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Using solar and ultraviolet light to degrade PCBs in sand and transformer oils

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Abstract

The present study describes the effect of the operating variables in the sensitized solar photolysis of sandy sediments contaminated by polychlorinated biphenyls (PCBs) in alkaline isopropanol. PCBs were almost completely removed in two weeks with stoichiometric release of chloride and biphenyl (BP) by a mechanism of reductive dechlorination. The concentration of the sensitizer (acetone) was the variable found to have most influence on the process. Under the same conditions, only partial dechlorination of the PCBs (34%) was observed in dielectric fluids without generating biphenyl to any appreciable extent.

Direct photolysis (ultraviolet light at 254 nm) of dielectric oils dissolved in alkaline isopropanol lead to 92% removal of PCBs in 60 min. The observed mechanism was again that of reductive dechlorination, with stoichiometric release of chloride, and the accumulation of biphenyl, quaterphenyl and condensation products of biphenyl with isopropanol.

Keywords: Degradation byproducts; Photodechlorination; Aroclor 1242; Kinetic

1. Introduction

Although several decades have passed since the manufacturers of PCBs stopped their production, there are currently still in existence a large number of transformers containing this type of fluid; this represents the largest volume still in use of material contaminated by PCBs. Moreover, uncontrolled disposals of PCBs resulted in the release of tens of thousands of tonnes of PCBs in the natural environment, causing severe soils, sediments and water contamination (Gschwend and Wu, 1985).

Incineration is the most commonly used technology to treat wastes with high concentrations of PCBs, particularly dielectric oils, and this achieves an elimination of almost 100%. But in spite of this, incineration also presents environmental risks (dioxins and benzofurans) and is limited by the high costs of handling, transport and elimination of the final contaminated material. Alternative treatments under development for this type of residue are: chemical reaction with an alkaline hydroxide in polyethyleneglycol (Maling, 1990); supercritical and wet oxidation (Ryoo et al., 1992); adsorption onto activated carbon-regeneration (Honda et al., 2001); and Fenton oxidation (Wlassics, 1994).

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Nomenclature

PCBs	polychlorinated biphenyls
MonoCBs	monochlorinated biphenyls
DiCBs	dichlorinated biphenyls
TetraCBs	tetrachlorinated biphenyls
PentaCBs	pentachlorinated biphenyls
BP	biphenyl
PTFE	polytetrafluoroethylene
GC/ECD	gas chromatography with electronic capture detector
HPLC	high performance liquid chromatography
HPLC/MS	high performance liquid chromatography–mass spectrometry
m/V	ratio of the mass of sediment to the volume of solvent
L/H	proportion between the low and high chlorinated homologues
$(L/H)^*$	the normalized ratio of homologues
$(L/H)_d$	the ratio of homologues corresponding to day d of the test
$(L/H)_0$	the ratio of homologues corresponding to day 0 of the test
ϕ	quantum yield of the reaction
Ia	velocity of absorption of light
HRT	hydraulic residency times
XRD	X-ray diffraction
ϕ	diameter

Wastes consisting of a large fraction of inert material, such as soils and sediments, also require alternative treatments to incineration. More notable among the technologies that are being researched for the remediation of soils and sediments contaminated by PCBs are: biodegradation, biodegradation in combination with photolysis, heterogeneous photocatalysis, dehalogenation by alkaline polyethylene glycol, and oxidation with ozone (Pignatello and Chapa, 1994).

With respect to photochemical treatments, the main concern of this paper, a distinction must be made with respect to the source of irradiation employed. When sources that emit at wavelengths above 300 nm are employed, such as sunlight, the absorption of light by the polychlorinated biphenyls is very small ($\varepsilon_{320} = 15\,\mathrm{M^{-1}\,cm^{-1}}$). In such case, in order that a reaction take place (sensitized photolysis), photosensitizers must be added (Lin et al., 1996). Hawari et al. (1991) observed that Aroclor 1254 was completely dechlorinated when dissolved in isopropanol (with NaOH as an additive so that the reaction is produced through a mechanism of reductive dechlorination), and that the stoichiometric quantities of chlorides and biphenyl were generated. In their assays artificial light at 300 and 350 nm was employed, and the used sensitizer was acetone. The objective in the present study is to use solar instead of artificial light to degrade PCBs adsorbed onto sediment or in a dielectric fluid.

Furthermore, if ultraviolet light is used as the source of irradiation, reactions of the direct photolysis type take place, since the PCBs absorb considerably in this region of the spectrum. Many studies have been carried out on PCBs in organic solvents, utilizing high-energy sources of ultraviolet irradiation (Shimura et al., 1996). We will also study photolysis (ultraviolet) of dielectric fluids contaminated by PCBs in alkaline isopropanol to determine the effect of oil on photodegradation process and to evaluate the potential of this technique.

2. Materials and methods

The dielectric fluid employed in the experiments was supplied by Electrical Company of Cádiz S.A. (Cádiz, Spain). This is a viscous fluid, yellowish in color, with a density of $1.550\,\mathrm{g\,ml^{-1}}$ (at 20 °C). The concentration of PCBs in the fluid, determined by gas chromatography with electronic capture detector, was $125\,\mathrm{g\,kg^{-1}}$, and, in terms of the congeners distribution, it was equivalent to Aroclor 1260.

The solid medium to be contaminated by PCBs was sand free of organic matter (<0.05% by weight), typical of the soil most commonly affected by leaks or discharges (Ravikumar and Gurol, 1994). The selected soil originated from the lower part of the river Guadalete basin (Southwest of Spain), specifically from the Arcos-San José del Valle zone. Its mineralogical analysis (Table 1) was conducted by X-ray diffraction (XRD) using a Philips PW 1830 diffractometer (Philips Ibérica, Madrid, Spain).

The sand was contaminated with Aroclor 1242 (Supelco, Bellefonte, PA, USA) according to the method of Barriault and Sylvestre (1993) up to a concentration of $100\,\mathrm{mg\,kg^{-1}}$. This concentration and distribution of congeners is within a realistic range (Sokol et al., 1994) and matches the values selected by other researchers (Barriault and Sylvestre, 1993).

The methodology adopted for the sensitized solar photolysis tests, both in sandy sediments and with the dielectric oil, is that employed by Hawari et al. (1992). The experiments were performed, in triplicate, in Pyrex glass test tubes (15 ml), transparent to solar

Table 1
Characterization of the sandy sediment employed in the experiments

Parameter (Technical)	Value (%)
Granulometry (sieved)	
$\phi > 1.5$ mm	0
1.5 mm $> \phi >$ 0.75 mm	2.78
0.75 mm $> \phi >$ 0.5 mm	10.13
0.5 mm $> \phi >$ 0.25 mm	80.64
0.25 mm $> \phi >$ 0.132	6.44
$\phi < 0.132$ mm	0.19
Humidity (104 °C, 24 h)	0.5
Mineralogy of the sands	
Monocrystalline quartz	91
Polycrystalline quartz	4
Potassium feldspar	<5
Associated heavy minerals	
Zircon	60
Garnet	<5
Rutile	10
Tourmaline	30
Andalucite	<5

irradiation with screwed lid and septum of polytetrafluoroethylene. The test tubes contained 1 g of sand (at different degrees of humidity) or 1 g of oil contaminated by PCBs, the appropriate volume of isopropanol and sodium hydroxide solution (0.05–0.2 N) for each assay and the photosensitizer, acetone, at different concentrations. In all the experiments, the test tubes were left in the horizontal position for 2 weeks (July–August, 1998) according to the methodology described by Hawari et al. (1992), with the rays of the sun falling perpendicularly on them and with daily agitation for 3 min. The controls, to determine the losses not attributable to the processes under investigation, were covered with aluminum foil to prevent the incidence of solar irradiation and were kept in the same conditions as the rest of the assays.

The direct photolysis tests of dielectric oils were conducted in a Waterex WR-10 photoreactor (Rex UV System, Oak Park, IL, USA) of 2 l capacity equipped with a low-pressure mercury ultraviolet (254 nm) lamp with 15 W power. In the batch experiments, the photoreactor was partially filled (200 ml with the dielectric fluids contaminated by PCBs in alkaline isopropanol) leaving the non-filled zone of the reaction chamber under a flow of nitrogen or air. The gas outlet was fitted with an activated carbon trap, in which no appreciable losses of the polychlorinated biphenyls by volatilization were detected. In the flow-through reactor, the experimental device (Kiwi, 1998) consisted of the photoreactor (low-pressure mercury lamp, 15 W), glass vessels for the effluent and the feed fluid (dielectric oil in basic isopropanol degassified by current of nitrogen) and a pumping system. The experiments were performed in duplicate and the controls were treated similarly but not irradiated, in order to determine the losses not due to the photochemical reaction.

The PCBs were analyzed by GC/ECD (Perkin Elmer Autosystem HRGC. Norwalk, CT, USA) following the method proposed by Ofjord et al. (1994) with hexachlorocyclohexane as internal standard. The procedure employed for the extraction of the PCBs from the contaminated sediment was that developed by Quensen et al. (1990), whereas the samples of dielectric oil were injected directly after dilution with hexane. The analysis of biphenyl (Motohashi et al., 1990) was performed by high performance liquid chromatography, HPLC, (Waters 510 pumps and U6K inyector) in reverse phase with fluorescence detection (Waters 470). Chlorides were analyzed by capillary electrophoresis (Waters Quanta 4000 CIA System, Bedford, MA, USA) in accordance with Waters method N601 and in compliance with American Society for Testing and Materials D1066 regulations. The identification of the resulting photoproducts was performed at the Central Services of Science and Technology of the University of Cádiz, by high performance liquid chromatography–mass spectrometry (HPLC/MS, Negative Electron Spray, Thermo. Finnigan-LCQ. San Jose, CA, USA).

3. Results and discussion

3.1. Sensitized solar photolysis of sand contaminated by PCBs

The variables tested were: the concentration of sodium hydroxide, the percentage of humidity of the sediment, the ratio of mass of sediment:solvent volume (m/V), and photosensitizer concentration. In non-irradiated controls, partial removal of penta- and hexachlorinated congeners (3–8% and 11–16%, respectively) was observed. These values were subsequently employed as correction factors for the results presented.

Table 2 summarizes the results obtained under the different experimental conditions. The ratio (L/H) establishes the proportion between the low and high chlorinated homologues. This ratio will increase during the reaction because of major tendency of high molecular weight PCB to be dechlorinated. It is calculated by means of the following expression:

$$\frac{L}{H}=\frac{\text{Low chlorinated homologues}}{\text{High chlorinated homologues}}=\frac{\text{mols of Mono DiCBs}}{\text{mols of Tri, Tetra, Penta, HexaCBs}}$$

Table 2
Experimental conditions and elimination of PCBs achieved in the sensitized solar photolysis of sediments contaminated by PCBs

Variable tested	[NaOH] (N)	Moisture (%)	m/V ($\mathrm{g\,ml^{-1}}$)	Photosensitizer (%)	Elimination[a] (%, 14 days)	$(L/H)^*$ 14 days
NaOH	0.05	0	1/5	4	45 ± 2	3.21
”	0.1	0	1/5	4	52 ± 2	3.53
”	0.2	0	1/5	4	54 ± 1	9.31
Moisture	0.1	0	1/5	4	52 ± 1	3.53
”	0.1	5	1/5	4	50 ± 3	3.24
”	0.1	10	1/5	4	53 ± 1	3.68
m/V	0.1	0	1/2	4	55 ± 2	5.34
”	0.1	0	1/5	4	52 ± 3	3.53
Photosensitizer	0.1	0	1/5	1	99.7 ± 1	16.01
”	0.1	0	1/5	4	52 ± 2	3.53
”	0.1	0	1/5	10	6 ± 4	2.15

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

If the ratio L/H is normalized, by dividing it by the value of L/H on day 0 of the test, the resulting expression is:

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

where $(L/H)^*$ = the normalized ratio of homologues, $(L/H)_d$ = the ratio of homologues corresponding to day d of the test, $(L/H)_0$ = the ratio of homologues corresponding to day 0 of the test.

In Table 2 it can be observed that the treatment becomes more effective on increasing the concentration of sodium hydroxide from 0.05 N to 0.1–0.2 N, the function of which in the reaction is to facilitate the mechanism of reductive dechlorination. Therefore, the 0.1 N concentration was selected.

In the assays conducted with different degrees of humidity, it was observed that the elimination percentage of PCBs does not appear to be affected by the different degrees of humidity tested; therefore it would not be necessary to carry out a prior step of dehydration of the residue, at least when the original humidity is less than 10%.

Regarding the influence of the ratio of mass of sediment to volume of basic isopropanol (m/V), the percentages of elimination of the polychlorinated biphenyls were similar for the 1/2 and 1/5 $\mathrm{g\,ml^{-1}}$ ratios, therefore the lower of these was selected.

Lastly, it was confirmed that the concentration of the photosensitizer (acetone) is the parameter that has most influence on the process. Hence, the treatment process reaches its maximum efficacy with a concentration of acetone of 1%, with PCBs elimination and the degree of dechlorination diminishing in line with the increasing concentration of the sensitizer. The explanation for this dependence lies in the mechanism proposed by Hawari et al. (1991) for the dechlorination at 254 nm of Aroclor 1254 in alkaline 2-propanol solution.

Initiation

$$\mathrm{Ar{-}Cl} \xrightarrow{h\nu} {}^{1}\mathrm{Ar{-}Cl} \xrightarrow{ISC} {}^{3}\mathrm{Ar{-}Cl} \tag{1}$$

$$^{3}\mathrm{Ar{-}Cl} \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{Cl}^{\bullet} \tag{2}$$

Propagation

$$\mathrm{Ar}^{\bullet}\ \text{or}\ \mathrm{Cl}^{\bullet} + (\mathrm{CH_3})_2\mathrm{CHOH} \rightarrow (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} + \mathrm{ArH}\ \text{or}\ \mathrm{HCl} \tag{3}$$

$$(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} + \mathrm{OH^-} \leftrightarrow (\mathrm{CH_3})_2\mathrm{CO}^{\bullet-} + \mathrm{H_2O} \tag{4}$$

$$(\mathrm{CH_3})_2\mathrm{CO}^{\bullet-} + \mathrm{Ar-Cl} \leftrightarrow (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{Ar}\overset{\bullet-}{\rightarrow}\mathrm{Cl} \tag{5}$$

$$\mathrm{Ar}\overset{\bullet-}{\rightarrow}\mathrm{Cl} \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{Cl}^{\bullet} \tag{6}$$

Termination

$$\left.\begin{array}{l} (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} \\ (\mathrm{CH_3})_2\mathrm{CO}^{\bullet-} + (\mathrm{CH_3})_2\mathrm{CO}^{\bullet-} \\ (\mathrm{CH_3})_2\mathrm{CO}^{\bullet-} + (\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{OH} \end{array}\right\rangle \longrightarrow \text{products} \tag{7}$$

The reversibility of the reaction (5) is the cause of the reduced yield observed when the concentration of acetone is increased. Fig. 1 shows the results by groups of homologues in the assays conducted with different concentrations of the sensitizer. An increase is observed, in consonance with the values of $(L/H)^*$ shown, of the mono and dichlorinated congeners at the expense of the more chlorinated ones, which confirms the mechanism of reductive dechlorination.

As a result of this reaction, using 1% acetone, a stoichiometric release of chlorides (determined by capillary electrophoresis) and biphenyls (by HPLC) is produced without any other degradation byproduct being

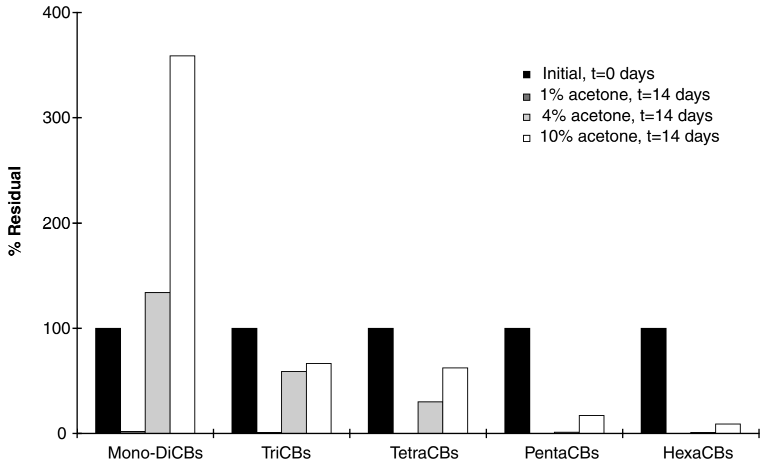

Fig. 1. Residual percentage of PCBs, by groups of homologues, in the experiment of sensitized solar photolysis conducted on sediments, adding different concentrations of acetone.

detected. Therefore the process of sensitized photolysis of sand contaminated by PCBs could be complemented with a later stage of aerobic biological treatment of the resulting biphenyl. The use of 2-propanol (rubbing alcohol) as an additive in the above photolysis is advantageous, since it is readily biodegradable and environmentally friendly.

3.2. Sensitized solar photolysis of PCBs in dielectric oils

Having optimized the conditions under which the PCBs adsorbed on particles are dechlorinated by the action of solar light, these were then applied to another type of waste material containing PCB: the dielectric oils used in electrical transformers and condensers. The variables tested were: the concentration of the photosensitizer (1% and 4%); and the degree of dilution with basic isopropanol (0.1 N NaOH) applied to the oil (mass of oil/volume of isopropanol, $m/V = 1/2$ and $1/5\,\mathrm{g\,ml^{-1}}$).

The results showed that PCBs were not degraded (<5%) under any of the conditions assayed, due to the high turbidity of the medium. The biphenyl analysis showed that it was not generated to any appreciable extent.

Fig. 2 shows the concentration of the chloride anion generated (index of dechlorination) in each of these experiments. It can be confirmed that the ratio m/V is the factor that has most effect on the dechlorination achieved, which increases as the dilution of the oil increases, as a result of the transmission of light through the mixture. Moreover, as in the sediment experiments, it is observed that the most appropriate concentration

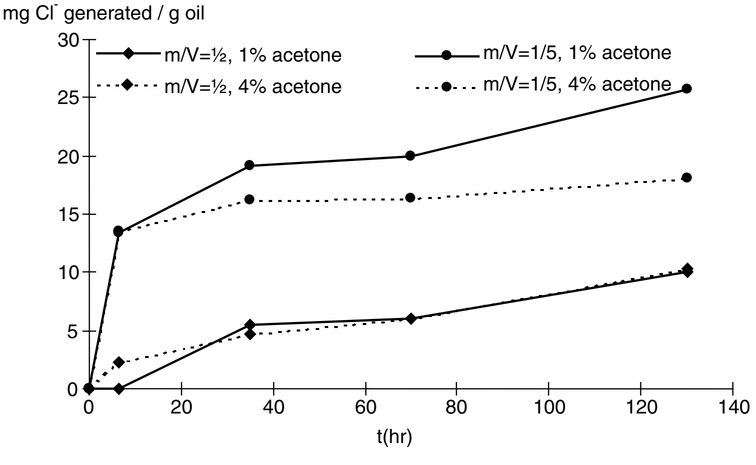

Fig. 2. Chloride generated during sensitized solar photodechlorination of oils contaminated by PCBs.

is 1% of acetone. Under these conditions, $m/V = 1/5\,\mathrm{g\,ml^{-1}}$ and acetone at 1%, the percentage of total dechlorination (calculated in the basis of an original chlorine content in the dielectric oil of $75\,\mathrm{mg\,Cl^-/g}$ oil) is 34%; within this total, 82% of the Octa and NonaCBs and 68% of the HeptaCBs (determined by GC/ECD) were transformed into less chlorinated biphenyls (4 to 6 chlorine atoms). However, in none of the groups of studied homologues total dechlorination was obtained.

In consequence, it must be concluded that the conditions considered optimum for the dechlorination of PCBs in sediments are not applicable for the PCBs in dielectric oil. To optimize the solar process for the latter, two possibilities would be possible: to increase considerably the degree of dilution of the oil, to a m/V ratio $>100\,\mathrm{g\,ml^{-1}}$, in order to obtain an appreciable reduction of turbidity, which would probably make the process economically unviable, or to carry out the dechlorination in photoreactors that would allow thin films of the waste oil to be treated, in conjunction with a system of concentration of the solar light.

3.3. Direct photolysis (at 254 nm) of PCBs in dielectric oils

A study has also been made of the influence on the photodegradation of the PCBs contained in dielectric oils exerted by a higher energy light source than sunlight, ultraviolet irradiation at 254 nm. The variables studied in the batch experiments were: the dilution of the oil, the time of reaction, and the atmosphere in which the photoreaction is performed. Subsequently, having optimized the conditions of operation and determined the kinetics of the process, the next step was to conduct flow-through experiments. In this group of experiments, the dilution of the dielectric fluid was performed simply in alkaline isopropanol, since a sensitizer (acetone) is not required for irradiation at 254 nm. In the controls, without irradiation, no losses of PCBs were observed to any appreciable extent.

In Fig. 3, the percentage of elimination of the PCBs at the various experimental conditions is shown. With respect to the dilution of the oil, it can be observed that the elimination of the PCBs is much greater in the experiment with a dilution of 1 g of oil in 100 ml of basic isopropanol, >99% in 2 h, than in that with a dilution of 1 g of oil in 10 ml (11% in 2 h). It can also be observed in Fig. 3 that the reaction is clearly inhibited by the presence of oxygen in the medium of reaction, which confirms a radical mechanism of reaction. In the phase of initiation, reactions (1) and (2), the triplet state of the polychlorinated biphenyl is generated; instead of giving rise to the radicals Ar$^\bullet$ and Cl$^\bullet$, this is deactivated by the O_2 that is a strong inhibitor of the triplet states.

Fig. 4 shows the ratio $(L/H)^*$, the index of the structural variation of the PCBs, during the experiment in nitrogen atmosphere and with a dilution factor of 100 of the dielectric oil. The ratio $(L/H)^*$ is calculated with the low chlorinated homologues considered to be those in which an increase in the concentration is observed during the reaction (i.e. Mono-TetraCBs). Once again we found that highly chlorinated congeners degraded faster than the lower chlorinated ones.

Table 3 gives the results of the fit of the experimental data, obtained in the experiment with dilution factor 100 in nitrogen atmosphere, to the first order kinetic model. This particular model was chosen because the velocity of a photochemical reaction can be expressed as the product of the quantum yield, ϕ, of the reaction and the velocity of absorption of light, Ia, of the reagent substance; also, when the concentration of the reagent is low, 3.6 mM Aroclor 1260 in the reagent mixture

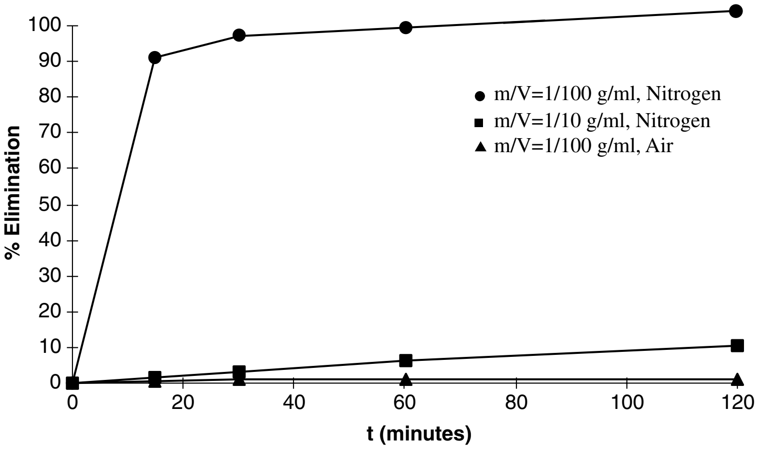

Fig. 3. Photolysis of Aroclor 1242 in dielectric oil at 254 nm (batch mode).

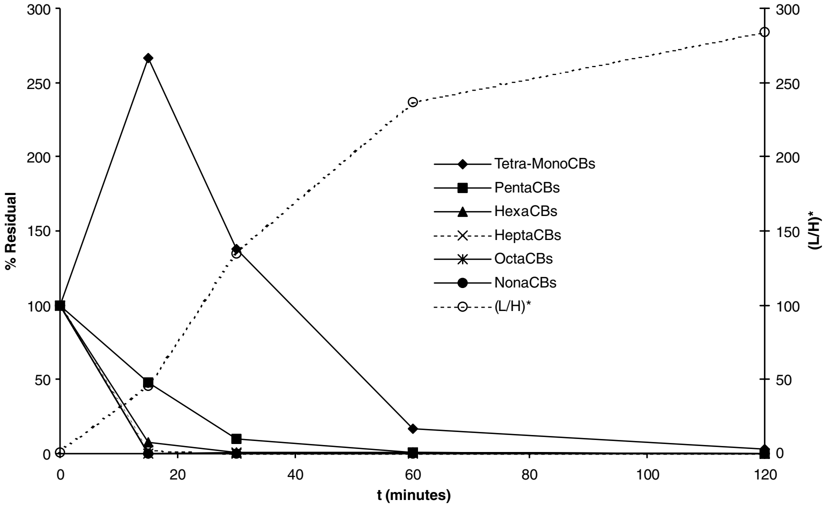

Fig. 4. Structural variation of the polychlorinated biphenyls during the batch mode experiment of direct photolysis of the dielectric oil (nitrogen atmosphere and dilution factor of 100).

Table 3
Parameters of fit to the first order model of the data obtained in the discontinuous experiment of direct photolysis of dielectric fluid with the optimized conditions

	TetraCB[a]	PentaCBs	HexaCBs	HeptaCBs	Octa-, NonaCBs[b]	Aroclor 1260
K' (min^{-1})	0.038	0.047	0.165	0.268	1.319	0.159
r^2	0.951	0.964	0.999	0.999	0.999	0.999

[a] The fit was performed without considering the new signals generated by the process of dechlorination. In the rest of the groups of homologues, there were no significant differences when these signals were not considered.

[b] The results obtained for both groups of homologues were similar.

($m/V = 1/100\,\mathrm{g\,ml^{-1}}$), first order kinetics are usually observed since *Ia* is proportional to the concentration (Beer–Lambert Law):

$$V = Ia\phi = k[\mathrm{PCBs}]\phi = k'[\mathrm{PCBs}]$$

Fig. 5 shows the quantity of chloride released as a result of the process of dechlorination. In the experiment conducted in an atmosphere of air, the release of chlorides to the medium was 6.9 mg $\mathrm{Cl^-}$/g of oil after of 2 h of irradiation (as against the 75 mg $\mathrm{Cl^-}$/g of oil that is the maximum that could have been generated), which represents a percentage of dechlorination of 9%. In contrast, when the presence of the inhibitor of radicals, oxygen, is eliminated, and with an oil dilution factor of 100, the total dechlorination of the PCBs is produced (compared with a 20% dechlorination produced with a dilution factor of 10). In addition, by performing the reaction in a nitrogen atmosphere, the risk associated with the inflammability of the solvent is reduced.

With regard to the biphenyl (BP) generated, in the experiment conducted in nitrogen atmosphere with a dilution factor of 100, it was found that the quantity released to the medium was 4.1 mg BP/g of oil, representing a percentage release of 8%, clearly lower than the quantity that should theoretically be generated (50 mg BP/g of oil). Therefore, it can be deduced that, if the PCBs have almost completely (>99%) disappeared, all the chlorine has been released to the medium and the concentration of biphenyl in the medium is less than 10% of the quantity that should be produced, then other non-halogenated organic substances must have been produced by parallel reactions. These products will be identified in the continuous tests.

Having studied the process in batch mode, flow-through experiments were then conducted. The oil was diluted by a factor of 100 in basic isopropanol ($m/V = 1/100\,\mathrm{g\,ml^{-1}}$), in a nitrogen atmosphere with hydraulic retention times (HRT) in the photoreactor of 30 and 60 min.

The percentages of elimination obtained were 68% and 92% for HRTs of 30 and 60 min. respectively; these are lower than the percentages calculated in the batch

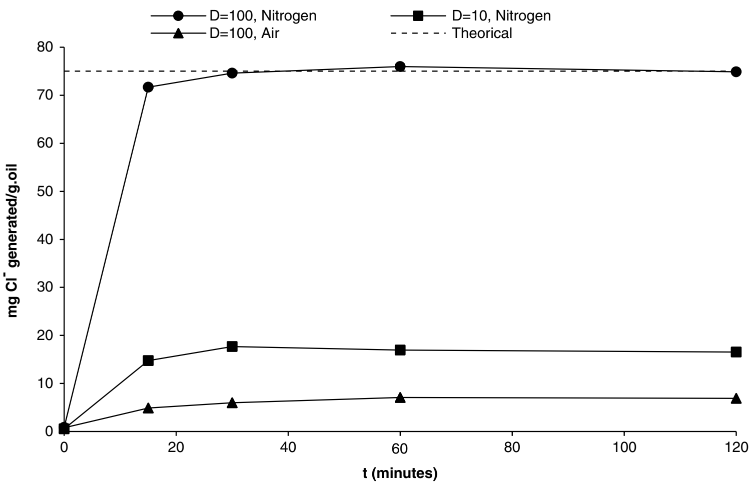

Fig. 5. Chloride generated during direct photolysis of dielectric fluids (batch mode).

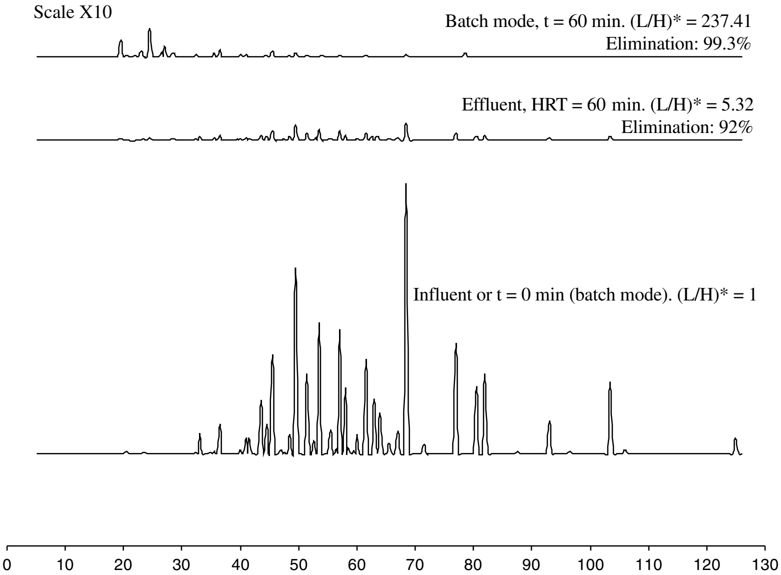

Fig. 6. Chromatographic signals corresponding to the influent and to the effluent with HRT of 30 and 60 min, in the experiment of direct photolysis of dielectric fluid ($m/V = 100\,\mathrm{g\,ml^{-1}}$, N_2 atmosphere).

tests, in which elimination rates of 97% and 99% at 30 and 60 min were obtained, respectively (Fig. 6). This is consonant with the great difference found for the values of $(L/H)^*$ between the discontinuous and continuous regimes for the same time of reaction (Fig. 6).

Furthermore, the resulting congeners are less toxic than those initially present and the continuous process could be optimized, both in respect of the elimination yield and in the kinetics of the process and the necessary dilution, employing higher intensity lamps and maximizing the surface/volume ratio of the photoreactor.

In Fig. 7 the concentration of chlorides and biphenyl in the effluent is presented. It is observed that, in the experiments with HRT of 30 min, 80% of the total chlorides (60.2 mg Cl^- generated/g of oil) has been released, whereas in those conducted with HRT of 60 min, the chlorides released represent 97% of the total (72.8 mg Cl^- generated/g of oil). In respect of the biphenyl generated, in the experiments with HRT of 30 min, this was 1.59 mg BP generated/g of oil, which represents only 4% of the biphenyl that should be produced if it was the only photoproduct of the reaction, whereas in

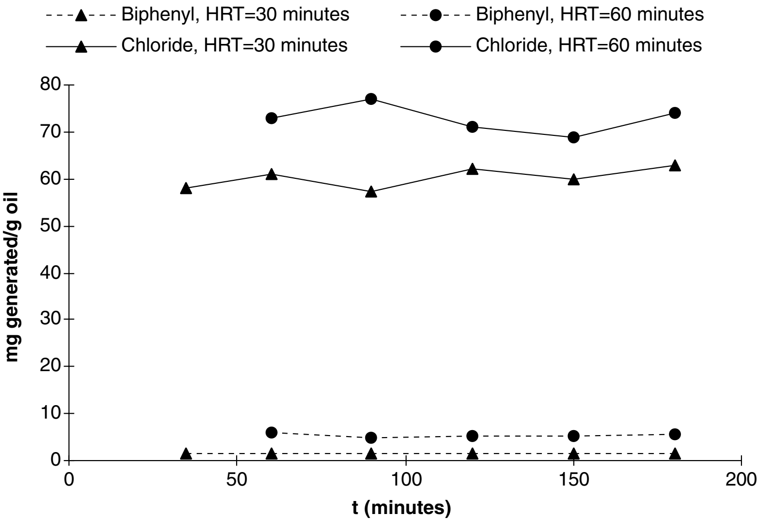

Fig. 7. Chloride and biphenyl generation during direct photolysis of dielectric fluid (flow-through mode).

those conducted with HRT of 60 min, the result was 4.5 mg BP generated/g of oil, representing 9% of the total biphenyl that could be generated.

The analysis of the organic photoproducts present in the effluent by HPLC/MS showed 3 principal signals, corresponding to substances with molecular weights that match those of quaterphenyl and those of biphenyl associated with 2 and 4 isopropyl groups, $^{\bullet}C(CH_3)_2OH$. These products would arise as a consequence of the dimerization of the biphenyl, since $BP^{\bullet}$ radicals are generated that may react with each other, or else there may be a reaction between the $BP^{\bullet}$ radical and the isopropanol solvent.

Dimerization involving the formation of carbon–carbon links is a well-known photochemical process; in fact, in the photodechlorination tests reported by Hawari et al. (1992), traces of quaterphenyl were detected when irradiating at 254 nm Aroclor 1254 dissolved in alkaline isopropanol. Moreover, in respect of the structures derived from the biphenyl associated with 2 and 4 isopropyl $^{\bullet}C(CH_3)_2OH$ groups, the results are similar to the products obtained for the photodechlorination of PCBs dissolved in methanol (Hutzinger et al., 1974); this process gives rise not only to biphenyl but also to products of the reaction between the biphenyl and the methanol ($BP–OCH_3$).

The rest of the minority signals (<2%) correspond to traces of unidentified compounds that probably result from the reaction between the radicals generated during the treatment and various compounds present in the oil.

From the results obtained it may be concluded that the photochemical detoxification at 254 nm of the PCBs contained in dielectric oils, after prior dilution with basic isopropanol, can be considered a feasible alternative to incineration, complemented by a subsequent step of separation of the isopropanol from the oil, so that it can be re-used.

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References

Barriault, D., Sylvestre, M., 1993. Factors affecting PCB degradation by an implanted bacterial strain in soil microcosm. Can. J. Microbiol. 39, 594–602.

Gschwend, P.M., Wu, S., 1985. On the constancy of sediment–water partition coefficients of hydrophobic organic pollutants. Environ. Sci. Technol. 19, 90–96.

Hawari, J., Demeter, A., Greer, C., Samson, R., 1991. Acetone-induced photodechlorination of Aroclor 1254 in alkaline 2-propanol: probing the mechanism by thermolysis in the presence of di-*t*-butyl peroxide. Chemosphere 22, 1161–1174.

Hawari, J., Demeter, A., Samson, R., 1992. Sensitized photolysis of polychlorobiphenyls in alkaline 2-propanol: dechlorination of Aroclor 1254 in soil samples by solar radiation. Environ. Sci. Technol. 26, 2022–2027.

Honda, K., Ouchi, M., Wakimoto, T., 2001. Treatment of oils containing PCB and its apparatus. Jpn. Kokai Tokkyo Koho JP 27, 5.

Hutzinger, O., Safe, S., Zitko, V., 1974. The Chemistry of PCBs. CRC Press, Boca Ratón, FL, USA.

Kiwi, J., 1998. Swiss Federal Institute of Technology, Lausanne, Switzerland. Personal communication.

Lin, Y., Gupta, A., Baker, J., 1996. Photodegradation of Aroclor 1254 using simulated sunlight and various sensitizers. Bull. Environ. Contam. Toxicol. 56, 566–570.

Maling, G., 1990. Chemical treatment of PCB containing mineral oil and oil-filled transformers. In: 10th International Meeting on Organohalogen Compounds, Bayreuth, Germany, vol. 2, p. 43.

Motohashi, N., Nagashima, H., Meyer, R., 1990. Simultaneous determination of fungicide residues in citrus. J. Liquid Chromatogr. 13, 345–355.

Ofjord, G.D., Puhakka, J.A., Ferguson, J.F., 1994. Reductive dechlorination of Aroclor 1254 by marine sediment cultures. Environ. Sci. Technol. 28, 2286–2294.

Pignatello, J.J., Chapa, G., 1994. Degradation of PCBs by ferric ion, hydrogen peroxide and light. Environ. Toxicol. Chem. 13, 423–427.

Quensen, J.F., Boyd, S.A., Tiedje, J.M., 1990. Dechlorination of four commercial polychlorinated biphenyl mixtures (Aroclors) by anaerobic microorganisms from sediments. Appl. Environ. Microbiol. 56, 2360–2369.

Ravikumar, J.X., Gurol, M.D., 1994. Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand. Environ. Sci. Technol. 28, 394–400.

Ryoo, K.S., Kapila, S., Puri, R.K., Yanders, A.F., Elseewi, A.A., 1992. Evaluation of carbon for removal of PCBs from transformer mineral oils. Chemosphere 25, 1569–1575.

Shimura, M., Koana, T., Fukuda, M., Kimbara, K., 1996. Complete degradation of polychlorinated biphenyls by a combination of ultraviolet and biological treatments. J. Ferment. Bioeng. 81, 573–576.

Sokol R.C., Kwon, O.S., Bethnoney, C.M., Rhee, G.Y., 1994. Reductive dechlorination of PCBs in St. Lawrence river sediments and variations in dechlorination characteristics. Environ. Sci. Technol. 28, 2054–2064.

Wlassics, I., 1994. Inquinamento 4, 91–92.