Available online at www.sciencedirect.com
SCIENCE DIRECT®
Radiation Physics and Chemistry 71 (2004) 423–426
Radiation Physics and Chemistry
www.elsevier.com/locate/radphyschem

Application of the electron-beam treatment for Ca, Si, P, Al, Fe, Cr, Zn, Co, As, Se, Cd and Hg removal in the simulated and actual industrial effluents

Márcia Almeida Ribeiro[a], Ivone Mulako Sato[a,*], Celina Lopes Duarte[b], Maria Helena Oliveira Sampa[b], Vera Lúcia Ribeiro Salvador[a], Marcos Antonio Scapin[a]

[a] *Centro de Química Meio Ambiente, Instituto de Pesquisas Energéticas e Nucleares-IPEN/CNEN/SP, Av. Prof. Lineu Prestes, 2242-Cidade Universitária, São Paulo SP 05508-900, Brazil*
[b] *Centro de Tecnologia das Radiações, Instituto de Pesquisas Energéticas e Nucleares-IPEN/CNEN/SP, Av. Prof. Lineu Prestes, 2242-Cidade Universitária, São Paulo SP 05508-900, Brazil*

Abstract

The removal of Ca, Si, P, Al, Fe, Cr, Zn, Co, As, Se, Cd and Hg was determined in the simulated and actual industrial effluents using electron-beam treatment. The actual effluents gave the following results: a removal of ca. 80% for Ca and P with 20 kGy irradiation doses; more than 96% for Al and Si with 100 kGy; more than 99% for Ca, Fe, Zn, Cr and Co with 200 kGy and Hg showed a 71.0% removal with 500 kGy. In the simulated industrial effluent solution, As and Hg showed 92.5% and 99% removal with 500 and 100 kGy irradiation doses, respectively. Se and Cd showed a 99.6% and 44.0% removal with 500 kGy. HCOONa solution was added for Hg and As removal, and irradiation process was done in the oxidant atmosphere.

Keywords: Electron beam treatment; Metal removal; Industrial effluent

1. Introduction

The strong industrial development associated with the population growth has been leading to consumption of water and industrial activity has been one of the largest pollution agents. The generation of different effluent types and the inadequate disposition of the residues associated with inefficient treatments have led to the strict laws for environmental protection. Therefore, more effective techniques and processes have been sought for industrial effluent treatments. Metals like Cr, Ni, Zn, As, Se, Cd, Pb and Hg are frequently found in industrial effluents. The activities that most contribute to the generation and emission of those metals are coating, inks, textile, batteries and chemical industries.

The ionizing radiation process has demonstrated the reduction of those metals, in liquid effluents, to its insoluble form, making its removal easy. Several authors (Kartasheva et al., 1997; Pikaev et al., 1997; Chaychain et al., 1998) verified the high efficiency of removing toxic metal ions from aqueous solution by ionizing radiation.

Water radiolysis produces very high reactive species like e^-, $H^\bullet$ and OH^-. These species react with organic and inorganic compounds, reducing them to less hazardous final products. The use of HCOONa, as scavenger, has been investigated for trace elements removal. The formed COO^- is a good reducing agent and reacts with metallic ions inducing their precipitation. Besides that, the reaction does not generate toxic products.

*Corresponding author.
E-mail address: imsato@ipen.br (I.M. Sato).

0969-806X/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.radphyschem.2004.03.017

In this work, the ionizing radiation was used to verify the level of removal of Ca, Si, P, Al, Fe, Cr, Zn, Co, As, Se, Cd and Hg elements, with and without the addition of HCOONa, in simulated and actual industrial effluents.

2. Experimental

Industrial effluent simulate solution was prepared from high purity chemical reagents (Ribeiro et al., 2002). Na, Al, P, S, K and Ca were added as majority composition ($g\,l^{-1}$) and elements Cr, Fe, Zn, Mn, As, Se, Cd and Hg at the trace level ($mg\,l^{-1}$), obtaining the final metal concentration at $79.1\,g\,l^{-1}$. In addition, the organic compound (dichloroethane, methylisobutilkentone, toluene, xylene, benzene, chloroform, tetrachloroethilene and tricloroethilene) were added, from certified standard solution, up to a final concentration at $840\,mg\,l^{-1}$ (Table 1).

Industrial effluent sample was collected at the industrial receiver point in the governmental wastewater treatment plant (ETE/SABESP) in Susano City, São Paulo State/Brazil. This Station receives domestic and industrial effluents, ca. of 60% of which are from industrial sources. The physical and chemical characterization of this sample is given in Table 1.

All effluent samples, simulated and actual, were appropriately fractioned: one part was added HCOONa and another one kept in its raw form.

The samples were irradiated at the IPEN's electron beam facility (RDI Inc. Dynamitron, 1.5 MeV and 37 kW). The irradiation was performed in a batch system using Pyrex glass vessels and the delivered doses were 20, 100, 200 and 500 kGy. The irradiation parameters were: 4.0 mm sample width, 112 cm (94.1%) scan and 6.72 m/min stream velocity.

Wavelength dispersive X-ray fluorescence spectrometer (Rigaku Co., model RIX 3000) was used for elemental determination. The sample preparation was carried out in thin film form. 1.0–5.0 ml of the sample was deposited onto 1.0 cm diameter filter paper. It was dried at 35°C temperature under a stirrer and it was protected between two Mylar leaves. Sensitivity curve was obtained using the Fundamental Parameters method (Lachance and Claisse, 1995; Wheller, 1998; Scapin et al., 2002). The accuracy of the method was verified by analysis of Johnson Matthey's multi-element standard solution.

3. Results and discussion

The validation of analytical methodology from standard solution analysis (Table 2) showed a relative standard deviation 1.6–16.6% except for Cd with was 25.0%; and a relative error from 3.3% to 12.0%, except for Al with was 39.0%.

Al, Si, P, Ca, Cr, Fe, Zn and Co removal levels were calculated for 20, 100 and 200 kGy irradiation doses in actual industrial effluent without HCOONa addition (Table 3). Al and Si showed a removal of 97.8% and 97.7%, respectively at 100 kGy and no additional removal was observed until 200 kGy irradiation doses. P showed a 81.8% removal at 20 kGy and kept same level until 200 kGy irradiation doses. Ca, Cr and Fe showed a removal $>99.9\%$ at 100 kGy. Zn and Co reached same removal at 20 and 200 kGy, respectively.

As, Se, Cd and Hg removal was studied in the simulated and actual industrial effluents, once they are usually presented at trace and ultra-trace level. In addition, their removal was carried out at 100, 200 and 500 kGy irradiation doses, with HCOONa addition (Table 3). As and Se showed a 92.5% and 96.5%

Table 1
Physical and chemical parameters of simulated and actual industrial effluents

Parameters	Effluent sample	Simulated solution
Chemical oxygen demand ($mg\,l^{-1}$)	1514.6	—
Biochemical oxygen demand ($mg\,l^{-1}$)	966.7	—
Total solids ($mg\,l^{-1}$)	3720.0	—
Total organic compounds ($mg\,l^{-1}$)	384.7	
Dissolved metals ($mg\,l^{-1}$)	253×10^{-3}	79.1
Organic compounds ($mg\,l^{-1}$)[a]	—	840
pH	8.08	1.0

[a] Sum of MIC, TEC, PE, BTX, CCl_4.

Table 2
Validation of analytical methodology. Johnson Matthey's multi-element standard solution analysis (Scapin et al., 2002)

Element	Certified values ($mg\,l^{-1}$)	Experimental values ($mg\,l^{-1}$)[a]	RSD (%)	RE (%)
Al	20	27.8 ± 2.4	8.6	39.0
Cr	4	4.32 ± 0.16	3.7	8.0
Mn	4	4.31 ± 0.07	1.6	7.7
Fe	4	4.34 ± 0.46	10.6	8.5
Co	4	4.29 ± 0.11	2.6	7.2
Zn	4	4.46 ± 0.74	16.6	11.5
Cd	1	1.12 ± 0.28	25.0	12.0
Pb	4	3.87 ± 0.10	1.6	3.3

[a] Number of repetition: 3; RSD: Relative standard deviation; RE: Relative error.

Table 3
Metal removal level for different irradiation doses

Element (initial conc. $g\,l^{-1}$)	Sample	% RL at 20 kGy (conc. $g\,l^{-1}$)	% RL at 100 kGy (conc. $g\,l^{-1}$)	% RL at 200 kGy (conc. $g\,l^{-1}$)	% RL at 500 kGy (conc. $g\,l^{-1}$)
Al	EF-1	63.6	97.8	97.8	—
(11.0)		(3.0)	(237×10^{-3})	(260×10^{-3})	—
Si	EF-1	28.5	97.7	98.7	—
(13.0)		(8.0)	(310×10^{-3})	(163×10^{-3})	—
P	EF-1	81.8	81.8	81.8	—
(3.0)		(3.0)	(2.0)	(2.0)	—
Ca	EF-1	82.4	99.94	99.95	—
(125.0)		(22.0)	(69×10^{-3})	(66×10^{-3})	—
Cr	EF-1	97.3	99.6	99.6	—
(2.0)		(54×10^{-3})	(9×10^{-3})	(8×10^{-3})	—
Fe	EF-1	96.2	99.9	99.9	—
(21.0)		(162×10^{-3})	$(<1\times10^{-3})$	$(<1\times10^{-3})$	—
Zn	EF-1	99.95	99.95	99.95	—
(2.0)		$(<1\times10^{-3})$	$(<1\times10^{-3})$	$(<1\times10^{-3})$	—
Co	EF-1	96.2	96.7	99.8	
(419×10^{-3})		(16×10^{-3})	(14×10^{-3})	$(<1\times10^{-3})$	
As	SS-1	—	53.6	43.2	92.5
(47×10^{-3})		—	(21.8×10^{-3})	(26.7×10^{-3})	(3.5×10^{-3})
Se	SS-2	—	29.1	61.5	96.5
(2×10^{-3})		—	(1.42×10^{-3})	(0.77×10^{-3})	(0.07×10^{-3})
Cd	SS-2	—	21.0	27.0	44.0
(15×10^{-3})		—	(11.85×10^{-3})	(10.95×10^{-3})	(8.4×10^{-3})
Hg-1	SS-1	—	7.5	96.7	96.7
(17×10^{-3})		—	(15.7×10^{-3})	(0.6×10^{-3})	(0.6×10^{-3})
Hg-2	SS-2	—	99.0	99.0	99.0
(17×10^{-3})		—	(0.2×10^{-3})	(0.2×10^{-3})	(0.2×10^{-3})
Hg-3	EF-2	—	24.0	52.0	71.0
(0.22×10^{-3})		—	(0.167×10^{-3})	(0.106×10^{-3})	(0.064×10^{-3})

% RL: Removal level percentage, EF-1: Actual effluent sample without HCOONa addition, EF-2: Actual effluent sample with HCOONa addition, SS-1: Simulated solution sample without HCOONa addition, SS-2: Simulated solution sample with HCOONa addition.

removal in actual effluent at 500 kGy; second one with HCOONa addition. Cd did not show good removal (44.0% at 500 kGy) because the whole experiment was performed in the oxidant atmosphere. Hg showed a 71.0% removal in actual effluent at 500 kGy and a 99.0% removal in the simulated solution at 500 kGy; both samples with HCOONa addition. This removal variation is due to different initial Hg concentrations in these samples: 0.22 and 17 $mg\,l^{-1}$, respectively.

4. Conclusions

The electron beam treatment seems to be a promising process for metals removal in industrial effluents. However, the metal removal levels depend strongly on initial sample characteristics, as inorganic, organic and biologic composition, organic matter content and pH, due to their competition for reactive specimens consumption produced by irradiation process.

Acknowledgements

To FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, Brazil) for financial support.

References

Chaychain, M., Al-Sheikhly, M., Silverman, J., McClaughlin, W., 1998. The mechanism of removal of heavy metals from water by ionizing radiation. Radiat. Phys. Chem. 53, 145–150.

Kartasheva, L.I., Chulkov, V.N., Didenko, O.A., Piek, V.K., Kim, D.K., Kim, Y., Han, B., 1997. Cadmium removal from water by electron-beam treatment in presence of a scavenger of OH radicals. High Energy Chem. 31 (5), 349–352.

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

Pikaev, A.K., Kartasheva, L.I., Zhestkova, T.P., Yurik, T.K., Chulkov, V.N., Didenko, O.A., Kim, D.K., Kim, Y., Han,

B., 1997. Removal of heavy metals from water by electron-beam treatment in the presence of a hidroxyl radical scavenger. Mendeleev Commn. 52–53.

Ribeiro, M.A., Sato, I.M., Duarte, C.L., Salvador, V.L.R., Sampa, M.H.O., 2002. Determinação de Grau de Remoção de Metais Tóxicos como As, Hg, Pb e Cd em Solução Simulada de Efluentes Industriais na Presença de "scavengers" após a Irradiação com Feixe de Elétrons. INAC/2002: International Nuclear Atlantic Conference, 11–16 August 2002, Rio de Janeiro, RJ, Brazil, E03-294.

Scapin, M.A., Sato, I.M., Duarte, C.L., Sampa, M.H.O., Salvador, V.L.R., Borrely, S.I., Ribeiro, M.A., Rela, P.R., Oikawa, H., 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 Analísis por Técnicas de Rayos X. ISSN 1515–1565 XI, 87–91.

Wheller, B., 1998. Chemical analysis of ferrous base alloys utilizing the fundamental parameters technique assisted by standards of similar and dissimilar materials. The Rigaku J. 15, 28–40.