

Transformation of Polychlorinated Biphenyls (PCBs) into Non-Hazardous Products by Electron Beam Treatment

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This study is focused on investigating the influence of the parameters for dechlorination of polychlorinated biphenyls (PCB) using electron beam. The dechlorination process was studied using concentrated solutions of polychlorinated biphenyls. 2-propanol with/without water, ethanol, 1,2,3,4-tetrahydronaphthalin and tetrahydrofurane were used as solvents. The results of the research showed that the electron beam irradiation is an efficient dechlorination method in the presence of sodium hydroxide and 2-propanol. The presence of sodium hydroxide is mandatory for the efficiency of the dechlorination process. Water has a negative effect on the value of the degree of dechlorination. Higher temperatures (50-70°C) are needed to ensure a higher solubility of sodium hydroxide into 2-propanol.

Keywords: PCB; dechlorination; electron beam

Polychlorinated biphenyls (PCBs) were used to produce electric equipment such as transformers and capacitors, but also as additives for lubricants, hydraulic fluids and adhesives, due to their unique combination of properties: chemical inertness, resistance to heat, non-flammability, low vapour pressure and high dielectric constant. The problems with PCBs derive from their toxicity to humans and to the environment. PCBs are resistant to biodegradation and have negative effects on life forms even at very low concentrations because they bioaccumulate in fatty tissues.

The production of PCBs has been banned all over the world since 1998. In Romania, the use of oils containing PCBs (with higher concentrations than 50 ppm for volumes larger than 5 dmc) in equipment must be eliminated until the year 2010 [1]. Also, year 2028 was set as the time limit for the implementing of environmental sound management of all PCBs wastes.

In Romania there are large quantities of transformer oils containing PCBs, in storage. For the existent quantities, a friendly environmental process must be developed and implemented.

At present, the destruction and/or treatment methods of PCBs include two types of processes:

- combustion at high temperatures [3] - is the most used process to destroy PCBs. However, evidence of environmental and public health impact of incinerators has created strong public opposition to incineration;

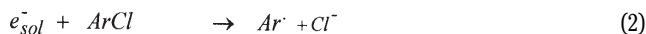
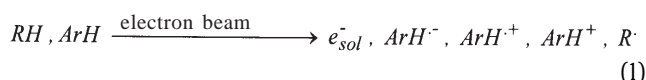
- physico-chemical processes - by which PCBs are transformed into environmentally friendly compounds or into reusable products such as biphenyl. The use of these technologies is limited because they imply the consumption of expensive reactive (metallic sodium) or severe temperature and pressure conditions (wet oxidation in supercritical conditions) [3-6].

A non-combustion method, which seems to be effective for the treatment of PCBs, is the radiolysis of PCBs using electron beam.

Radiolysis with electron beam (EB) can be achieved in an aqueous environment [7] with PCBs dispersed in an

emulsion form (low reaction rates) or in an organic environment (high reaction rates) [8-11].

The chemical transformations are generated by the interaction between the "target" molecules and the reactive species generated by the attack of electrons on the substrate (1-6) [12].



To stabilize the formed aromatic radicals, a compound with the ability to donate easily hydrogen atoms is needed. Such compounds are alcohols. Also, basic compounds (sodium and potassium hydroxide) are needed in order to prevent the oxidation of Cl⁻ ions to Cl₂ [13].

The aim of our study is to investigate the radiolytic dechlorination of PCBs with electron beam in the presence of NaOH and solvents.

Experimental part

PCBs (with an average number of chlorine atoms of 5), 2-propanol, ethanol, 1,2,3,4-Tetrahydronaphthalin, tetrahydrofurane (THF) and NaOH were of analytical grade and used without further purification. The dechlorination reactions were carried out in 100 mL vessels with magnetic stirrer and covered with aluminum foils. The samples were prepared as described in the table 1. The samples were irradiated using a linear electron beam

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Table 1
CHARACTERISTICS OF THE SAMPLES SUBJECTED TO IRRADIATION WITH ELECTRON BEAM

Sample	Volume of sample [mL]	Solvent	Concentration of PCB [g/L]	NaOH quantity [g]	Absorbed dose of irradiation [kGy]	Temperature [°C]
pcb-01	45	100% 2-propanol	32,6	0,3	40	65
pcb-02	45	100% 2-propanol	32,6	1,5	40	65
pcb-03	45	100% 2-propanol	32,6	3,0	40	65
pcb-04	45	100% 2-propanol	48,9	3,0	40	65
pcb-05	45	100% 2-propanol	16,3	3,0	40	65
pcb-07	45	67% 2-propanol + 33% water	32,6	3,0	40	65
pcb-08	45	50% 2-propanol + 50% water	32,6	3,0	40	65
pcb-09	45	33% 2-propanol + 67% water	32,6	3,0	40	65
pcb-10	45	100% ethanol	32,6	3,0	40	65
pcb-11	45	100% tetraline	32,6	3,0	40	65
pcb-12	45	100% THF	32,6	3,0	40	65
pcb-13	45	100% 2-propanol	32,6	1,5	32	30
pcb-14	45	100% 2-propanol	32,6	1,5	32	65
pcb-15	45	100% 2-propanol	32,6	1,5	32	75

accelerator ALIN-10 (6.23MeV, 100W). The analyses of reagents and reaction products were performed with a Buck Scientific 910 Gas Chromatograph equipped with two detectors: FID (sensitive to all organic compounds) and DELCD (sensitive only to chlorinated compounds). Helium was used as carrier gas. Products were separated on a Stabilwax capillary column (MXT-1 0.53 x 60M, I.D. 5.0u, DB1).

Results and discussion

The dechlorination process was evaluated by computing two parameters:

-conversion of PCB into biphenyl :

$$CB(\%) = \frac{[Biphenyl]_{final}}{[PCB]_{initial}} \times 100 \quad (7)$$

- degree of dechlorination:

$$DD(\%) = \frac{[PCB]_{initial} - [PCB]_{final}}{[PCB]_{initial}} \times 100 \quad (8)$$

where:

$[Biphenyl]_{final}$ is the concentration of biphenyl obtained after the irradiation process;

$[PCB]_{initial}$ is the initial concentration of PCBs;

$[PCB]_{final}$ is the final concentration of PCB after the treatment with electron beam.

Effect of solvent type

2-propanol, 1,2,3,4-tetrahydronaphthalin (tetraline), ethanol, and tetrahydrofurane (THF) were used as solvents for the dechlorination of PCBs. Figure 1 shows that 2-propanol ($DD=91.4\%$) is the best solvent for dechlorination of PCBs using electron beam. This observation is in agreement with results from other researches [7-9, 12, 13]. When using 1,2,3,4-tetrahydronaphthalin as solvent, the dechlorination occurs with much lower value of DD (68.8%) compared to 2-propanol. In solvents like THF and ethanol the value of DD is very low, less than 6%. The solvents have the same behaviour concerning the values of the conversion to biphenyl (CB).

Effect of PCBs initial concentration

Concentrated solutions of PCBs, with concentrations of 16.3, 32.6 and 48.9 g/l (0.05, 0.1 and 0.15 M) were used in order to observe the effect of PCBs initial concentration on their dechlorination. At concentrations lower than 32.6 g/L, the degree of dechlorination and conversion to biphenyl are high ($CB > 89\%$ and $DD > 95\%$). At 48.9 g/L initial

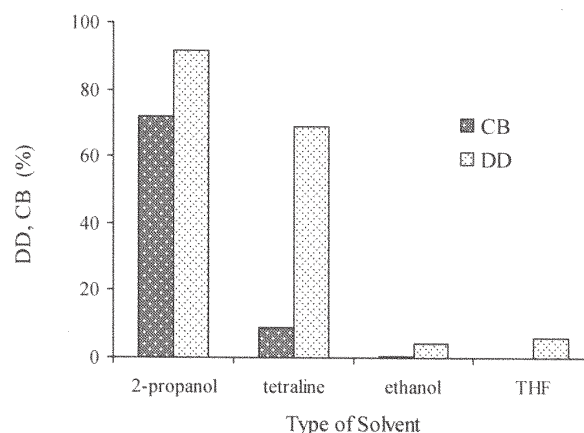


Fig. 1. Influence of the solvent type on dechlorination of PCBs. (Dose of irradiation = 40kGy, $[PCB]_{initial} = 32.6$ g/L, NaOH = 1.5g, temp. 65°C)

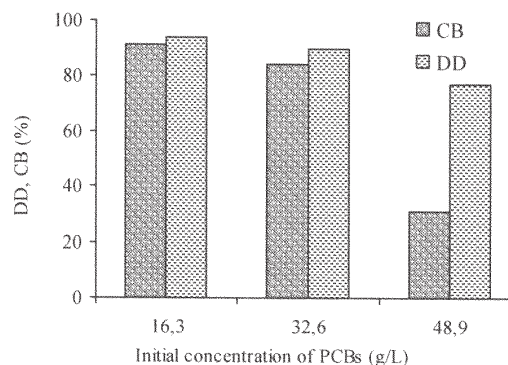


Fig. 2. Influence of PCB initial concentration on dechlorination of PCBs. (Dose of irradiation = 40kGy, solvent - 2-propanol, 3g NaOH, temp. 65°C)

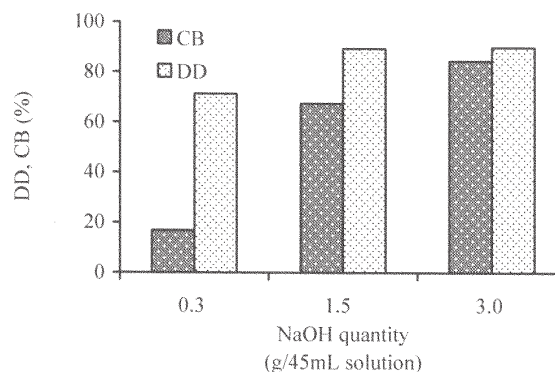


Fig. 3. Influence of NaOH amount on dechlorination of PCBs. (Dose of irradiation = 40kGy, solvent - 2-propanol, $[PCB]_{initial} = 32.6$ g/L, temp 65°C)

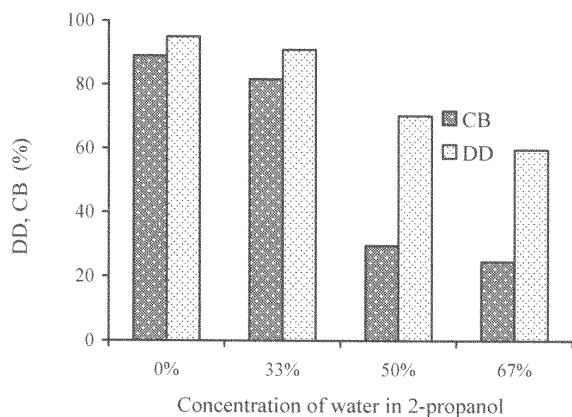


Fig. 4. Influence of the 2-propanol - water composition on dechlorination of PCBs. (Dose of irradiation = 40kGy, $[PCB]_{initial} = 32.6 \text{ g/L}$, NaOH = 3g, temp. 65°C)

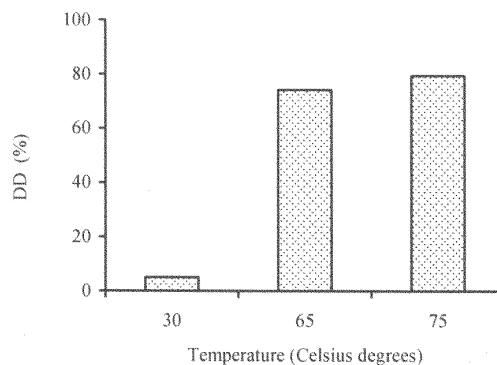


Fig. 5. Influence of the temperature on dechlorination of PCBs. (Dose of irradiation = 32 kGy, $[PCB]_{initial} = 32.6 \text{ g/L}$, NaOH = 1.5 g, 45 ml 2-propanol)

concentration of PCBs, the degree of dechlorination decreases to a value of 75% (fig. 1).

Effect of NaOH amount

Three different quantities of NaOH were used to study their effect on the degree of dechlorination. Assuming that the PCB molecules have an average number of chlorine atoms equal to 5, the initial concentration of the PCBs is 32.6 g/L, and the quantities of NaOH are 0.3, 1.5 and 3g, the following molar ratio NaOH/Chlorine are obtained: 0.35, 1.76 and 3.5. As can be seen in figure 3, when the molar ratio NaOH/Chlorine is less than one, the dechlorination degrees are low. These results are consistent with the fact that NaOH must be added in sufficient quantity to ensure the capture of all chlorine ions that are released in solution by cleavage of the C-Cl bonds.

Effect of amount of water added in 2-propanol

The effect of water on dechlorination of PCBs was studied by mixing water with 2-propanol (water concentrations of 0, 33, 50 and 67%). The best results in terms of degree of dechlorination and conversion of PCBs into biphenyl were obtained when 2-propanol was free of water, as shown in figure 4. When the solvent was pure 2-propanol, the dechlorination had the maximum values, i.e. CB = 92% and DD = 96%. When low quantities of water (<33%) are added to the solvent, the dechlorination still has high values, CB = 81%, DD = 92%. Higher concentrations of water – 50 and 66% - lead to a high decrease in the values of DD and CB.

The influence of the temperature

The degree of dechlorination has a strong dependence on the temperature (fig. 5). At normal temperature (30°C) the degree of dechlorination has a low value due to the fact that the solubility of NaOH into 2-propanol has also a low value. At higher temperatures (50,70°C) the solubility of NaOH into 2-propanol increases and the degree of dechlorination increases as well.

Conclusion

The aim of the researches was to study the influence of the most important factors that affect the dechlorination of PCBs by irradiation with electron beam: the type of

solvent used, the quantity of NaOH to be added, the temperature of the process.

Based on the experiments that were carried out, were observed the following aspects:

- the dechlorination of PCBs occurs with the highest values of DD and CB when 2-propanol is used as solvent and as hydrogen donor;
- NaOH must be present in sufficient amount to capture all chlorine anions released in solution by cleavage of C-Cl bonds;
- the presence of large amounts of water into the solvent has a negative effect on the degree of dechlorination;
- the temperature at which dechlorination is performed is very important because the solubility of NaOH into 2-propanol increases with the increase of the temperature.

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Manuscript received: 24.11.2008