. Higher amounts of catalyst (200-500 mg/L) were employed to treat the soil washing extracts. Experiments without TiO₂ were also performed in order to estimate the possible contribution of photolysis to the degradation. The primary degradation kinetics of each pollutant was followed by sampling and analysing the dispersions after different irradiation times. An equal volume of acetonitrile (5 mL) was added to the irradiated dispersions in order to minimize the adsorption of the residual pollutants on the catalyst particles, then the hydroorganic dispersions were stirred for 20 minutes and filtered before the analysis through a 0.1 μ m Anotop 25 Plus inorganic membrane filter (Whatman).

3 Results and discussion

3.1 Soil washing experiments

The surface tension of the filtered soil extracts was measured in order to assess the presence of micellar aggregates in the washing waste. This is an important test since it is well known that the washing efficiency largely depends on micellar solubilization, being negligible the contribution arising from the surfactant monomers.

The profiles of surface tension as a function of surfactant concentration are shown in Figure 1 for washing wastes containing 4-tert-butylphenol. The dilution ratio (d_r) is given by V_d/V_0 , where V_d is the volume of the washing waste after dilution with pure water and V_0 is the initial volume of the filtered washing solution. It can be seen that micellar aggregates were still present in all the investigated solutions. Strictly similar profiles were also obtained for washing wastes containing the other two examined pollutants.

The alkylphenols recoveries and the corresponding standard deviation values, estimated from five replicated extractions, are reported in Table 1. After 5 hours washing, the micellar solutions allow to achieve significant pollutants recoveries. Solubilization in pure water was noticeable only for 4-methylphenol and decreased with the increasing hydrophobicity of solutes. The SDS solution also gave good extraction yields for 4-methylphenol, but the extraction of the more hydrophobic derivatives was more difficult. Similar trends were shown by the nonionic surfactants, being Brij 35 the best candidate for the recovery of 4-ethylphenol and 4-tert-butylphenol. The results obtained using surfactant mixtures suggest that mixed micelles of C₁₂E₈ and SDS could be used as alternative washing systems, whereas the mixed aggregates of Brij 35 and SDS are less effective.

However, a convenient selection of the washing system cannot be done without considering the behaviour of such solutions during the washing waste treatment step.

3.2 Preliminary Photocatalytic tests

We initially investigated the photocatalytic degradation of each organic compound in aqueous TiO₂ dispersions containing the examined surfactants at concentrations higher than their cmc. The relative abatement of the organic substrate concentration (C) with respect to its initial concentration (C₀) was followed as a function of the irradiation time. Figure 2 shows the corresponding kinetic profiles of the substrate degradation (primary process), which follows a pseudo first-order kinetic law:

$$-\ln (C/C_0) = k_{\text{obs}} t \quad (5)$$

Figure 3 shows that linear plots according to eqn. (5) are obtained up to ca. 70% of 4-tert-butylphenol abatement (each point represents the mean of 3 replicated measurements). Similar linear profiles were obtained by fitting the degradation of the other examined alkylphenols.

Experiments performed in the presence of lower concentrations of nonionic surfactants (one tenth of those employed in soil washing runs) showed a relevant increase of the degradation rate, suggesting that wastes dilution with water could be applied in order to speed up the treatment. The SDS solution was not diluted since this surfactant was only slightly above its cmc.

The examination of Fig. 2 indicates that SDS allows to perform faster degradations, roughly comparable with those observed in water, whereas C₁₂E₈ strongly inhibits the pollutants abatement. Also Brij 35 induces a noticeable inhibition, but much lower than that observed in the presence of C₁₂E₈. For the more hydrophobic phenols, the treatment of wastes containing the C₁₂E₈-SDS mixture give results similar to those obtained with Brij 35, whereas faster degradations can be obtained using Brij 35-SDS. However this last mixture is less efficient in the washing step. Table 2 summarizes the corresponding kinetic data; the uncertainties calculated from 4-5 repeated runs, were found in the range 4-6%.

The inhibition of the photocatalytic pollutants degradation, observed when working in the presence of surfactants, can be in part due to the fact that the surfactant itself is degraded (Hidaka et al 1990; Eng et al. 2010), thus competing with the substrate for the active sites at the catalyst/solution interface. Moreover, other effects arising from the solute partitioning between the bulk solution and the micelles (see Figure 4) should also be considered.

The influence of pH on surfactants adsorption onto TiO₂ plays a significant role. The initial pH of the washing solutions was in the range 7.2-7.5, after 120-180 min irradiation the pH in the cells was slightly lower (6.8-7.0), whereas the final pH of the treated wastes after long term irradiations (5-6 hours) was around 6.3-6.5, which corresponds to the isoelectric point of TiO₂ P-25 (Lee et al. 2003). A negligible adsorption of SDS on TiO₂ can be, thus, expected on the basis of the electrostatic repulsion operating between the amphiphile and the negatively charged semiconductor particles. This effect reasonably reduces the competition between SDS and substrate molecules for the active sites of TiO₂, justifying the higher degradation rates observed.

On the other hand, the different adsorption mechanism of nonionic surfactants suggests that their adsorption onto the TiO₂ particles is possible. Among the two examined amphiphiles, C₁₂E₈ has the smaller polyoxyethylene head group and interactions between the hydrophobic tails can occur, giving rise to the formation of admicellar structures on hydrophilic surfaces much more easily than Brij 35 (Koopal 2003). This higher tendency to adsorb can justify the relevant inhibition observed using C₁₂E₈.

The concentration of micelles is also very important. It was found that, upon increasing the number of micelles, the pollutant degradation becomes slower due to its decreased availability at the semiconductor/solution interface (Fabbri et al. 2006). At constant surfactant concentration, the degradation of 4-tert-butylphenol is much slower than that observed for the less hydrophobic phenols, as expected considering the higher tendency of hydrophobic solutes to bind to micellar aggregates.

3.3 Photocatalytic treatment of soil washing extracts

The pollutants degradation in the soil washing extracts was examined using the better surfactant candidates: SDS 1.5x10⁻² M, Brij 35 1.0x10⁻² M, and the mixture C₁₂E₈ 5.0x10⁻³ M-SDS 5.0x10⁻³ M, in the presence of different TiO₂ concentrations (200 and 500 mg/L, respectively). Blank experiments were also performed in the absence of TiO₂, in order to evaluate the possible beneficial effects attributable to the dissolved organic matter, in particular humic acids, present in the soil (Alleman and Leeson 1997).

Figure 5 shows the degradation of 4-ethylphenol in soil washing extracts containing Brij 35, SDS and C₁₂E₈-SDS mixture. It can be seen that Brij 35 allows to obtain faster degradation rates. For this surfactant, experiments were also performed under the same working conditions but without the presence of soil, in order to estimate the contribution of soil components to the degradation kinetics. The significant increase of inhibition evidenced in the presence of soil confirms the results reported in previous studies (Fabbri et al. 2008). This effect can be in part due to the fact that humic compounds can be themselves degraded (Minero et al. 1999) and in part attributed to the joint influence of humic matter and surfactants on pollutants solubility (Lippold et al. 2008), which can significantly modify the solute-micelle binding, altering the substrates partitioning in the heterogeneous system. The same general behaviour shown in Fig. 5 was also found for the other examined phenols.

The peculiar properties of humic components, known to act as sensitizers of photodegradation (Kamiya and Kameyama 1998), can also justify the non negligible substrates degradation observed in the absence of TiO₂. In fact, ca. 36% of the initial 4-ethylphenol was degraded after 2 hours irradiation in Brij 35 soil washing wastes, whereas the degradation of ca. 22% and ca. 10% of this pollutant was observed in SDS and C₁₂E₈-SDS wastes, respectively. Similar degradations in the absence of TiO₂ were also observed for 4-methylphenol and 4-tert-butylphenol, with a marked effect found in the presence of Brij 35.

The kinetic data summarized in Table 3 confirms that aqueous Brij 35 allows to perform a faster photocatalytic treatment of the soil washing wastes.

4 Conclusions

The effective removal of alkylphenols from the polluted soil samples can be performed using the investigated amphiphiles, but the choice of the proper soil washing system needs also to consider the possible further treatment of the wastes. SDS allows to obtain rather good extraction yields, however the photocatalytic treatment of the washing wastes is slow. The nonionic amphiphile C₁₂E₈ and the mixture C₁₂E₈-SDS are less suitable for washing due to the observed relevant inhibition of the photocatalytic step, whereas Brij 35 can be proposed as the best candidate since it allows to obtain higher recoveries of more hydrophobic alkylphenols and the photocatalytic treatment of the corresponding wastes is faster. Taking into account that the organic components of soil can also inhibit the photocatalytic process and drastically alter the micellar performances, their specific contribution to the selection of the washing systems must be carefully evaluated.

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Figure Captions

Fig. 1 Surface tension of washing wastes containing 4-tert-butylphenol as a function of dilution ratio (∇ Brij 35 1.0×10^{-2} M; \square C₁₂E₈ 1.0×10^{-2} M; \blacktriangledown SDS 1.5×10^{-2} M; \circ Brij 35 and SDS 5.0×10^{-3} M).

Fig. 2 Photocatalytic degradation profiles of 4-methylphenol (a), 4-ethylphenol (b) and 4-tert-butylphenol (c). (\bullet H₂O; ∇ Brij 35 1.0×10^{-2} M; \square C₁₂E₈ 1.0×10^{-2} M; \blacktriangledown SDS 1.5×10^{-2} M; dotted lines: \circ Brij 35 and SDS 5.0×10^{-3} M, \blacklozenge C₁₂E₈ and SDS 5.0×10^{-3} M).

Fig. 3 Plots of $-\ln(C/C_0)$ versus time for the degradation of 4-tert-butylphenol in the presence of different washing solutions (\bullet H₂O; ∇ Brij 35 1.0×10^{-2} M; \square C₁₂E₈ 1.0×10^{-2} M; \blacktriangledown SDS 1.5×10^{-2} M; dotted lines: \circ Brij 35 and SDS 5.0×10^{-3} M, \blacklozenge C₁₂E₈ and SDS 5.0×10^{-3} M).

Fig. 4 Solute partition equilibria between bulk solution (W), micelles (M) and surfactant-modified semiconductor particles (TiO₂).

Fig. 5 Photocatalytic degradation of 4-ethylphenol in soil washing wastes: \blacksquare Brij 35 1.0×10^{-2} M soil extract, TiO₂ 500 mg/L; \blacktriangledown Brij 35 1.0×10^{-2} M soil extract, TiO₂ 200 mg/L; \bullet Brij 35 1.0×10^{-2} M blank, TiO₂ 500 mg/L; \blacklozenge Brij 35 1.0×10^{-2} M blank, TiO₂ 200 mg/L; \square SDS 1.5×10^{-2} M soil extract, TiO₂ 500 mg/L; ∇ SDS 1.5×10^{-2} M, soil extract TiO₂ 200 mg/L; dotted lines: \star C₁₂E₈ and SDS 5.0×10^{-3} M, TiO₂ 500 mg/L, \circ C₁₂E₈ and SDS 5.0×10^{-3} M, TiO₂ 200 mg/L).

Fig. 1

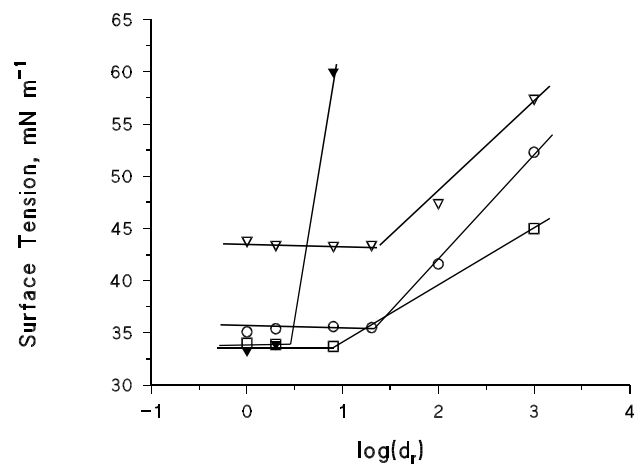


Fig. 2

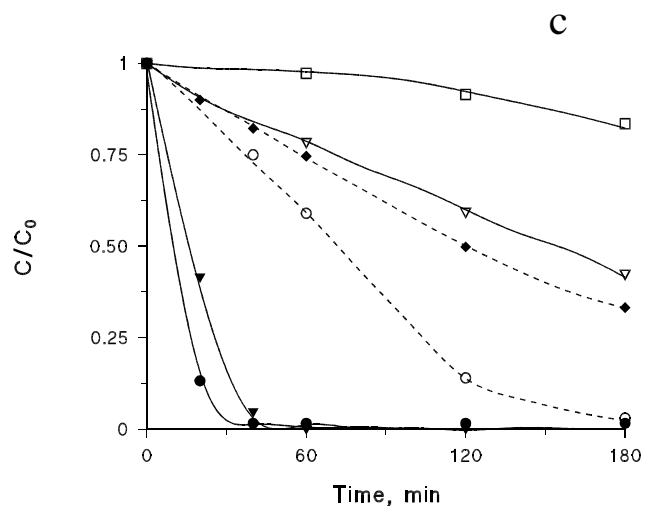
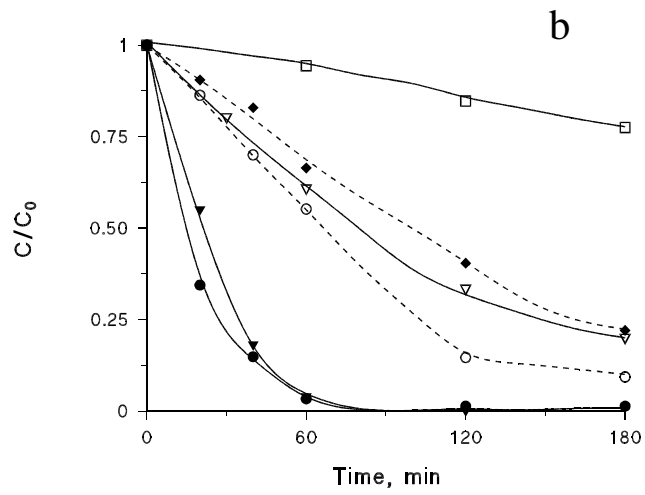
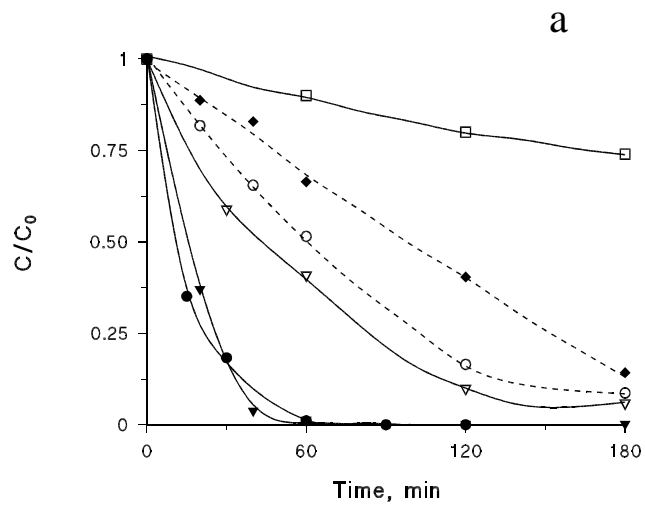


Fig. 3

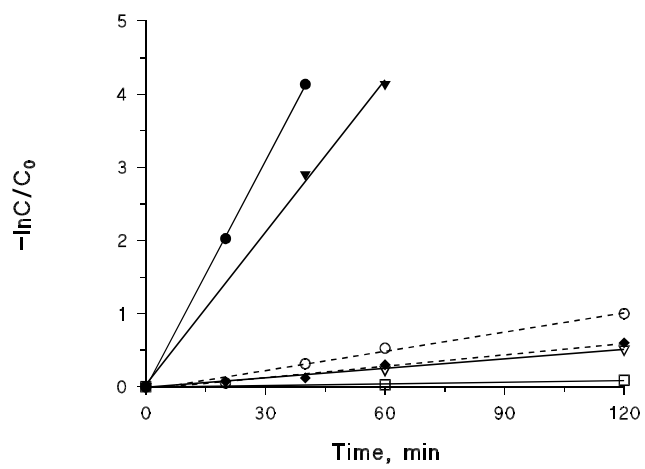


Fig. 4

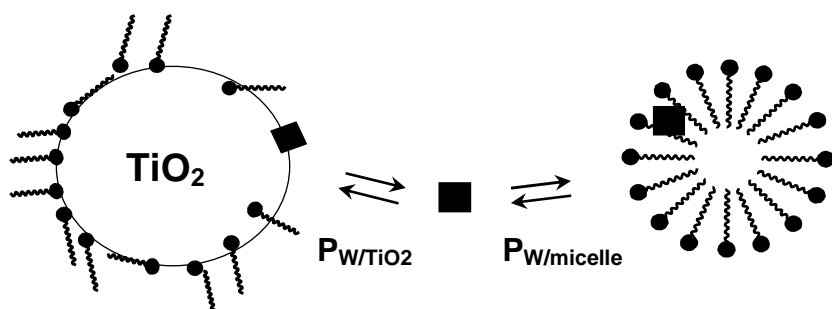


Fig. 5

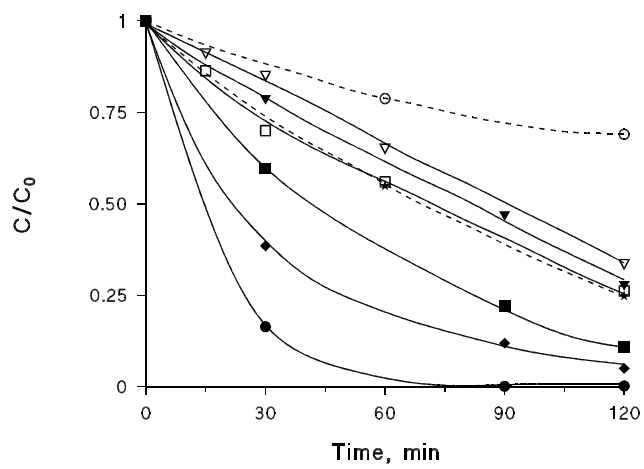


Table 1 Recoveries of the investigated alkylphenols after the soil washing experiments.

Soil washing solution	4-methylphenol		4-ethylphenol		4-tert-butylphenol	
	% Recovery	SD	% Recovery	SD	% Recovery	SD
Acetone/n-hexane	93.4	2.1	93.5	4.7	95.9	3.9
H ₂ O	74.6	14.4	56.3	9.5	41.8	4.3
BRIJ 35 1.0x10 ⁻² M	86.2	6.8	71.8	4.6	72.1	1.7
C ₁₂ E ₈ 1.0x10 ⁻² M	77.7	8.3	61.4	6.0	52.2	4.9
SDS 1.5x10 ⁻² M	89.1	5.2	65.3	4.2	55.1	5.7
BRIJ 35 - SDS, 5.0x10 ⁻³ M ^(*)	75.7	7.0	65.7	8.7	60.9	3.0
C ₁₂ E ₈ - SDS, 5.0x10 ⁻³ M ^(*)	92.4	5.0	67.9	5.0	69.8	4.0

^(*) concentration of each surfactant; SD: standard deviation

Table 2 Rate constants of the primary degradation of alkylphenols in the presence of surfactants.

Washing solution	k_{obs} (min^{-1})		
	4-methylphenol	4-ethylphenol	4-tert-butylphenol
H ₂ O	8.6×10^{-2}	5.5×10^{-2}	4.4×10^{-2}
BRIJ 35 1.0×10^{-2} M	1.9×10^{-2}	9.1×10^{-3}	4.3×10^{-3}
BRIJ 35 1.0×10^{-3} M	2.1×10^{-2}	2.1×10^{-2}	1.7×10^{-2}
C ₁₂ E ₈ 1.0×10^{-2} M	1.8×10^{-3}	1.5×10^{-3}	1.3×10^{-3}
C ₁₂ E ₈ 1.0×10^{-3} M	3.7×10^{-3}	4.7×10^{-3}	3.6×10^{-3}
SDS 1.5×10^{-2} M	8.2×10^{-2}	4.3×10^{-2}	3.9×10^{-2}
BRIJ 35 - SDS 5.0×10^{-3} M (*)	1.1×10^{-2}	1.0×10^{-2}	8.7×10^{-3}
C ₁₂ E ₈ - SDS 5.0×10^{-3} M (*)	9.4×10^{-3}	6.6×10^{-3}	5.9×10^{-3}

(*) concentration of each surfactant

Table 3 Rate constants of the primary degradation of alkylphenols in the washing wastes.

	k_{obs} (min⁻¹)		
	4-methylphenol	4-ethylphenol	4-tert-butylphenol
Brij 35 1.0 x 10 ⁻² M soil extract; TiO ₂ 500 mg/L	3.1x10 ⁻²	1.8x10 ⁻²	1.6x10 ⁻²
Brij 35 1.0 x 10 ⁻² M soil extract; TiO ₂ 200 mg/L	1.3x10 ⁻²	8.6x10 ⁻³	4.9x10 ⁻³
Brij 35 1.0 x 10 ⁻² M blank; TiO ₂ 500 mg/L	8.6x10 ⁻²	7.6x10 ⁻²	4.5x10 ⁻²
Brij 35 1.0 x 10 ⁻² M blank; TiO ₂ 200 mg/L	3.0x10 ⁻²	2.3x10 ⁻²	2.3x10 ⁻²
Brij 35 1.0 x 10 ⁻² M; without TiO ₂	4.8x10 ⁻³	3.6x10 ⁻³	3.4x10 ⁻³
SDS 1.5 x 10 ⁻² M soil extract; TiO ₂ 500 mg/L	2.7x10 ⁻²	9.3x10 ⁻³	7.0x10 ⁻³
SDS 1.5 x 10 ⁻² M soil extract; TiO ₂ 200 mg/L	1.5x10 ⁻²	7.3x10 ⁻³	3.4x10 ⁻³
SDS 1.5 x 10 ⁻² M; without TiO ₂	2.8x10 ⁻³	1.7x10 ⁻³	1.2x10 ⁻³
C ₁₂ E ₈ and SDS 5.0 * 10 ⁻³ M soil extract; TiO ₂ 500 mg/L	1.9x10 ⁻²	1.2x10 ⁻²	5.4x10 ⁻³
C ₁₂ E ₈ and SDS 5.0 * 10 ⁻³ M soil extract; TiO ₂ 200 mg/L	5.1x10 ⁻³	3.1x10 ⁻³	8.5x10 ⁻⁴
C ₁₂ E ₈ and SDS 5.0 * 10 ⁻³ M; without TiO ₂	1.1x10 ⁻³	5.1x10 ⁻⁴	1.6x10 ⁻⁴