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ELECTRON BEAM IRRADIATION AND ZEOLITES ADSORPTION APPLIED TO DYEING EFFLUENTS

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ABSTRACT

Wastewater generated from the textile industries contain large amount of azo dyes and many of them present low biodegradability capability. Today several countries are facing with evidences that water pollution is related to toxicity, mutagenicity and carcinogenic nature. Once reactive dyes are commercial products they will be discharged to the waterways and rivers causing ecological damages and health problems. The aim of this paper was to consider the potential of two techniques for colour and toxicity removal: ionizing radiation and adsorption by zeolites synthesized from fly ash. Real effluents from chemical and textile industries (hardly coloured) were submitted to radiation and adsorption using zeolites. It was necessary to dilute some effluents prior the treatments in order to get any success. When electrons irradiation was performed radiation doses applied were from 0.5kGy up to 20kGy. This radiation process accounted for a partial decolouring as higher doses were implemented. Coal fly ashes were used as starting material for zeolite synthesis by means of hydrothermal treatment with alkaline medium. The adsorption was performed by batch experiments. It was obtained about 77% - 90% color removal from dye wastewater after 24h of contact time with two types of zeolite. The irradiation accounted for 72% of the initial toxicity. The ionizing radiation and adsorption by zeolites synthesized from fly ash can be used as an alternative for the treatment of aqueous waste containing dyes.

1. INTRODUCTION

Many industries such as textile and printing use dyes and pigments and thus produce highly colored waste effluents. Disposal of these wastes into waters causes environmental problems Due to your own nature, the color is detected by human eyes, even if in concentrations for 1mg/L [1]. This characteristic results principally from dyes that are applied in operations of dyeing [2]. Additionally, the discard of dyes in rivers and lakes damage the absorption of luminous energy, alternating the aquatics ecosystems, affect also the effluent on esthetic and the solubility of gas into the water [3]. New technologies have been developed to the degradation or immobilization of these compounds for textile effluents [4].

Adsorption techniques employing solid adsorbents are widely used for removal of certain chemical pollutants from waters [5; 6; 7]. If the adsorbent is not expensive the adsorption process may provide an attractive alternative for dye removal from wastewater [8]. Zeolite synthesized from fly ash have been used as low-cost adsorbents for the removal of metals from aqueous solution [9; 10; 11; 12; 13]. Adsorption of metals onto zeolites synthesized from Brazilian coal ashes was investigated [14; 15]. A recent study has shown that modification of fly ash by chemical treatment could improve the adsorption capacity of fly ash for dye removal [16].

On the other hand, ionizing radiation started to be studied with gamma rays (^{60}Co and ^{137}Cs) for effluent treatment. The electron accelerators were applied some years later. Today the accelerating irradiators have been preferred to the cobalt irradiators, specially for environmental purposes. The ionizing radiation products interact with the water and its pollutants promoting the disinfection, organic compounds degradation, reduction of the organic load and color reduction for many industrials effluents. The treatment with electron beam does not generate radioactive residues and can be applied as previous treatment related to biological and than disposal [17].

In this study, zeolites synthesized from fly ashes and electron beam irradiation were used to treat actual textile wastewater. The efficacy for toxicity reduction using two lived organisms (*Daphnia similis* crustacean and *Vibrio fischeri* bacteria) was evaluated and color removal as well.

2. MATERIALS AND METHODS

Samples from two different sources were used in this study (code identification). The radiation process and zeolites adsorption are the two techniques applied to reduce the color of liquid effluents and the biological effects of both processes are evaluated by acute toxicity reduction. The real samples: A01 and A02 – from manufacture of dyes and the sample B01 - a textile industry. The samples have been submitted to the irradiation at CTR/IPEN and to the zeolite adsorption at CQMA/IPEN.

2.1. Electron Beam Irradiation

The irradiation was applied with an industrial electron beam accelerator, high energy until 1.5 MeV, fixed at 1.4MeV for all the experiments. Varied was the electric current applied in accordance with the radiation dose required by each effluent. The thickness of 4 mm for liquid sample layer was controlled by the volume of material conditioned in the container.

2.2. Zeolite Synthesis

Coal fly ash was used as starting material for zeolite synthesis by means of hydrothermal treatment. The samples of fly ash from baghouse filter and cyclone filter were obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil. Fly ash was modified with sodium hydroxide varying the solution concentration, reaction time, temperature and ratio fly ash/solution (Table 1). The synthesis conditions were selected from prior studies which gave zeolitic products with high adsorption capacities for methylene blue [16].

Table 1. Synthesis conditions and zeolitic products

[NaOH] (mol L^{-1})	t (h)	T (°C)	Fly ash / NaOH solution (g mL^{-1})	Zeolitic products
3.5	24	100	0.125	ZC
4.0	21	90	0.1	ZBH

For synthesis experiment, fly ash was heated in oven with NaOH solution. At the end of synthesis process, the solid phase was separated by filtration, washed with deionized water in excess and dried in an oven at 50^{o}C for 12 h.

2.3. Efficacy of Decolorization

Prior to the treatment, the actual textile wastewater was suitably diluted to evaluate the adsorption cause was highly colored. The adsorption was performed by batch experiments. Kinetic experiments were carried out by agitating 100 ml of dye solution with 1g of zeolite at room temperature (25^{o}C) at a constant agitation speed of 120 rpm. Samples were pipetted out using a 10mL-syringe at different time intervals. The collected samples were then centrifuged. Absorption spectra for the dyeing effluent before and after treatment with zeolite and electron beam irradiation were recorded on a UV/VIS spectrophotometer (Cary 1E – Varian). The maximum absorbance wavelength (λ_{max}) was used for all absorbance readings. Percentage of color removal was calculated by comparing the absorbance values for the waste after treatment to the absorbance value for the original dye waste and was defined as:

$$\text{Decolorization (\%)} = 100 \times (\text{Absorb}_{untr} - \text{Absorb}_{after\ treatment}) / \text{Absorbance}_{untreated} \quad (1)$$

2.4. Biological Effects of Samples and their Treatments

2.4.1. *Daphnia similis* crustacean

Young *D. similis,* aged between 6 and 24 h, were exposed to the effluent samples during the study. The immobility or death resulted from the exposition due to the contaminants on the sample. Data were registered after 24h periods and 48h exposition. Control samples were kept during all the biological assays and twenty organisms were exposed at control in the same water used for maintenance. No feeding during the assay. Validation of assay: control does not allow immobility or death higher than 10% [17].

2.4.2. *Vibrio fischeri* bacteria

The assay that uses the *V. fischeri* bacterium consists, basically, of the initial reading of the luminescence (I_0) and in the second reading (I_{15}), when some concentrations of the sample already had been added to the buckets whose (I_0) were already measured. The second reading occurs 15 min after the exposition. Based on the rude data of the displayed concentrations of the sample and the loss of the luminescence of the concentration of the sample, the value of the EC (I)50 with assistance of the curve of linear regression is calculated [17].

2.5. Treatment Efficacy on Toxicity Reduction

The effectiveness of treatment for toxicity was evaluated through the EC50 (effective concentration that cause immobility in 50% of the exposed organisms). The value of EC50 was calculated by Trimmed Spearman Karber Method. This values were transformed into Toxic Units (UTs), and the difference between treated and untreated samples show the benefits. The values of the EC50 and UTs, are inverse, therefore lesser the CE50 is, more toxic is the effluent sample. The UTs values, directly proportional to the toxicity, were gotten by Equation 2:

$$UT = \frac{100}{CE50} \qquad (2)$$

3. RESULTS AND DISCUSSION

3.1. Decolorization of Dye Industry Effluents

The radiation effects on color effluents demanded several experiments and different radiation doses. Results are presented in Figure 1 for radiation treatment and Figure 2 for zeolites adsorption.

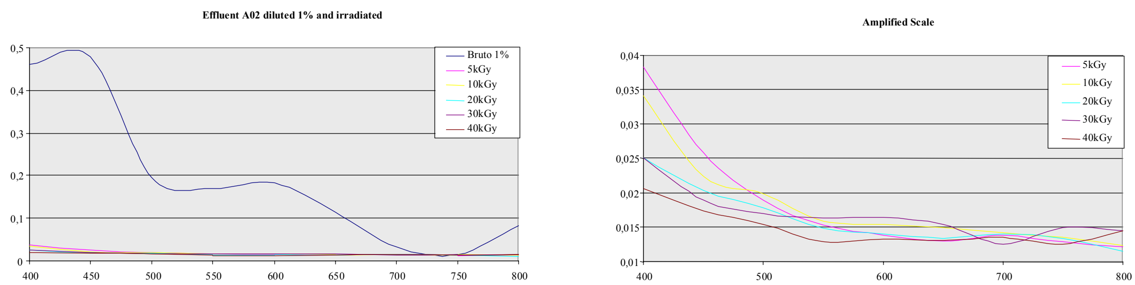

Fig. 1 Spectra of 1% effluent before and after electron beam irrad. (sample A02).

This effluent required a 5kGy radiation dose, which represented 94,60% color reduction. On the other hand, previous samples required higher radiation doses.

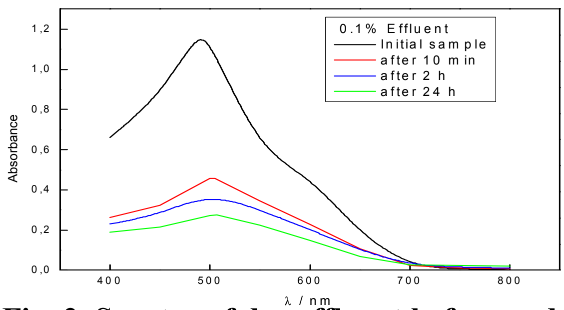

Fig. 2. Spectra of dye effluent before and after treatment with ZC for 0.1% diluted sample A01.

There wasn't a remarkable diminution in the absorbance values for less diluted samples. The diminution in the peak obtained at 487 nm took place due to the removal of dyes after adsorption on ZC. The percentage of color removed was improved with increasing contact time. The percentage dye removal by ZC increased from 61%, 68% and 77% for 10 min, 120 min and 1400 min contact time, respectively. The time of 1400 min was fixed as the optimum contact time.

The results of color removal, treated by ZC, were compared with those treated by ZBH. Treatment of the dyeing effluent by ZC and ZBH resulted in a significant loss of color after 1400 min of contact time. ZC decolorized 77% of the dyeing effluent while the ZBH decolorized 90% under identical experimental conditions.

3.2. Toxicity Reduction

The zeolite ZC showed more efficient than zeolite ZBH in relation to the reduction of toxicity with *D. similis* for 0.1% diluted sample (A01). A reduction of the toxicity for *D. similis* with zeolite ZBH for the A02 effluent was not obtained with dilutions that varied of 0.1 to 1.4% in preliminary tests.

The effects of radiation on toxicity are shown in Table 2. Each sample required different radiation dose and toxicity reduction varied from 36% up to 72%, at the experimented condition.

Table 2: Toxicity after application of electron beam irradiation

Effluents	Dose Irradiation	Organism	CE50	Toxic Units	Effectiveness
A02	No irradiated	*D. similis*	1.88 (0.90–3.92)	53.19	
A02	20 kGy	*D. similis*	6.73 (5.99–7.56)	14.86	**72.06%**
B01	No irradiated	*D. similis*	3.81 (2–7.25)	26.24	
B01	0.5 kGy	*D. similis*	6.45 (4.18–9.94)	15.50	**40.92%**
B01	No irradiated	*V. fischeri*	25.53 (8.68–75.11)	3.91	
B01	2.5 kGy	*V. fischeri*	39.99 (19.27–82.98)	2.50	**36.06%**

The effluent A01 presented an initial CE50 0.75 (0.64 – 0.87) or 133.33 UTs for *D. similis,* extremely toxity. After 20kGy both toxicity and colour still remained. On the contrary, when the A02 effluent (50% diluted – pH adjusted) was irradiated it resulted in 72,06% less toxic. As the B01 effluent was originally less toxic, no dilution was required. These samples required 0.5 kGy to 2.5 kGy, for further toxicity reduction.

3. CONCLUSIONS

The effluents from industry that fabrics dyes were very complex. Big efforts are needed to remove color and toxic effects. The toxicity of such effluent was higher compared to the effluents from textile industry.

It was concluded that electron beam irradiation and zeolites synthesized from fly ash were effective for the decolorization from industrial effluents dyes. Several conditions for irradiation and adsorption are being investigated.

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