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Photocatalytic degradation of chlorophenols in soil washing wastes containing Brij 35. Correlation between the degradation kinetics and the pollutants-micelle binding.

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ABSTRACT

The photocatalytic degradations of 4-chlorophenol (CP), 4-chloro-2-methylphenol (CMP), 4-chloro-3,5-dimethylphenol (CDMP) and 4-chloro-2-isopropyl-5-methylphenol (CIMP) were investigated in water and in simulated soil washing wastes containing Brij 35 (polyoxyethylene(23)dodecyl ether) in the presence of TiO₂ dispersions. A neat inhibition of substrates decomposition proportional to their growing hydrophobicity was observed in the washing wastes for CP, CMP and CDMP whereas CIMP showed a different behaviour. The mineralization of the organic chlorine of CP and CIMP was relatively fast and complete, whereas it was much slower for CMP and CDMP. Micellar solubilization and substrate adsorption onto the semiconductor play opposite roles on the degradation kinetics and a break-point between the corresponding induced effects was evidenced when the pollutants become completely bound to the micellar aggregates.

KEYWORDS: chlorophenols, Brij 35, soil washing, photocatalysis

1. INTRODUCTION

Soil washing, a remediation technology largely based on the use of aqueous surfactant solutions (Edwards et al. 1991; Deshpande et al. 1999) exploits the solubilization of contaminants present in soil by surfactant micelles and the simultaneous lowering of the interface tension between the washing solution and the soil particles, facilitating the pollutants desorption from the solid phase pores (Gotlieb et al. 1993; Chu and So 2001; Chu and Chan 2003).

Nonionic surfactants have been often employed for soil washing due to their high solubilization capabilities towards hydrophobic solutes. Moreover, they exhibit low critical micelle concentrations and do not originate precipitates in the presence of ionic components of soil (Zheng and Obbard 2002). Hydrophilic non-ionic surfactants are, in particular, suitable candidates since they generally show lower adsorption on the solid soil particles, thus reducing the surfactant consumption during the washing.

A typical problem arising from soil washing is that the obtained wastes must be further disposed or treated using proper chemical or biological degradation procedures. Among the possible chemical treatments, heterogeneous photocatalysis is an advanced oxidation method largely used in the past years for the effective degradation of a wide variety of organic pollutants present in aqueous wastes. One of the main advantages of this process is that it allows to obtain the effective decomposition and in most cases the complete mineralization of a great variety of substrates (Ollis et al. 1989; Pichat et al. 1993; Bahnemann et al. 1994; Hoffmann et al. 1995; Alfano et al. 2000; Malato et al. 2002).

The photocatalytic treatment of aqueous wastes containing surfactants coming from soil washing was previously successfully applied in real cases (Fabbri et al. 2008). However this treatment is a very complex process which needs to be carefully considered since it is known that surfactants are themselves degraded (Hidaka et al. 1990), thus competing with the target pollutants for the active sites of the semiconductor. Moreover, the presence of surfactant micelles and

surfactant structures adsorbed onto the semiconductor drastically alter the partition equilibria of substrates between the solution and the catalyst, with noticeable effects on the degradation kinetics.

In fact, it was generally found that the degradation of organic pollutants is largely inhibited in the presence of surfactants (Pramauro et al. 1998; Bianco Prevot et al. 1999; Fabbri et al. 2004), but beneficial kinetic effects were also observed in some peculiar cases (Tada et al. 2002; Fabbri et al. 2006). In particular, in a very recent work the positive role played by the accumulation of the target pollutant in the admicellar structures formed on the semiconductor was clearly confirmed (Zhang et al. 2012).

Although these contradictory results have been noticed and tentative explanations have been proposed, there is still a lack of information concerning the mechanisms of the photocatalytic treatments performed in the presence of surfactants due to the complexity of the heterogeneous reaction media. In particular, the existence of useful relationships between the kinetic effects and the interactions operating between the substrates and the different components present (micelles, admicelles, semiconductor particles and bulk solution) need to be more deeply examined.

In order to give insight into these aspects, the application of photocatalysis to treat soil washing wastes containing some chlorophenolic derivatives was investigated, looking at the opposite influence exerted on the primary degradation kinetics by pollutants adsorption onto the TiO₂ particles and by their binding to the micellar aggregates. All the examined compounds contain a common moiety (4-chlorophenol) and different alkyl substituents contributing to the whole molecule hydrophobicity. The evolution of the substrates mineralization was also examined by monitoring the chloride release during the treatment.

Taking into account the good performances exhibited by the nonionic surfactant Brij 35 in previous investigations (Davezza et al. 2011), it was selected as suitable and unique candidate for the soil washing and the successive photocatalytic experiments.

2. MATERIALS AND METHODS

2.1 Soil samples

A clean sandy clay loam having an organic carbon content of ca. 2.5% was sampled from the 0-15 cm soil horizon, 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 pollutants determinations were performed using an HPLC Merck-Hitachi, equipped with L-6000 and L-6200 pumps and a UV-VIS L-4200 detector. The chloride analysis was performed using a Dionex DX500 ionic chromatograph, equipped with a Dionex AS9HC anionic column (200 mm long x 4 mm i.d.) and a conductometric ED40 Dionex detector.

A microwave digestion system MARSX (from CEM Corporation) was used for the exhaustive extraction of the soil samples. Surface tension measurements were performed with a digital tensiometer (K10, Krüss).

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 measured temperature within the solarbox was ca. 53°C.

Some ultrafiltration experiments were also performed on the pollutants-containing soil washing wastes using an ALC PK 131 R centrifuge (Milan, Italy).

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.

Methanol (Lichrosolv, Merck) was used as eluent. The surfactant Brij 35 (from Aldrich), was 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-QTM system (Millipore). Pure standards of CP (Aldrich), CMP (Fluka), CDMP and CIMP (from Alfa Aesar) were used as received.

3. EXPERIMENTAL PROCEDURES

3.1 Soil Spiking

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 forced ventilation in hood for 24 hours to obtain the complete removal of the organic solvent. The spiked soil samples were kept in refrigerator.

3.2 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 the present study.

To 2 g of soil were added 12.5 mL of the surfactant-containing washing solutions, then the dispersions were placed in a rotatory mixer (rotation speed: ca. 10 rpm). The contact time was 5 h. 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) and analyzed via HPLC using a mobile phase composed of methanol/water (50:50 v/v for CP; 60:40 v/v for CMP and 70:30 v/v for CDMP and CIMP, respectively). A 100 RP-C18 column (Lichrospher, 4 mm i.d x 125 mm long, 5 μm particle size) was used. Isocratic elutions were performed at a flow rate of 1 mLmin⁻¹; the detector wavelength was 220 nm.

3.3 Microwave-assisted extraction (MAE) of the spiked soil samples

Prior to the washing runs the spiked soil 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 the room temperature and the suspensions were filtered through 0.45 µm Millex–LCR filters (Millipore). Acetone was finally replaced by methanol before the HPLC analysis.

3.4 Pollutants adsorption onto TiO₂

In order to verify the tendency of each pollutant to adsorb onto the semiconductor particles, adsorption runs were performed in the dark. Soil washing solutions containing 20 mgL⁻¹ of alkylchlorophenols were placed in the Solarbox cells together with the proper amount of TiO₂ (1000 mgL⁻¹). The cells, completely covered with aluminium foil, were kept under constant stirring for ca. 4 hours, time which ensures to reach the complete equilibration of the system. The dispersion was then filtered (always in the dark) through a 0.45 µm Millipore membrane and analyzed by HPLC.

3.5 Micellar ultrafiltration tests

10 mL of soil washing solutions obtained from clean soil, containing 20 mg L⁻¹ of each examined pollutant, were placed in centrifuge tubes equipped with YM 10 ultrafiltration membranes (Millipore) having a molecular weight cut-off of 10 kDa. After centrifugation at ca. 6000 rpm for 8 min the collected permeate was analyzed by HPLC.

3.6 Photocatalytic degradation tests

The experiments were carried out in Solarbox on 5 mL of soil washing wastes containing 20 mgL⁻¹ of each individual pollutant and 1000 mgL⁻¹ of added TiO₂. Blank runs were also performed in water for comparison purposes.

The primary degradation kinetics of each pollutant was followed by sampling and analyzing the dispersions after different irradiation times. An equal volume of methanol (5 mL) was added to the irradiated dispersions in order to dissolve the pollutant adsorbed on the catalyst particles, then the hydroorganic dispersions were stirred for 20 min and filtered before the HPLC analysis through a 0.45 µm Millex–LCR filters (Millipore).

4. RESULTS AND DISCUSSION

4.1 Soil washing experiments

The presence of micelles in the soil washing solutions is required to ensure the solubilization of hydrophobic pollutants, but it is known that the surfactant critical micellar concentration (CMC) increases in the presence of soil particles due to the surfactant adsorption (Zheng and Obbard 2002). In order to verify the presence of micellar aggregates after the equilibration of the washing solution with the soil, the effective CMC (CMC_{eff}) was determined by means of surface tension measurements.

As expected, the measured CMC_{eff} of the washing extracts (2.6×10^{-4} M) was above the CMC values reported for Brij 35 in pure water (9×10^{-5} M) (Borgerding and Hinze 1985). Taking into account the total surfactant concentration employed, the presence of micellar aggregates in the extracts was then confirmed.

Although the mean aggregation number of surfactants slightly changes in the presence of other solutes, a rough estimate of micelle concentration (assuming the aggregates as macromolecules) can be done for Brij 35 starting from its reported aggregation number in water (ca. 40 at room temperature (Phillies et al. 1995; Borbély 2000)). Then, the ratio (R) between the substrate and micelle concentrations can be calculated according to the following equation:

$$R = \frac{\frac{C_{sub}}{MW}}{(C_{tot} - CMC_{eff})} \cdot N_{AG} \quad \text{Eq. (1)}$$

Where C_{sub} is the substrate concentration (2×10^{-2} gL⁻¹), MW is the substrate molecular weight (gmol⁻¹), C_{tot} is the surfactant concentration in the washing solution and N_{AG} is the surfactant aggregation number. Values of $R \leq 1$ largely favour the substrates solubilization.

The molar concentrations of the examined compounds vary between ca. 1.1×10^{-4} M for CP and ca. 1.6×10^{-4} M for CIMP. Since the concentration of Brij 35 micelles in the starting washing

solutions is ca. 2.4×10^{-4} M, the corresponding R values were: 0.64 (CP), 0.58 (CMP), 0.53 (CDMP) and 0.44 (CIMP), respectively.

Under the reported working conditions the effective extraction of the examined chlorophenols from the spiked soil samples was obtained. Table 1 reports the percent recoveries and their standard deviations (from five replicated measurements) after the soil washing runs. The recoveries obtained with water and with Brij 35 washing solutions were calculated in respect to those obtained using the exhaustive MAE procedure with acetone/hexane. The higher recovery of the relatively hydrophilic CP reflects the lower adsorption of this compound on the soil in comparison with the more hydrophobic alkyl derivatives.

4.2 Photocatalytic runs

The fundamental aspects of the photocatalysis are well known (Ollis et al. 1989; Pichat et al. 1993; Bahnemann et al. 1994; Hoffmann et al. 1995; Alfano et al. 2000; Malato et al. 2002) and will be not remembered here. The influence of surfactants on these processes, largely due to their tendency to adsorb onto the semiconductor, has been recognized and must be carefully considered. In particular, detailed studies on surfactants adsorption onto hydrophilic solids (Koopal 2003) indicated that, within a homologous series of alkyloxyethylene surfactants having the same hydrophobic moiety, the extent of adsorption onto oxides significantly decreases with the increase of the hydrophilic head size. In these cases, the formation of admicellar structures onto the semiconductor particles becomes negligible. Brij 35 has been chosen in this light in order to reduce the competitive adsorption between surfactant and pollutant on the active semiconductor oxide, thus allowing a faster pollutant abatement.

Both the degradation of the chlorophenolic substrates (primary process) and the formation of the chloride ions generated during the mineralization process were followed as a function of the irradiation time. The TOC analysis during the waste treatment is precluded due to the simultaneous degradation of the surfactant.

Fig. 1 illustrates the degradation profiles of the investigated compounds. Linear plots up to ca. 75% of substrate degradation were obtained by fitting the degradation data with Eq. (2), confirming the typical pseudo-first order kinetics observed in most photocatalytic experiments.

$$-\ln\left(\frac{C}{C_0}\right) = -k_{\text{obs}} t \quad \text{Eq. (2)}$$

In Eq. (2) C_0 is the initial substrate concentration before to start the run and C is the substrate concentration measured after the irradiation time t . Table 2 summarizes the measured rate constants of the examined pollutants. Each reported k_{obs} value represents the mean of four repeated runs.

A general decrease of the degradation rate with the increasing hydrophobicity of the substrates is observed in the presence of Brij 35. A contribution to the degradation inhibition also arises from the presence of organic components of soil (Davezza et al. 2011) since it is known that also humic compounds undergo photocatalytic degradation, thus competing with the pollutants for the occupation of the semiconductor active sites (Minero et al. 1999; Al-Rasheed and Cardin 2003). Surprisingly, it can be observed that the degradation rate of CIMP is higher than that of CDMP and similar to that of CP.

Taking into account that the pH of the collected washing wastes lies in the range 6.6-6.9 and that the measured pH values of the corresponding TiO_2 dispersions after long term irradiation (5-6 h) were found in the range 6.4-6.7, the presence of ionic interactions between the pollutants and the semiconductor can be excluded. In fact, the isoelectric point of TiO_2 P-25 is around 6.5 (Lee et al. 2003), whereas the reported $\text{p}K_a$ of CP is 9.38 (Liang et al. 2007) and higher $\text{p}K_a$ values are expected for the alkylchlorophenols.

As previously reported in the literature, the negative influence of micellar solubilization on the solutes degradation rate can be related to the tendency of pollutants to bind to the host micellar aggregates, whereas the pollutants adsorption onto the semiconductor favours their degradation.

Then, the evaluation of substrates-micelle binding constants, K_B (not found in the literature) and the measurement of substrates adsorption on TiO_2 have been performed looking at the possible existing correlations between these data and the observed kinetic effects.

As far as the mineralization evolution is concerned, Fig. 2 shows a nearly stoichiometric formation of Cl^- in water after ca. 3 h for CP and CIMP, whereas the chloride ion release is slower and incomplete in the irradiated washing wastes for CMP and CDMP. Even after long term irradiation (5 h), the measured Cl^- concentration was found to be far from the expected stoichiometric value for CMP and CDMP (ca. 60% and ca. 30%, respectively).

4.3 Effect of substrate hydrophobicity on the primary process kinetics

The solute-micelle binding constant, K_B , was chosen as suitable parameter for the estimation of the substrates hydrophobicities. The correlations between this parameter and the equilibria regulating the solutes partitioning in the surfactant-containing semiconductor dispersions were investigated.

4.3.1 Measurement of solute-micelle binding constants using micellar HPLC

The retention of solutes in micellar HPLC (Armstrong and Nome 1981) depends on the surfactant concentration in the mobile phase and on the partition coefficients of the solutes between stationary, aqueous and micellar phase, according to the following equation:

$$\frac{V_s}{V_e - V_m} = \frac{1}{P_{MW}} + \frac{V \cdot (P_{MW} - 1)}{P_{SW}} \cdot C_M \quad \text{Eq. (3)}$$

where V_s is the stationary phase volume, V_e is the elution volume of the solute and V_m is the void volume of the column, V is the partial molar volume of the surfactant and C_M is the micellized surfactant concentration in the mobile phase ($C_M = C_{tot} - CMC$). P_{MW} is the solute partition coefficient solute between the micellar and aqueous phases and P_{SW} is the solute partition coefficient between the stationary and the aqueous phase. The solute-micelle binding constant, K_B , is in turn defined by the equation (Berezin et al. 1973):

$$K_B = V \cdot (P_{MW} - 1) \quad \text{Eq. (4)}$$

The K_B values can then be estimated from the slope/intercept ratio of the plots according to Eq. (3). The volume of the stationary phase in the column was calculated from the difference between the total column volume and the void volume, in turn determined from the retention time of injected NO_3^- , analyte which do not interact with the C_{18} stationary phase. All the measurements were performed at room temperature (25°C).

As reported in previous studies concerning Brij 35 (Borgerding et al 1988) the phase ratio remains constant over the surfactant concentration range examined in our experiments (0.06-0.09 M). It was also found that working with relatively low surfactant concentrations, as in our case, the uncertainties in the K_B determinations are lower (Kord 1991).

Fig. 3 shows the variation of the chromatographic parameter $V_s/(V_e-V_m)$ as a function of the micellized Brij 35 concentration in the mobile phase for CP and CMP. The binding constant of phenol (P) was also determined for comparison purposes and its value was found in good agreement with previously reported data (Marina et al. 1989). It can be seen that the linear behaviour predicted by Eq. (3) is obeyed.

Table 3 summarizes the data arising from the micellar HPLC measurements. The uncertainties of the measured K_B were in the range $\pm 5 - 10 \%$, as expected on the basis of previous results concerning solutes having similar K_B values (Khaledi et al. 1987). For highly hydrophobic solutes the large increase of the term P_{sw} and the corresponding decrease of the intercept of Eq. (3) lead to a noticeable uncertainty of the intercept determination, precluding the application of the micellar HPLC method (Borgerding et al. 1988). The K_B values of CDMP and CIMP were then estimated using an alternative approach.

4.3.2 Evaluation of K_B for CDMP and CIMP.

A correlation exists between the free energy of transfer of solutes from water to micelles and their corresponding binding constants (Bunton and Sepulveda 1979):

$$\Delta\mu_t^0 = \mu_{mic}^0 - \mu_w^0 = -RT \ln (55.5 K_B) \quad \text{Eq. (5)}$$

In homologous series the free energy of transfer of complex molecules can be related to the individual contributions of the various substituent groups to the starting moiety. In particular for the examined alkylchlorophenols the following equation holds:

$$\Delta\mu_{\text{t molecule}}^0 = \Delta\mu_{\text{t Clphenol}}^0 + n\Delta\mu_{\text{t C}}^0 \quad \text{Eq. (6)}$$

where $\Delta\mu_{\text{t C}}^0$ represents the contribution of each aliphatic carbon atom of the alkyl substituents to the free energy of transfer of the starting 4-chlorophenol molecule. The hydrophobic contribution of the chlorine atom to the free energy of transfer of 4-chlorophenol, $\Delta\mu_{\text{t Cl}}^0$, was found to be -0.7 kJ mol^{-1} , as expected from the measured $\Delta\mu_{\text{t}}^0$ of P and CP ($-23.0 \text{ kJ mol}^{-1}$ and $-23.7 \text{ kJ mol}^{-1}$, respectively).

The contribution of each aliphatic carbon group ($\Delta\mu_{\text{t C}}^0 = -1.2 \text{ kJ mol}^{-1}$) was in turn estimated from equation Eq. (6) starting from the $\Delta\mu_{\text{t}}^0$ values of CP and CMP ($-23.7 \text{ kJ mol}^{-1}$ and $-24.9 \text{ kJ mol}^{-1}$, respectively) calculated from the measured K_{B} using Eq. (5). On the other hand, from the calculated $\Delta\mu_{\text{t}}^0$ of CDMP and CIMP ($-26.1 \text{ kJ mol}^{-1}$ and $-29.7 \text{ kJ mol}^{-1}$, respectively), their corresponding K_{B} values (680 and $1,800 \text{ M}^{-1}$) were evaluated.

4.3.3 Determination of the percentage of pollutants bound to the micelles in the washing wastes

In order to evaluate the extent of pollutants binding to the Brij 35 micelles, some ultrafiltration experiments were performed on blank soil washing solutions obtained from clean soil samples. A fixed amount of each investigated chlorophenol (20 mg L^{-1}) was dissolved in these solutions, previously filtered through a 0.45 m filter, then the ultrafiltration runs were performed as previously described and the permeate was analyzed by HPLC. The percentage of rejection, defined by Eq. (7), was then calculated.

$$\%R = \left(\frac{C_{\text{p}}}{C_{\text{o}}} \right) \cdot 100 \quad \text{Eq. (7)}$$

In Eq. (7) C_{p} is the measured concentration of each pollutant in the permeate and C_{o} is the initial concentration before ultrafiltration. The obtained %R values were the following: 85.0 ± 3.4 (CP),

94.5±3.3 (CMP), 99.9±2.5 (CDMP) and 100.0±2.7 (CIMP). Each reported rejection value was the mean of five repeated runs. The obtained rejection data confirmed that, as previously reported (Pramauro et al. 1993), the complete binding of solutes to micelles occurs for K_B values in the range 800-1000 M^{-1} . Under these conditions the presence of free solute molecules in the aqueous bulk becomes negligible and it was recognized that, in these cases, the direct transfer of highly bound solutes from the host micelles to a solid/solution interphase becomes slower and difficult (Borgerding et al 1988). Then, it can be expected that the negative effect exerted by micelle–solute binding on degradation kinetics tends to level off for highly hydrophobic compounds.

4.3.4 Evaluation of substrates adsorption onto TiO_2

A significant adsorption of the examined chlorophenols onto the TiO_2 particles has been evidenced. The adsorption of the three less hydrophobic compounds was between 32.6% for CP and 39.6% for CDMP, whereas a neat increase was observed for CIMP (ca. 70%). As shown in Fig. 4 the substrates adsorption increases monotonically with increasing K_B . In the same figure the plot of %R vs. K_B (shown for comparison purposes) indicates that for higher K_B values the substrates can be considered completely bound to the aggregates.

The degradation rate of CIMP, higher than that of CDMP, can be justified on the basis of the dominant contribution of adsorption to the faster degradation of highly hydrophobic compounds, in agreement with previously reported data (Tada et al. 2002; Fabbri et al. 2006).

5. CONCLUSIONS

The non-ionic surfactant Brij 35 allows to obtain satisfactory recoveries of the investigated chlorophenols present in spiked soil samples, then it can be proposed as suitable solubilizing agent for the removal of these pollutants from contaminated soil. The further photocatalytic treatment of the washing wastes allows to degrade the extracted pollutants, being the kinetics of the process mainly dependent on the solute hydrophobicity.

For the less hydrophobic compounds (CP, CMP and CDMP) the decrease of the primary degradation rate with respect to the corresponding values in water can be directly related to the increase of the solute hydrophobicity, whereas a neat change of this tendency was observed for CIMP. The observed behaviour can be explained in terms of competition between micellar solubilization, proportional to K_B and limited by the complete binding of substrates to micellar aggregates, and substrates adsorption onto the semiconductor, growing monotonically with increasing K_B . The obtained results suggest that adsorption plays a dominant role for solutes having K_B values higher than a threshold limit of ca. 1000 M^{-1} , leading to a relative increase of their degradation rate.

The evolution of the mineralization process, markedly slower than the pollutants abatement, for CMP and CDMP, suggests that a longer treatment time of the corresponding wastes should be necessary in order to minimize the presence of residual chlorinated by-products.

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REFERENCES

Alfano OM, Bahneman D, Cassano AE, Dillert R, Goslich R (2000) Photocatalysis in water environments using artificial and solar light. *Catal Today* 58:199-230

Al-Rasheed R, Cardin DJ (2003) Photocatalytic degradation of humic acid in saline waters. Part 1. Artificial seawater: influence of TiO₂, temperature, pH, and air-flow. *Chemosphere* 51:925-933

Armstrong DW, Nome F (1981) Partitioning Behavior of Solutes Eluted with Micellar Mobile Phases in Liquid Chromatography. *Anal Chem* 53:1662-1666

Bahnemann D, Cunningham J, Fox MA, Pelizzetti E, Pichat P, Serpone N (1994) Photocatalytic treatment of waters. In Helz GR, Zepp RG, Crosby DG (eds) *Aquatic and Surface Photochemistry*. Lewis, Boca Raton (FL), pp 261-316

Berezin IV, Martinek K, Yatsimirskii AK (1973) Physicochemical foundations of micellar catalysis. *Russ Chem Rev* 42:787-802

Bianco Prevot A, Pramauro E, De la Guardia M (1999) Photocatalytic degradation of carbaryl in aqueous TiO₂ suspensions containing surfactants. *Chemosphere* 39:493-502

Borbély S (2000) Aggregate structure in aqueous solutions of Brij-35 nonionic surfactant studied by small-angle neutron scattering. *Langmuir* 16:5540-5545

Borgerding MF, Hinze WL (1985) Characterization and evaluation of the use of nonionic polyoxyethylene(23)dodecanol micellar mobile phases in reversed-phase high-performance liquid-chromatographyanal. Chem 57:2183-2190

Borgerding MF, Quina FK, Hinze WL, Bowermaster J, McNair HM (1988) Investigation of the retention mechanism in nonionic micellar liquid-chromatography using an alkylbenzene homologous series. Anal Chem 60:2520-2527

Bunton CA, Sepulveda L (1979) Hydrophobic and coulombic interactions in the micellar binding of phenols and phenoxide ions. J Phys Chem 83:680-683

Chu W, Chan KH (2003) The mechanism of the surfactant-aided soil washing system for hydrophobic and partial hydrophobic organics. Sci Total Environ 307:83-92

Chu W, So WS (2001) Modeling the two stages of surfactant-aided soil washing. Water Res 35:182-188

Davezza M, Fabbri D, Bianco Prevot A, Pramauro E (2011) Removal of alkylphenols from polluted sites using surfactant-assisted soil washing and photocatalysis. Environ Sci Pollut Res 18:783-789

Deshpande S, Shiau BJ, Wade D, Sabatini DA, Harwell JH (1999) Surfactant selection for enhancing ex situ soil washing. Water Res 33:351-360

Edwards DA, Luthy RG, Liu Z (1991) Solubilization of polycyclic aromatic-hydrocarbons in micellar nonionic surfactant solutions. Environ Sci Technol 25:127-133

Fabbri D, Bianco Prevot A, Pramauro E (2004) Kinetic effects of SDS on the photocatalytic degradation of 2,4,5-trichlorophenol. *Appl Catal B: Environ* 49:233-238

Fabbri D, Bianco Prevot A, Pramauro E (2006) Effect of surfactant microstructures on photocatalytic degradation of phenol and chlorophenols. *Appl Catalysis B: Environ* 62:21-27

Fabbri D., Bianco Prevot A., Zelano V., Ginepro M., Pramauro E. (2008) Removal and degradation of aromatic compounds from a highly polluted site by coupling soil washing with photocatalysis. *Chemosphere* 71:59–65.

Gotlieb I, Bozelli JW, Gotlieb E (1993) Soil and water decontamination by extraction with surfactants. *Sep Sci Technol* 28:793-804

Hidaka H, Yamada S, Suenaga S, Zhao J, Serpone N, Pelizzetti E (1990) Photodegradation of surfactants. 6. Complete photocatalytic degradation of anionic, cationic and nonionic surfactants in aqueous semiconductor dispersions. *Mol Catal* 59:279-290

Hoffmann MR, Martin ST, Choi W, Bahnemann DW (1995) Environmental applications of semiconductor photocatalysis. *Chem Rev* 95:69-96

Khaledi MG, Peuler E, Ngeh-Ngwainbi J (1987) Retention behavior of homologous series in reversed-phase liquid-chromatography using micellar, hydroorganic, and hybrid mobile phases. *Anal Chem* 59:2738-2747

Koopal LK (2003) Modelling association and adsorption of surfactants. In: Ezumi K, Ueno M (eds) Structure-performance relationships in surfactants. Surfactant Science Series. Marcel Dekker, New York 112(2):11–187

Kord AS, Strasters JK, Khaledi MG (1991) Comparative-study of the determination of solute micelle binding constants by micellar liquid-chromatography and micellar electrokinetic capillary chromatography. *Anal Chim Acta* 246:131-137

Lee HS, Hur T, Kim S, Kim JH, Lee HI (2003) Effects of pH and surface modification of TiO₂ with SiO_x on the photocatalytic degradation of a pyrimidine derivative. *Catal Today* 84:173–180

Liang J, Komarov S, Hayashi N, Kasai E (2007) Improvement in sonochemical degradation of 4-chlorophenol by combined use of Fenton-like reagents. *Ultrasonics Sonochemistry* 14:201-207

Malato S, Blanco J, Vidal A, Richter C (2002) Photocatalysis with solar energy at a pilot-plant scale: an overview. *Appl Catal B: Environ* 37:1-15

Marina ML, Vera S, Rodriguez AR (1989) Determination of the micelle-solute association constants of some benzene and naphthalene derivatives by micellar high-performance liquid-chromatography. *Chromatographia* 28:379-384

Minero C, Pelizzetti E, Sega M, Friberg SE, Sjoblom J (1999) The role of humic substances in the photocatalytic degradation of water contaminants. *J Dispersion Sci Technol* 20:643–661

Ollis DF, Pelizzetti E, Serpone N (1989) Heterogeneous photocatalysis in the environment: application to water purification. In: Serpone N, Pelizzetti E (Eds.) *Photocatalysis: Fundamentals and Applications*. Wiley, New York, USA, pp 603–637

Phillies GDF, Hunt RH, Strang K, Sushkin N (1995) Aggregation number acid hydrodynamic hydration levels of Brij-35 micelles from optical probe studies. *Langmuir* 11:3408-3416

Pichat P, Guillard C, Maillard C, Amalric L, D'Oliveira JC (1993) TiO₂ photocatalytic destruction of water aromatic pollutants: intermediates; properties-degradability correlation; effects of inorganic ions and TiO₂ surface area; comparisons with H₂O₂ processes. In Ollis DF, Al-Ekabi H (eds) *Photocatalytic purification and treatment of water and air*. Elsevier, Amsterdam, pp 207-223

Pramauro E, Bianco Prevot A, Savarino P, Viscardi G, De la Guardia M, Peris Cardells E (1993) Preconcentration of aniline derivatives from aqueous-solutions using micellar-enhanced ultrafiltration. *Analyst* 118:23-27

Pramauro E, Bianco Prevot A, Vincenti M, Gamberini R (1998) Photocatalytic degradation of naphthalene in aqueous TiO₂ dispersions: Effect of nonionic surfactants. *Chemosphere* 36:1523-1542

Tada H, Matsui H, Shiota F, Nomura M, Ito S, Yoshihara M, Esumi K (2002) Heterosupramolecular photocatalysis: oxidation of organic compounds in nanospaces between surfactant bilayers formed on TiO₂. *Chem Commun* 16:1678-1679

Zhang Y, Wu H, Zhang J, Wang H, Lu W (2012) Enhanced photodegradation of pentachlorophenol by single and mixed cationic and nonionic surfactants. *J Hazardous Materials* 221-222:92-99

Zheng Z, Obbard JP (2002) Evaluation of an elevated non-ionic surfactant critical micelle concentration in a soil/aqueous system. *Water Res* 36:2667-2672

CAPTIONS

Fig. 1 Primary process: ■ CP, ● CMP, ▼ CDMP and ★ CIMP in presence of Brij 35 1.0×10^{-2} M (soil washing extracts). Substrates concentration: 20 mgL^{-1} , TiO_2 : 1000 mgL^{-1} .

Fig. 2 Chloride evolution: □ CP, ○ CMP, ▽ CDMP and ☆ CIMP in presence of Brij 35 1.0×10^{-2} M (soil washing extracts). Substrates concentration: 20 mgL^{-1} , TiO_2 : 1000 mgL^{-1} .

Fig. 3 Variation of $V_s/(V_e - V_m)$ with the micellized concentration of Brij 35 (□ P, ○ CP, ◆ CMP).

Fig. 4 Percentage of adsorption and rejection vs K_B for the pollutants analyzed.

Fig. 1

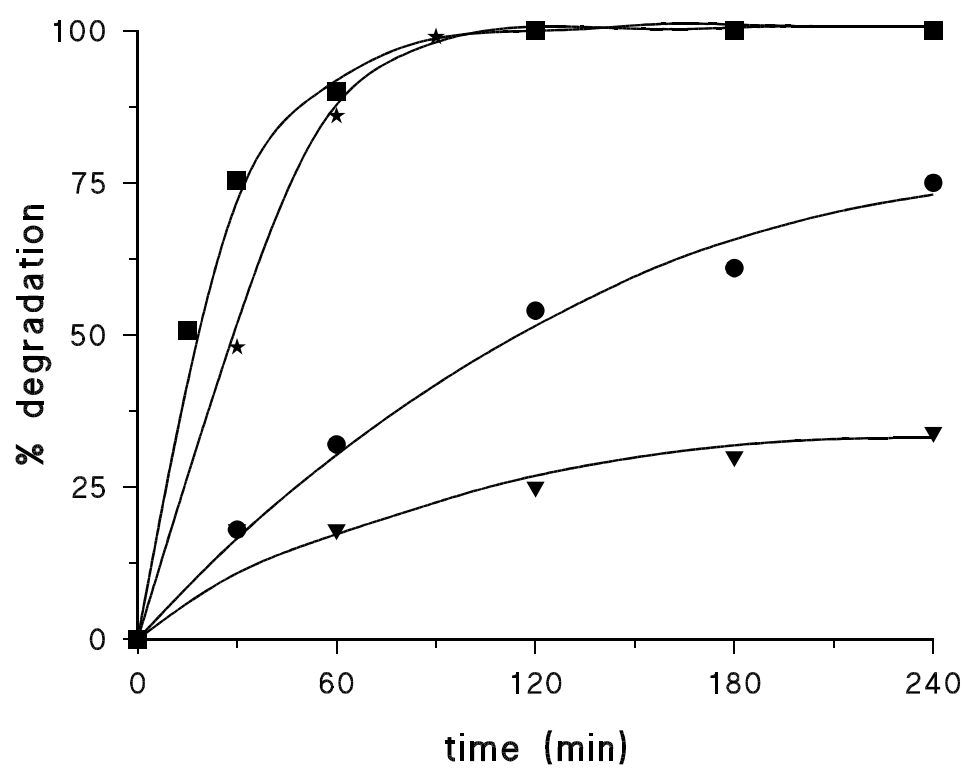


Fig. 2

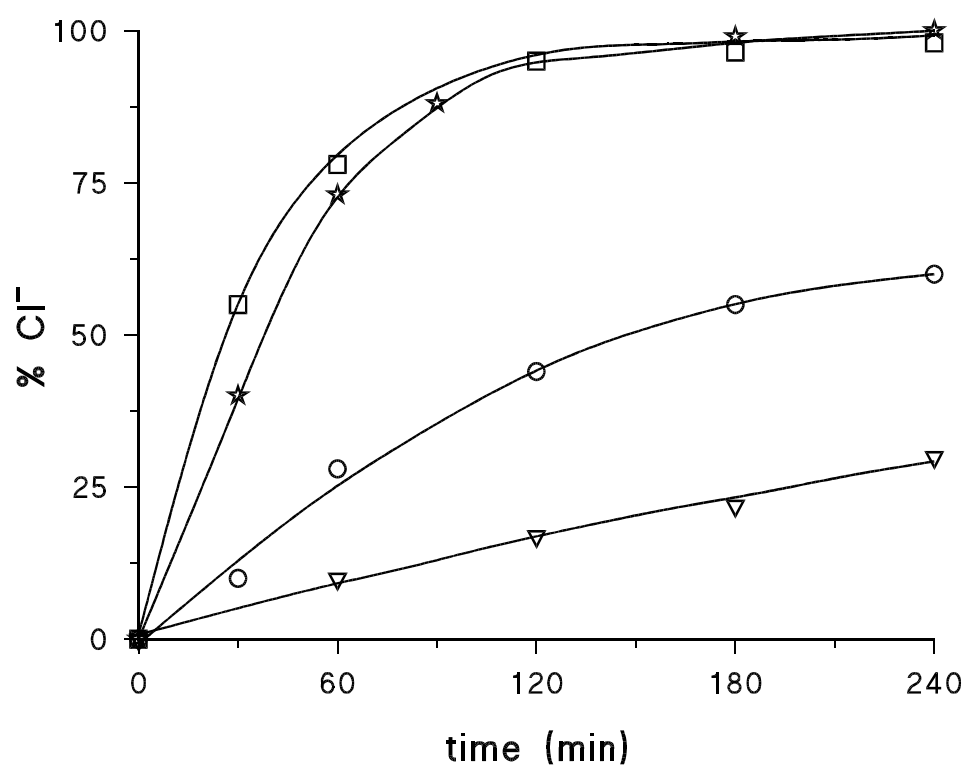


Fig. 3

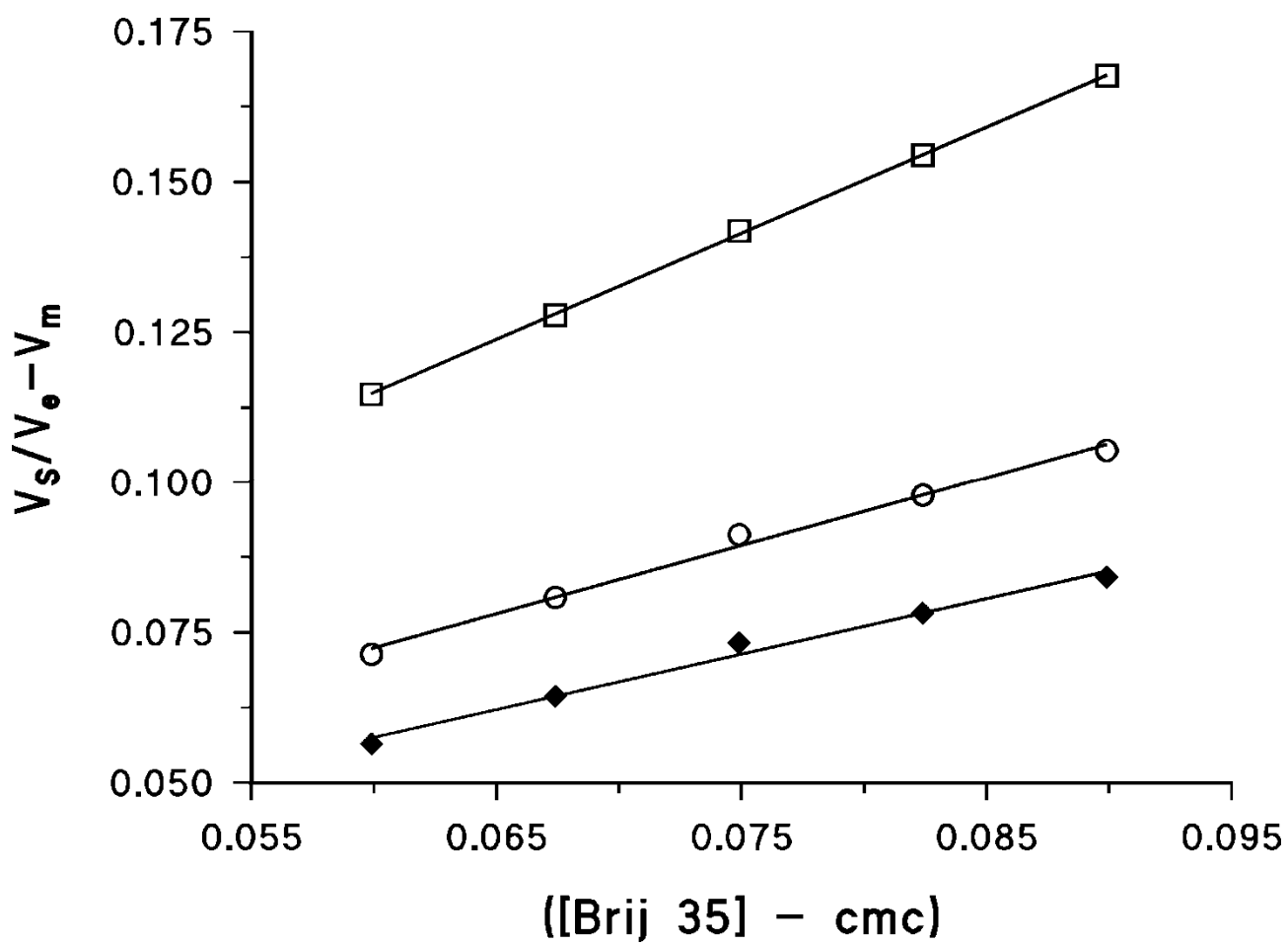


Fig. 4

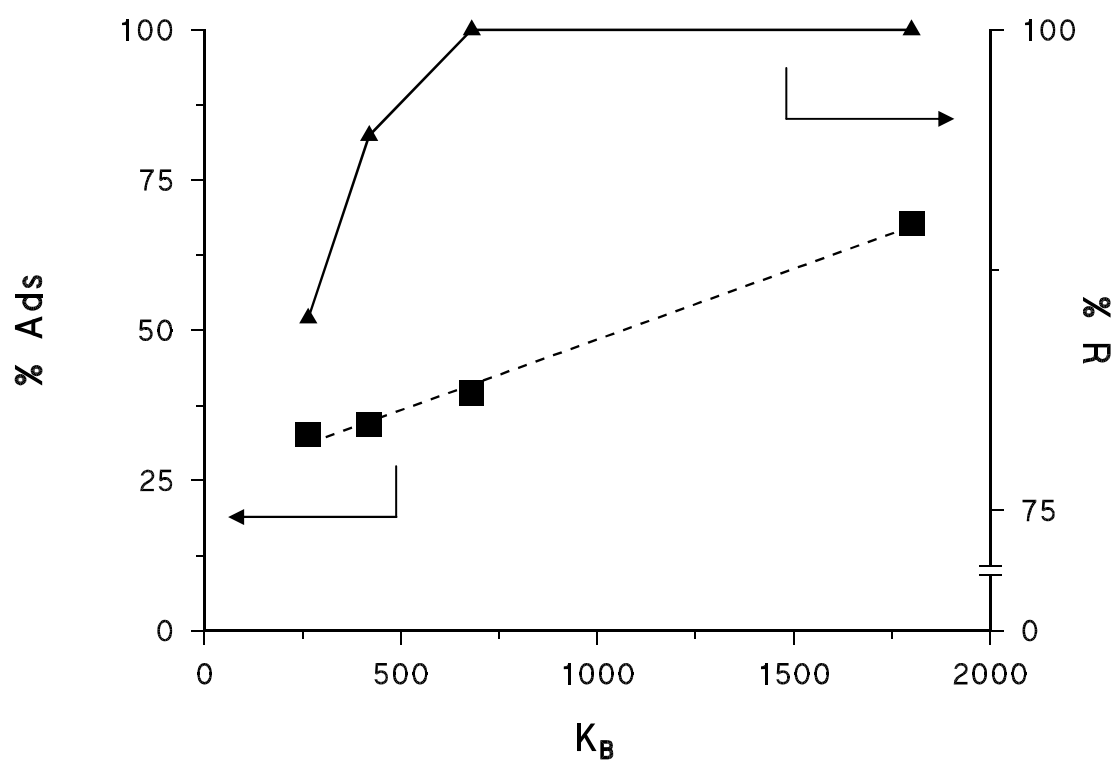


Table 1 Recoveries of the investigated chlorophenols after soil washing.

Soil washing solution	Acetone/n-hexane		Brij 35 1.0×10^{-2} M	
	% Recovery	Standard Deviation	% Recovery	Standard Deviation
CP	97.6	0.5	100	2.3
CMP	100	2.3	95.2	4.6
CDMP	100	3.9	91.4	1.7
CIMP	100	2.4	90.2	4.6

Table 2 Primary degradation rate constants of alkylchlorophenols.

Compounds	k_{obs}(min⁻¹)	
	H₂O	Brij 35 1.0x10⁻² M soil washing extracts
CP	2.1x10 ⁻¹	5.1x10 ⁻²
CMP	1.2x10 ⁻¹	5.4x10 ⁻³
CDMP	4.7x10 ⁻²	2.4x10 ⁻³
CIMP	7.0x10 ⁻²	3.2x10 ⁻²

Table 3 Association constants of P, CP and CMP to Brij 35 micelles

Solute	Intercept	Slope	r²	K_B (M⁻¹)	P_{SW}	P_{MW}^a
P	9.3x10 ⁻³	1.76	0.999	196	111	872
CP	4.3x10 ⁻³	1.13	0.990	264	233	1174
CMP	2.2x 10 ⁻³	0.92	0.985	419	454	1863
CDMP^b	-	-	-	680	-	-
CIMP^b	-	-	-	1,800	-	-

^a The Partial molar volume of Brij 35 is 0.225 L mol⁻¹ (Borgerding et al 1988).

^b **The determination of the value for these compounds is not possible via HPLC and the K_B was evaluated using the approach detailed in the section 4.3.2.**