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RADIATION DEGRADATION OF PCBS IN SEDIMENTS: COMPARISON BETWEEN TWO METHODS

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Abstract. Polychlorinated biphenyls are toxic compounds which have accumulated in river sediments in Eastern Slovakia. Bioaccumulation could cause even cancer. Radiation degradation with electrons is new and perspective method to dechlorinate PCBs in sediment matrix. We tested the influence of two difference chemical pretreatments and electron irradiation on PCB contaminated sediments.

Keywords: PCBs, $CuSO_4 \cdot 5\,H_2O$, electron beam, irradiation, sediment.

1. Introduction

Polychlorinated biphenyls (PCBs) were used as additives for lubricants, adhesives in transformers and capacitors. Chemical and physical properties are following: inertness, resistance to heat, non-flammability and high dielectric constant. PCBs were produced all over the world, but the production was banned in 1998. In Slovakia the producer of PCBs was the chemical company Chemko Strážske Ltd. Probably, a part of produced PCBs was released to the environment through the Strážske channel. Over the years the sediments in surrounding area of the chemical factory (the Laborec river and the Zemplínska Šírava lake) were contaminated with PCBs. The contamination in Strážske channel exceeds 400-times the limit, which is allowed in Slovakia for the sediment matrix. Behavior of PCBs in the soil is strongly dependent on the basic soil properties. Great attention has been devoted to the PCBs problem in soil contamination in United Kingdom, USA, Canada, Japan and Sweden. In Slovakia, the monitoring of PCBs was carried out, but specific solution has not been given [1, 2].

Irradiation of PCBs with electron beam has not been used very often and it is new technology, which could provide non-combustion method for PCBs degradation in soil sediments. Water is a product produced during radiolysis and it is also presented in soil samples contaminated by PCBs. The presence of oxygen during the irradiation process has negative effect to radiolytic dechlorination of PCBs contaminated sediments. Soil matrice is rich of organic and anorganic compounds. The dechlorination yields of PCBs were reduced, due to the organic content of the soil, which could compete with required free radiacal reactions [3].

Due to the hydrophobicity of PCB, organic-rich sediments could be easily solubilized in water with the use of organic co-solvent. During the radiolysis, hydroxyl radicals react with PCBs through the addition to the phenyl rings to produce various isomeric PCB radicals (ArCl(OH)) [4].

2. PCBs Degradation with Electron Beam

2.1. Simple PCBs irradiation with electron beam

Electrons interact at high energies predominantly by elastic scattering by bound electrons. The chemical changes in PCBs occur through secondary reactions of radiolytic species with PCBs (Fig. 1). Hydrogen atoms and hydroxyl radicals react with PCBs via addition to the phenyl rings, producing PCBs radicals. PCBs that remain in association with or within the sediment phase may undergo dechlorination by thermalized electrons [5, 6].

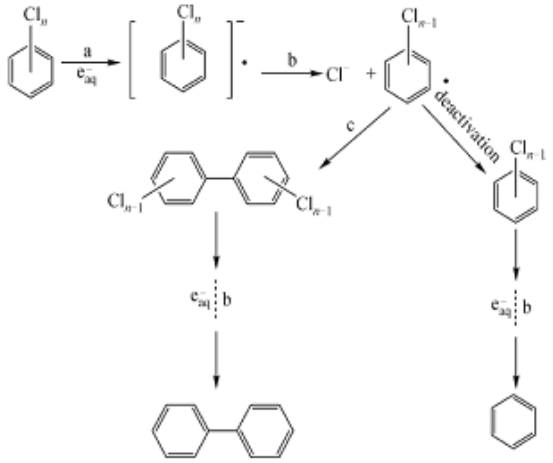

Figure 1. Mechanism of radiation dechlorination of PCBs [5].

2.2. Chemical pretreatment and electron irradiation of PCBs

Due to the fact that PCBs are hydrophobic compounds, it is required to use co-solvent. Very often is used as co-solvent propan-2-ol, which assist with the dechlorination process of PCBs.

It is essential to stabilize the formed aromatic radicals, that´s why it is need the compound which could easily donate hydrogen atoms, which could stabilize the aromatic cycle.

Such compounds are alcohols. Trifan et al. [7] tested the influence of propan-2-ol, ethanol, THF and electron beam irradiation for PCBs destruction in transformer oils and solutions (Fig. 2). The best results in terms of degree of dechlorination and convertion of PCBs into biphenyls were obtained when propan-2-ol was used. Also, NaOH or KOH are needed for basic environment, which prevent the oxidation of Cl^- ions to Cl_2 [7].

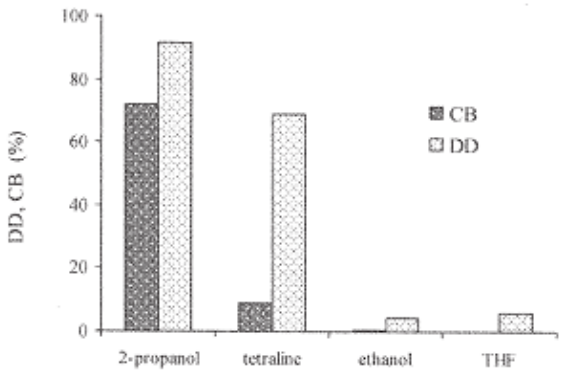

Figure 2. Influence of the different solvent type on dechlorination of PCBs (Dose of irradiation = 40 kGy, [PCBs] = 32.6 g dm^{-3}, NaOH = 1.5 g, temp. 65 °C, CB = conversion of PCB into biphenyl, DD = degree of dechlorination) [7].

3. Methodology

Our study was aimed to compare our method of chemical pretreatment and electron irradiation of samples to results obtained by colleagues from South Korea, who chemically pretreated and irradiated the samples of soil contaminated by PCB from Slovakia. They used lower energy of electrons, 2.5 MeV. After irradiation at EB-Tech to a dose of 400 kGy the total concentration of PCBs in soil samples decreased by more than 53 % (Fig. 3).

3.1. Chemical pretreatment and electron irradiation of PCBs

In our experiment we used 5 MeV electrons and chemical pretreatment: $CuSO_4 \cdot 5\,H_2O$ and K_2CO_3. 20 g of wet sediment was mixed with 2 g of K_2CO_3, which provided stable pH $\sim$ 10 which is essential to keep Cl^- anions during reaction. Our samples were rich

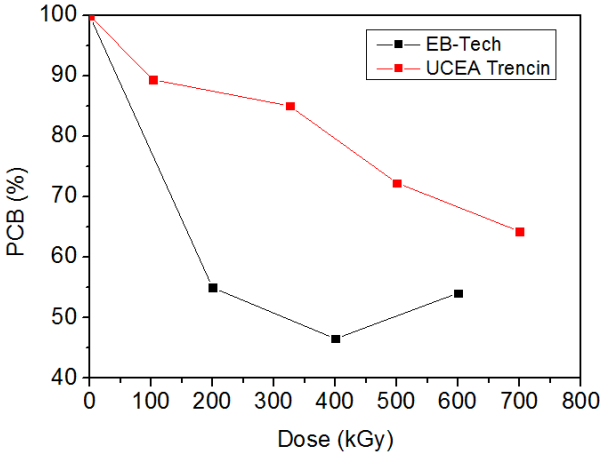

Figure 3. PCB concentration in soil sample as a function of dose irradiated by EB-Tech vs. UCEA Trenčín.

of water and water molecules are competitive compounds in the process of PCBs irradiation. Due to this fact, 1 g of $CuSO_4 \cdot 5\,H_2O$, as a water scavenger, was added to the sample. Samples were irradiated in the test tubes by electron accelerator with scanning beam UELR-5-1S at the University Centre of Electron Accelerators (UCEA) of the SMU in Trenčín.

We applied doses: 100, 300, 500 and 700 kGy to chemical pretreated samples. Determination of PCB in sediment was done at the Department of Toxic Organic Pollutants of the SMU in Bratislava. Isotope-dillution method by using of ^{13}C-labeled standard solution was used. About 0.15 g of dried homogenized irradiated sediment was Soxhlet extracted with toluene (8 hours). An 1/50 aliquot of the extract was applied on multi-layer silica column (44 % sulphuric acid/potassium hydroxide/silver nitrate on activated silica gel). The PCB extract was carefully concentrated and after dilution coupled with high-resolution mass spectrometry (HRGC). The initial total content of PCBs was intended to 1842.69 ng g^{-1}.

4. Results and Discussion

Fig. 3 shows that with increasing dose, the total amount of PCB congeners is decreasing at our experiments. At dose 700 kGy the PCB degradation falls to 46 %. From the Fig. 4, it is seen, that PCBs groups are decreasing with increasing dose, but also the increase occurs, when higher chlorinated PCBs are converting to lower ones. For environmental purposes, it is required to degrade PCB with higher efficiency. Our methodology (UCEA) was less efficient than the methodology of EB-Tech, as we reached only 46 % decrease of total amount of PCBs at 700 kGy in comparison to their 53 % decrease at 400 kGy. It could be caused by energy of electrons and also by the chemical pretreatment method. For this purpose we are going to find better chemical pretreatment methodology in our future research.

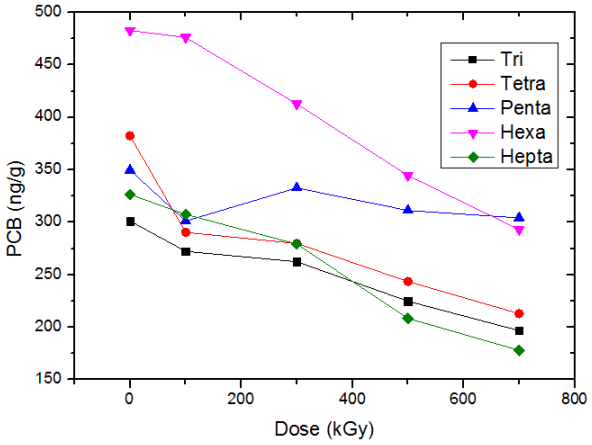

FIGURE 4. Concentration of PCB groups in soil samples chemically pretreated by $CuSO_4 \cdot 5\,H_2O$ and K_2CO_3 as a function of increasing dose of electrons.

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