



REMOVAL OF COLOR FROM INDUSTRIAL EFFLUENTS BY ADSORPTION USING UNMODIFIED AND SURFACTANT-MODIFIED ZEOLITE FROM CYCLONE ASH

REMOÇÃO DE COR DE EFLUENTES INDUSTRIAIS POR ADSORÇÃO USANDO ZEÓLITA DE CINZAS CICLONE NÃO MODIFICADA E MODIFICADA POR SURFACTANTE

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ABSTRACT

Treatment of wastewater is one of the biggest problems faced by textile and dyestuff manufacturers. The purpose of the present study was to investigate the suitability of using zeolitic materials as low cost media for removal of color from dye effluents. Zeolite synthesized from cyclone ash (ZCA) was modified with hexadecyltrimethylammonium bromide and the adsorption efficiencies for unmodified and surfactant-modified zeolite (SMZCA) were studied using a batch equilibration method. SMZCA presented higher color removal efficiency than ZCA, removing 60-100% of color for textile effluents and around 39% for effluent of dyestuff manufacturing industry. The effects of dilution on color removal were evaluated. The pH values of the treated effluent were according to the Brazilian legislation. It can be concluded that surfactant modified-zeolite from cyclone ash is a promising low-cost adsorbent for color removal from textile wastewater.

Palavras-chave: *effluent treatment; organozeolite; coal ash; dyes*

RESUMO

O tratamento de águas residuais é um dos maiores problemas enfrentados pelas indústrias têxteis e fabricantes de corantes. O propósito do presente estudo foi investigar a possibilidade de utilizar materiais zeolíticos como um meio de baixo custo para a remoção da cor de efluentes coloridos. Zeólita sintetizada a partir de cinzas ciclone (ZCA) foi modificada com brometo de hexadeciltrimetilamônio e as eficiências de adsorção para a zeólita não modificada e modificada por surfactante (SMZCA) foram estudadas usando o ensaio de equilíbrio em batelada. SMZCA apresentou maior eficiência de remoção da cor do que ZCA removendo de 60-100 % da cor para efluentes têxteis e cerca de 39% para efluente de indústria de fabricação de corante. Os efeitos da diluição na remoção de cor foram avaliados. Os valores de pH do efluente tratado estavam de acordo com a legislação Brasileira. Pode-se concluir que a zeólita de cinzas ciclone de carvão modificada por surfactante é um adsorvente de baixo custo promissor para a remoção da cor das águas residuais da indústria têxtil.

Keywords: *tratamento de efluente; organozeólita; cinzas de carvão; corantes*

INTRODUCTION

The textile industries have great significance in terms of economic contribution as well as employment in Brazil. Brazil is the fifth largest textile producer in the world generating 1.7 million direct jobs. But this sector is a major cause of pollution in water. Textile wastewater usually contains a high concentration of colorants (dyes and pigments), which come from the textile dyeing and printing processes (Bafana and Chakrabarti, 2011; Ventura-Camargo and Marin-Marales, 2013).

Dyes are also used to color the final products of others industries, such as paper and pulp mills, cosmetics, food, leather, rubber, etc.

The extensive use of dyes in different kinds of industries often poses pollution problems in the form of colored wastewater discharged into environmental water bodies.

The removal of color is often more important than the removal of colorless substances which typically contribute more to the overall pollution of the waste stream as measured by the biochemical oxygen demand of the water. Moreover, most of the dyes can cause allergy, dermatitis, skin irritation (Brookstein, 2009) and also provoke cancer (Carneiro *et al.*, 2010) and mutation in humans (Lima *et al.* 2007; Carneiro *et al.*, 2010; Kant, 2012)

Aquatic toxicity of aqueous solution of Reactive Red 198 and Reactive Black 5 was evaluated in an acute toxicity study using *Daphnia similis* as an aquatic experimental animal model and the 48-h EC50 value was 13.6 mg L⁻¹ and 12.9 mg L⁻¹, respectively (Magdalena, 2010; Ferreira, 2011).

Traditional biological systems are not effective in removing color and currently there is no general or economically feasible method for decolorizing waste streams (Singh and Arora, 2011).

Adsorption is one of the most commonly employed methods for the removal of synthetic dyes from aqueous effluents due its simplicity and high efficiency, as well as the availability of a wide range of adsorbents that can be applied. This process transfers the dyes from the aqueous effluent to a solid phase, remarkably decreasing dye bioavailability to live organisms. The decontaminated effluent can be released to surface water or reutilized in the industrial process (Bafana and Chakrabarti, 2011; Singh and Arora, 2011).

Most commercial systems currently use activated carbons and organic resins as adsorbents to remove the dye in wastewater because of their excellent adsorption abilities. However, these materials are costly and lower-cost adsorbents have been investigated for the removal of pollutants from water. The technical feasibility of various nonconventional low-cost adsorbents for dye removal from contaminated water has been reviewed (Gupta and Suhas, 2009; Gupta *et al.*, 2009; Bhatnagar and Sillanpaa, 2010; Ahmaruzzaman, 2011; Kyzas *et al.*, 2013).

Zeolite synthesized from coal fly ash has been extensively investigated for water treatment, showing high adsorptive capacity for pollutants (Cunico *et al.*, 2011; Magdalena *et al.*, 2011; Fungaro *et al.*, 2009, 2010, 2011; Shoumkova, 2011). Coal fly ash is a solid waste generated in large amounts in Brazil and its productive reuse is important.

The surface of zeolites is negatively charged and hydrophilic in nature, so little affinity toward other organic pollutants such as anionic, ionizable and non-ionizable organic chemicals is thus expected. In order to enhance the adsorption capacity of zeolite, the surface of material has been successfully modified using cationic surfactants (Bowman, 2003; Haggerty and Bowman, 1994; Li and Bowman, 1997).

The modified zeolite by hexadecyltrimethylammonium cations was applied to remove dyes from aqueous solutions (Fungaro and Magdalena, 2012, 2014; Fungaro *et al.*, 2013).

This paper investigates color removal from real dye-containing wastewaters using zeolite from fly ash modified with hexadecyltrimethylammonium bromide. It is proposed that cyclone ash be used as raw material for zeolite synthesis. A comparison of the adsorbent before and after modification for the removal of color from samples was performed.

EXPERIMENTAL

2.1. Materials

All the reagents used for experimental studies were of analytical grade. The sample of coal fly ash from cyclone filter (CFA) was obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil.

The quaternary ammonium salt hexadecyltrimethylammonium bromide (HDTMA-Br, Merck), with molar mass $364.46 \text{ g mol}^{-1}$ and minimum 99% active substance, was used.

The wastewater samples were collected from textile industry (SW1, SW2 and SW3) and dyestuff manufacturing (SW4 and SW5) located in São Paulo, Brazil. All the effluent samples were highly colored. The sampling bottle was cleaned and rinsed carefully with distilled water and then filled with the effluent. The samples were stored at $5 \text{ }^{\circ}\text{C}$ within one to two hours of sample collection. Samples SW1 and SW3 were collected after biological treatment and sample SW2 was collected after pH correction and without any treatment. Sample SW4 was collected after treatment with photo-Fenton and sample SW5 was collected without any treatment.

2.2. Synthesis of zeolites from fly ash

CFA (30 g) was mixed with 240 mL of $3.5 \text{ mol}\cdot\text{L}^{-1}$ aqueous NaOH solution in a 300 mL Teflon vessel. This mixture was heated to $100 \text{ }^{\circ}\text{C}$ in oven for 24 h. After finishing of the process, the suspension was filtered with 4A quantitative filter paper. The zeolite from cyclone fly ash (ZCA) was repeatedly washed with deionized water until the pH of washing water reach ~ 11 and dried at $50 \text{ }^{\circ}\text{C}$ for 12 h (Henmi, 1987). Twenty-five grams of ZCA were mixed with 0.5 L of 9 mmol L^{-1} HDTMA-Br. The mixture of zeolite and HDTMA-Br solution was stirred for 7 h at 120 rpm and $25 \text{ }^{\circ}\text{C}$. The suspension was filtered and the solid was dried in oven at $50 \text{ }^{\circ}\text{C}$ for 12 h (Fungaro and Borrelly, 2012). The characterizations of the materials have been described in detail in previous paper (Fungaro and Magdalena, 2012; Fungaro *et al.*, 2013a, 2013b).

2.3. Decolorization of dyeing effluent

The adsorption was performed using the batch procedure. Kinetic experiments were carried out by shaking 0.1 g of adsorbents with 10 mL of effluent at room temperature ($25 \pm 2 \text{ }^{\circ}\text{C}$) in a shaker operated at 120 rpm for 24 h in glass bottles. The collected samples were then centrifuged. Absorption spectra for the dyeing effluents before and after treatment with zeolite were recorded on a UV/VIS spectrophotometer (Cary 1E – Varian). The maximum absorbance wavelength or the area under the absorbance spectra were utilized to monitor the percentage of

the dye mixture removed from the effluents. The solution pH was recorded using a digital precision pH meter (Quimis modelo Q-400 H -versão 1.06).

RESULTS AND DISCUSSION:

3.1. Characterization of materials

Coal fly ash is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from the flue gas by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones (Shanthakumar *et al.*, 2008).

The cyclone fly ash is the ash fraction that has been carried through the flue gas channels into the cyclone and precipitated there. Cyclones are low-cost, low-maintenance centrifugal collectors that are typically used to remove particulates in the size range of 10–100 microns.

Cyclone ash samples contained larger particles than fabric filter and electrostatic precipitator ash samples and showed lower cytotoxicity, very little mutagenicity and lower concentrations of trace elements (Mumford and Lewtas, 1984; Depoi *et al.*, 2008).

Table 1 summarizes the concentration of major element contents in the studied cyclone ash sample and some important physicochemical characteristics. The chemical composition was quite similar to others coal ash samples (Fungaro *et al.*, 2013b).

Cyclone ashes are particularly rich in silica (SiO_2), alumina (Al_2O_3) and ferric oxide (Fe_2O_3). Quantities below 2.5% of K_2O and CaO were also observed.

The pH value indicated that cyclone ash was moderately alkaline in nature. The alkaline cations (K^+ , Na^+ , Ca^{2+} and Mg^{2+}) combined with carbonates, oxides or hydroxides cause the alkalinity of the ash suspension (Fungaro *et al.*, 2013b). Cyclone ash shows a very low moisture and high conductivity, which is characteristic of samples from Figueira coal-fired power plant.

Loss on ignition (LOI) which represents the unburnt carbon present in coal ash is one of the important parameters for assessing the quality of ash (Wesche, 1991). Carbon has a low density and can absorb significant amounts of water. This means that the maximum dry density and optimum moisture content of ash are influenced by the LOI. Generally, the lower the carbon content and the finer the ash particles, the better prospects for ash utilization, principally in cement-based formulations. Cyclone ash

presented an intermediate value of LOI.

Table 1. Physicochemical properties of cyclone ash

Characteristics	Obtained Values
SiO ₂ (wt. %)	40.4
Al ₂ O ₃ (wt. %)	15.2
Fe ₂ O ₃ (wt. %)	10.6
K ₂ O (wt. %)	2.23
CaO (wt. %)	1.60
Others (wt. %)	0.98
pH in water	8.18
Conductivity (μS·cm ⁻¹)	201
Humidity (%)	1.59
Loss on ignition (%)	8.18
Specific surface area (m ² g ⁻¹)	3.31
Real density (g cm ⁻³)	2.33
CEC* (meq ·g ⁻¹)	0.0791

(*)Cation exchange capacity

The particle size distribution is an important parameter not only for coal ash utilization, but for health risk assessment, as well. The cumulative distribution of cyclone fly ash particles was determined by laser granulometric analysis and showed the following values for d₁₀, d₅₀ and d₉₀: 13.6, 43.6 and 174.8 μm, respectively.

The mineralogical composition of ashes as a rule is very complicated and depends on parent coals petrography, as well as the boiler type, combustion temperature, the rate of cooling etc.

The identification of corresponding crystalline and mineralogical characteristics of materials from powder X-ray diffraction patterns were made by comparing the diffraction data against a database provided by "Joint Committee on Powder Diffraction Standards" and "International Centre for Diffraction Data" (not shown). The common crystalline phases identified in CFA and zeolitic materials are quartz (ICDD 001-0649) and mullite (ICDD 002-0430). The XRD analyses of zeolitic materials showed that hydroxysodalite (ICDD 00-011-0401) was the major zeolitic phase.

The structural parameters of SMZCA are very close to that of corresponding unmodified zeolite ZCA which indicate that the crystalline nature of the zeolitic material remained intact after required chemical treatment with HDTMA molecules and heating treatment for drying.

3.2. Analysis of Color Removal Efficiency

Color removal efficiency was analyzed by measuring the presence of color in untreated effluents and effluents treated with ZCA and SMZCA. The color removal values are reported in Table 2.

Absorption spectra in the visible region of the effluents before and after treatment with adsorbents were shown in Figs. 1 and 2.

Table 2. Percentage of color removal from dye effluents

Sample	Color Removal (%)	
	ZCA	SMZCA
SW1	13.2	100
SW2	61.2	100
SW3	21.0	59.7
SW4	0	38.5
SW5	0	39.9

According to the experimental results, it was obvious that SMZCA, with complete adsorption for samples SW1 and SW2, was the most effective adsorbent with the percentages color removal range from 39 to 100%.

As expected, non-modified zeolite (ZCA) had quite low efficiency for color removal from effluents with adsorption efficiencies between 13 and 61% for textile effluent and there was no removal for effluents from the dyestuff manufacturing.

Zeolites have almost no affinity for anions or non-polar organics. By treating the zeolite with the cationic surfactant HDTMA, an organic coating is created on the external zeolite surfaces. The surfaces of organically modified zeolite have hydrophobic properties. Anions are retained on the modified zeolite via anion exchange, while non-polar organic molecules partition into the surfactant coating (Bowman, 2003).

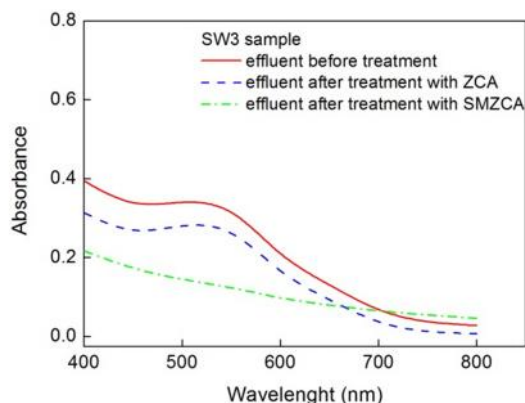
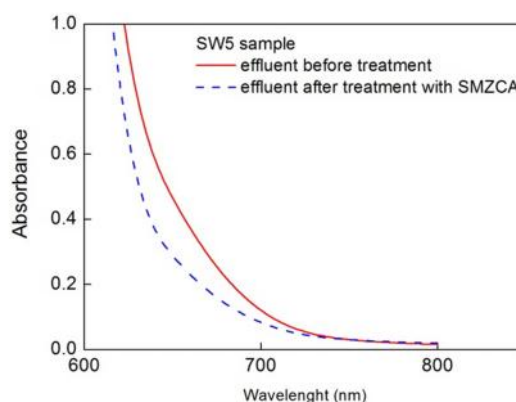
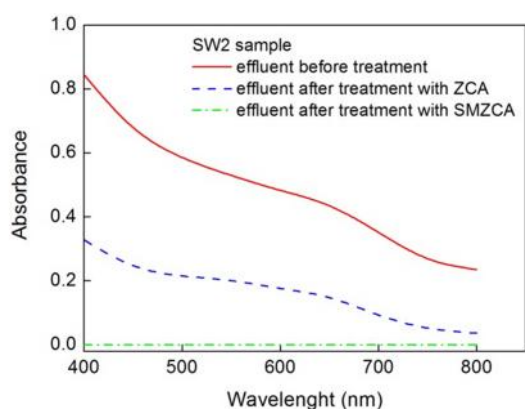
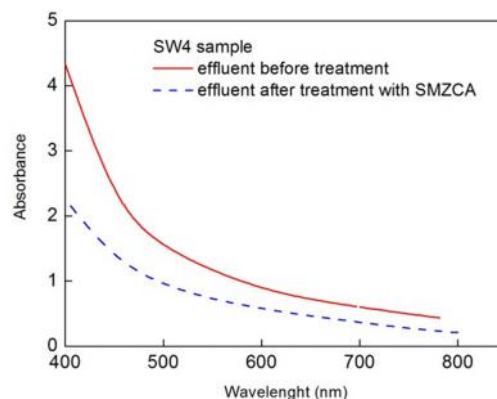
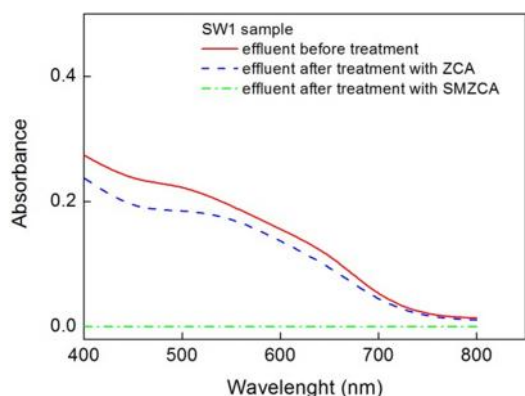


Figure 2. Absorption spectra in the visible region of the effluents from the dyestuff manufacturing before and after treatment with SMZCA

Previous studies have shown that the surfactant concentration affects the adsorptive properties of the modified zeolite (Torabian *et al.*, 2010; Ghadiri *et al.*, 2010; Lin *et al.*, 2011; Fungaro and Magdalena, 2012).

The experimental data showed that zeolite from fly ash modified with initial concentration of $9 \text{ mmol} \cdot \text{L}^{-1}$ of surfactant presented optimal loading for color removal from textile effluents.

The theoretical critical micelle concentration (CMC) of HDTMA-Br is about $0.9 \text{ mmol} \cdot \text{L}^{-1}$ (Li and Bowman, 1997) and the initial concentration used in this study exceeds the critical micelle concentration of the surfactant. It is therefore envisaged that these micelles attach as such to the external surface and then rearrange to form a patchy mono-layer and/or bi-layers that tends to impart anionic exchange and hydrophobic characteristics to the adsorbent

Figure 1. Absorption spectra in the visible region of the effluents from the textile industry before and after treatment with ZCA and SMZCA

(Fungaro and Borrelly, 2012; Guan *et al.*, 2010; Li, 1999; Li and Bowman, 1998; Rozi *et al.*, 2019).

Figure 3 show a photograph of the effluents from the textile industry before and after treatment with SMZCA.

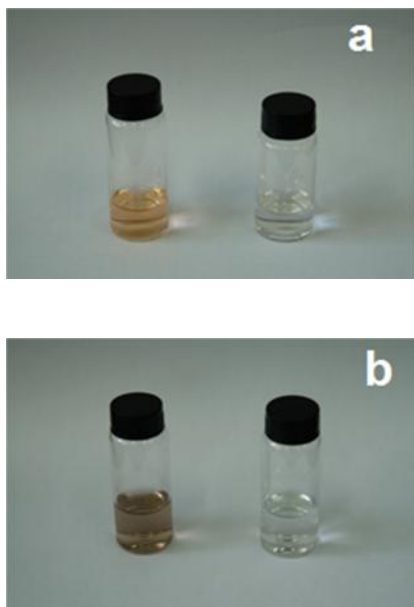


Figure 3. Photographs of SW1 (a) and SW2 (b) effluent samples before and after treatment with SMZCA. Left: Dark color contaminated effluent before treatment. Right: Crystal clear reusable water after the treatment.

The results show that in the case of decolorization of wastewater samples collected from dyestuff manufacturing, the zeolite should have been modified by HDTMA at surfactant concentrations higher than $9 \text{ mmol}\cdot\text{L}^{-1}$ because usually increasing the surfactant loading on the zeolites resulted in an increase in efficiency adsorption.

Fixed-bed column study was conducted to find out the effectiveness of natural zeolite modified with hexadecyltrimethylammonium bromide for color removal from real textile wastewater. Taguchi method was applied as an experimental design to determine optimum conditions for color removal. Optimum modification conditions of natural zeolite were found as lower values of surfactant concentration (1 g L^{-1}) and flow rate (0.015 L min^{-1}), textile flow rate = 0.025 L min^{-1} and bed height = 50 cm for higher color removal (Ozdemir *et al.*, 2009; Engin *et al.*, 2008).

The wastewater from dyestuff

manufacturing contained a high color concentration. Therefore, the effect of dilution on color removal of samples SW4 and SW5 was studied. The dilution of wastewater samples was carried out because adsorption is suitable for tertiary step to further treat the remaining pollutants in wastewater where adsorbate concentration is not high to meet the environmental standards.

Wastewater samples SW4 and SW5 were diluted to 50%, 75% and 95% with deionized water, thus, lower color intensities were obtained. The percentage of color removal for original wastewater and diluted wastewaters were presented in Table 3. The removal efficiency of two effluents increased significantly as the degree of wastewater dilution increased. The color removal efficiency increased from 38.5% to 100% and 40% to 100% for SW4 and SW5, respectively. The complete color removal was only effective with a 95% dilution of the original sample. This fact indicated that adsorption onto modified-zeolite from fly ash may be included at the end of dye treatment processes as a fail-safe mechanism. This will prevent the release of untreated dyes or toxic degradation intermediates into the environment.

Table 3. Decolorization Reduction in 0, 50, 75 and 95% diluted effluent after treatment with SMZCA

Sample	Dilution (%)	Color removal (%)
SW4	0	38.5
	50	74.0
	75	87.0
	95	100
SW5	0	40.0
	50	82.0
	75	86.0
	95	100

An investigation demonstrated that acute toxicological studies with *Daphnia Similis* done with the wastewater obtained after the treatment with coal fly ash and zeolite from fly ash for reactive dyes removal caused 100% organisms death when the adsorbent used was coal fly ash. When the zeolite from fly ash was the adsorbent and the treated water was neutralized (pH of about 7) acute toxicological demonstrated that the toxicity was eliminated (Magdalena, 2010; Ferreira, 2011).

Acute toxicity using *D. Similis* and *V. Fischeri* was determined for methylene blue solutions before and after treatment with zeolite synthesized from fly ash. Both lived-organisms evidenced that the proposed treatment resulted in a less toxic liquid residue (Fungaro *et al.*, 2010).

After treatment, final pH values of wastewater were determined. The pH is one of the most important operational water quality parameters (Benerji, 1993). Table 4 indicates that initial pH of effluents was in the range of 2 - 8. After treatment with SMZCA, the pH of samples SW1 to SW4 was found to increase, but the pH of sample SW5 remained unchanged even after treatment. The final pH value of the effluents after treatment was according the established limits recommended by the Brazilian Water Quality Legislation for effluent discharge (CONAMA 430/2011). The careful attention should be given to pH control at all the stages of water treatment to ensure the satisfactory water classification and disinfections.

Table 4. pH of wastewater samples before and after treatment with SMZCA

Sample	pH	
	Initial	Final
SW1	7.2	8.5
SW2	7.4	8.7
SW3	8.3	8.8
SW4	2.0	5.0
SW5	5.2	5.2

CONCLUSION:

Zeolite was synthesized from cyclone ash (ZCA) and modified with the surfactant hexadecyltrimethylammonium bromide. The zeolitic materials were examined for the removal of color from real dye effluents. Although ZCA showed low performance, the adsorption by surfactant-modified zeolite (SMZCA) was high.

The wastewater treatment employed SMZCA showed high color removal efficiency for textile wastewater with performance in the range 60-100% within an acceptable pH. In contrast, SMZCA presented low performance for color removal (~39%) from dyestuff manufacturing wastewaters. Decolorization was more efficient at greater dilutions as compared to more concentrated dilutions. So, treatment to decolorize complex dyestuff wastewaters from dyestuff manufacturing must be a combination of

methods involving adsorption onto organozeolite as a possible post-treatment.

As a result, organozeolite from cyclone fly can be used satisfactorily for the bleaching of textile materials. Moreover, the wastewater after treatment may be used as non-potable water reuse.

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