Chemical dechlorination for the treatment of PCBs present in transformer oil (Sovtol-10): parameter study

Margie Zorrilla Velazco[a*], Petra G. Velazco Pedroso[a], Gretel Villanueva Ramos[b], Herman Van Langenhove[c]

[a]Study Center of Applied Chemistry. [b]Faculty of Chemistry and Pharmacy. Central University "Marta Abreu" of Las Villas. Road to Camajuani Km. 5 ½, CP 54830, Villa Clara, Cuba. [c]Research Group EnVOC, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B9000, Belgium.

Descloración química para el tratamiento de PCBs presente en aceite de transformador (Sovtol-10): parámetro de estudio

Descloració química per al tractament de PCBs presents en olis de transformador (Sovtol-10): paràmetre d'estudi

Recibido: 21 de febrero de 2012; aceptado: 24 de mayo de 2013

RESUMEN

Este trabajo está dirigido a la evaluación de diferentes parámetros por el tratamiento de PCBs presente en el aceite de transformador Sovtol-10 mediante el proceso de descloración química con el alcóxido del polietilenglicol (KPEG). Utilizando KOH en perlas fue determinado primeramente el efecto de la relación en peso de KPEG/aceite, la relación molar KOH/PEG y el peso molecular del polietilenglicol. La influencia de otros dos parámetros: el KOH en polvo y el ultrasonido fue investigada con los valores óptimos obtenidos del experimento anterior. Los resultados se calcularon en términos de eficiencia en la destrucción – eliminación de PCBs (DRE). Una reducción del 93.7 % en el % de DRE fue obtenido bajo las siguientes condiciones experimentales: PEG 400, relación en peso KPEG/aceite de = 30 y relación molar KOH/PEG = de 2 para dos horas de reacción. A los 10 minutos de reacción el ultrasonido incrementa el DRE en un 8 %. Después de los 120 minutos de reacción no hay diferencias significativas en el DRE cuando utilizamos el ultrasonido.

Palabras claves: Bifenilos policlorados, descloración, proceso KPEG, sovtol, ultrasonido.

SUMMARY

Different parameters for the treatment of PCBs present in transformer oil (Sovtol-10) using chemical dechlorination with polyethylene alkoxide (KPEG) were evaluated. The effect of the KPEG/oil weight ratio, KOH/PEG mole ratio and polyethylene glycol molecular weight (PEG) using KOH in pellets were determined first. With the optimal values obtained the influence of two other parameters: KOH in powder and ultrasound was investigated. The overall dechlorination performance was assessed in terms of the destruction and removal efficiency (DRE) of PCBs. Average DRE of 93.7 % was obtained under the following conditions: PEG 400, KPEG/oil weight ratio of 30 and KOH/PEG mole ratio 2 for 2 hours of reaction. The ultrasound initially increases DRE of PCBs by 8 % after 10 min of reaction time. After a reaction time of 120 min no difference in DRE was measured when using ultrasound.

Keywords: Polychlorinated biphenyls, dechlorination, KPEG process, sovtol, ultrasound.

RESUM

Aquest treball està dirigit a l'avaluació de diferents paràmetres pel tractament de PCBs presents en l'oli de transformador Sovtol-10 utilitzant la descloració química amb l'alcòxid del polietilenglicol (KPEG). Al utilitzar KOH en perles es va determinar primerament l'efecte de la relació en pes de KPEG/oli, la relació molar KOH/PEG i el pes molecular del polietilenglicol. La influència dels dos paràmetres: el KOH en pols i el ultrasò va ser investigada amb els valors òptims obtinguts de l'experiment anterior. Els resultats es van calcular en termes d'eficiència en la destrucció-eliminació de PCBs (DRE). Una reducció del 93.7% en el % d'DRE va ser obtingut sota les següents condicions experimentals: PEG 400, relació en pes KPEG /oli = 30 i relació molar KOH/PEG = 2 per a dues hores de reacció. Als 10 minuts de reacció l'ultrasò incrementa el DRE a un 8%. Després dels 120 minuts de reacció no hi ha diferències significatives en el DRE quan utilitzem el ultrasò.

Paraules claus: bifenils policlorats, descloració, procés KPEG, sovtol, ultrasò.

---

*Corresponding author: margiezv@uclv.edu.cu; Tel.: (53) (42)-281510. Fax: (53) (42)-81608

INTRODUCTION

Polychlorinated biphenyls (PCBs) are amongst the world's most widespread hazardous environmental contaminants. They have been detected in most environments (indoor and outdoor atmospheres, surface and subsurface waters, soils and foodstuffs). Relatively considerable quantities of PCBs have been, and continue to be, released into the environment due to inadequate draining practices, losses and accidental spills in a wide range of industrial installations (UNEP, 2002).

The term of polychlorinated biphenyls makes reference to a class of synthetic organic products called chlorinated hydrocarbons. Theoretically there are 209 PCBs congeners but only about 130 congeners are found in commercial products. The PCBs internationally commercialized are a mixture of congeners that have been chlorinated to different degrees, according to its final use. Their excellent stability and thermal properties make PCBs suitable as a heat transfer medium and dielectric liquids in electrical transformer and capacitors. Later, PCBs are considered as Persistent Organic Contaminants; they remain in the environment for long periods and are included in the "Dirty Dozen", a list of the twelve most hazardous contaminants known (UNEP, 1999).

In Cuba, the principal use of PCBs is largely concentrated in electrical transformers and capacitors. These are installed indistinctly, according to its necessity, in the electrical grids that supply power to the residential, industrial and commercial production sectors. The Department of Power Supply of the Ministry of Basic Industry owns and operates approximately 90 % of the existing electrical transformers throughout the country, but other sectors own and operate entirely imported industrial PCBs containing equipment as well.

Until now, no technology for the treatment of electrical equipment containing PCBs is available in Cuba. As a result of the ever increasing stocks of these equipment's being taken out of service, the national strategy has been the temporary confinement under specific criteria that ensures the lowest risks possible to health and the environment. PCBs containing oil known as Sovtol-10 constitutes 62.1 % of the quantities of fluid used in Cuba. The principal origin of the import was the former USSR up to a few years ago (CITMA, 2004).

In the former USSR, PCBs were first synthesized in 1934 and industrial production was launched in 1939 and between 1987 and 1993 production of PCBs in Russia was terminated. In this period technical mixtures of PCBs were produced mainly at Russia territory but also in Kazakhstan, Armenia, Uzbekistan and Ukraine (Amirova et al., 2001).

There are three different mixtures of Sovol (a mixture of mainly tetra- and pentachlorinated PCBs) and trichlorobenzenes (TCBZ). Sovtol-1 is composed of 75 % Sovol and 25 % TCBZ; Sovtol-2 has 64 % of Sovol and 36 % TCBZ, and Sovtol-10, 90 % of Sovol and 10 % TCBZ (Wyrzykowska et al., 2006). The dielectric oil that contains Sovtol-10 is commercially named as Sovtol-10 too; this was imported by Cuba for several years.

The destruction of PCBs requires breaking the molecular links by thermal or chemical energy. In the last twenty years there have been many investigations for PCBs removal and destruction of contaminated products, and many processes have been developed. The more conventional approach is the high temperature controlled incineration (UNEP, 2004). This incineration technology is effective for destruction of PCB; however, it is hampered by the costs of disposal and the exclusion of reusable materials as well as measures that have to be taken to avoid production and emission of highly toxic products such as dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). Some other alternative techniques seem viable, environmentally acceptable and cost-competitive for reducing of PCBs concentration in many selected wastes (Rahuman et al., 2000). For that reason different methods for the destruction of PCBs have been proposed such as wet-air oxidation (Yak 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) and a number of other chemical methods, based on laboratory experiments only.

Wu (Wu et al., 2005) applied a practical and efficient disposal method for hydrodechlorination of polychlorinated biphenyls (PCBs) in transformer oil. Transformer oil containing PCBs was treated by nanometric sodium hydride (nano-NaH) and transition metal catalysts. High destruction and removal efficiency (89.8 %) can be attained by nano-NaH alone under mild conditions. The process exhibits apparent characteristics of a first order reaction.

Literature search reveals that papers about the polyethylene glycol (PEG)/base chemical process are rather uncommon, although the process appears promising from an industrial point of view (De Filippis et al., 1997; Lopera and Aguirre, 2006; Ryoo et al., 2007). These processes are based on the reaction between PCBs and PEG alkoxide, a group of reagents generically referred to as "APEG" (alkali metal polyethylene glycolate) has been developed.

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 the former are easier to dehalogenate. 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 all studies mentioned treatment was performed on oil samples contaminated with PCB at levels less than 1 g/kg.

To our knowledge there are no studies treating transformer oil with high PCBs concentrations using the KPEG process. Only 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.

The aim of this study was to explore the possibility of using the KPEG process for the dechlorination of oil containing high levels of PCBs as technique which might be more adapted to local situation in Cuba than incineration. The effect of operational parameters (PEG molecular mass, KOH/PEG ratio, applying ultrasound or not) on the dechlorination was investigated.

MATERIALS AND METHODS

Experiments were carried out with transformer oil known as Sovtol-10 recovered from industrial transformers. All chemicals (PEG 300, PEG 400 and PEG 600; pellet and powdered KOH and n-hexane) were analytical grade and provided by Fluka. Standards Aroclor 1254 1000 μg/ mL in n-hexane was used for the determination of PCBs in the transformer oil and the evaluation of the nine individual indicator congeners. Standard Aroclor 1254; 1, 2, 4-TCBZ; 1, 2, 3-TCBZ and 1, 3, 5-TCBZ were purchased from Supelco.

The congener 52 (2, 2, 5, 5’- tetrachlorobiphenyl) was used as “internal standard” to calculate relative retention times. Polyethylene glycol (PEG) of three different molecular mass (300, 400 and 600 g/mole) was used as a reagent. Pelleted or powdered potassium hydroxide (KOH) was dissolved in PEG at 70 °C before addition to the oil under treatment.

The dehalogenation reaction was carried out in a batch reactor. The reactor included a double jacket reaction vessel (160 mm height and 100 mm diameter), and temperature control system. Contaminated oils were heated, and the KOH solution in PEG is added into the reaction vessel, to a temperature of 90 ± 1 °C under continuous stirring with a turbine impeller at a rotation speed of 1000 rpm. 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. With ultrasound, the reactor was directly immersed in the bath. An ultrasonic bath Model Branson 2200 operating at about 47±6 kHz was used in this study.

All runs were operated in batch mode with two hours duration. Aliquots of 4 mL were collected at fixed times to analyze the PCBs content. Analyses were performed gas chromatographically after separating the glycolic phase (heavy) from organic phase (light).

An Agilent 7890A gas chromatograph (GC) with flame 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 flow 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 and the (DRE in percentage) was calculated by the equation (1):

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

Where: A_1 and A_2 are the total area of peaks for mixture of the PCBs congeners before and after treatment. For the statistical analysis the STATGRAPHICS Centurion XV program was used.

RESULTS AND DISCUSSION

As an example a typical chromatogram of 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.

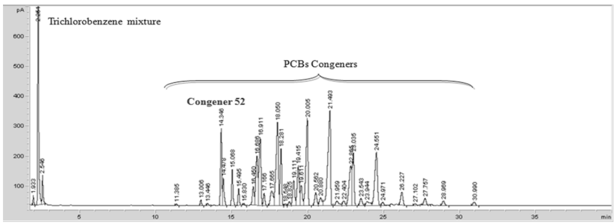

Figure 1. *GC FID Chromatogram of blank (Sovtol-10) used in this study*

The PCBs concentration calculated in the Sovtol-10 for the nine congeners that are in higher concentrations in PCBs mixture, was 76.7 g PCBs/kg of oil, this nine congeners were identified using the standard CEN PCB Congener Mix-1. The method used shows a good precision and reproducibility for the analysis of congeners, what is corroborated by relative standard deviation (% RSD) value, smaller than 5 % (n=3), which indicates consistence on the measurements. The analytical characteristics of the calibration present linearity higher than 99 % with limit of detection (LoD = 17 **μg**/mL) and limit of quantification (LoQ = 48.7 **μg**/mL) what enables the identification and quantification of PCBs in transformer oils (Zorrilla et al., 2011).

Effect of molecular weight of PEG in the PCBs dechlorination reaction

Figure 2 represents typical DRE time profiles for the dechlorination reaction using PEG with molecular mass 300, 400 and 600 using KOH/PEG ratio 2.0 (mole) and KPEG/oil ratio 30 (weight). PEG acts both as the reagent and as a phase transfer agent. Reaction products formed are extracted into the glycol phase, and their immiscibility with the non-polar Sovtol-10 ensures at the same time efficient removal of the reaction product driving the reaction towards adduct formation.

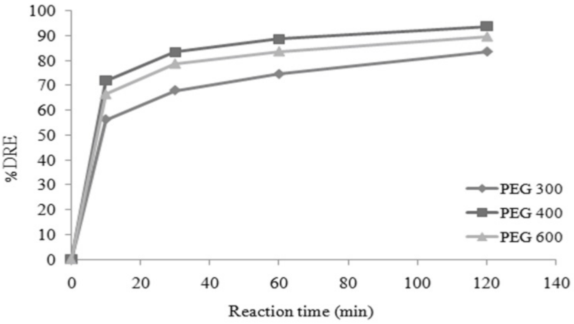

Figure 2. *Percent of Destruction and Removal Efficiency (DRE) as a function of reaction time: effect of Polyethylene Glycol (PEG) molecular weight.*

As shown in Figure 2 there is an initial fast increase in DRE up to 50-70 % during the first 10 min of the reaction. Then DRE increases more slowly with reaction time attaining values between 80-95 % after 120 min. Figure 2 also indicates that DRE efficiency changes with PEG MW in the following order: PEG 400 > PEG 600 > PEG 300.

When PEG 400 was used as phase transfer agent for dechlorination reaction, the removal after 2 hours was 93.7 %, which is higher than 89.5 % using PEG 600, and 83.4 % using PEG 300. Statistical comparison (using Statgraphics Program) between the means for the PEG 300, PEG 400 and PEG 600, showed no significant difference at the 95.0 % confidence level when comparing the PEG 300 with PEG 600 or PEG 400 with PEG 600. However, when the means for PEG 300 and PEG 400 are compared there is a statistically significant difference for the two samples at the 95.0 % confidence level. These results are different than those obtained by Brunelle and Singlenton (Brunelle and Singlenton, 1983) where the effectiveness of PEG increases somewhat with increasing molecular weight, and Cafissi (Cafissi et al., 2007); those authors used PEG 1000; PEG 600 and PEG 300. After 3 h reaction time, the DRE efficiency decreased in the following order PEG 1000 > PEG 300 > PEG 600. After 4 h, the behavior was changed with a higher DRE for PEG 300 than PEG 1000. However no statistical evaluation of these results was reported.

From our results the PEG 400 gives better dechlorination results than both PEG 300 and PEG 600. So there is no linear relation between PEG molecular weight a DRE. This indicates that exist a combined effect of several factors counteracting on the dehalogenation reaction when varying the molecular mass of the PEG. Mass transfer is influenced by both viscosity (mixing between PEG and oil) and PCB diffusion coefficients. Both factors will increase with decreasing PEG molecular weight. The density of reactive groups (hydroxyl functions at the end position of the polymer chains) will increase with decreasing PEG molecular weight. More detailed mechanistic research which is out of this parameter study will be necessary the check the hypothesis that de effect of PEG is the result of counteracting mass transfer parameters and the density of reactive OH-groups.

Effect of KPEG/oil ratio and KOH/PEG ratio in the PCBs destruction and removal efficiency (DRE)

The effects of KPEG/oil ratio (wt.) and KOH/PEG ratio (mole) on the PCBs destruction and removal efficiency (DRE) were determined using an experimental design 2^2. Reaction time was 120 min. The data obtained at 120 min are summarized in Table 1 where: X_1 is KOH/PEG ratio (mole) 1.5 and 2; X_2 is KPEG/oil ratio (weight) 22 and 30 and Y_1 and Y_2 destruction and removal efficiency DRE of PCBs.

A multiple linear regression model describes the relationship between DRE and the two independent variables at a specific reaction time. The equation of the fitted model (2) at 120 min of reaction is:

$$DRE = 91.46 + 1.2 X_1 + 1.51 X_2 - 0.52 X_1X_2$$

With X_1 = KOH/PEG ratio and X_2 KPEG/oil ratio

Table 1. *Overview of experimental design and overall DRE as a function of KOH/PEG and KPEG/oil ratio (reaction time 120 min)*

Run	KOH/ PEG ratio	KPEG/ oil ratio	Average DRE (%)	Standard deviation	RSD (n=2) (%)
1	+1	+1	93.7	0.16	0.17
2	+1	-1	91.7	0.10	0.11
3	-1	+1	92.3	0.09	0.10
4	-1	-1	88.2	0.40	0.45

The results obtained for the factorial design 2^2, show that both independent variables KOH/PEG ratio and KPEG/oil ratio and their interaction significantly influence the % DRE. The KPEG/oil ratio shows the most significant effect. The R-Squared statistic indicates that the model as fitted explains 99.3706 % of the variability in DRE.

Figure 3 shows chromatograms of Sovtol-10 treated in the 2^2 design experiment. The influence of KPEG/oil ratio can be analyzed by comparing run 1 and run 2 (Run 1: KPEG/oil ratio (30:1) and Run 2: KPEG/oil ratio (22:1)) and the blank. In Run 1, PCBs congeners of high molecular mass disappear from the chromatogram and highly halogenated compounds tend to be converted into molecules of low number of chlorine atoms, however in the Run 2 two high molecular congeners not disappear. In the Run 2 the total area for congener 52 and other congeners are larger than in the Run 1 and the efficiency removal destruction is smaller. This value is similar to the obtained for other authors (De Filippis et al., 1999; Kaštánek and Kaštánek, 2005), who reported lower efficiency at lower ratio KPEG/oil.

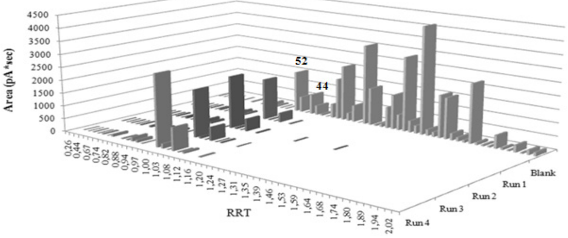

Figure 3. *3D Chromatograms of PCBs dehalogenation in Sovtol-10 treated in each experiment.*

When the chromatograms for Run 1 and Run 3 are compared (KOH/PEG effect) it is observed that, for both runs the congeners of high molecular mass disappear of the chromatogram at 2 hours of reaction, although the total area of the PCBs congeners in Run 3 is slightly greater than in the Run 1.

Analyzing these chromatograms 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 a 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. There were also some compounds which were present already in the blank but also increased in concentration as 52 and 44 PCBs congeners.

The treatment with the experimental conditions used is effective for the mixture of trichlorobenzenes too, because complete removal is achieved after 60 minutes of reaction (Figure 4). The best results are obtained under the following conditions: PEG 400, KPEG/oil weight ratio of 30 and KOH/PEG mole ratio 2.

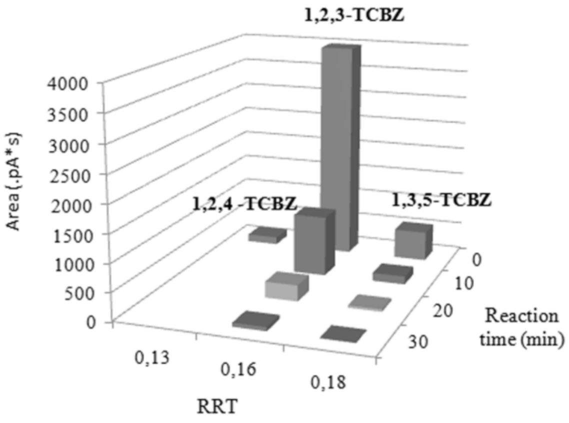

Figure 4. *Trichlorobenzene mixture treatment at 10, 20 and 30 minutes*

Influence of powdered KOH and ultrasounds

With the best experimental conditions obtained in the previous experiment the influence of powdered KOH and applying ultrasound on the DRE was examined. (Table 2)

Table 2. *The Removal and Destruction Efficiency (DRE) of Sovtol-10 using powdered KOH with and without ultrasound for different reaction times*

Time (min)	with US			without US		
	DRE (%)	Standard deviation	RSD (n=2) (%)	DRE (%)	Standard deviation	RSD (n=2) (%)
10	68.8	0.33	0.48	60.5	0.84	1.39
20	79.4	1.10	1.39	78.3	1.11	1.42
30	83.3	0.64	0.77	82.0	1.21	1.48
60	87.9	0.94	1.07	86.8	0.08	0.09
120	95.1	0.02	0.02	93.8	0.34	0.36

When powdered KOH is used, there are no significant difference in the PCBs removal at 10, 30 and 120 min. Neither there is a statistically significant difference comparing the results for the powdered KOH and as pellets at the 95.0% confidence level. The ultrasound application increases by DRE of PCBs 8 % at 10 min of reaction time. After a reactions time of 120 min no difference in DRE was measured when using ultrasound. The use of ultrasounds only initially leads to better efficiency compared to the results performed without ultrasounds.

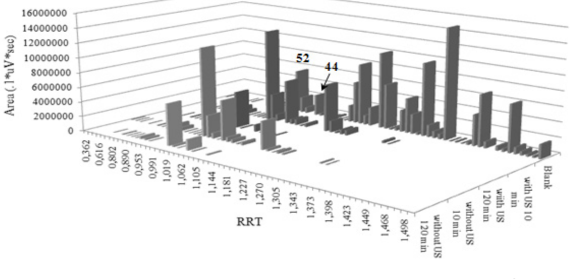

Figure 5. *Ultrasound effect: 3D chromatogram of PCBs dehalogenation in Sovtol-10 treated after 10 and 120 min.*

Analysis of the results also reveals that PCBs dehalogenation of Sovtol-10 involves all congeners (Figure 5). In particular, congeners of high molecular mass (penta- and hexachlorinated) disappear from the chromatogram after 30 minutes treatment. The less chlorinated congeners as 52 and 44 increase 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 and Singlenton (Brunelle and Singlenton, 1983). This fast dechlorination of the highly chlorinated PCBs is particularly favorable from the ecological environmental point of view since they are the most dangerous to the human body. To understand the mechanism of this reaction is required a detailed study of the kinetics of formation and destruction of each of these congeners.

The KPEG process with the experimental conditions used is also effective for the mixture of trichlorobenzene present in the Sovtol-10, attained its complete removal after 30 min of reaction.

CONCLUSIONS

The KPEG process was studied to remove TCBZ and PCBs from Sovtol-10. The effect of molecular mass was investigated for PEG 300, PEG 400 and PEG 600. PEG 400 gave the best results in terms of dehalogenation rate (DRE). PEG 300 was significantly less performance and results of PEG 600 were in between and did not differ significantly from results obtained with PG 300 or PEG 400.

Using PEG400 best results were obtained with a KPEG/oil weight ratio of 30 and a KOH/PEG mole ratio 2. The removal of PCBs is strongly affected by KPEG/oil weight ratio and KOH/PEG mole ratio, in this order.

The ultrasound application increases by DRE of PCBs 8 % at 10 min of reaction time. After a reactions time of 120 min no difference in DRE was measured when using ultrasound. PCBs dehalogenation in Sovtol-10 by the KPEG process is faster for penta - and hexachlorinated congeners that disappear from the chromatogram in all runs.

ACKNOWLEDGMENTS

This work has been financially supported by Project 7, Environmental Education and Development of Clean Technologies of VLIR Program. Besides, we would like to thank the Prof. Herman Van Langenhove from Ghent University, Faculty of Bioscience Engineering, Belgium, for his help and technical support.

BIBLIOGRAPHY

1. UNEP (2002). Chemical, PCB Transformer and Capacitor: From Management to Reclassification and Disposal. United Nations Environment Programme, Geneva, Switzerland.
2. UNEP (1999). Guidelines for the Identification of PCBs and Material Containing PCBs. United Nations Environment Programme, Geneva, Switzerland.

3. CITMA (Ciencia Tecnología y Medio Ambiente), (2004). Inventario Nacional de PCBs y Plaguicidas en Desuso. La Habana, Cuba.
4. AMIROVA, Z.; KATSNELSON, B. AND BERESNEVA, O. (2001). “Sovtol” (commercial PCBs) neutralization: toxicological assessment of technology. *Organohalogen Compounds,* 54:167-181.
5. WYRZYKOWSKA, B.; BOCHENTIN, I.; NOBUYASU, H.; ORLIKOWSKA, A.; FALANDYSZ, J., HORII, Y. AND YAMASHITA, N. (2006). Source determination of highly chlorinated biphenyl isomers in pine needles – Comparison to several PCB preparations. *Environmental Pollution,* 143(1), 46-59.
6. UNEP, (2004). Inventory of World – wide PCBs Destruction Capacity.
7. RAHUMAN, M.; PISTONE, L.; TRIFIRO, F. AND MIERTUS, S. (2000). Destruction Technologies for Polychlorinated Biphenys (PCBs), ICS-Union Publications. Proceedings of Expert Group Meetings on POPs and Pesticides Contamination: Remediation Technologies and on Clean Technologies for the Reduction and Elimination of POPs. 48 p.
8. YAK, H. K.; LANG, Q. AND WAI, C.M. (2000). Relative resistance of positional isomers of polychlorinated biphenyls toward reductive dechlorination by zerovalent iron in subcritical water. *Environ. Sci. Technol.,* 34, 2792–2798.
9. ANITESCU, G.; TAVLARIDES, L. L. (2000). Oxidation of Aroclor 1248 in supercritical water: a global kinetic study. *Ind. Eng. Chem. Res.,* 39, 583–591.
10. SAKO, T.; SUGETA, T.; OTAKE, K.; KAMIZAWA, C.; OKANO, M.; NEGISHI, A. AND TSURUMI, C. (1999). Dechlorination of PCBs with supercritical water hydrolysis. *Journal of Chemical Engineering of Japan,* 32(6),830-832.
11. WONG, K. H.; WONG, P. K. (2006). Degradation of polychlorinated biphenyls by UV-catalyzed photolysis. *Human and Ecological Risk Assessment,* 12(2), 259-269.
12. MATSUNAGA, A. AND YASUHARA, A. (2002). Reductive Dechlorination of Polychlorinated Biphenyls. *Journal of Environmental Chemistry,* 12(1), 33-43.
13. WU, W. H.; XU, J.; ZHAO, H. M.; ZHANG, Q. AND LIAO, S. J. (2005). A practical approach to the degradation of polychlorinated biphenyls in transformer oil. *Chemosphere,* 60(7), 944-950.
14. DE FILIPPIS, P., CHIANESE, A. AND POCHETTI, F. (1997), Removal of PCBs from Mineral Oils. *Chemosphere,* 35(8), 1659-1667.
15. LOPERA, P. E AND AGUIRRE, C. J. (2006). Purification of mineral insulating oil contaminated with polychlorinated biphenyls (PCB’s). Dyna 150, 75-88. Medellin, ISSN 0012-7353.
16. RYOO, K. S.; KO, S.; HONG, Y. P.; CHOI, J.; CHO, S.; KIM, Y. AND BAE, Y. J. (2007). Destruction and Removal of PCBs in Waste Transformer oil by a Chemical Dechlorination Process. *Bull. Korean Chem. Soc.,* 28(4), 520-528.
17. BRUNELLE, D. J. (1982). Method for removing polyhalogenated hydrocarbons from nonpolar organic solvent solutions. General Electric Company, US Patent 4,351,718, September 18.
18. DE FILIPPIS, P.; SCARSELLA, M. AND POCHETTI, F. (1999).Dechlorination of polychlorinated biphenyl: a kinetic study of removal of PCBs from mineral oil. *Ind. Eng. Chem. Res.,* 38, 380–384.
19. KAŠTÁNEK, F. AND KAŠTÁNEK, K. (2005). Combined decontamination process for waste containing PCBs. *Journal of Hazardous Materials,* B117, 185–205.
20. CAFISSI, A.; BEDUSHI, S.; BALACCO, V.; SACCHI, B. AND TRASATTI, S. P. (2007).Chemical dechlorination of polychlorinated biphenyls (PCBs) from dielectric oils*. Environ. Chem. Lett.,* 5, 101-106.
21. ZORRILLA, M.; VELAZCO, P.; VILLANUEVA, G. AND VAN LANGENHOVE, H. (2011).Partial validation of an analytical method for determination of polychlorinated biphenyls (PCBs) in transformer oil using gas chromatography and Aroclor 1254. *Afinidad,* 28(554), 341-347.
22. BRUNELLE, D.J; SINGLENTON, D. A. (1983). Destruction/removal of polychlorinated biphenyls from non-polar media. Reaction of PCB with poly (ethylene glycol)/KOH. *Chemosphere* 12, 183-196.