Removal and degradation of aromatic compounds from a highly polluted site by coupling soil washing with photocatalysis

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REMOVAL AND DEGRADATION OF AROMATIC COMPOUNDS FROM A HIGHLY POLLUTED SITE BY COUPLING SOIL WASHING WITH PHOTOCATALYSIS.

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ABSTRACT

The possible application of two environmental remediation technologies – soil washing and photocatalysis – to remove and decompose various aromatic pollutants present in excavated soils of a contaminated industrial site has been investigated. Aqueous solutions containing the non ionic surfactant Brij 35 were used to extract the contaminants from the soil samples. The photocatalytic treatment of the obtained washing wastes, performed in the presence of TiO_2 suspensions irradiated with simulated sunlight, showed a slow abatement of the toxic compounds due to the relevant concentrations of organics in the waste. A neat improvement of the process performances, obtained by operating in the presence of added potassium peroxydisulfate, suggests a feasible treatment route.

KEYWORDS: soil-washing, surfactants, photocatalysis, aromatic pollutants

Introduction

Soil washing, a treatment technology used for removing contaminants from polluted soils, is largely based on the use of aqueous surfactant solutions and exploits both the solubilization capabilities of micelles and the lowering of the interface tension between the washing liquid and the soil particles, thus facilitating the solutes desorption and their exit from the soil pores (Edwards et al., 1991; Gotlieb et al., 1993; Chu and So, 2001; Chu and Chan, 2003). Surfactant-enhanced remediation (SER) has been, in particular, proposed as a suitable approach for removal of hydrophobic organic pollutants and the performances of different amphiphiles have been reported (Edwards et al., 1991; Desphande et al., 1999).

Among the proposed amphiphiles, nonionic surfactants have been often employed on the basis of their high solubilization capabilities and low critical micelle concentrations, CMC (that is the amphiphilic concentration at which the aggregation of monomer occurs, giving rise to the formation of micelles) (Zheng and Obbard, 2002), whereas anionic surfactants have been usually selected taking into account their lower adsorption on the soils. However, it is well known that ionic surfactants exhibit higher CMC values and this implies the presence of higher surfactant concentrations in the residual washing wastes. The use of mixtures of non-ionic and ionic surfactants has been also reported in the literature (Zhu and Feng, 2003; Yang et al. 2006), as well as the possible application of solvent/surfactant mixtures (Chu and Kwan, 2003).

However, further problems arise after the soil washing since the collected wastes must be adequately disposed or treated by applying suitable microbial or chemical degradation procedures. Heterogeneous photocatalysis, one of the more promising advanced oxidation processes developed in the past, has been proposed for the treatment of a wide variety of washing wastes. This process allows not only to perform the effective degradation of a great number of organic pollutants present at moderate concentration levels in aqueous wastes (Ollis et al., 1989; Pichat et al., 1993; Bahnemann et al., 1994; Hoffmann et al., 1995; Alfano et al., 2000; Malato et al., 2002), but in most cases leads to the complete mineralization of such compounds.

The possible applications of photocatalysis to treat complex aqueous wastes, including those containing surfactants, have been recently considered. In these cases it must be recalled that surfactants are themselves degraded (Hidaka et al., 1990) and that a competition between these molecules and the target pollutants for the active sites of the semiconductor usually occurs. In some previous investigations we have, in fact, found that the degradation of various aromatic pollutants is inhibited in the presence of surfactants (Pramauro et al., 1998; Bianco Prevot et al., 1999; Fabbri et al., 2004), but beneficial kinetic effects due to the accumulation of hydrophobic substrates in the adsorbed surfactant layers covering the TiO_2 particles have been also observed (Tada et al., 2002; Fabbri et al., 2006). It is, thus, essential to study in detail the evolution of the process in order to find the suitable experimental conditions under which the treatment could be effectively performed.

The aim of the present work was to investigate the possible application of photocatalysis to treat soil washing wastes arising from a vast contaminated site located in Cengio (Savona, Italy), where a former chemical plant was involved in the production of many chemicals for the synthesis of dyes. The nonionic aliphatic surfactant Brij 35 has been chosen to perform the soil washing step, whereas different experimental conditions have been examined in order to optimize and speed up the photocatalytic treatment of the surfactant-containing wastes.

EXPERIMENTAL SECTION

Materials and methods

Soil samples

The reported mean composition of the sampled soil (previously determined in different points of the site) was in the following range: sand: 50-55%; silt: 40-43%; clay: 4-5%, organic carbon: around 3%. Soil samples were sieved to < 2 mm to remove the bigger particles (in particular the rock pieces) and were mechanically homogenized. Various aromatic pollutants having different toxicities have been found in the contaminated soil samples.

Reagents

Polycrystalline TiO_2 Degussa P25 (composed of c.a. 80% anatase and 20% rutile) was employed in all the photodegradation experiments. In order to remove any organic impurity this oxide was washed with water and irradiated with simulated solar light for about 12 h. The washed semiconductor was then dried in the oven at 80 °C. The resulting powder was resuspended in water by sonication immediately before use.

Acetonitrile (Lichrosolv, Merck) and potassium acetate (99.5%, Carlo Erba) were used to prepare the eluents. Pure standards of the analytes (purchased from Aldrich, Merck, Carlo Erba) were used for calibration runs and for preliminary photocatalytic experiments. Brij 35 (Aldrich) was used for soil washing. Acetone (from Aldrich) and n-hexane (from Aldrich) were used for the exhaustive extraction of the soil samples. Pure water was produced using a Milli-QTM system (Millipore).

Instruments

The following instruments were used: HPLC Merck-Hitachi, equipped with L-6200 pumps and a UV-VIS L-4200 detector; GC-MS: Varian 3400 gas chromatograph interfaced to a Varian Saturn 4D ion trap detector equipped with a Supelco MDN-5S column (30 m, 0.25 mm i.d. with 0.25 μm film thickness); microwave digestion system MARSX from CEM Corporation. Surface tension measurements were performed with a digital-tensiometer (K10, Krüss).

Analytical procedures

Soil samples analysis

The soil samples have been analyzed according to the following procedure: ca. 3 g of soil were directly weighed in the teflon microwave vessel and 20 mL of solution acetone/hexane (50:50, v/v) was added. Then the sample was micro-waved at 110 °C and 689 kPa for 20 min. The liners were cooled to 25 °C, then the solution was filtered through 0.45 μm Millex –LCR filters (Millipore).

All the analytes were identified by means of GC-MS analysis and from the match of their HPLC retention properties and UV spectra with those of the corresponding authentic standards.

The GC temperature program conditions were: 60 °C isothermal for 1 min, ramped to 160 °C in 15 min and then isothermal for 8 min. The mass spectrometer was operated in EI-mode at electron energy of 70 eV. The ion source temperature was 200 °C.

The quantification of each compound has been performed by HPLC, according to two different elution procedures: i- For the analysis of 2-naphthol, 3,4-dichloroaniline and 2,4-dichloroaniline the employed eluent was: acetonitrile and an aqueous solution of potassium acetate 20 mM (45:55 v/v); a column 100 RP-C18 (Lichrospher, 4 mm i.d.×125 mm, 5 μm) was used, working in isocratic condition at a flow rate of 1 mL min^{-1}; the detector wavelength was 240 nm; ii- A mixture of acetonitrile and water (55:45 v/v) was employed as eluent for the analysis of all the remaining analytes. A column 100 RP-C18 (Lichrospher, 4 mm i.d. × 250 mm, 10 μm) was used. The detector wavelength was 200 nm.

Soil washing experiments.

Most extraction experiments were performed on 2 g of soil extracted with 25 mL of washing solution, placed in stopped tubes in a rotatory mixer (rotation speed: ca. 10 rpm). The standard contact time was 5 h.

The obtained soil dispersions were centrifuged at 5000 rpm for 10 min and aliquots of the surnatant clear solutions were sampled for the analysis and filtered through a 0.45 μm Millex LCR hydrophilic PTFE membranes (Millipore). The concentration of each analyte was successively determined on the filtered solution by HPLC, following the previously detailed procedures.

Preliminary degradation experiments.

A series of preliminary photocatalytic runs were performed in stirred cylindrical closed cells (40 mm i.d. x 25 mm high, made of Pyrex glass) on 5 mL of aqueous dispersions containing 6 mg L^{-1} of each individual pollutant and 500 mg L^{-1} of TiO_2. The concentration of Brij 35 was 2.5×10^{-2} M. Similar experiments were also performed on the washing extract diluted (1:2) with water to have the same surfactant concentration.

A 1500 W Xenon lamp source (Solarbox, CO. FO. MEGRA, Milan, Italy) equipped with a 340 nm cut-off filter was employed to furnish simulated solar irradiation. The temperature within the cells was ca. 55 °C. The dispersions were collected from the cells at the end of the programmed irradiation period, then were filtered before the analysis.

Degradation runs performed in laboratory photoreactor.

Another series of experiments were performed using an annular photoreactor (from Helios-Italquarz, Milan) equipped with a medium pressure mercury lamp (125 W). This light source better simulates the treatment conditions of real wastes in plants. The irradiated solutions were kept saturated with air during the treatment.

Degradations were performed on 500 mL of waste solutions containing 500 mg L^{-1} of TiO_2 (and eventually other additives). The temperature was kept at 25 °C. The starting pH of the irradiated suspensions was around 7.5. Samples (1-2 mL) of irradiated dispersion were taken from the reactor at different times; all the analytical determinations were performed after filtration.

RESULTS AND DISCUSSION

Analysis of the contaminated soil samples

The soil samples, analyzed following the procedures detailed in the previous section showed the presence of relevant amounts of aromatic compounds (ca. 3 g kg^{-1}). The concentrations of the identified main pollutants are given in Table 1. The standard deviations of the found values, estimated from five replicated measurements, were in the range 4-7%.

It has to be noted that anthraquinone and benzanthrone, which are well known dyestuff intermediates employed for the production of anthraquinonic dyes, are the more abundant components found in the contaminated soil. Traces of benzene have also been detected.

Soil washing performances

The surfactant Brij 35 –poly(oxyethylene)$_{23}$ dodecyl ether- was chosen on the basis of its high solubilization capability towards aromatic solutes and taking into account its low CMC (1.0×10^{-4} M, see inset in Fig. 1). Moreover, due to the non-aromatic nature of this surfactant, the interferences with the soil pollutants during the photocatalytic runs are expected to be less important. After the established contact period (5 h) all the soil extracts showed a yellowish colour.

The surface tension measurements performed on the filtered soil extract and on the solutions obtained after its dilutions clearly indicates (see Fig. 1) that, under the described working conditions, micellar aggregates are present in the washing solutions, even in the presence of surfactant adsorption on the soil. This condition is important since micellar solubilization plays a crucial role in the removal of adsorbed hydrophobic pollutants from soils (Liu et al., 1992).

Another set of surface tension measurements was performed in order to confirm the presence of micellar aggregates after the equilibration of the washing solutions with the proper amount of TiO_2. The surface tension of filtered washing solutions was measured after equilibration in the dark for 30 min. Also in this case the presence of surfactant aggregates was evident.

Due to the complexity of the solid matrix and to the abundance of organic pollutants (including those coming from alterations of the initially present compounds and/or from the organic soil fraction), the components listed in Table 1 were chosen as reference pollutants and their evolution was investigated. They have been divided into two distinct groups representing both highly hydrophobic and moderately hydrophobic contaminants present in the soil samples:

Group 1**:** moderately hydrophobic compounds. Measured retention times (min): 2-naphthol = 4.2; 3,4-dichloroaniline = 6.1; 2,4-dichloroaniline = 8.0. Group 2**:** more hydrophobic compounds. Retention times (min): chlorobenzene = 10.2; 9,10-anthraquinone = 11.4; 1,4-dichlorobenzene = 15.8; 7[H]-benz[de]-anthracen-7-one (benzanthrone) = 19.5; 1,2,4-trichlorobenzene = 25.8; 1,2,3,4-tetrachlorobenzene = 37.2; 1,2,4,5-tetrachlorobenzene = 43.6.

The recovery yields after 5 h extraction with Brij 35 0.05 M, calculated with respect to the corresponding recoveries obtained using the microwave-assisted extraction with organic solvents, are reported in Table 2.

The standard deviations of the found values, estimated from five replicated measurements, were in the range 4-8% for most pollutants. For chlorobenzene a higher uncertainty was found (ca. 15%).

Compounds of Group 1 are significantly extracted after 5 h, whereas for analytes pertaining to Group 2 the extraction yields are generally lower and largely vary depending on the solutes structures. It has to be underlined that the extraction of chlorobenzene was scarcely reproducible and that, due to its higher volatility, relevant amounts of this component were detected in the gas phase and lost during the soil washing runs. Also 9,10-anthraquinone exhibited modest recovery yields under the examined conditions.

Photocatalytic degradation experiments

The fundamentals of photocatalysis have been abundantly reported in the literature (Ollis et al., 1989; Pichat et al., 1993; Bahnemann et al., 1994; Hoffmann et al., 1995). Basically, the light-induced formation of electron-hole pairs leads to the formation of reactive species (in particular the oxidizing OH radicals) able to attack and degrade the organic pollutants. The contribution of reductive pathways involving the electrons present in the conduction band can be also present in some cases (Muneer and Bahnemann, 2002).

i) Degradation of individual pollutants in Solarbox: In order to examine and compare the pollutants evolution during the photocatalytic treatment, the primary degradation of each reference contaminant was investigated in the presence of Brij 35 0.025 M, corresponding to the surfactant concentration of soil washing extracts after dilution 1:2 with water. The obtained data fit well a pseudo-first order kinetic law, as typically found in most photocatalytic degradations of organics (see Fig. 2).

As for most similar experiments the formation of transient intermediate species, which in turn undergo degradation, has been observed. The transformation of the organic carbon of the investigated substrates to CO_2 cannot be followed under the described experimental conditions due to the presence of the large excess of added surfactant.

It can be seen that the degradation of polychlorobenzenes is much slower than that of the other aromatic substrates. Moreover, a noticeable induction period ranging from ca. 2 h for 1,4-dichlorobenzene up to ca. 4 h for tetrachlorobenzenes has been observed before the beginning of the effective degradation process. During this induction time a negligible degradation (less than ca. 5%) of the pollutants was observed, whereas after this period the substrate degradation becomes faster and follows the expected kinetic behaviour. The two tetrachlorobenzene isomers, which showed the same degradation rate, were reported together. For comparison purposes, the kinetic plots shown in Fig. 2 do not include the induction period.

In order to estimate the effective pollutants persistency during the treatment, their half-life times ($t_{1/2}$) have been measured. The obtained $t_{1/2}$ values (min) were: 9,10-anthraquinone: 8; 2-naphthol: 10; 2,4-dichloroaniline: 37; 3,4-dichloroaniline: 47; benzanthrone: 60; 1,4-dichlorobenzene: 120; 1,2,4-trichlorobenzene: 300; tetrachlorobenzenes: 620.

Although a detailed study of the factors which are at the basis of the observed slow steps in the degradation of polychlorobenzenes was out of the scope of this work, the scarce tendency of these pollutants to transfer from micelles to the surfactant coated TiO_2 particles (where the degradation reactions can initiate) could play a significant role. In fact, it is known from micellar chromatography experiments that the mass transfer of highly bound solutes from micelles to adsorbed surfactant layers covering solid surfaces is a very slow process which involves a peculiar direct transfer mechanism (Borgerding et al., 1988).

In order to verify the extent of micelle-solute binding, the binding constants (K_B) of the examined polychlorobenzenes to Brij 35 micelles have been estimated starting from available literature data for benzene and chlorobenzene (Marina et al., 1989), exploiting the well known existing correlation between the free energy of transfer of solutes from water to micelles and their corresponding binding constants (Bunton and Sepulveda, 1979):

$$\Delta\mu^\circ_t = \mu^\circ_{mic} - \mu^\circ_w = - RT \ln (55.5\ K_B) \qquad (1)$$

Since the free energy of transfer of polysubstituted molecules can be calculated from the individual contributions of the substituent groups, the following equation holds for polychlorobenzenes having n chlorine atoms:

$$\Delta\mu^{\circ}_{t\ \mathrm{molecule}} = \Delta\mu^{\circ}_{t\ \mathrm{benzene}} + n\ \Delta\mu^{\circ}_{t\ \mathrm{chlorine}} \qquad (2)$$

From K_B and $\Delta\mu°t$ values reported for benzene (K_B = 34 M^{-1}, $\Delta\mu°t$ = -18.71 kJ mol^{-1}) and chlorobenzene (K_B = 239 M^{-1}; $\Delta\mu°t$ = -23.53 kJ mol^{-1}), the contribution of each chlorine atom to the free energy of transfer of the chlorinated molecules was estimated to be -4.81 kJ mol^{-1}. The free energies of transfer of the investigated polychlorobenzenes were then calculated using Eq. 2 and the corresponding K_B values of polychlorobenzenes were obtained by applying Eq. 1. These values (1,670 M^{-1} and 11,640 M^{-1} for 1,4-dichlorobenzene and 1,2,4-trichlorobenzene, respectively) largely justify the assumption that the solutes are completely bound to the micelles and, thus, their slow release from the host aggregates is expected. The estimated K_B value for tetrachlorobenzenes is even much higher (around 80,000 M^{-1}).

ii) Degradation of soil-washing extracts in Solarbox: In order to examine the degradation kinetics of the pollutants mixture present in the real waste, some experiments were also performed on the soil washing extracts (diluted 1:2 with water) in the presence of 500 mg L^{-1} of TiO_2. From the examination of the HPLC profiles I and II (see Figs. 3a and 3b), corresponding to the initial composition and that obtained after 1 h irradiation, respectively, it can be seen that the pollutants abatement is negligible for compounds belonging to Group 1, whereas for those of Group 2 only the neat abatement of 9,10-anthraquinone is observed together with the formation of a transient intermediate peak (*), which successively disappears.

In order to increase the degradation rate, the amount of TiO_2 can be increased, but it is known that the maximum amount of added photocatalyst is limited by the scattering of impinging light in the dispersion. The introduction of suitable additives was thus considered as a possible way to improve the treatment performances.

Various additives capable to trap e^-_{CB}, delaying electron-hole recombination, and to favour the formation of active oxidizing radicals have been proposed. Among them, peroxydisulfates can offer relevant beneficial effects which can be explained taking into account both the electron scavenging action of $S_2O_8^=$ (Eqs. 3 and 4) and the possible participation of strong oxidizing sulfate radicals ($SO_4\bullet^-$) in oxidation reactions with organic substrates (Neta et al., 1977).

The following reactions give rise to the formation of radical active species:

$$S_2O_8^= + e^-_{CB} \rightarrow SO_4^= + \bullet SO_4^- \quad (3)$$

$$\bullet SO_4^- + H_2O \rightarrow SO_4^= + \bullet OH + H^+ \quad (4)$$

The sulfate radical anion can then attack organic compounds via: i) hydrogen atom abstraction from saturated carbon, ii) addition to unsaturated or aromatic carbon, iii) removal of electrons from some reactive groups, such as carboxylate anion. These peculiar properties suggest the addition of peroxydisulfate to enhance both the degradation rate and the mineralization extent in various photocatalytic processes. This approach has been successfully applied to increase the photocatalytic degradation/mineralization rates of different pollutants, such as organophosphorous compounds (Gratzel et al., 1990), dioxins, chlorophenols and atrazine (Pelizzetti et al. 1991), chlorinated hydrocarbons (Martin et al., 1995), anthraquinonic dyes (Bianco Prevot et al., 2001) and others.

On these basis we decided to perform photocatalytic experiments in the presence of $K_2S_2O_8$ (500 mg L^{-1}), added at the beginning of the runs. From the examination of profiles III in Figs. 3a and 3b, the beneficial effect due to the additive is evident.

iii) Treatment of the soil washing waste in the photoreactor: Table 3 reports the evolution of substrates degradation as a function of irradiation time (up to 6 h), in the presence of both TiO_2 and $K_2S_2O_8$ (500 mg L^{-1}). It can be seen that, under the examined conditions, the removal of Group 1 compounds (naphthol and chloroanilines) and of some components of Group 2 (anthraquinone, 1,4-dichlorobenzene and benzanthrone) is effective, whereas the much slower degradation of polychlorinated benzenes is evident. For these last mentioned compounds longer irradiation times become necessary in order to obtain their complete degradation.

CONCLUSIONS

Taking into account the complex composition of the examined wastes, their high content of aromatic pollutants, the contribution to the total organic matter arising from the organic soil fraction and the presence of relevant amounts of added surfactant (ca. 60 g L^{-1}), the reported results are promising since they support the feasibility of the photocatalytic procedure based on the use of TiO_2 dispersions under simulated solar light irradiation, even under these unfavourable starting conditions. The addition of $K_2S_2O_8$ to the wastes enhances remarkably the rate of degradation of the examined substrates.

The different reactivities exhibited by the investigated pollutants can be, at least in part, related to their tendency to partition between the surfactant micelles and the bulk aqueous phase before their transfer to the active sites of the irradiated semiconductor, although other factors such as the specific influence of substrate and surfactant structures and the nature and evolution of surfactant layers adsorbed onto the semiconductor surface, should be also considered and examined more deeply. Studies in these directions are actually in progress in our laboratory.

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REFERENCES

Alfano, O.M.; Bahneman, D., Cassano, A.E., Dillert, R., Goslich, R., 2000. Photocatalysis in water environments using artificial and solar light. Catal. Today 58, 199-230.

Bahnemann, D., Cunningham, J., Fox, M.A., Pelizzetti, E., Pichat, P., Serpone, N., 1994. Photocatalytic treatments of waters. In: Helz, G.R., Zepp, R.G., Crosby, D.G. (Eds.). Aquatic and Surface Photochemistry. Lewis, Boca Raton (FL), pp. 261-316.

Bianco Prevot, A., Pramauro, E., De la Guardia, M., 1999. Photocatalytic degradation of carbaryl in aqueous TiO_2 suspensions containing surfactants. Chemosphere 39, 493-502.

Bianco Prevot, A., Baiocchi, C., Brussino, M.C., Pramauro, E., Savarino, P., Augugliaro, V., Marcì, G., Palmisano, L., 2001. Photocatalytic degradation of Acid Blue 80 in aqueous solutions containing TiO_2 suspensions. Environ. Sci. Technol. 35, 971-976.

Borgerding, M.F, Quina, F.H, Hinze, W.L, Bowermaster, J, McNair, H.M, 1988. Investigation of the retention mechanism in nonionic micellar liquid chromatography using an alkylbenzene homologous series. Anal. Chem. 60, 2520-2527.

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

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

Chu, W., Chan, K.H., 2003. The mechanism of the surfactant-aided soil washing system for hydrophobic and partially hydrophobic organics. Sci. Total Environ. 307, 83-92.

Chu, W., Kwan, C.Y., 2003. Remediation of contaminated soil by a solvent/surfactant system, Chemosphere 53, 9-15.

Desphande, S., Shiau, B.J., Wade, D., Sabatini, D.A., Harwell, J.H., 1999. Surfactant selection for enhancing ex-situ soil washing. Water Res. 33, 351-360.

Edwards, D.A., Luthy, R.G., Liu, Z. B, 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. Catal. B-Environ. 62, 21-27.

Gotlieb, I., Bozelli, J.W., Gotlieb, E., 1993. Soil and water decontamination by extraction with surfactants. Separ. Sci. Technol. 28, 793-804.

Gratzel, C.K., Jirousek, M., Gratzel, M., 1990. Decomposition of organophosphorus compounds on photoactivated TiO_2 surfaces. J. Mol. Catal. 60, 375-387.

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. J. Mol. Catal. 59, 279-290.

Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W., 1995. Environmental application of semiconductor photocatalysis. Chem. Rev. 95, 69-96.

Liu, Z.B., Edwards, D.A., Luthy, R.G., 1992. Sorption of non-ionic surfactants onto soil. Water Res. 26, 1337-1345.

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, M.L., Vera, S., Rodriguez, A.R., 1989. Determination of the micelle-solute association constants of some benzene and naphthalene derivatives by micellar high performance liquid chromatograph. Chromatographia 28, 379-384.

Martin, S., Lee, A.T., Hoffmann, M.R., 1995. Chemical mechanism of inorganic oxidants in the TiO_2/UV process - increased rates of degradation of chlorinated hydrocarbons. Environ. Sci. Technol. 29, 2567-2573.

Muneer, M., Bahnemann, D., 2002. Semiconductor-mediated photocatalyzed degradation of two selected pesticide derivatives, terbacil and 2,4,5-tribromoimidazole, in aqueous suspension. Appl. Catal. B-Environ. 36, 95-111.

Neta, P., Madhavan, V., Zemel, H., Fessenden, R.W., 1977. Rate constants and mechanism of reaction of sulfate radical anion with aromatic compounds. J. Am. Chem. Soc. 99, 163-164.

Ollis, D.F., 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, pp. 603-637.

Pelizzetti, E., Carlin, V., Minero, C., Gratzel, M., 1991. Enhancement of the rate of photocatalytic degradation on TiO_2 of 2-Chlorophenol, 2,7-Dichlorodibenzodioxin and atrazine by inorganic oxidizing species. New. J. Chem. 15, 351-359.

Pichat, P., Guillard, C., Maillard, C., Amalric, L., D’Oliveira, J. C., 1993. TiO_2 photocatalytic destruction of water aromatic pollutants. Intermediates, properties-degradability correlation, effect of inorganic ions and TiO_2 surface area. In: Ollis, D. F., Al-Ekabi, H. (Eds.). Photocatalytic Purification and Treatment of Water and Air. Elsevier, Amstedam, pp. 207-223.

Pramauro, E., Bianco Prevot, A., Vincenti, M., Gamberini, R., 1998. Photocatalytic degradation of naphthalene in aqueous TiO_2 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 TiO_2. Chem. Commun. 16,1678-1679.

Yang, K., Zhu, L., Xing, B., 2006. Enhanced soil washing of phenanthrene by mixed solutions of TX100 and SDBS. Environ. Sci. Technol. 40, 4274-4280.

Zheng, Z.M., Obbard, J.P., 2002. Evaluation of an elevated non-ionic surfactant critical micelle concentration in a soil/aqueous system. Water Res. 36, 2667-2672.

Zhu, L.Z., Feng, S.L., 2003. Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed anionic-nonionic surfactants. Chemosphere 53, 459-467.

Captions

Figure 1 Surface tension versus dilution factor of Brij 35 in washing solution (○) and in washing solution after contact with TiO_2 in the dark (☆).

Figure 2 Linear plots of -ln A/A_o versus time of degradation, obtained for analytes of Group 1 (dashed lines) and Group 2 (continuous lines). (□ 2-naphtol; △ 3,4-dichloroaniline; ○ 2,4-dichloroaniline, ♦ 1,4-dichlorobenzene; ★ 1,2,4-trichlrobenzene; ● 1,2,3,4-tetrachlorobenzene; ■ 9,10-antraquinone, ▲ benzanthrone)

Figure 3 HPLC profiles of soil washing extract following the chromatographic conditions employed for Group 1 (a) and Group 2 (b). Profile I): sample diluted 1:2 with water; II) after 1 h of degradation in the presence of TiO_2 (500 mg L^{-1}); III) after 1 h of degradation in the presence of TiO_2 (500 mg L^{-1}) and $K_2S_2O_8$ (500 mg L^{-1}). Group 1: 1) 2-naphthol, 2) 3,4-dichloroaniline, 3) 2,4-dichloroaniline. Group 2: 4) chlorobenzene; 5) 9,10-anthraquinone, 6) 1,4-dichlorobenzene; 7) 7[H]-benz[de]-anthracen-7-one (benzanthrone), 8) 1,2,4-trichlorobenzene, 9) 1,2,3,4-tetrachlorobenzene, 10) 1,2,4,5-tetrachlorobenzene.

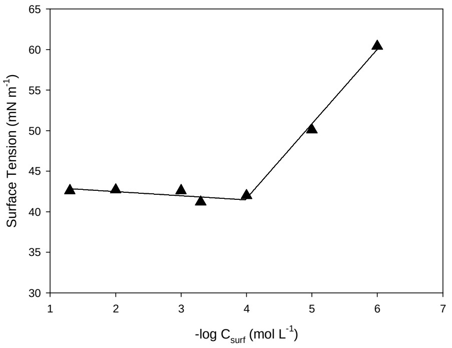

Figure 1

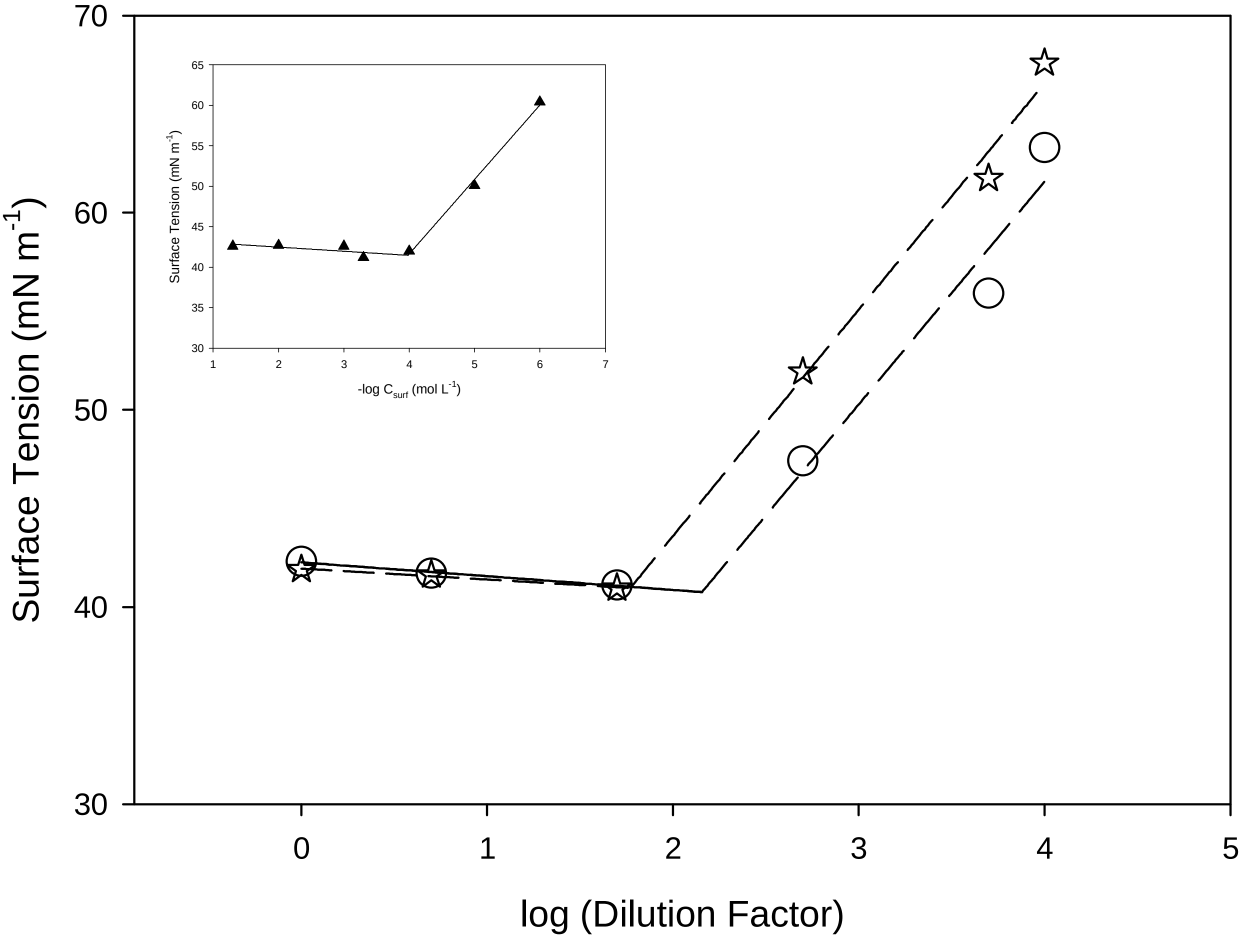
70
60
50
40
30
0
1
2
3
4
5
Surface Tension (mN m-1)
log (Dilution Factor)
65
60
55
50
45
40
35
30
1
2
3
4
5
6
7
Surface Tension (mN m-1)
-log Csurf (mol L-1)

Figure 2

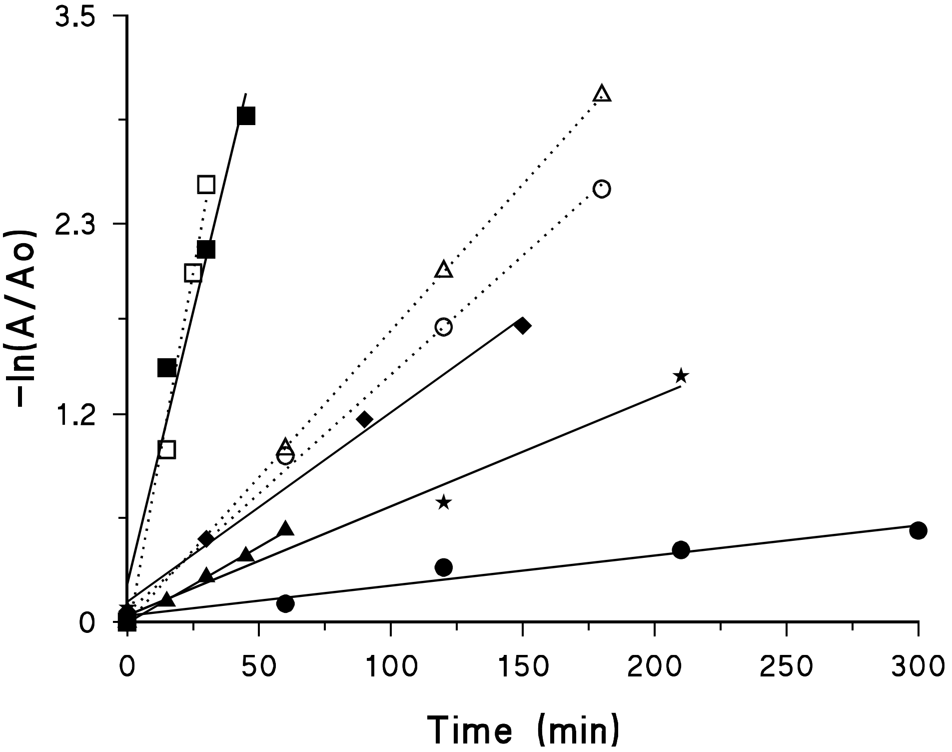

Figure 3

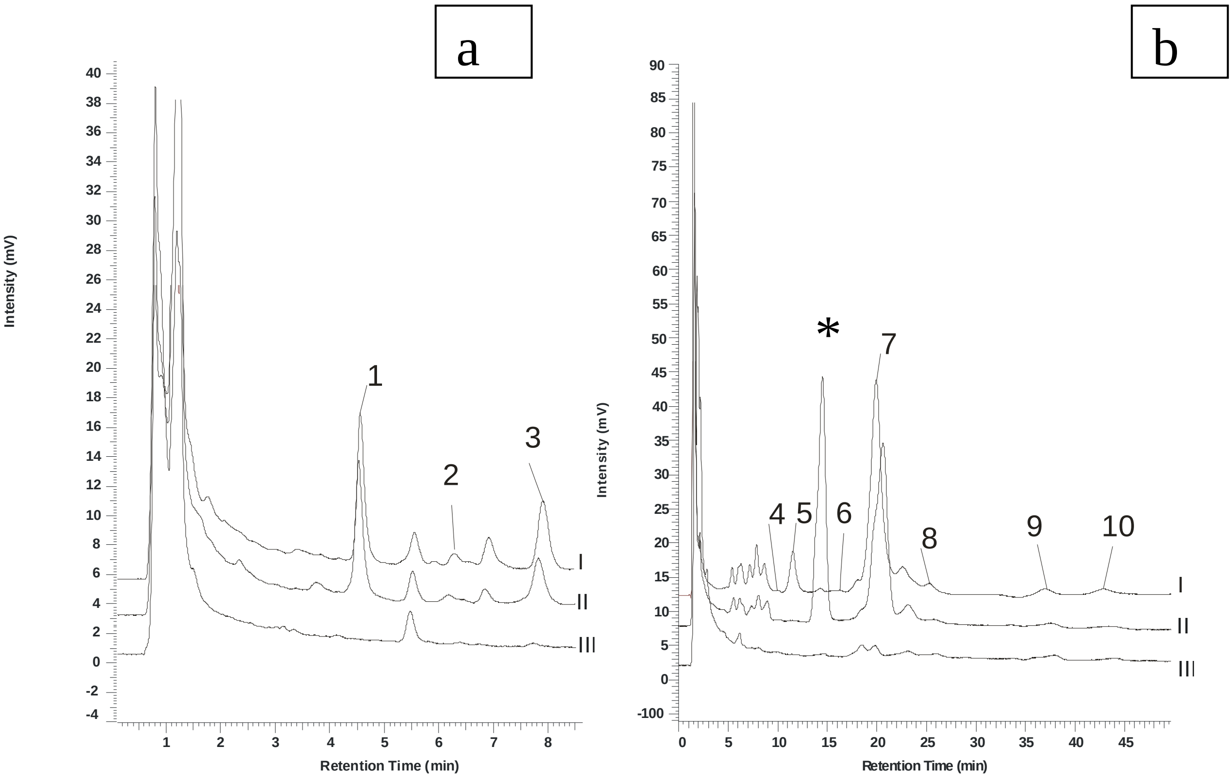
a
b
Intensity (mV)
Retention Time (min)
1
2
3
I
II
III
Intensity (mV)
Retention Time (min)
*
4
5
6
7
8
9
10
I
II
III

Table1: Aromatic pollutants found in the contaminated soil.

Pollutant	**Concentration in soil (mg kg^{-1})**
2-naphtol	66
2,4-dichloroaniline	126
3,4-dichloroaniline	30
Chlorobenzene	76
1,4-dichlorobenzene	114
1,2,4-dichlorobenzene	76
1,2,3,4-tetrachlorobenzene	79
1,2,4,5-tetrachlorobenzene	67
9,10-anthraquinone	670
Benzanthrone	1706
Benzene	traces

Table 2: Amount of pollutant recovered (mg kg^{-1}) after 5 h extraction with Brij35 0.05 M and recovery yields in respect to the exhaustive extraction.

Pollutant	**Amount recovered (mg kg^{-1})**	**% Recovery**
2-naphtol	39	59
2,4-dichloroaniline	87	69
3,4-dichloroaniline	13	43
Chlorobenzene	7	≈ 9
1,4-dichlorobenzene	29	25
1,2,4-dichlorobenzene	30	40
Tetra chlorobenzenes	72	49
9,10-anthraquinone	92	14
Benzanthrone	761	45

Table 3: Percent of pollutants removal as a function of the irradiation time. Photoreactor runs.

Pollutant	**Time (h)**		
Group 1	2	4	6
2-naphtol	98	100	100
2,4-dichloroaniline	99	100	100
3,4-dichloroaniline	87	93	95
Group 2			
1,4-dichlorobenzene	31	54	100
1,2,4-trichlorobenzene	28	40	50
Tetrachlorobenzenes	37	47	60
9,10-anthraquinone	100	100	100
Benzanthrone	91	93	94