

Adsorption properties of methylene blue on hectorite: kinetic and Thermodynamics studies

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Keywords: Hectorite, methylene blue, kinetic, thermodynamics

Abstract. Hectorite has been designed and synthesized by hydrothermal way, which is used for removal of methylene blue (MB) from aqueous solution. The experiment data was analyzed using pseudo-second-order kinetics, intra-particle diffusion and film diffusion. The characteristic parameters for each model have been determined. Thermodynamic parameters such as activation(E_a), standard free energy(ΔG^0), the enthalpy(ΔH^0) and the entropy(ΔS^0) were also evaluated. The negative value of ΔG^0 (kJ/mol) and ΔH^0 (kJ/mol) indicates the spontaneous and exothermic nature of the reactions. The data of E_a shows the physisorption process of MB on hectorite.

Introduction

The main pollution source of textile effluent emerged from the dyeing process. The effluent discharged was highly colored. The disposal of this colored water was not only caused damage to aquatic life, but also to human beings by causing mutagenic or carcinogenic effect[1]. Accordingly, to protect humans and recover ecosystem from contamination, the dyes must be eliminated from the dye-contained wastewater before being released into the environment. Therefore, the removal of dyes from waste effluents was important. During the past three decades, different methods such as coagulation, electro coagulation, flotation, chemical oxidation, filtration, membrane separation and microbial degradation have been developed for the removal of synthetic dyes from waters and wastewaters to decrease its impact in the environment [2-4]. Among the numerous techniques of dye removal, adsorption is the procedure of choice giving the best results as it can be used to remove certain classes of chemical pollutants from water. Conventional industries used activated carbon as adsorbent for wastewater treatment. Because of its high cost, researchers are testing the efficiency of various other low cost adsorbents for the textile effluents. A lot of works have employed natural and synthetic clays for removing the dyes from wastewater [5-7].

Hectorite, which is 2:1 smectite clay, has been used as an adsorbent for the removal of cationic dyes and metal ions [8-10]. Due to unique structure with interior channels which allows penetration of organic and inorganic ions bounding together with solutes into the structure of hectorite, it is one of the best adsorbents for removing dyes from relatively concentrated wastewater. However, the adsorption processes of MB onto hectorite such as equilibrium model, dynamics, and thermodynamic were few reported .

In this paper, using hydrothermal way, we synthesized hectorite and proposed the use of hectorite for the adsorption of methylene blue(MB). Experiment data was analyzed using kinetic and thermodynamics equations. The characteristic parameters for each model have been determined.

Experimental procedures

Adsorption experiments.

All adsorption experiments were carried out in a thermostatic orbital shaker at different temperatures (293, 303, 313 and 323K). The shaking was continued till the equilibrium time was reached. The adsorption isotherm experiment was carried out by agitating aqueous dispersions of MB (200 mL, various concentrations) and adsorbent (100 mg). The dispersion was centrifuged and the concentration was measured by UV-Vis spectroscopy (T-6 UV-VIS spectrophotometer) at 665 nm. The amount of MB adsorbed by hectorites, q_e (mg/g), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e) \frac{v}{w} \quad (1)$$

Where C_0 and C_e are the initial and equilibrium solution concentrations of MB, respectively (mg/L), v is the volume of the solution (L) and w is the mass (g) of the adsorbent used.

The kinetic studies were carried out in 200 mL MB solutions (180 mg/L) by adding 100 mg adsorbent at different temperatures (293, 303, 313 and 323K). At given irradiation time intervals, the dispersion was centrifuged and the concentration was measured.

Results and discussion

The pseudo-second-order kinetic model.

The study of adsorption dynamics described the solute adsorption rate. This rate controlled the residence time of adsorbate adsorption onto hectorite was analyzed using pseudo-first-order, pseudo-second-order, intra-particle diffusion kinetics models.

The amount of MB adsorbed onto hectorite increased as the time increased. Most of MB molecules adsorption took place at the initial 30 min of the experiment. As the time progressed, there was a weak increase in adsorption even after long time.

The linear form of the pseudo-second-order kinetic model [11] was given as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where k_2 was the equilibrium rate constant of pseudo-second-order adsorption [$g/(mg \cdot min)$]. The straight line plots of t/q_t against t were tested to obtain rate parameters (Fig. 1 and Table 1).

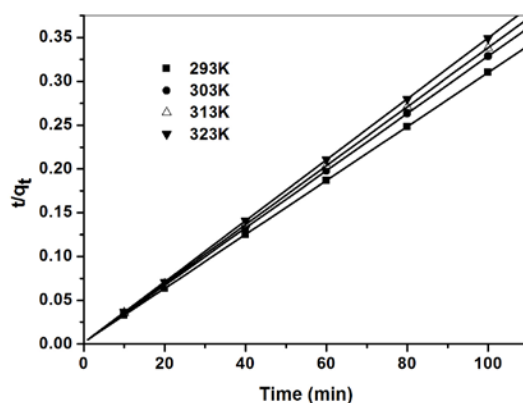


Fig.1 The pseudo-second-order kinetics for the adsorption of MB onto hectorite

The correlation coefficients (r^2) of the pseudo-second-order model were higher (Table 1). The experimental q_e values studied for hectorite were close to q_e values calculated from the pseudo-second-order kinetic model. It could be concluded that the mechanism of adsorption was pseudo-second-order reaction.

Table 1 The kinetic parameter constants for the adsorption MB onto hectorite

Adsorption	Experimental q _e (mg/g)	Pseudo-second-order kinetic model		
		q _e (mg/g)	k ₂	r ₂ ²
293K	338	325	0.0048	0.9994
303K	330	306	0.0063	0.9996
313K	317	297	0.0067	0.9995
323K	301	287	0.0078	0.9998

Intraparticle diffusion and film diffusion kinetics.

Intraparticle model used here referred to the theory proposed by Weber and Morris. The linear form of intraparticle diffusion model was given as,

$$q_t = K_p t^{1/2} + C \tag{3}$$

where *C* was the intercept and *K_p* was the intra-particle diffusion rate constant [*mg/(g·min^{1/2})*]. According to this model, plot of *q_t* versus *t^{1/2}* should be linear if intra-particle diffusion was involved in the adsorption process [11]. If these lines passed through the origin, then intra-particle diffusion was the rate controlling step. When these lines did not pass through the origin, this was indicative of some degree of boundary layer control and this further showed that the intra-particle diffusion was not the only rate limiting step. The values of *K_p* and *C* were given in Table 2. In this experiment, the plots did not pass through the origin, which indicated the intra-particle diffusion was not only the rate controlling step. The result was consistent with the previous study [12].

If the film diffusion was one of the rate limiting steps, the calculated film diffusion coefficient (*D_F*) value will be in the range 10⁻⁶ to 10⁻⁸ cm²/s. The film diffusion coefficient (*D_F*) values were calculated using the following equation

$$D_F = (0.23r_0\delta C_s)/(C_L t_{0.5}) \tag{4}$$

where *r₀* and *t^{0.5}* have the same meaning as above, *δ* is the film thickness (10⁻³ cm) [13], *C_s* and *C_L* are the concentrations of adsorbate in solid and liquid phase at *t* = *t* and *t* = 0, respectively. The calculated *D_F* value are found to be in the order of 10⁻⁸ cm²/s (Table 2), which implied the film diffusion was one of the rate limiting steps.

Based on all the explanation, the pseudo-second-order model was the best fit model for the adsorption of MB onto cobalt doping hectorite. The adsorption process was controlled by both intra-particle diffusion and film diffusion. The initial section indicated the external surface adsorption. The second indicated the final equilibrium stage where the intra-particle diffusion starts to slow down due to extremely low solute concentrations in the solution.

Table 2 Intra-particle diffusion model parameter and film diffusion coefficient for the adsorption of MB onto hectorite at different temperature

Adsorption	Intraparticle diffusion model			Film diffusion coefficient
	K _p	C (mg/g)	r _p ²	(D _F) (cm ² /s)
293K	1.3121	311	0.8951	1.4792×10 ⁻⁸
303K	1.0300	295	0.8946	1.7211×10 ⁻⁸
313K	0.81735	288	0.8941	1.7243×10 ⁻⁸
323K	0.6110	280	0.9748	1.8745×10 ⁻⁸

Thermodynamics studies.

The pseudo-second-order rate constant of MB adsorption was expressed as a function of temperature by Arrhenius type relationship

$$\ln k_2 = -\frac{E_a}{RT} + \ln A \tag{5}$$

where *E_a* is the Arrhenius activation energy of sorption, representing the minimum energy which reactants must have to proceed, *A* is the Arrhenius factor, *R* is the gas constant and is equal to 8.314

$J/mol \cdot K$, and T is the solution temperature. When $\ln k$ is plotted vs $1/T$ (Fig.2), a straight line with slope $-E_a/R$ is obtained. The magnitude of activation energy gives an idea about the type adsorption, which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5-40 kJ/mol , while higher activation energies (40-800 kJ/mol) suggest chemisorptions [14]. The result obtained is 12.00 kJ/mol , which are in the typical activation energy range for physisorption. This conclusion was also inferred from the dispersive interaction between MB and surface of hectorite.

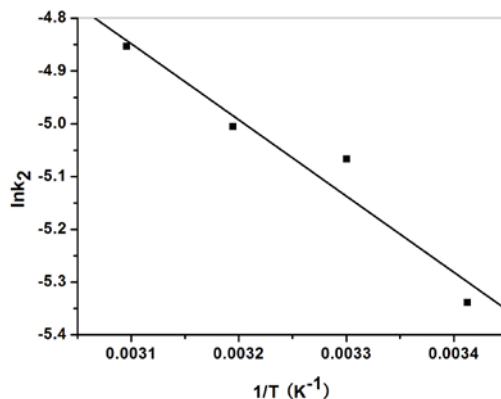


Fig.2 Arrhenius plots for the adsorption of MB onto hectorite

The thermodynamic parameters such as change in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined by using the following equations and were given in Table 3.

$$K = \frac{C_A}{C_S} \tag{6}$$

$$\Delta G^0 = -RT \ln K \tag{7}$$

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{8}$$

where K was the equilibrium constant, C_A was the amount of MB adsorbed on the adsorbent at equilibrium (mg/g), and C_S was the equilibrium concentration (mg/L) of the MB in the solution. T was the solution temperature (K) and R was the gas constant.

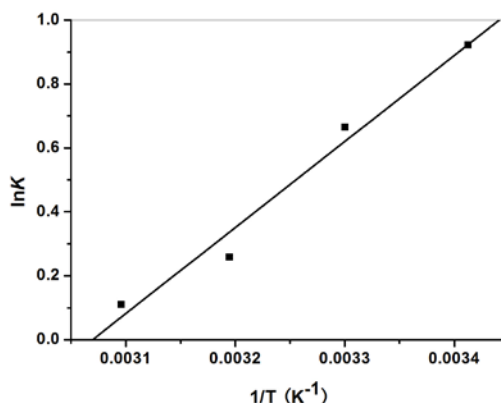


Fig.3 Plot of $\ln K$ vs. $1/T$ for MB onto hectorite. K is distribution coefficient, T is temperature 293K, 303K, 313K, 323K

Table 3 Thermodynamic parameters for the adsorption of MB onto hectorite

Adsorption	K	E_a ($kJ \cdot mol^{-1}$)	ΔG^0 ($kJ \cdot mol^{-1}$)	ΔH^0 ($kJ \cdot mol^{-1}$)	ΔS^0 ($J \cdot K^{-1} \cdot mol^{-1}$)
293K	2.5128		-2.245		
303K	1.9429	12.00	-1.673	-22.39	-68.74
313K	1.2931		-0.669		
323K	1.1165		-0.296		

ΔH^0 and ΔS^0 were determined from the slope and intercept of van't Hoff plot of $\ln K$ versus $1/T$, which were shown in Fig. 3 and Table 2. The obtained values of ΔH^0 and ΔS^0 are -22.39 kJ/mol and $-68.74 \text{ J/mol}\cdot\text{K}$, respectively. It means that adsorption of MB on hectorite is an exothermic process, so raising the temperature leads to lower affinity and less MB being adsorbed at equilibrium.

Conclusion

Hectorite was synthesized successfully. With large pore volumes and high specific surface area, the samples demonstrated the remarkable adsorption capacity of methylene blue. The kinetic data were represented by pseudo-second-order kinetic model. Adsorption activation energy was found to be 12.00 kJ/mol , which were the typical activation energy range for physisorption. The enthalpy change (ΔH_0) and entropy change (ΔS_0) for adsorption are estimated to be -22.39 kJ/mol and $-68.74 \text{ J/mol}\cdot\text{K}$, respectively. The Gibbs free change (ΔG_0) for the adsorption was estimated to be -2.245 , -1.673 , -0.669 and -0.296 kJ/mol at 293, 303, 313 and 323K, respectively. Therefore, the adsorption was a spontaneous exothermic process.

Acknowledgement

The authors are grateful for the financial support from the National Natural Science Foundation of China (reference 21106171) and Open fund of Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources.

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