

APPLICATION OF IONIZING RADIATION FOR DEGRADATION OF ORGANIC POLLUTANTS IN WATERS AND WASTES

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Abstract: Anthropogenic organic pollutants of natural waters discharged to environment in municipal and industrial wastes can be removed by the use of various technologies. Among numerous chemical technologies of advanced oxidation, a particular effectiveness is exhibited by methods based on the use of γ radiation or electron beam that was already demonstrated both in batch processes and in flow installations and also in a mobile treatment station. Their application is based on a unique interaction of oxidizing hydroxyl radicals and/or reducing hydrated electrons with organic pollutants. Both these reactive species are formed in a very rapid process of radiolysis of water and can be utilized in different ways in processes of degradation of organic pollutants depending on applied conditions. The results of own research on application of this technology for removal of selected chlorophenols and herbicide 2,4-D from aqueous solutions are given with detailed analytical data on the yield of processes and their products in different irradiation conditions. The optimization of these processes using both γ and electron beam irradiation has been carried out in regards of magnitude and rate of the irradiation dose, chemical conditions of the process, presence of scavengers and changes of toxicity of irradiated solutions.

Numerous studies have shown that irradiation using high energy electron beam or γ radiation from ^{60}Co sources can be efficient for the destruction of several classes of hazardous organic compounds, such as halogenated alkyl hydrocarbons, aromatic hydrocarbons and chlorobenzenes (1). The efficiency of removal of organic chemicals from contaminated water depends on radiation dose, initial concentration of contaminant, pH and turbidity. A descriptive, empirical model was developed for estimating the removal of selected organic compounds as a function of these factors and also for estimating the dose required to meet specific treatment objectives (2). The developed model, however, can overstate the removal of compounds sensitive to particular radicals in waters with higher concentrations of scavengers.

Phenol and chlorophenols are widely distributed at low concentrations in natural waters. They have detrimental effects on water quality and are toxic for aquatic life. Radiolytic degradation of phenol, and especially chlorophenols for environmental purposes has not focused so far much attention in the literature. The aim of this study was to identify the products of radiolytic degradation of various chlorophenols and pesticide 2,4-D and to determine the effect of the various experimental factors on removal and influence of natural matrix of river water on the effectiveness of radiolytic degradation.

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The efficiency of radiolytic degradation of phenol and chlorophenols was monitored mainly by reversed-phase HPLC and ion-chromatography, but also by GC-MS. The products of radiolytic degradation were preconcentrated using solid-phase extraction. Bioindicative measurements of toxicity based on bioluminescence of bacteria *Vibrio fischeri* were carried out using Microtox M500 Toxicity Analyzer MICROBIX. The determination of total organic content (TOC) was performed using Shimadzu TOC-500 analyzer.

The results obtained for irradiation of aqueous solutions of various chlorophenols without scavengers demonstrate efficient removal of all examined species by irradiation doses from 1 to 2 kGy. The most difficult to decompose is simple phenol, which is also a product of radiolysis of all chlorophenols except pentachlorophenol, occurring largest concentrations (up to several ppm). Doses up to 2.0 kGy have not decomposed it completely. Degradation of chlorophenols in synthetic aqueous solutions takes place almost completely at 0.2 kGy dose, however, for river water matrix containing scavengers such as carbonates or oxygen it requires a larger dose. For the same dose used for degradation of higher chlorophenols in river water, smaller amounts of difficult to decompose phenols are produced.

More detailed studies on effect of various factors on radiolytic degradation have been carried out for 2,4-dichlorophenol (2,4-DCP) (3, 4), one of the most frequently occurring chlorophenolic pollutant in the environment and product of decomposition of numerous organic biocides. At doses not exceeding 1 kGy, the yield of decomposition essentially depends on initial concentration of 2,4-DCP. For 50 ppm 2,4-DCP, only 40% has been decomposed, and a dose 10 kGy is needed for complete decomposition. The efficiency of radiolytic degradation is additionally decreased in the presence of scavengers such as nitrate. The presence of 20 ppm nitrate at 1 kGy dose results in decrease of degradation yield of 20 ppm 2,4-DCP as much as 60%, and complete degradation in such conditions requires 20 kGy dose. It was found, that even 20 kGy dose does not cause total mineralization of 2,4-DCP at 20 ppm level. According to earlier suggestions (5), dehalogenation of 4-chlorophenol leads to formation of di- and trihydroxybenzenes, and then to opening of aromatic ring and formation of various carboxylic acids. A similar mechanism can be expected in case of 2,4-DCP and the presence of several carboxylic acids was found in this study in ion-chromatography measurement of irradiated 2,4-DCP solutions. At doses above 10 kGy the presence of formic and acetic acids were found as main products in irradiated samples. Such species as oxalate, muconate or chlorine oxoanions have not been found on the level detected by ion-chromatography.

The fundamental purpose of radiation treatment of polluted waters or wastes is not only decomposition of particular species, but first of all a decrease of total toxicity of these solutions. In this stage of the study, additional investigations were initiated to examine toxicity using bioluminescence test Microtox. As a function of applied dose up to 20 kGy, the changes of toxicity of 2,4-DCP solutions were examined with and without addition of other substances or laboratory wastes from Institute of Nuclear Chemistry and Technology spiked with 20 ppm 2,4-DCP. At 20 ppm 2,4-DCP level, a complete reduction of toxicity has been obtained at 10 kGy dose, while for 50 ppm 2,4-DCP solution a certain residual level of toxicity was found even at 20 kGy dose. The presence of nitrate decreases the reduction of toxicity with increase of dose. Both in the absence of nitrate, and especially in its presence at low radiation dose up to 1 kGy, a certain initial increase of toxicity has been found (at 50 ppm nitrate even about 60%). This can be explained by the formation at low doses of polyhydroxybenzenes, much more toxic against

bacteria used in Microtox than 2,4-DCP. For instance the toxicity of hydroquinone is about two orders of magnitude higher than 2,4-DCP (6). The broadening of chromatographic diagnostics of radiolytic degradation of 2,4-DCP with TOC and toxicity measurements allows additional conclusions on this method of water and waste treatment. Because of side effects of various scavengers and different toxicity of various compounds formed during radiolysis, a doses estimated for effective radiolytic degradation of given pure chemical species usually requires several times increase in practical applications.

2,4-dichlorophenoxyacetic acid (2,4-D) is a common herbicide widely used in agriculture, on pastures and lawns, in parks and for protection of rail roads. In living organisms, as well as in natural environment, as result of metabolic processes of 2,4-D, various toxic and cancerogenic chloro-organic compounds are formed, mostly 2,4-dichlorophenol. In Poland and in several other countries also, one of severe environmental problems is a storage of unused and unwanted expired pesticides including large amounts of 2,4-D. They are stored in concrete tombs and their leakage to soil and underground waters has been already reported because of aging and gradual destruction of all protective materials used. A search for appropriate technology of their destruction is an important environmental issue. The aim of this environmentally oriented work was to study the effect of various experimental factors on effectiveness of radiolytic degradation of 2,4-D and toxicity changes of irradiated solutions.

At 50 mg/l level of 2,4-D the complete radiolytic decomposition of substrate in aerated neutral solutions requires at least 5 kGy dose, but complete release of inorganic chloride occurs at about 7.5 kGy dose. This is due to transient formation of different other chloroorganic compounds such as mono- and dichlorophenols. Using ion-chromatography with conductivity detection for determination of other ionic products than chloride, as main products (at doses up to 20 kGy), formate and acetate were found. A complete mineralization of aqueous 2,4-D solutions requires, however, much larger doses. Experiments performed with electron beam irradiation and infrared TOC determination have shown that in 20 mg/l 2,4-D solution at 200 kGy, only 50% mineralization occurs. In 100 mg/l 2,4-D solutions irradiation with 20 kGy dose results in 10% decrease of TOC, only. The yield of 2,4-D degradation can be substantially reduced in the presence of other competing scavengers of hydroxyl radicals. A strong indirect scavenging effect was found for nitrate present in irradiated 2,4-D solutions. In the presence of 50 mg/l nitrate, decomposition of 50 mg/l 2,4-D requires a 10 kGy dose which is twice larger dose than in the absence of nitrate. A similar increase of needed dose was found in the presence of 400 mg/l bicarbonate in neutral irradiated solutions of 2,4-D.

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