



Adsorptive Removal of Methylene Blue by Mn-Modified Tourmaline

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 14-06-2017

Accepted: 21-08-2017

Key Words:

Mn-modified tourmaline
Methylene blue
Adsorption kinetics
Isotherm

ABSTRACT

Adsorbent Mn-modified tourmaline was creatively prepared by wet impregnation in a MnSO_4 solution and subsequent calcination procedure. The prepared Mn-modified tourmaline was used for the adsorptive removal of a cationic dye methylene blue (MB). The experimental data under different solution pH conditions were simulated using both linear and non-linear kinetic models. Linear pseudo-second-order model and non-linear Elovich kinetic model were found to be more suitable to describe the adsorption kinetics. This indicates that the adsorption of MB onto the Mn-modified tourmaline is possibly a chemisorption process in which the rate-determining step is diffusion in nature. The adsorption isotherms were also investigated and the experimental data were fitted by both Langmuir and Freundlich models. Using Langmuir model, the calculated maximal adsorption capacities for MB achieved 158.5 mg/g at 298 K. Thermodynamic analysis indicates that the changes of enthalpy and entropy of the adsorption processes are 55.6 KJ mol⁻¹ and 199.0 J mol⁻¹ K⁻¹, respectively. The negative value of Gibbs free energy change and the positive value of enthalpy also indicates that the adsorption process is spontaneous and endothermic.

INTRODUCTION

Natural minerals such as tourmaline, smectite and diatomite have been widely studied and applied in environmental remediation and chemical industries. They have potential applications in practical water purification as well. Tourmaline is a kind of complex borosilicate mineral. More importantly, tourmaline is a type of intelligent and functional ecological material which can be used for environmental protection (Fuat 1997). It is capable of radiating far infrared energy, permanently releasing negative ions, producing an electric field and releasing rare microelements (Ruan et al. 2004). Interestingly, the solution pH in the presence of tourmaline can be automatically controlled to near neutral pH (Wang et al. 2011). As such, it is deduced that tourmaline could have a wide application in environmental purification.

Further, tourmaline was mainly used as a substrate for the preparation of environmental functional materials. Recently, it was reported that tourmaline was utilized to improve the photocatalytic activity of the photocatalyst involved (Yu et al. 2016). Nevertheless, it is scarcely reported on the adsorptive removal of organic pollutants by tourmaline and tourmaline-related sorbent. Our previous study indicated that tourmaline was an excellent substrate to enhance the adsorptive removal of phosphate from aqueous solution (Li et al. 2015). As we know, adsorption process can transfer the pollutants from one phase to another effi-

ciently, and no toxic intermediates are generated. It is accepted as one of the most powerful, efficient and cost-effective water treatment technologies so far. From above, natural minerals including tourmaline are the best choice of adsorbent substrate for environmental remediation. Additionally, various studies demonstrated that composite adsorbents exhibited excellent performance as they could combine the properties and advantages of each of their components (Qu 2008). From this point of view, tourmaline could be an ideal candidate as an adsorbent substrate for water and wastewater treatment.

In this research, the natural functional mineral tourmaline was selected as an adsorbent substrate for the preparation of Mn-modified tourmaline. The modified adsorbent was innovatively prepared by wet impregnation method and subsequent calcination procedure. Then the prepared Mn-modified tourmaline was used for the adsorptive removal of a cationic dye methylene blue (MB). The adsorption kinetics under different solution pH conditions was investigated and the experimental data were fitted by typical kinetic models. The adsorption isotherm was also investigated and thermodynamic parameters were calculated. Adsorption mechanism was also discussed.

MATERIALS AND METHODS

Chemicals: Methylene blue (mass fraction > 98.5%, chemical pure) was purchased from Tianjin Chemical Reagent

Research Institute. The other chemicals used were of analytical grade. Deionized (DI) water was used throughout the study.

Preparation of the Mn-modified tourmaline: A MnSO_4 solution with a concentration of 0.10 mol/L was used for the wet impregnation of the raw tourmaline as our preliminary study indicated that this concentration could generate the highest adsorption capability. The tourmaline/solution ratio was 1 g/10 mL. The mixture of tourmaline and MnSO_4 solution was agitated in an orbital shaker at 140 rpm and room temperature for 24 h. The modified tourmaline was collected by filtration and dried at 100°C overnight. Finally, the treated tourmaline was calcined at 500°C for 2 h. The prepared 0.10 mol/L MnSO_4 modified tourmaline is denoted as Mn-modified tourmaline.

Batch adsorption studies: Stock solutions of MB (500 mg/L) were prepared in DI water. All working solutions were prepared by diluting the stock solution with DI water to the desired concentration. Adsorption of methylene blue (MB) onto the Mn-modified tourmaline was conducted in a series of conical flasks. A desired amount of Mn-modified tourmaline (10 mg) was added to a conical flask containing 50 mL of MB solution with a concentration of 10 mg/L. For kinetic experiments, the adsorbent dosage was 200 mg in 1000 mL MB solution. Constant stirring was maintained by mechanical agitation for 24 h. Finally, samples were collected and filtered through a 0.45 μm pore-size membrane before measurement. The reaction temperature was controlled at a constant temperature of 25°C unless otherwise stated. All the solution pH were maintained at neutral pH except for the pH effect study. The solution pH adjustment was conducted by addition of dilute HCl or NaOH solution.

Analysis of MB: The concentration of MB was analysed using an UVmini-1240 spectrophotometer (Shimadzu) by monitoring at the wavelength of maximum absorption (664 nm). The adsorption capacity (q_e and q_t) was calculated by the following equation:

$$q_e = \frac{V \times (C_0 - C_t)}{m} \quad \dots(1)$$

$$q_t = (C_0 - C_t) V/W \quad \dots(2)$$

Where, q_e and q_t (mg/g) are the adsorption capacity at equilibrium and t min, respectively; C_0 is the initial concentration of MB in solution, while C_e and C_t (mg/L) are the concentrations of MB at equilibrium and t min, respectively; V (L) is the volume of solution, and W (g) is the mass of the Mn-modified tourmaline prepared.

RESULTS AND DISCUSSION

Linear adsorption kinetics of MB on the Mn-modified tourmaline: The adsorption kinetics for the adsorption of MB on the Mn-modified tourmaline were explored at 5.0, 7.0 and 9.0 pH. Pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental data. The mathematical representations of the linear and non-linear models of pseudo-first-order and pseudo-second-order kinetics are given as (Lagergren 1898, Ho & McKay 1999):

$$q_t = q_e(1 - e^{-k_1 t}) \quad \dots(3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(4)$$

$$q_t = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)} \quad \dots(5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(6)$$

Where, q_e and q_t are the adsorption capacities (mg/g) of MB at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) and k_2 ($\text{g/mg} \cdot \text{min}$) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

As illustrated in Fig. 1, the simulated linear adsorption kinetic curves at pH 5.0, 7.0 and 9.0 are presented. Apparently, the experimental points are quite close to the curves simulated by pseudo-second-order kinetic model. Pseudo-second-order kinetic model is more suitable to describe the adsorption kinetics than pseudo-first-order model. Meanwhile, at all the pH conditions, the values of correlation coefficient (R^2) of pseudo-second-order model are higher than 0.996, which is much higher than those of pseudo-first-order model. From Table 1, the calculated q_e values from pseudo-second-order model at pH 5.0, 7.0 and 9.0 are

Table 1: Linear kinetic model parameters for the adsorption of MB onto the Mn-modified tourmaline.

	Linear pseudo-first-order kinetics			Linear pseudo-second-order kinetics		
	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	R^2
pH=5.0	0.00524	7.21	0.804	0.00391	18.7	0.999
pH=7.0	0.00427	11.2	0.914	0.00174	22.5	0.998
pH=9.0	0.00303	12.4	0.869	0.00118	23.6	0.996

18.7, 22.5 and 23.6 mg/g, respectively. They are much closer to the experimental data than those of pseudo-first-order model as well. Accordingly, pseudo-second-order kinetic model is better to simulate the adsorption kinetics, indicating the MB adsorption process is chemisorption.

Non-linear adsorption kinetics of MB on the Mn-modified tourmaline: As a comparison, the experimental data were also simulated by non-linear kinetic models including pseudo-first-order, pseudo-second-order and Elovich models. The Elovich kinetic model can be written as (Kithome et al. 1988):

$$q_t = a \ln(t) + b \quad \dots(7)$$

Where, a (g·mg/min) and b (mg/g) are constants.

As the simulated curves at pH 5.0, 7.0 and 9.0 showed similar adsorption behaviours, only the simulated curves at pH 7.0 are illustrated in Fig. 2. It is observed that the experimental data are in correlation with the simulated Elovich curves as the experimental points are evidently closer to the simulated Elovich curves than pseudo-first-order and pseudo-second-order models. Nevertheless, at pH 7.0, the values of correlation coefficient (R^2) of pseudo-first-order, pseudo-second-order and Elovich models are 0.840, 0.930 and 0.996, respectively. As we know, Elovich model is used to describe chemisorption in which the rate-determining step is diffusion in nature (Aharoni et al. 1991, Pavlatou et al. 1988). Accordingly, the adsorption of MB onto the Mn-modified tourmaline could be a chemisorption process in which the rate-determining step is diffusion in nature.

Non-linear adsorption isotherms of MB on the Mn-modified tourmaline: Isotherm studies for the uptake of MB onto the Mn-modified tourmaline were carried out at 288, 298 and 308 K. As shown in Fig. 3, both Langmuir and Freundlich models were used to fit the experimental data. The saturated monolayer Langmuir isotherm can be represented as (Langmuir et al. 1916):

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad \dots(8)$$

Where, q_e is the amount of MB adsorbed onto the Mn-modified tourmaline (mg/g), C_e is the equilibrium concentration (mg/L), q_m is the maximal adsorption capacity of the sorbent (mg/g) and k_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg).

Freundlich isotherm is commonly written as (Freundlich et al. 1906):

$$q_e = k_F C_e^{\frac{1}{n}} \quad \dots(9)$$

Where, k_F and n are the Freundlich constants related to

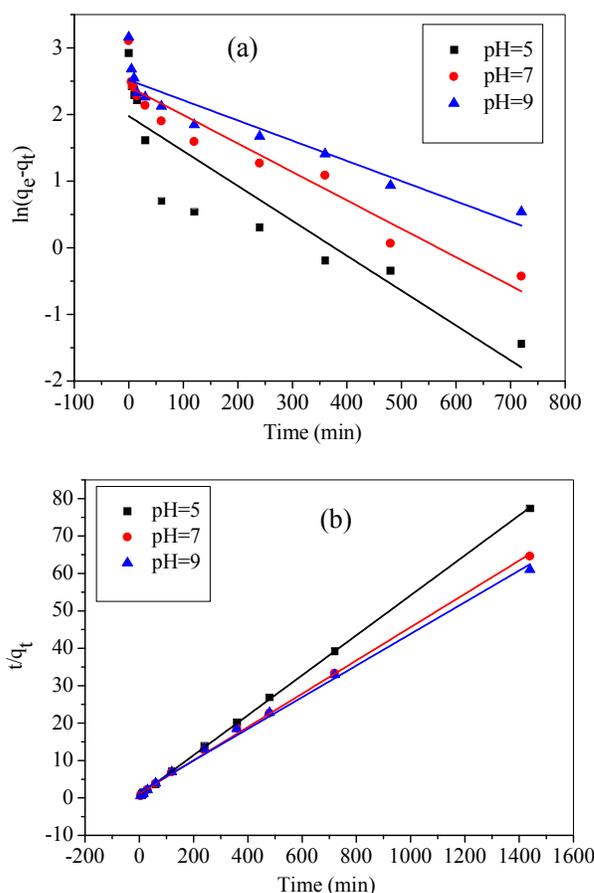


Fig. 1: Linear adsorption kinetics for pseudo-first-order (a) and pseudo-second-order (b) kinetic simulation of MB onto the Mn-modified tourmaline.

the adsorption capacity and adsorption intensity of the sorbent, respectively.

As presented in Fig. 3 and Table 2, both isotherm models could describe the adsorption isotherm well, although the Freundlich model is only slightly better than the Langmuir model judged from the values of correlation coefficients (R^2). Using Langmuir model, the calculated maximal adsorption capacities for MB achieved 134.3, 158.5 and 185.3 mg/g at 288, 298 and 308 K, respectively. It is evident that the uptake of MB increased with an increase in the reaction temperature, indicating the endothermic nature of the adsorption process.

Thermodynamic analysis: Thermodynamic parameters associated with the adsorption process such as standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated using the following equations:

$$\Delta G^0 = -RT \ln K_0 \quad \dots(10)$$

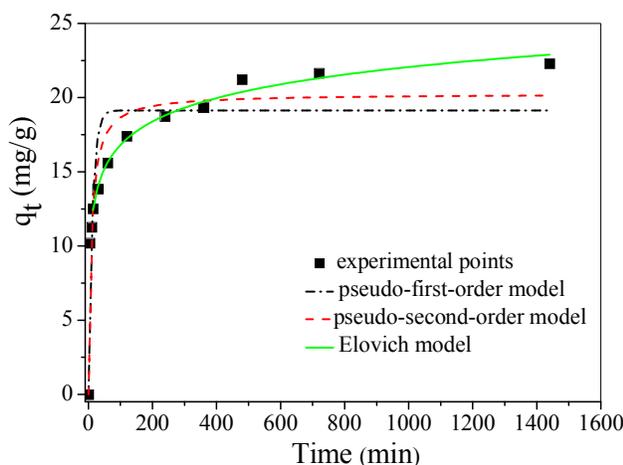


Fig. 2: Non-linear adsorption kinetic fitting for the experimental points at pH 7.0.

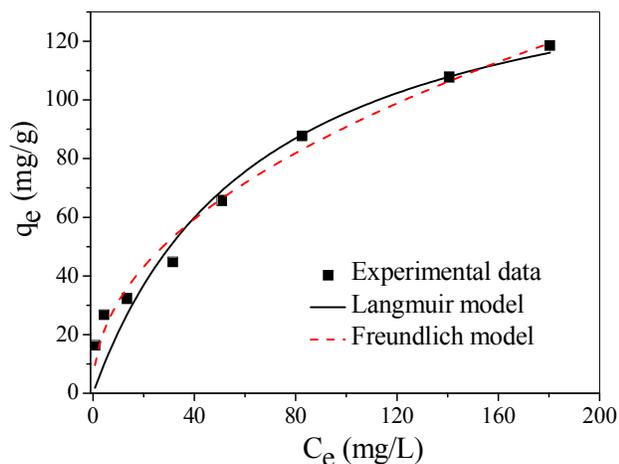


Fig. 3: Experimental points and fitted non-linear isotherm curves by Langmuir and Freundlich models at 298 K.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \dots(11)$$

$$\ln k_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \dots(12)$$

Where, the thermodynamic equilibrium constant K_0 for the adsorption process was determined by plotting $\ln q_e/C_e$ versus q_e and extrapolating to zero q_e using a graphical method (Lyubchik et al. 2004). Regression straight lines were fitted through the data points by the least-squares method. The intersection with the vertical axis gives the value of $\ln K_0$ at the three different temperatures. In these equations, T is in Kelvin; ΔH^0 is the enthalpy of adsorption and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of a plot $\ln k_0$ versus the reciprocal of absolute

Table 2: Non-linear Langmuir and Freundlich isotherm parameters for the adsorption of MB onto the Mn-modified tourmaline.

	Nonlinear method		
	288 K	298 K	308 K
Langmuir model			
$q_{max} \text{ (mg/g)}$	134.3	158.5	185.3
$k_L \text{ (L/mg)}$	0.0156	0.0152	0.0126
R^2	0.921	0.933	0.939
Freundlich model			
$k_F \text{ (mg/g)}$	9.05	10.75	9.86
n	2.14	2.16	2.00
R^2	0.975	0.979	0.966

temperature ($1/T$).

As presented in Table 3, the changes of enthalpy and entropy of the adsorption process are found to be 55.6 KJ mol^{-1} and $199.0 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The positive value of the reaction enthalpy implies that the uptake of MB increases with a rise in the reaction temperature, which is consistent with the aforementioned results. The negative values of ΔG^0 -1.71 , -3.28 and $-5.68 \text{ KJ mol}^{-1}$ at 288, 298 and 308 K, respectively, suggest the spontaneous nature of MB adsorption. The positive value of enthalpy change also indicated that the adsorption process is endothermic.

CONCLUSION

A composite adsorbent, Mn-modified tourmaline, was prepared by wet impregnation and subsequent calcination procedure. It was used for the efficient adsorptive removal of a cationic dye methylene blue (MB). Linear pseudo-second-order model and non-linear Elovich kinetic model were found to be more suitable to describe the adsorption kinetics. This indicates that the adsorption of MB onto the Mn-modified tourmaline is possibly a chemisorption process in which the rate-determining step is diffusion in nature. The adsorption isotherms were also investigated and the experimental data were fitted by Langmuir and Freundlich models. The maximal adsorption capacities for MB increased with increasing reaction temperature. Thermodynamic analysis indicated that the changes of enthalpy and entropy of the adsorption processes are 55.6 KJ mol^{-1} and $199.0 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The negative value of Gibbs free energy change and the positive value of enthalpy also indicated that the adsorption process is spontaneous and endothermic.

ACKNOWLEDGEMENTS

The authors thank for the financial support from the North China University of Water Resources and Electric Power to Dr. Gangfu Song and the foundation for university key youth teacher by Henan Province of China (2013GGJS-088).

Table 3: Values of thermodynamic parameters for MB adsorption at different temperatures.

T (k)	lnk ₀	ΔG ⁰ (kJ·mol ⁻¹)	ΔH ⁰ (kJ·mol ⁻¹)	ΔS ⁰ (J·mol ⁻¹ ·K ⁻¹)
298	0.713	-1.71	55.64	199.0
308	1.322	-3.28	55.64	199.0
318	2.281	-5.68	55.64	199.0

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