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Adsorption behaviors of the methylene blue dye onto modified sepiolite from its aqueous solutions

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ABSTRACT

The natural sepiolite was modified by nitric acid followed by a heat treatment, and then used as adsorbent for the removal of methylene blue (MB) dye from aqueous solution. The adsorbents were characterized by Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Batch adsorption experiments were carried out to study the effect of various parameters, such as the initial MB concentration, adsorbent dosage, contact time, pH value, and temperature on the adsorption of MB dye. The isotherm analysis indicated that the adsorption data can be represented by the Langmuir isotherm model; the maximum adsorption capacity was up to 90.211 mg/g. Kinetic studies showed that the adsorption data followed the pseudo-second-order model. Thermodynamic studies suggested that the adsorption of MB dye on modified sepiolite was a spontaneous and exothermic process. The results indicate that the modified sepiolite has excellent physical and chemical properties and can serve as a promising adsorbent for the removal of MB dyes from aqueous solutions.

Keywords: Modified sepiolite; Methylene blue; Adsorption; Kinetics

1. Introduction

The discharge of effluents containing dyes into the environment, even at low concentrations, can cause harmful environmental and public problems [1]. Most dyes usually have complex aromatic rings which are non-biodegradable, highly toxic, carcinogenic, and mutagenic for human being and aquatic life [2–8]. Methylene blue (MB), a cationic dye, it is a heterocyclic aromatic compound commonly used substance for dying cotton, wood, and silk [9]. Wastewater containing MB is difficult to treat due to their complicated aromatic molecular structures, and the MB has recalcitrant nature which causes difficulty in its degradation [10,11]. Although MB is not considered to be a very toxic dye, when in higher concentrations, it can cause some harmful effects, such as hypertension, precordial pain, fever, and mental confusion, acute renal failure and hemolytic anemia [12]. Therefore, MB-containing wastewater should be treated before discharge [13–15].

Various conventional physicochemical methods involve flocculation, reverse osmosis, photocatalytic degradation, ion-exchange, bioaccumulation, and advance oxidation process have been used to treat wastewater containing dyes [16–19]. However, application of those techniques has been tightly limited due

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to vast energy consumption, complicated process design, and multiple production operations [20–22]. Moreover, those methods may generate harmful byproducts and become ineffective at low MB concentration. Biological methods have got much attention as they possess advantages over the conventional physicochemical treatments, while it requires a strict experimental condition, toxicity of some chemicals, less flexibility in design, operation, and their application is often restricted because of technical constraints [23,24]. In this regard, the adsorption is an attractive method to remove MB in low concentration due to its low-cost, simplicity of design, ease of operation, insensitivity to toxic pollutants, and smaller amounts of harmful substances [25–27]. Various adsorbents have been studied for adsorption of MB from aqueous solutions, however, in many of these adsorbents, there are still some limitations: the specific surface area is low, the chemical resistance is poor, or the price is high [28–32]. Because natural mineral materials have advantages such as wide sources, low prices, and more extensive industrial application prospects, they have started to become an area of much research [33–36].

Sepiolite is a natural, fibrous clay mineral with fine microporous channels running parallel to the length direction of the fibers [37]. The unique properties and structures give sepiolite good adsorption properties. Sepiolite can have a very high specific surface area, as much as 900 m^2/g in theory [38], which is much greater than other natural clay mineral materials. Furthermore, sepiolite is abundant and cost-effective. Recently, sepiolite has been studied as an effective and economical sorbent material for wastewater treatment, including the removal of dyes and pigments [39,40], and the removal of heavy metal ions [41,42]. However, natural sepiolite has the shortcomings of weak surface acidity, small channel, and poor stability of thermal [43,44], to improve its adsorption capacity, modification before used as the adsorbent is very necessary.

The main objective of the present work is to study the adsorption characteristics and behaviors of the modified sepiolite toward MB. Concretely, the natural sepiolite was firstly modified, and then used as adsorbent for removal of MB, different experimental conditions, involving initial MB concentration, adsorbent dosage, contact time, pH value, and temperature, are investigated to understand the adsorption characteristics for the removal of MB from aqueous solution. Meanwhile, behaviors and mechanisms of MB adsorption are comprehensively explored by adsorption isotherm, kinetics studies, and thermodynamic parameters.

2. Materials and methods

2.1. Materials

The sepiolite used in this study was obtained from Guangda Co. in Hunan, China. Reagent-grade nitric acid (MW: 63.01 g/mol, Aaaay: 65–68%), sodium hydroxide (MW: 40 g/mol, Aaaay: 65–68%), and MB (Chemical formula: $C_{16}H_{18}ClN_3S{\cdot}3H_2O$, MW: 373.90 g/mol, AR) were obtained from Tianjin Benchmark Chemical Reagent Co., Ltd, in, Tianjin, China. All of the water utilized throughout the experimental procedures was deionized (DI) water at room temperature.

2.2. Preparation of modified sepiolite sample

About 25.0-g sample of natural sepiolite was mixed with 300 mL of deionized water and stirred for 3 h at room temperature, then filtered under vacuum, and washed several times. Then, the wet sample was dried at 100℃ in an oven for 24 h and shattered to 80-mesh particle size. The sepiolite was mixed with 2.0 mol/L HNO_3 in solid–liquid ratio of 1 g/20 ml, and the mixture was stirred continuously for 2 h at 40℃. Then, the sepiolite solid was filtered under vacuum and washed several times, then dried in a vacuum oven at 100℃ [38,44]. Next, the treated sample was calcined under vacuum at 250℃ for 3 h. After cooled, the samples were shattered to 100-mesh particle size, to obtain the “modified sepiolite.”

2.3. Batch adsorption experiments

Batch adsorption experiments were carried out on a water bath temperature-controlled shaker (SHZ-82A, Ningbo Jiangnan Instrument Factory, China) using a 100-mL glass conical flask. The desired concentration of dye was obtained by diluting a stock solution of MB (1,000 mg/L). All experiments were repeated at least three times to ensure accuracy of the obtained data.

At the end of the adsorption, the adsorbent was separated from solution by centrifugation at 7,000 rpm for 8 min. The concentration of MB in the solution was measured using a UV–vis spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd, China) at 664 nm. The effect of MB concentration on the adsorption was tested by adding 80 mg of sepiolite into 20 mL of solution with MB concentration ranging from 5.0 to 30.0 mg/L (step size: 2.5 mg/L) at pH kept the raw value. The effect of sepiolite dosage on the adsorption was conducted by adding different sepiolite amounts (1–20 mg) into 20 mL of solution with initial MB concentration of 12.5 mg/L. The solution pH was kept the raw value and temperature was controlled at 298 K. The contact time study was performed with initial MB concentration of 12.5 mg/L and 10-mg modified sepiolite at 298 K. The influence of pH on MB removal was studied by varying the solution pH from 2.0 to 11.0 using HNO_3 or NaOH solution with appropriate concentration. The initial MB concentration, adsorbent dosage, and temperature were 12.5 mg/L, 10 mg, and 298 K, respectively.

The adsorption isotherm studies were carried on with different initial MB concentrations (20–120 mg/L, a step size of 20 mg/L) at 298 K. To evaluate the thermodynamic properties, 10 mg of modified sepiolites were added into 20 mL solutions with initial MB concentration ranging from 20 to 120 mg/L in a step size of 20 mg/L. The samples were shaken at 298, 308, 318, and 328 K, respectively.

3. Results and discussion

3.1. Characterization of the sepiolite

The physical properties of catalysts are tested by the BET, the results show that the modified sepiolite exhibited a high specific surface area (423.2 m^2/g), which was more than three times higher than that of the natural sepiolite (124.5 m^2/g), the increased specific surface area may be due to the formation of new pore structures [45], and the pore size of the modified sepiolite increased largely compared to that of the natural sepiolite, which was in favor of the adsorption property of the modified sepiolite. It was in accordance with the previous literature findings [46].

The XRD patterns of natural sepiolite and modified sepiolite are investigated. After the modification of the natural sepiolite, the relative intensity of the peak at 7.5° decreased significantly, even close to disappear in the modified sepiolite, the same phenomenon occurred when the 2θ value at 27.5°, it indicated that the structure of sepiolite had changed, which could be ascribed to the acid- and heat-treated sepiolite removes Mg^{2+} ions from its original structure and resulting in the formation of many highly active silanol groups (Si–OH), and the removal of the zeolitic water during the calcination process, these treatments also changed the pore structure and physicochemical properties of sepiolite structure [38,47]. The sharp diffraction peak of the natural sepiolite at $2\theta = 30.0°$ corresponds to the $CaCO_3$, after modification process, the characteristic $CaCO_3$ peak was disappeared, which can be assigned to the action of acid, calcium carbonate existed in the sepiolite channel had been removed.

The surface morphology of the natural and modified sepiolite is conducted by SEM. The surface of natural sepiolite particle was compact and smooth, after the acid and heat treatment, the surface structure was destroyed, and the surface became loose, and appeared obvious layered structure, the change was beneficial to the adsorption. The result agrees well with that of the XRD analysis.

3.2. Methylene blue adsorption

3.2.1. Effect of initial MB concentration

The initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases [48]. The effect of initial MB concentration on MB removal is shown in Fig. 1(a), it was observed that the MB removal varies with different initial MB concentration, as the initial MB concentration increases from 5 to 30 mg/L, the MB removal rate by modified sepiolite decreases from 98.3 to 61.5%, whereas the adsorption capacity increases from 12.5 to 43.8 mg/g. The MB removal rate is very high when the initial concentration below 12.5 mg/L, and thereafter the sorption rate decreases and finally reaches saturation after the initial concentration higher than 25.0 mg/L. The high removal of MB particles at the beginning is attributed to the occurrence of solute transfer only due to adsorbate and adsorbent interactions, with negligible interference due to solute–solute interactions [49]. In addition, the adsorption capacity is greater for higher initial MB concentration, because the resistance to the MB removal decreases as the mass transfer driving force increases.

3.2.2. Effect of adsorbent dosage

The effect of adsorbent dosage on MB adsorption was conducted by varying adsorbent dosages from 2 to 20 mg/20 mL MB solution. Fig. 1(b) shows that the removal rate increases sharply from 13.4 to 98.5% with increasing adsorbent dosage from 2 to 10 mg and then it remains almost constant. The initial rapid increase in adsorption with adsorbent dosage could be attributed to the increased surface area and active adsorption sites [50]. The following slight increase might be due to partial aggregation of the adsorbent at higher adsorbent concentration, which results in a decrease in effective surface area for the adsorption. It was also observed from Fig. 1(b) that the adsorption capacity decreases with the increase in adsorbent dosage. This may be due to the fact that almost all active sites are completely exposed and utilized at lower adsorbent dosage, while the active sites of at higher adsorbent dosage are much more than the saturated threshold

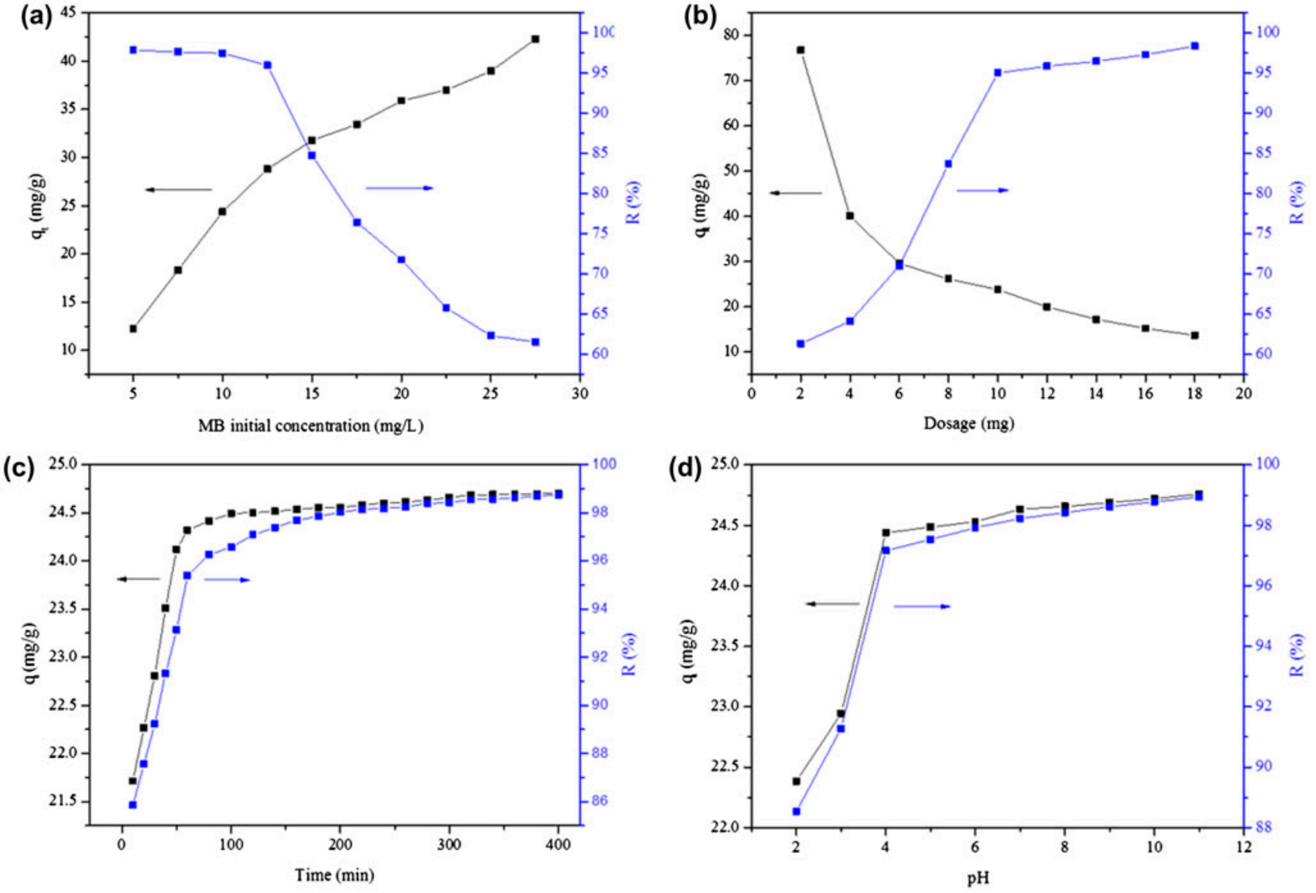

Fig. 1. Effect of different factors on MB adsorbed by modified sepiolite: (a) MB initial concentration, (b) adsorbent dosage, (c) contact time, and (d) pH value.

adsorption point and only part of active sites can be occupied by MB molecules, leading to the decrease of adsorption capacity.

3.2.3. Effect of contact time

The effect of contact time on MB removal is shown in Fig. 1(c), the initial adsorption stage is rapid for the first 60 min, which is due to the adsorption of the molecules on the external surface of the particles. The following stage is a slow adsorption process, it is attributed to that the MB molecules slowly diffuse into the porous structure of the adsorbent, because many of the available external sites have been occupied at initial stage. It was also observed that when the time is 60 min, reaching a constant value beyond which no more MB is removed from solution. At this point, the adsorbed amount of MB onto sepiolite is in a state of dynamic equilibrium with the amount of the MB desorbing from the adsorbent. The time required to attain the state of equilibrium is termed the equilibrium time, and the adsorbed amount of MB at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under these operating conditions.

3.2.4. Effect of pH value

The pH of the aqueous solution is an important factor to affect the MB dye adsorption process through changing the surface charge of an adsorbent as well as the ionization behavior of adsorbent and adsorbate [15,51]. It can be seen from Fig. 1(d) that the adsorption capacity of modified sepiolite increases with an increase in pH, which can be ascribed to that MB is a kind of cationic dye, and the zeta potential of modified sepiolite was tested. It shows that the modified sepiolite has an isoelectric point at around pH 4.0. In this case, the modified sepiolite has a negative zeta potential above pH 4.0, therefore, the strong electrostatic interaction between the negative-charged sepiolite surface and MB cationics, would then be responsible for the increased adsorption capacity of MB onto sepiolite.

3.3. Effect of temperature and adsorption isotherm

The effect of temperature on the adsorption of MB onto the modified sepiolite was carried out at different temperatures of 298, 308, 318, and 328 K, respectively. Fig. 2 shows that the equilibrium adsorption capacity of MB decreases as the temperature increases. As the temperature increases from 298 to 328 K, the maximum adsorption of modified sepiolite decreases from 38.45 to 28.63 mg/g. The result demonstrates that the adsorption MB onto the modified sepiolite is an exothermic process.

The adsorption isotherm model is commonly used to describe the interactive behavior between the adsorbate and adsorbent and to predict the adsorption capacity of the adsorbent. Isotherm models such as Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (D–R) have been widely used to fit the adsorption data, Fig. 3 shows the adsorption isotherm of methylene blue absorbed by modified sepiolite.

The Langmuir equation hypothesizes that the adsorption process happens on a homogeneous surface in the monolayer pattern, and the sorption energies are equivalent. The Langmuir equation can be expressed as follows:

$$Q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \tag{1}$$

where C_e (mg/L) is the the equilibrium concentration of MB, $q_{\max}$ (mg/g) represents the maximum adsorption capacity, K_L (L/mg) is the Langmuir constant related to the energy of adsorption and represents the affinity within adsorbent and adsorbate. The values of $q_{\max}$ and K_L were programmed using the (Eq. (1)) to fit the adsorption isotherm data and they were 90.211 mg/g and 0.027L/mg, respectively. The determination coefficient of the Langmuir equation is 0.9622, which suggests that the Langmuir equation can be used in this experiment to assess the maximum MB adsorption capacity.

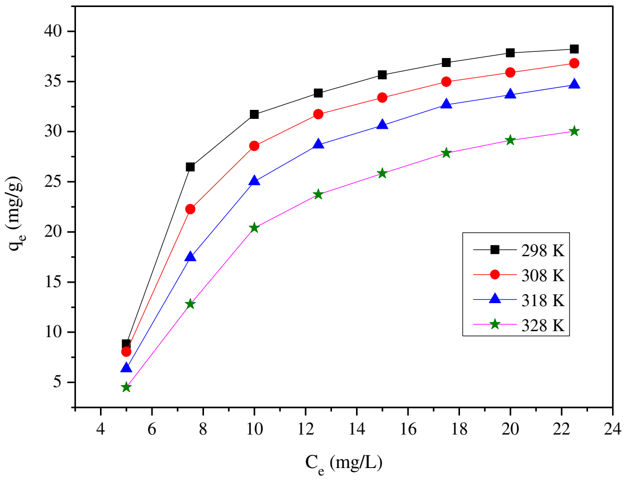

Fig. 2. Effect of temperature on adsorbed by modified sepiolite.

The Langmuir isotherm can be expressed as a dimensionless parameter (R_L) [52]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{2}$$

where C_0 is the highest initial concentration of MB (mg/L), the value of R_L indicates that whether the discussed Langmuir isotherm is favorable ($0 < R_L < 1$) or not ($R_L > 1$ means unfavorable, $R_L = 1$ means linear, $R_L = 0$ means irreversible). In this study, the calculated R_L is 0.574, indicating that methylene blue adsorbed by modified sepiolite is favorable [53].

3.4. Kinetic studies

Adsorption kinetic is used to predict the rate at which MB is removed from the aqueous solutions. Several kinetic models including pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion [54] are available to understand the behavior of the adsorbate adsorbed by the adsorbent and to determine the controlling mechanism of the adsorption process.

The pseudo-first-order model is one of the most widely used equations to describe the adsorption rate based on the adsorption capacity. The pseudo-first-order equation was expressed as follows [55]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

where k_1 is the rate constant of adsorption (1/min), q_e and q_t are the amounts of MB adsorbed at equilibrium and at time t (min), respectively. The values of k_1 and q_e can be calculated from the slope of the plots of log ($q_e - q_t$) vs. t (Fig. 4(a)) and they are 0.014 min and 1.691 mg/g, respectively. The determination coefficient r^2 is as lower as 0.8860, which indicates the data does not comply with the pseudo-first-order kinetic model [56].

The linearized-integral form of the pseudo-second-order model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

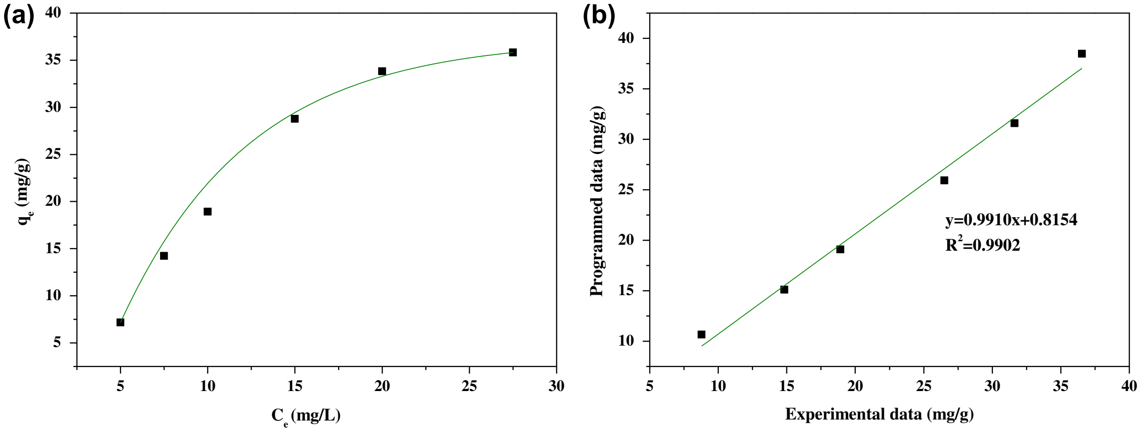

Fig. 3. (a) The Langmuir isotherm of MB adsorbed by modified sepiolite and (b) outcome assessment of fitting the experimental data according to the Langmuir isotherm theory.

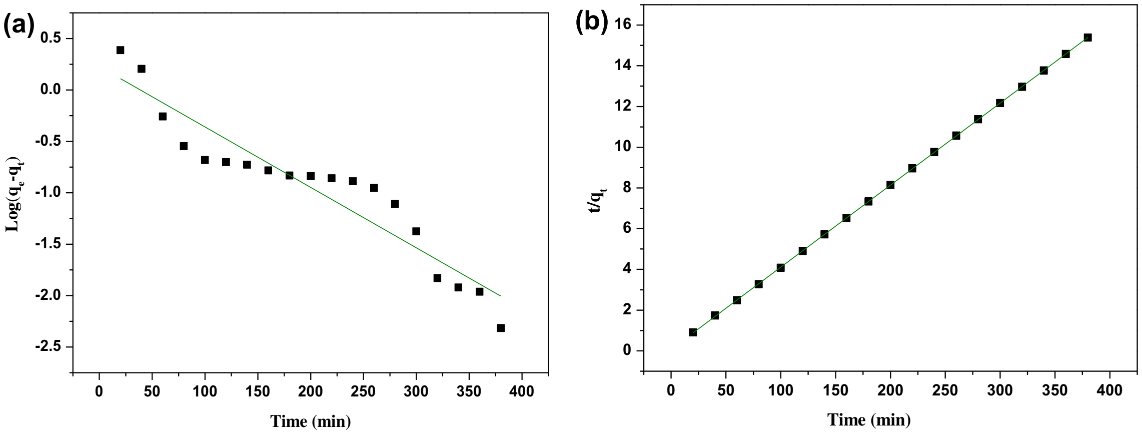

Fig. 4. Adsorption kinetics of MB adsorbed by modified sepiolite: (a) pseudo-first-order model and (b) pseudo-second-order model.

where k_2 (g/(mg min)) is the rate constant of pseudo-second-order adsorption. From the slopes and vertical intercept of the linear charts obtained by plotting t/q_t against t (Fig. 4(b)), the values of k_2 and q_e can be calculated and are 0.021 mg/(mg min) and 24.820 mg/g, respectively. The high determination coefficient of r^2 (0.9992) and the similarity between the calculated capacity and the experimental data (24.6998 mg/g) shows that the adsorption of MB onto sepiolite fits the pseudo-second-order model well. Moreover, the overall rate of the MB dye adsorption is likely monitored by chemically sharing of electrons or by covalently exchanging of electrons between adsorbent and adsorbate [57].

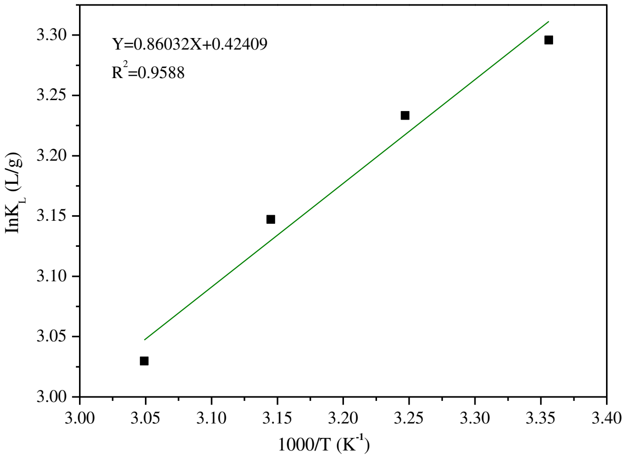

Fig. 5. Arrhenius plot for the adsorption of MB on modified sepiolite.

3.5. Thermodynamic studies

Aiming to appraise the contribution of temperature in this experiment, the thermodynamic parameters, for

Table 1
Thermodynamic parameters for MB adsorbed by modified sepiolite

T/K	K_L/L g^{-1}	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	ΔG/kJ mol^{-1}
298	27.00	−7.15	3.53	−8.17
308	25.36			−8.28
318	23.27			−8.32
328	20.69			−8.26

instance, Gibbs free energy (ΔG), standard enthalpy change (ΔH), and standard entropy change (ΔS) are calculated at different temperatures using the following equations:

$$\Delta G = -\mathrm{RT}\ln K_L \tag{5}$$

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{\mathrm{RT}} \tag{7}$$

where R (8.3145 J/(mol K)) is the universal gas constant, K_L (L/g) is the Langmuir constant, and T (K) is the absolute temperature (in Kelvin). The values of ΔH and ΔS can be calculated from the slopes and the intercept of the linear straight by plotting ln a_c against $1/T$ in Fig. 5, and the values of ΔG can be calculated in accordance to (Eq. (7)).

Table 1 shows the values of ΔH, ΔS, and ΔG at different initial MB concentrations and temperatures. The obtained values of energy ΔG are from −8.32 to −8.17. The negative values at four tested temperatures indicate that the adsorption of MB dye onto sepiolite is a spontaneous and feasible process. The values of ΔG (between −20 and 0 kJ/mol) reveal that the adsorption process is physisorption. However, the absolute value of ΔG increases with increasing the temperature, suggesting that the adsorption of MB dye becomes less favorable at higher temperature. The negative standard enthalpy change (ΔH) suggests that the adsorption is an exothermic reaction and the adsorption process is energetically stable. The positive standard entropy change (ΔS) reveals the increased randomness at the solid–solution interface during the adsorption progress. As temperature increases, the increased mobility of MB molecules causes the molecules to escape from the solid phase to the liquid phase, and the amount of MB adsorbed by sepiolite consequently increases [58].

4. Conclusions

A modified sepiolite has been prepared by nitric acid impregnation and a heat treatment. The specific surface area of the modified sepiolite is up to 412.7 m^2/g, which has been greatly improved compared with natural sepiolite with a specific surface area of 125.2 m^2/g. The adsorption properties of MB dye by the modified sepiolite have been studied in detail through investigating related factors such as the initial MB concentration, adsorbent dosage, contact time, pH value, and temperature. The results showed that pH higher than 4.0 conditions benefited for MB adsorption and the adsorption capacity reached 24.82 mg/g. The adsorption capacity decreased from 38.45 mg/g to 28.63 mg/g with increasing temperature from 298 K to 328 K. The experimental data can be well fitted with the Langmuir isotherm equation. Kinetic studies show that adsorption process follows the pseudo-second-order reaction model. Thermodynamic investigations indicate that the adsorption reaction is a spontaneous and exothermal process. It suggests that modified sepiolite is a promising adsorbent candidate to remove MB from aqueous solutions.

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