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Sustainable decontamination of an actual site aged PCB polluted soil by a biosurfactant-based washing followed by a photocatalytic treatment

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A two phases processing consisting of a Soya lecithin (SL)-based soil washing process followed by the photocatalityc treatment of resulting effluents was developed and applied at the laboratory scale in the remediation of an actual-site soil historically contaminated by 0.65 g/kg of polychlorinated biphenyls (PCBs). Triton X-100 (TX) was employed in the same process as a control surfactant. SL and TX displayed a comparable ability to remove PCBs from the soil. However, SL solution displayed a lower ecotoxicity, a lower ability to mobilize soil constituents and a higher soil detoxification capacity with respect to the TX one. The photocatalytic treatment resulted in marked depletions (from 50 to 70%) of total organic carbon (TOC) and PCBs initially occurring in the SL and TX contaminated effluents. Higher PCB depletion and dechlorination yields along with lower increases of ecotoxicity were observed in SL-containing effluents with respect to the TX ones at the end of 15 days of treatment. The two phases process developed and tested for the first time in this study seems to have the required features to become a challenging procedure for sustainable remediation of PCB-contaminated soils.

1. Introduction

Polychlorinated biphenyls (PCBs) are toxic xenobiotics widely distributed in the environment, mainly in soils and sediments. PCBs occurring in soils can be partially biodegraded by aerobic consortia of PCB-cometabolizing and chlorobenzoic acid (CBA)-mineralizing bacteria. However, the bioremediation of aged PCB-contaminated soils is very often adversely affected by the low bioavailability of PCBs, which are hydrophobic and tend to adsorb strongly onto soil organic matter, thus becoming poorly available in the soil water phase, where the PCB- and CBA-degrading microorganisms are mainly located (Fava et al., 2003a). Poorly biotreatable aged contaminated soils might be remediated through a surfactant-aided ex-situ soil-washing treatment (Chu et al., 2003). Satisfactory decontamination yields have been obtained with this technique on a variety of hydrocarbons polluted soils, but the generally used synthetic chemical surfactants were found to persist and exert toxic effects both in the soil resulting from washing and in the resulting aqueous effluents (Berselli et al., 2004). This limitation of conventional soil washing procedure can be mitigated by replacing synthetic surfactants with biogenic

pollutant mobilizing agents able to provide marked pollutant mobilization activity along with complete biodegradability and none toxicity (Berselli et al., 2006). Some commercial phytogenic surfactants, like Soya Lecithin (SL), have been found to be very effective hydrophobic pollutants-mobilizing agents in the semisolid bioremediation of PCBs contaminated soils (Fava et al., 2001). Anyway, little is generally known about the efficiency of soil washing procedures in the clean-up of actual site contaminated soils, and in particular of those polluted with PCBs. Further, the conventional soil washing procedure is also inhered by generation of large volumes of contaminated aqueous streams, which are generally not easily detoxified through conventional or advanced biological treatments. These effluents might be decontaminated through photocatalytic treatments based on the use of dispersed or fixed-bed TiO_2 catalysts (Camera Roda et al., 2005).

2. Materials and methods

2.1 Soil characteristics and soil washing

The aged contaminated soil employed, supplied by Area SpA (Ravenna, Italy), was homogenised, air-dried, sieved through a 0.2 cm sieve and analysed for its contents of organic pollutants.

Soil washing experiments were performed as described by Berselli et al. (2004). 150.0 g of air-dried soil were suspended in 1.0 L of distilled water, or a water solution of SL or TX at 2.25 g/L, in identical 3L-baffled flasks placed on a rotary shaker (120 rpm; 20 ± 2 ºC) for 72 h. Each washing agent was tested in two parallel identical reactors. At the end of the washing operations, the reactors were removed from the shaker and their content was allowed to settle down for 3 h. Then, the soil and the water phases were separated. Soil phases were air-dried for 2 days and then subjected to accelerated solvent extraction (ASE) followed by GC analysis of the resulting organic extract, and ecotoxicity analysis with the *Lepidium sativum* test organism. The water phases were subjected to batch solvent extraction, TOC and ecotoxicity analysis with *Vibrio fisheri* organism.

2.2 Photocatalytic treatment

TiO_2 powder was added to the effluents (0.5 g/L) in a 1L hermetically closed reservoir equipped with a magnetic stirring device. Then, the TiO_2 slurries were sent to the annular photocatalytic reactor. The light source was a linear fluorescent lamp (UVA in the 330-400 nm wavelength interval). The reactor (0.2 L) worked under batch mode conditions at 20 ± 2 ºC. TiO_2 slurry was continuously circulated through the reactor by means of a membrane pump. 50 mL samples were withdrawn from the medium mixing tank at the beginning and after 1, 7, 12, 15 days of photocatalytic treatment. 10 mL of each sample were subjected to batch solvent extractions to recover organic pollutants and the extracts were analyzed by GC-ECD. Polar (chloro)aromatic compounds were batch extracted from 10 mL of collected samples by diethyl-ether. The remaining water phase was centrifuged at 5,000 rpm for 10 min and the supernatant obtained was subjected to TOC and chloride ions analysis. The ecotoxicity of aqueous phase resulting after 15 days of

photocatalytic treatment was performed by applying the *Vibrio fischeri* test on 10 mL of sample.

2.3 Pollutant extraction and other procedures

PCBs and related compounds of the soil were extracted from the original soil samples resulting from washing through an ASE system operating at 140 atm and 100 ºC with a mixture of hexane-acetone (1:1). PCBs and related pollutants occurring in the washing effluents and in the aqueous phases subjected to photocatalytic treatment were recovered through two successive batch extractions with a mixture hexane-acetone according to Fava and Di Gioia (2001). The qualitative and quantitative analysis of PCBs occurring in the organic extracts obtained were performed through a gas chromatograph equipped with a capillary column (30m x 0.25mm) and an electron capture detector (ECD). Qualitative analysis of PCBs was performed by comparing the retention time (relative to Octafluoronaphtalene added as an hexane solution) of each of the GC peaks obtained with those of pure congeners and PCBs of standard Aroclor 1242 and Aroclor1260 (2003b). The TOC of the washing solution, as well as of the soil washing effluents before, during and at the end of the photocatalytic treatment, was determined by using a Shimadzu TOC-500 analyser as reported by Camera Roda et al. (2005). The ecotoxicity of the original soil and of the soil samples resulting from the washing experiment was measured by using the *Lepidium sativum* root and shoot elongation inhibition test as reported by Fava and Bertin (1999). Ecotoxicity of the solutions applied in the washing operations and that of effluents obtained before and after their photocatalytic treatment was determined as reported by Bolelli et al. (2006) employing the *Vibio fisheri* organism and the procedure recommended by the European standard EN ISO 11348.

3. Results

3.1 Soil decontamination through washing

The air-dried soil employed was found to contain about 650 mg per kg of dried soil of total PCBs ascribed to Aroclor 1242 and Aroclor 1260.

An extensive removal of PCBs was achieved through the washing operations. The two surfactants mediated a comparable overall PCB removal yields (~60%) which were not significantly influenced by the chlorination degree and pattern of eluted molecules (Table I).

		Average PCBs removal percentages in the soil after washing with	
	Initial concentration (mg/kg dry soil)	**SL**	**TX-100**
Overall PCBs concentration	640.11 ± 0.21	257.90 ± 4.68	242.15 ± 3.07
Average PCBs removal %		59.71 ± 2.03	62.17 ± 1.48

Table I. Initial PCBs concentration and average removal % after washing in the presence of SL and TX (± standard deviation).

Washing operations resulted in small changes of TOC of the washing solutions applied; TX mobilized larger extents of soil constituents than SL did (Table II).

Agent	Washing solutions TOC (mg/L)	Effluents TOC (mg/L)	TOC changes %
SL	1177.0 ± 1.7	1026.1 ± 18.1	-14.7
TX-100	1711.0 ± 78.5	1857.0 ± 53.0	+7.8

Table II. TOC of SL- and TX-amended washing solutions before and after their use in the washing operations (± standard deviation).

A remarkable depletion of original soil ecotoxicity was obtained with washing operations, in particular when SL was employed. However, the soil detoxification observed in the SL-washed soil was higher than that obtained with the TX-amended washing solution. The ecotoxicity of TX washing solution increased markedly with the washing operation (data not shown).

3.2 Photocatalytic treatment of the soil washing effluents

Comparable concentrations and composition of PCBs were observed in the two washing effluents sent to photocatalytic treatment. Marked depletions of such PCBs were generally observed at the end of effluent irradiation. Significantly higher PCB removal yields were observed in SL amended effluents with respect to the TX ones (76% vs 58%) (Table III).

	SL		TX	
	Initial concentration (mg/L)	**Removal %**	**Initial concentration (mg/L)**	**Removal %**
Initial concentration (mg/L) and average pollutants removal %	52.65	76.38	56.50	58.69

Table III. PCBs initially detected in the SL or TX effluents (average concentration ± standard deviation) and their average removal % attained at the end of photocatalytic treatment.

TOC was removed more extensively and rapidly in the SL amended effluents than in the TX ones. In particular, in the SL effluents, TOC decreased faster than total PCBs concentration during the first 7 days of irradiation, while the degradation rate of pollutants was higher than that of TOC during the remaining 8 days of treatment. In the TX effluents, instead, the degradation rate of PCBs and that TOC were comparable (Figure 1).

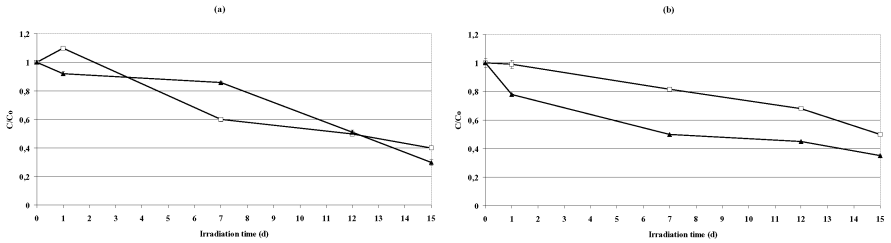

Figure 1. Fate of overall PCBs (▲) and TOC (□) in SL affluents (a) and in the TX ones (b) throughout the photocatalytic treatment as a functionof irradiation time. [C=concentration (mg/L) of total PCB ot TOC at each time, C_0 =initial concentration (mg/L) of total PCB or TOC].

A marked release of chlorine ions was observed in SL and TX effluents throughout the 15 days of treatment (Figure 2). However only about 50% of organic chlorine holds by depleted PCBs was detected as chloride ions in both types of effluents at the end of the treatment.
The photocatalytic treatment also resulted in marked increases of effluents ecotoxicity, in particular in the case of the TX amended ones (data not shown).

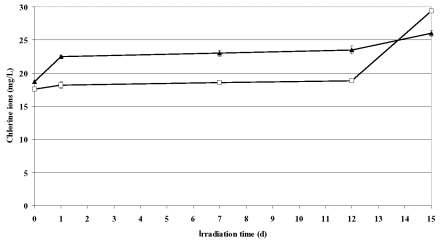

Figure 2. Change in chlorine concentration (mg/L) in the SL (▲) and TX (□) effluents throughout the whole photocatalytic treatment (error bars represent standard deviation).

4. Conclusion

In the present study, a two-phases process consisting of a biogenic surfactant assisted soil washing procedure followed by a TiO_2-photocatalytic treatment of resulting streams was developed.
SL based washing procedure provided very promising results. Indeed, SL was found to be an effective PCB mobilizing agent, by mediating, comparably to TX, the removal of about 60% of total PCBs originally occourring in the soil (Table I). Further, SL mobilized lower amounts of soil organic constituents with respect to TX (Table II) by also mediating, with respect to TX, a higher depletion of the soil initial ecotoxicity. These findings indicate that SL is a very promising soil washing

assisting agent as it as not costly biogenic agent capable of combining high and selective PCBs mobilizing activity with high biocompatibility and soil detoxification potential.

The photocatalytic treatment of effluents generally resulted in an extensive degradation of soil eluted PCBs (76% and 58% in SL and TX effluents respectively). However, PCBs disappeared through different rates and extents in the SL and TX effluents, and it suggests that surfactants affected the production of free radicals in the reactor (Table III).

The depletion of TOC was generally lower and slower than that of total PCBs (Figure 1). This finding along with the evidence that only 50% of organic chlorine was detected in the effluents at the end of the treatment (Figure 2) suggest that remarkable amounts of chlorinated intermediates of PCBs accumulated in the reactor troughout the treatment. However, none known intermediates were detected (trough CG and HPLC procedures) in the effluents.

In conclusion, the two phases process developed in this study seems to have all featurs required for being an effective new treatment for the clean-up of actual site PCBs-contaminated soils.

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