

Efficiency of organic compounds removal by electron-beam irradiation in presence of high metal concentration

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Abstract

The high efficiency of electron-beam irradiation process in removing organic compounds from industrial effluents has been established. The actual chemical, textile, pharmaceutical and industrial effluents contain a high level of organic and inorganic compounds. In this study, the organic compounds removal was evaluated in the simulated industrial effluents, using electron-beam irradiation. The samples were prepared by adding Na, Cl, Ca, P, K, Si, Al, Zn, Fe, Mn, Cd, Pb, As and Hg elements and dichloroethane, methylisobutylketone, toluene, xylene, benzene, chloroform, tetrachloroethylene and trichloroethylene organic compounds. The samples were irradiated in a batch system and delivered irradiation doses were 20 and 50 kGy. The free metals sample showed a more than 99% organic compounds removal at 20 kGy irradiation doses. The same level of removal had reached at 50 kGy irradiation doses for sample-containing metals.

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Keywords: Electron-beam processing; Organic compounds removal; Metals analysis

1. Introduction

The oxidation process using OH radicals has high efficiency in destroying organic compounds. The interaction of ionizing radiation with water is the most simple and efficient method for generating OH radicals. The reactive species formed by the water irradiation are solvated electron (e-aq), H atoms and radical hydroxyl OH. This reactive species reacts with organic compounds in the water inducing their decomposition (Nickelsen and Cooper, 1992).

A program to study toxic and refractory organic pollutants removal and degradation and pathogenic microorganisms disinfecting from wastewater,

has been developed at Nuclear Research Institute, IPEN (Duarte et al., 2002, 2000; Borrelly and Sampa, 2000). This program has been applied to local industries and governmental wastewater treatment plants.

In the industrial effluents, the organic compounds faced a great problem due to their deposition and having remained in the environment for a long time. This fact has caused serious damage to human health, animals and plants. Moreover, the toxic metals such as Cr, Mn, Ni, Fe, Zn, Cu, Pb, Cd, Hg and As are frequently found in industrial effluents and usually they are mixed with organic compounds.

This paper presents the metal presence influence in organic compounds degradation in the simulated industrial effluents samples, using electron-beam irradiation process.

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2. Experimental

2.1. Sample preparation

Typical simulated industrial effluents samples were prepared from dichloroethane, methylisobutylketone, toluene, xylene, benzene, chloroform, tetrachloroethylene and trichloroethylene standard solutions. In addition, Na, Cl, Ca, P, K, Si, Al, Zn, Fe, Mn, Cd, Pb, As and Hg elements were added from certified standard solutions. The high-metal concentration sample was named A and the low one as B. In the same way, a free metal sample was prepared, this one named C. All the inorganic and organic compositions are given in Table 1.

2.2. Chemical analysis

An X-ray fluorescence spectrometer (Rigaku Co, model RIX3000) was used for elemental determination. 1.0 ml of the solution was deposited onto a 1.0 cm diameter filter paper. A sensitivity curve was obtained from B to U pure oxides, using fundamental parameters method (Lachance and Claisse, 1995; Wheller, 1998; Scapin, 2002).

The organic compounds determination, before and after irradiation processing, was performed using a gas chromatograph coupled with a mass spectrometer (CG/MS -Shimadzu, model CGMS QP-5000). The Helium gas carrier, DB5 capillary column and 1.0 μ l injection volume were used for analysis (Duarte et al., 2002).

2.3. Sample processing

The samples were irradiated with 1.5 MeV electrons, provided by the IPEN's Electron Beam Facility (Dynamitron from Radiation Dynamics Inc.). The irradiation was performed in a batch system using Pyrex glass vessels and delivered irradiation doses were 20 kGy and 50 kGy. The irradiation parameters of electron-beam accelerator were 4.0 mm sample width, 112 cm (94.1%) scan and 6.72 m/min solution stream velocity.

3. Results and discussion

The free metal sample C showed a removal of more than 99.9% at 20 kGy irradiation doses for organic compounds, except for methylisobutylketone and benzene, a 99.4 and 99.3% removal, respectively. At

Table 1
Initial organic and inorganic composition in simulated samples

Organic compounds	Sample C (mg l ⁻¹)	Sample A (mg l ⁻¹)	Sample B (mg l ⁻¹)
Methylisobutylketone	124.24	123.06	122.97
Dichloroethane	84.95	83.67	85.39
Chloroform	145.12	140.36	141.19
Trichloroethylene	138.91	135.15	139.74
Tetrachloroethylene	130.57	129.58	127.73
Benzene	77.18	75.13	74.28
Toluene	82.65	79.72	78.14
Xylene	76.86	75.45	76.84
Total	860.48	842.12	846.28
<i>Element</i>			
Fe	—	128.3 ± 1.5	35.9 ± 0.3
Cu	—	11.5 ± 0.3	4.4 ± 0.1
Cr	—	58.5 ± 0.5	13.7 ± 0.3
Se	—	7.48 ± 0.3	7.2 ± 0.1
Al	—	374.7 ± 8.9	92.3 ± 1.7
Na	—	652 ± 31	229 ± 12
K	—	321 ± 5	116 ± 2
Ca	—	1355 ± 22	449 ± 4
Mn	—	12.9 ± 0.3	4.3 ± 0.1
Ni	—	13.5 ± 0.3	4.6 ± 0.1
Zn	—	59.9 ± 0.9	22.8 ± 0.2
As	—	4.8 ± 0.2	2.1 ± 0.2
Cd	—	3.9 ± 0.8	11.7 ± 0.1
Hg	—	3.3 ± 0.1	6.8 ± 0.1
Pb	—	6.5 ± 0.5	5.9 ± 0.4
Total	—	3013 ± 39	1006 ± 13

50 kGy, all the organic compounds showed a removal of more than 99.9%. The high metal sample A showed organic compounds removal less than low metal sample

B. At 20 kGy, sample A showed a removal 44.69–73.31% and at 50 kGy a 84.1–99.9% removal. Further, sample B showed a 52.86–86.12% and 90.2–99.9%

Table 2

Organic compounds removal (%) after electron-beam processing in simulated industrial effluent, at 20 and 50 kGy absorbed doses

Organic compounds	Organic compounds removal (%)					
	20 kGy			50 kGy		
	Sample C	Sample A	Sample B	Sample C	Sample A	Sample B
Methylisobutylketon	99.4	44.69	52.86	99.9	85.6	90.4
Dichloroethane	99.9	49.00	62.07	99.9	94.4	98.1
Chloroform	99.9	62.70	69.41	99.9	91.6	92.4
Trichloroethylene	99.9	64.37	72.99	99.9	98.4	99.3
Tetrachloroethylene	99.9	73.31	86.12	99.9	97.0	99.9
Benzene	99.3	58.57	78.89	99.9	84.1	90.2
Toluene	99.9	60.21	63.99	99.9	98.0	99.4
Xylene	99.9	64.94	75.48	99.9	99.9	99.9

Sample C: free metal; Sample B: 1006 ± 13 mg metal ions l^{-1} ; Sample A: 3013 ± 39 mg metal ions l^{-1} .

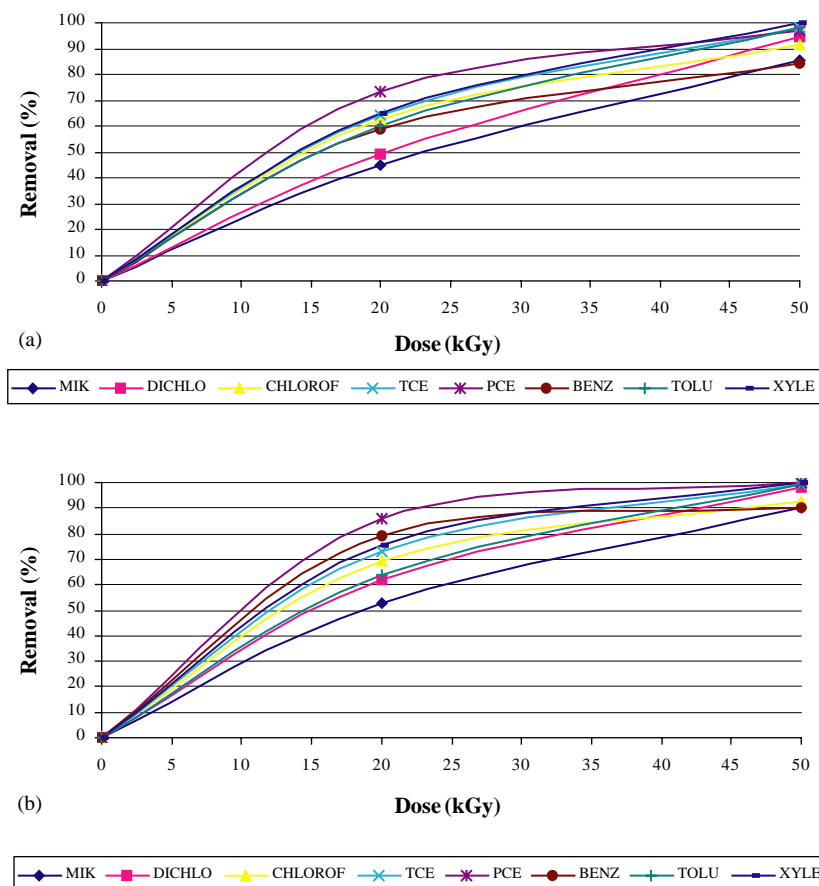


Fig. 1. Organic compounds removal, at 20 and 50 kGy irradiation doses, for samples A and B, containing 3013 ± 39 and 1006 ± 3 mg metal ions l^{-1} , respectively.

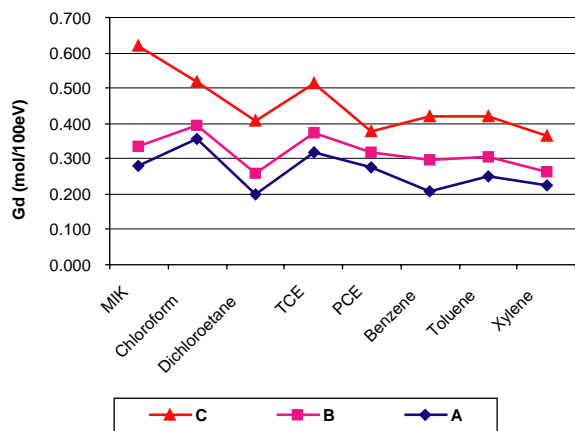


Fig. 2. Organic compounds $G_d \times 10^3$ (mol/J) values for free metal sample C and samples A and B, containing 3013 ± 39 and 1006 ± 3 mg metal ions L^{-1} , respectively, at 20 kGy irradiation doses.

removal, respectively at the same irradiation doses. All the results are given in Table 2 and Fig. 1. The organic compounds methylisobutylketone, dichloroethane, chloroform and benzene showed more restriction for their degradation in metal presence. The metal presence leads to necessarily higher irradiation doses for the organic compounds removal, once a part of the primary radicals of water radiolysis is consumed by metal ions.

The organic compounds removal, after irradiation, is described as the destruction of Gd value and is defined by solute disappearance in aqueous solution. Usually, it is experimentally determined, using the following equation (Nickelsen and Cooper, 1992):

$$G_d = \Delta RD N_A / D (6.24 \times 10^{15}) = \text{mol J}^{-1},$$

where ΔRD is the change in organic solute concentration (mol l^{-1}) at a given dose, D is the dose (kGy), and $6.24 \times 10^{15} \text{ kGy}$ in 100 eV l^{-1} converting constant and N_A is Avogadro's number. The Gd values were obtained for the organic compounds at 20 kGy an absorbed dose and the results are given in the Fig. 2. The Gd values showed behaviour similar to the removal values. The free metal sample C showed the highest Gd values

followed the samples B and A, containing, 1006 ± 3 and 3013 ± 39 mg metal ions L^{-1} respectively.

4. Conclusion

The efficiency in destroying organic compounds by the electron-beam process is affected in the metal presence. Formerly one part of the reactive specimens produced by water radiolysis is consumed by the metal ions. The selected organic compounds irradiation-induced degradation proves to be an efficient process even in the metal ions presence.

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