RADIATION INDUCED DECOMPOSITION OF 1,2-DICHLOROETHANE IN WATER SYSTEMS

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Abstract

The paper presents the results of the studies regarding the influence of dose rate and some scavengers (bicarbonates, nitrates, sulfates) on the efficiency of radiation degradation of 1,2-dichloroethane (DCE) - water system. Experiments were performed on laboratory scale with synthetic aqueous samples at the concentrations ranging from 10^{-4} to 10^{-3} mol.l^{-1} of target compound and 10^{-4} – 10^{-3} mol.l^{-1} for the scavengers. All samples were air saturated. GC measurements showed that DCE was completely decomposed in the range of doses 2-4 kGy, but many various degradation products containing different number of organic bound chlorine were found. Radiation degradation of these products occured at the dose range 16-32 kGy depending on the DCE concentration. Inhibition effect of scavengers increases in the order nitrates, bicarbonates and sulfates, respectively. Based on the results obtained, study of radiation purification of real waste water systems in large volume pilot plant is planned.

Introduction

In the field of environmental technologies (especially waste water and ground water purification), increasing attention is focused on processes involving formation of free radicals. Radiolytic degradation of target toxic species (mainly various chlorinated organic compounds) is one of these processes. During irradiation of water various free radicals (OH, H, e_{aq}) are formed. These products may react with the most of organic compounds present in water systems. Efficiency of the process depends not only on the amount of free radicals (applied dose), but also on their consumption in parallel reactions, caused by the presence of other components in irradiated system. Presence and quantity of these components significantly affect economy of treatment processes. Another important effect with radiation processing was found: Application of gamma rays (radionuclide sources – low dose rates) leads to the greater radiation yields G (number of decomposed molecules per 100 eV absorbed energy) than the utilization of electron beam (EB) processing (high dose rates, but low electrons penetration in water). Advantage of instrumental electron sources (treatment of larger quantities of water at reasonable conditions), on the one hand, is limited by less effectivity i.e. less economy, than gamma irradiation, on the other hand.

The aim of this study was investigate influence of irradiation conditions (dose rate effect) and influence of some scavengers (bicarbonates, nitrates, sulfates) on the efficiency of radiation degradation of 1,2-dichloroethane (DCE) - water system.

Methods

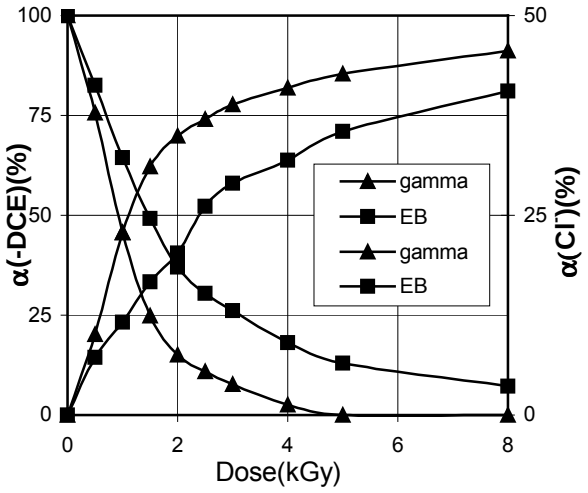
The irradiated samples were prepared by dilution of DCE - saturated water solution in distilled water or in solutions of relevant scavengers. The study was performed in the presence of oxygen in irradiated systems. The experiments were conducted in the concentration range 10^{-4} – 10^{-3} mol.l^{-1} of target compound and 10^{-4} – 10^{-3} mol.l^{-1} of scavengers. Samples were bottled to the glass ampoules (20 ml), sealed and irradiated. Electron irradiation (4,5MeV) was performed using linear pulse accelerator UR-4-1200 Tesla (dose rate 1,5 kGy/s). Gamma irradiation was performed using Gammacell 220 (dose rate 1,5 kGy/hod). Doses were applied in the range 0-32 kGy. Dosimetry was ensured by means of Fricke dosimeter. Course of DCE degradation was monitored using gas chromatography (GC), (CHROMPACK model CP 9002, ECD, DATA-APEX integrator). Amount of inorganic forms of chlorine was determined by selective chloride electrode.Course of DCE degradation was characterized by

degree of degradation α(-DCE)=100.c/c_0, where c and c_0 are actual and initial concentration of DCE and by degree of dechlorination $\alpha(Cl^-)$=100.c_{Cl^-} / 2c_0 where c_{Cl^-} represents actual concentration of Cl^- ions.

Results

Comparison of gamma and EB irradiation (dose rate effect). The degree of degradation α(-DCE) decreases with increasing dose for gamma irradiation more sharply then for EB irradiation – FIG.1. α(-DCE) of about 10 % was reached at the dose 2,5 kGy for gamma and 8 kGy for EB. The degree of dechlorination $\alpha(Cl^-)$ reaches the value of about 50 % at the dose 8 kGy with both gamma and EB irradiation. The rest of organic bound chlorine remains in the solution as the degradation products, especially dimers containing different number of chlorine. Degradation of these products occured at the doses 16-32 kGy, depending on the DCE concentration (determined by GC).

Figure 1: Dependence of the degree of degradation α(-DCE) and dechlorination $\alpha(Cl^-)$ on the dose D(kGy) for gamma and EB irradiation. (Initial concentration of DCE 10^{-3} mol/l.)



Initial radiation yields G_i(-DCE) for EB irradiation were calculated from the dependence of DCE concentration on the dose - FIG.2. G_i(-DCE) increases with increasing initial concentration of DCE - FIG.3 and reaches value of about 1,6 $100^{-1}eV^{-1}$. Radiation degradation proceeds as a reaction of DCE with primary products of water radiolysis.

Figure 2: Dose dependence of DCE and Cl^- concentration on initial DCE concentration

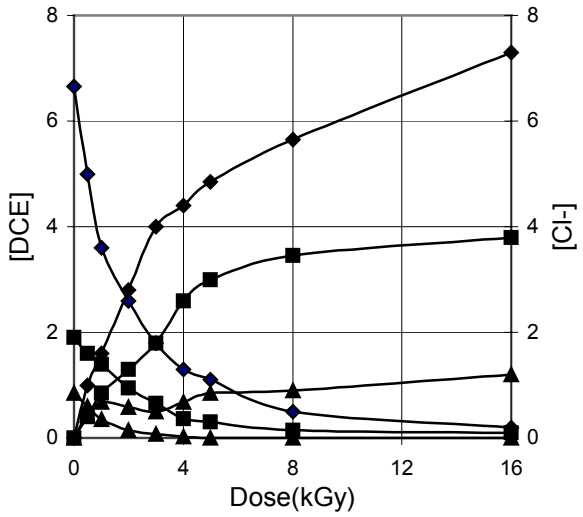
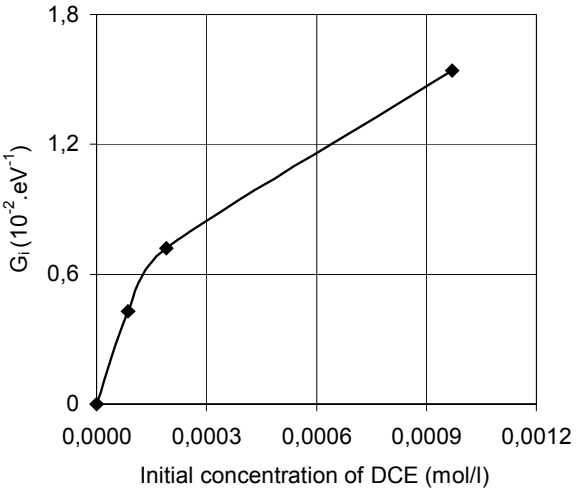
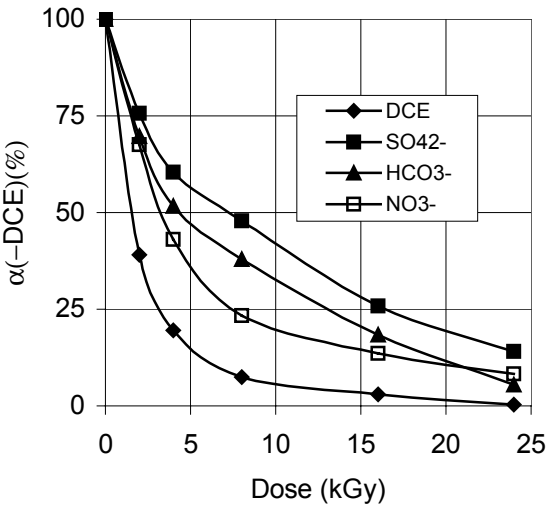


Figure 3: Dependence of the initial radiation yield G_i(-DCE) on the initial concentration of DCE



The results shown in FIG.4 indicate that presence of selected scavengers (10^{-3} mol/l) significantly influences the efficiency of radiation degradation of DCE in water. Inhibition effect increases in the order nitrates, bicarbonates, sulphates. Lower concentration of nitrates (10^{-4} mol/l) leads to the decrease of the scavengers influence - FIG.5.

Figure 4: Influence of the SO_4^{2-}, HCO_3^- and NO_3^- ions (10^{-3} mol/l) on the degree of DCE degradation



Conclusions

Irradiation of the DCE-water system by accelerated electron leads to approximately double decrease of the degradation effectiveness, when compared with gamma irradiation

Practically total DCE degradation may be achieved with the doses 4 – 8 kGy

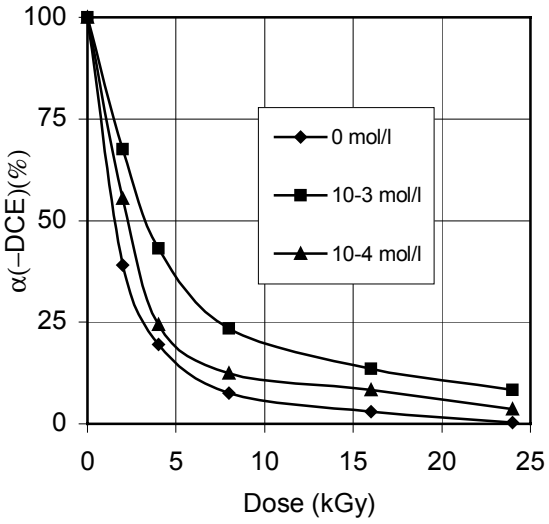
About 50 % of organic bound chlorine remains in the solution as the degradation products. Degradation of these products may be performed at the doses 16-32 kGy depending on the DCE concentration

G_i(-DCE) increases with increasing initial concentration of DCE and reaches value of about 1,6 100^{-1} eV^{-1}.

Inhibition effect was found when SO_4^{2-}, HCO_3^-, NO_3^- ions are present. Inhibition effect increases in the order nitrates, bicarbonates, sulfates. This influence decreases with decreasing scavengers concentration.

Based on the obtained results, study of radiation purification of real waste water systems in large volume pilot plant is planned.

Figure 5: Influence of the NO_3^- concentration on the degradation of DCE



Acknowledgements
This study was performed under the auspices of the Grant Agency of the Czech Republic, Contract No. 104/98/0466.

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