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Adsorptive properties of acid-heat activated rectorite for Rhodamine B removal: equilibrium, kinetic studies

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ABSTRACT

The acid-heat activated sodium rectorite (AH-R) was prepared and used to remove Rhodamine B (RhB) from aqueous solution. The AH-R showed higher adsorbility than the raw sodium rectorite and the rectorite modified by acid or by heat treatment. The effects of pH, adsorbent dosage, initial dye concentration, reaction temperature and ionic strength were studied. The Rhodamine B adsorption on the AH-R was a fast process and the equilibrium was reached in 60 min. The Langmuir and Freundlich isotherm models were applied to the equilibrium data and the Langmuir model was applied to the equilibrium data better. The maximun adsorption capacity was found to be 59.1 mg/g, and the kinetic data followed the pseudo-second-order kinetics. Thermodynamic parameters were obtained and it was found that the adsorption of Rhodamine B dye onto the AH-R was an endothermic and spontaneous process at the temperatures under investigation.

Keywords: Rectorite; Acid-heat activation; Rhodamine B; Low cost adsorbent; Adsorption capacity; Adsorption kinetics

1. Introduction

Dye-containing wastewater is a matter of concern for both toxicological and esthetical reasons, and the removal of dyes from wastewater has received considerable attention over the past decades [1,2]. Various techniques, including coagulation, chemical oxidation, membrane separation, electrochemical process and adsorption techniques, have been evaluated to decrease the dyes discharge into the water bodies [3–10]. In addition of easy access, adsorption is one of the most effective methods employed in the treatment of wastewaters containing different classes of dyes [1,11,12]. Due to the versatility and the high adsorption capacity, activated carbon is a widely used adsorbent [13–15]. However, higher operating cost and problems of regeneration limit its commercial application. Nowadays, many researchers have focused on the alternative low-price adsorbents such as bottom ash, rice husks, wheat husk, Red Mud and clays [16–22]. The wide usefulness of clay is a result of its high specific surface area, its physico-chemical properties, and its typical structural properties [23–26]. Rectorite is an interstratified layered silicate mineral consisting of a regular (1:1) stacking of mica-like layers and montmorillonite-like layers. The cations of Na^+, K^+ and Ca^{2+} lie in the interlayer region between 2:1mica-like layers and 2:1 montmorillonite-like layers, while the exchangeable hydrated cations reside in the latter. Its structure has provided rectorite with good adsorption properties [27]. The physico-chemical behaviour of rectorite is governed by the extent and the nature of their external surface, which can be modified by suitable acid

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or thermal treatments [28,29]. However, there were few reports about both acid and thermal modified rectorite to adsorb organic dyes.

Rhodamine B (RhB), an extensive used colorant in food and textile industries, was considered as the model compound to represent the dyes that are released in effluents from the textile and food industries [30,31]. The physical contact with the dye may cause severe eye and skin irritation. Its ingestion may cause gastrointestinal irritation with nausea, vomiting, and diarrhea and irritation to the respiratory tract.

In this paper, the acid-heat activated sodium rectorite (AH-R) was prepared for the removal of Rhodamine B (RhB) in aqueous solution. The effects of pH, adsorbent dosage, initial dye concentration, reaction temperature and ionic strength were also investigated. The kinetics and thermodynamics of the RhB adsorption in aqueous solution onto the AH-R were studied.

2. Experimental

2.1. Materials

The rectorite used in the present experiments was obtained from Zhongxiang (Hubei, China). Sodium hydroxide (NaOH, SCRC, China), hydrochloric acid (HCl, SCRC, China) and Sodium Chloride (NaCl, SCRC, China) were of analytical reagent grade and were used without further purification. Deionized water was used in the whole experiment. Rhodamine B (RhB, TSRC, China) (AR) with a molecular weight of 479.02 g/mol was supplied by the Third Shanghai Reagents Co., China. The molecular structure of the RhB was shown Fig. 1.

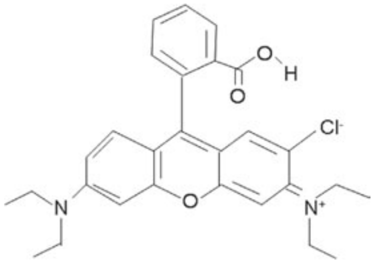

Fig. 1. Molecular structure of the RhB.

2.2. Preparation of adsorbent

A saturated sodium form of rectorite (Na-rectorite) was prepared by modifying rectorite with 1 mol/l NaCl solution [32]. The chemical compositions of Na-rectorite are listed in Table 1.

Acid-heat activated sodium rectorite (AH-R) samples were prepared according to the following procedures: 10.0 g of Na-rectorite powders were dispersed in 100 ml hydrochloric acid (10 wt.%), the resulting suspension was stirred for 3 h, then left it to stand statically for 24 h at room temperature. The obtained products was centrifuged and washed with distilled water for several times to remove residual acid and other impurities, and then was dried in an oven at 373 K (AH-R-373) and ground in an agate mortar. The AH-R-373 sample was calcined at 473, 573, 673 and 773 K for 2 h (which were labeled as AH-R-473, AH-R-573, AH-R-673, AH-R-773, respectively), and the AH-R powders were obtained [33].

2.3. Characterizations of adsorbent

The as-prepared samples were characterized by powder X-ray diffraction (XRD) using a D/MAX-RB powder X-ray diffractometer (Rigaku, Japan), which equipped with high-intensity Cu Kα radiation (λ=1.54060Å), and the accelerating voltage and the applied current were held at 40 kV and 50 mA, respectively. The morphologies and chemical compositions of the samples were examined using a scanning electron microscope (SEM) (JSM-5610LV, Japan) with energy-dispersive X-ray spectroscopy (EDS) analysis (Phoenix, U.S.A.). The specific surface area of the samples was measured by BET (Brunauer-Emmett-Teller) method in an AUTOSORB-1 (Quantachrome Instruments, U.S.A.) nitrogen adsorption apparatus.

2.4. Adsorption experiments

The adsorbents were mixed in 100 ml of RhB aqueous solutions with different concentration. The pH value of the initial solution was adjusted with 0.6 mol/l HCl or 0.6 mol/l NaOH solutions. The mixtures were shaken (150 rpm) in a thermostatic shaker bath (THZ-82, Guohua Apparatus Company, China) for 120 min, and then the suspensions were centrifuged to remove the adsorbents. The absorbance of the RhB aqueous solution was analyzed using a UV-vis spectrophotometer

Table 1
The compositions of the Na-rectorite

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	MnO	P_2O_5
Mass (%)	44.30	35.50	1.55	2.99	0.33	2.46	1.12	2.22	0.01	0.41

(UV-2102, UNICO, China). The RhB concentrations were calculated by the adsorption calibration curve of the RhB aqueous solution.

For the kinetic studies, 0.3 g of the adsorbent was added to 100 ml RhB solution. The initial concentrations of RhB solution were 10, 50, 100, 150 and 180 mg/l, and the experiments were carried out at 298, 318 and 338 K, respectively. The aliquots were then collected at different time intervals and were centrifuged. The concentration of RhB in the solution after adsorption was analyzed as before.

The data obtained in batch model studies was used to calculate the equilibrium RhB adsorption quantity. It was calculated for adsorptive quantity of RhB by using the following expression [34,35]:

$$\text{Removal\%} \;=\; (C_0 - C_e)\,/\,C_0 \times\; 100\% \qquad (1)$$

$$q = (C_0 - C)\,V\,/\,m \qquad (2)$$

where C_0 (mg/l) is the initial concentration; q (mg/g) is the adsorption capacity; C (mg/l) is the liquid-phase concentration of solutes; V (l) is the volume of solution and m (g) the mass of adsorbent.

3. Results and discussion

3.1. Structural analysis

XRD patterns of the Na-rectorite and the AH-R-673 are shown in Fig. 2. It can be observed that the Na-rectorite shows a strong (001) diffraction peak at 2θ = 3.34° and a (002) diffraction peak at 2θ = 6.68°. After being acid-heat treated, the (001) and (002) characteristic peak were markedly weakened compared with that of the Na-rectorite, and the peak at 16.8° was absent in AH-R-673. These results are probably caused by the destruct of the crystal structure of the Na-rectorite during acid-heat treatment [21].

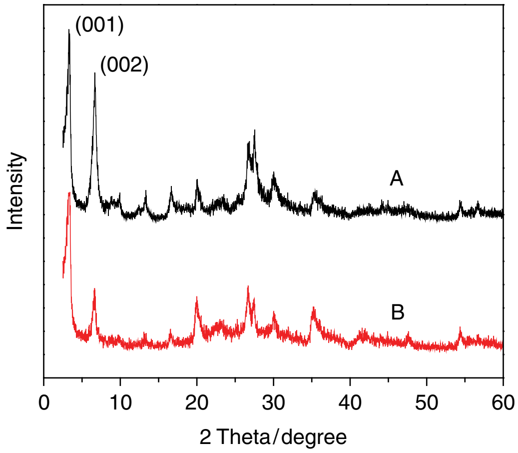

Fig. 2. XRD patterns of (A) the Na-rectorite and (B) the AH-R-673.

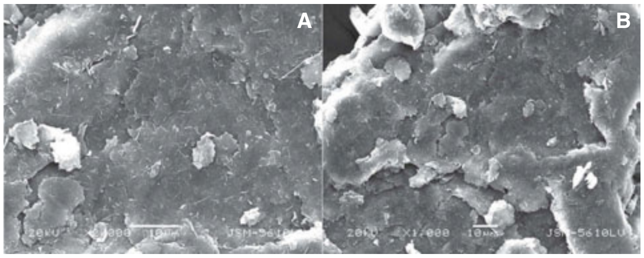

Fig. 3. SEM micrographs of (A) raw rectorite and (B) AH-R-673.

Table 2
S_{BET}, pore volume and pore size of the Na-rectorite and the AH-R

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Rectorite	15.5	0.36	48.5
AH-R-373	78.4	0.39	60.5
AH-R-473	85.6	0.40	61.1
AH-R-573	90.4	0.45	64.9
AH-R-673	95.6	0.54	65.0
AH-R-773	70.3	0.38	60.3

SEM micrographs of the Na-rectorite and the AH-R-673 are shown in Fig. 3. From Fig. 3, the Na-rectorite only exhibits a smooth and dense surface, while the AH-R-673 shows a relatively loose surface, and this kind of surface is more favorable to improve adsorbility.

The S_{BET}, pore volume and pore size of the Na-rectorite and the AH-R were shown in Table 2. After acid-heat treatment, the S_{BET} and the pore volume increased rapidly, from 15.5 to 95.6 m^2/g and from 0.36 to 0.54 cm^3/g, respectively. The S_{BET} and the pore volume increased when the temperature increased from 473 K to 673 K, which was probably caused by the water evaporation and the decomposition of organic compounds [36]. As the temperature continually increased from 673 K to 773 K, the S_{BET} and the pore volume decreased, which indicated that the high temperature decomposed the Na-rectorite's layer structures, and resulted in the layers being folded and the pores being blocked.

3.2. Effect of pH on adsorption

The pH of the aqueous solution is an important parameter which influences the adsorption of dyes at the solid-liquid interfaces [37]. The effect of pH ranging from 2.0 to 9.0 on the removal of RhB (20 mg/l) by the AH-R-673 was investigated, and the results are shown in

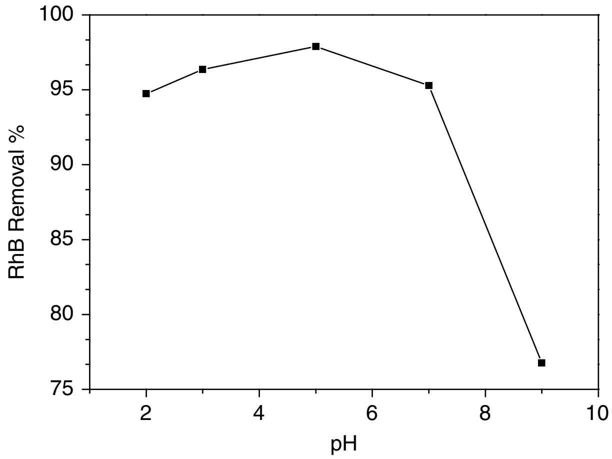

Fig. 4. Effect of pH on adsorption.

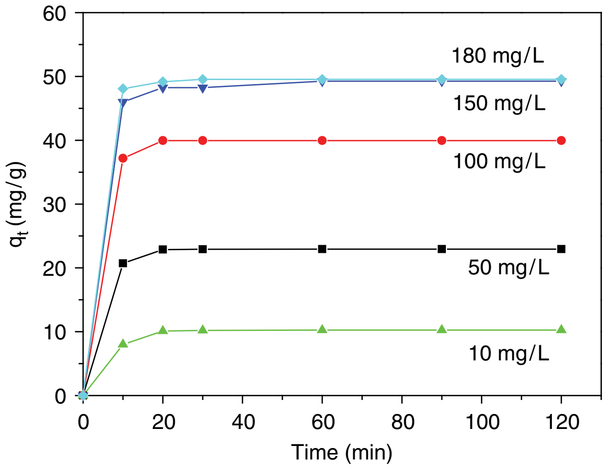

Fig. 5. Effect of adsorption time on adsorption.

Fig. 4. From the Fig. 4, it can be seen that the removal of RhB is the maximum at pH 5.0. Low pH value (2.0–5.0) leads to an increase of H^+ ion concentration in the system and more positive charge of the AH-R surface by adsorbing the H^+ ions, and this result is agreement with the previous study [38]. At higher pH (>5.0), the lower adsorption of RhB was resulted from an increased repulsion between the positively charged RhB and the positively charged surface sites.

3.3. Effect of initial dye concentration on adsorption

The initial concentration provides an important driving force to overcome all mass transfer resistance of ions between the aqueous and solid phases. Fig. 5 shows the effect of initial dye concentration (ranging from 10 to 180 mg/l, at pH 5.0, at 298 K) on the RhB adsorption. The equilibrium adsorption capacity increased with the increasing initial RhB concentration, which may result from the increased number of ions competing for the available binding sites in the surface of the AH-R-673 [39,40]. Meanwhile, the adsorbance of RhB had little increase at higher concentrations than 150 mg/l, which indicates that the adsorption saturation was reached. It can be seen that the rate of adsorption decreases with time and gradually reaches a plateau. The contact time to reach the equilibrium was about 60 min.

3.4. Effect of adsorbent dose on adsorption

Various dosages of the adsorbents ranging from 1 to 8 g/l were used to study the effect of adsorbent dose on the adsorption of RhB (150 mg/l). The effect of adsorbent dose on the removal (%) and adsorption amount q_e (mg/g) of RhB were shown in Fig. 6. As the adsorbent dose (m_s) was increased from 1 to 8 g/l, for AH-R-673, the RhB removal efficiency increased from 59.4% to 95.6%, whereas, the equilibrium adsorption amount q_e decreased from 50.0 to 17.9 mg/g. The increased percentage removal of RhB with increasing AH-R-673 dose could be due to increased absolute adsorption surface. However, the decreased equilibrium adsorption capacity q_e could be attributed to the increased resistance in diffusion and the unsaturated adsorption sites [21].

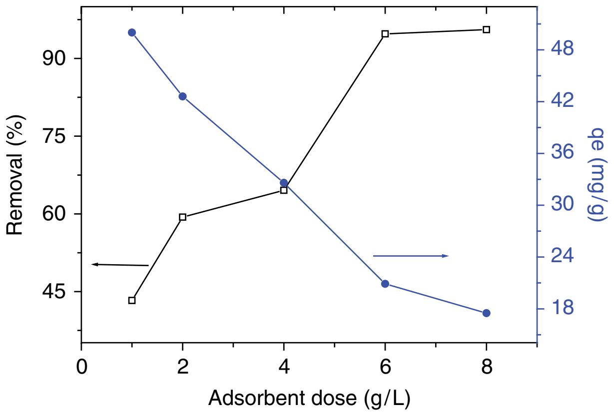

Fig. 6. Effect of absorbent dosage on adsorption (pH=5.0; 298 K).

3.5. Effect of temperature on adsorption

The effects of the temperature (at 298 K, 318 K and 338 K) on adsorption are shown in Fig. 7. As can be seen in Fig. 7, the equilibrium adsorption capacity of RhB was increased with the increasing temperature from 30.5 mg/g at 298 K to 35.0 mg/g at 318 K and to 48.0 mg/g at 338 K. The uptake of RhB by AH-R-673

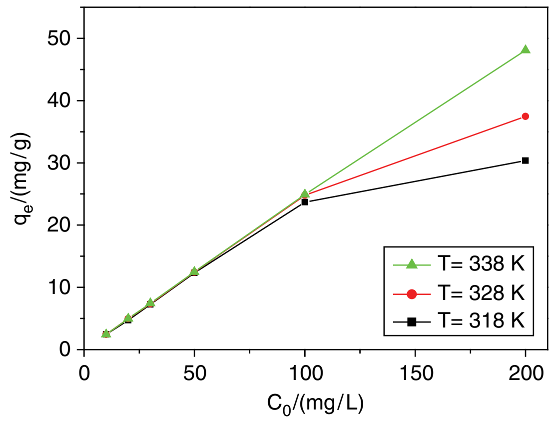

Fig. 7. Effect of Temperature on RhB adsorption (initial RhB concentration is 150 mg/l; pH=5.0).

increased with an increase in temperature implied that the enthalpy change had positive values, and the adsorption process was endothermic.

3.6. Effect of ionic strength on the RhB adsorption

The ionic strength of the solution is one of the factors which control both electrostatic and non-electrostatic interactions between the adsorbate and the adsorbent surface. The effects of NaCl (ranging from 0.01 M to 0.20 M) on the RhB removal efficiencies of the AH-R-673 are shown in Fig. 8. As can be seen in Fig. 8, the increase of the ionic strength causes an increase of the adsorption of RhB onto the AH-R-673 surface. As the ionic strength increase, the AH-R-673 will be negatively charged, which result in the attractive forces between the RhB cation and the AH-R-673 surface increasing, and the RhB adsorbtion amount was increased accordingly [41–43].

3.7. Adsorption isotherms

In order to determine the mechanism of RhB adsorption on the AH-R-673, the Langmuir and Freundlich models were applied to the experimental data [44–45]. The Langmuir adsorption isotherm has been successfully applied to many real sorption processes. The linearized Langmuir isotherm is represented by following equation:

$$C_e \ / \ q_e \ = \ 1 \ / \ Q_0 b \ + C_e \ / \ Q_0 \qquad (3)$$

where C_e is the dye concentration at equilibrium (mg/l), q_e is the adsorption capacity in equilibrium (mg/g), b is the Langmuir adsorption constant (l/mg), and Q_0 is the maximum adsorption capacity(mg/g).

The Freundlich isotherm model is an empirical equation based on adsorption on a heterogeneous surface, and is applicable to multi-layer adsorption. The relationship between the amount of RhB adsorbed at equilibrium (q_e, mg/g) and the equilibrium concentration of RhB (C_e, mg/l) in the aqueous solution is shown as follows:

$$\ln q_e = \ln K_F + (1 / n) \ln C_e \qquad (4)$$

where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively, which indicate whether the nature of adsorption is either favorable or unfavorable.

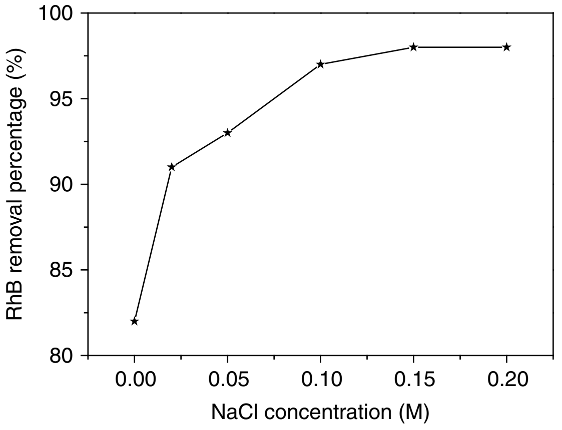

Fig. 8. Effect of ionic strength on adsorption of RhB onto AH-R-673 (contact time is 60 min; initial RhB concentration is 150 mg/l; pH=5.0).

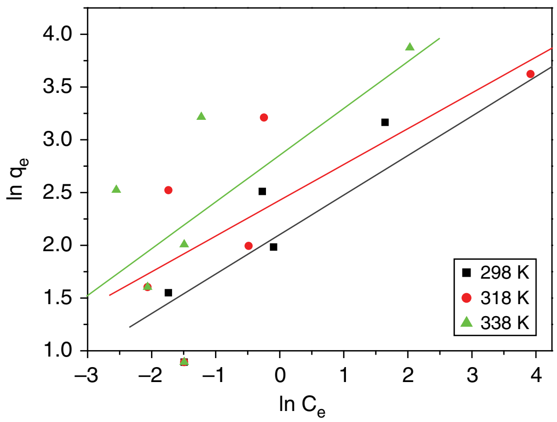

Fig. 9. Freundlich adsorption isotherms for the adsorption of the RhB onto the AH-R-673 at different temperatures (pH=5.0).

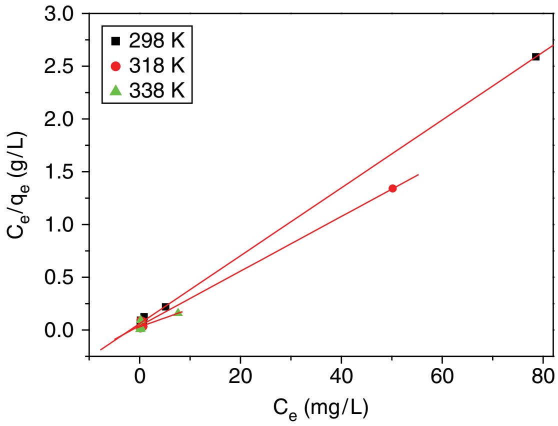

Fig. 10. Langmuir adsorption isotherms for the adsorption of the RhB onto the AH-R-673 at different temperatures (pH=5.0).

Table 3
Parameters of Langmuir and Freundlich adsorption isotherm models for the RhB on the AH-R-673 (pH=5.0)

T (K)	Langmuir			Freundlich		
	Q_0 (mg/g)	b (l/Mg)	R^2	K_F	n	R^2
298	50.08	0.532	0.9997	8.18	0.67	0.7845
318	56.58	0.638	0.9982	11.32	3.01	0.5407
338	59.10	0.565	0.9605	17.36	2.26	0.4385

Fig. 9 and Fig. 10 show the Freundlich ($\ln q_e$ versus $\ln C_e$) and the Langmuir (C_e/q_e versus C_e) plots for the removal of RhB at different temperatures, respectively. Table 3 shows the Freundlich and Langmuir adsorption isotherm constant and correlation coefficients. The results show that the Langmuir model yields a better fit than that of the Freundlich model by comparing the values of R at different temperatures. The value of Q_0 increases with temperature increase, and which further confirms that the process is endothermic. At 338 K, the maximum adsorption capacities were determined as 59.10 mg/g for RhB.

3.8. Adsorption kinetics

The adsorption data were analyzed using the pseudo-first-order and pseudo-second-order kinetic models [46–48].

The pseudo-first-order kinetic model can be expressed as follows:

$$\mathrm{d}q_t \,/\, \mathrm{d}t = k_1\left(q_e - q_t\right) \tag{5}$$

Table 4
Kinetic parameters of Pseudo-first-order and pseudo-second-order for the adsorption of RhB with different concentrations by the AH-R-673 (pH=5.0; 298 K)

C0 (mg/l)	Pseudo-first-order			Pseudo-second-order		
	$q_{e,\exp}$ (mg/g)	K_1 (1/min)	R	$q_{e,\exp}$ (mg/g)	K_2 (g/(mg min))	r
20	16.5	0.099	0.8771	16.5	0.998	0.9985
50	24.5	0.105	0.7830	24.5	0.247	0.9975
100	42.6	0.252	0.6937	42.6	0.412	0.9982

where q_e and q_t are the amount of dye adsorbed per unit of adsorbent at equilibrium and at time t, respectively (mg/g), and k_1 is the rate constant (1/min).

Integrating and applying the boundary condition (t = 0 and q_t = 0) to (t = t and q_e = q_t), Eq. (5) takes the linear form as:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{6}$$

On the other hand, the pseudo-second-order kinetic model may be expressed in the form [49]:

$$\mathrm{d}q_t \,/\, \mathrm{d}t = k_2\left(q_e - q_t\right)^2 \tag{7}$$

where k_2 is the rate constant of pseudo-second-order adsorption kinetic model (g/mg/min). Integrating and applying the boundary condition (t = 0 and q_t = 0) to (t = t and q_e = q_t), Eq. (7) takes the linear form as:

$$t \,/\, q_t = 1 \,/\, k_2 q_e^{\,2} + t \,/\, q_e \tag{8}$$

The rate constant k, the calculated adsorption capacity $q_{e,cal}$ and the correlation coefficient r for the pseudo-first-order kinetic model and the pseudo-second-order kinetic model are listed in Table 4. The first-order kinetic curves of all AH-R-673 did not fit well with the experimental data. The linear plots t/q_t versus t for the RhB adsorption onto the AH-R-673 is shown in Fig. 11. The correlation coefficients are in the range of 0.9975–0.9985, confirming a very good agreement with experimental data.

3.9. Thermodynamic parameters

The thermodynamic parameters such as change in standard free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were determined using the following equations and are given in Table 5 [50–52]:

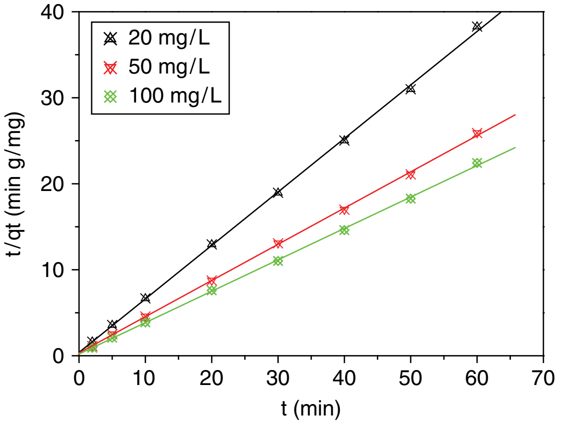

Fig. 11. Test of pseudo-second-order kinetic model for the adsorption of RhB with different concentrations by the AH-R-673 (pH=5.0; 298 K).

Table 5
Thermodynamic parameters of RhB adsorption on AH-R-673

Temperature (K)	K_C	ΔG^0 (kJ/mol)	ΔS^0 (J/K mol)	ΔH^0 (kJ/mol)
298	0.597	–1.278	17.32	6.473
318	0.662	–1.172		
338	0.814	–0.587		

$$K_C = C_A / C_S \tag{9}$$

$$\Delta G^0 = -RT\ln K_C \tag{10}$$

$$\ln K_C = \Delta S^0/R - \Delta H^0/RT \tag{11}$$

where K_C is the distribution coefficient for the adsorption. C_A is the amount of dye (mol) adsorbed on the adsorbent per dm^3 of the solution at equilibrium, and C_S is the equilibrium concentration (mol/dm^3) of the dye in the solution. T is the solution temperature (K) and R is the gas constant (8.314 J/mol K). ΔH^0 and ΔS^0 were calculated from the slope and intercept of van't Hoff plots of ln K_C versus $1/T$ (see Fig. 12). As could be noted, the adsorption process is spontaneous with the negative values of ΔG^0. The standard enthalpy change (ΔH^0) for the adsorption on AH-R-673 is positive indicating that the process is endothermic in nature. The positive value of ΔS^0 shows increased disorder at the solid/solution interface during the adsorption of dye.

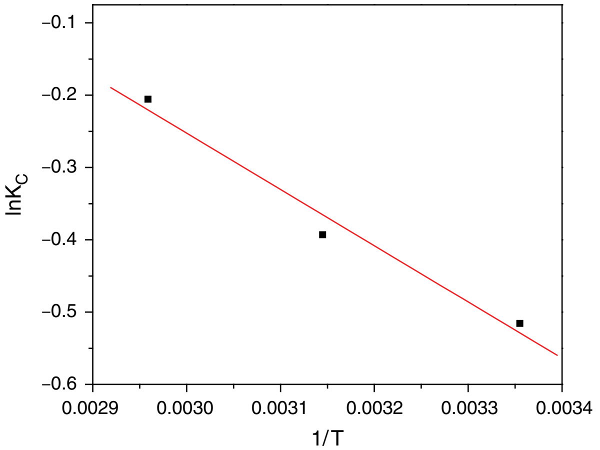

Fig. 12. Van't Hoff plot for the adsorption of RhB onto AH-R-673.

4. Conclusion

The acid-heat rectorite (AH-R) showed a suitable adsorption capacity for the removal of RhB from aqueous solution. The acidic condition was favorable for the adsorption, and the AH-R has good adsorption capacity which is comparable with the some low-cost adsorbent reported for the removal of similar and other ionic dyes using low-cost adsorbents (Table 6). AH-R is cheap and easily available material thus it is a better replacement of activated carbon. The increase of the adsorption with the increase of ionic strength could be attributed to the minimization of the repulsion. The pseudo-second-order rate model and the Freundlich isotherm model were applied to the experimental data better. Adsorption of RhB was found to be spontaneous at the temperatures

Table 6
Comparison with other low-cost adsorbent for dye removal on the basis of their adsorption capacity

Adsorbent	Dye	Maximum adsorption capacity, Q_0 (mg/g)	Ref.
Red Mud	Rhodamine B	0.06	[17]
Activated clay	Acid blue 9	57.8	[1,18]
Activated carbon	Safranin-T	3.18	[15]
Kaolnite	Metomega chrome orange	0.65	[1,10]
Peat	Acid Bhre 25	8.84	[44]
Acid-heat rectorite	Rhodamine B	59.1	Present study

under investigation (298 K-338 K) as indicated from the negative values of free energy (Δ*G*). The study concludes that the AH-R could be employed as low-cost adsorbents for the removal of dyes from wastewater.

Acknowledgement

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