Remediation of Contaminated Soils with PCBs Using an Integrated Treatment: Desorption and Oxidation

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Abstract: During most of the past century, large quantities of substances were produced and utilized that subsequently proved harmful. This is the case with polychlorinated biphenyls (PCBs) which only became prohibited by law in the 1970s. As a result of their physicochemical properties, these substances are now present everywhere, although they are mainly found in soils, since they are hydrophobic in character. The present study evaluates an innovatory treatment for the remediation ex situ of soils contaminated by PCBs. This treatment consists of a first stage of desorption using a surfactant agent, followed by a second stage of oxidation with the object of transforming the PCBs into innocuous substances through successive oxidations using the photo-Fenton process. The results obtained (87% remediation in the desorption and 100% in the oxidation stages) show this new treatment to be a highly effective alternative, which does not generate dangerous residues of any type.

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CE Database subject headings: Soil pollution; PCB; Desorption; Oxidation.

Introduction

Polychlorinated biphenyls (PCBs) are produced by the chlorination of biphenyl with anhydrous chlorine and iron filings as a catalyst. The resulting chlorobiphenyls form a complex mixture of compounds that have different numbers of chlorine atoms per molecule. Because they are chemically inert and have good thermal and electrical insulating properties, PCBs have been widely used in many different applications. Since 1929, in the world as a whole, somewhere between 1.3 and 2 millions of tons of PCBs have been discharged as waste (US Department of Commerce 1972; Safe 1994; Ockenden et al. 2003).

Due to the toxicity of PCBs for the environment and humans, the first laws prohibiting their use appeared in the 1970s. At the present time their production has been stopped and the total amount of PCBs in use and distributed in the environment has been estimated in thousands of tons.

Because of their hydrophobicity and persistence, PCBs are distributed mainly in soils, silts, or particles in suspension (Gschwend and Wu 1985). Thus soils represent the primary environmental reserve in the terrestrial environment (Cousins et al. 1999) and the contamination is caused mainly by industrial and anthropogenic activities (Motelay-Massei et al. 2004). As a result of this situation PCBs are not readily available for the mechanisms of natural and artificial remediation.

Several treatments have been studied for the remediation of contaminated soils, and mixed results have been obtained (Pignatello and Chapa 1994; Ravikumar and Gurol 1994; Singer et al. 2001; Chu and Kwan 2003). This study presents an innovative method of remediating soils contaminated with PCBs and, by extension, with other hydrophobic organic compounds. It consists of an integrated two-stage treatment.

First, there is a stage of ex situ desorption of PCBs from the soil using a surfactant (dodecylbenzenesulfonic acid sodium salt or LAS) in aqueous phase that maintains PCBs in solution, thus increasing their accessibility by means of the micellas formed by the surfactant molecules. After completing this stage, the soil is free of PCBs.

Then there is the second stage or chemical oxidation (photo-Fenton process) of the extract obtained from the desorption process, in order to degrade and transform the PCBs and LAS into innocuous substances and to reuse the water in subsequent treatment cycles.

The Fenton process (Fenton 1894) consists of the generation of the hydroxyl radical ($HO^{\bullet}$) by means of the reaction between a ferrous ion and hydrogen peroxide [chemical reaction (1)]. This radical is highly oxidizing and can react indiscriminately with different organic compounds. The process does not need irradiation since the reaction takes place easily, due to the ferrous ion being recycled, as indicated in the chemical reaction (2) below. However, if an illumination source is used (photo-Fenton reaction), this increases the yield and velocity of the process due to increased effectiveness in the photoreduction of the ferric to the ferrous ion [chemical reaction (3)], where an extra hydroxyl radical is generated if the ferric ion is solvated with water molecules

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$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (2)$$

$$Fe(H_2O)_5OH^{2+} + h\nu \rightarrow Fe(H_2O)_5^{2+} + HO^{\cdot} \quad (3)$$

Experiment

Soil Contamination

The soil employed in the experiments was sandy quartz (X-ray diffraction model PW 1830, Phillips Ibérica, Madrid, Spain) from Guadalete River (south-west of the Iberian Peninsula) containing very low levels of organic matter ($<0.7\%$ by weight). The procedure used to contaminate the soil artificially was described previously by Barriault and Sylvestre (1993) and is similar to the methods used by Chang et al. (2000) and Huang and Hong (2000). A concentration of 73.55 mg/kg dry soil was obtained. The Aroclor 1242 commercial mixture (Supelco Code 48585) was used as the source of PCBs. This contaminated soil was controlled for one year to check that it did not suffer from aging process and, therefore, the PCBs concentration was always the same.

Experimental Methodology

LAS (Fluka Code 44200) was used in the desorption study. The study was carried out in Pyrex glass flasks with a capacity of 100 mL. A quantity of 1 g of soil containing PCBs was introduced and a suitable volume of surfactant solution was added. Agitation was carried out with a J. P. Selecta Agimatic-N magnetic agitator. The agitation rate was 6 and a polytetrafluoroethylene magnet of 4 cm length suitable for sediments was used. A Heidolph Reax 2 rotational agitator was used in previous desorption experiments. The soil was separated from the extract by sedimentation and was washed twice with a volume of water equal to the surfactant solution volume in order to remove the rest of the surfactant solution with PCBs. These two aqueous extracts were added to the surfactant extract from the sedimentation.

The chemical oxidation study of the extract resulting from the desorption process was carried out in a tubular photoreactor (Pyrex glass cylinder with the illumination source on the longitudinal axis and a volume of 1.1 L) in discontinuous mode. Prior to filling the reactor, the surfactant solution with PCBs was prepared as described for the desorption stage. Subsequently, the iron source was added ($FeCl_3 \cdot 6H_2O$, Scharlau HI0336), the pH value was adjusted to 2.8 with H_2SO_4 (c) and 1 M NaOH. Hydrogen peroxide 33% ppv (Panreac 131077) was added and the photoreactor was filled with this mixture. Finally the illumination source (Philips TL-D 36W/18 blue, SLV TL-D 36W/08 SLV, and TUV TL-D 36W/08 SLV, centered at 440, 366, and 254 nm, respectively) was activated.

Methodology of Analysis

To assure the effectiveness of the desorption stage and to measure the concentration of PCBs in the soil after applying the LAS surfactant solution, three ultrasonic cycles were carried out using a Sonics VCX 750 to extract the PCBs from the soil. Each cycle took 6 min at 450 W power in 30 mL of hexane-acetone mixture (1:1) surrounded with ice. Subsequently, the acetone was eliminated from the organic mixture with two washes using 2% NaCl aqueous solution (50 mL) by means of manual agitation for 2 min, and the organic phases were collected. The aqueous phase was washed with 10 mL of hexane in order to extract traces of PCBs from the water. This new organic phase was added to the previous extract and dried with Na_2SO_4 (anhydrous) to eliminate water traces. The next step was to concentrate the organic phase to a volume of about 2–3 mL on a Heidolph Laborota 4001 Efficient rotavapor at 40°C under vacuum. This extract was purified through a chromatography column of Florisil [$MgO:SiO_2$ (15:85), 0.15–0.25 mm, 100/60 mesh ASTM, Macherey-Nagel 815710] which had been deactivated previously with water (2% ppv) and horizontal agitation for 4 h. In the upper part of the column, 2 g of Na_2SO_4 (anhydrous) were added, and glass wool in the lower part. After introducing the extract, hexane was added and the first 100 mL were collected and filtered under vacuum with PVDF and 0.22 mm filters (Durapore membrane filters GVWP02500). The resulting mixture (PCBs in hexane) was concentrated to a final volume of 3 mL.

To extract the PCBs from the aqueous phase (the surfactant solution from the desorption stage and the reaction mixture in the chemical oxidation stage) a new method was developed. The starting point for this development is the 6630B method of American Public Health Association (APHA)–WWWA-WPCB (1992) and the method proposed by Huang and Hong (2000). It consisted on carrying out three washes of 2 min each with 50 mL of a hexane–methylene chloride (85:15) mixture. After combining the different organic phases, starting from this point, the treatment is similar to that described in the previous paragraph.

A gas chromatograph with an electronic capture detector (GC-EDC, Perkin Elmer Autosystem HRGC) was used to determine the PCBs and biphenyl following the method proposed by Ofjord et al. (1994). Total organic carbon (TOC) measurements were carried out to follow the mineralization process, indicative of the total degradation, using a Shimadzu 5050A TOC Analyzer.

The evolution of hydrogen peroxide during the experiments was measured semiquantitatively by means of the Merkoquant test which detects peroxides between 1 and 100 mg/L of H_2O_2 and between 100 and 1000 mg/L of H_2O_2 (Merck 110081 and 110337).

The LAS toxicity test was carried out with luminescent bacteria *Vibrio ficheri* 11177 (Dr. Bruno Lange GmbH, LCK480).

Results and Discussion

Desorption Stage

The object of the present study is to measure the desorption capacity of LAS for PCBs in soils. To optimize this process, several variables were studied: concentration of LAS (0–5,000 ppm), time of contact (0–72 h), type of agitation (magnetic and rotational), molar ratio (1 g of soil per 10, 25, and 50 mL of surfactant solution), and number of reextractions (0–3 times after the first extraction). The temperature was always 25°C. Table 1 summarizes the best experimental conditions found. Fig. 1 shows the results obtained in the desorption stage using these optimum experimental conditions and the LAS toxicity. An increase of the desorption percentage is observed when the time of contact between soil and surfactant solution is increased until an asymptotic regime is reached. The time of 10 min could have been selected

Table 1. Optimal Conditions in the Two Stages of the Integrated Treatment: Desorption and Oxidation

Desorption stage	
Variable	Value
[LAS]	300 ppm
Time	120 minutes
Agitation	Magnetic
m/v ratio	1 g/10 mL
Reextractions	No
Temperature	25 °C
Oxidation stage	
[LAS]	300 ppm
[PCBs]	8 ppm
λ	254 nm
H_2O_2/(LAS+PCBs) molar ratio	100
Iron salt	$FeCl_3 \cdot 6H_2O$
$[Fe^{3+}]$	1 ppm
pH	2.80
Temperature	25°C

but the time of 120 min was selected as more appropriate since it gave the best desorption percentage (87%) and 2 h is not an excessive time of agitation.

To verify that the desorbed PCBs stayed in the aqueous solution due to the effect of the surfactant, a mass balance was carried out under the conditions selected as optimum. The total PCB content was measured in aqueous solution, in the soil, and in the desorption reactor. The mass balance was 89.6% satisfied, the losses being quantified at 10.4%, with more than 90% of that adhering to the Pyrex glass reactor. These values are considered acceptable results since they show the capacity of the LAS to maintain the PCBs in solution.

In respect of the toxicity study, the concentrations of LAS used ranged from 12.5 to 250 ppm. The toxicity of the reference solution was assayed (25 ppm $ZnSO_4 \cdot 7H_2O$) to check the reliability. The value obtained was 47.8%, which is between 40 and 60% of luminescence inhibition. This value assured the validity and quality of the results obtained according to the DIN 38412 L 34, L341 standard and verified that the activity of the bacterial population was within the normal range. The LAS toxic effect envelope of the luminescent bacteria is presented in Fig. 1. This shows the inhibition percentages at different LAS concentrations for an exposure time of 30 min. It can be observed that the LAS concentration that produces a 50% inhibition in 30 min $[EC_{50}(30)]$ is 42.6 ppm. This result is relatively high compared with other surfactant toxicity results obtained by our research group (perfluorinated surfactants around 20 ppm). Therefore, after the desorption process, the soil could be returned to its place of origin without any prior washing, because of the low toxicity and the high biodegradation rate of the LAS.

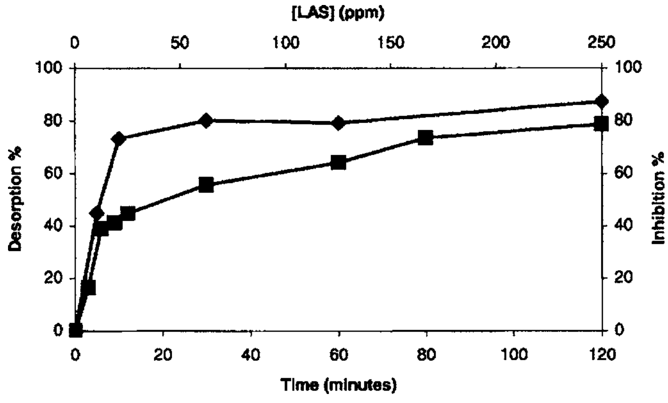

Fig. 1. Evolution of the PCB desorption percentage (◆) and of the luminescence inhibition (toxicity) (■)

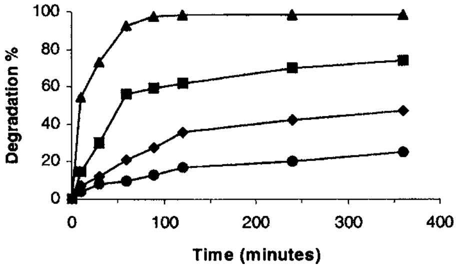

Fig. 2. Primary degradation percentage [molar ratio of H_2O_2 with 100 and 1 ppm of iron (III)] using different illumination sources: (◆) 440 nm, (■) 366 nm, (▲) 254 nm, and (●) control (darkness)

Oxidation Stage

The initial conditions for performing the study of the oxidation stage were the following: the H_2O_2/(LAS+PCBs) molar ratio was 100; 1 ppm of iron (III); and, based on the results of the previous desorption stage study, 300 ppm of LAS (optimal concentration) and 8 ppm of PCBs. (The experimental concentration in the desorption stage was lower than 8 ppm. Nevertheless, it was rounded up in order to obtain an exact value and to test higher concentrations of PCBs in dissolution.)

Wavelength (λ) of the Illumination Source

Fig. 2 shows the effect of the wavelength of the illumination source on the primary degradation of the PCBs. The lamps used in this study were 440 nm (visible), 366 nm (UV-visible), and 254 nm (UV). A control assay in darkness was also conducted (Fenton process).

It can be observed that the rate and the degradation percentage depend on the wavelength of the illumination source, with the lamp centered at 254 nm giving the best results (54, 93, and 97% in 10, 60, and 90 min, respectively). This is due to the iron (III) complexes absorbing more radiation at 254 nm and, therefore, photoreducing to iron (II) in a more rapid and effective way compared with the other wavelengths assayed (440 and 366 nm). The results of carrying out the experiment in darkness are also shown. This is the Fenton process [chemical reactions (1) and (2)]. Further, the 254 nm wavelength promotes a low photolysis of hydrogen peroxide and the loss of chlorine atoms from the PCBs that makes them more susceptible to oxidation since the number of positions without chlorine atoms is increased. Therefore, it can be concluded that the process proceeds in the following sequence: $254 > 366 > 440$ nm > darkness.

The slowest aspect of the Fenton process is the restrictive step of regenerating the iron (II) ions, as described by chemical reaction (2). This result agrees with those found by other authors (Andreozzi et al. 1999; Yoon et al. 2001; Kavitha and Palanivelu 2004).

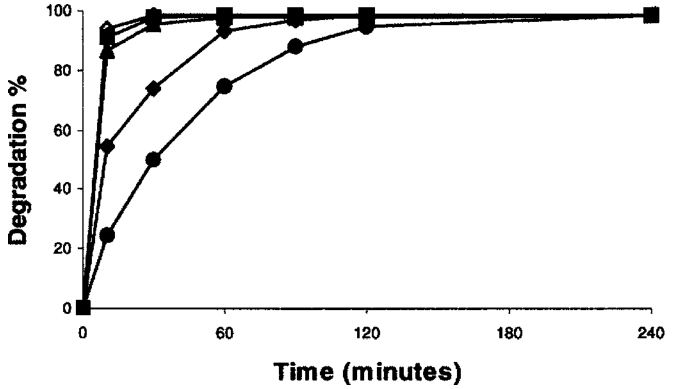

Fig. 3. Primary degradation percentage of PCBs using different molar ratios with iron ions: $R=$(◆) 1000, (■) 100, (▲) 10, (●) 0 (without H_2O_2), and (◇) $R=100$ without Fe

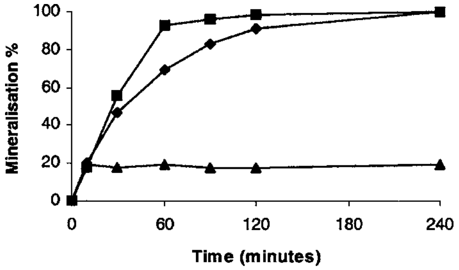

Fig. 4. Mineralization percentage of LAS+PCBs using different molar ratios with or without iron ions: $R=$(◆) 100 with Fe ions (■) 100 without Fe, and (▲) 10 with Fe ions

An important aspect to keep in mind in the assay carried out at 254 nm was to verify that the disappearance of the PCBs was due to the oxidation of the hydroxyl radical and not to the loss of chlorine atoms at this wavelength. To make this verification, an assay at 254 nm under the previous experimental conditions was carried out. The homologous groups of PCBs and biphenyl evolution were measured. It was observed that there was no significant increase of the homologous concentration with a low degree of chlorination and the initial biphenyl concentration in the original Aroclor 1242 mixture. This indicated that the oxidation process occurred rapidly and even more rapidly than the dechlorination process. In other words, the chlorine is lost but the molecules formed will be oxidized easily since they have fewer chlorine atoms than originally.

Dose of Hydrogen Peroxide

The hydrogen peroxide is a fundamental reagent in the photo-Fenton process since it is consumed. This affects the extent of the process; therefore, it was necessary to optimize the dose applied to reduce its consumption and to achieve maximum possible efficacy. This study was carried out by varying the H_2O_2/organic matter molar ratio (R). Since the hydrocarbonated surfactant is degraded at the same time as the PCBs, the previous molar ratio became $H_2O_2/(LAS+PCBs)$. Consequently, four experiments were carried out where R took the values 1000, 100, 10, and 0 (without hydrogen peroxide) ($\approx$1000, 100, 10, and 0 ppm, respectively).

For $R=0$, a few hydroxyl radicals were formed due to the photoreduction of iron (III) to iron (II) as indicated by chemical reaction (3). When the different analyses and calculations of degradation percentages were made, the biphenyl concentration in each sample, in addition to the concentration of PCBs, was taken into account, since PCBs suffer the loss of chlorine atoms at 254 nm; this gives biphenyl as the final product, with the consequent disappearance of the analytic signal of the PCBs.

Fig. 3 shows the evolution of the degradation percentage of total PCBs at different molar ratios. For $R=100$ and $R=10$, the rate and degradation percentages are very similar, although slightly higher for $R=100$. High degradation percentages were obtained in a short time, reaching values of more than 97 and 95% in 30 min for molar ratios of 100 and 10, respectively.

On the other hand, it can also be observed that the PCB degradation was lower when the hydrogen peroxide dose was higher (except for $R=0$). This result is consistent with the process chemistry, since, starting from a certain dose, increase of hydrogen peroxide did not improve the yield, due to the hydroxyl radical scavenging.

Last, it is necessary to highlight the high degradation percentage obtained for $R=0$. This finding can be explained by the contributions of two processes. First, the loss of chlorine atoms of the PCBs at 254 nm facilitates their oxidation, and, second, hydroxyl radicals are generated by the photoreduction of iron (III) to iron (II) if the iron (III) is complexed with water molecules [chemical reaction (3)].

To select the optimum dose of hydrogen peroxide, R values of either 10 or 100 could be taken. To determine the most appropriate molar ratio, it became necessary to study the mineralization process or total degradation to CO_2 and H_2O. Fig. 4 shows the evolution of mineralization for the molar ratios of 10 and 100. It can be observed that the process takes place faster for $R=100$, reaching values of 92 and 96% in 60 and 90 min, respectively. However, for $R=10$, the mineralization process seems to stop at around 19%. This is because there is not enough hydrogen peroxide to mineralize 308 ppm of organic matter (LAS+PCBs), so the process ends with a majority intermediate product that gives a yellow color to the solution.

Based on the results obtained, the value of 100 was taken as a good molar ratio, and this is used in the following assays.

Effect of Iron Ions in Solution

When the photo-Fenton process is applied using an illumination source centered at 254 nm, hydrogen peroxide photolysis could take place, with hydroxyl radicals being generated (Pera-Titus et al. 2004). Therefore, it is possible that the degradation of PCBs takes place in the absence of iron ions. To check this hypothesis, two assays were carried out: using an iron (III) concentration in solution of 1 ppm, contributed as FeCl3·6H2O, and in the total

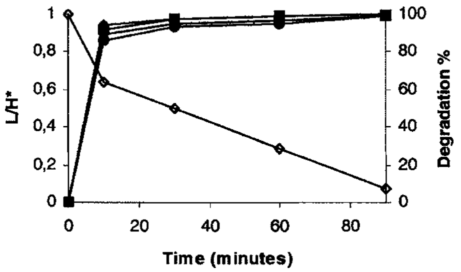

Fig. 5. Primary degradation percentages for homologous groups: (◆) di-, (■) tri-, (▲) tetra-, and (●) penta-, and (◇) $(L/H)^*$

Table 2. Correlation Coefficients (R^2) for the Different Kinetic Models Applied and Parameters Calculated for the Chan-Chu Kinetic Model

	Total PCBs	
	Primary degradation	Mineralization
	Correlation coefficients	
Order 1	0.3733	0.9233
Order 2	0.5152	0.8586
Chan-Chu	0.9999	0.9660
	Chan and Chu kinetic model	
ϱ	0.4279	27.7040
$-1/\varrho$	−2.3369	−0.0360
σ	1.0101	0.8464
$1/\sigma$	0.9900	1.1814
%	99.00	118.14

	Homologous Groups			
	Di-	Tri-	Tetra-	Penta-
	Correlation coefficients			
Order 1	0.6591	0.7215	0.8176	0.8417
Order 2	0.9790	0.9633	0.8766	0.7746
Chan-Chu	0.9999	0.9999	0.9999	0.9993
	Chan and Chu kinetic model			
ϱ	0.6045	0.8853	1.5519	2.1539
$-1/\varrho$	−1.6542	−1.1295	−0.6443	−0.4642
σ	1.0041	1.0017	0.9967	0.9951
$1/\sigma$	0.9959	0.9983	1.0033	1.0049
%	99.59	99.83	100.33	100.49
Equation	$y=1.0041x+0.6045$	$y=1.0017x+0.8853$	$y=0.9967x+1.5519$	$y=0.9951x+2.1539$

absence of iron ions. The results obtained are presented in Fig. 3. It can be observed that the degradation is similar for $R=100$ both with and without iron ions in solution.

The initial small differences in favor of the assay without iron may be due to the hydroxyl radical generated reacting with the organic matter present, in this case the LAS and PCBs. On the other hand, the iron ions are competing for the hydroxyl radical with organic matter, as shown in the following chemical reaction (4) (Buxton and Greenstock 1988; Xu et al. 2004)

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-} \quad (4)$$

Therefore, the assay without iron in solution would be selected as the optimum. To verify this choice, mineralization assays were carried out. The results obtained are presented in Fig. 4. It is observed that the mineralization of LAS and PCBs is practically complete in both cases, reaching percentages close to 100% in 240 min. However, the process takes place faster when there are iron ions in solution in the reaction medium, reaching percentages above 90% in 60 min, whereas, without iron, the reaction takes 120 min to reach similar mineralization percentages. In view of the results obtained, the process with iron ions was selected as the more appropriate.

Optimal Conditions

The effectiveness of the process as a function of the homologous groups (degree of chlorination) and the kinetics was then studied under these optimum conditions.

Homologous Group. Fig. 5 shows the evolution of the primary degradation percentage for the different homologous groups. It is observed that the rate and extent of the degradation is higher when the degree of chlorination decreases. In other words, the number of positions without chlorine that can be attacked by the hydroxyl radical increases. Therefore, the process takes place in the following sequence for the different homologous groups: di- > tri- > tetra- > pentachlorinated biphenyls.

As for the degradation percentages, in 30 min all the homologous groups have exceeded 90%; even in the first 10 min there are groups like di- and tri-chlorinated compounds that have reached this percentage. In 60 min the process has been practically completed for all the groups. This is due to the effect of the illumination source centered at 254 nm, which promotes the loss of chlorine atoms from the PCBs and/or the hydrogen peroxide photolysis.

The evolution can also be observed of the $(L/H)^*$ normalized molar ratio between low and high chlorinated homologous groups, which is defined as

$$\left(\frac{L}{H}\right)^* = \frac{\left(\frac{L}{H}\right)_t}{\left(\frac{L}{H}\right)_0}$$

where $(L/H)_t$=molar ratio at instant t between the di- and tri- congeners (L) and the tetra- and penta- congeners (H); $(L/H)_0$=initial molar ratio between the di- and tri- congeners (L) and the tetra-and penta- congeners (H).

It is observed that the $(L/H)^*$ molar ratio decreases during the entire process. In the first 10 min, the slope is higher, since the congeners with fewer chlorine atoms are oxidized faster. The $(L/H)^*$ molar ratio was 0.64 after 10 min, and starting from that time, the slope is lower and practically constant until the end of the process where almost identical moles of (L) and (H) congeners are oxidized.

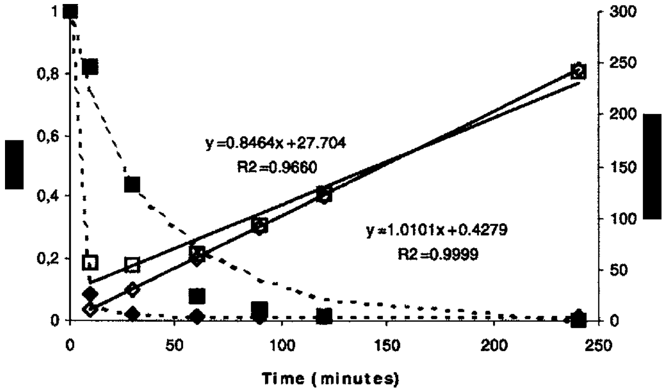

Fig. 6. Linear fit obtained with the Chan-Chu kinetic model. Experimental data: (♦,◇) primary degradation and (■□) mineralization. Theoretical values: (···) and (—).

Based on the results obtained and before extrapolation to pilot scale, the integrated process can be considered an effective treatment for extracting and degrading sorbed PCBs in soils. This treatment could also be applied to remediate soils contaminated with other hydrophobic organic compounds, and other surfactants could be used.

Kinetic Study. *Kinetic Study of the Primary Degradation.* To study the kinetics of the primary degradation results, the following kinetic models were applied: order 1, order 2, and the model developed by Chan and Chu (2003). The regression coefficients obtained are given in Table 2. The model of Chan and Chu was chosen on the basis of the theoretical results obtained and the physical meaning of their parameters.

The parametric equation of the Chan-Chu kinetic model is presented next. The main characteristic is the physical meaning of its parameters ϱ and σ through the values of $-1/\varrho$ and $1/\sigma$, respectively. The first is related to the initial oxidation capacity while the second is related to the final oxidation capacity or theoretical oxidation percentage

$$\frac{t}{1 - C/C_0} = \rho + \sigma t$$

where t=reaction time; C_0=initial concentration; and C=concentration at instant t.

Fig. 6 shows the fit obtained by applying this model to the experimental data. The consonance between experimental data and model can also be observed.

The various parameters of the Chan-Chu kinetic model are given in Table 2. The initial oxidation capacity $(-1/\varrho)$ acquires an absolute value of 2.3369 while the theoretical oxidation percentage $(1/\sigma)$ is 99%, which indicates that PCBs have been oxidized to practically 100%. This last result is in consonance with the experimental data.

Kinetic Study of the Mineralization of LAS and PCBs. The same kinetic models were applied as in the primary degradation study. The correlation coefficients obtained are given in Table 2. It can be observed that the best fit corresponds to the model developed by Chan and Chu, although the advantage is not as clear cut as with the primary degradation. The linear fit and the consonance between experimental data and kinetic model are presented in Fig. 6.

The parameters of the kinetic model are given in Table 2. The initial oxidation capacity $(-1/\varrho)$ acquires a value of −0.0360. This indicates that initial mineralization takes place more slowly than the initial primary degradation, which took a value of −2.3369. There are two reasons for this: the higher number of oxidations for the biphenyl molecule in the mineralization process until CO_2 and H_2O are obtained, and the higher concentration of organic matter in the mineralization (308 ppm) compared with the primary degradation (8 ppm). On the other hand, the theoretical oxidation capacity $(1/\sigma)$ reaches a value of 118.14%, which is equivalent to the experimental 100%.

Kinetic Study of the Homologous Groups. Table 2 shows the regression coefficients obtained for each homologous group. It can be observed that the best results for all the cases are provided by the Chan-Chu kinetic model.

The parameters of the Chan-Chu kinetic model are shown in Table 2. The absolute value of the initial oxidation capacity $(-1/\varrho)$ is higher when the number of chlorine atoms decreases, which is indicative of the stronger resistance to being oxidized. The theoretical oxidation capacity $(1/\sigma)$ reaches values around 100% for all the homologous groups, as found experimentally.

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