



Adsorption and kinetic studies of methylene blue on zeolite synthesized from fly ash

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ABSTRACT

Batch sorption experiments were carried out to remove methylene blue from its aqueous solutions using zeolite synthesized from fly ash as an adsorbent. Nearly 10 min of contact time are found to be sufficient for the adsorption of dye to reach equilibrium. Equilibrium data have been analyzed using Langmuir and Freundlich isotherms and the results were found to be well represented by the Freundlich isotherm equation. Adsorption data were fitted to both Lagergren first-order and pseudo-second-order kinetic models and the data were found to follow pseudo-second-order kinetics. Thermodynamic calculations suggest that the adsorption of methylene blue on zeolite synthesized from fly ash is spontaneous and exothermic reaction.

Keywords: Zeolite; Methylene blue; Dye adsorption; Adsorption Kinetics; Thermodynamics

1. Introduction

Many industries use dyes and pigments to color their products. The remaining dye molecules are common water pollutants in trace quantities in the wastewater. Their presence in water, even at very low concentrations, is highly visible and undesirable and may significantly affect photosynthetic activity in aquatic life due to reduced light penetration. Some dyes are also toxic and even carcinogenic.

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 [1]. 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 [2]. 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 as adsorbents because of their higher adsorption capacities [3–5]. However, because of its relatively high cost, numerous low-cost materials have been investigated as adsorbent for contaminants removal from wastewater [6].

Utilization of industrial solid wastes such as fly ash for the treatment of wastewater could be helpful not only to the environment in solving the solid waste disposal problem, but also in terms of economy [7]. Fly ash is produced by burning of coal in coal-fired power stations and is the industrial solid waste most generated in southern Brazil: approximately 4 millions tons/y. Only 30% of this total is reused or recycled mainly for construction purposes. Thus, continuous research is needed to

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develop an alternative technology for more value-added utilization of coal ash materials.

It is possible to convert fly ash into zeolitic products by hydrothermal treatment with alkaline medium [8–13]. The synthesized zeolite has a significantly increased surface area when compared to the raw ash and exhibit important characteristic properties like cation exchange capacity, adsorption, molecular sieving and catalysis. Several environmental technologies can emerge with substantial benefits from zeolite based materials.

Zeolitic materials have been widely used as low-cost adsorbents for the removal of metals from aqueous solution [14–22]. However, few investigations have focused on the removal of dye pollutant of potential waste streams.

Several papers have reported that various types of zeolites could be obtained by changing the source of fly ash [23,24]. Fly ash composition seriously changes depending on the origin of coal sources as well as differences in the design of coal-fired boilers. Recently, Australian [25–27] and South African [28] fly ashes have been used as raw material for synthesizing zeolites and were tested for removal of dyes from wastewater. Zeolite from different fly ash may be different in their adsorption behaviors. It was, therefore, thought desirable to convert fly ashes from Brazilian thermal power plant and to investigate their application for the wastewater treatment.

In this study, zeolite synthesized from Brazilian fly ash was evaluated as an adsorbent for removal of cationic dye from aqueous solution. Batch kinetic experiments were performed to provide appropriate equilibrium times. The Langmuir and Freundlich isotherm models were used to model the isotherm data for their applicability.

2. Materials and methods

2.1. Materials

Methylene blue (CI = 52015) was AR-grade chemical and has a molecular weight of 373.90 g mol⁻¹, which corresponds to methylene blue hydrochloride with three groups of water. 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 baghouse filter were obtained from a coal-fired power plant located at Figueira County, in Paraná State, Brazil.

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 90°C in an

oven for 21 h with 200 mL of 4 mol L⁻¹ NaOH solution. The zeolitic material was repeatedly washed with deionized water and dried at 100°C for 24 h.

2.2.2. Characterization techniques

The physicochemical characteristics of materials were determined using standard procedures. Bulk density was determined by a helium pycnometer (Micromeritics, Accupyc 1330). The surface area was determined by N₂ adsorption isotherm with relationship using NOVA 1200 (Quantachrome). Before adsorption experiments, the samples were degassed at 150°C for 12 h. The BET surface area was obtained by five points at p/p^0 between 0.05 and 0.20 applying the BET equation to the adsorption data. The phases of the zeolite were determined by XRD analyses with an automated Rigaku multiflex diffractometer with a Cu anode using Co K α radiation at 40 kV and 20 mA over the range (2θ) of 5–80° with a scan time of 1°/min. The chemical composition of zeolite was determined by a RIX-3000 RIGAKU X-ray fluorescence spectrometer (XFR). A scanning electron micrograph was obtained by using an XL-30 Philips scanning electron microscope (SEM). The cation exchange capacity (CEC) value was determined using ammonium solutions [23]. The pH of zeolite was measured as follows: 0.1 g of samples were mixed with 10 mL of distilled water and shaken for 24 h. After filtration, the pH of solution was determined by a pH meter (Onda ion analyzer).

2.2.3. Adsorption studies

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°C) at 120 rpm. A quantity of 2.5 mL of uniform dispersion was 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 $\lambda_{\text{max}} = 650$ nm and pH = 5. Adsorption isotherms were carried out by shaking 1 g of zeolite with 100 mL of methylene blue over the concentration ranging from 3.2 to 96 mg L⁻¹ for 10 min, which is sufficient time to reach equilibrium. The effect of pH on adsorption was studied by adjusting initial pH of the dye solutions using 0.1 mol L⁻¹ HNO₃ or 0.5 mol L⁻¹ NaOH. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg g⁻¹), was calculated by:

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

where C_0 and C_e (mg L⁻¹) are the liquid-phase con-

centrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of adsorbent used (g).

3. Results and discussion

3.1. Characterization of materials

The chemical composition of fly ash determined by X-ray fluorescence is shown in Table 1. XFR measurement shows that the most of chemical compounds in fly ash are alumina, silica with some iron oxide and sodium oxide. The fly ash from the baghouse filter has a very low $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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.

Some physical properties of zeolitic material synthesized from fly ash are given in Table 2. X-ray diffraction analysis of sample revealed that the product obtained was NaP1 zeolite ($\text{Na}_6\text{Al}_6\text{Si}_8\text{O}_{32}\cdot 12\text{H}_2\text{O}$) with traces of hydroxysodalite, quartz and mullite. The synthesized zeolite exhibit strong basicity suggesting the negative charge on the solid surface in aqueous solution.

Fig. 1 shows the SEM images of zeolitic material synthesized from fly ash. The absence of the spherical

particles in zeolitic product indicates high conversion on fly ash to crystalline zeolite on hydrothermal treatment. The surface is rough, indicating that zeolite crystals were deposited on the surface of underlying fly ash particles during the hydrothermal treatment. Most of the crystallites are small (<1 μm in length) because the presence of a multitude of impurities in the ash leads to rapid nucleation at the expense of crystal growth [29].

3.2. Adsorption kinetics

Fig. 2 shows the effect of initial dye concentration on amount of dye adsorbed (mg g^{-1}) at different contact time for different initial methylene blue concentrations. The amount of dye uptake, q (mg g^{-1}), increased with the increase in agitation time and initial dye concentration.

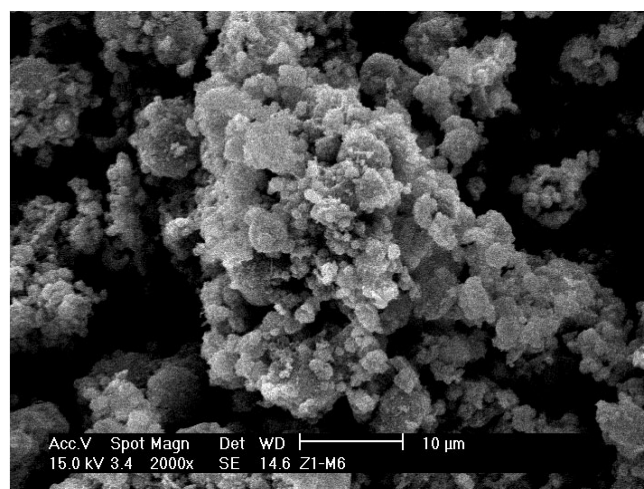


Fig. 1. Typical SEM micrograph of zeolite from fly ash.

Table 1
Chemical composition of coal fly ash

Components	Composition (wt %)
SiO_2	18.4
Al_2O_3	18.8
Fe_2O_3	5.78
Na_2O	0.975
CaO	0.733
K_2O	2.51
TiO_2	0.55
SO_3	0.731
MgO	0.406
ZnO	0.219
As_2O_3	0.25
P_2O_5	0.14
$\text{SiO}_2/\text{Al}_2\text{O}_3$	0.98

Table 2
Some physical properties of zeolitic material synthesized from fly ash

pH (in water)	11
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	131.5
Specific gravity (g cm^{-3})	2.36
Pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.25
CEC ($\text{meq } 100 \text{ g}^{-1}$)	152.2

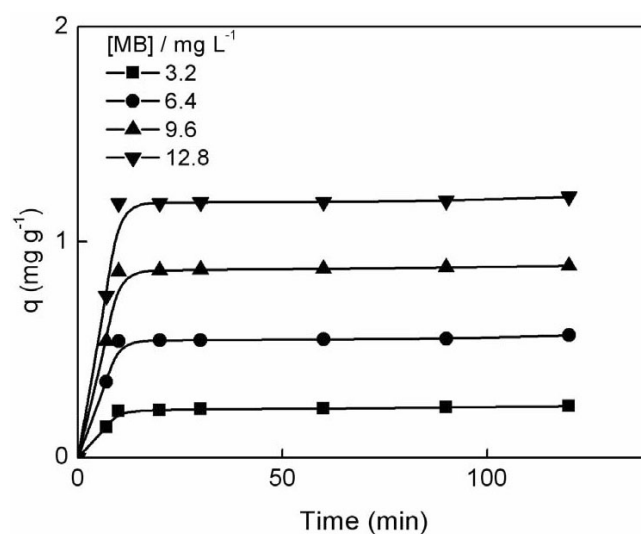


Fig. 2. Adsorption kinetics for methylene blue onto zeolite.

The adsorption of methylene blue on zeolite reached equilibrium at around 10 min at all initial dye concentrations. These observations show that the initial dye concentration has no effect on equilibrium time. Further, larger fractions (~70–92% of total amount of color adsorbed) of dye were removed within the first rapid uptake phase, i.e., the first 10 min. This is due to the decrease in flux (concentration gradient) with time due to transfer of solute onto solid phase. 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 [30]. Moreover, the percentage removal rate increased with an increase in the dye concentration, which is due to the availability of adsorption active sites for the initial dye concentration range studied.

3.3. Kinetic models

The transient behavior of the batch sorption process at different initial concentrations was analyzed using the Lagergren pseudo-first-order kinetic model and Ho and McKay's pseudo-second-order model.

The pseudo-first-order kinetic model, proposed by Lagergren, has been widely used to predict the dye adsorption kinetics. The dye adsorption kinetics following the pseudo-first-order model is given by [31]:

$$\frac{dq}{dt} = K_1(q_e - q) \quad (2)$$

where q and q_e represent the amount of dye adsorbed (mg g^{-1}) at any time t and at equilibrium time, respectively, and K_1 represents the adsorption rate constant (min^{-1}). Integrating Eq. (2) with respect to boundary conditions $q = 0$ at $t = 0$ and $q = q$ at $t = t$, then Eq. (2) becomes:

$$\log(q_e - q) = \log q_e - K_1 t / 2.303 \quad (3)$$

Thus the rate constant K_1 (min^{-1}) can be calculated from the plot of $\log(q_e - q)$ vs. time t .

The kinetic data were further analyzed using a pseudo-second-order relation proposed by Ho et al. [32] which is represented by:

$$\frac{dq}{dt} = K_2(q_e - q)^2 \quad (4)$$

where K_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) and q_e and q represent the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time t . Separating the variables in Eq. (5) gives

$$\frac{dq}{(q_e - q)^2} = K_2 dt \quad (5)$$

Integrating Eq. (5) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$ gives

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

A plot of t/q vs. t gives the value of the constants K_2 ($\text{g mg}^{-1} \text{min}^{-1}$), and also q_e (mg g^{-1}) can be calculated.

Because the above two equations cannot give definite mechanisms, the intraparticle diffusion model was tested. According to Weber and Morris [33], an intraparticle diffusion coefficient K_i is defined by the equation:

$$K_i = q/t^{0.5} \quad (7)$$

Thus the K_i ($\text{mg g}^{-1} \text{min}^{-0.5}$) value can be obtained from the slope of the plot of q (mg g^{-1}) vs. $t^{0.5}$ ($\text{min}^{0.5}$). Previous studies showed that such plots may present a multi-linearity, which characterizes the two or more steps involved in the adsorption process [34].

Fig. 3 shows the fitting results using various kinetic models and the parameters for all models are presented in Table 3.

The calculated correlation coefficient values (R^2) for first-order and second-order kinetics were found to be greater than 0.9, which shows the applicability of both these kinetic models. The linearity of fitting lines in plots q vs. $t^{0.5}$ (Fig 3c) points to the presence of intraparticle diffusion. However, the deviation of the lines from the origin indicates that the pore diffusion is not the only rate controlling step [33]. The average value of K_i was found to be $2.9 \times 10^{-3} \text{ mg g}^{-1} \text{min}^{-0.5}$. From Table 3 it is observed that the R^2 values were found to be higher than that of R_1^2 and R_i^2 at all initial dye concentrations. The higher R^2 values confirm that the sorption process follows a pseudo-second-order mechanism.

3.4. Adsorption equilibrium

The analysis and design of adsorption process requires the relevant adsorption equilibrium. Adsorption equilibria provide fundamental physicochemical data, which are important for optimizing the efficiency of the process. In the present investigation the equilibrium data were analyzed using the Freundlich and Langmuir isotherm expression given by the equations:

- Freundlich:

$$q_e = K_f C_e^{1/n} \quad (8)$$

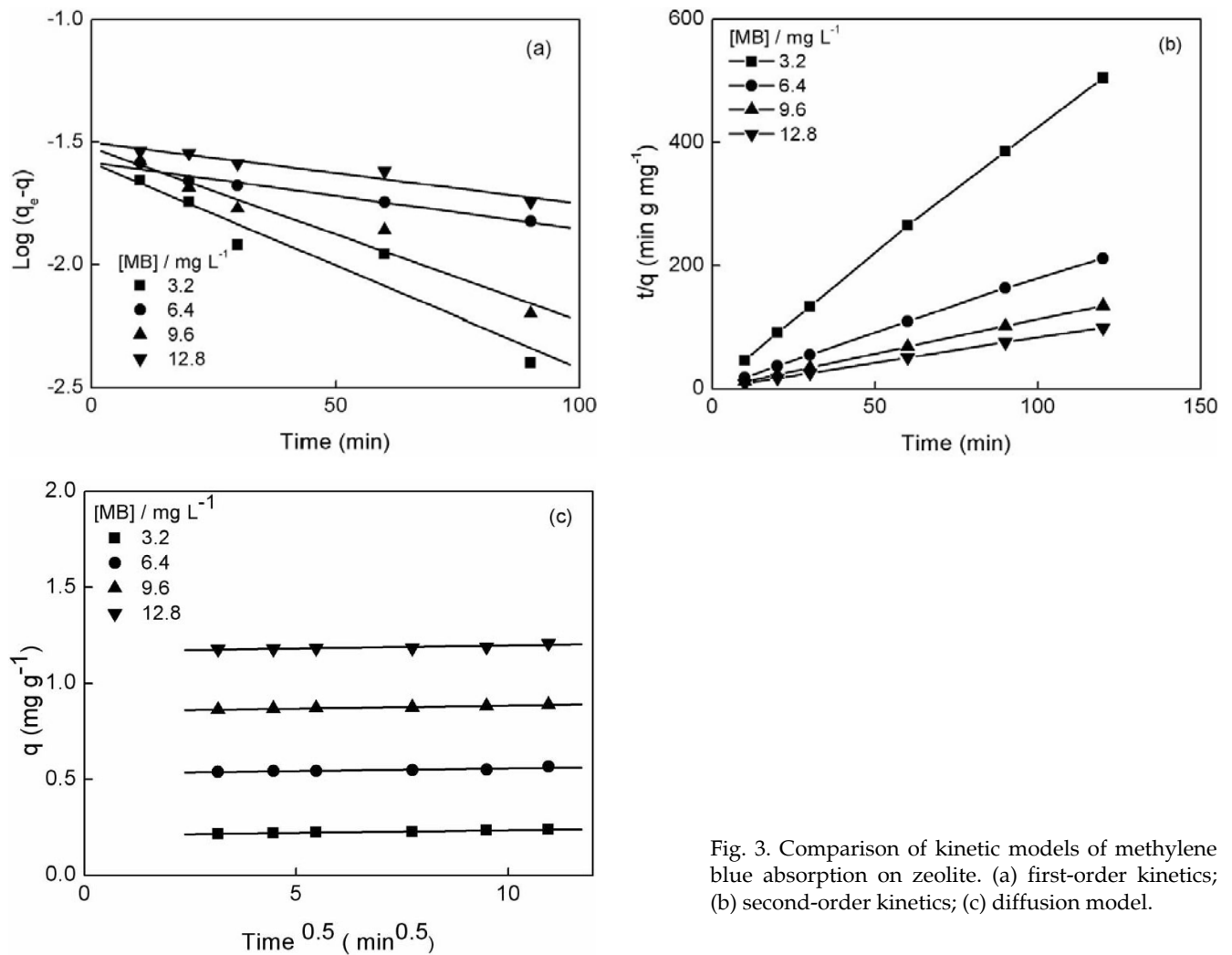


Fig. 3. Comparison of kinetic models of methylene blue absorption on zeolite. (a) first-order kinetics; (b) second-order kinetics; (c) diffusion model.

Table 3
Kinetic constants for methylene blue onto zeolite

[MB] (mg L ⁻¹)	Pseudo-first-order		Pseudo second-order		Diffusion model	
	$K_1 \times 10^{-2}$ (min ⁻¹)	R_1^2	K_2 (g mg ⁻¹ min ⁻¹)	R_2^2	$K_d \times 10^{-3}$ (mg g ⁻¹ min ^{-0.5})	R_d^2
3.2	1.930	0.9574	2.01	0.9998	2.72	0.9812
6.4	0.624	0.9814	1.64	0.9998	2.81	0.9042
9.6	1.630	0.9745	1.88	0.9999	3.14	0.9872
12.8	0.573	0.9710	1.36	0.9999	3.23	0.8765

where K_f (mg g⁻¹) (L mg)^{-1/n} and n are Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents. The value of n falling in the range of 2–10 indicates favorable adsorption [35].

- Langmuir:

$$q_e = Q_0 b C_e / (1 + b C_e) \quad (9)$$

where q_e is the solid-phase adsorbate concentration at equilibrium (mg g⁻¹), C_e is the 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 and Langmuir equations can be written as follows:

$$\log q_e = \log K_f + 1/n (\log C_e) \quad (10)$$

$$C_e/q_e = 1/bQ_0 + C_e/Q_0 \quad (11)$$

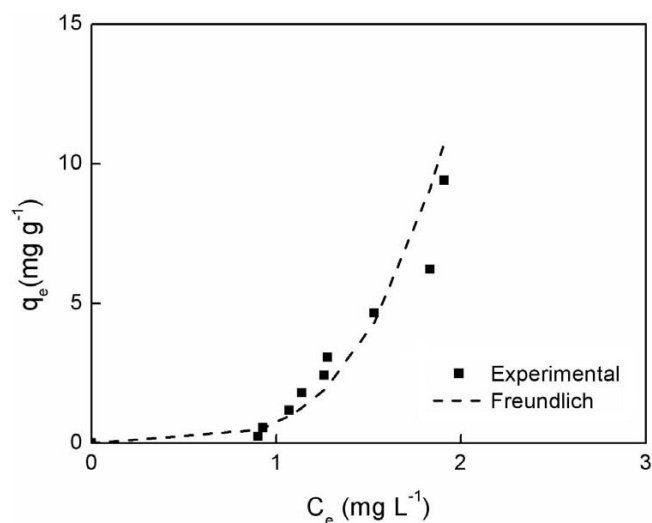


Fig. 4. Adsorption isotherm of methylene blue onto zeolite synthesized from fly ash.

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 vs. C_e gives a straight line of slope $1/Q_0$ and intercept $1/Q_0 b$.

Equilibrium data of methylene blue onto zeolite synthesized from fly ash is shown in Fig. 4. The isotherm shapes are largely determined by the adsorption mechanism and can therefore be used to diagnose the nature of the adsorption [36]. 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 S3 type curve, indicative of multilayer or aggregate formation at the interface at higher coverage.

The isotherm constants and correlation coefficients calculated for Freundlich and Langmuir equations are given in Table 4. 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. Zeolitic material contains mineral oxides and minor unconverted fly ash and its surface will provide active vacancies for dye adsorption with different characteristics.

The adsorption isotherm can be fitted very well using Freundlich model evidenced from the correlation coefficient ($R^2 > 0.90$). The value of n below one is indicative for a cooperative sorption in sites with different bonding energies [37,38]. The adsorption of methylene blue onto original coal fly ash was also studied for comparison. It was seen that the maximum adsorption of capacity was $0.0886 \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}^{-1/n}$. The capacity of the zeolite from

Table 4

Equilibrium isotherm constants for methylene blue onto zeolite from fly ash

Freundlich:	
$K_f \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}^{-1/n}$	0.738
n	0.241
R^2	0.950
Langmuir:	
$Q_0 \text{ (mg g}^{-1}\text{)}$	-0.465
$b \text{ (L mg}^{-1}\text{)}$	-0.563

Table 5

Freundlich constants for methylene blue adsorption by various adsorbents reported in the literature

Adsorbent	$K_f \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}^{-1/n}$	References
Fly ash	0.00216	25
Zeolites from fly ash	1.42–1.93	25
Natural zeolite	0.0537	26
Synthetic zeolite MCM-2	0.116	39
Fly ash	0.3544	40
Fly ash treated with HNO_3	0.0139	41
Fly ash	0.00438	42
Zeolite from fly ash	0.738	This work

fly ash for methylene blue had increased 8-fold when compared to the raw ash. The enhancement in adsorption can be attributed to increase in surface area. Table 5 compares the adsorption capacity of methylene blue on various adsorbents.

3.5. Effect of initial pH

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The adsorption of charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent which is in turn influenced by the solution pH.

Fig. 5 shows the effect of pH on amount of dye adsorbed $q_e \text{ (mg g}^{-1}\text{)}$ at an initial dye concentration of 6.4 mg L^{-1} . It was observed that there is no significant effect of pH on methylene blue adsorption by zeolite from fly ash at the experiments carried out over the pH range from 2 to 11.

The fact that the adsorption of dye onto zeolite from fly ash is not significantly affected with changing of initial pH of the dye solution may be attributed to the weak electrostatic interaction between the dye molecules and the electron-deficient sites on the surface of the zeolite particles. On the other hand, the alkaline character of zeolite from fly ash can neutralize the acidic pH of the dye

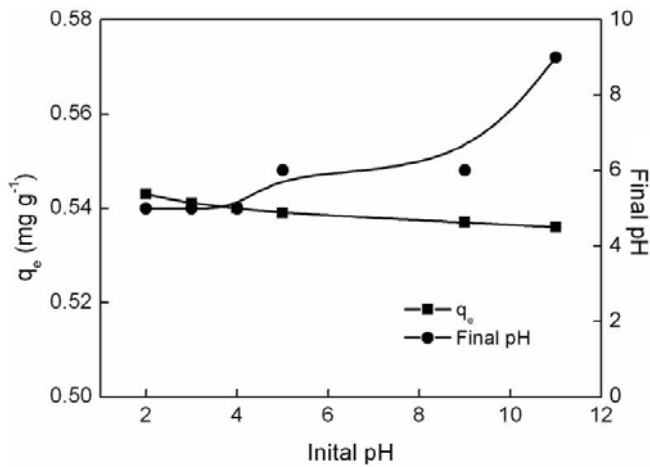


Fig. 5. Effect of pH on the removal of methylene blue onto zeolite from fly ash.

solution, significantly decreasing the effect of pH on the adsorption.

3.6. Effect of the adsorbent dosage

To determine the effect of adsorbent dosage on the amount of adsorption, the adsorbent concentration was varied from 2.5 to 25 g L⁻¹, while initial methylene blue concentration was held constant at 6.4 mg L⁻¹. As expected, the percentage of methylene blue removal increased with increasing zeolite dosage at the same initial dye concentration. As seen from Fig. 6, the removal yield increased from 71 to 82% for the given adsorbent dosage at the duration of adsorption of 10 min. The increase in methylene blue removal with the adsorbent dose can be attributed to increased surface area and the sorption sites.

Initially the rate of increase in the percentage of dye removal was found to be rapid, which then slowed down as the dose increased. This phenomenon can be explained, based on the fact that at a lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher. The rate of adsorption is higher in the beginning as sites are available and the unimolecular layer increases. Adsorption and desorption occur together and the rates become equal at a stage called adsorption equilibrium when isotherms are applied. The subsequent slow rise in the curves is due to adsorption and intra-particle diffusion taking place simultaneously with the dominance of adsorption.

Results obtained for the adsorption of methylene blue are shown in Fig. 6. It is clear that an increase in the mass of zeolite resulted in a decrease in adsorption capacity (q_e) values despite the fact that methylene blue uptake increased. The drop in adsorption capacity is basically due to sites remaining unsaturated during the adsorption

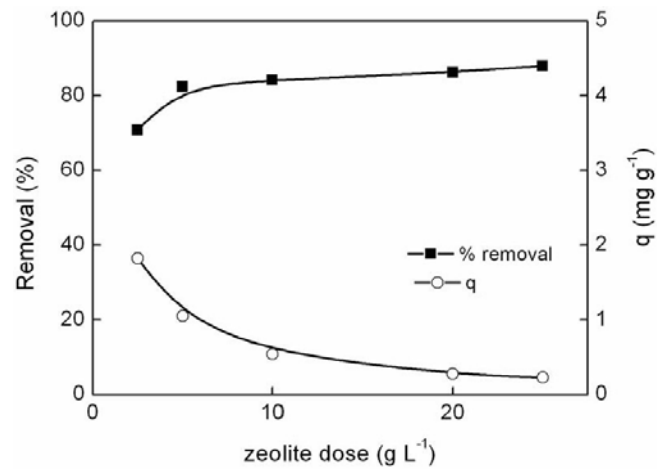


Fig. 6. Effect of adsorbent dose on the removal of methylene blue onto zeolite from fly ash.

reaction. Another reason may be the inter-particle interaction, such as aggregation, resulting from a high adsorbent dose. Such aggregation would lead to a decrease in the total surface area of the zeolite and an increase in diffusional path length [43]. As the adsorbent dose was increased from 2.5 to 25 g L⁻¹, the equilibrium adsorption capacity decreased from 1.82 to 0.225 mg g⁻¹ for methylene blue.

3.7. Thermodynamic parameters

In environmental engineering practice, both energy and entropy considerations must be taken into account in order to determine what process will occur spontaneously. The adsorption of methylene blue from aqueous solutions on the zeolite at different temperatures was studied. The variation in the extent of adsorption with respect to temperature has been explained on the basis of thermodynamic parameters viz., changes in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0). These were calculated by using the following equations:

$$K_c = \frac{C_{\text{adsorv}}}{C_e} \quad (12)$$

where C_{adsorv} is the equilibrium concentration of the dye ions on adsorbent (mg L⁻¹) and C_e is the equilibrium concentration of the dye ions in the solution (mg L⁻¹).

$$\Delta G^0 = -2.303 RT \log K_c \quad (13)$$

$$\Delta H^0 = 2.303 R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \log \frac{K_{c_2}}{K_{c_1}} \quad (14)$$

Table 6

Thermodynamic parameters for adsorption of methylene blue onto zeolite from fly ash at different temperatures

T (°C)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J K ⁻¹ mol ⁻¹)
25	-5.05	-19.7	-49.1
30	-2.08	-6.49	-14.5
40	-2.06		

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (15)$$

where R is the gas constant, T is temperature on the absolute scale and K_c , K_{c1} and K_{c2} are the equilibrium constants at temperature T , T_1 and T_2 , respectively. The values of these parameters were calculated and are presented in Table 6.

It is obvious from this table that the negative and small values of free energy change (ΔG^0) are an indication of the spontaneous nature of the adsorption process. The negative values of standard enthalpy change (ΔH^0) at different temperatures are indicative of the exothermic nature of the adsorption process. The negative values of (ΔS^0) suggest the decreased randomness at the solid/solution interface during the adsorption of the methylene blue onto zeolite from fly ash.

4. Conclusions

The present study showed that the zeolite synthesized from Brazilian fly ash can be used as an adsorbent for the removal of methylene blue from aqueous solution. The amount of dye uptake increased with increasing initial dye concentration and contact time. The maximum adsorption capacity for methylene blue was rapidly attained within 10 min and the adsorption was between 70 and 98% under the conditions studied. The equilibrium data followed the Freundlich isotherm with a sorption capacity of $0.738 \text{ (mg g}^{-1}) \text{ (L mg}^{-1})^{-1/n}$. Kinetics data tend to fit well in pseudo-second-order rate expressions. Thermodynamic calculations indicated that the adsorption of methylene blue on zeolite synthesized from fly ash is spontaneous and exothermic reaction. The use of the southern Brazilian coal ashes generated in power plants for the production of zeolites can constitute an alternative and noble use for a residue which has contributed to the degrading of vast areas.

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