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PRESENT STATUS OF ENVIROMENTAL APPLICATION OF ELECTRON BEAM ACCELERATOR IN BRAZIL

Celina Lopes Duarte, Hiroshi Oikawa, Manoel Nunes Mori, Maria Helena O. Sampa

Instituto de Pesquisas Energéticas e Nucleares - IPEN-CNEN/SP
Av. Lineu Prestes 2.242
05508-000 , São Paulo, SP, Brasil
clduarte@ipen.br

Abstract. The necessity to decrease the environmental contamination caused by toxic flue gases, liquid and solid effluent delivered by industries, have resulted in search of new treatment technologies. The oxidation processes with OH radicals are the most efficient to mineralize organic compounds, and there are various methods to generate OH radicals as the use of ozone, hydrogen peroxide and ultra-violet radiation (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 irradiation of aqueous solutions with high-energy electrons results in the excitation and ionizing of the molecules and rapid (10^{-14} - 10^{-9} s) formation of reactive intermediates. The most reactive species are the reducing radicals solvated electron (e^{-}_{aq}), and $H^{\cdot}$ atoms and the oxidizing radical hydroxyl, OH, the unique process that produce the reducing specie $e\text{-}_{aq}$ is the electron beam irradiation These reactive species will react with organic compounds present in industrial effluent inducing their decomposition. The primary products from water irradiation tend to react with the functional groups present in an organic molecule rather than with the molecule as a whole. This paper presents the evaluation of ionising radiation effectiveness in actual effluents from different industries such as chemical, petroleum, wastewater treatment plant, and drinking water, using Electron Beam Facility with a 1.5 MeV, Dynamitron from Radiation Dynamics Inc. The ionising radiation was efficient on destroying organic compounds delivered in industrial effluents, independent on the physical-chemical characteristics and origin. The efficiency of ionizing radiation in presence of Titanium dioxide (TiO_2) catalyzed photoreaction, to treat industrial effluent with high organic pollutant concentration is discussed. The main objective to combine these technologies is to improve the efficiency for high-contaminated effluents and decreasing the required absorbed doses for future implementation to large-scale design.

1. Introduction

There are various methods to generate OH radicals that are called Advanced Oxidation Process, AOP, as the use of ozone, hydrogen peroxide and ultra-violet. The most simple and efficient method for generating OH radicals in situ is the interaction of ionising radiation with water [9]. 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 [3,8,9,12,13].

This paper presents the evaluation of the efficiency of ionizing radiation treatment of actual effluents and samples from different origin, distinct physical chemical characteristics and organic compound concentrations, such as drinking water, wastewater treatment plant, industrial, and petroleum production. These results were obtained from 1994 to 2002 research group from Institute for Energetic and Nuclear Research, IPEN [2,5,6,7,14].

1.1 Drinking Water Treatment

The cyanobacteria, or blue-green algae, owe their name to the presence of photosynthetic pigments. Freshwater cyanobacteria are known to occur throughout the world. The main responsible organic composites for the taste and odor type earth and mould of surface waters used to supply throughout the world are geosmin (GEO) and 2-methylisoborneol (MIB). Geosmin (*trans*-1, 10-dimethyl-*trans*-decalol) is and 2-methylisoborneol is compounding produced by several species of cyanobacteria (blue-green algae) and is extremely difficult to degrade microbiologically. Conventional treatment processes of surface water are not effective in removing or destroying the cyanobacteria toxins. However, certain oxidation procedures as well as activated charcoal were found to be effective [4,10,15,16].

1.2. Effluent From Wastewater Treatment Plant

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 are from chemical, pharmaceutical, textile and dyes industries origin [6]. 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.

1.3. Effluent From Industrial Complex

The effluents were from an industrial complex composed by eight separated production units named: Intermediary Organic Products (IOP), Poly Vinyl Acetate (PVA), Resins (RES), Especial Products (SP), Detergents (DET), Sulphonation (SULF), Thiodan (THIO) and Azo dyes (AZO). Each unit delivered its effluent to the small treatment station, where they were mixed and the pH was neutralized. One effluent sample from each of eight separate industrial units (POI, PVA, RES, SP, DET, SULF, THIO and AZO) and 5 samples from the mixed effluent (ME1 to ME5), were irradiated at IPENs Pilot Plant [7].

1.4. Effluent From Petroleum Production

During the offshore oil production large volumes of aqueous waste with high salinity are produced. The produced water originates mainly from the oil-bearing formation but may also include seawater, which has been injected to maintain reservoir pressure. This water is normally separated from oil on the platform generating aqueous effluent with metals, sulfite, ammonium and organic compounds. The conventional treatment used includes filtration, flotation, ionic change and adsorption in activated charcoal, but the high salinity of this water decreases the efficiency of those treatments [11].

2-Experimental Details

2.1. Radiation Processing

The water samples from Water Treatment Plant of Alto Boa Vista – SABESP, were irradiated with the following absorbed doses: 0.5 kGy, 1.0 kGy, 2.0 kGy and 3.0 kGy using gamma irradiation with a Co-60 source (Gammacell, 11,000 Ci) in a batch system. Fricke dosimeter was employed to determine the absorbed dose rate of the system. The samples of Wastewater Treatment Plant and effluents from petroleum production were irradiated at the Electron Beam Facility with a 1.5 MeV Dynamitron from Radiation Dynamics Inc. The irradiation was performed in a batch system using Pyrex glass. 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. Effluents from industrial chemical complex were irradiated at the IPEN's Electron Beam Pilot Plant that was set up to treat wastewater and industrial effluents and was described elsewhere. The absorbed dose was 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. The sample stream had a medium flow rate of 30L/min; the electron beam with 1.5MeV energy and the current was varied from 1.2mA to 10.6mA in order to obtain the desired doses [6, 14].

2.2. Chemical Characterization

The irradiation treatment efficiency was evaluated by the chemical analysis of the duplicate samples before and after irradiation. The organic compounds were analyzed by
Gas chromatograph associated to mass spectrometry using Gas Chromatograph associated to Mass Spectrometer Shimadzu model GCMS-QP 5000 using 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) and 1uL of injection volume.

3. Results and Discussion

3.1. Drinking Water Treatment

The results of quantitative analyses of organic compounds GEO and MIB in the three kinds of water samples before and after gamma irradiation with 0.5 kGy, 1.0 kGy, 2.0kGy and 3.0 kGy are showed in the Table I. There was a total removal of GEO and MIB with 0,5 kGy of absorbed dose and the concentrations were near 100 ngL^{-1} in case of sedimented water and final water, raw water present lower reduction. In the case of samples, which concentrations were near to 1000 ngL^{-1}, it was necessary higher doses to remove 90% of GEO and MIB. For final and sedimented water it was necessary 2.0 kGy to remove 99%. It was not observed acute toxicity in the samples before neither after irradiation. The absence of acute toxicity mainly when 3kGy of absorbed dose was applied is important to verify that no toxic substances were formed after the radiation processing [2].

Table I. Removal of the odorific organic compounds with applied absorbed doses in water samples from Guarapiranga reservoir

ABSORBED DOSE (kGy)	**RAW WATER**		**SEDIMENTED WATER**		**FINAL WATER**	
	GEOSMIN (ng.L^{-1})					
0.0	160	860	960	88	800	92
0.5	135	106	134	<4	70	<4
1.0	100	40	20	<4	10	<4
2.0	20	18	<4	<4	<4	<4
3.0	<4	13	<4	<4	<4	<4
METHYLISOBORNEOL (ng.L^{-1})						
0.0	93	900	1130	89	930	45
0.5	15	194	204	<4	206	<4
1.0	13	56	56	<4	50	<4
2.0	<4	22	<4	<4	<4	<4
3.0	<4	5,6	<4	<4	<4	<4

3.2. Effluent From Wastewater Treatment Plant

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, resulting in very high Total Organic Carbon; but this organic load represents proteins, carbohydrates, oils and greases but not toxic organic pollutants. 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 Table II.

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

Phenol presented negative results on removal in the steps IRU, CBS and MBS when irradiated at doses of 10kGy and 20kGy (Table II), that is because it was observed an increase in its concentration when lower doses were applied. This occurrence suggest a phenol molecule formation as a by-product of others aromatic compounds, because this, the Gd of phenol presented lower values than the others studied organic compounds (Table V).

3.3. Effluent From Industrial Complex

The physical chemical characterization of these samples showed the complexity and differences of these effluents. The pH ranged from 1.40 (IOP) to 12.80 (AZO), Chemical Oxygen Demand (COD) was from 466 mgO_2/L (THIO) to 29,000 mgO_2/L (DET), sulfates from 70 mg/L (SP) to 22,780 (AZO), oil and greases from 21 mg/L (ME5) to 285 mg/L (DET) and the suspended solids from 58 mg/L (SULF) to 494 mg/L (DET).

The concentration of the most important pollutants found in the studied were chloroform, dichloroethane, methyl isobutyl ketone, toluene, xylene and phenol, are presented in Table III. The necessary dose to removal 90% of these contaminants are represented in italic, for the most compounds and effluents 20 kGy dose was enough to remove about 90%.

TABLE II - Minimum and maximum concentration of the main organic compounds present in steps of WTP

ORGANIC COMPOUNDS	**IRU**	**CBS**	**MBS**	**PD**	**FE**
	Concentração (mg/L)				
Methilisobutyiketon	1.00 - 22.30 *(20)*	1.30 - 7.85 *(20)*	0.22 - 3.52 *(20)*	0.98 - 2.69 *(10)*	<dl
Dichoroethane	1.30 - 25.70 *(20)*	1.10 - 16.00 *(20)*	1.86 - 5.58 *(20)*	0.98 - 3.69 *(10)*	0.40- .85*(10)*
Toluene	0.80 - 12.00 *(50)*	1.00 - 72.00 *(50)*	0.51 - 2.57 *(20)*	0.85 - 1.60 *(10)*	0.32-1.97*(10)*
Xylene	1.50 - 67.00 *(50)*	0.50 - 25.70 *(50)*	1.22 - 3.51 *(20)*	0.96 - 1.82 *(10)*	0.12 - 4.00*(10)*
Phenol	3.20 - 7.80 *(50)*	3.20 - 16.40 *(50)*	0.96 - 2.00 *(20)*	0.86 - 1.60 *(10)*	0.50 - 0.86 *(10)*

dl = detection limit = 0.03 mg/L Variation = 10% *() Necessary Absorbed Dose to 90% removal*

3.4. Effluent from petroleum production

Although originated of the same process, samples from *Production Unit A* and *Production Unit B* showed very different physical chemical characteristics, such as the higher ammonium concentration and lower sulfite concentration of the samples from *Production Unit A*, and the pH ranged from 9.28 to 9.88 in *Production Unit A* and from 7.88 to 8.07 in *Production Unit* B.

The most important organic pollutants in both effluent samples were benzene, toluene, etilbenzene, xylene (TableIII); all these pollutants present higher concentration in the samples from *Production Unit A* than *Production Unit B* and so were the TOC (Table V). Phenol was found in relative low concentration but was considered due to its toxicity and because phenol is formed as first byproduct of the degradation of benzene and toluene. From these results the complexity and differences of these effluents can be observed.

After radiation processing, the organic compounds content showed a substantial reduction, but with very high absorbed doses. For samples from *Production Unit A*, a dose of 100 kGy was necessary to remove more than 90% of all organic compounds, and in the case of *Production Unit B* a dose of 20 kGy was enough to remove 90% of BTEX and phenol in all samples except SB4 (Table III). The exact influence of ammonium concentration is presently not clear enough, but the results would suggest a positive effect in the removal of organic compound after electron beam processing, since the *SA*2 and SA4 with higher ammonium concentration have the higher yield (Gd) for BTEX and apposite happened with SA3 (Table IV).

The degradation yield of the substrate depends on its starting concentration, hence the process was more effective when high number of organic molecules was present, because the reaction among reactive transients produces more radicals and the process continue, but it is not a direct proportion. E.g. in the case of Benzene in samples from PUA has higher concentration than samples from PUB (Table III), about three times, but the Gd values (Table IV) was almost the same.

4. Conclusion

The electron beam processing has shown high effectiveness in removing organic compounds in complex effluents. In terms of yield *Gd* values, the process showed more effectiveness when high organic molecules number are present, because the reaction among reactive transients produces more radicals continuing the process.

The results of the mass spectrometry analysis showed that no different by-products were formed after irradiation, even in very complex industrial effluent, but it was detected by liquid chromatography a significant increase of organic acids concentration mainly oxalic, tartaric, ascorbic and formic when BTEX were present.

Besides the high necessary absorbed doses, it is a promising process for future field implementation because, the high complexity of the effluent become its treatment by others technologies, very expensive and not so efficient. For future implementation in Brazil, it was detect the necessity of building a mobile system to disposal this new technology to industries and governmental installation’s.

TABLE III – Organic Compounds concentration in the effluents from industrial complex and petroleum production

Sample	**Dichloroethane**	**Methyl isobutyl ketone**	**Benzene**	**Toluene**	**Xylene**	**Phenol**
INDUSTRIAL COMPLEX EFFLUENT						
ME1	87.9 *(20)*	na	*	6.3 *(20)*	9.3 *(15)*	2.8 *(50)*
ME2	2.6 *(20)*	na	*	1.1 *(20)*	1.5 *(20)*	3.2 *(50)*
ME3	0.2 *(20)*	na	*	1.8 *(20)*	0.1 *(20)*	0.1 *(50)*
ME4	51.3 *(20)*	24.2 *(20)*	*	13.1 *(20)*	24.3 *(30)*	2.3 *(50)*
ME5	65.7 *(30)*	34.0 *(20)*	*	25.3 *(10)*	27.2 *(10)*	1.9 *(50)*
RES	<0.010	na	<0.10	<0.10	0.6 *(50)*	0.6 *(50)*
PVA	<0.010	na	6.2 *(50)*	<0.10	1.6 *(50)*	1.6 *(50)*
DET	<0.010	na	0.3 *(50)*	<0.10	1.9 *(50)*	1.9 *(50)*
POI	<0.010	na	0.3 *(50)*	0.2 *(50)*	1.1 *(50)*	1.1 *(50)*
SULF	28.4 *(50)*	na	<0.10	<0.10	0.6 *(50)*	0.6 *(50)*
THIO	0.1 *(50)*	na	<0.10	<0.10	<0.10	<0.10
AZO	1.8 *(30)*	na	<0.10	<0.10	0.4 *(50)*	0.4 *(50)*
PETROLEUM PRODUCTION						
SA1	*	*	99,30 (100)	134,49 (100)	307,00 (100)	4,24 (50)
SA2	*	*	146,80 (100)	218,22 (100)	585,06 (50)	3,27 (50)
SA3	*	*	119,79 (100)	195,36 (100)	333,44 (100)	1,47 (50)
SA4	*	*	111,71 (100)	216,93 (100)	243,24 (50)	1,39 (50)
SB1	*	*	22,46 (20)	8,53 (20)	6,61 (20)	3,73 (20)
SB2	*	*	42,17 (50)	27,12 (50)	24,40 (50)	1,92 (20)
SB3	*	*	35,30 (20)	20,83 (20)	12,65 (20)	1,65 (20)
SB4	*	*	49,05 (20)	27,33 (20)	17,70 (20)	0,98 (20)

() Necessary Absorbed Dose to 90% removal
* = Under the detection limit

TABLE IV- Obtained Gd x 10^3 (mol/J) values for mainly organic compounds in the effluent

Sample	Dichloroethane	Methyl isobutyl ketone	Benzene	Toluene	Xylene	Phenol
WASTEWATER TREATMENT PLANT						
RUI	33.9	25.6	*	15.0	51.6	5.2
CBS	36.4	17.6	*	69.4	29.5	10.7
MBS	27. 1	14.0	*	8.0	9.7	4.8
PS	23.1	9.2	*	7.9	4.8	4.9
FE	11.1	*	*	10.2	19.5	11.0
INDUSTRIAL COMPLEX EFFLUENT						
ME1	288.9	*	*	38.3	391.0	2.6
ME2	18.5	*	*	14.2	18.2	0.0
ME3	1.0	*	*	6.4	0.6	-0.6
ME4	226.8	101.7	*	64.8	42.2	4.6
ME5	265.1	150.0	*	256.2	121.0	3.7
RES	*	*	*	10.8	*	-3.4
PVA	*	*	*	0.5	*	1.4
DET	*	*	*	0.1	0.5	1.0
POI	20.0	*	*	*	*	1.0
SULF	0.4	*	*	*	*	*
THIO	4.6	*	*	*	*	0.5
AZO	35.2	*	*	5.91	74.3	-3.4
PETROLEUM PRODUCTION						
SA1	*	*	121,2	132,9	302,4	8,7
SA2	*	*	179,1	214,7	1152,4	6,7
SA3	*	*	145,2	384,1	327,9	3,0
SA4	*	*	135,4	212,7	478,7	2,8
SB1	*	*	137,0	42,0	32,5	7,7
SB2	*	*	102,9	53,4	48,1	3,9
SB3	*	*	215,3	102,4	62,3	3,4
SB4	*	*	299,2	134,4	87,2	5,0

* Under the detection limit

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