Dehalogenation of Polychlorinated Biphenyls (PCBs) using chemical dechlorination

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Deshalogenación de Bifenilos Policlorados (PCBs) utilizando descloración química

Deshalogenació de bifenils policlorats (PCBs) mitjançant la descloració química

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RESUMEN

El objetivo de este estudio es evaluar los efectos del ultrasonido, la relación en peso KPEG/aceite y el peso molecular del polietilenglicol en el tratamiento de PCBs presentes en aceites de transformadores utilizando la descloración química. Los resultados se evaluaron en términos de eficiencia en la remoción-destrucción de PCBs, expresado en porciento. Para la determinación de los PCBs fue utilizado un cromatógrafo gaseoso Agilent 7890A con detector de ionización por llama. Los mejores resultados (DRE igual a 88.55%) fueron obtenidos bajo las siguientes condiciones: relación KPEG/aceite de 30 y PEG 600. La deshalogenación en el Sovtol-10 incluye a todos los congéneres con alta eficiencia. En particular, congéneres de alto peso molecular desaparecen del cromatograma en todas las corridas. La remoción de los PCBs está fuertemente afectada por la relación KPEG/aceite, PEG y la interacción KPEG/aceite-PEG, en este orden.

Palabras claves: PCBs, descloración, aceite de transformador.

SUMMARY

The objective of this study is concerned about the effects of ultrasound, KPEG/oil weight ratio and polyethylene glycol (PEG) molecular weight in the treatment of PCBs present in transformer oil using chemical dechlorination (KOH/PEG). The dechlorination performance was assessed in terms of the destruction and removal efficiency (DRE) of PCBs. DRE value was expressed as percentage. An Agilent 7890A Gas Chromatograph (GC) fitted with a flame ionization detector (FID) and a capillary column (HP-5) was used for the determination of PCBs. The best results (average DRE of 88.55 %) were obtained under the following conditions KPEG/oil ratio of 30 and PEG 600. PCBs dehalogenation in Sovtol-10 involves all congeners with high efficiency. In particular, congeners of high molecular mass disappear from the chromatogram in all runs. The removal of PCBs is strongly affected by KPEG/oil ratio, PEG and KPEG/oil ratio-PEG interaction, in this order.

Keywords: PCBs, Dechlorination, Transformer oil.

RESUM

L'objectiu d'aquest estudi és avaluar els efectes de l'ultrasò, la relació en pes KPEG/oli i el pes molecular del polietilenglicol en el tractament de PCBs presents en olis de transformadors utilitzant la descloració química. Els resultats es van avaluar en termes d'eficiència en la remoció-destrucció de PCBs, expressat en tant per cent. Per a la determinació dels PCBs va ser utilitzat un cromatògraf de gasós Agilent 7890A amb detector de ionització per flama. Els millors resultats (DRE igual a 88,55%) van ser obtinguts en les següents condicions: relació KPEG/oli de 30 i PEG 600. La deshalogenació al Sovtol-10 inclou a tots els congèneres amb alta eficiència. En particular, congèneres d'alt pes molecular desapareixen del cromatograma en totes les curses. La remoció dels PCBs està fortament afectada per la relació KPEG/oli, PEG i la interacció KPEG/oli-PEG, en aquest ordre.

Paraules claus: PCBs, descloració, oli de transformador.

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INTRODUCTION

Polychlorinated biphenyls (PCBs) are compounds artificially synthesized from the substitution of hydrogen atoms by chlorine atoms in the biphenyl molecule. This substitution is possible in any position and in combinations of 1 to 10 chlorine atoms in each molecule. The interest of the PCBs as an environmental pollutant began in 1966 when they were catalogued as hazardous waste. These compounds are chemically stable, a property that represents an economical advantage but that constitutes a disadvantage and risk from the environmental perspective. The 209 possible PCBs congeners only 150 congeners have been reported in environmental samples (Robles et al., 2005).

In Cuba the principal use of polychlorinated biphenyls (PCBs) is largely concentrated in electrical transformers and capacitors. These are installed indistinctly, as demands require, in the electrical grids that supply power to the residential, industrial, and commercial sectors. PCBs are amongst the world's most widespread hazardous environmental contaminants. Until now, In Cuba there is not an available technology for the treatment of electrical equipment containing PCBs. The national strategy has been one of temporary confinement under specific criteria that ensures the lowest risks possible to health and the environment. Sovtol-10 (a mixture consisting of 10 % of trichlorobenzene and 90 % of Cl_2-Cl_7 PCBs) constitutes 62.12 % of the quantities of fluid used in diverse applications nationwide (CITMA, 2004). This corresponds with the principal origin of the imports (former USSR) up to a few years ago.

The most conventional disposal for PCBs transformer is high temperature controlled incineration (UNEP, 2004). The incineration technology is quite effective for destruction of PCBs. However, it is hampered by the disposal costs and the exclusion of reusable materials, as well as by highly toxic by-products such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). For that reason different methods for the destruction of PCBs have been proposed and include wet-air oxidation (Yat et al., 2000), super or supra-critical oxidation (Sako et al., 1999; Anitescu and Tavlarides, 2000), photolysis in the presence of hydrogen donors and oxidants (Wong and Wong, 2006), electrolytic reduction (Matsunaga and Yasuhara, 2002), biologic treatment (Kim et al., 2002; Ling et al. 2006) and a number of other chemical methods, based on laboratory experiments only. Moreover, these methods typically involve one or more drawbacks, such as the use of expensive reagent, inert atmospheres, extensive temperature control, complex apparatus, substantial energy consumption and the like. However, an among non-destructive decontamination process (selective PCBs removal) those based on the reaction between PCBs and alkoxide appear as most promising from an industrial point view.

Scrutiny of the literature reveals that papers on the chemical PEG/base process are scanty, while such a process is of remarkable industrial interest (De Filippis et al., 1997; Lopera and Aguirre, 2006; Ryoo et al., 2008). Brunelle (Brunelle, 1982) carried out an extensive study of Aroclor 1260 dechlorination in such non-polar media as heptane and toluene and found that PCBs react with polyethylene glycols and potassium hydroxide (KPEG) under mild conditions, following a simple nucleophilic substitution by a polyethylene glycol alkoxide, probably occurring in the glycol phase. De Filippis (De Filippis et al., 1982; 1999) applied the same chemical process to remove PCBs from contaminated dielectric and lube oils, concluding that a first-order kinetic was observed for each PCB as well as with respect to the PEG concentration. The reaction was also affected by the KOH/PEG ratio. In other study, Kaštánek and Kaštánek (Kaštánek and Kaštánek, 2005) use PCBs concentrations in the order of 15 g/kg of oil (sum of seven indicative congeners) but using the modified KPEG process with powdered aluminum at higher temperatures. This process has drawbacks because requires inert atmospheres and extensive temperature control.

In addition, the occasional investigation has, in fact, indicated that the use of ultrasounds reveals high potentialities not yet sufficiently explored. The use of ultrasound (US) in the KPEG dechlorination process for transformer oils with PCBs content of 320 and 800 mg/kg of oil was investigated and they concluded that the use of ultrasounds can lead to less severe operating conditions in terms of both temperature and duration of treatment (Cafissi et al., 2007).

On the basis of the above considerations, the aim of this study is concerned about the possibility of using the KPEG process for the dehalogenation of oil containing high concentration of PCBs and to determinate the influence of ultrasound, KPEG/oil ratio and polyethylene glycol (PEG) applying an experimental design 2^3.

MATERIALS AND METHODS

Experiments were carried out with transformer oil known as Sovtol-10 recovered from industrial transformer. The 52 (2, 2', 5, 5'- tetrachlorobiphenyl) congener was taken as an "internal standard" to calculate relative retention times. The effects of the KPEG/oil ratio, the polyethylene glycol molecular weight (PEG) and the effect of ultrasound (35 kHz) were determinate using an experimental design 2^3 as is shown in Table 1.

Table 1 *Experimental design 2^3*

	KPEG/oil X_1	PEG X_2	US X_3
1	30	600	yes
2	30	300	yes
3	15	600	yes
4	15	300	yes
5	30	600	no
6	30	300	no
7	15	600	no
8	15	300	no

The dehalogenation reaction was carried out in a 500 mL double jacket glass vessel under continuous stirring at a rotation speed to 1000 rpm. Temperature was of 90 – 91 °C all time; same temperature was used with ultrasounds. Cafissi (Cafissi et. al., 2007) determined that very low efficiency was observed with temperatures lower than 90 °C and that speed rotation less that 1000 rpm proved ineffective for the good mixing of reagent.

Chemical reagents consisting of a polyethylene glycol 600 (PEG 600 or PEG 300) and potassium hydroxide (KOH) were prepared by dissolving KOH in PEG at 70°C before addition to the oil under treatment. The KOH/PEG mole ratio was 2.0. All chemicals were analytical grade.

Contaminated oils were heated in the reaction vessel to a given temperature under stirring and the KOH solution in PEG added. The KPEG/oil mass ratio was 30 or 15. With ultrasounds, the reactor was directly immersed in the bath. Ultrasound at about 35 kHz was used in this study. Aliquots of 4 mL were collected at 120 minute to analyze the PCBs content.

An Agilent 7890A gas chromatograph (GC) with fame ionization detector (FID) was used. The separation of congeners was done in 30 m x 320 µm x 0.25 µm 5 % phenyl 95 % dimethylpolixiloxane capillary column (HP-5). The GC experimental conditions were as follows: nitrogen as carrier gas and as makeup gas with fow rates of 4 and 25 mL/min, respectively; injection temperature, 250 °C; detector temperature, 300 °C. The GC oven program was the following: initial temperature 110 °C, retained for 2 min, then increased at a rate of 5 °C/min to 180 °C, retained for 2 min, after increased at a rate of 2 °C/min to 230 °C, retained for 2 min and finally increase at a rate of 5 °C/min to 280 °C. The injection volume was 1µL in the splitless mode; n-hexane was used as solvent. The choice of this detector is carried out starting from several considerations: after hexane extraction, as proven by GC-MS, only chlorinated benzenes and PCB compounds are in the samples; concentration levels are not a critical factor since experiments are done in a controlled way and is possible to decide them, and the GC-FID measurements are supported and backed up by GC-MS in some experiments. The performance of this study was assessed in terms of the destruction and removal efficiency (DRE) of PCBs. DRE value was expressed as percentage and it was calculated by the equation 1.

$$DRE = \left(\frac{A_1 - A_2}{A_1}\right) * 100 \qquad (1)$$

Where: A_1 and A_2 are the sum of the area of each peak for trichlorobenzene and PCBs congeners present in the chromatogram before and after treatment.

For the statistical analysis the STATGRAPHICS Centurion XV program was used.

RESULTS AND DISCUSSION

The chromatogram of initial sample (a mixture of PEG and Sovtol-10) is shown in the Figure 1. In this chromatogram three trichlorobenzene (1, 2, 4-TCBZ; 1, 2, 3-TCBZ and 1, 3, 5-TCBZ) and a variety of tetra-, penta- and hexa-PCBs congeners were identified.

The PCBs concentration calculated in the sample for nine congeners that are in higher concentrations in the PCBs mixture, was 76.7 g PCBs/kg of oil, this nine congeners were identified using the standard CEN PCB Congener Mix-1 (Zorrilla et al., 2010). The PCBs congeners identified in the sample are shown in the Table 2.

Table 2 *PCBs congeners identified in the sample***.**

Ballschmitter number	PCBs Congener	RRT	
		PCB Mix 1	Sample
18	2, 2’,5-trichlorobiphenyl	0.803	0.802
31	2,4’,5- trichlorobiphenyl	0.912	0.910
52	2,2’,5,5’-tetrachlorobiphenyl	1.000	1.000
44	2,2’,3,5-tetrachlorobiphenyl	1.053	1.052
101	2,2’,4,5,5’-pentachlorobiphenyl	1.226	1.227
118	2,3’,4,4’,5-pentachlrobiphenyl	1.371	1.373
153	2,2’,4,4’,5,5’-hexachlorobiphenyl	1.414	1.414
138	2,2’,3,4,4’,5’-hexachlorobiphenyl	1.463	1.464

The PEG/base process is a typical nucleophilic reaction where polyethyleneglycolate, formed as a base is added to PEG, selectively attacks active sites (halogen groups) of the polychlorobiphenyl molecule (Brunelle, 1982). The effects of ultrasound, ratio KPEG/oil and polyethylene glycol (PEG) are summarized in the Table 3.

Table 3 *Results of experimental design 2^3***.**

Runs	Average DRE (%)	Standard Deviation	RSD (n=2)(%)
1	80.1	0.46	0.6
2	83.2	2.44	2.9
3	56.2	3.50	6.2
4	68.0	3.86	5.7
5	88.6	0.22	0.3
6	83.4	2.98	3.6
7	53.3	0.89	1.7
8	67.2	2.73	4.1

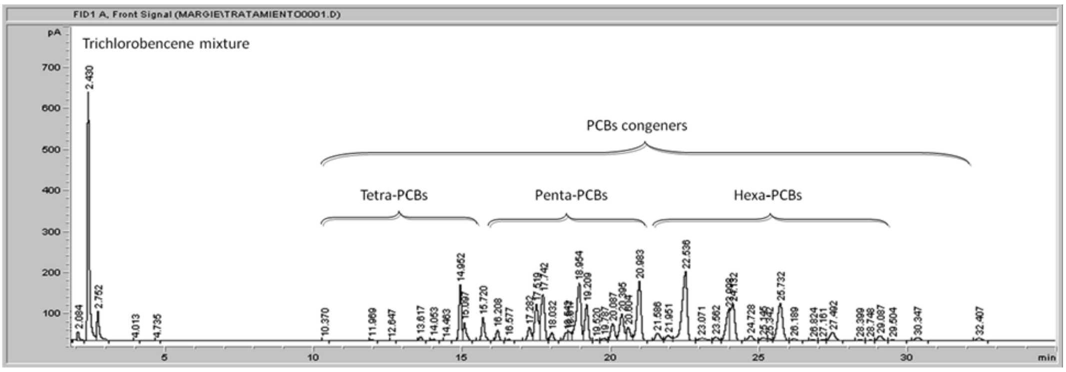

Figure 1 *GC FID Chromatogram of initial sample used in this study.*

Using in the statistical analysis the STATGRAPHICS Centurion XV program, a multiple linear regression describes the relationship between DRE and the three independent variables at a specific reaction time. The equation of the fitted model (2) at 120 min of reaction is:

$$\% \text{ DRE} = 72.4 + 11.3X_1 - 2.9X_2 - 0.6X_3 + 3.5X_1X_2 - 1.5X_1X_3 - 0.8X_2X_3 - 1.3X_1X_2X_3 \quad (2)$$

With X_1 = KPEG/oil ratio; X_2 = PEG molecular weight and X_3 = US

There is a statistically significant relationship between the variables at the 95.0 confidence level, except for the US since the P-value is greater to 0.05. The R-squared statistics (97.9947 %) indicate that the model as fitted explains 96.2401 % of variability in % DRE.

The results obtained for the factorial design 2^3, show that the studied independent variables X_1 and X_2 were significant with relationship to % DRE, being the relationship KPEG/oil the variable that evidences a highly significant influence on the behaviour of the dependent variable. Under these conditions the US did show a negative effect when increases PEG 300 to PEG 600. It can be attributed to low ultrasound intensity (35 kHz) and the high viscosity of the reaction mixture used in this study.

Figure 2 show the ratio KPEG/oil effect, keeping constant during each run the other two variables, Run 1 ratio KPEG/oil (30:1) and Run 3 ratio KPEG/oil (15:1). In both runs PCBs congeners of high molecular mass disappear from the chromatogram and highly halogenated compound tend to be converted into molecules of low number of chloro atoms. In the Run 3, the total area for congener 52 and other PCBs congeners are larger than in the Run 1 (KPEG/oil 30:1). The Run 3 shows efficiency removal destruction smaller. This value was chosen according to De Filippis (De Filippis et al., 1999) and Kaštánek and Kaštánek (Kaštánek and Kaštánek, 2005) were it was reported that low efficiency is observed at lower KPEG/oil ratio.

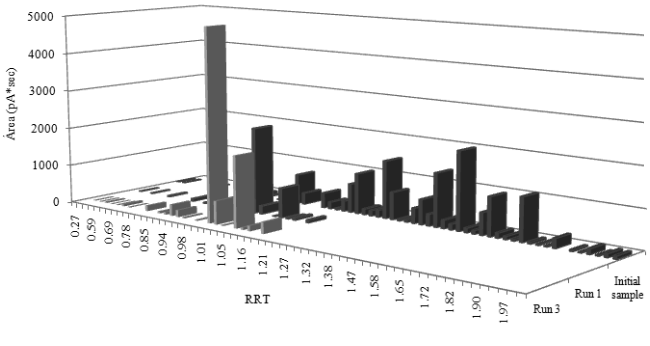

Figure 2 *3D chromatogram of PCBs dehalogenation: effect of KPEG/oil ratio.*

When compare the chromatograms for Run 1 and Run 2 (PEG effect, Figure 3), keeping constant during each run the other two variables, is observed that for the Run 2 (PEG 300) two high molecular congeners not disappear of chromatogram at 2 hours of reaction, although the total area is lower. An explanation may be as following: PEG 300 is relatively small molecule with respect to PEG 600 so as to substitute more than one chloro atom at the same time.

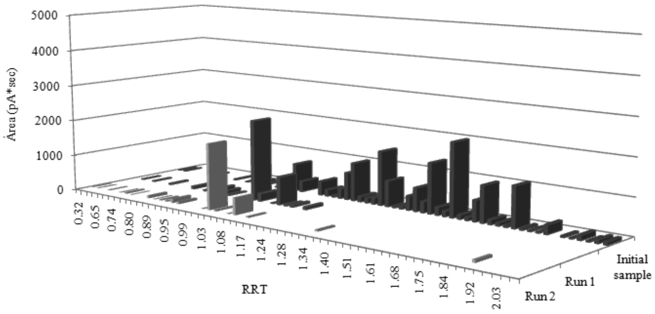

Figure 3 *3D chromatogram of PCBs dehalogenation: effect of Polyethylene Glycol (PEG) molecular weight.*

The chromatograms for Run 1 and Run 5 (ultrasound effect, Figure 4) show a similar behavior. However, the tendency for highly halogenated molecules to be converted into lighter compounds is confirmed. The ultrasound application increases by DRE of PCBs 8% at 10 minute of reaction time. After a reactions time of 120 minute no difference in DRE was measured when using ultrasound. This behavior could be due to the low ultrasound frequency used in the experiment (35 kHz). The use of ultrasound only initially leads to better efficiency compared to the results performed without ultrasound.

The results obtained in these chromatograms show that, when dehalogenation occurs, highly halogenated compound tend to be converted into molecules with lower number of chlorine atoms, hence congeners of high molecular mass disappear from the chromatogram in all runs.

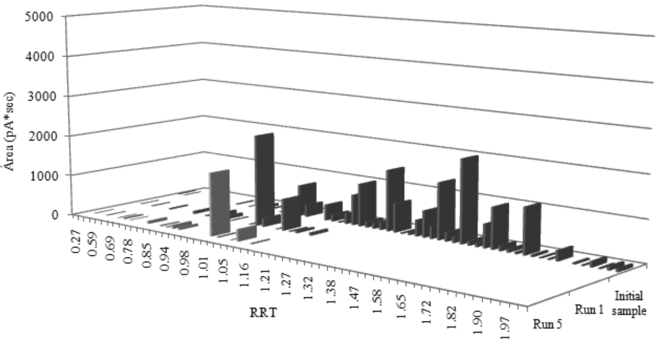

Figure 4 *3D chromatogram of PCBs dehalogenation: ultrasound effect*

These were also some compounds which were present already in the initial sample but also increased in concentration as 52 and 44 PCBs congeners. The behavior for these congeners at different reaction times are summarized in the Table 4 as percentage of reduction (minus sign) or increment (plus sign) after 1 h and 2 h, respectively of treatment. Analysis of the result reveals there is an evidence of a pronounced increase of presence of di- and tri-chrorinated congeners, which were not detected in the original sample e.g. at relative retention times of 0.44, 0.67, 0.74, 0.82 and 0.99. It seems that these compounds have emerged probably as a result of chemical changes in the course of contact of congeners having three and four chlorine atoms with the alkali environment, with simultaneous substitution reaction. The less chlorinated congeners as 52 and 44 increased in the first 10 minutes, which might indicate that the high molecular mass congeners are converted in low molecular mass compounds that behavior is not explained for the mechanism of nucleophilic aromatic substitution proposed for Brunelle (Brumelle and Singlenton, 1983). This fast dechlorination of highly chlorinated PCBs is particularly favorable form the ecological environmental point of view since they are the most dangerous to the human body.

The KPEG process with the experimental conditions used is also effective for the mixture of trichlorobenzene present in the sample, attained its complete removal after 30 minute of reaction as is showed in the Figure 5.

Table 4 *Result of PCBs dehalogenation for 52 and 44 congeners*

	% of reduction (or increment) of congeners			
	52 2,2',5,5' tetrachlorobiphenyl		44 2,2',3,5 tetrachlorobiphenyl	
Runs	after 1 h	after 2h	after 1 h	after 2h
1	76.0	-11.8	25.8	-65.9
2	115.6	16.2	51.0	-54.8
3	75.2	-0.2	30.1	-56.3
4	75.2	-0.2	30.1	-56.3
5	81.3	0.3	40.5	-47.4
6	145.3	30.8	72.4	-50.8
7	87.7	7.1	31.4	-57.4
8	183.9	37.2	104.6	-49.4

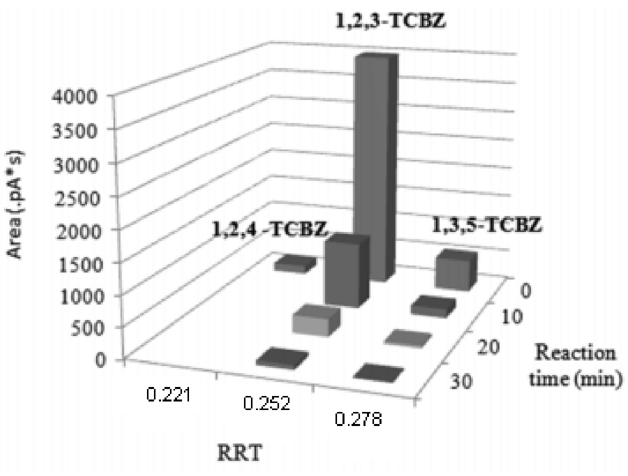

Figure 5 *3D chromatogram of trichlorobenzene treatment using KPEG process***.**

CONCLUSION

PCBs dehalogenation in the studied sample involves all congeners with high efficiency. In particular, congeners of high molecular mass disappear from the chromatogram in all runs. The best results were attained under conditions KPEG/oil ratio of 30 and PEG 600. Average DRE of PCBs, as show in the Table, was 88.55 %. The removal of PCBs is strongly affected by KPEG/oil ratio, PEG and KPEG/oil ratio-PEG interaction, in this order. However, the US and US-PEG interactions does not appear to have a significant influence. The KPEG process with the experimental conditions used is also effective for the mixture of trichlorobenzene present in the sample. The chemical reagents PEG and KOH used in this study are common and fairly inexpensive and the operation of the reactor system is simple a safe, requiring no special precautions.

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