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ZEOLITES SYNTHESIZED FROM FLY ASH AS A LOW-COST ADSORBENT FOR TREATMENT OF METHYLENE BLUE-CONTAINING WASTEWATER

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Abstract

The adsorption of methylene blue from aqueous solution was carried out using zeolites synthesized from fly ash as low-cost adsorbents. The effect of contact times, initial dye concentrations and temperatures was investigated. The adsorption was between 74 and 96% under the conditions studied. It was also determined that the adsorption isotherm followed Freundlich model. It is found that the zeolite synthesized from fly ash exhibits a much higher adsorption capacity than raw fly ash. From thermodynamic studies, it was seen that the adsorption was spontaneous and endothermic.

Keywords: Adsorption; Kinetic; Isotherm; Thermodynamic; Methylene blue

Resumo

A adsorção do azul de metileno em solução aquosa foi realizada usando zeólitas sintetizadas a partir da cinza leve como adsorventes de baixo custo. O efeito dos tempos de contato, das concentrações iniciais do corante e das temperaturas foi investigado. A adsorção estava entre 74 a 96% sob as condições estudadas. Foi também determinado que a isoterma de adsorção seguiu o modelo de Freundlich. A zeólita sintetizada a partir da cinza leve exibiu uma capacidade de adsorção muito maior do que aquela encontrada para a cinza leve. Os estudos termodinâmicos indicaram que a adsorção foi espontânea e endotérmica.

Palavras-chave: Adsorção; Cinética; Isoterma; Termodinâmica; Azul de metileno

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INTRODUCTION

Dyes are widely used by textile industries to color their products. One of the major problems concerning textile wastewaters is colored effluent. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms. Methylene blue (MB) dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition, and methemoglobinemia. MB is the most commonly used material for dying cotton, wood, and silk. Therefore the treatment of effluent containing such dye is of interest due to its impacts on receiving waters.

The most widely used methods for removing dyes from wastewater systems include physicochemical, chemical, and biological methods, such as flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation, and fungal decolorization (Dabrowski, 2001). However, wastewaters containing various dyes, due to their complex aromatic structure, are very difficult to treat using conventional wastewater treatment methods, since the dyes are generally stable under the influence of light and oxidizing agents, and reactive dyes are especially resistant to aerobic digestion (Orthman et al., 2003). 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 them relatively high cost, there have been attempts to utilize low-cost adsorbents (Sanghi and Bhattacharya, 2002).

Utilization of industrial solid wastes for the treatment of wastewater could be helpful not only to environment in solving the solid waste disposal problem, but also the economy. Fly ash is produced by burning of coal in coal-fired power stations and is the industrial solid waste most generated in southern Brazil: about 4 millions tones/year. Only 30% of this total is reuse mainly for construction purposes. Thus continuous research is needed to develop an alternative technology for utilizing these fly ash materials.

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 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 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).

The focus of the research was to evaluate the adsorption potential of zeolites synthesized from fly ashes for methylene dye due to the fact that the fly ash is a very abundant and inexpensive material. Methylene blue was chosen in this study because of its known strong adsorption onto solids and often serves as a model compound for removing organic contaminants and colored bodies from aqueous solutions. The kinetic data and equilibrium data of adsorption studies were processed to understand the adsorption mechanism of the dye molecules onto the synthetic zeolite.

MATERIALS AND METHODS

Materials

Methylene blue was obtained from Merck and used as received. A stock solution (3.2 g L^{-1}) was prepared in deionized water (Millipore Milli-Q) and the solutions for adsorption tests were prepared by diluting. The samples of fly ash from cyclone filter were obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil. The chemical composition of fly ash determined by X-ray fluorescence analysis (XRFS RIX 3000 - Rigaku) is shown in Table 1.

Table 1. Chemical composition of coal fly ash

Components	Composition (wt %)
SiO_2	18.9
Al_2O_3	15.2
Fe_2O_3	10.6
Na_2O	0.988
CaO	1.18
K_2O	2.23
TiO_2	0.468
SO_3	0.366
MgO	0.348
SiO_2/Al_2O_3	1.2

The fly ash from cyclone filter has a very low SiO_2/Al_2O_3 ratio compared with the most coal fly ashes (~ 2 w/w). This feature coupled with the relatively low impurities content (Fe, Ca and S oxides) confers a high potential for the use of this sample as a starting material for the synthesis of low-Si zeolites.

Zeolite synthesis

Coal fly ash was used as starting material for zeolite synthesis by means of hydrothermal treatment. Fly ash was modified with sodium hydroxide varying the solution concentration, reaction time, temperature and ratio fly ash/ solution (Table 2). The synthesis conditions were selected from prior studies (Fungaro et al., 2005) to obtain zeolitic products with high adsorption capacities for methylene blue.

Table 2. Synthesis conditions and zeolitic products

[NaOH] (mol. L^{-1})	t (h)	T (^{o}C)	Fly ash / NaOH solution (g. mL^{-1})	Zeolitic products
4.0	21	90	0.1	Z1
3.5	24	100	0.125	Z2

In synthesis experiment, fly ash was heated in oven with NaOH solution. The zeolitic material obtained was repeatedly washed with deionized water and dried at 100 ^{o}C for 24 h. X-ray diffracion analysis (Rigaku model RINT-2000) of sample revealed that the product obtained was NaP1 zeolite with traces of hydroxysodalite, quartz and mullite. The cation exchange capacity value of 1.1 meq g^{-1} was determined using ammonium solutions (Scott et al., 2002).

Adsorption studies

A typical basic dye, methylene blue, was selected for adsorption test because it is an important dye widely used for printing, textural dyeing and medicinal purpose.

The adsorption was performed by batch experiments. Kinetic experiments were carried out by agitating 100 ml of dye solution of known initial dye concentration with 1 g of zeolite at room temperature (25 ^{o}C) at a constant agitation speed of 120 rpm. Samples were pipetted out using a 10 mL-syringe at different time intervals. The collected samples were then centrifuged and the concentration in the supernatant solution was analyzed using a UV spectrophotometer (Cary 1E – Varian) by measuring absorbance at λ_{max} = 650 nm and pH=5. Adsorption isotherms were carried out by contacting 1 g of zeolite with 100 mL of methylene blue over the concentration ranging from 3.2 to 96 mg L^{-1}. The agitation was made for 10 min, which is sufficient time to reach equilibrium. The methylene blue adsorption performance of the original coal fly ash was also studied for comparison.

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time on adsorption process was investigated at various initial dye concentrations. It can be seen from Fig. 1 and 2 that the adsorption of methylene blue on zeolite occurred very quickly within the first 10 min after which a maximum value of adsorption capacity was attained.

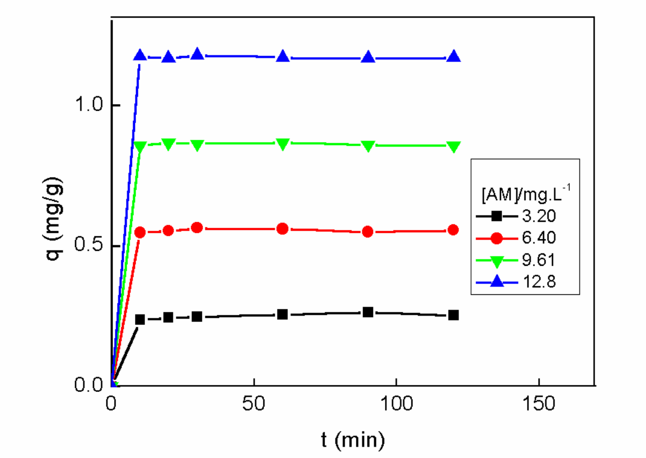

Figure 1. Adsorption kinetics for methylene blue onto zeolite Z1.

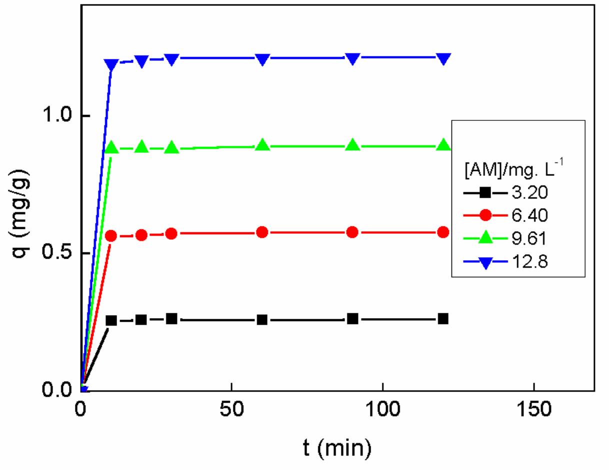

Figure 2. Adsorption kinetics for methylene blue onto zeolite Z2.

The rapid uptake of dye particles for the first 10 min is due to the occurrence of solute transfer only due to adsorbate and adsorbent interactions with negligible interference due to solute–solute interactions (Varshney et al., 1996). The equilibrium of the adsorption process was attained so fast that the kinetic data could not be modeled.

Adsorption isotherms

The analysis and design of adsorption process requires equilibrium to better understand the adsorption process. Adsorption equilibria provide fundamental physiochemical 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.

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

$C_e/q_e = 1/bQ_o + C_e/Q_o$ (1)

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:

$\log q_e = \log K_f + 1/n (\log C_e)$ (2)

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 logC_e. Similarly a plot of C_e/q_e versus C_e gives a straight line of slope $1/Q_0$ and intercept $1/Q_0b$.

Equilibrium data of methylene blue onto zeolite synthesized from fly ash are shown in Fig. 3 and 4. 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. The equilibrium isotherm has the shape of L3 type curve and indicates that the second layer of dye can form readily.

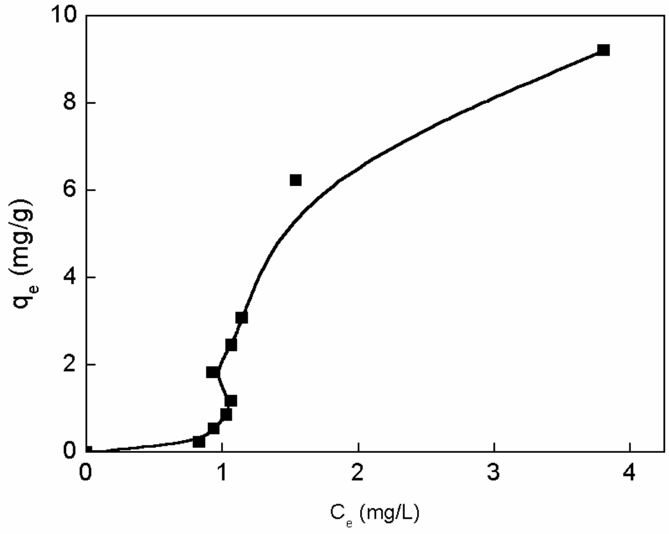

Figure 3. Adsorption isotherm of methylene blue onto zeolite Z1

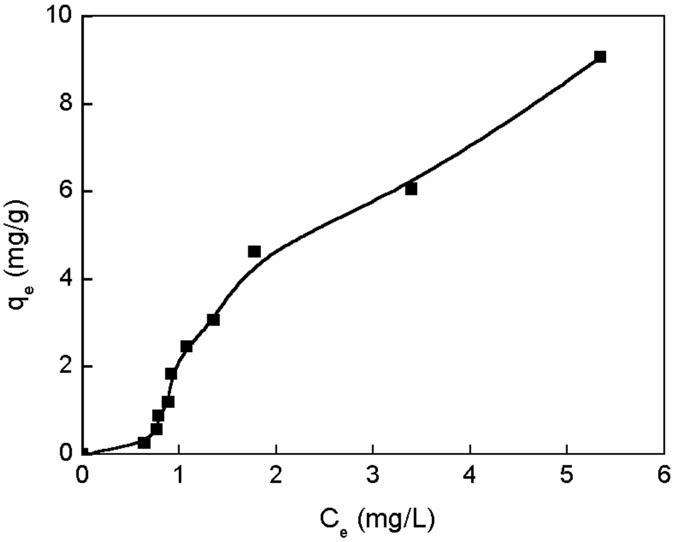

Figure 4. Adsorption isotherm of methylene blue onto zeolite Z2.

The parameters obtained from the isotherm are given in Table 3. Langmuir constants are not given in Table 3 due this poor fit to experimental data. Negative values for the Langmuir isotherm constants imply that this model is not suitable to explain the adsorption process, since these constants are indicative of the surface binding energy and monolayer coverage. This suggests that some heterogeneity in the surface or pores of the zeolite synthesized from fly ash will play a role in dye adsorption.

Table 3. Freundlich parameters for the adsorption of methylene blue onto adsorbents

Adsorbent	Freundlich		
	K_f *	n	R^2
Z1	1.15	0.512	0.778
Z2	1.28	0.701	0.890
Fly ash **	0.389	1.70	0.829

(*) $(mg\ g^{-1})\ (L\ mg^{-1})^{1/n}$; (**) [AM] = 3.2 – 12.8 mg L^{-1}; t_{equilt} = 2 h

The adsorption isotherm can be fitted using Freundlich model with correlation coefficient between 0.80 - 0.90. The value of n below one is indicative for a cooperative sorption in sites with different bonding energies (Atkins, 1970).

The adsorption of methylene blue onto original coal fly ash was also studied for comparison (Table 3). The adsorption capacities of methylene blue on the adsorbents decreased as Z2> Z1> fly ash. The original coal fly ash had the lowest adsorption capacity of the methylene blue. Samples using zeolite needed shorter periods of agitation before reaching equilibrium and were able to remove more methylene blue from aqueous solution than the fly ash.

The adsorption capacity can be correlated with the variation of surface area and porosity of the adsorbent. Higher surface area and pore volume will result in higher adsorption capacity. Zeolites synthesized from fly ash presents the highest surface area and pore volume than raw ash. These products show increased affinity for cationic dye adsorption when compared to the fly ash. (Woolard et al., 2002).

The effect of treatment conditions on methylene blue removal was less pronounced. Although the synthesis parameters were different, the adsorption capacities of two zeolites obtained were similar. The adsorption capacity of Z2 was only 10% higher than Z1.

Thermodynamics Parameters

In understanding better the effect of temperature on the adsorption, it is important to study the thermodynamic parameters such as standard Gibbs free energy change (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o). The Gibbs free energy of adsorption by using equilibrium constant (K_c) is calculated from the following equation:

$$\Delta G^o = - 2.0303\ RT \log K_C \quad (3)$$

Standard enthalpy, (ΔH^o), and standard entropy, (ΔS^o), of adsorption can be estimated from van’t Hoff equation given in

$$\text{Log } K_C = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (4)$$

where R is the gas constant, K_c is adsorption equilibrium constant. The K_c value is calculated from the equation [5]

$$K_C = \frac{C_{Ae}}{C_{Se}} \quad (5)$$

where C_{Ae} is the equilibrium concentration of the dye ions on adsorbent (mg L^{-1}) and C_{Se} is the equilibrium concentration of the dye ions in the solution (mg L^{-1}).

The plot of log K_c against $1/T$ (in Kelvin) should be linear. The slope of the van’t Hoff plot is equal to - ΔH^o / 2.303 R, and its intercept is equal to ΔS^o / 2.303 R. The van’t Hoff plot for the adsorption of MB onto zeolite synthesized from fly ash is given in Fig. 5. Thermodynamic parameters obtained are given in Table 4.

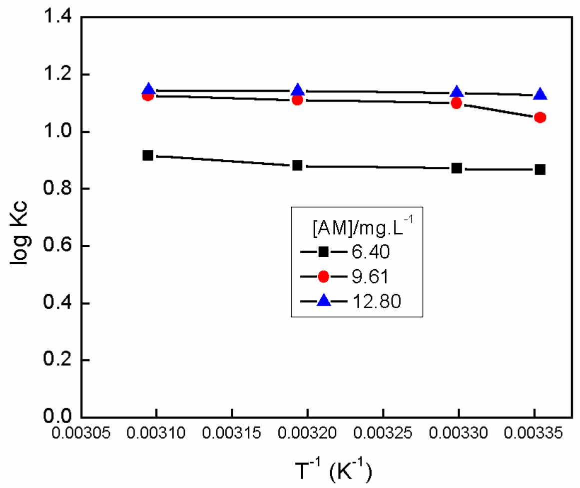

Figure 5. Van´t Hoff plot of methylene blue adsorption onto zeolite Z2.

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Table 4. Thermodynamic parameters for the adsorption of MB onto zeolite Z2

[AM] mg. L^{-1}	ΔH k.J.mol^{-1}	ΔS J. $mol^{-1}.K^{-1}$	ΔG (k.J.mol^{-1})			
			298.15 K	303.15 K	313.15 K	323.15 K
6.40	9.27	46.43	-4.37	-5.05	-5.28	-5.67
9.61	4.89	36.79	-5.98	-6.39	-6.65	-6.96
12.8	1.25	25.82	-6.44	-6.59	-6.83	-7.08
Average	5.14	36.35	-5.61	-6.01	-6.26	-6.57

As shown in the table, the negative values of ΔG^o at different temperatures indicate the spontaneous nature of the adsorption process. Positive ΔH^o reveals endothermic adsorption. The positive value of ΔS^o suggests the increased randomness at the solid/solution interface during the adsorption of the dye onto zeolite synthesized from fly ash. A similar trend has been reported for the adsorption of Methylne blue onto synthetic zeolite MCM-22 [Wang et al., 2006].

CONCLUSIONS

The present study showed that the zeolite synthesized from fly ash could be used as an effective adsorbent for the removal of methylene blue from its wastewaters. It is observed from the experiments that about 74-96% removal is possible. The equilibrium data followed Freundlich isotherm with a sorption capacity around 1.2 – 1.3 (mg/g)(L/mg)$^{1/n}$. The coal fly ahs based adsorbent may be an alternative to more costly adsorbents for the treatment of aqueous waste containing methylene blue.

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