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ENVIRONMENTAL RECOVERY BY DESTRUCTION OF TOXIC ORGANIC COMPOUNDS USING ELECTRON BEAM ACCELERATOR

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Abstract. The Government of the State of São Paulo has a program for the treatment of water in the Tietê River, located in the São Paulo Metropolitan Region (SPMR). The main objective of this program is to reduce substantially the pollution of this river. A study using the IPEN's Liquid Effluent Irradiation Pilot Plant in the Electron Beam Facility was undertaken. Electron beam irradiation was shown to be efficient in destroying organic compounds mainly chloroform, dichloroethane, methyl isobutyl ketone, benzene, toluene, xylene and phenol in rivet water.

1. INTRODUCTION

Damages to human health related to improper treatment of residues have led strict environmental protection laws and consequently the need for research in new technologies for the treatment of effluents mainly from industrial origin. The variables involved in the environment's preservation are numerous, mainly those that are originated by the chemical compounds and raw material used by the industries. Organic compounds, especially synthetic ones from industrial effluents are difficult to be treated by conventional methods.

The effluent generate by the industries in São Paulo are one of the main causes for the environmental pollution, most of these contaminants biodegrade very slowly, becoming dangerous for men, plants and animals. The conventional treatment and available technologies to treat such waste have low efficiency, and industries are searching for alternative technologies to degrade chemical compounds to get a better quality of effluent and consequently improve the environmental conditions.

The Government of the State of São Paulo has a program for the treatment of water in the Tietê River, located in the São Paulo Metropolitan Region (SPMR). The main objective of this program is to reduce substantially the pollution of this river which has been transformed into an open sewer in the middle of an urban area. Today the river receives sewer and industrial flows of $40m^3/s$, which represent 60% of the natural flow during dry periods. The program proposes to invest in new sewer systems, collectors and, five new treatment plants, besides specific industrial treatment. São Paulo Metropolitan Region has a population of the 17.4 million and 40,000 registered enterprises; 1,250 of these industries are responsible for 90% of the pollution .

The industries that contribute most to the SPMR are metallurgical (including mechanical and automobile), followed by the textile, food, chemical, electrical and cellulose and paper industries. The metallurgical and chemical industries produce 87% of inorganic load, while chemical, food and textile industries produce 79% of organic load discharged into the Tietê river without any treatment .

The State Environmental Pollution Control Regulation establishes that the enterprises need to control and treat liquid effluents before delivery to the river or to the Public Wastewater Treatment System.

Considering these aspects the Government of São Paulo State and the Industries are concentrating a major effort in a program on decontamination of the main rivers and water reservoirs located close to industrial areas, through the implementation of new Wastewater Treatment Plants. As these plants have a low efficiency for the removal of refractory pollutants, mainly organochloride compounds, there is a need for an alternative technology to be used in conjunction with the conventional treatment to improve the reduction of pollutants.

The oxidation process has attracted many researchers because of the capacity to mineralize organic compounds. The most efficient oxidation is the use of OH radicals. There are various methods to generate OH radicals as the use of ozone, hydrogen peroxide and ultra-violet (AOP - Advanced Oxidation Process). The most simple and efficient method for generating OH radicals in situ is the interaction of ionizing radiation with water.

The reactive species formed by the water irradiation are the reducing radical's solvated electron (e^-_{aq}), and H atoms and the oxidizing radical hydroxyl OH. The reactive species will react with organic compounds in the water inducing their decomposition. The use of ionizing radiation has great ecological and technological advantages, especially when compared to physical-chemical and biological methods. It degrades organic compounds, generating substances that are easily biodegraded without the necessity of adding chemical compounds. The purpose of the radiation treatment is the conversion of these substances to biodegradable compounds; sometimes the complete decomposition is not necessary for this conversion [4,5].

2. EXPERIMENTAL PROCEDURES

Seven effluent samples (E1 to E7) from a mixture of chemical, pharmaceutical, textile and dyes industries origin were irradiated using the IPEN's Liquid Effluent Irradiation Pilot Plant in the Electron Beam Facility with a 1.5 MeV Dynamitron from Radiation Dynamics Inc. The IPEN's pilot plant used to irradiate these samples was set up to treat wastewater and industrial effluents and was described elsewhere [2,3,7].
The absorbed dose is measured by calorimetric system using a temperature transducer type, WCOTT, Wire Current Output temperature transducer, - Intensil, GE-AD590, that allows to obtain in real time the average absorbed doses [7].
The sample stream had a medium flow rate of 30L/min; the electron beam with 1.5MeV energy and the current was fixed from 1.2mA to 10.6mA 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 [1]. Analyses of Total Organic Carbon (TOC) were performed too, using Total Organic Carbon Analyzer, Shimadzu, model TOC 5000A. The degree of improvement was evaluated by the control of organic compound composition through the chemical analysis by gas chromatograph associated to mass spectrometer analysis, Shimadzu model GCMS-QP 5000, after pentane extraction. 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.

3. RESULTS

The physical chemical characterization of these samples is presented in Table 1.

Table 1 - Physical chemical characterization of the studied industrial effluent samples

SAMPLE	Total Organic Carbon TOC (mg/L)	Chemical Oxygen Demand COD (mgO_2/L)	Biochemical Oxygen Demand BOD (mgO_2/L)	Suspended Solid (mg/L)	pH
E1	315	1200	601	624	8.3
E2	340	1040	641	552	7.4
E3	390	1513	1330	182	9.6
E4	362	2000	686	353	7.8
E5	364	1075	7520	254	8.1
E6	380	1029	672	151	8.3
E7	407	2193	1430	181	8.9

The concentration of the most important pollutants found in the studied effluents are presented in the Figure 1 and the main organic compounds found in term of concentration were dichloroethane, toluene, xylene, benzene, methilisobutylketone and phenol.

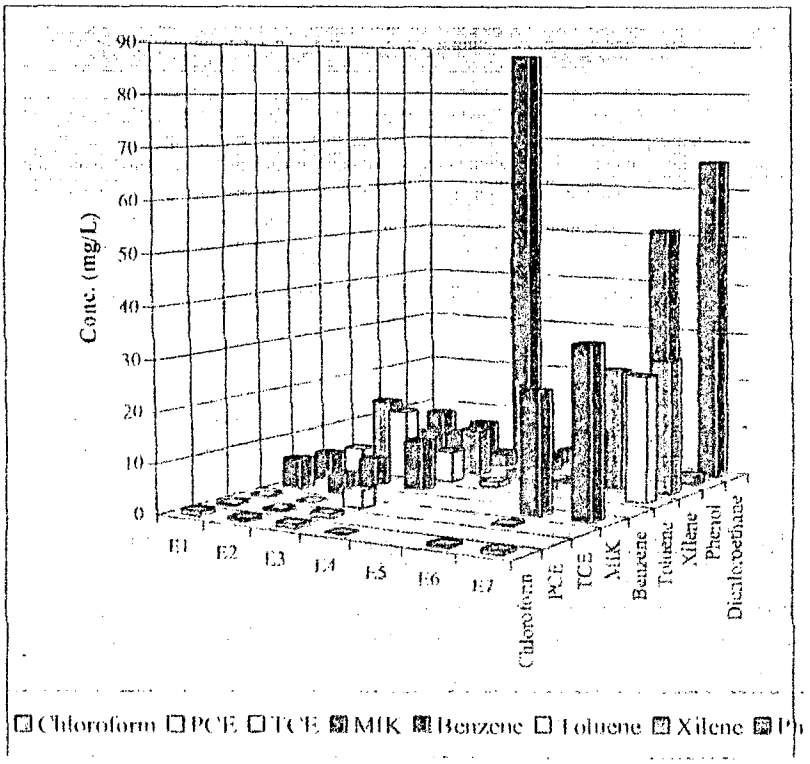

FIG. 1. Main organic compounds present in the industrial effluent sample E1 to E7.

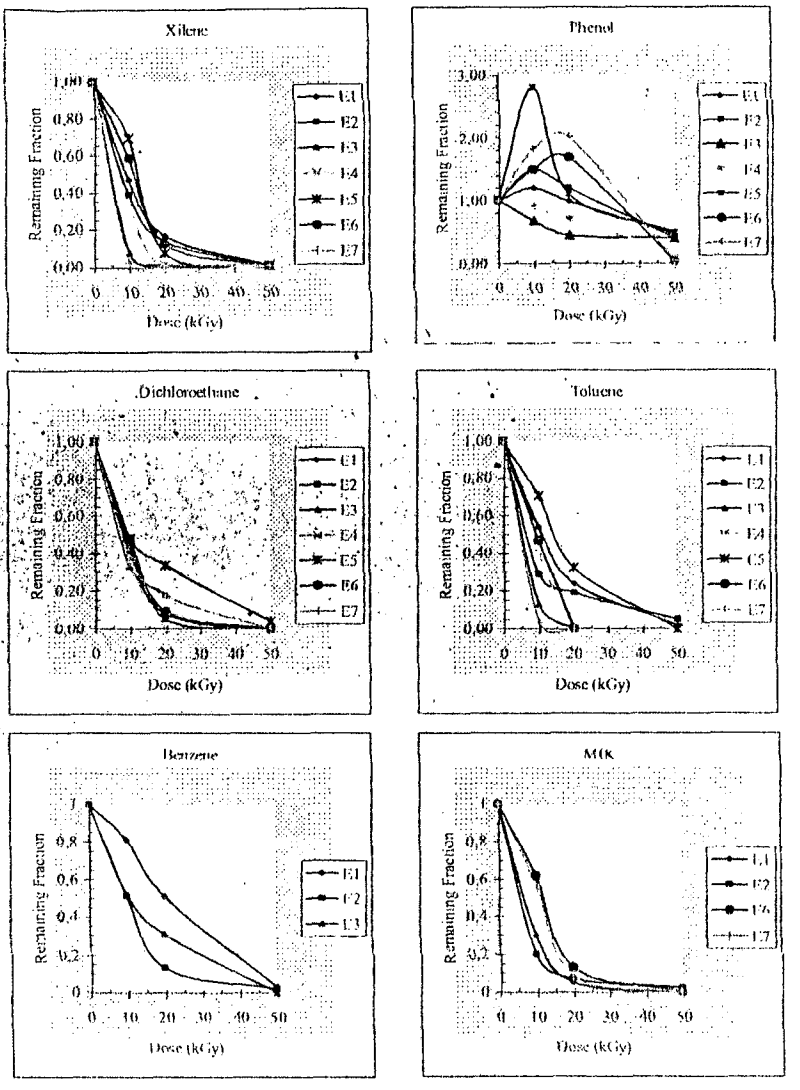

FIG. II. Organic compounds destruction after electron beam irradiation of the industrial effluent sample.

The electron beam irradiation showed be efficient on destroying the organic compounds delivered in these effluents mainly chloroform, dichloroethane, methyl isobutyl ketone, benzene, toluene, xylene and phenol as it is showed in the graphics of the Figure III. To remove 90% of the most organic compounds present in the complex sample it was necessary a 50 kGy dose. The phenol concentration increase at low doses as a by product of aromatic organic compound as benzene and toluene [4,6].

Analysing the TOC results in different doses presented at the Figure IV and the results of toxic organic compounds destruction by radiation (Figure III), it can be concluded that even after toxic organic compound destruction the samples presented high TOC indicating the presence of organic carbon. A great part of that organic carbon can be simple organic acids formed by the destruction of toxic and complex organic molecule as showed in the graphics of the Figure IV, where is represented the formation of the less toxic organic acids as formic, acetic, tartaric and oxalic when the irradiation absorbed dose is increased.

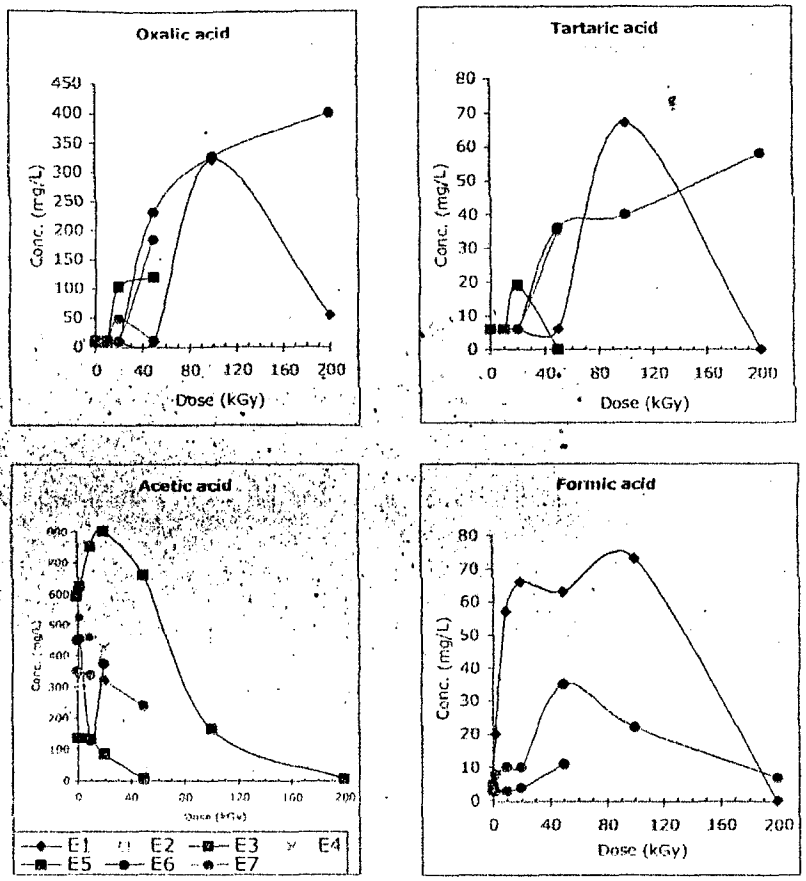

FIG. III Main organic acid formed as byproduct of organic compounds destruction after e-beam irradiation of the industrial effluent sample (E1 to E7).

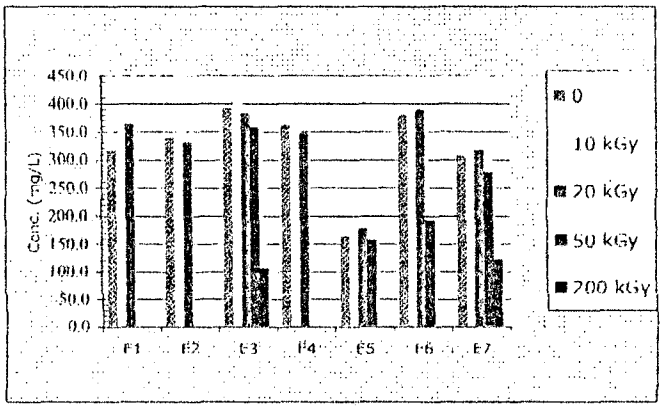

FIG. IV TOC variation after e-beam irradiation of industrial effluent (E1 to E7)

The removal of these organic compounds after irradiation were described 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 [6]:

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

Where ΔRD is the change in organic solute concentration (mol L^{-1}) at a given dose. D is the dose (kGy), 6.24 x 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 1.

The obtained results show the high efficiency of irradiation process on destroying organic compounds even for effluent with different complexity.

Table 2- Obtained Gd x 10^3 (mol/J) values for mainly organic compounds

Sample	Dichloroethane	Chloroform	Methyl isobutilketon	Toluene	Xylene	Phenol
E1	33.9 (20)	3.9 (20)	25.6 (10)	15.0 (20)	51.6 (20)	5.2 (50)
E2	36.4 (20)	2.3 (20)	17.6 (10)	69.4 (20)	29.5 (20)	10.7 (50)
E3	288.9 (15)	4.3 (15)		38.3 (15)	391.0 (02)	2.6 (15)
E4	18.5 (05)	1.8 (05)		14.2 (05)	18.2 (05)	0.0 (05)
E5	1.0 (20)	0.8 (20)		6.4 (20)	0.6 (15)	-0.6 (30)
E6	22.8 (20)	2.9 (10)	101.7 (20)	64.8 (10)	42.2 (50)	4.6 (50)
E7	265.1 (20)	1.8 (05)	150.0 (20)	256.2 (30)	121.0 (10)	3.7 (50)

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

4. CONCLUSIONS

Based on research studies performed in association with the industry, the obtained results are able to accelerate the development, demonstration and use of new technology that offer permanent cleanup alternative for hazardous wastes.

In the present stage of this project we are evaluating the applicability in industry for specific waste plants and develop a reliable engineering performance and cost data for this innovative treatment technology to environmental recovery.

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