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Advanced oxidation process by electron-beam-irradiation-induced decomposition of pollutants in industrial effluents

C.L. Duarte*, M.H.O. Sampa, P.R. Rela, H. Oikawa, C.G. Silveira, A.L. Azevedo

Institute for Energetic and Nuclear Research-IPEN-CNEN/SP, Radiation Technology Center-TE, P.O. Box 11049-CEP 05499-970, São Paulo, Brazil

Abstract

Electron-beam irradiation considered on advanced oxidation process induces the decomposition of pollutants in industrial effluent. Experiments were conducted using a radiation dynamics electron beam accelerator with 1.5 MeV energy and 37 kW power. The effluent samples from an industrial complex were irradiated using the IPEN's liquid effluent irradiation pilot plant. The experiments were conducted using one sample from each of eight separate industrial units and five samples of a mixture of these units. The physical–chemical characterization of these samples is presented. The electron beam irradiation was efficient in destroying the organic compounds delivered in these effluents, mainly, chloroform, dichloroethane, methyl isobutyl ketone, toluene, xylene and phenol. The necessary dose to remove 90% of the most organic compounds from industry effluent was 20 kGy. The removal of organic compounds from this complex mixture was explained by the destruction G value (Gd) that was obtained for those compounds with different initial concentrations and was compared with literature.

Keywords: Advanced oxidation process; Electron beam accelerator; Organic compound destruction; Industrial wastewater treatment

1. Introduction

The variables involved in the environment's preservation and recovery are numerous. One such problem results from damage by hazardous chemicals and the raw materials used and discharged by industries.

Organic compounds have been a problem of environmental pollution because, once in the environment, they may cause problems in human health, animals and plants. Traditional treatment methods are not efficient in removing theses compounds and the advanced oxidation process (AOP) such as electron-beam irradiation is a promising technology in the destruction of these pollutants in industrial effluent (Duarte et al., 2000), decreasing this toxicity (Borrely and Sampa, 2000).

This paper presents a study of the electron-beam treatment, using effluents from an industrial complex, in order to evaluate the effectiveness of this technology to degrade organic compounds in effluents with various physical–chemical characteristics and organic compound concentration.

The effluents were from an industrial complex composed of eight separated production units namely: Intermediary Organic Products (IOP), Poly Vinyl Acetate (PVA), Resins (RES), Especial Products (SP), Detergents (DET), Sulfonation (SULF), Thiodan (THIO) and Azodyes (AZO). Each unit delivered its effluent to the small treatment station, where they were mixed and the pH was neutralized.

The IPEN's pilot plant used to irradiate these samples was set up to treat wastewater and industrial effluents and is described elsewhere (Sampa et al., 1995). The absorbed dose is measured by a calorimetric system using a temperature transducer type, WCOTT, Wire Current Output temperature transducer—Intensil, GE-AD590, that allows to obtain the average absorbed doses in real time (Rela et al., 2000).

*Corresponding author.
E-mail address: clduarte@net.ipen.br (C.L. Duarte).

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2. Experimental

One effluent sample from each of eight separate industrial units (POI, PVA, RES, SP, DET, SULF, THIO and AZO) and five samples from the mixed effluent (ME1–ME5), were irradiated at IPENs Pilot Plant (Fig. 1). The variables that have been examined are the absorbed radiation dose, physical–chemical characterization and organic solute concentration.

A special truck with 10001 capacity was used to transport the liquid wastes from the industry to the IPEN's electron beam pilot plant and they were irradiated using the following doses: 5, 10, 15, 20, 30 and 50 kGy. The sample stream had a medium flow rate of 30 l/min; the electron beam with 1.5 MeV energy and the current was varied from 1.2 to 10.6 mA in order to obtain the desired doses.

The physical–chemical characterization was performed according to the Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1997).

The irradiation treatment efficiency was evaluated by the chemical analysis of the duplicate samples before and after irradiation. The following analyses were performed:

- chloroform and dichloroethane analysed by a gas chromatograph, model CG-90, with electron capture detector (ECD), after pentane extraction;
- toluene, xylene, phenol and methyl isobutyl ketone analysed by a gas chromatograph and mass spectrometry, Shimadzu model GCMS-QP 5000, after pentane extraction.

3. Results and discussion

The physical–chemical characterization of these samples is presented in Table 1. From these results, the complexity and differences of these effluents are obvious. The pH ranged from 1.40 (IOP) to 12.80 (AZO), chemical oxygen demand (COD) was from 466 (THIO) to 29,000 mgO_2/l (DET), sulfates from 70 (SP) to 22,780 mg/l (AZO), oil and greases from 21 (ME5) to 285 mg/l (DET) and the suspended solids from 58 (SULF) to 494 mg/l (DET).

The concentrations of the most important pollutants found in the study, chloroform, dichloroethane, methyl isobutyl ketone, toluene, xylene and phenol, are presented in Table 2. The necessary dose to removal 90% of these contaminants are represented in italic, for the most compounds and a 20 kGy dose of effluents was enough.

The removal of these organic compounds after irradiation was explained by the destruction G value (Gd) that is defined by the disappearance of the solute in aqueous solution and is determined experimentally using (Nickelsen and Cooper, 1992)

$$\mathrm{Gd} = \Delta \mathrm{RD}\, N_A / D\, (6.24 \times 10^{15})(\mathrm{mol/J}),$$

where ΔRD is the change in organic solute concentration (mol/l) at a given dose, D is the dose (kGy), 6.24×10^{15}

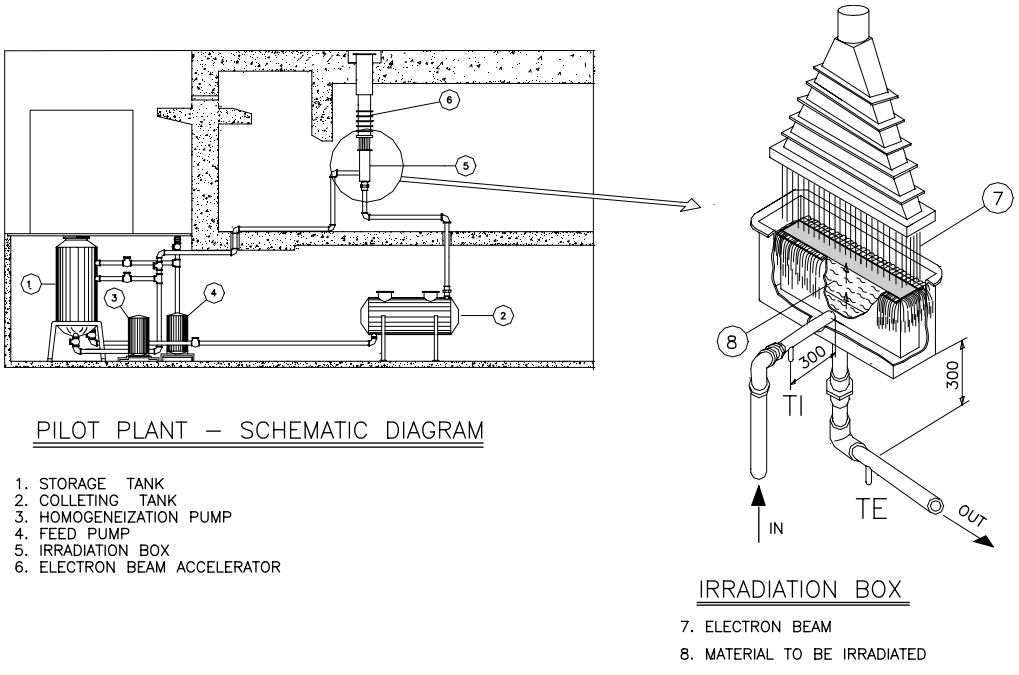

Fig. 1. Schematic diagram of the Pilot Plant for liquid wastewater treatment.

Table 1
Physical chemical characterization of the studied industrial effluent[a]

Sample	pH	COD (mgO_2/l)	Sulfates (mg/l)	Oil & grease (mg/l)	Suspended solids (mg/l)
Mixed effluent (ME)					
1	9.60	951	584	100	182
2	7.83	1728	482	na	353
3	8.12	1254	352	na	254
4	8.29	na	na	na	151
5	7.93	2315	1644	21	181
Separated units					
POI	1.40	8349	18,080	43	92
PVA	4.17	2524	250	65	110
Resins	12.20	1618	117	279	118
Special products	6.72	2912	70	78	276
Detergents	7.61	29,000	302	285	268
Sulfonation	6.66	1320	110	94	58
Thiodan	7.54	466	233	69	64
Azodyes	12.80	1844	22,780	56	494

[a] na—not analyzed.
Standard deviation: pH = ±5%; COD = ±10%; suspended solids = ±20%.

Table 2
Mainly organic compounds and its concentration in the various studied effluents[a]

Sample	Dichloro ethane (mg/l)	Chloroform (mg/l)	Methyl isobutyl ketone (mg/l)	Toluene (mg/l)	Xylene (mg/l)	Phenol (mg/l)
Mixed effluent (ME)						
1	87.9 (*20*)	0.8 (20)	na	6.3 (20)	9.3 (*15*)	2.8 (*50*)
2	2.6 (*20*)	0.2 (20)	na	1.1 (20)	1.5 (*20*)	3.2 (*50*)
3	0.2 (*20*)	<0.010	na	1.8 (20)	0.1 (*20*)	0.1 (*50*)
4	51.3 (*20*)	0.5 (20)	24.2 (20)	13.1 (20)	24.3 (*30*)	2.3 (*50*)
5	65.7 (*30*)	0.8 (20)	34.0 (20)	25.3 (10)	27.2 (*10*)	1.9 (*50*)
Separated units						
SP	<0.010	<0.010	na	<0.10	<0.10	0.6 (50)
RES	<0.010	<0.010	na	6.2 (*50*)	<0.10	1.6 (50)
PVA	<0.010	<0.010	na	0.3 (*50*)	<0.10	1.9 (50)
DET	<0.010	<0.010	na	0.3 (*50*)	0.2 (*50*)	1.1 (50)
IOP	28.4 (*50*)	<0.010	na	<0.10	<0.10	0.6 (50)
SULF	0.1 (*50*)	<0.010	na	<0.10	<0.10	<0.10
THIO	1.8 (*30*)	<0.010	na	<0.10	<0.10	0.4 (50)
AZO	11.4 (*50*)	0.2 (20)	na	<0.10	2.1 (*20*)	<0.10

[a] na—not analyzed.
( )—Necessary dose to 90% removal.

is the constant to convert kGy into 100 eV/l, and N_A is Avogadro's number.

For Gd calculation in this study, the minimum dose required to detect 90% removal of each pollutant was considered. The Gd values so obtained are shown in Table 3.

The phenol results of Gd values in the samples ME3, RES, and AZO, were negative, indicating a formation at the lower doses. These increases suggest that phenol is formed as a byproduct of other aromatic compounds, as reported by others (Getoff, 1991; Nickelsen and Cooper, 1992).

The Gd values obtained in this work for chloroform, toluene and xylene are comparable to those presented in the literature (Table 4), when less complex samples were used as aqueous solutions, and, in some situations, only one kind of organic compound is presented.

4. Conclusion

The electron-beam irradiation was shown to be an efficient process for destroying chloroform, dichloroethane, methyl isobutyl ketone, toluene, xylene and

Table 3
Obtained Gd $\times 10^3$ (mol/J) values for mainly organic compounds[a]

Sample	Dichloroethane	Chloroform	Methyl isobutil keton	Toluene	Xylene	Phenol
Mixed effluent (ME)						
1	288.9 (*15*)	4.3 (*15*)	*	38.3 (15)	391.0 (2)	2.6 (15)
2	18.5 (*5*)	1.8 (*5*)	*	14.2 (5)	18.2 (5)	0.0 (5)
3	1.0 (*20*)	0.8 (*20*)	*	6.4 (20)	0.6 (15)	−0.6 (30)
4	226.8 (*20*)	2.9 (*10*)	101.7 (20)	64.8 (10)	42.2 (50)	4.6 (50)
5	265.1 (*20*)	1.8 (*5*)	150.0 (20)	256.2 (30)	121.0 (10)	3.7 (50)
Separated units						
RES	*	*	*	10.8 (30)	*	−3.4 (30)
PVA	*	*	*	0.5 (30)	*	1.4 (30)
DET	*	*	*	0.1 (30)	0.5 (30)	1.0 (30)
POI	20.0 (*30*)	*	*	*	*	1.0 (30)
SULF	0.4 (*30*)	*	*	*	*	*
THIO	4.6 (*30*)	*	*	*	*	0.5 (20)
AZO	35.2 (*30*)	*	*	5.91 (30)	74.3 (30)	−3.4 (30)

[a]( )—Radiation dose (kGy) considered for Gd calculation.
*—organic compound which concentration in the effluent was under the detection limit.

Table 4
Comparison of obtained Gd values (mol/J) obtained in this work with those from literature for organic compounds in different initial concentration (Ic) and matrix

Ic (mg/l)	Gd $\times 10^3$	Ref.	Ic (mg/L)	Gd $\times 10^3$	Ref.
Chloroform			Toluene		
0.09	**5.3**	Cooper et al. (1993)	6.07	**318.0**	Kurucz et al. (1995)
0.83	*4.3*	ME1(this work)	1.00	**68.0**	Nickelsen and Cooper (1992)
0.18	*1.8*	ME2 (this work)	6.30	*38.0*	ME1 (this work)
0.23	*0.8*	ME3 (this work)	1.10	*14.2*	ME2 (this work)
0.51	*2.9*	ME4 (this work)	1.8	*6.4*	ME3 (this work)
0.83	*1.8*	ME5 (this work)	13.1	*64.8*	ME4 (this work)
			25.3	*256.2*	ME5 (this work)
			6.2	*10.8*	RES
			0.3	*0.5*	PVA
			0.1	*0.1*	DET
			26.1	*5.9*	AZO
Xylene			Phenol		
1.00	**34.0**	Nickelsen and Cooper (1992)	56.40	**525.9**	Kurucz et al. (1995)
1.50	**18.0**	Nickelsen and Cooper (1992)	9.40	**964.1**	Getoff (1991)
9.30	*391.0*	ME1 (this work)	2.80	*2.6*	ME1 (this work)
1.50	*18.2*	ME2 (this work)	3.20	*0.0*	ME2 (this work)
0.13	*0.6*	ME3 (this work)	0.04	*−0.6*	ME3 (this work)
24.30	*42.2*	ME4 (this work)	2.32	*4.6*	ME4 (this work)
27.20	*121.0*	ME5 (this work)	1.92	*3.7*	ME5 (this work)
0.25	*0.5*	DET	1.60	*-3.4*	RES
32.54	*74.3*	AZO	0.40	*1.4*	PVA
			1.10	*1.0*	DET
			0.30	*1.0*	IOP
			0.10	*0.5*	THIO
			7.10	*−3.4*	AZO

phenol in complex mixtures. The Gd values obtained in this work for chloroform, toluene and xylene are comparable with those presented in the literature when less complex samples were used.

The results showed that this technology might be an efficient and promising treatment of real industrial effluents.

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