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IMPROVEMENT OF CONVENTIONAL PARAMETERS OF ACTUAL INDUSTRIAL EFFLUENT BY ELECTRON BEAM IRRADIATION

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Abstract

The ordinary process to treat wastewater from the dye, textile, chemical, pharmaceutical and paper mill industries do not degrade easily the colored substances and organic compounds. A study on the improvement on this treatment using high energy electron irradiation was carried out. Experiments were conducted using samples from the public Wastewater Treatment Plant (WTP) that receives about 80% of wastewater from industrial sources and 20% from domestic sources. A large amount of industrial wastewater comes from chemical and textile industries changing every day the quality, quantity and color, these characteristics depend on the production line of each particular industry. Samples from WTP influent and effluent were collected every 15 days and irradiated in a batch system, the delivered doses were 3.0 kGy, 4.0 kGy, 6.0 kGy, 8.0 kGy and 10.0 kGy. For the non irradiated and irradiated samples the following parameters were analyzed: chemical oxygen demand (COD), fixed and volatile total solids and fixed and volatile suspended solids, absorption spectrum (300 -700nm) and gas chromatography. For samples from effluent irradiated with 3.0 kGy dose, the COD value presented a reduction average of 45%, and this result was fix for higher doses, however the COD of influent sample did not show signifcn change for all the delivered doses.

1. INTRODUCTION

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[1,2].

Industrial wastewater differs from domestic sewage by the nature of pollutants content and their higher concentration, normally with substances that are toxic and difficult to be degraded, among such substances are dyes, detergents, organic compounds, etc.

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: 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[3,4].

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 $OH^\cdot$, the unique process that produce the

reducing specie e^-_{aq} is the electron beam irradiation These reactive species will react with organic and inorganic compounds in the water inducing their decomposition, the products of these reactions will depend on the compounds present in solution. 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 [4,5].

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[5,6].

This technology has been extensively studied by many researches [7,8,9,10,11,12] most of the experiments have been conducted in samples of pure water spiked with the contaminant. It is very important to study reactions and degradation mechanisms, however when actual industrial effluents are used, the mixture of different kinds of pollutants can take to side reactions not observed in pure water.

The tests shown in the presented work were performed using samples from industrial wastewater collected at the Public Wastewater Treatment Plant in São Paulo State. This Wastewater Treatment Plant (WTP) receives about 80% industrial sources and 20% from domestic origin, the activated sludge process is used as treatment and the sludge dewatering is made by filter press. A large amount of industrial wastewater comes from chemical industries and its characteristics of quality, quantity and color changes every day resulting in a low efficiency of the wastewater treatment plant, even after the treatment some organic compounds and colored substances remain in the effluent, allowing the discharge of dangerous products to the environment.

The aim of this work is to evaluate the efficiency of the electron beam irradiation to improve the conventional parameters of actual wastewater, before and after the conventional treatment process. The combination of irradiation and biological oxidation can increase the efficiency and economy of decomposition of refractory pollutants, the choice of combination of methods depends on the biological chemical and physical properties of the pollutants and their behavior in irradiation process.

2. EXPERIMENTAL

Irradiation were performed using the IPEN's Electron Beam Facility with a 1.5MeV Dynamitron system from Radiation Dynamics Inc., the beam current range is from 1 mA to 25 mA, the electron beam is scanned on a 60 cm length and 4 cm width area, at a frequency of 100 Hz[13].

The influent and effluent samples from WTP were collected three times each 15 days and irradiated in a batch system, using Pyrex glass vessels (500 mL), the delivered doses were 3.0 kGy, 4.0 kGy, 6.0 kGy, 8.0 kGy and 10.0 kGy with 1.5 MeV electron energy and currents in the range of 0.1 mA to 25 mA to reach the desired doses. Wastewater layer thickness (4 mm) and the conveyor velocity (6.72 m/min) were kept constant during irradiation. For the non irradiated and irradiated samples, the chemical oxygen demand (COD) and fixed (103-105^{0}C) and volatile total solids (550^{0}C) and fixed and volatile suspended solids (using Millipore filter type AP40) analyses, were determined in accordance with Standard Methods for the Examination of Water and Wastewater [14].

To evaluate the radiation effect on the decoloration of the sample, the absorption spectra (300 -700 nm) was obtained using a Shimadzu Spectrophotometer UV-Visible, Model 1601. The gas chromatography analysis were made using a Gas chromatography CG -90, just to observe the degradation of the organic compounds and not to identify or quantify the byproducts.

3. RESULTS

The COD of effluent samples presented a reduction about 45% when 3.0 kGy dose was applied , at the higher doses the COD values approaches a fixed value for all the series, as it was reported in the literature, at small doses the COD value appears to be more sensitive to dose change and at the higher doses the COD approaches a fixed value, however the COD of the three series of influent sample did not change for all the irradiation doses. The COD results of three series from WTP influent, and of three series from effluent samples were used to built the graphic Dose vs COD presented in the Fig. 1.

The Tables I and II and the Figs. 2 and 3 show the results of solids analysis of the three series for non irradiated and irradiated samples. The influent samples present a higher total solid concentration than effluent samples and the percentage of suspended solid is higher in the first case. The total fixed solid represent almost the totality of total solids in both cases. The volatile suspended solid from the effluent represents almost the totality of the total suspended solid, it means that the most part of suspended solid are organic material remaining after conventional treatment.

Even after conventional treatment organic compounds remain in the samples, as can be seen by the gas chromatogram spectra showed in the Fig. 4 from the irradiated and non irradiated sample of WTP effluent, the degradation of organic compounds can be observed by the reduction of the peaks when the sample was irradiated at 3.0 kGy dose.

The Fig. 5 shows the absorption spectra UV-VIS of irradiated and non irradiated effluent samples that presented more colored substances, the delivered doses were 3 kGy and 10 kGy. The reduction of color is visible with 3.0 kGy dose and for higher doses it was not significant

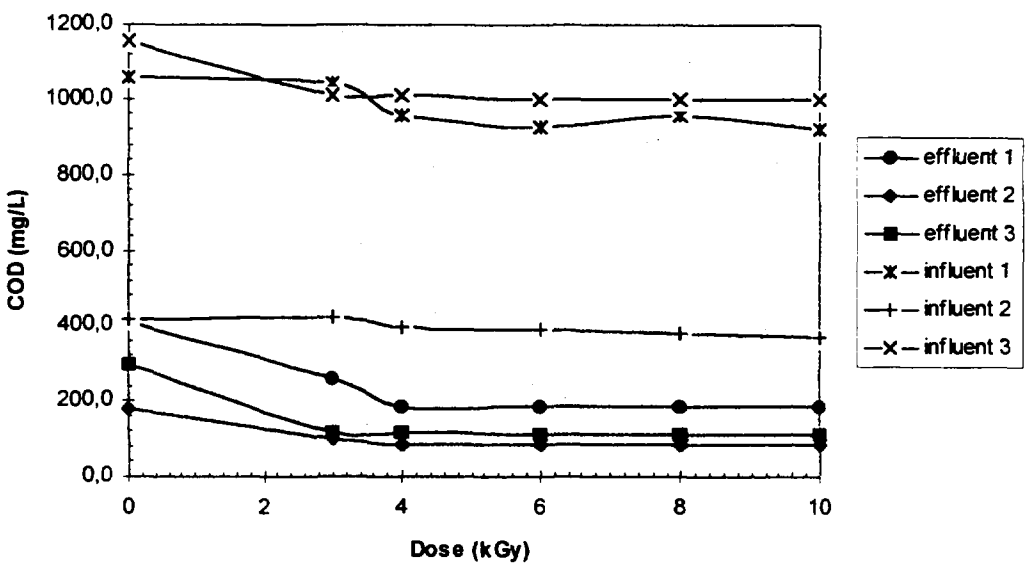

FIGURE 1 COD vs irradiation dose of samples from WTP

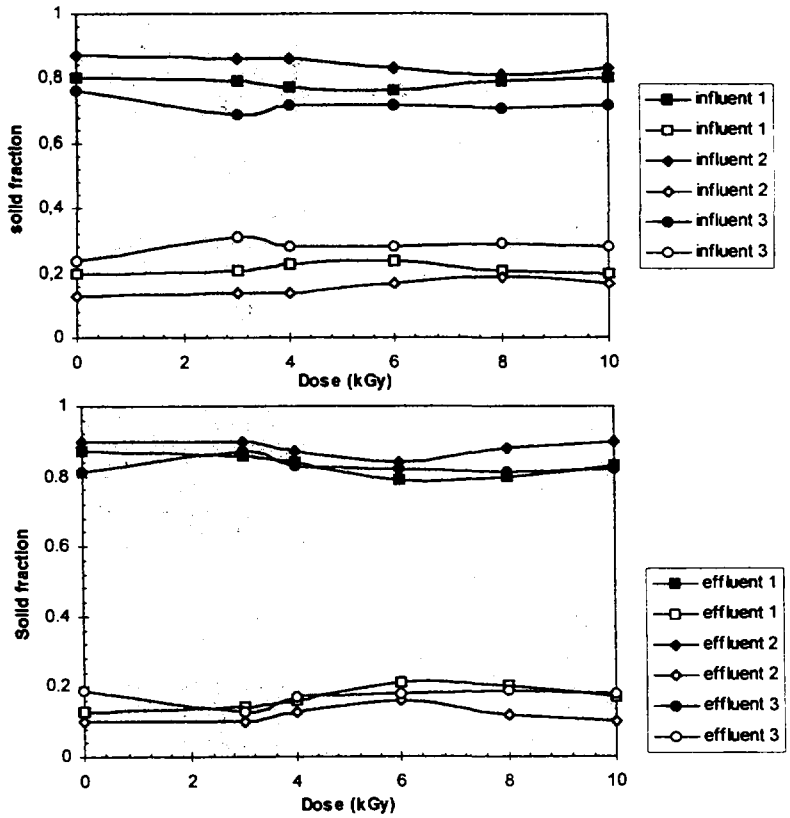

FIGURE 2 Fraction of total fix and total volatile solid vs irradiation dose of samples from WTP influent and effluent

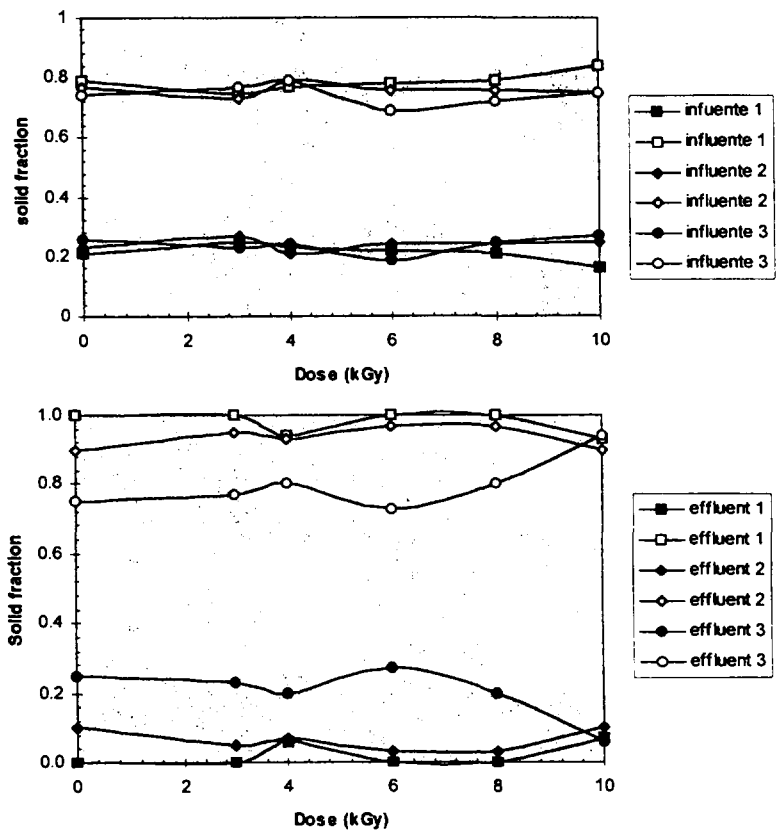

FIGURE 3 Fraction of total suspended fix and total suspended volatile solid vs irradiation dose of samples from WTP influent and effluent

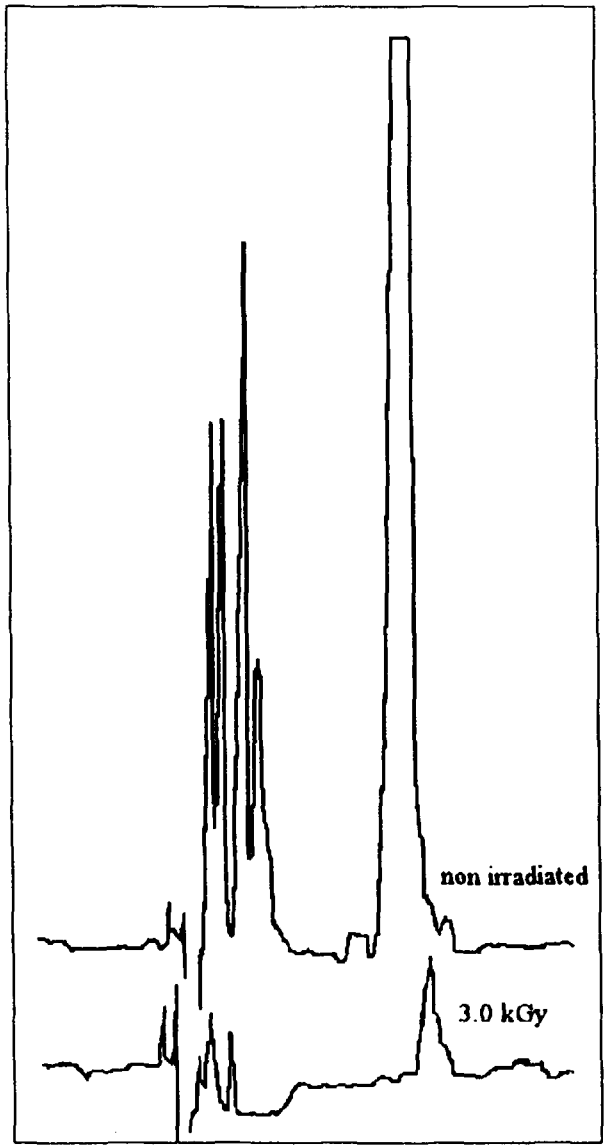

FIGURE 4 Chromatograms of WTP effluent 1

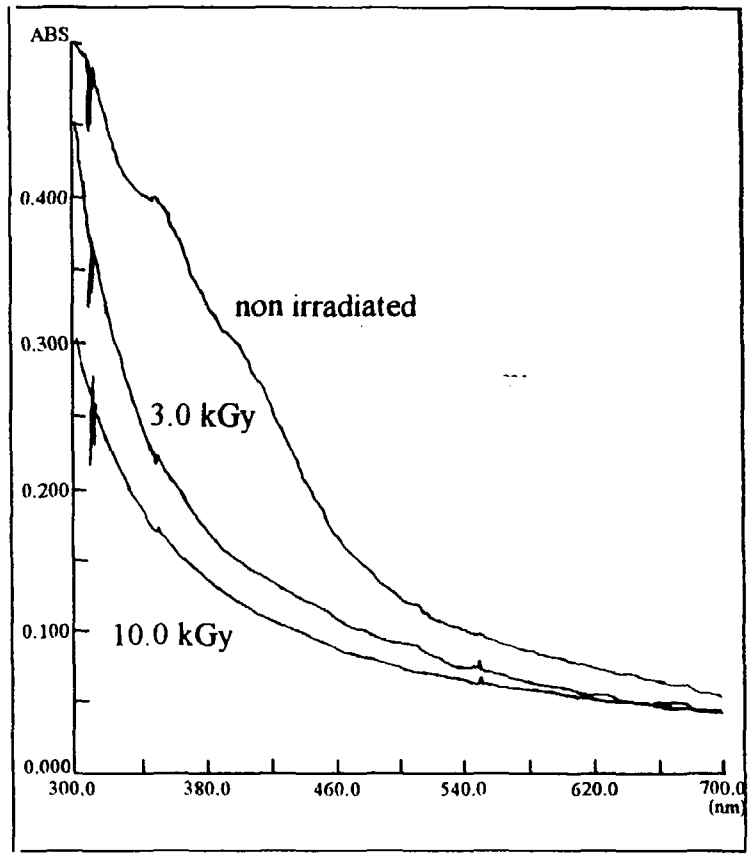

FIGURE 5 Absorption spectra of WTP effluent 1

TABLE I. SOLIDS CONCENTRATION OF SAMPLES OF INFLUENT FROM WTP

Dose (kGy)	Total solid (g/L)	Total fix (g/L)	Total volatile (g/L)	Total suspended (g/L)	Suspended fix (g/L)	Suspended volatile (g/L)	Suspended (%)
Serie 1							
0.0	2.44	1.96	0.48	0.19	0.04	0.15	7.7
3.0	2.48	1.95	0.53	0.21	0.06	0.15	8.3
4.0	2.50	1.93	0.57	0.19	0.05	0.14	7.5
6.0	2.48	1.89	0.51	0.17	0.04	0.13	6.9
8.0	2.45	1.94	0.51	0.15	0.03	0.12	5.9
10.0	2.43	1.95	0.48	0.11	0.02	0.09	4.5
Serie 2							
0.0	1.69	1.46	0.22	0.07	0.02	0.05	4.2
3.0	1.69	1.45	0.24	0.05	0.01	0.04	2.9
4.0	1.70	1.47	0.23	0.04	0.01	0.03	2.5
6.0	1.75	1.45	0.29	0.07	0.02	0.06	4.2
8.0	1.79	1.46	0.33	0.07	0.02	0.06	4.1
10.0	1.79	1.49	0.30	0.05	0.01	0.04	2.9
Serie 3							
0.0	2.14	1.62	0.51	0.31	0.08	0.23	14.3
3.0	2.3	1.59	0.71	0.30	0.07	0.23	13.2
4.0	2.27	1.63	0.64	0.30	0.08	0.24	13.2
6.0	2.23	1.60	0.63	0.30	0.07	0.21	13.4
8.0	2.21	1.57	0.65	0.26	0.06	0.19	11.9
10.0	2.22	1.61	0.61	0.26	0.07	0.19	11.5

TABLE II. SOLIDS CONCENTRATION OF SAMPLES OF EFFLUENT FROM WTP

Dose (kGy)	Total solid (g/L)	Total fix (g/L)	Total volatile (g/L)	Total suspended (g/L)	Suspended fix (g/L)	Suspended volatile (g/L)	Suspended (%)
Serie 1							
0.0	1.45	1.26	0.19	0.013	0.000	0.013	0.9
3.0	1.47	1.27	0.19	0.021	0.000	0.021	1.4
4.0	1.52	1.28	0.23	0.019	0.001	0.018	1.3
6.0	1.56	1.24	0.33	0.005	0.000	0.005	0.3
8.0	1.57	1.26	0.31	0.014	0.000	0.014	0.9
10.0	1.50	1.25	0.25	0.010	0.003	0.007	0.5
Serie 2							
0.0	1.39	1.25	0.14	0.026	0.003	0.023	1.8
3.0	1.41	1.27	0.14	0.012	0.000	0.012	0.8
4.0	1.47	1.28	0.18	0.015	0.001	0.014	1.0
6.0	1.46	1.23	0.23	0.015	0.000	0.015	1.0
8.0	1.46	1.28	0.16	0.016	0.000	0.016	1.1
10.0	1.44	1.29	0.14	0.016	0.001	0.015	1.1
Serie 3							
0.0	1.51	1.23	0.28	0.024	0.006	0.018	1.6
3.0	1.48	1.29	0.19	0.030	0.007	0.023	2.0
4.0	1.56	1.30	0.26	0.025	0.012	0.020	1.6
6.0	1.54	1.27	0.27	0.030	0.008	0.022	2.0
8.0	1.55	1.26	0.29	0.020	0.004	0.016	1.3
10.0	1.57	1.29	0.27	0.017	0.001	0.016	1.1

4. CONCLUSION

The general improvement of the WTP effluent was acquired when irradiated at 3,0 kGy dose, nevertheless the irradiation of WTP influent do not show a visible change by the analyses methods employed in the present investigation.

As the influent samples had no treatment and the industrial contributors had a lot of different kinds of contaminants that were not identified, these contaminants could actuated as a scavenger of reactive species interfering during the irradiation process, another reason of interference could be the presence of high quantity of fix solids (metals and others).

Studies of the changes on biochemical oxygen demand (BOD) of the irradiated influent are being performed to evaluate the degradation of the contaminants in easily intermediate biodegradable compounds.

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REFERENCES

1-SANEAMENTO BÁSICO DO ESTADO DE SÃO PAULO- SABESP- Bulletin, São Paulo, 7 (1991).

2-POMPEIA, S. L. Áreas degradadas por poluição - Procedimentos técnicos para recuperação. Saneamento Ambiental, 37 (1996) 14-18.

3-GEHRINGER, P.; ESCHWEILER, H.; SZINOVATZ, W.; FIEDLER, R.; STEINER, R.; SONNECK, G. Radiation-induced OH radical generation and use for groundwater remediation. Radiat. Phys. Chem., 42 (1993) 711-714.

4-COOPER, W.J.; NICKELSEN, M.G.; LIN, K.; SUTNICK, M.; MAK, F.T.; KURUCZ, C.N.; WAITE, T.D. E-Beam treatment of aqueous based toxic organic wastes. Proceedings on radiation curing conference exposition, held in Boston (1992) 509-513.

5-WANG, T.; WAITE, T.D.; KURUCZ, C.; COOPER, W.J. Oxidant reduction and biodegradability improvement of paper mill effluent by irradiation. Wat. Res., 28 (1994) 237-241.

6-PIKAEV, A.K. Current state of radiation processing. Russian Chem. Rew. 64 (1995) 569-598.

7-GEHRINGER, P.; PROKSCH, E.; ESCHWEILER, H.; SZINOVATZ, W. Remediation of groundwater polluted with chlorinated ethylene's by ozone-electron beam irradiation treatment. Appl. Radiat. Isot., 43(1992) 1107-1115.

8-GETOFF, N. Purification of drinking water by irradiation. A review. Proc. Indian Acad. Sci., 105(1993) 373-391.

9-MATTHEWS, S.M., BOEGEL, A.J., LOFTIS, J.A. Radiolytic decomposition of environmental contaminants and site remediation using an electron accelerator. Remediation, 3(11993) 459-481.

10-PODZOROVA, E., A. New developments in radiation-chemical technology of sewage treatment. Radiat. Phys. Chem., 46 (1995) 1129-1132.

11-NICKELSEN, M.G.; COOPER, W.J. Removal of benzene and selected alkyl-substituted benzene's from aqueous solution utilizing continuous high-energy electron irradiation. Envir. Sci. Technol., 26(1992).

12-SILVA, B.L.R.; SAMPA, M.H.O.; AVOLIO, R.M.; SOMESSARI, E.S.R.; VIEIRA, J. M.; RELA, P.R. Estudo da degradação de tricloroetileno e tetracloroetileno utilizando feixe de elétrons de alta energia gerado em acelerador industrial. III Encontro Nacional de Aplicações Nucleares, Aguas de Lindóia, (1995) 257-261.

13-SAMPA, M.H.O., BORRELY, S.I., VIEIRA, J.M.; RELA, P.R.; CALVO, W.A.P.; NIETO, R.C.; DUARTE, C.L.; PEREZ, H.E.B.; SOMESSARI, E.S. The use of electron beam accelerator for the treatment of drinking water and wastewater in Brazil. Radiat. Phys. Chem., 46 (1995) 1143-1146.

14-AMERICAN PUBLIC HEALTH ASSOCIATION. STANDARD. Methods for the Examination of Water and Wastewater. 17 ed. Washington, DC. APWA, AWWA, WPCF (1997).