

Adsorption of Reactive Orange 16 onto zeolite synthesized from fly ash: kinetics and equilibrium studies

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The adsorption of Reactive Orange 16 from aqueous solution was carried out using zeolite synthesized from fly ash as low-cost adsorbent. The dye adsorption equilibrium was attained with 120 min of contact time. Adsorption isotherms were analyzed using Freundlich and Langmuir equations. Equilibrium adsorption data followed both Langmuir and Freundlich isotherms, attaining a maximum adsorption capacity of 0.58 mg g⁻¹. The data obtained with biological assays showed that at least 40% of the total toxicity of Reactive Orange 16 may be removed from the solutions after adsorption process.

Keywords: Zeolite, Fly ash, Adsorption, Reactive Orange 16

1 INTRODUCTION

Dyes are widely used by industries such as textiles, food, paper, plastics, cosmetics and leather, for coloring their products. The discharge of colored wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain.

Commonly used methods for removing dyes from wastewater systems include physico-chemical (chemical and biological methods, such as flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation, and fungal decolorization (Dabrowski, 2001)). Of the numerous techniques mentioned, adsorption in particular, is an effective process for the removal of dyes from waste effluents. Currently, the most common procedure involves the use of activated carbons (Pelekani and Snoeyink, 2000; Walker and Weatherley, 2000; Meshko et al., 2001) as adsorbents because of their higher adsorption capacities. However, because of their relatively high cost, there have been attempts to utilize low-cost adsorbents as an alternative to activated carbons (Sanghi and Bhattacharya, 2002).

Utilization of industrial byproduct for the treat-

ment of wastewater could be helpful not only to environment but also the economy. Fly ashes are produced by burning of coal in coal-fired power plants and are the industrial byproduct most generated in southern Brazil: about 4 millions tones/year. Only 30% of this total is reused, mainly for construction purposes. Thus continuous research is needed to develop an alternative technology for utilizing coal ashes.

It is possible to convert fly ash into zeolitic products by hydrothermal treatment with alkaline medium (Henmi, 1987; Querol et al., 1997; Poole et al., 2000; Rayalu et al., 2000; Kolay et al., 2001; Murayama et al., 2002). The treated product has a significantly increased surface area and cation exchange capacity when compared to the raw ash.

Zeolitic materials have been used as low-cost adsorbents for the removal of metal ions from aqueous solution (Singer and Berkgaut, 1995; Lin and Hsi, 1995; Amrhein et al., 1996; Querol et al., 2001, 2002). Adsorption of metals onto zeolites synthesized from Brazilian coal ashes was investigated (Fungaro and Silva, 2002; Fungaro et al., 2004). However, few investigations have focused on the organic component of potential waste streams (Woolard et al.,



2002; Fungaro et al., 2005).

In this study, zeolite synthesized from fly ash was used as an adsorbent for removal of an anionic reactive dye. Batch kinetic experiment was performed to provide appropriate equilibrium time. The Langmuir and Freundlich isotherm models were used to model the isotherm data for their applicability. The zeolite efficacy for toxicity reduction using two lived organisms (*Daphnia similis* and *Vibrio fischeri*) was evaluated too. The results were based on the percentage of reducing effects into the tested-organisms after the zeolite adsorption (immobility and light emission).

2 MATERIALS AND METHODS

2.1 Materials

All chemicals used in this study were of analytical grade. Reactive Orange 16 (RO16), which was used as a model reactive dye in this work, was purchased from Sigma-Aldrich. A stock solution was prepared in deionized water (Millipore Milli-Q) and the solutions for adsorption tests were prepared by diluting. The sample of fly ashes from cyclone filter was obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil. As shown in Fig. 1, RO 16 has two sulfonate groups, which have negative charges in aqueous solution. The general characteristics of RO 16 are summarized in Table 1.

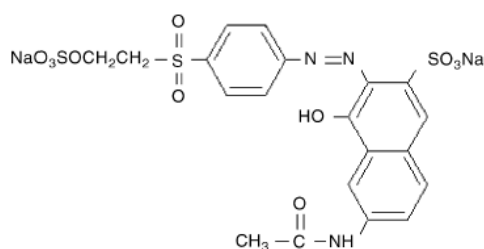


Figure 1

Chemical structure of Reactive Orange 16.

Table 1

General characteristics of RO-16.

Chemical Formula	$C_{20}H_{17}N_3Na_2O_{11}S_3$
Molar Mass	617.54
Color index Number	17757
λ_{max} (nm)	493

2.2 Methods

2.2.1 Zeolite synthesis

Coal fly ash was used as starting material for zeolite synthesis by means of hydrothermal treatment. In synthesis experiment, 20 g of ash was heated to 100°C in an oven for 24 h with 160 mL of 3.5 mol L⁻¹ NaOH solution. The zeolitic material (ZC) was repeatedly washed with deionized water and dried at 100°C for 24 h.

2.2.2 Adsorption studies

The adsorption was performed by batch experiments. Kinetic experiments were carried out by agitating 25 mL of dye solutions of known initial dye concentration with 0.25 g of zeolite at room temperature (25°C) at a constant agitation speed of 120 rpm for 30-180 min. The samples were removed from the shaker at different time intervals, centrifuged and the concentration in the supernatant solution was analyzed using a UV spectrophotometer (Cary 1E – Varian) by measuring absorbance at $\lambda_{max} = 493$ nm and pH = 5. Adsorption isotherms were carried out by contacting 0.25 g of zeolite with 25 mL of RO 16 over the concentration ranging from 1.85 to 13.7 mg L⁻¹. The agitation was made for 120 min, which is sufficient time to reach equilibrium. The amount of adsorption, q (mg g⁻¹), was calculated by:

$$q = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where C_0 and C_e (mg L⁻¹) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of adsorbent used (g).

2.2.3 Toxicity evaluation

Daphnia similis: tested-organisms were obtained from own culture at LEBA Laboratory which keeps the cultures at natural waters adjusting the hardness at 46 mg/L CaCO₃. The same natural water was used for diluting the samples in order to get five different sample concentrations (10% up to 100%). During the ecotoxicity assay 20 organisms were exposed at each sample concentration for 24 h and 48 hours at 20°C ± 0.5. Once the assay ended, the crustacean immobility obtained at each sample concentration were submitted to Trimmed Spearman Karber Statistics Test. Final results will show the average

concentration which represented the immobility for 50% of the total exposed number, expressed as EC₅₀ (%) (ABNT, 2004).

Vibrio fischeri: acute toxicity for luminescent bacteria was carried out with Microtox System – model 500 (Azur Environment, USA). The bacterial luminescence was measured after 15 minutes exposition and the lost sign was related to the sample effect, according to the dye concentration. This biological assay was expressed as EC₅₀, which is the effective concentration that causes 50% of light inhibition after 15 min exposure and 15°C.

ABNT and ISO methods were used and EC₅₀ results were transformed to Toxic Units, once as lower the EC₅₀ higher is the toxicity. The ZC zeolite adsorbent efficacy was calculated as the percentage of toxicity reduction comparing the toxic unit.

3 RESULTS AND DISCUSSION

3.1 Effect of contact time

Figure 2 shows the dynamic adsorption of RO16 on zeolite from fly ash different at initial concentration of 3.9 mg L⁻¹. The results showed that the extent of adsorption increased rapidly in the initial stages before 60 min and then approaches equilibrium around 120 min. The amount of RO16 uptake is increasing with contact time. The removal curves obtained are single smooth and continuous suggesting the formation of monolayer of adsorbate on the surface of the adsorbent (zeolite). During the initial stage of adsorption, a large number of vacant surface sites are available for adsorption. After lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid surface and the bulk phase.

3.2 Adsorption isotherms

The analysis and design of adsorption process requires equilibrium to better understand the adsorption process. Adsorption equilibria provide fundamental physico-chemical calculations are given by data for evaluating the applicability of adsorption process as an unit operation. The two most commonly used equilibrium relations are Freundlich and Langmuir isotherm equations and were selected in this study to analyze the equilibrium data.

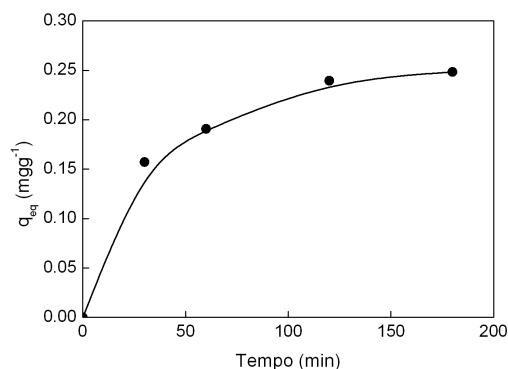


Figure 2

Dynamic adsorption of RO16 on zeolite from fly ash

The linear form of the Langmuir expression may be written as:

$$C_e/q_e = 1/bQ_0 + C_e/Q_0 \quad (2)$$

where q_e is solid-phase adsorbate concentration at equilibrium (mg g⁻¹), C_e is aqueous-phase adsorbate concentration at equilibrium (mg L⁻¹), Q_0 (mg g⁻¹) is the maximum amount of adsorbate per unit weight of adsorbent to form a complete monolayer on the surface, and b is the Langmuir isotherm constant (L mg⁻¹), related to the affinity of the adsorption sites.

The linearized forms of the Freundlich equation can be written as follows:

$$\log q_e = \log K_f + 1/n(\log C_e) \quad (3)$$

where K_f [mg/g(L/mg)^{1/n}] and n are Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents.

Thus the Freundlich constant K_f and n can be calculated from the intercept and slope of plot between $\log q_e$ and $\log C_e$. Similarly a plot of C_e/q_e versus C_e gives a straight line of slope $1/Q_0$ and intercepts $1/Q_0b$.

Equilibrium data of RO16 onto zeolite synthesized from fly ash is shown in Fig. 3. The isotherm shapes are largely determined by the adsorption mechanism and can therefore be used to diagnose the nature of the adsorption (Giles et al., 1960). The adsorption isotherm for solution may be classified into four main classes relating to their shapes termed S, L, H and C and subgroups 1, 2, 3, 4 or max. Figure 3 clearly shows that adsorption isotherms are L2 type.

In L2-type isotherms, the adsorption of solute on the adsorbent proceeds until saturation (Giles et al., 1960).

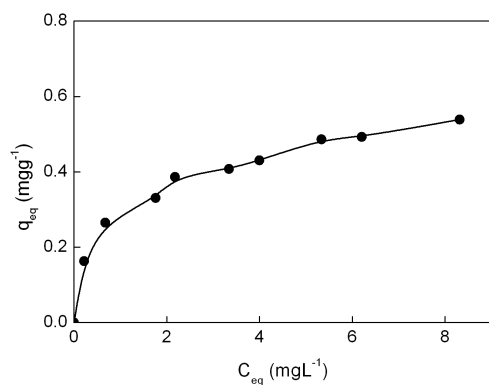


Figure 3

Adsorption isotherm of RO16 onto zeolite synthesized from fly ash

Figures 4 and 5 depict linear Langmuir and Freundlich plots for the adsorption of RO16 onto zeolite synthesized from fly ash. The isotherm constants and determination coefficients calculated for Freundlich and Langmuir equations are given in Table 2.

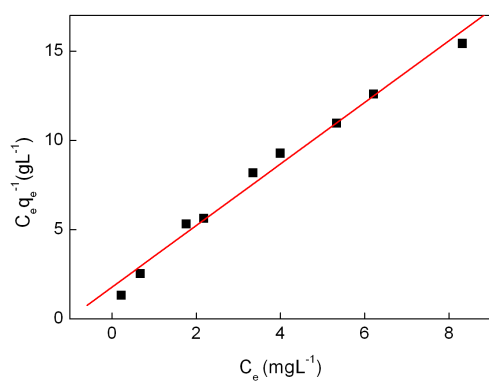


Figure 4

Langmuir plots for the adsorption of RO16 onto zeolite synthesized from fly ash

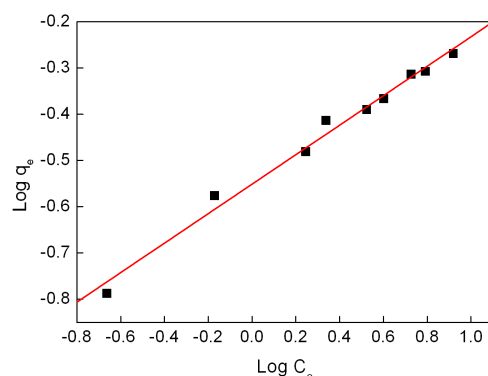


Figure 5

Freundlich plots for the adsorption of RO16 onto zeolite synthesized from fly ash

Table 2

Langmuir and Freundlich parameters for the adsorption of RO16 onto zeolite from fly ash

Langmuir isotherm	
Q_0 (mgg ⁻¹)	0.58
b (L mg ⁻¹)	0.97
R^2	0.9863
R_L	0.070
Freundlich isotherm	
K_f [(mg g ⁻¹)(L mg ⁻¹) ^{1/n}]	3.56
n	3.14
R^2	0.9870

It can be observed from the Table 2 that the according the determination coefficients criterion (R^2), equilibrium adsorption data followed both Langmuir and Freundlich isotherms.

The Langmuir isotherm can also be represented in terms of a dimensionless constant separation factor or an equilibrium parameter:

$$R_L = 1/(1 + bC_0) \quad (4)$$

where b is the Langmuir constant and C_0 the initial concentration of dye. R_L values between 0 and 1 indicate favorable adsorption (Hall *et al.*, 1966). The calculated R_L value (Table 2) was 0.07 indicating the favorable condition for adsorption process. The Freundlich parameters K_f and n were also presented in Table 2. The n value was higher than 2 indicating

the dye ions were adsorbed favorably onto adsorbent (Helby, 1952).

3.3 Toxicity evaluation

The acute toxicity results showed that the effective concentration that caused effect (immobilization) for *Daphnia* varied from 7.16 ppm up to 8.04 ppm and the effective concentrations that promoted 20% of light reduction from *V. fischeri* were 3.50 ppm. The RO-16 acute toxicity was observed through the *V. fischeri* EC₂₀ (% , 15min) and for *Daphnia* (EC₅₀) evidenced a huge biological effect which means that less than 10ppm of RO-16 may represent death for fifty percent of lived tested organisms. Regarding zeolite adsorption an improvement in terms of biological effect was evidenced mainly with *Vibrio fischeri*. The data obtained with biological assays showed that with this bacteria at least 40% of the total toxicity may be removed from the solutions (or effluents) during the ZC adsorption process. These results are very significative if we consider that this effluent can pass through adsorbent and after for a classic biological treatment process.

4 CONCLUSION

The present study shows that the zeolite synthesized from fly ash is an effective adsorbent for the removal of azo dye Reactive Orange 16 from aqueous solution. Adsorption followed both the Langmuir and Freundlich isotherms. The adsorption capacity was found to be 0.58 mg g⁻¹. The data obtained with biological assays showed that at least 40% of the total toxicity of RO-16 may be removed from the solutions after adsorption process. The results would be useful for the fabrication and designing of wastewater treatment plants for the removal of dye. Since the raw material fly ashes is freely available in large quantities in coal-fired power plant the treatment method seems to be economical.

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