Available online at www.sciencedirect.com
SCIENCE DIRECT®
Radiation Physics and Chemistry 71 (2004) 443–447
Radiation Physics and Chemistry
www.elsevier.com/locate/radphyschem

Treatment of effluents from petroleum production by electron beam irradiation

Celina Lopes Duarte[a,*], Lucia Limoeiro Geraldo[b], Oswaldo de Aquino P. Junior[b], Sueli Ivone Borrely[a], Ivone Mulako Sato[a], Maria Helena de Oliveira Sampa[a]

[a] *Instituto de Pesquisas Energéticas e Nucleares, IPEN, CNEN/SP, Av. Lineu Prestes 2.242, São Paulo, SP 05508-900, Brazil*
[b] *PETROBRAS/CENPES, Cidade Universitária, Quadra 7, Ilha do Fundão, Rio de Janeiro, RJ 21949-900, Brazil*

Abstract

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 treatment efficiency. The high efficiency of electron beam irradiation on removing organic compound in industrial effluent has been shown, and the primary aim of this study is to evaluate the efficiency of this new technology to treat the oil water production. Experiments were conducted using samples from two platforms processed in the radiation dynamics electron beam accelerator with 1.5 MeV energy and 37 kW power. The results showed that the electron beam technology has high efficiency in destroying organic compounds even in the presence of high salinity and complex effluent.

Keywords: Electron beam accelerator; Organic compound removal; Petroleum production effluent

1. Introduction

Organic compounds have been a problem of environmental concern because once in the environment they may cause problems to the human health, animals and plants. Traditional treatment methods are not efficient in removing these compounds and advanced oxidation process (AOP), such as electron beam irradiation, is a promising technology for the removal of these pollutants from the industrial effluent (Duarte et al., 2002; Nickelsen and Cooper, 1992; Kurucs, et al., 1995) and thus decreasing its toxicity (Borrely and Sampa, 2000).

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 include filtration, flotation, ionic change and adsorption in activated charcoal, but the high salinity of this water decreases the efficiency of those treatments.

This paper presents a study of the electron beam treatment, using effluents from two different petroleum production units, in order to evaluate the effectiveness of this technology to degrade organic compounds in effluents with high salinity, different physical chemical characteristics and organic compound concentrations.

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

0969-806X/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.radphyschem.2004.03.021

Table 1
Chemical characterization of the petroleum effluent

Sample	TOC (mg/l)	SULFITE (mg/l)	AMMONIUM (mg/l)	pH
Production unit A				
PUA1	450.2	Na	Na	9.88
PUA2	478.5	0.3	1500.0	9.45
PUA3	582.0	0.2	307.4	9.54
PUA4	427.7	1.7	2817.0	9.28
Production unit B				
PUB1	142.8	Na	Na	8.01
PUB2	135.7	11.2	182.5	7.89
PUB3	217.2	28.8	72.0	8.07
PUB4	291.5	91.3	64.9	7.88

Standard deviation: pH = ±5%, TOC = ±10%.
Na = not analyzed.

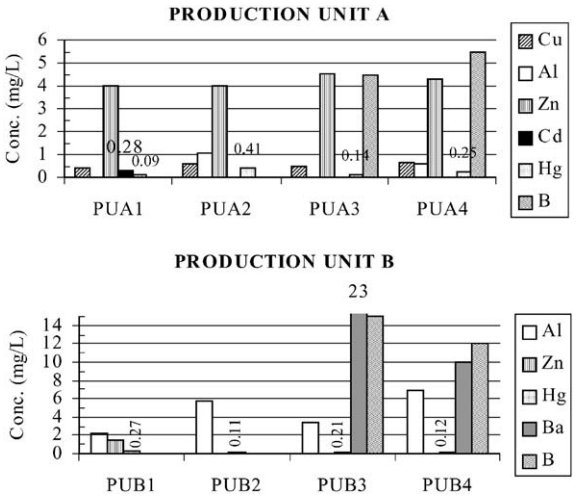

Fig. 1. Main metals in the *Production Unit A* and *B* samples.

2. Experimental

2.1. Sampling

Effluent samples of produced water from platforms of two different petroleum production units named "Production Unit A" (PUA) and "Production Unit B" (PUB) were collected. The assay scheduled, such as 4 samples with 10 l volume were collected in 1-month intervals, transported to the laboratory and processed on the same day.

2.2. Processing

The irradiation was performed in a batch system using Pyrex glass vessels with 250 ml, and the effluent samples were processed at radiation dynamics electron beam accelerator with 1.5 MeV energy and 37 kW power. They were irradiated with the following absorbed doses: 20, 50, 100 and 200 kGy, the current of the electron beam was varied from 1.2 to 10.6 mA in order to obtain the desired absorbed doses.

2.3. Chemical analysis

The physical chemical characterization was performed according to the standard methods for the examination of water and wastewater (American Public Health Association, 1997).

The organic analyses before and after irradiation processing were performed using Gas chromatograph associated to mass spectrometry using the Shimadzu, model GCMS QP-5000, with Head Space concentrator using gas Helium, 20 ml of volume sample and the following conditions:

- Capilar column DB5,
- Mass detector operation in electron impact mode (EI), using 1.50 kV of ionizing voltage and temperature 250°C,

Table 2
Main organic compounds in the effluent

Sample	Benzene (mol/l)	Toluene (mol/l)	Etilbenzene (mol/l)	Xylene (mol/l)	Phenol (mol/l)
Production unit A					
PUA1	1255.21	1377.55	576.72	3132.65	45.11
PUA2	1855.64	2224.49	1220.97	5969.39	34.79
PUA3	1504.23	1989.80	626.92	3397.59	15.64
PUA4	1403.11	2204.08	530.47	2479.59	14.79
Production unit B					
PUB1	283.91	87.04	16.77	67.35	39.68
PUB2	533.06	276.73	62.16	248.98	20.43
PUB3	446.21	212.24	27.22	129.08	17.55
PUB4	620.02	278.57	44.83	180.61	10.43

- Interface temperature 240°C and continuous operation mode (SCAN).

For metal analysis, 1.0 ml of the solution was deposited into the 1.0 cm diameter filter paper fixed on the double face adhesive ribbon. It was dried at 35°C temperature under a stirrer and protected between two mailer leaves. Following the same procedure, three samples from multielement standard solution (Johnson Matthey) were prepared (Lachance and Claisse, 1995). The elements were determined using the Rigaku modified fundamental parameters method installed at the X-ray spectrometer (Scapin and Sato, 2002). The irradiation treatment efficiency was evaluated by the chemical analysis of the duplicate samples before and after irradiation.

2.4. Radiation processing efficiency

The radiation processing yield was evaluated by the destruction G value (Gd), that means the number of destroyed molecules by absorption of 100 eV energy, as previously described (Duarte et al., 2002).

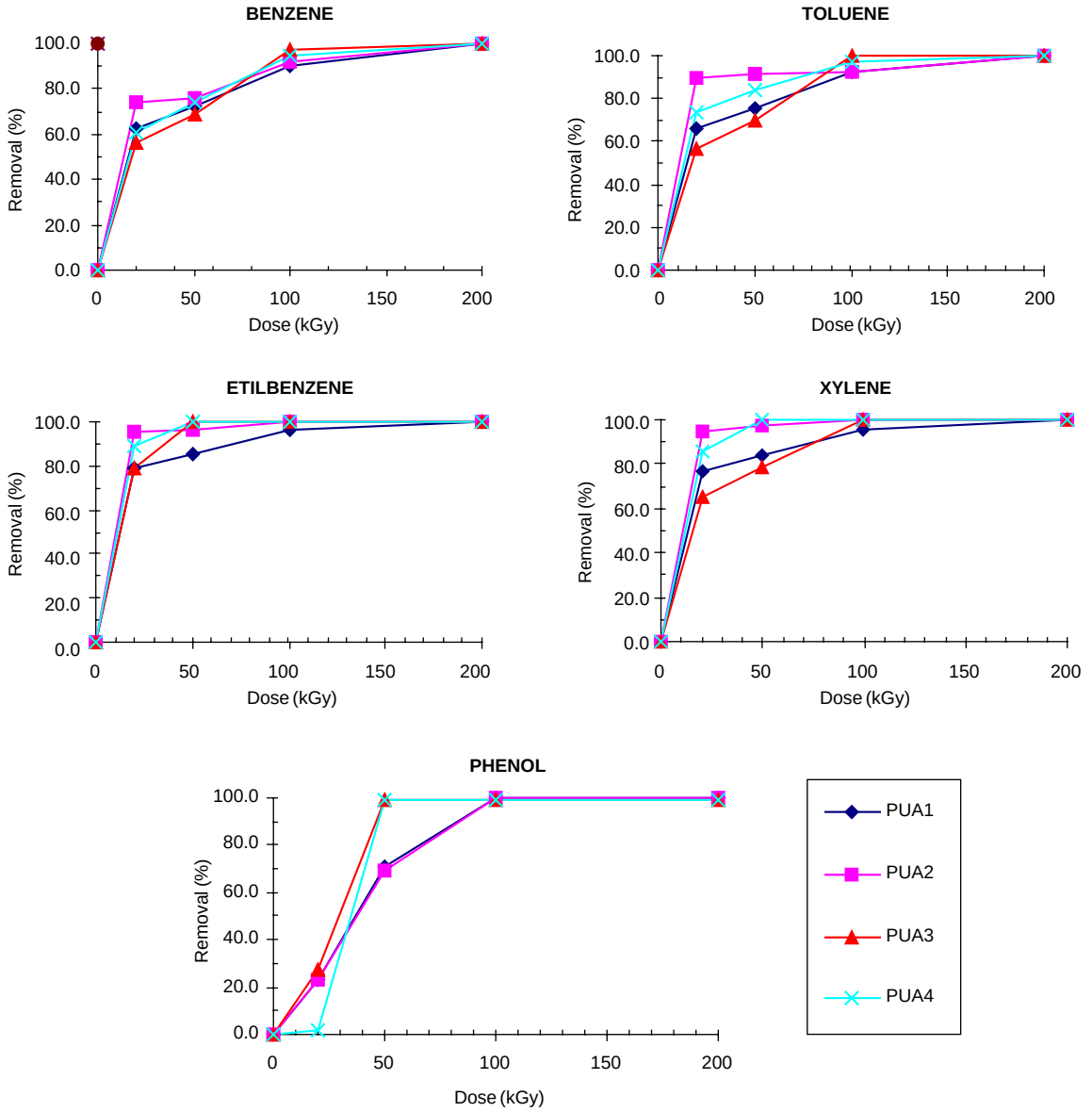

Fig. 2. Removal of organic compounds from *Production Unit A* after electron beam irradiation.

3. Results and discussion

Although originated of the same process, samples from PUA and PUB showed very different physical chemical characteristics, such as the higher ammonium concentration and lower sulfite concentration of the samples from PUA, and the pH ranged from 9.28 to 9.88 in PUA and from 7.88 to 8.07 in PUB (Table 1).

The results of metal analysis show the presence of Cu, Al, Zn, Cd, Hg and B in the PUA samples and Al, Zn, Hg, Ba and B in PUB samples (Fig. 1). The metal concentration is an important parameter, because it has been found by corresponding experiments that part of the primary radicals of water radiolysis are consumed by the metals ions.

The most important organic pollutants in both effluent samples were benzene, toluene, etilbenzene, xylene (Table 2); all these pollutants present higher concentration in the samples from PUA than PUB and so were the TOC (Table 1). 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 compound content showed a substantial reduction, but with very high absorbed doses. For samples from PUA, a dose of 100 kGy was necessary to remove more than 90% of all organic compounds (Fig. 2), and in the case of PUB a

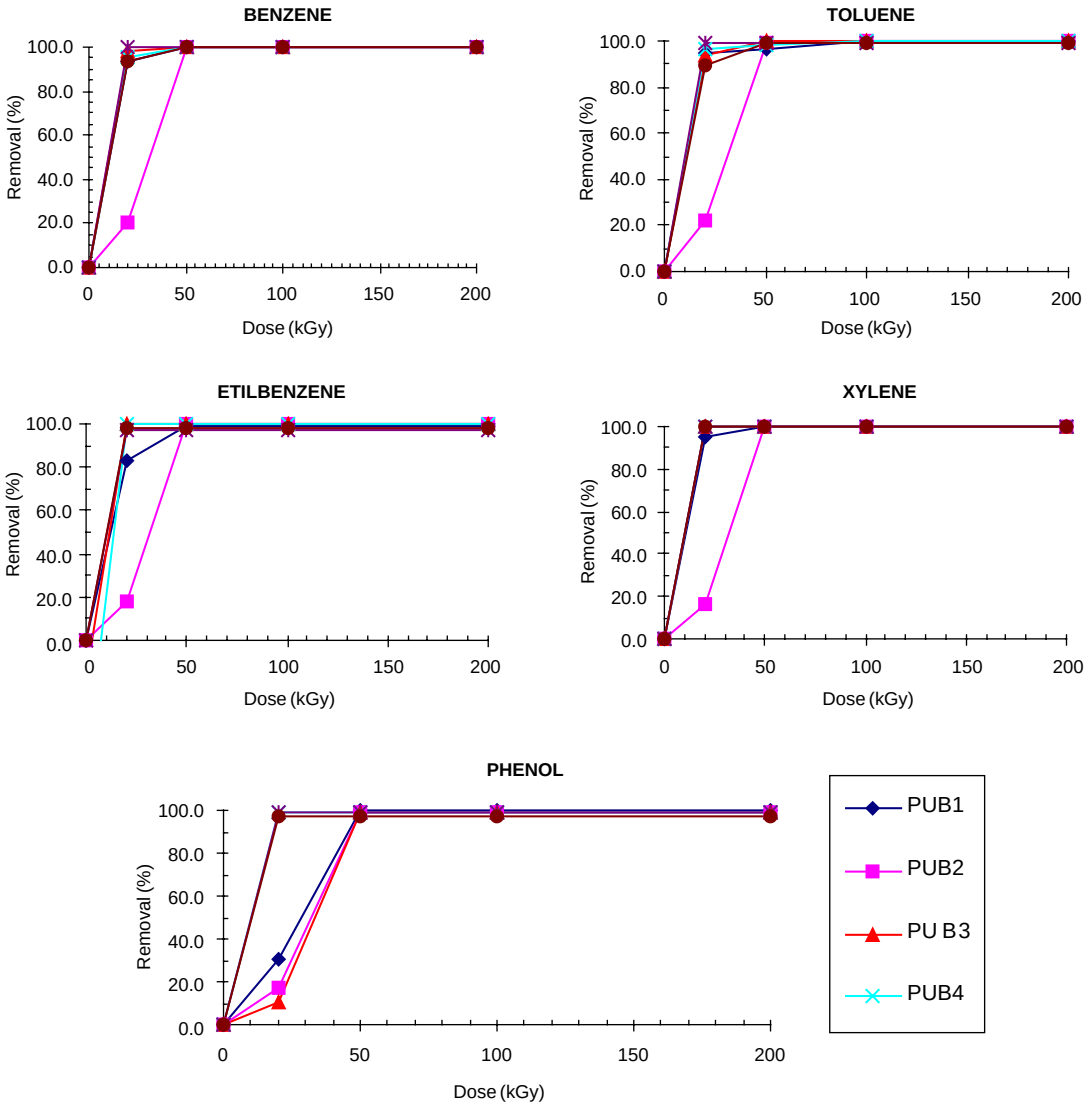

Fig. 3. Removal of organic compounds from *Production Unit B* after electron beam irradiation.

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

Sample	Benzene (mol/J)	Toluene (mol/J)	Xylene (mol/J)	Phenol (mol/J)
PUA1	121.2	132.9	302.4	8.7
PUA2	179.1	214.7	1152.4	6.7
PUA3	145.2	384.1	327.9	3.0
PUA4	135.4	212.7	478.7	2.8
PUB1	137.0	42.0	32.5	7.7
PUB2	102.9	53.4	48.1	3.9
PUB3	215.3	102.4	62.3	3.4
PUB4	299.2	134.4	87.2	5.0

dose of 20 kGy was enough to remove 90% of BTEX and phenol in all samples except SB4 (Fig. 3).

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 PUA2 and PUA4 with higher ammonium concentration have the higher yield (Gd) for BTEX and opposite happened with PUA3 (Fig. 2 and Table 3).

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. In the case of Benzene, e.g. samples from PUA have about three times the concentration of the samples from PUB (Table 2), but the Gd values (Table 3) was almost the same.

4. Conclusion

The removal of organic compounds such as benzene, toluene, xylene and phenol from petroleum production water by irradiation processing was shown to be very significant. Despite the necessity of very high absorbed doses, it is a promising process for future field implementation because, the high complexity of the effluent makes its treatment by other technologies very difficult and expensive.

References

American Public Health Association. Standard, 1997. Methods for the Examination of Water and Wastewater. 17th Edition. APWA, AWWA, WPCF, Washington, DC.

Borrely, S.I., Sampa, M.H.O., 2000. Radiation processing of wastewater evaluated by toxicity assay. Radiat. Phys. Chem. 57, 507–511.

Duarte, C.L., Sampa, M.H.O., Rela, P.R., Oikawa, H., Silveira, C.G., Azevedo, A.L., 2002. Advanced oxidation process by electron-beam-irradiation induced decomposition of pollutants in industrial effluents. Radiat. Phys. Chem. 63, 647–651.

Kurucs, C.N., Waite, T.D., Cooper, W.J., Nickelsen, M.G., 1995. Empirical models for estimating the destruction of toxic organic compounds utilizing electron beam irradiation at full scale. Radiat. Phys. Chem. 45 (5), 805–816.

Lachance, G.R., Claisse, F., 1995. Quantitative X-ray Fluorescence Analysis—Theory and Application. Wiley, London.

Nickelsen, M.G., Cooper, W.J., 1992. Removal of benzene and selected alkyl-substituted benzene from aqueous solution utilizing continuous high-energy electron irradiation. Environ. Sci. Technol. 26, 144–152.

Scapin, M.A., Sato, I.M., 2002. Determination of Na, Al, Si, P, K, Ca, Fe, Co, Ni, Cu and Zn by WD-XRF Spectrometry in industrial effluents after an electron-beam treatment. Avances in Analisis por Técnicas de Rayos. XI, 87–91.