2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-05-2**

ELECTRON BEAM IRRADIATION AND ADSORPTION AS POSSIBILITIES FOR WASTEWATER REUSE

Sueli I. Borrely[1] , Marcela C. Higa[1], Alessandro Pinheiro[1], Aline V. Morais, Denise A. Fungaro[2]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
sborrely@ipen.br

[2] Centro de Quimica e Meio Ambiente (IPEN/CQMA)

ABSTRACT

The importance of water for life and for the industrial processes is forcing the development of combined technologies for wastewater improvement. The limitations of biological treatment for reducing micro-pollutants and the constant introduction of different chemical into environment make Ionizing Radiation a more interesting technique for pollutants abatement. Electron Accelerators are the main radiation source for cleaning waters purpose. Remazol Orange and Black B were decomposed by Electron Beam Irradiation. Another research consisted in reuse of burnt coal for cleaning wastewater and the Orange and Red dyes were adsorbed onto zeolitic material. Both color and toxicity were the main parameters to evaluate the efficacy of the process and also the recommended criteria which allow further industrial reuse. Real effluents were also treated by both technologies in batch scale. The radiation dose suggested for real effluents varied from 2.5kGy up to 5kGy. The characteristics of obtained zeolite will be presented. The removal of color and toxicity was enough to allow the industrial reuse of those products (wastewater).

1. INTRODUCTION

The water is a basic resource for life maintenance as it is indispensable for industrial activities. At textile industries the water and the dyes are the principal resources, beyond the fibers and textiles. During the manufacture of cotton textile water usage may reach from 100 to 300 $L.kg^{-1}$ of textile product. On the other hand new generation of dyes were developed to attend the environment criteria, reducing loses of dyes during their application and to manage other negative impacts. Nevertheless there are still some improvements to be done, in order to achieve the targets for industrial reuse of water. From the biological point of view some effects of dyes for living organisms will be further discussed and are important for both situations: the efficacy of biological treatment at the industrial site and after to protect biota when effluents are discharged.

The dyes are not completely consumed during dying processes and part is removed from fibers during final washing. These are some of the reasons why the textile effluents may present 10 to 25 mg/L of dyes, according to the type of dye and applied dying process (Pinheiro, 2011; Hassemer, 2006). In these sense the reuse of water is really important and the requirements for internal reuse is reported by CIESP, 2011. The reduction in color units is mandatory [1,2,3].

Concerning radiation technology for wastewater improvement, there are interesting expertise in South Korea and United States. The first is related to EB Machines especially designed for treating colored effluents from Daegu and after it was designed a mobile system [4]. On the other hand, USA developed an important program in Maiami Wastewater Treatment Plant which evaluated the EB Technology for several years for disinfection and improvement of final effluents [5]. Working on real textile effluents the Brazilian Studies included many types of pollutants such as dyes, surfactants, organic solvents among others [6].

Besides this technology, several other methods are being proposed and adsorption processes have been reported. In Brazil one of them is related to the burnt of coal, which would be a very good way to recycle a solid residue from energy production once zeolitic material can be produced from them. The coal fly ash, transformed into zeolites, were effective for the removal of Methylene Blue from water and accounted for efficient reduction of whole toxicity [7]. When cyclone ash as adsorbent was used for the removal of reactive Orange 16 from aqueous solution satisfactory results for color were obtained. Nonetheless it is necessary to reduce acute toxic effects promoted by the surfactant-modified zeolite [8].

Ionizing Radiation is one of the possibilities to be applied for water reuse during textile manufacture. South Korean Project installed two accelerator for dyeing treatment. They applied 1-2kGy before the effluent be treated by a secondary activated sludge system. In Brazil the reactive dyes decoloration were studied by Pinheiro et all, 2011 and Real Effluent submitted separately to RB irradiation and coal zeolites were carried by Higa [9].

The decoloration of final effluent is necessary for environment and also for wastewater directly reuse. CIESP, 2011 Manual was published to facilitate and offer the requirements for wastewater reuse [3].

2. **METHODOLOGY**

The Electron Beam Accelerator was used for the decomposition of reactive dyes and for the decoloration from real effluents and for toxicity removal. Most of the samples were also submitted separately to the adsorption process which were based on the transformation of coal fly ash into zeolotic material. Ecotoxicological correlated aspects of the compounds treated by radiation and untreated are reported. The samples were treated and subjected to toxicity assays with *Vibrio fischeri* and *Daphnia similis*. The research carried out with reactive dyes qualitative analysis was performed by UV-Vis spectrophotometry. At figure 1 both techniques were presented.

<u>Samples</u>: Reactive dyes, 8 samples from textile SP, two treatments, toxicity for water flea (*D.similis*) and luminescent bacteria (*V.fischeri*)

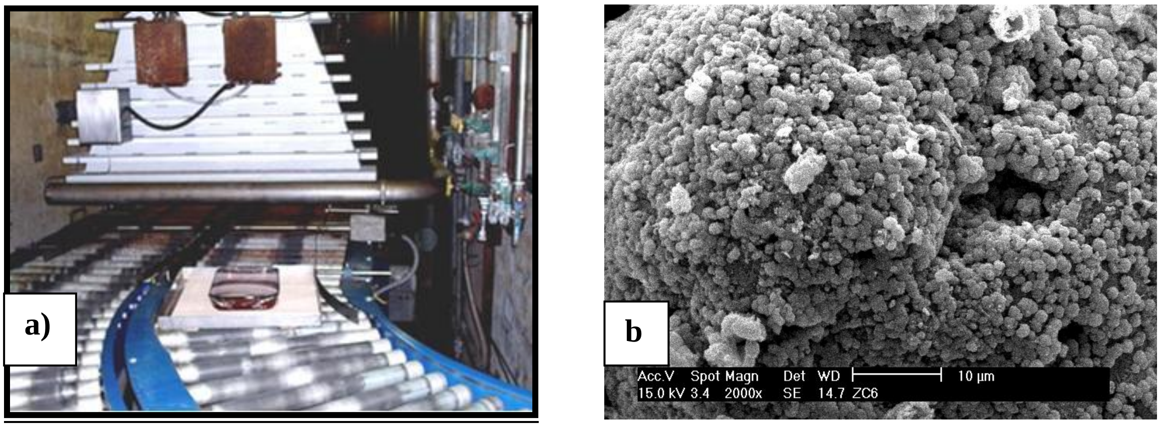

Figure 1 - Developing Technologies for removal of reactive dyes from wastewater:
a) EB irradiation of effluent; b) Photomicrography of zeolites obtained from coal

The experimental conditions during the research are presented separately. Irradiations: A Dynamitron® Electron Beam Accelerator was used during the irradiations and fixed parameters were: 37.5 kW power, 1.4 MeV energy. The electric current varied according to the required dose from 0 up to 25mA. Radiation doses applied were 2.5, 5.0, 7.5, 15.0 and 20.0 kGy. During the *Vibrio fischeri* luminescence assays an screening information was obtained to verify the effective radiation doses for the decomposition of 5 mg L^{-1} FH.

Zeolites: The raw material for the obtaining zeolite was Cyclone Coal fly Ash from Figueira da Foz Thermic Power Plant (CCA). Material preparation: 30g of CCA was mixed with 240mL of 3.5mol L-1 aqueous NaOH solution in a 300mL Teflon vessel. This mixture was heated to 100°C in oven for 24h. After this process, the suspension was filtered with 4A quantitative filter paper. The zeolite from cyclone fly ash (ZC) was repeatedly washed with deionized water until the pH of washing water reach ~ 11 and dried at 50°C for 12h. The following step was the general evaluation of zeolites: characterization, adsorption studies and kinetcs [7,8].

Before and after the adsorption treatment be applied to the dye solution, the acute toxicity was measured for two classes of aquatic organisms according to Brazilian Standard ABNT methods [10,11].

Toxicity: a) using the Microtox System® to measure the luminescence of bacteria *Vibrio fischeri* and related effects meaning losing luminescence. b) the immobility of crustacean Daphnia similis was also related to the dyes effects. In this case the organisms are obtained from a proper Laboratory cultivation in natural water.

3. RESULTS AND DISCUSSION

The research comprised two types of samples and two completely different treatment technologies. In this sense the toxicity of all reactive dyes and also real effluents evaluated during the researches is presented at Table 1.

The toxicity values were expressed by the medium effective concentration (EC50), which refers to the concentration of the dye in a given standard solution or to the percentage of a raw sample which is lethal to 50% of exposed living-organism within a specified exposure time. It is often used the Toxic Units (TU) to calculate the efficiency of treatment processes for reducing toxicity, once EC50 is an inverse function, it means that the lower the EC50 higher is the toxicity.

Table 1 – Average values of toxicity (EC50) for the studied solutions before the treatment processes

S a m p l e	**EC50[1] (% or ppm)**	**EC50[2] (% or ppm)**	**References**
BTV 01	23.44	14.26	Higa, 2011
BTV 02	14.83	42.44	Higa, 2011
BTV 03	29.12	68.45	Higa, 2011
R e a c t i v e D y e s			
Black B*	28.15	96.21	Pinheiro, 2011
Orange 3R*	13.02	4.41	Pinheiro, 2011
Orange 16_p	16.72	92.10	Fungaro et al, 2013

EC50[1] - *V. fischeri* (15 min); EC50[2] - *D. similis* (48h);
Reactive dyes* (133% - industrial distribution: dying potency*);*
Orange 16p – pure compound as standard.

3.1 – EB Radiation for decoloration and detoxification of reactive dyes and effluents

Regarding color removal by radiation processing, at Figure 1 it was presented the efficacy of the radiation for the reactive dyes black B and Orange 3R, both irradiated for several doses.

3.2 – Zeolites adsorption of textile effluent and reactive dyes

At Table 2 it was presented the main results obtained during adsorption process for textile effluents sampled at different days (BTV 01, BTV 02 and BTV 03) and for dyes standard solution.

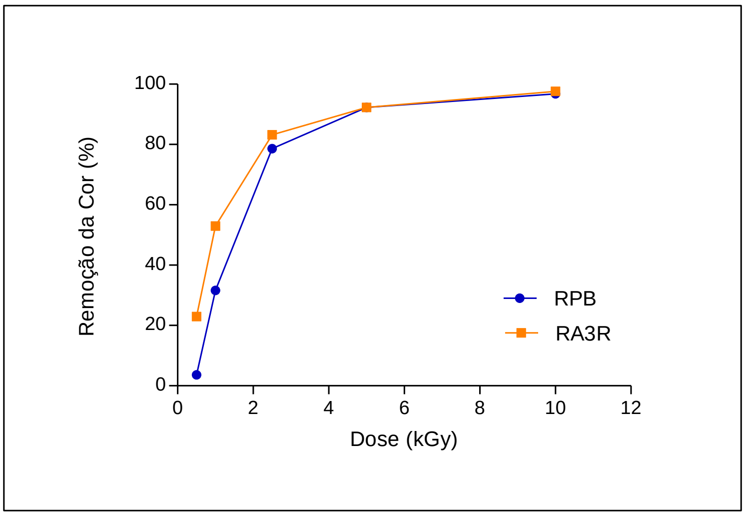

Figure 2: Color removal versus Radiation Dose (EB Techlology)

Table 2 – Acute toxicity removal on textile effluent treated by zeolites adsorption

Sample	**Zeolite**	**TUi**	**TUf**	**Removal (%)**	**Assay**
BTV 01	ZC6	4.35	2.97	31.72	*V. fischeri*
BTV 02	ZC6	7.01	1.47	79.03	*D. similis*
BTV 03	ZC6	7.01	1.77	74.75	*D. similis*
Dyes RO16	CCA	5.80	-	-	*V.fischeri*
Dyes RO16	SMZCA-20	5.80	8.24	increase	*V.fischeri*

According to obtained results it is possible to confirm that the reactive dyes are very toxic specially for *Vibrio fischeri* and the same pattern was observed for the BTV effluents toxicity (Table 1). From this table only once we observed the higher toxicity for *Daphnia similis* (4.41 ppm) compared to *V.fischeri* (13.02 ppm): Orange 3R* with 4.41 ppm meaning three times more toxic on *D. similis* than to the *V. fischeri* bacteria. Very important removal of total color was obtained by radiation on standard dye solutions and also on real effluents.

At Figure 2 it was presented the color removal from reactive dyes as a function of radiation dose (kGy). The doses from 2kGy up to 5kGy was good enough for color removal in this research and also during experiments carried by Higa, 2011 using BTV effluents.

Concerning the adsorption technology, the data for effluents and dyes solutions treated by coal's zeolite are presented at Table 2. Regarding toxicity data, it was obtained good results but the higher efficacy was obtained for *Daphnia similis* crustacean than for *Vibrio fischeri* bacteria. Removal percentage > 70 for acute toxicity. This technique is important not only due to the reuse of a solid waste (burnt coal) but also because it can be applied in batch systems during dying process and remove color of real effluents with a relatively low cost.

The reuse of water is part of obligation and management for several industrial water used in Brazil. Textile activities are important for economy and the water consumption during their processes are very high. The final textile effluents often are discharged with hard variation of contaminants due to the variety of chemical used during textile manufacture.

Regarding industrial water reuse, there is the "Manual de Conservação e Reuso de Água para a Indústria", which was published by CIESP, 2011 [8]. This document recommend that for most types of textile reuse of water the following targets need to be achieved: color < 5 UH, hardness < 25 $CaCo_3$, Mn: 0.01 < Mn < 0.05; pH: 3.5 – 10.5 (except for starching process); 100 ppm and 5 ppm for TDS and SS, respectively.

In general the color is apparently the worst irregular number for effluent reuse in textile activities and the reactive dyes are widely applied for cotton benefits (important manufacture in Brazil). On the other hand, the discharge of such a type of residue into the rivers requires the control of toxicity.

Another question is the residual toxicity which is variable with the time, according to the daily manufacture and chemicals used during their processes. Most of the time biological process is applied for final effluents and when very high toxic charge are discharged into the treatment system it damage the activated sludge system. In this direction both mentioned technologies may contribute to reduce toxic charge as a previous treatment, improving the further biological step of treatment allowing suitable water reuse of a safety discharge of treated effluent to the environment.

In terms of chemical structure, colorants may either be inorganic or organic compounds (both groups natural or synthetic).While pigments consist of small particles that are practically insoluble in those media in which they are applied, dyes are applied to various substrates (textiles, leather, paper, hair etc) from a liquid in which they are completely, or at least partly, soluble. Reactive dyes as organic compounds are suitable for radiation degradation and many efforts are continuously done by the zeolites group in terms of getting chemical modification in order to improve the adsorption capacity of this material.

3. CONCLUSIONS

The residual color and toxicity of effluents are discussed and two distinct treatment processes were evaluated. EB Irradiation is one of them and the doses from 1kGy up to 5kGy may be succeffully applied for industrial reuse of wastewater. The same importance may be given to the coal zeolites which are suitable for the decoloration of dyed solutions and wastewater accounting also for the reduction of whole acute toxicity.

ACKNOWLEDGMENTS

To the IAEA for the grants (RC Project); CNPQ for the financial support of post-graduation students and Research Contract (Universal). CNEN for the student financial support during PHD.

REFERENCES

1. A.S. Pinheiro. Avaliação da toxicidade e genotoxicidade dos corantes azo reativos Remazois Preto B e Alaranjado 3R e da eficácia da radiação com feixe de elétrons na redução da cor e efeitos tóxicos. (Tese de Doutorado) Instituto de Pesquisas Energéticas e Nucleares. 2011.
2. M.E.N. Hassemer, 2006 Oxidação fotoquímica - UV/H_2O_2 – para degradação de poluentes em efluentes da indústria têxtil. Dissertação (Mestrado em Engenharia Ambiental). Universidade Federal de Santa Catarina.
3. CIESP, 2011. Manual de conservação e reúso de agua para a indústria. www.ciesp.gov.br.
4. B. Han, J. Kim, Y. Kim, J.S. Choi, I.E. Makarov, A.V. Ponomarev. Electron beam treatment of textile dyeing wastewater: operation of pilot plant and industrial plant construction, *Water Science and Technology*, **52** (10-11), pp. 317-324 (2005).
5. W.J. Cooper; D.E.Meacham; M.G.Nickelsen; L.Lin, D.B.Ford; C.N. Kurucz; T.D.Waite. The removal of tri-(TCE) and tetrachloroethylene (PCE) from aqueous solutions using high energy electrons. J.Air Waste Manag.Assoc. **43**: 1358-1366. 1993.
6. S.I. Borrely, A.A. Gonçalves, H. Oikawa, C.L. Duarte, F.R. Rocha, "Electron beam accelerator for detoxification of effluents. When radiation processing can enhance the acute toxicity?", *Radiation Physics and Chemistry*, **71**, pp. 453 -456 (2004).
7. D.A.Fungaro, S.I.Borrely, T.E.M.Carvalho. Surfactant modified zeolite from Cyclone ash as adsorbent for removal of reactive Orange 16 from aqueous solution. *American Journal of Environmental Protection, 2013,* **Vol. 1**, n. 1, 1-9 (DOI: 10.1269/env-1-1-1).
8. D.A.Fungaro, S.I.Borrely, T.E.M.Carvalho. Adsorption of reactive orange 16 onto zeolite synthesized from fly ash: kinetics and equilibrium studies. Proc. Symp. Brazil-Japan in Economy, Science and Technological Innovation. Sao Paulo, Brazil. June 2008.
9. HIGA, M. Aplicação de ensaios de toxicidade na avaliação da eficiência da radiação ionizante e da adsorção em zeólitas para o tratamento de efluentes coloridos. (Dissertação de Mestrado). Instituto de Pesquisas Energéticas e Nucleares. 2011.
10. Associação Brasileira de Normas Técnicas (ABNT NBR 12713). Ecotoxicologia Aquática – Toxicidade Aguda - Método de Ensaio com *Daphnia spp* (CLADOCERA, CRUSTACEA). 21 p. 2004.
11. Associação Brasileira de Normas Técnicas. "Ecotoxicologia aquática – Determinação do efeito inibitório de amostras de água sobre a emissão de luz de *Vibrio fischeri* (Ensaio de bactéria luminescente) Parte 3: Método utilizando bactérias liofilizadas", ABNT NBR 15411-3 (2006).