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Removal of methylene blue using acid and heat treatment of clinoptilolite

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ABSTRACT

The adsorption of methylene blue from aqueous solution onto clinoptilolite has been studied under various experimental conditions. Heat treatment and acid treatment have also been applied to modify the clinoptilolite. It is found that heat treatment and acid treatment can significantly change the adsorption capacity. The treatment of clinoplites has the higher adsorption capacity than untreated ones. The adsorption data have been analyzed using Langmuir and Frendlich isotherms. The results indicate that the Langmuir model provides the better correlation of the experimental data. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy and entropy of adsorption. For heat treatment of clinoptilolite, adsorption of methylene blue is endothermic reaction with ΔH_{ads} at 50.67 kJ/mol.

Keywords: Clinoptilolite; Methylene blue; Adsorption; Modify

1 Introduction

Dye, a constituent that is widely used in textile, paper, plastic, food and cosmetic industries is an easily recognized pollutant. It is not only aesthetically displeasing, but also impedes light penetration in the treatment processes within the treatment plant. It also increases the BOD, and cause lack of dissolved oxygen to sustain aquatic life. In addition, many dyes are toxic to some microorganisms, and may cause direct destruction or inhibition of their catalytic capabilities [1]. Its presence, even in very low concentration, is highly visible and will affect aquatic life as well as food web. Many dyes are difficult to degrade, as they are resistant to aerobic digestion [2]. Hence, contaminations due to dyes pose not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and non-biodegradable characteristics.

The conventional methods of color removal from industrial effluents include ion exchange, activated carbon adsorption, membrane technology and coagulation [3]. Adsorption has been used extensively in industrial processes for many purposes of separation and purification. The removal of colored and colorless organic pollutants from industrial wastewater is considered as an important application of adsorption processes using suitable adsorbent [4–6].

At present, there is growing interest in using low cost, commercially available materials for the adsorption of dyes. A wide variety of materials such as fly ash [7], peat, phenolic resin, wood, maise cob, natural clays, activated sludge, wood chips, jift, palm-fruit bunch particles, nanosize modified silica, sugar beet pulp, activated carbon from fertilizer waste, olive mill products and diatomaceous silica, are being used as low cost materials for the adsorption of dyes [8]. Gupta et al. have made major contribution in this aspect [9–11]. They have studied the adsorption of dyes by a wide variety of materials such as bottom ash [12–15],

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bagasse fly ash [16], industrial waste products [17], red mud [18], TiO_2 [19], wheat husk [20], carbon slurry [21,22].

Clinoptilolites are highly porous aluminosilicates with different cavity structures. Their structures consist of a three-dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations which are exchangeable with certain cations in solutions. Clinoptilolites consist of a wide variety of species, more than 40 natural species. However, the most abundant and frequently studies zeolites is clinoptilolite, a mineral of the heulandite group. Its characteristic tabular morphology shows an open reticular structure of easy access, formed by open channels of 8-10 membered rings. Clinoptilolite has been shown to have high selectivity for certain pollutants [23,24].

High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively low prices, make zeolites attractive adsorbents [25]. Therefore, an inexpensive residual management technology is needed for the disposal or beneficial uses this material.

The natural clinoptilolite applied into adsorption of dye is low efficiency, so it was limited in the water treatment. In this study, acid treatment and thermal treatment of clinoptilolite was attempted to enhance the adsorptive capabilities of clinoptilolite for dyes. The effect of some operational parameters such as initial dye concentration, and temperature on the adsorptive capacity of the clinoptilolite was tested. The equilibrium, kinetic and thermodynamic data of the adsorption process then were studied to understand the adsorption mechanism of molecules onto the treatment of clinoptilolite. Based on the above researches, it will support its application into the treatment of water with theory.

2 Materials and methods

2.1. Adsorbent materials

The clinoptilolite sample used in these experiments was obtained from Zeolite Company in the P.R. of China. The main chemical composition of the sample is 78% SiO_2, 1.25% CaO, 3.24% K_2O, 0.03% SO_3, 12.3% Al_2O_3, 1.05% MgO, 0.02% TiO_2, 0.05% P_2O_5, 1.35% Fe_2O_3 and 0.35% Na_2O(wt). Properties of the sample are 0.5–1.0 mm particle size, porosity of 0.425, solid density of 2.32 g/cm^3, and particle density of 1.25 g/cm^3. To modify the clinoptilolite, the samples were treated by the following methods. One portion of the sample was heat treated at 823 K for 4 h and one portion of the sample was treated in 5 M H_2SO_4 solution for 6 h at room temperature (30 g clinoptilolites in 60 mL solution). After that, it was filtrated, washed and dried at 383 K for 12 h.

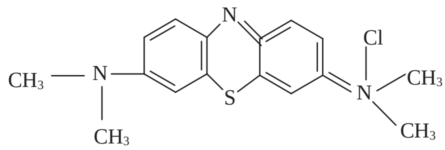

Fig. 1. Chemical structures of methylene blue.

2.2. Adsorbates

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 chemical structures of methylene blue are illustrated in Fig. 1.

2.3. Adsorption studied

The equilibrium time was determined by a preliminary investigation. It has been found that the adsorption equilibrium can be established in 6–8 h [26]. The adsorption was performed by batch experiments. 2 g of solid in 100 mL of dye solution of varying concentration was shaking at 100 rpm for 8 h at varying temperatures (293, 303 and 313 K). To investigate the effect of pH on adsorption, the pH of the solution was adjusted to the required value by adding either 1.0 M HCl or 1.0 M NaOH. Buffer solution of 1.0 mM potassium phosphate was added to the dye solution to enable better control of the pH, due to the characteristic of methylene blue. Preliminary samples of the dye solution and potassium phosphate were scanned between 300 and 700 cm^{-1} to check if there is chemical interaction between the dye and potassium phosphate. Results indicated that there were no such interactions.

2.4. Analytical method

The concentration of dye was measured with a UV-1600 spectrophotometer at a wavelength corresponding to the maximum absorbance of 665 nm for methylene blue. The uptake rate of dye was calculated by the following formula:

$$Q = \frac{A_0 - A_t}{A_0} \times 100\%, \tag{1}$$

where Q is the uptake rate (%), A_0 is the absorbency of initial dye, and A_t is the absorbency of equilibrium dye. The value of pH was measured with a pH probe.

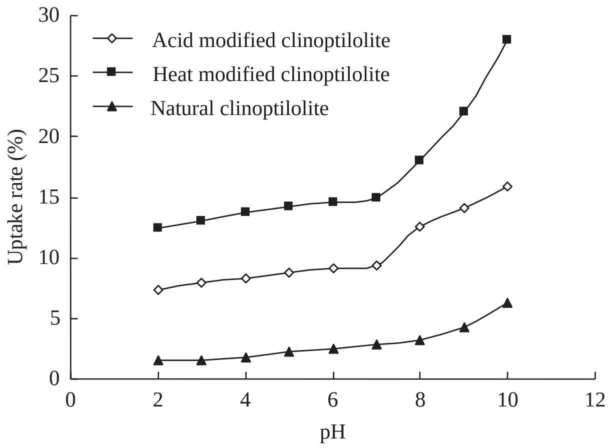

Fig. 2. Effect of pH on methylene blue adsorption on acid and heat treatment of clinoptilolite at 303 K.

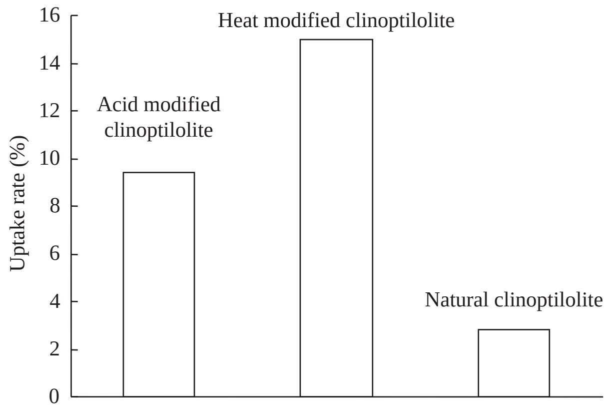

Fig. 3. Compared uptake rates (%) for methylene blue removal on natural, acid and heat modified treatment of clinoptilolite at 303 K and pH 7.0.

3. Results and discussion

3.1. Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The adsorption behaviour of methylene blue using acid and heat treatment of clinoptilolite and the natural clinoptilolites in both acidic and alkaline solutions was studied. That is, 2 g of solid in 100 mL of 10 mg/L methylene blue was shaking at 100 rpm for 8 h at 303 K. The dependencies of the dye sorption on pH are shown in Fig. 2.

As can be seen from Fig. 2, the percentage uptake increased with increase in pH from 2 to 10. The adsorption increased slowly in pH from 2 to 7, but the adsorption increased steeply in pH from 7 to 10. Similar adsorption behavior with variation in solution pH has been reported in the literature [27,28]. It is known that ionic dyes upon dissolution release colored dyes anions or cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent surface which is in turn influenced by the solution pH. Methylene blue is a basic dye. In water, it produces cation (C^+) and reduced ions (CH^+). If the solution pH is above the zero point of charge the negative charge density on the surface of the acid and heat treatment of clinoptilolite, which favors the sorption of basic (cationic) dyes [29]. In addition, the basic dye will become protonated in the acidic medium and the positive charge density would be located more on the dye molecules at low pH, resulting in the lower uptaking [23].

3.2. Effect of treatment methods

Fig. 3 shows the equilibrium adsorption of methylene blue on clinoptilolite. As shown, high-temperature treatment and sulphuric acid treatment both result in an important effect on the adsorption of methylene blue on clinoptilolite. Treatment of natural clinoptilolite by temperature and acid will have higher capacity. In addition to, it is clear from the figure that adsorption of methylene blue on the treatment of natural clinoptilolite by heat shows higher adsorption capacity than that on the treatment of natural clinoptilolite by acid. Acid treatment can dissolve the minerals in clinoptilolite and thus increase in adsorption. Higher temperature treatment will result in the decomposition of some organics and hydroxyl groups, which results in the increase in surface area and pore volume, and thus increase in adsorption.

3.3. Adsorption isotherms

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. The significance of the adsorbate molecules are distributed between the solution and the adsorbent at the equilibrium conditions and the effect of equilibrium conditions.

The Langmuir isotherms and the Freundlich isotherms [29,30] are available and selected in this study.

The theoretical Langmuir isotherm equation can be represented as,

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \tag{2}$$

where K_L is the Langmuir constant related to the energy of adsorption (l mg^{-1}), q_e is equilibrium the solid-phase concentration(mg g^{-1}) and q_m is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg g^{-1}). q_m is able to be calculated the following formula [31]:

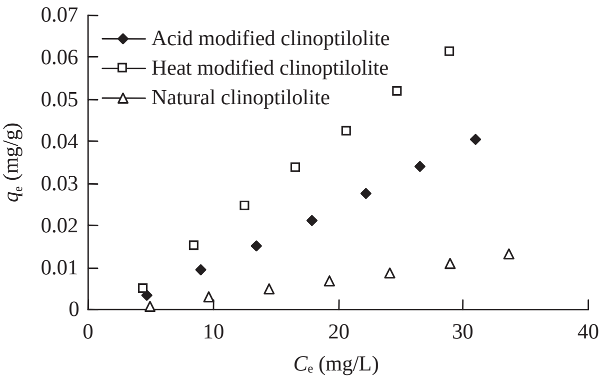

Fig. 4. The adsorption isotherms of methylene blue using the natural, acid and heat modified treatment of clinoptilolite at 303 K and pH 7.0

$q_m = \frac{(C_i - C_e) \times V}{1000m}$. C_e is the equilibrium liquid-phase concentration (mg L^{-1}). The constants K_L and q_m can be determined from the following linearised form of

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \times \frac{1}{C_e}. \tag{3}$$

The essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called the separation factor or equilibrium parameter (R_L). Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous treatment of the natural clinoptilolite surface.

The Freundlich isotherm can be used for non-ideal sorption that involves heterogeneous surface energy systems and is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}}, \tag{4}$$

where K_F is a rough indicator of the adsorption capacity ($\left(\frac{1}{\text{mg}}\right)^{\frac{1}{n}}$) and $\frac{1}{n}$ is the adsorption intensity. In general, as the K_F value increases the adsorption capacity of an adsorbent for a given adsorbate increases. Eq. (3) may be linearised by taking logarithms:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e). \tag{5}$$

We used the above two nonlinear equations for curve fitting by employing a commercial available software Excell2003. Fig. 4 shows the adsorption isotherms of methylene blue using the three types of clinoptilolite at 303 K and pH 7. It can be seen that acid or heat treatment of clinoptilolite could improve its loading capacity.

According to Eq. (2), Eq. (4) and experimental data in Fig. 4, a comparison of adsorption isotherms for fitting of the experimental results with the Langmuir model and the Freundlich model were studied. The models parameters from two isotherms obtained from nonlinear regression are presented in Table 1.

As seen that the Langmuir model is better than the Freundlich model in simulation of the adsorption isotherm (as evident from correlation coefficients). This suggests that the adsorption of methylene blue by clinoptilolite is characterized by monolayer coverage of the adsorbate molecules on the adsorbent outer surface. In addition, this adsorption has a homogenous nature or equal activation energy for each adsorbed molecule.

3.4. Effect of temperature

The temperature has two major effects on the adsorption process. Increasing the temperature is able to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [22].

Table 1
The models parameters obtained from fitting the experimental equilibrium data with isotherm models

Model	Parameters		R^2
Heat modified clinoptilolite			
Langmuir isotherm	Q_m= 1.273 mg/g	K_L = 0.152 l/mg	0.992
Freundlich isotherm	K_F = 0.305 [(l/mg)$^{1/n}$]	n = 2.578	0.965
Acid modified clinoptilolite			
Langmuir isotherm	Q_m= 0.607 mg/g	K_L =0.318 l/mg	0.985
Freundlich isotherm	K_F = 0.182 [(l/mg)$^{1/n}$]	n = 2.506	0.951
Natural clinoptilolite			
Langmuir isotherm	Q_m= 0.324 mg/g	K_L= 0.571 l/mg	0.981
Freundlich isotherm	K_F = 0.031 [(l/mg)$^{1/n}$]	n = 1.592	0.968

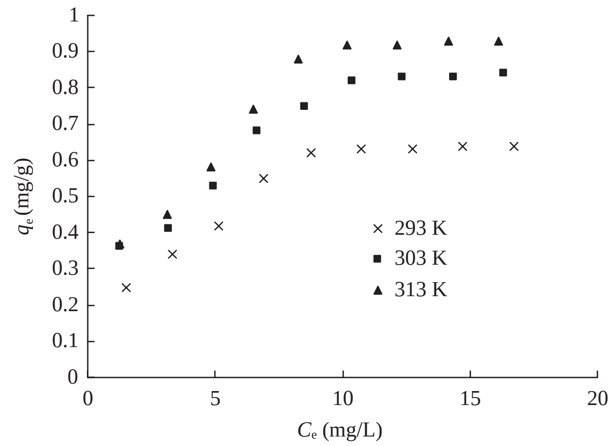

Fig. 5. Adsorption isotherms of methylene blue on the heat modified clinoptilolite at different temperatures.

The adsorption of methylene blue on the heat modified clinoptilolite was studied at temperatures of 293, 303 and 313 K, which these adsorption isotherms being shown in Fig. 5.

As shown in Fig. 5, the adsorption capacity of dye increased at higher temperatures, which indicates that adsorption of dye in this system was an endothermic process.

The free energy of adsorption (ΔG_{ads}) was calculated from the following equation [23]:

$$\Delta G^0 = -RT \ln K_{\mathrm{L1}}, \tag{5}$$

where K_{L1} is Langmuir constant at T_1, R is the gas constant (8.314 J/mol K). The apparent enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) were calculated from adsorption data at different temperatures using the Van't Hoff equation (Namasivayam and Kavitha, 2002):

$$\ln(K_{\mathrm{L}}) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \tag{6}$$

where K_{L} is the Langmuir constant and T is the solution temperature (K). The magnitude of ΔH_{ads} and ΔS_{ads} was calculated from the slope and y-intercept from the plot of $\ln K_{\mathrm{L}}$ vs $\frac{1}{T}$, with these thermodynamic parameters being given in Table 2.

From Table 2, the change in enthalpy for the heat treatment of clinoptilolite was found to be positive. The positive values confirm the endothermic nature of adsorption. The positive values of the entropy change show the increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent and an affinity of the adsorbent toward methylene blue. The increase in dye adsorption with increasing temperature might also be due to the enhanced rate of intraparticle diffusion of the adsorbate, as diffusion is an endothermic process [28].

Table 2
Thermodynamic parameters for methylene blue adsorption on the heat modified clinoptilolite under different temperatures

T (K)	K_{L} (l/mg)	Q_{m} (mg/g)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol·K)
293	0.302	0.771	9.14	50.67	141.74
303	0.152	1.273	14.88		
313	0.147	1.451	15.64		

4. Conclusions

In this study, it was found that acid and heat treatment can significantly change the adsorption capacity of clinoptilolite. Adsorption isotherm data were fitted to both Langmuir and Freundlich models, in which the Langmuir model was the better one. For heat treated clinoptilolite, adsorption of methylene blue is endothermic reaction with $\Delta H_{\mathrm{ads}} = 50.67$ kJ/mol.

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