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Photocatalytic degradation of bentazone in soil washing wastes containing alkylpolyoxyethylene surfactants

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ABSTRACT

Three alkylpolyoxyethylene surfactants bearing the same hydrophobic chain and a different number of oxyethylene groups were investigated as suitable candidates for the soil washing treatment of contaminated soil samples containing bentazone. Comparable good recoveries of the pesticide were obtained working with these surfactants. The photocatalytic treatment of the collected washing wastes, performed in the presence of suspended TiO_2 particles under irradiation with simulated sunlight, leads to the effective degradation of bentazone residues after a time depending on the nature and concentration of the chosen amphiphile. Brij 35 was found to be the best surfactant candidate, giving the faster abatement of the pesticide in the collected wastes. The overall treatment time depends on the bentazone mineralization kinetics, markedly slow in the presence of surfactants. Useful information about the photocatalytic degradation route was obtained from the HPLC–MS analysis of transient intermediates formed in water.

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1. Introduction

Contamination of soils due to the presence of pesticides is of great environmental concern since these generally toxic compounds can be adsorbed onto soil and the starting molecules and their degradation products can reach surface waters or percolate into ground waters. The remediation of pesticide-contaminated soils is thus necessary.

Among the proposed treatments, soil washing is an effective and diffuse remediation procedure (Castelo-Grande et al., 2010). It is largely based on the use of aqueous surfactant solutions and exploits both the solubilization capabilities of micelles towards the pollutants and the lowering of the interface tension between the washing solution and the soil phase (Gotlieb et al., 1993; Chu and Chan, 2003). The removal of a great variety of organic pollutants was reported using this approach (Desphande et al., 1999). Non-ionic surfactants are often the preferred candidates for soil washing due to their lower critical micellar concentration (CMC), which allows to reduce the amount of surfactant employed (Zheng and Obbard, 2002). Moreover, these amphiphiles exhibit lower interferences with ionic components present in soils, reducing the risks of surfactant precipitation.

An important problem arising from soil washing is that the washing wastes must be further disposed or treated before discharge or reuse. Heterogeneous photocatalysis can be proposed as suitable treatment since it allows the effective degradation of a wide variety of organic pollutants present in water and wastewater (Ollis et al., 1989; Bahnemann et al., 1994; Hoffmann et al., 1995; Fujishima et al., 2000; Malato et al., 2002).

The mechanism of photocatalysis was extensively investigated (Serpone and Pelizzetti, 1989; Ollis and Al-Ekabi, 1993; Hoffmann et al., 1995; Malato et al., 2002). It is essentially based on the generation of electron–hole pairs at the semiconductors surface upon irradiation of the photocatalyst with light having energy higher than its band gap. The generated holes can oxidize adsorbed water or hydroxide ions originating strong oxidizing agents, in particular $^{\cdot}OH$, which can attack the organic compounds leading to the formation of final non toxic or less toxic products. The complete mineralization of the starting molecules is in some cases obtained (Legrini et al., 1993). Reduction reactions involving conduction band electrons can also occur during the process (Muneer and Bahnemann, 2002).

When photocatalysis is applied to treat aqueous wastes, the presence of surfactants in such wastes leads in most cases to a significant inhibition of pollutants degradation (Bianco Prevot et al., 1999; Fabbri et al., 2004). This effect is not unexpected since the surfactant itself is degraded (Hidaka et al., 1990; Eng et al., 2010) and can compete with the substrate for the active sites of the semiconductor.

In the present work we investigated the treatment of soil samples containing bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide), a contact herbicide often used for selective control of broadleaf weeds and seeds in beans, corn, peanuts and especially in rice fields.

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Soil washing experiments were performed using nonionic surfactants pertaining to the same class but having a different hydrophobic/hydrophilic balance in order to investigate the effect of this parameter on the bentazone removal from the soil. The effect of amphiphiles structure on the photocatalytic treatment of the wastes was evaluated by following both the kinetics of the pesticide abatement and the formation and evolution of the degradation end products. In order to exclude the accumulation of harmful products during the treatment, the nature and persistence of transient intermediates arising from bentazone degradation were also investigated.

2. Materials and methods

2.1. Reagents

Polycrystalline TiO_2 P25 (from Degussa) was employed to perform all the photodegradation tests. In order to remove organic impurities the semiconductor was washed with water and irradiated in solarbox with simulated solar light for ca 12 h. The washed catalyst was then dried in the oven at 80 °C. The TiO_2 dispersions were sonicated in water immediately before use. Acetonitrile (Lichrosolv, Merck) was used as eluent.

Laboratory grade monodisperse poly(oxyethylene)$_5$dodecyl ether ($C_{12}E_5$) and poly(oxyethylene)$_8$dodecyl ether ($C_{12}E_8$) were obtained from Nikkol; poly(oxyethylene)$_{23}$dodecyl ether (Brij 35), purity >97%, was from Aldrich.

Acetone and n-hexane (from Aldrich) were used for the microwave-assisted exhaustive extraction of the soil samples. Pure water was produced using a Milli-Q system (Millipore). Bentazone (Pestanal, Sigma-Aldrich) was used throughout the work.

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; microwave digestion system MARSX (from CEM Corporation); double beam spectrophotometer CARY 100 SCAN (Varian); digital tensiometer (K10, from Krüss); HPLC–MS ThermoFinnigan Surveyor MSQ, equipped with a photodiode array detector, an electrospray ionization interface and a single quadrupole analyzer.

The irradiation experiments were carried out in Solarbox (CO.FO. MEGRA, Milan), where stirred cylindrical closed cells (40 mm id; 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 solarbox was ca 55 °C.

2.3. Experimental procedures

2.3.1. Preparation of the spiked soil samples

A clean soil (sandy clay loam) with an organic carbon content of ca 2.5% and a water content of ca 2.6% was used. Samples of the soil were dried at room temperature, grinded in a mortar and sieved to <2 mm to remove the bigger particles.

The soil was spiked according with the following procedure: 50 g of soil samples were treated with 50 mL of an acetone solution containing the proper amount of dissolved bentazone. The slurry was stirred for about 1 h and then allowed to stand at room temperature under hood with forced ventilation, for ca 24 h. During this step the spiked soil was homogenized several times in order to facilitate the complete evaporation of the organic solvent. The concentration of bentazone in soil samples was selected in order to have a final pesticide concentration of ca 40 mg L^{-1} in the washing wastes. All the homogenized (clean and spiked) soil samples were kept in refrigerator.

2.3.2. Microwave-assisted extraction of spiked soil samples

Exhaustive extraction runs with organic solvents were performed prior to the soil washing experiments for comparison purposes. The soil samples were treated following a standard EPA procedure (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 sample was then micro-waved at 110 °C and 689.4 kPa 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.

2.3.3. Soil washing runs

Aqueous washing solutions containing $C_{12}E_5$, $C_{12}E_8$ and Brij 35 were prepared. The surfactant concentrations were 5 and 10 mM. Soil washing experiments were typically performed on 2 g of spiked soil to which were added 12.5 mL of the investigated surfactant solutions, placed in stopped tubes in a rotatory mixer (rotation speed: ca 10 rpm, standard contact time: 5 h). The obtained soil dispersions were centrifuged at 5000 rpm for 10 min, then aliquots of the supernatant solutions were filtered through a 0.45 μm Millex-LCR hydrophilic PTFE membrane (Millipore). All the washing tests were performed on relatively fresh (1 wk) spiked soil samples. The effect of ageing was not investigated.

2.3.4. Bentazone determination

The bentazone determination was performed by HPLC on the filtered solutions, using a mobile phase composed of a mixture of acetonitrile/water 50:50 (v/v), to which 0.3 mL of phosphoric acid (85%) were added. In order to avoid bentazone losses due to the pesticide adsorption onto the semiconductor, an equal volume of acetonitrile was added to the aliquots of irradiated solutions sampled, then the mixtures were filtered through a 0.45 μm Anotop 25 Plus membrane (Whatman) and injected in the column.

A 100 RP-C18 column (Lichrospher, 4 mm id × 125 mm long, 5 μm particle size) was used. Isocratic elutions were performed at a flow rate of 1 mL min^{-1}. The detector wavelength was 225 nm.

2.3.5. Analysis of the ionic end products

The ionic end products were analyzed using suppressed IC, employing a Dionex DX instrument equipped with an ED 40 conductimeter detector (Dionex). Nitrate was determined using an AS9HC column (4 mm id × 200 mm long) from Dionex. Elution with a solution of K_2CO_3 12 mM and $NaHCO_3$ 5 mM (50:50 v/v) was performed with a flow rate of 1 mL min^{-1}. The determination of ammonium was performed using a CS12A column (4 mm id × 200 mm long), from Dionex. Methanesulphonic acid 25 mM was used as eluent at flow rate of 1 mL min^{-1}.

2.3.6. LC–MS analysis of transient organic intermediates formed in water

The MS operational parameters were: spray voltage 3 kV, temperature of the heated capillary 300 °C and cone voltage 90 kV. Mass spectra were collected in full scan negative mode in the range 50–900 *m/z*.

The chromatographic separations were conducted using a Lichrosphere 100 RP-18e (250 mm × 4 mm id particle size 10 μm). An aqueous solution of acetic acid 0.5% (v/v) and acetonitrile (50:50 v/v) was used as eluent under isocratic condition, at a flow rate of 0.5 mL min^{-1}.

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