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Removal of rhodamine B from wastewater by rectorite and sepiolite-kinetic study and equilibrium isotherm analyses

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Abstract. Adsorption removal of a cationic dye, rhodamine B (RhB) from water onto rectorite and sepiolite was investigated. The rectorite and sepiolite were characterized by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). Attempts were made to fit the isothermal data using Langmuir and Freundlich equations. The experimental results have demonstrated that the equilibrium data are fitted well by a Freundlich isotherm equation. Pseudo-first-order and pseudo-second-order models were considered to evaluate the rate parameters. The experimental data were well described by the pseudo-second-order kinetic model. The results indicate that the rectorite exhibited higher adsorption capacity for the removal of RhB than sepiolite and could be employed as a low-cost alternative in wastewater treatment for the removal of cationic dyes.

Introduction

Water contamination resulted from dyeing and finishing in textile industry is a major concern. The wastewaters containing dyes diminish the transparency of the water and affect the growth of the organisms in the water [1]. Moreover, they may also be carcinogenic and mutagenic to aquatic life or to human beings [2]. Hence, it is necessary to reduce and eliminate these dyestuffs from wastewater before it is discharged.

Among several chemical and physical methods, adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater. Activated carbon, as an adsorbent has been widely investigated for the adsorption of dyes [3]. However, its applications have been limited greatly by the high costs of manufacturing and regeneration [4]. In recent years, clays as environment-friendly and low cost adsorbents have been attracted many attentions. Large specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), etc., have made the clays excellent adsorbent materials [5].

Sepiolite is a natural clay mineral consisting of magnesium hydro silicate which belongs to the group of silicates [6]. It has a fibrous structure which is formed as a result of stowage of tetrahedral and octahedral oxide layers; it has canal cavities along the fibber [7]. Its peculiar structure provides high sorption capacity. Rectorite is a sort of regularly interstratified clay mineral with alternate pairs of a non-expansible dioctahedral mica-like layer and an expansible dioctahedral smectitelike layer existing in a 1:1 ratio. The interlayer cations of montmorillonite-like layers can be exchanged easily by either organic or inorganic cations. It is well known that wide variety of organic molecules can intercalate between the interlayer regions of expandable clays [8].

This paper reports on the ability of sepiolite and rectorite to remove rhodamine B (RhB) from aqueous solution. The pseudo-first-order and pseudo-second-order models were used to predict the adsorption rate constants. Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined.

Material and methods

Materials

The rectorite used came from Zhongxiang, Hubei, P.R. China. The sepiolite used was obtained from Hunan P.R. China. The sepiolite and rectorite were pretreated with 1 mol/L NaCl solution. Rhodamine B (RhB) has a molecular weight of 479.029 g/mol. The molecular structure of RhB is shown in Fig. 1.

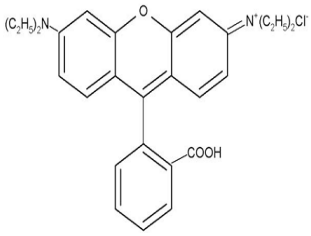

Fig. 1. Chemical structure of RhB.

Characterizations

The morphologies were examined using a scanning electron microscope (SEM, JSM-5610LV). The chemical bonds on the surface of the sorbents were detected by the Fourier transform infrared (FTIR) spectroscopy (Nexus, Thermo Nicolet).

Adsorption experiments

All adsorption experiments was carried out on a thermostated shaker (THZ-82, Guohua apparatus company, China) operated at 150 rpm. Adsorption kinetic experiments were carried out by adding 0.3 g the adsorbents to 100 mL RhB solution at 25 °C. Aliquots were removed from the suspension at different time intervals and centrifuged at 3000 rpm. For adsorption isotherms determination, RhB solutions of different concentrations (20, 50, 100, 150, 180 and 200 mg/L) were agitated with known amount of adsorbents till the equilibrium was achieved.

Results and discussion

Characterization of adsorbents

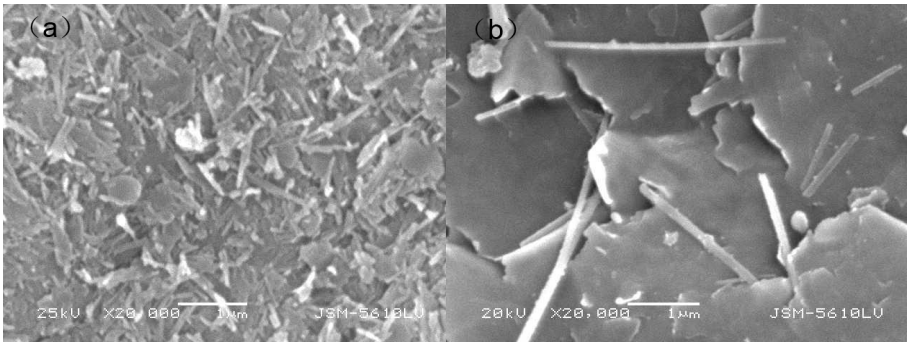

Fig. 2. SEM images of (a) sepiolite and (b) rectorite.

The SEM images of the sepiolite and the rectorite are shown in Fig. 2. As can be seen from Fig. 2, the microstructure and surface properties of the sepiolite and the rectorite are quite different. The sepiolite exhibits a coarse surface and fluffy structure, while the rectorite presents a smooth and dense surface.

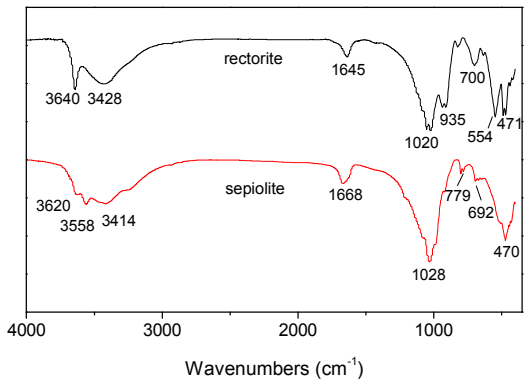

Fig. 3. FTIR spectra of sepiolite and rectorite.

The infrared spectra of the sepiolite and the rectorite are shown in Fig. 3. The broad bands between 3770 and 2880 cm^{-1} for the clays are due to the O–H stretching vibration of the silanol (Si–OH) groups from the solid and HO–H vibration of the water molecules adsorbed on the surface. The spectral band at 1645 cm^{-1} for rectorite and 1668 cm^{-1} for sepiolite are respectively reflects the bending of the HO–H bond of water molecules, which is retained in the silica matrix. The strong band at 1020 and 1028 cm^{-1} represents the Si–O–Si groups of the tetrahedral sheet. The bands in the region of 400–790 cm^{-1} are due to the deformation and bending modes of the Si–O bond.

Adsorption kinetics

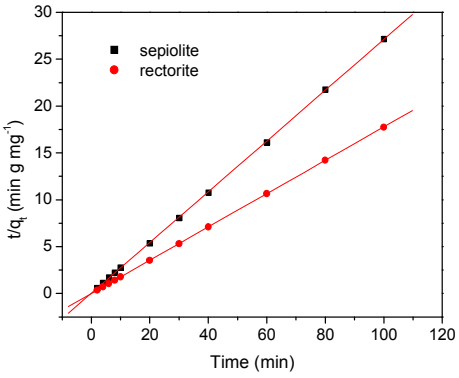

Fig. 4. The pseudo-second-order models for the adsorption of RhB onto sepiolite and rectorite

Table 1 Pseudo-first-order and pseudo-second-order kinetic parameters for the adsorption of RhB onto sepioilite and rectorite.

Adsorbent	$q_e(exp)$ (mg g^{-1})	$q_e(cal)$ (mg g^{-1})	$k_1(min^{-1})$	R^2
Pseudo-first-order				
sepiolite	3.72	0.36	0.1543	0.9397
rectorite	5.63	0.068	0.1353	0.9913
Adsorbent	$q_e(exp)$ (mg g^{-1})	$q_e(cal)$ (mg g^{-1})	k_2(g mg^{-1} min^{-1})	R^2
Pseudo-first-order				
sepiolite	3.72	3.69	2.0856	0.9999
rectorite	5.63	5.63	0.2081	1

In order to analyze the adsorption kinetics of RhB onto the rectorite and the sepioilite, the pseudo-first-order and pseudo-second-order models were used.

The pseudo-first-order equation can be expressed as [9]:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (1)$$

where q_t is the amount of adsorbate adadsorbed at time t (mg g^{-1}), q_e is the adsorption capacity at equilibrium (mg g^{-1}), and the k_1 is the pseudo-first-order rate constant (min^{-1}).

The pseudo-second-order model is based on the assumption of chemisorptions of the adsorbate on the adsorbents. This model is given as [10]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (2)$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}).

The sorption rate constant k_1, k_2 and q_e along with correlation coefficients for the two kinetic models are shown in Table 1. As can be seen from Table 1, for the pseudo-first-order kinetic model, the calculated q_e(cal) are much lower than the experimental q_e(exp). Therefore, the adsorption of RhB onto the sepiolite and rectorite is not suitable for the pseudo-first-order reaction. The linear plot of t/q_t versus t for the pseudo-second-order kinetic model is shown in Fig.6. The pseudo-second-order rate constant k_2 and the value of q_e(cal) were determined from the model and the results are presented in Table 1. The R^2 values are much greater in this case in the range of 0.99-1.00, and the q_e(cal) is closer to the q_e(exp). These results indicate that the adsorption of RhB on sepiolite and rectorite conform well to the pseudo-second-order kinetic model, which is based on the assumption that rate-limiting step may be chemical sorption involving valence forces through sharing or exchange electrons between adsorbent and adsorbate.

Adsorption isotherms

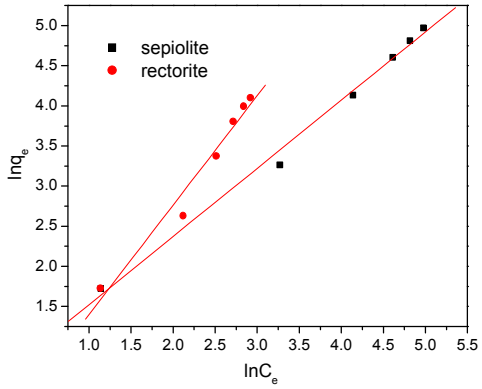

Fig. 5. Freundlich adsorption isotherms for the adsorption of RhB onto sepiolite and rectorite.

Table 2 Langmuir and Freundlich constants for the adsorption of RhB onto the sepiolite and rectorite.

Adsorbent	k_f *(mg* g^{-1}*)(L/mg)*$^{1/n}$	*n*	R^2
Freundlich constants			
sepiolite	1.9588	1.1768	0.9966
rectorite	1.0348	1.7330	0.9842

Adsorbent	k_b (L mg^{-1})	q_m (mg g^{-1})	R_L	R^2
Langmuir constants				
sepiolite	0.01641	26.70	0.2335~0.7529	0.9823
rectorite	0.02989	49.83	0.1433~0.6259	0.8354

In order to describe the adsorption progress and investigate mechanisms of adsorption, Langmuir and Freundlich models are adopted to calculate the adsorption isotherms in this study. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [11], whereas in the Langmuir theory the basic

assumption is that the sorption takes place at specific homogeneous sites within the adsorbent [12].

The Langmuir adsorption isotherm is given as:

$$C_e/q_e = C_e/q_m + 1/(q_m k_b) \quad (3)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), k_b is the langmuir constants (L/mg), and q_m is the theoretical maximum adsorption capacity (mg/g).

The essential characteristic of a Langmuir isotherm, related to the isotherm shape, can be expressed in terms of a dimensionless constant separation factor, also called equilibrium parameter, R_L, which is defined according by the following equation [13]:

$$R_L=1/(1+k_b C_0) \quad (4)$$

The value of R_L indicates the nature of the adsorption process to be either favorable ($0< R_L <1$), unfavorable ($R_L > 1$), linear ($R_L =1$) or irreversible ($R_L = 0$).

The Freundlich adsorption isotherm can be expressed as:

$$\ln q_e = \ln k_f + (\ln C_e)/n \quad (5)$$

where n and k_f are Freundlich adsorption isotherm constants, n indicates of how favorable the adsorption process is, and k_f is the adsorption capacity of the adsorbent.

Fig. 5 shows the plot of $\ln q_e$ versus $\ln C_e$ for the testing of the Freundlich isotherm. Similarly, Langmuir isotherm was tested by the plot of C_e/q_e versus C_e (not shown). The constants calculated from the linear forms of the two isotherms are given in Table 2. As seen, the Freundlich isotherm fits better to the experimental data than the Langmuir isotherm for RhB adsorption on the sepiolite and the rectorite, which is indicative of the heterogeneity of the adsorption sites on the clay particles. From Table 2, it is noted that the values of n are bigger than 1, reflecting the beneficial adsorption. Furthermore, all the R_L for the adsorption of RhB onto the sepiolite and rectorite are in the ranges of 0.2335~0.7529 and 0.1433~0.6259 respectively, which shows that the adsorption process are favorable.

References

[1] T. Akar, T.A. Demir, I. Kiran, A. Özcan, A.S. Özcan and S. Tunali: J. Chem. Technol. Biotechnol. Vol. 81 (2006), p. 1100.

[2] M. Arami, N.Y. Limaee, N.M. Mahmoodi and N.S. Tabrizi: J. Hazard. Mater. Vol. 135 (2006), p. 171

[3] P. Nigam, G. Armour, I.M. Banat, D. Singh and R. Marchant: Bioresource Technol. Vol. 72 (2000), p. 219–226.

[4] Tamai H, Nagoya H and Shiono T: J. Colloid Interface Sci. Vol. 300 (2006), p. 814–817.

[5] K.G. Bhattacharyya, S.S. Gupta: Adv. Colloid Interfac. Vol. 140 (2008), p. 114–131.

[6] K. Brauner and A. Preisenger: Miner Petrogr Vol. 6 (1956) p. 40–120.

[7] M. Alkan, Ö. Demirbas and M. Doğan: Microporous Mesoporous Mater. Vol. 101 (2007), p. 388–396.

[8] S. Akyuz, T. Akyuz and J.E.D. Davies: J. Inclusion Phenom. Vol. 18 (1994), p. 123.

[9] S. Lagergren: Handlingar Vol. 24 (1898), p. 1–39.

[10] Y.S. Ho and G. McKay: Chem. Eng. J. Vol. 70 (1998), p. 115–124.

[11] H. Chen and A.Q. Wang: J. Colloid Interface Sci. Vol. 307 (2007) p. 309–316.

[12] Z. Bouberka, A. Khenifi, N. Benderdouche and Z. Derriche: J. Hazard. Mater. Vol. 133 (2006), p. 154–161.

[13] I. Langmuir: J. Am. Chem. Soc. Vol. 40 (1918), p. 1361–1403.