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Microbial Degradation and Chemical Oxidation of Sandy Sediment Contaminated with Polychlorinated Biphenyl

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ABSTRACT

This paper reports the results of various biodegradation experiments on polychlorinated biphenyl (PCB)-contaminated sandy sediment employing a mixed culture of acclimatized bacteria. Following the optimization of different variables, the elimination rate achieved of Aroclor 1242 in slurry phase reactors was 61% after 4 months of treatment. The presence of biphenyl as a cosubstrate was the most important factor affecting PCB biodegradation. The biodegradation occurred as a first-order process, and proved most effective with respect to dichlorinated (100% removal), followed by trichlorinated (92%) and tetrachlorinated biphenyls (24%). The results of the treatment of polychlorinated biphenyl (PCB) contaminated sandy sediment with the Fenton advanced oxidation process (AOP) confirm that the oxidation process occurs on the PCBs adsorbed to particles, producing 98% elimination of the original PCB structure after 72 h. The degree of elimination was found to be dependent on the level of congener chlorination, and the process follows pseudo first-order kinetics. In addition, the Fenton chemical oxidation process may be complemented by subsequent aerobic biologic degradation which, after 15 days, produces 70% mineralization of the products generated during the chemical oxidation process.

Key words: biodegradation; advanced oxidation process; integrated chemical biological treatment; sandy sediment remediation; kinetics

INTRODUCTION

AWARENESS OF THE TOXICITY OF PCB has led to increased research into the development of PCB waste treatment technology. Although incineration is currently the most frequently used method of dealing with waste containing a high concentration of PCB, waste products containing a large proportion of inert material such as soils and sediments require other alternatives (Watts *et al.*, 1993).

One of the options for this type of waste is aerobic biologic treatment, made attractive by its low cost and operative simplicity. Although considerable efforts have been made (Abramowicz, 1990), the mechanisms involved in the biodegradation of PCBs sorbed on particles are not yet fully established. This is due to the difficulty in correlating the results of the different researchers in the field, and to the fact that most work has been carried out in the aqueous phase. One objective of this research

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has been to study the aerobic biodegradation of PCB adsorbed to sand particles by employing a mixed culture of acclimatized bacteria. Three alternatives to enhance the process have been tested: addition of organic supplements (cometabolism); biostimulation, and bioaugmentation; and the addition of a nonionic surfactant.

Another innovative approach to the treatment of PCB-contaminated sediments may be the application of a strong oxidizing agent such as Fenton's reagent. The Fenton-oxidation process consists of a catalytic breakdown of hydrogen peroxide to produce hydroxyl radicals. These generate nonspecific oxidations, and react with the organic compounds, RH, at a bimolecular rate constant in the order of 10^7 to 10^{10} L/mol · s, producing organic radicals as transitory intermediates, which are subsequently oxidized by electron transfer chain reactions (Tyre *et al.*, 1991).

This chemical oxidation process has been used for 70 years to treat refractory organic compounds. Research has concentrated, however, on the aqueous phase, with Watts *et al.* (1990) being the first to use the Fenton oxidation process for the elimination of organic compounds (pentachlorophenol) in soils. The work done by Sato *et al.* (1993) is probably the only study that used PCB-contaminated sand. A point of interest is whether the hydroxyl radicals are able to react with the adsorbed contaminants or, on the contrary, whether they react with the dissolved fraction. The hydrophobic organic contaminants tend to be associated with the solid phase, while radical hydroxyls are generated in aqueous solution and react immediately, and this may hinder the oxidation of adsorbed contaminants. To assess further the potential of this technology and clarify reaction mechanisms, more research work is required.

METHODS

PCB-contaminated sandy sediment

The solid matrix contaminated by PCB employed in the experiments was sandy quartz (X-Ray Diffraction, Phillips PW 1830) from the Guadalete river (South-West of the Iberian Peninsula) containing very low levels of organic material (<0.05% weight). Sand was selected because the surface soils—the region most affected by an accidental spill—is often predominantly made up of sand (Ravikumar and Gurol, 1994). Furthermore, due its low natural organic composition, this sand was expected to have low interaction with PCB and thus result in better interpretation of the experimental data. Using Aroclor 1242 (Supelco, Bellefonte, PA), and following the method described by Barriault and Sylvestre (1993), the sediment was contaminated to a concentration of 100 mg/kg (dry weight).

Acclimatized PCR degrading culture

The mixed culture of PCB degrading bacteria was acquired from New York State Center for Hazardous Wastes Management (Buffalo, NY). The mixed culture of micro-organisms was isolated by biphenyl enrichment from PCB contaminated sediment. To isolate the mixed culture, 5 g of sediment and 0.1 g of biphenyl were placed in 100 mL of a phosphate-buffered mineral nutrient solution (Furakawa, 1982).

This culture consisted mainly of Gram-negative strains exhibiting Type II organism PCB biodegradation patterns. Type II organisms are *Pseudomonas* that biodegrade similar congener profiles to the *Pseudomonas* strain LB400 (U. Gosh, 1996, personal communication). The mixed culture was grown on biphenyl, aqueous PCB solutions, and a phosphate-buffered mineral nutrient solution (Furakawa, 1982).

Generation of aqueous PCB solution (glass bead generator columns)

To obtain aqueous solutions of PCB, needed for the inoculation reactor feed and for biodegradation experiments in an aqueous medium, bidistilled water was passed through a column (Pyrex®, ϕ = 2.5 cm, L = 20 cm) filled with glass beads (ϕ = 0.15–0.212 mm, G 9018, Supelco) impregnated with Aroclor 1242 at a rate of 0.035 mL/cm^2/min (Gosh *et al.*, 1998). The composite sample from the column effluent contained a greater quantity of di- (21%) and trichloro biphenyls (44%) than Aroclor 1242 (14% DiCBs; 34% TriCBs), and a minor quantity of the higher chlorinated congeners (23% TetraCBs; 8% PentaCBs) than Aroclor 1242 (34% TetraCBs; 15% PentaCBs). The altered distribution of PCB homolog in solution is expected owing to the differences in aqueous solubilities. The average overall concentration of PCB in the composite sample was 261 μg/L.

Aerobic PCB biodegradation studies

Before performing biodegradation experiments on sediments, the effectiveness of the inoculum was tested in the aqueous phase. Batch testing was conducted in 125 mL amber-colored glass bottles with Teflon® septums. The aqueous PCB solution (100 mL) used for this experiment was obtained from the glass bead generator column and the aqueous concentration was approximately 71 μg/L for the sum of eight congeners. The medium contained the phosphate-buffered mineral nutrient solution (Furakawa, 1982) and biphenyl was supplied at an initial concentration of 100 mg/L as a cosubstrate directly to the sample bottles. The acclimatized mixed culture was supplied at approximately 2×10^5 active cells/mL. Oxygen was supplied by starting

the experiment with a 20% (v/v) oxygen headspace in each bottle. After setup, the sample bottles were placed on an orbital shaker (Heidolph, Unimax 2010; Heidolph Instruments, Cinnaminson, NJ) rotated at 200 rpm in the upright position at room temperature (25 ± 2°C).

After confirming aerobic biodegradation of soluble phase PCB, a study was conducted to assess the effect of different variables in the biodegradation of PCB-contaminated sediment. The experiments were conducted in 15 mL Pyrex glass test tubes, with screw tops and PTFE septums.

Each tube contained 1 g of PCB-contaminated sediment, 10 mL (except in those cases where the purpose of the experiment was to determine the optimum value of volume of the cell suspension) of the phosphate-buffered mineral salts medium with the inoculum (approximately 10^6 active cells/mL), and the oxygen headspace saturated (33% v/v) by flushing with oxygen (weekly). Biphenyl was supplied at an initial concentration of 1,000 mg/L (except in those cases where the purpose of the experiment was to determine the dosage of the cosubstrate) as a cosubstrate directly to the sample test tubes. After setup, the test tubes were placed on an orbital shaker (Heidolph, Unimax 2010) rotated at 260 rpm in horizontal position at room temperature (25 ± 2°C) for 4 months.

Subsequently, experiments in stirred tank reactors (STR) were conducted to assess the effect of scaleup. These experiments were performed, using the optimum conditions found in test tube experiments, in 2.5-L Pyrex glass vessels, covered with aluminum foil and stirred with steel agitators at 200 rpm, at a temperature of 23 ± 3°C.

Chemical oxidation studies

The ferric sulfate and hydrogen peroxide (35%) employed in the chemical oxidation experiments were supplied by Sharlab (La Jota 86, 08016, Barcelona, Spain). The experiments, to optimize variables in the chemical treatment of PCB-contaminated sediment, were performed in screw-top 10-mL Pyrex glass test tubes with PTFE septums. Each tube contained 1 g of PCB-contaminated sediment, 5 mL of the hydrogen peroxide solution, and 0.4 mL of the ferric sulfate solution (except in those experiments to determine the optimum ratio of sediment mass/volume of oxidizing solution), with subsequent adjustment of pH to 2.75, with either NaOH or H_2SO_4 1 N (Kang and Hwang, 2000). All the test tubes were kept shaken (260 rpm) and submerged in a thermostated bath at 15 ± 0.5°C (except in those experiments to determine the temperature of the reaction). Subsequently, experiments in STRs were conducted to assess the effect of scaleup. These experiments were performed, using the best conditions found in test tube experiments, in 2.5-L Pyrex glass vessels, stirred with steel agitators at 200 rpm, at a temperature of 22 ± 1°C.

Quality assurance/quality control in the experiments

All experiments—in bottles, test tubes, and STRs—were performed in duplicate (in addition, two samples were taken from the STR), with controls to determine the losses not attributable to the processes under investigation (with the addition of $HgCl_2$ in the biodegradation tests to ensure cessation of biologic activity and with distilled water in place of oxidizing solutions in the chemical oxidation experiments).

These loss percentages were nonsignificant ($\alpha = 0.95$) in the case of the bottles and test tube assays (including those where flushing with oxygen was conducted) due to the application of the extraction procedure in the same reaction vessels. Loss percentages in the STR was (1) nondiscernible in the chemical experiments, and (2) depended on the group of homologs (4.6% for DiCBs, 5.7% for TriCBs, 9% for TetraCBs, and 24.7% for PentaCBs) in the biologic experiments due to wall sorption (determined by solvent extraction).

In the STR experiments (biologic and chemical), these control reactors contained activated carbon traps to determine losses due to evaporation. Analysis of the activated carbon in the atmospheric emissions trap revealed that no appreciable losses occurred.

Analytical methods

The PCBs were analyzed by capillary gas chromatography using an electron capture detector (ECD). All samples were run on a Perkin-Elmer (Norwalk, CT) Autosystem HRGC equipped with a 30 m × 0.32 mm i.d. fused silica column (SPB-5, Supelco Inc). The chromatographic protocol employed was that of Ofjord *et al.* (1994) employing hexachlorocyclohexane as an internal standard. Multiple injections were performed from a single sample stock solution to assess the reproducibility of the GC PCB analysis (RSD, 1.2%). PCB extraction was performed using the method developed by Quensen *et al.* (1990). Extraction efficiency for Aroclor 1242 in the sandy sediment was 89 ± 3%, and more than 95% for liquid samples. Eight congeners were selected for specific congener analysis (DiCBs: 23′–24′; TriCBs: 22′5–234′; TetraCBs: 22′45′–22′35′; PentaCBs: 22′345′–233′4′6) based on their Aroclor (all of them constituted a quantifiable percentage of 1,242 and encompassed a majority of the homolog groups in 1,242) and GC characteristics (they eluted with relatively discrete peaks during the GC analysis). Their mean detec-

Table 1. Degradation of Aroclor 1242 by PCB acclimitized mixed culture in liquid medium after 7 days.

Congeners	*Initial concentration*[a] *(μg/L)*	*% Biodegradation*[a]	*% Biodegradation (by homolog group*[a,b]*)*
23′	2.26	100	99.8 (DiCB)
24′	9.74	99.8	
22′5	19.43	89.2	94.5 (TriCB)
234′	10.09	99.7	
22′45′	11.42	82.1	90.1 (TetraCB)
22′35′	13.38	97.7	
22′345′	2.06	75.2	76.3 (PentaCB)
233′4′6	2.54	83.9	
			Total 94.9%

[a]Values are given as the mean of two replicates; [b]% biodegradation was calculated considering all quantifiable peaks in Aroclor 1242.

tion limits ranged between 0.11 μg/L for congener 252′ and 0.61 μg/L for congener 24′.

Evaluation of the active and total number of aerobic micro-organisms was determined with the Epifluorescence Microscope (Nikon AFX-DX; Melville, NY) using the following reagents as fluorochromes (Winding *et al.*, 1994): 5-cyano-2,3-ditolyl-tetrazolium chloride (CTC) and 4,6-diamido-2-phenylindole, respectively (DAPI). A total organic carbon analyzer (Shimadzu TOC-5050A, Shimadzu Corp., Columbia, MD), operating in accordance with the standard method of infrared combustion, was used to establish the dissolved organic carbon in liquid samples (Clesceri *et al.*, 1989). To evaluate the evolution of organic carbon in the contaminated sediment, the dichromate oxidation method developed by Osman (1985) was used. In determining the chlorides, Capillary Electrophoresis (Waters Quanta 4000 CIA System, Waters, Milford, MA) was employed, in accordance with Waters method N601 and in compliance with ASTM D1066 regulations. To determine pH, temperature, and dissolved oxygen concentration, selective electrodes were used in accordance with standard methods (Clesceri *et al.*, 1989).

Table 2. Effect of variables on extent of aerobic PCB biodegradation in sandy sediment after 4 months.

Variable	*Surfactant*	*m/V (g/mL)*	*Biphenyl*	*Biostimulation and bioaugmentation*	*% Biodegradation*[b,c]
Effect	—	1/10	—	—	32.1 ± 4
of cosubstrate	—	1/10	1,000 mg/L[a]	—	53.7 ± 1
(biphenyl)	—	1/10	1,000 mg/L/month	—	41.4 ± 3
	—	1/10	100 mg/L/2 days	—	59.9 ± 1
Effect of Biost.	—	1/10	1,000 mg/L[a]	+++	55.1 ± 2
and Bioaugm.	—	1/10	1,000 mg/L[a]	—	53.7 ± 1
Effect of	—	1/10	1,000 mg/L[a]	—	53.7 ± 1
m/V ratio	—	1/5	1,000 mg/L[a]	—	45.2 ± 3
	—	1/2	1,000 mg/L[a]	—	42.3 ± 2
	—	1/10	1,000 mg/L[a]	—	53.7 ± 1
Effect of	1 mg/L	1/10	1,000 mg/L[a]	—	29.1 ± 3
surfactant	10 mg/L	1/10	1,000 mg/L[a]	—	25.8 ± 1
	100 mg/L	1/10	1,000 mg/L[a]	—	19.9 ± 3

[a]Biphenyl was supplied at an initial concentration of 1,000 mg/L; [b]Values are given as the mean of two replicates (sampling was conducted after 0, 15, 30, 60, and 120 days); [c]% biodegradation was calculated considering all quantifiable peaks in Aroclor 1242.

DISCUSSION

Aerobic biodegradation of PCB in an aqueous phase

The mixed culture used in this research demonstrated an ability to biodegrade all congeners contained in Aroclor 1242. The results revealed that after 3 days only 20.3% of the original PCB remained unamenable to degradation, and after 7 days only 5.1%. It is also clear (Table 1) that the degree of chlorination is an influencing factor, given that a high chlorine content has the effect of reducing the extent of biodegradation.

These results reflect those obtained by Bedard *et al.* (1987), and are higher than those obtained by Barriault and Sylvestre (1993), due probably to the fact that in our experiments a mixed culture was used which, generally, leads to greater levels of elimination (Grady, 1985).

Influence of variables in the bioremediation of PCB-contaminated sandy sediments

Experiments were performed with PCB-contaminated sediments to evaluate the influence of the following variables: (1) biostimulation (10% increase per month of the inorganic nutrients) and bioaugmentation (addition of 10^8 active cells/gram sediment/month); (2) ratio of sediment mass/volume of solution (m/V); (3) addition of a nonionic surfactant (nonylphenol polyethoxylated, Empilan NP8, Albright & Wilson, Yarraville, Australia) at different concentrations; and (4) addition of a cosubstrate (biphenyl) at different concentrations and frequencies.

Table 2 summarizes the results obtained in the different assays. The conclusions that may be arrived at based on the results obtained in this study are as follows: (a) the concentration of biphenyl is the variable that exerts the greatest influence on the process and optimal conditions are obtained by the addition of small but frequent amounts of biphenyl; (b) the amount of nutrients added initially is sufficient, and it is not necessary to reinoculate with fresh bacteria; (c) there is little difference between the levels of biodegradation achieved with m/V ratios of 1/2 and 1/5 g/mL, but there is a slight change when the m/V ratio is 1/10 g/mL probably due to the fact that a greater proportion of PCB was in the aqueous phase at this level; and (d) the results obtained in the experiments performed with the addition of the surfactant Empilan NP8 showed an inhibition of the biodegradation process. This may be due to the toxicity of nonylphenol polyethoxylated (NPEO) or its metabolites (Manzano *et al.*, 1999), in contrast with recent studies (Maguire, 1999) that show no toxic effects of NPEO in soils under aerobic conditions. Nevertheless, more results are necessary to establish precise conclusions.

Bioremediation of PCB-contaminated sandy sediments in stirred tank reactors

The experiment in the STR was surfactant-free, and bioaugmentation and biostimulation techniques were not

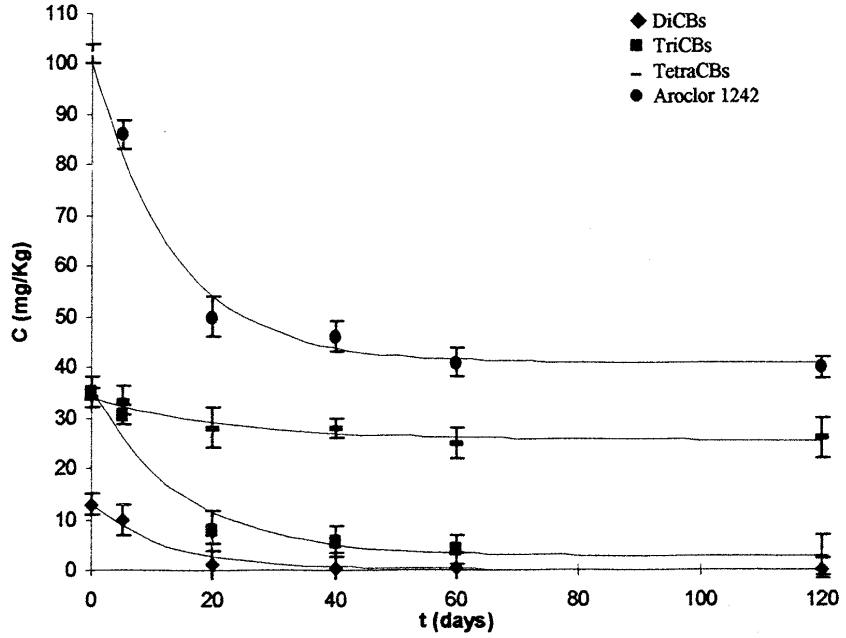

Figure 1. Depletion of overall and homolog PCB concentration in stirred tank reactor. Bullets represent experimental values, and continuous lines represent those predicted by the Middleton Model. The error bars represent the standard deviation from the mean of four samples.

Table 3. Degradation of eight target congeners by PCB acclimatized mixed culture in stirred tank reactor after 120 days.

Congeners	*% Biodegradation*	*Congeners*	*% Biodegradation*
23′	100 ± 2	22′45′	27 ± 7
24′	98 ± 2	22′35′	19 ± 4
22′5	89 ± 9	22′345′	ns
234′	95 ± 3	233′4′6	ns

Note: Degradation percentage was calculated relative to a sterile control. Values are given as the mean of four replicates ± SD. ns., no significant degradation, less than 10%, or less than 2 SD from the control.

applied. The m/V ratio was 1/10 g/mL and the cosubstrate was added every 2 days at a level of 100 mg/L of biphenyl. Figure 1 shows depletion of total and homolog PCB concentrations, including those experimentally obtained (represented by bullets) and those predicted by the Middleton Model (Middleton *et al.*, 1991) (represented by a continuous line).

The results show that Aroclor levels in the slurry decrease rapidly in the experiment under the optimized conditions (15.7% at 5 days and 50.8% over the first 20 days of the experiment). After 120 days, the total duration of the experiment, the biodegradation rates achieved with acclimatized bacteria were 60.9%. As before (see biodegradation of PCBs in aqueous phase), an increase in the level of chlorination resulted in a lower extent of biological degradation (100% DiCBs; 92% TriCBs; 24% TetraCBs; nonappreciable degradation for PentaCBs after 120 days). Table 3 shows the biodegradation percentages for eight selected congeners. It may be concluded that, in comparison with the values in water, the presence of particles causes a decrease in the degree of biodegradation of high chlorinated PCB, probably due to their hydrophobicity.

The proposed equation in the Middleton model is as follows:

$$C_t = C_r + (C_o - C_r)e^{-kt} \quad (1)$$

where C_t is concentration of the organic compound at time t (mg/kg), C_o is initial concentration of the organic compound (mg/kg), C_r is concentration of the organic compound that is resistant to biodegradation or has no bioavailability (mg/kg), and k is first-order rate constant (t^{-1}). The fitted parameters C_r and k are presented in Table 4. The model was applied successfully, as is evident from the correlation coefficients obtained. The results also show how an increase in the number of congener chlorines is accompanied by an increase in relative residual amounts and a decrease in the kinetic constants of the degradation rate.

With regard to the evolution of PCB concentration in the aqueous phase of the experiments performed with acclimatized bacteria and in the abiotic assays (Fig. 2), the results show that the PCB concentration was less in the micro-organism assays than in the abiotic assays. However, PCB were not entirely eliminated in the aqueous phase and, consequently, biostabilization of the sediment did not occur.

With regard to the evolution of total and viable microorganisms, the results from the experiment performed with PCB degrading inoculum show that initially the bacterial population was so small (3.5×10^7 total cells/mL and 10^6 active cells/mL), that it increased with each application of biphenyl, and stabilized after 20 days at values for total and active cells ranging between $4–5 \times 10^8$ to $1.5–3 \times 10^7$ cells/mL, respectively (5% viable). The pH, temperature, and inorganic anion values all remained within an optimum range for bacterial development.

Influence of variables on Fenton oxidation of PCB-contaminated sandy sediments

Figure 3 shows elimination (%) of Aroclor 1242 in the experiments performed with different concentrations of iron and hydrogen peroxide. It may be concluded that the elimination levels of the polychlorinated biphenyls (1) diminish as the concentration of iron increases over the range studied [these results are consistent with those obtained by Watts *et al.* (1993), who attributed this behavior to a loss in efficiency of the process—increased number of H_2O_2 mol required to degrade 1 mol of PCB—due,

Table 4. Fitted model parameters for Aroclor 1242 and homolog group (bioremediation of PCB-contaminated sandy sediments in stirred tank reactors).

	DiCB	*TriCB*	*TetraCB*	*Total*
C_r (mg/kg)	0.12	2.62	25.41	40.7
k (days^{-1})	0.0823	0.0654	0.044	0.074
r^2	0.982	0.967	0.966	0.987

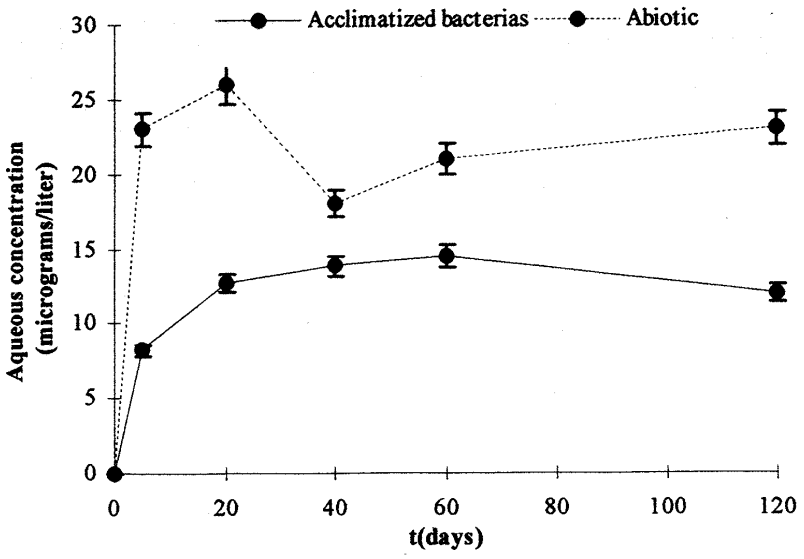

Figure 2. PCB concentrations (considering all quantifiable peaks in Aroclor 1242) in the aqueous phase of the experiment performed with acclimatized bacteria and in the abiotic assay. The error bars represent the standard deviation from the mean of four samples.

in turn, to the reduced availability of soluble iron as a result of precipitation]; and (2) increase with hydrogen peroxide concentration, due to the presence in the medium of a higher concentration of hydroxyl radicals (the slight difference existing between the degree of elimination achieved with 5 and 10% H_2O_2 is the result of a process of deactivation of the hydroxyl radicals, deriving from their high levels of concentration in the medium).

Based on these results, the operational conditions selected were 5% hydrogen peroxide and 100 ppm Fe^{3+}. The choice of 5% concentration of hydrogen peroxide is due, apart from economic factors, to the fact that high levels of degradation are achieved of all the congeners (100% DiCBs, 96–97% TriCBs, 91–96% TetraCBs, and 71–90% PentaCBs). In the case of lightly chlorinated PCB-contaminated sandy sediment, 1% hydrogen peroxide may be sufficient, because this concentration achieves very high levels of removal (98–100% DiCBs, 89–90% TriCBs, 80–85% TriCBs, and 52–75% PentaCBs).

The influence of the following variables were also studied: temperature of reaction, ratio of sediment mass/volume of oxidizing solution (m/V), agitation, and influence on the reaction of open or closed environment. Table 5 summarizes the results obtained in the different assays.

The conclusions that may be arrived at based on the results obtained are as follows: (1) the extent of the chemical oxidation reaction is slightly affected by changes in temperature, but the expenses incurred in the raising of the temperature would not be justified; (2) it was noted

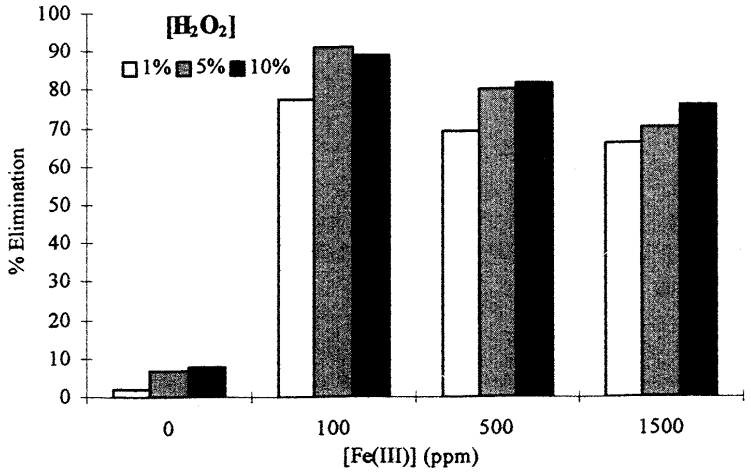

Figure 3. Effect of H_2O_2 and Fe^{3+} concentration on extent of chemical PCB oxidation in sandy sediment after 24 h. Values are given as the mean of two replicates. Elimination (%) was calculated considering all quantifiable peaks in Aroclor 1242.

Table 5. Effect of variables on extent of chemical PCB oxidation in sandy sediment after 24 h.

Variable	*T (°C)*	*m/V (g/mL)*	*Agitation (260 rpm)*	*System*	*% Elimination*[a,b]
Temperature	15	1/5	Yes	Closed	92.2
	30	1/5	Yes	Closed	94.4
	50	1/5	Yes	Closed	96.8
Agitation	15	1/5	Yes	Closed	92.2
	15	1/5	No	Closed	67.1
System	15	1/5	Yes	Open	66.3
	15	1/5	Yes	Closed	67.1
M/V ratio	15	1/1	Yes	Closed	50.7
	15	1/3	Yes	Closed	92.2
	15	1/5	Yes	Closed	93.1

[a]Values are given as the mean of two replicates; [b]% elimination was calculated considering all quantifiable peaks in Aroclor 1242.

that agitation has a beneficial effect on Aroclor 1242 removal, deriving from the enhanced opportunity for contact between the oxidizing reagents and the contaminated sediment; (3) the fact that the reactor is closed or open to the atmosphere does not appear to affect the result; and (4) the lowest levels of Aroclor 1242 elimination were achieved with an m/V ratio of 1/1 g/mL. However, tests with m/V ratios of 1/3 and 1/5 g/mL produced very similar results, and consequently, the m/V ratio of 1/3 g/mL was chosen.

The operational conditions selected in these preliminary experiments are within the economic margins established by Watts and Dilly (1996), who concluded that for the treatment of contaminated soil to be economically viable, the concentration of hydrogen peroxide should be between 0.1 and 2.0 M (in the present trials the concentration is 1.5 M), and the m/V ratio should be within the range 1/0.5 to 1/3.

Chemical oxidation by the Fenton reaction of PCB-contaminated sandy sediments in stirred tank reactors

Following the optimization of the conditions (5% H_2O_2; 100 ppm Fe^{+3}; m/V = 1/3 g/mL; with agitation; room temperature, 23 ± 3°C), experiments were performed in 2.5-L stirred tank reactors to simulate an on-

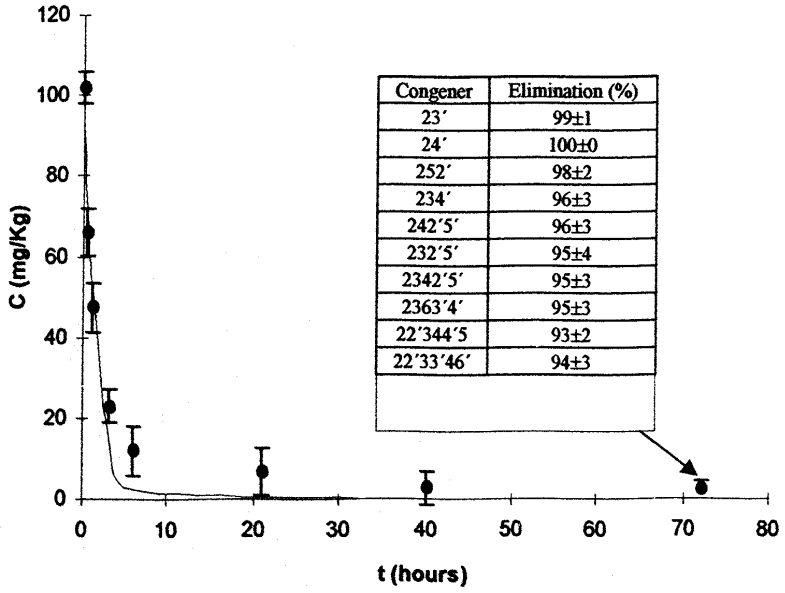

Figure 4. Rate of elimination of Aroclor 1242 in the Fenton oxidation experiments. The errors bars represent the standard deviation from the mean of four samples. Percent elimination was calculated considering all quantifiable peaks in Aroclor 1242.

Table 6. Fitted model parameters for Aroclor 1242 and homolog group (chemical oxidation by the Fenton reaction of PCB-contaminated sandy sediments in stirred tank reactors).

	DiCB	*TriCB*	*TetraCB*	*PentaCBs*	*Aroclor 1242*
K'_{OH} (h^{-1})	1.582	0.773	0.457	0.421	0.632
r^2	0.968	0.989	0.964	0.921	0.946

site treatment in slurry phase. Figure 4 shows that the residual level of Aroclor 1242 in the experiment was 1.9% after 72 h of treatment. These results reflect those obtained by other authors for the Fenton oxidation of pentachlophenyl (Watts *et al.*, 1993), trichloroethylene (Gates and Siegrist, 1995) and combustible diesel oil (Watts and Dilly, 1996). On the other hand, the most rapid rate of elimination (35.3%) is produced within the first half hour of treatment.

With respect to the different groups of homologues present in Aroclor 1242, it was observed that as the level of chlorination increased, the degree of elimination decreased. Consequently, after 3 h of the experiment, the following elimination levels were recorded: 87, 84, 70, and 68% for the Di-, Tri-, Tetra-, and PentaCBs, respectively. These differences level out after 72 h, when the degradation levels of all the congeners ranged between 96% for PentaCBs and 99.7% for DiCBs.

The kinetics of the PCB oxidation reaction in the presence of particulates is, on the one hand, a result of the reversible adsorption–desorption reactions, and on the other, a result of the reactions with the hydroxyl radicals in solid and aqueous phase. A model capable of predicting the kinetics of this reaction should at least take into account the following reactions:

$$\text{PCB} = \text{S} \rightarrow \text{PCB} + \text{S} \ (k_d \text{ and } k_a) \quad (2)$$

$$\text{PCB} = \text{S} + \text{OH}\cdot \rightarrow \text{PCB-OH} \ (k_{OH_1}) \quad (3)$$

$$\text{PCBaq} + \text{OH}\cdot \rightarrow \text{PCB-OH} \ (k_{OH_2}) \quad (4)$$

where PCB = S represents particle-associated PCB; PCBaq are the dissolved PCB; S are the particles; OH· are the hydroxyl radicals, and PCB-OH are the hydroxylated PCB.

As to whether the oxidation reaction of the polychlorinated biphenyls takes place in aqueous medium or when the PCB are adsorbed to the particles, it seems evident to conclude, due to the high degree of hydrophobicity of PCB (the average PCB concentration in aqueous phase was 17 ± 4 ppb after 72 h in a desorption experiment conducted with the same soil–water ratio) and the speed with which the oxidation process took place (Fig. 4), that the oxidation reaction occurred with the polychlorinated biphenyls adsorbed to the particles and that the hydroxyl radicals may cross the liquid–solid interface in conditions of aggressive oxidation.

Based on the supposition that oxidation occurs in the solid phase, the principal reaction to take place would be as follows:

$$\text{OH}\cdot + \text{PCB} = \text{S} \rightarrow \text{PCB-OH} \ (k_{OH}) \quad (5)$$

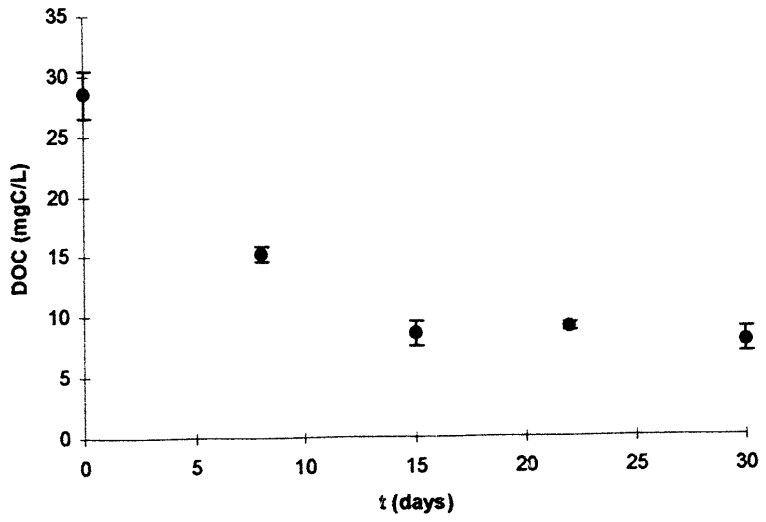

Figure 5. Evolution of dissolved organic carbon during the aerobic biodegradation process (T = 22 ± 2°C, pH = 7.05). The error bars represent the standard deviation from the mean of three samples.

with the associated kinetic expression:

$$-d[\text{PCB}]/dt =$$

$$-d[\text{PCB} = \text{S}]/dt = k_{\text{OH}}\,[\text{PCB} = \text{S}][\text{OH}\cdot] \quad (6)$$

Due to the high concentration of hydrogen peroxide employed ($nPCB/nH_2O_2$ = 1:12.400), it is to be assumed that the very high levels of hydroxyl radicals will persist throughout the reaction and, as a result, the transformation of Aroclor 1242 may be considered a pseudo first-order process with a pseudo first-order constant $k'_{\text{OH}} = k_{\text{OH}}\,[\text{OH}\cdot]$. The concentration of PCB at any given time is expressed by the following equation:

$$[\text{PCB}] = [\text{PCB}]_0\, e^{(-k'_{\text{OH}}t)} \quad (7)$$

Table 6 illustrates the results obtained after fitting of the experimental data from the tests in the agitator tank reactor to the pseudo first-order kinetic model. In the first place, it may be observed that the adjustment has been appropriate, with coefficients above 0.9. In addition, from the data expressed in Table 6, it may be deduced that the rate of reaction diminishes as the degree of chlorination of the congeners increases, as shown by the values of the kinetic constant k'_{OH}, which decrease as the levels of chlorination rise. The rate constant of the PCB reaction with the OH· radicals diminishes by a factor of 3.7 when passing from DiCBs to PentaCBs, rather higher than the factor of 2 recorded by Sedlak and Andren (1991) for aqueous-phase oxidation of PCBs by hydroxyl radicals.

Integrated chemical–biologic treatment in stirred tank reactors

The high level of PCB elimination obtained with Fenton oxidation means that the aerobic biological treatment of sandy sediment that has previously been chemically oxidized would have practically no appreciable effect in terms of the elimination of the original PCB structure. This is because aerobic biodegradation is primarily effective on lightly chlorinated congeners, which have, to a large extent, disappeared.

On the other hand, the concentrations of organic carbon in the solid and aqueous phase prior to chemical treatment were 74 mg C/kg and 1.7 mg C/L, respectively; following chemical treatment, after 72 h, the content was less than 5 mg C/kg in the solid phase and 28.5 mg C/L in liquid phase. It may, therefore, be deduced that the PCB have not been mineralized during the chemical treatment, but have given way to a series of soluble products, concentrated in the supernatant liquid.

The aerobic biodegradation experiment was performed on the supernatant liquid following neutralization with NaOH 1 N, and subsequent to the addition of the phosphate buffer (0.05 M) and the mineral nutrient solution combined with the inoculum. After 15 days of the experiment, the levels of dissolved oxygen fell from an initial value of 8.1 to 6.8 ppm. With regard to the viable bacterial population, this increased from 1.1×10^6 cells/mL to 3.2×10^7 over the same period of time. Figure 5 shows the evolution of dissolved organic carbon in this experiment and illustrates how, after 30 days of biological treatment, 72% mineralization occurred of the products generated by Fenton oxidation. This would indicate that chemical pretreatment gives rise to easily biodegradable products.

CONCLUSIONS

The surface soils, the region most affected by an accidental spill, is often predominantly made up of sand. One of the options for this type of waste contaminated by PCR is aerobic biological treatment but it is only effective for low chlorinated homologs as the results obtained have shown (100% DiCBs; 92% TriCBs; 24% TetraCBs; non-appreciable degradation for PentaCBs after 120 days). Another alternative for the PCB-contaminated sand is the Fenton advanced oxidation process. This chemical treatment produces 98% elimination of the original PCB structure after 72 h, but the PCB are not mineralized (if we use operational conditions within economic margins).

The results obtained show that one possible solution for this kind of residue with low organic content could be the integrated chemical–biological treatment, due to the fact that, as result of the Fenton treatment, biodegradable products are easily released.

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