DECOMPOSITION OF ORGANIC POLLUTANTS IN INDUSTRIAL EFFLUENT INDUCED BY ADVANCED OXIDATION PROCESS WITH ELECTRON BEAM

C.L. DUARTE, M.H.O. SAMPA, P. R. RELA, H. OIKAWA, C.G. SILVEIRA

INSTITUTE FOR ENERGETIC AND NUCLEAR RESEARCH –IPEN –CNEN/SP
Radiation Technology Center – TE
P.O. Box 11049 – CEP 05499-970 - São Paulo BRAZIL
E-mail – clduarte@net.ipen.br

ABSTRACT

Advanced Oxidation Process (AOP) by electron beam irradiation 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. Experiments were conducted using samples from a Governmental Wastewater Treatment Plant (WTP) that receives about 20% of industrial wastewater; with the objective of use the electrons beam technology to destroy the refractory organic pollutants. Samples from WTP main Industrial Receiver Unit influent (IRU), Coarse Bar Screens effluent (CBS), Medium Bar Screens effluent (MBS), Primary Sedimentation effluent (PS) and Final Effluent (FE) were collected and irradiated in the electron beam accelerator in a batch system. The electron beam irradiation showed be efficient on destroying the organic compounds delivered in these effluents mainly dichloroethane, methilisobutylketon, toluene, xylene, phenol. To remove 90% of the most organic compounds was necessary a 20 kGy to 50 kGy dose for IRU, CBS and MBS and 10 kGy to 20 kGy for PS and FE. The removal of organic compounds from this complex mixture were described by the destruction G value (Gd) that were obtained for those compounds in different initial concentration and compared with literature.

KEYWORDS

Advanced Oxidation Process, electron beam accelerator, organic compound decomposition, industrial wastewater treatment

INTRODUCTION

Organic compounds has been a great problem of environmental pollution because most of them are deposited to environment and stayed there for a long time causing problems to the human health, animals and plants. The traditional methods are not efficient on removing theses compounds and Advanced Oxidation Process (AOP) by electron beam irradiation is a promissory technology that induces the destruction of these pollutants.

This paper presents a study about the organic compounds degradation by electron beam irradiation, 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 Suzano Wastewater Treatment Plant (WTP) has a processing capacity of 1.5m^3/s, receiving domestic and industrial wastewater from five different cities. About 30% of wastewater in this plant is from chemical, pharmaceutical, textile and dyes industries origin (Duarte 2000, Duarte 1997).

EXPERIMENTAL

Five steps of the conventional treatment of the WTP were selected for sampling: Industrial Receiver Unit influent (IRU), Coarse Bar Screens effluent (CBS), Medium Bar Screens effluent (MBS), Primary Sedimentation effluent (PS) and Final Effluent (FE). The IRU and CBS receive exclusively effluent from industrial origin. The samples were collect following the schedule: four sampling each two hours from each step (composed samples), biweekly during 8 months.

The samples were irradiated at the IPEN's Electron Beam Facility with a 1.5 MeV Dynamitron from Radiation Dynamics Inc. The irradiation was performed in a batch system using Pyrex glass vessels and the delivered doses were: 5kGy, 10kGy, 15kGy, 20kGy, 30kGy and 50kGy. The irradiation parameters of electron beam accelerator were: 4.0 mm sample width, scan of 112cm (94.1%) and stream velocity of 6.72 m/min.

To physical chemical characterization of the samples were performed analysis of the Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Volatile Solids dried at 550 ^{0}C and Total Solids dried at 103-105^{0}C; these parameters were analyzed according to the Standard Methods for the Examination of Water and Wastewater [1]. Analyses of Total Organic Carbon (TOC) were performed too, using Total Organic Carbon Analyzer, Shimadzu, model TOC 5000A.

The qualitative and quantitative analysis of organic compounds were performed by mass spectrometry after penthane extraction using the Gas Chromatograph associated to Mass Spectrometer Shimadzu model GCMS-QP 5000 in the following conditions:

- Capilar column DB5,
- Mass detector operation in electron impact mode (EI), using 1.50 kV of ionising voltage and temperature 250°C,
- Interface temperature 240°C and continuo operation mode (SCAN),
- 1 uL of injection volume.

The incomplete oxidation of the pollutants can result in the formation of organic acids, which can be considered as a by-product of the radiation process. This was evaluated by the Chromatographic analysis of organic acids using the High-Performance Liquid Chromatograph - HPLC-Shimadzu LC10. The analysis were performed after solid sedimentation, using:

- UV-Vis detector SPD-6A, Shimadzu Co, 210 nm wavelength,
- Column Shim-pack SCR-102H, Shimadzu Co
- Perchoric acid 10 mM as mobile fase, 0.8 mL/min. flow, column temperature 60oC and 20 uL injection volume

RESULTS AND DISCUSSION

The physical chemical characterization of these samples is presented in Table 1. Samples from IRU and CBS are mainly of industrial origin, resulting high COD and BOD, in the MBS point occur the reception of domestic wastewater then the organic load increase, that can be seen by the TOC values presented in the Table 1, but this

organic load represents proteins, carbohydrates, oils and greases but not toxic organic pollutants.

The pH of the samples from different collect point didn't present significant variations.

The minimal and maximum concentrations of the main organic compound in each collect point are presented in the Table 2. The steps that presented more toxic organic compounds were IRU and CBS and the main organic compounds found were dichloroethane, toluene, xylene, methilisobutylketon and phenol.

By the results presented in the Table 2, it is possible to see the decrease of organic compounds concentration in the PS step, may be because the organic compounds are deposited adsorbed in the solid particulates.

The removal of these organic compounds after irradiation were described by the removal percentage in each irradiation (Table 3) and by the destruction G value (Gd) that is defined by the disappearance of the solute in aqueous solution and is determined experimentally using the following equation (Nickelsen, 1992):

$$Gd = \Delta RDN_A/D(6.24 \times 10^{15}) = \text{mol } J^{-1}$$

Where:

ΔRD is the change in organic solute concentration (mol L^{-1}) at a given dose,

D is the dose (kGy),

6.24×10^{15} is the constant to convert kGy in 100 eVL^{-1}, and

N_A is Avogadro's number.

For Gd calculation in this study it was considered the maximum dose of higher removal detected, in different initial concentration. The Gd values so obtained are showed in Table 4.

Samples from the IRU, CBS and MBS steps presented the highest concentrations of organic compounds then it was necessary doses from 20kGy to 50kGy to remove 90%, while samples from PS needed doses from 10kGy to 20kGy and FE needed 10kGy doses. Although the MBS samples presented lower concentrations of organic

compounds than IRU and CBS steps (Table 2), the necessary dose to remove 90% of the main organic compounds was the same, it may be because the highest organic load concentration that compete to the oxidation by radiation. This can be seen by the Gd value obtained for MBS that is lower than Gd value obtained for IRU and CBS in all studied organic compounds.

The Gd values obtained in this work for toluene and xylene are compatible with those presented in the literature (Table 5), when less complex samples as aqueous solutions were used, and in some situations only one kind of organic compound is presented. It was not found any data of removal for methylisobutylketon and dichloroethane in the literature to compare.

Phenol presented negative results on removal in the steps IRU, CBS and MBS when irradiated at 10kGy and 20kGy doses, that is because it was observed an increase in its concentration when lower doses were applied. These increases suggest a phenol molecule formation as a byproduct of others aromatic compounds, because this Gd of phenol presented lower values than the others studied organic compounds.

As byproduct after irradiation it was found oxalic acid, tartaric acid and formic acid at mg/L concentrations in all steps of WTP.

By the pictures presented in the Figure 1 it can be seen an example of the color differences on samples from each step, these color change every day depending on the production line of the industries. It is important to find out that the Final Effluent remain colored even after biological treatment and the radiation contributed to the clarification in all steps of WTP.

CONCLUSION

The electron beam irradiation showed high efficiency on destroying organic compounds mainly dichloroethane, methylisobutylketon, toluene, xylene and phenol present in the complex samples from industrial effluent. The Gd values obtained in this work for chloroform, toluene and xylene are compatible with those presented in the literature when less complex samples were used.

By the clarification of the samples the decomposition of the corants is deduced, making possible the reuse of treated wastewater.

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Table 1 - Average of the conventional parameters in different steps of WTP during the studied time

SAMPLE	COD (mgO_2/L)	BOD (mgO_2/L)	TOC (mg/L)	Total Solid (mg/L)	T. Volatile Solid (mg/L)	pH
IRU	1362 ±445	854 ±318	330 ±74	3599 ±982	624± 237	8.3 ±0.3
CBS	1044 ±547	545 ±183	212±79	2648 ±1025	552±224	7.4 ±0.2
MBS	663 ±126	315 ±68	465 ±278	2691 ±690	583 ±328	7.5 ±0.4
PS	713 ± 396	410 ±266	428 ±245	1333 ±377	450 ±284	7.8 ± 0.5
FE	153 ±56	28 ±15	185 ±133	632 ±372	203 ±109	7.8 ±0.4

Table 2 - Minimum and maximum concentration of the main organic compounds present in different steps of WTP

ORGANIC COMPOUNDS	UNA	GG	GM	DP	EF
	Concentração (mg/L)				
Methilisobutyiketon	1.00 - 22.30	1.30 - 7.85	0.22 - 3.52	0.98 - 2.69	<dl
Dichoroethane	1.30 - 25.70	1.10 - 16.00	1.86 - 5.58	0.98 - 3.69	0.40 - 1.85
Toluene	0.80 - 12.00	1.00 - 72.00	0.51 - 2.57	0.85 - 1.60	0.32 - 1.97
Xylene	1.50 - 67.00	0.50 - 25.70	1.22 - 3.51	0.96 - 1.82	0.12 - 4.00
Phenol	3.20 - 7.80	3.20 - 16.40	0.96 - 2.00	0.86 - 1.60	0.50 - 0.86

dl = detection limit = 0.03 mg/L
Variation = 10%

Table 3 - Removal (%) of the main organic compounds present in different steps

Organic Compound (mg/L)	Dose (kGy) 10	20	50
INDUSTRIAL RECEPTION UNIT			
Methilisobutylketon	70.1 ± 8,5	95.1 ± 8,9	99.9 ± 0,0
Dichoroethane	59.3 ± 8.3	92.1 ± 9,2	99.8 ± 0,2
Toluene	46.3 ± 7,0	76.2 ± 8,1	88.4 ± 3,3
Xylene	53.4 ± 8.3	82.7 ± 9.5	96.6 ± 5,5
Phenol	-17.3 ± 7,7	-0.7 ± 4.8	52.6 ± 2,0
COARSE BAR SCREEN			
Methilisobutylketon	79.9 ± 8,6	93.3 ± 10.4	98.4 ± 1.5
Dichoroethane	55.6 ± 8,5	95.3 ± 8.9	99.9 ± 0.0
Toluene	70.6 ± 8.2	80.6 ± 7.2	95.0 ± 6.6
Xylene	60.9 ± 8,1	86.3 ± 7.2	99.2 ± 8.1
Phenol	-52.9 ± 9.7	-55.0 ± 9.4	59.5 ± 5.1
MEDIUM BAR SCREEN			
Methilisobutylketon	89.1 ± 8.4	97.8 ± 0.9	99.9 ± 0.1
Dichoroethane	85.0 ± 6.7	93.4 ± 7.1	99.1 ± 0.0
Toluene	71.7 ± 9.0	76.1 ± 6.8	95.3 ± 0.0
Xylene	89.1 ± 9.8	99.9 ± 0.0	>99.9
Phenol	-35.2 ± 9.8	-25.9 ± 6.5	59.5 ± 3.5
PRIMARY SEDIMENTATION			
Dichoroethane	87.8 ± 1.7	>99.9	
Toluene	88.4 ± 2.4	>99.9	
Xylene	92.0 ± 3.5	>99.9	
Phenol	73.3 ± 7.7	>99.9	
FINAL EFFLUENT			
Dichoroethane	99.2 ± 0.4	>99.9	
Toluene	97.4 ± 0.6	>99.9	
Xylene	99.9 ± 0.0	>99.9	
Phenol	42.5 ± 0.3	>99.9	

Table 4 - Obtained Gd x 10^3 (mol/J) values for mainly organic compounds

Sample	Dichloroethane	Methyl isobutyl keton	Toluene	Xylene	Phenol
RUI	33.9 (25)	25.6 (10)	15.0 (20)	51.6 (20)	5.2 (50)
CBS	36.4 (20)	17.6 (10)	69.4 (20)	29.5 (20)	10.7 (50)
MBS	27. 1 (10)	14.0 (10)	8.0 (10)	9.7 (10)	4.8 (2)
PS	23.1 (5)	9.2 (5)	7.9 (10)	4.8 (5).	4.9 (10)
FE	11.1 (5)		10.2 (10)	19.5 (5)	11.0 (10)

( ) = Radiation dose (kGy) considered for Gd calculation

Table 5 – 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

TOLUENE		
Ci (mg/L)	Gd x 10^3	Reference
6.07	**318.0**	KURUCS
1.00	**68.0**	NICKELSEN
5.00	15.0	IRU
13.92	69.4	CBS
1.04	10.2	FE
XYLENE		
Ci (mg/L)	Gd x 10^3	Referência.
1.00	**34.0**	NICKELSEN
1.50	**18.0**	NICKELSEN
13.78	51.6	IRU
7.34	29.5	CBS
1.63	19.9	FE
PHENOL		
Ci (mg/L)	Gd x 10^3	Referência.
56.40	**525.9**	KURUCS
7650	**2981**	GETOFF
9.40	**964.1**	GETOFF
5.45	5.2	IRU
6.09	10.7	CBS
6.60	11.0	FE

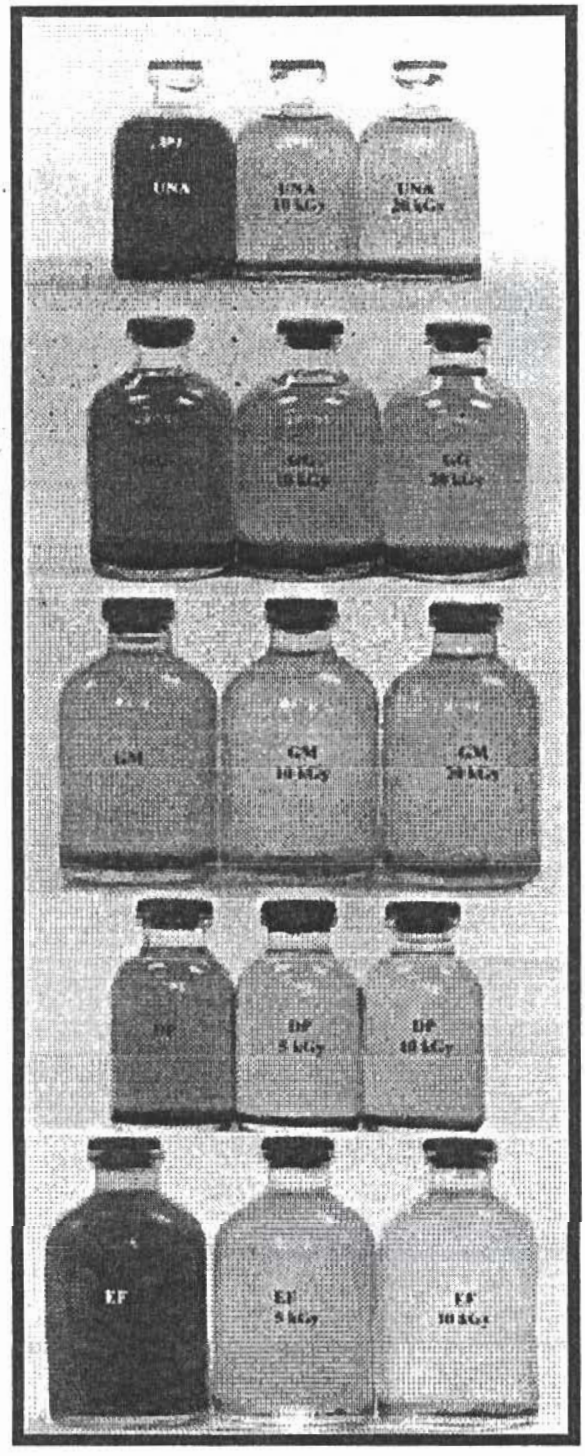

Figure 1 – The clarification of the industrial effluent from different WTP steps after electrons beam irradiation

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Figure 1 – The clarification of the industrial effluent from different WTP steps after electrons beam irradiation