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Research Article

Adsorption of Basic Brown and Chrysophenine from Water Solution by Magnesium Silicate Gel

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Noncrystalline, high surface area magnesium silicate gel was successfully prepared by hydrothermal method. Such product was characterized by BET and XRD to determine surface area 576.4 $m^2 \cdot g^{-1}$, average pore width 2.76 nm, and amorphous surface. The adsorption behaviors of Basic Brown and Chrysophenine on magnesium silicate gel were investigated through changing initial concentration, adsorbent dosage, solution pH, contact time, and temperature. The experimental data was analyzed by the adsorption isotherms and kinetics. The results showed the adsorption progress was fast for Basic Brown, and the adsorption equilibrium was finished in 2 h, while the adsorption equilibrium of Chrysophenine was finished in 7 h. Freundlich isotherm model and second-order kinetic models described the adsorption process very well.

1. Introduction

At present, dyes have been widely used in many fields, such as printing and dyeing, papermaking, textile, and food [1, 2]. While the extensive usage makes such dyes attract considerable attention, the reason is that they may be toxic and nondegradable due to their syntheses from polyaromatic ring organics. Therefore, much effort has been dedicated to the pollution problem of dyes. So far, numerous treatment methods have been reported in removal of dyes from aqueous solution [3–6]. Among them, adsorption technique is recognized as a great potential based on the adsorbents presenting environmental friendliness, without second-pollution, high capacity, ease of use, and so on. One kind of the most used adsorbent is activated carbon [7]. However, to some extent, the natural properties of activated carbon, including high cost and nondegradability, greatly confine its usage in industry. Thus, it is of great importance to decrease the cost of wastewater treatment and explore new, inexpensive, high-efficient adsorbents.

A survey revealed that many materials including chitosan, bagasse pith, peat, rice husk, fly ash, wood, and some natural minerals, such as bentonite, montmorillonite, alunite, sepiolite, zeolite, and diatomite, have been used as adsorbents to remove the dyes from solution [8–11]. A wide range of silicate materials had silanol group and magnesium hydroxide activated group accumulated on the surface. Some synthesized magnesium silicates displayed the common feature compared with that of natural materials and have been applied widely in removal of dyes, organics, and metal ions from the industry wastewater [12–23]. Our group also prepared some magnesium silicate materials with the similar surface activated groups and successfully removed the methylene blue and malachite green from water solution [17]. The other relative studies also have been reported [18–21, 24–26].

Herein, we synthesized a kind of new, high special surface area and multiporous magnesium silicate gel through hydrothermal method. The adsorption experiments were performed by investigating the removal behavior of Basic Brown and Chrysophenine on the as-prepared magnesium silicate gel from water solution. This study provides the theory evidence and practice support for industrial wastewater treatment.

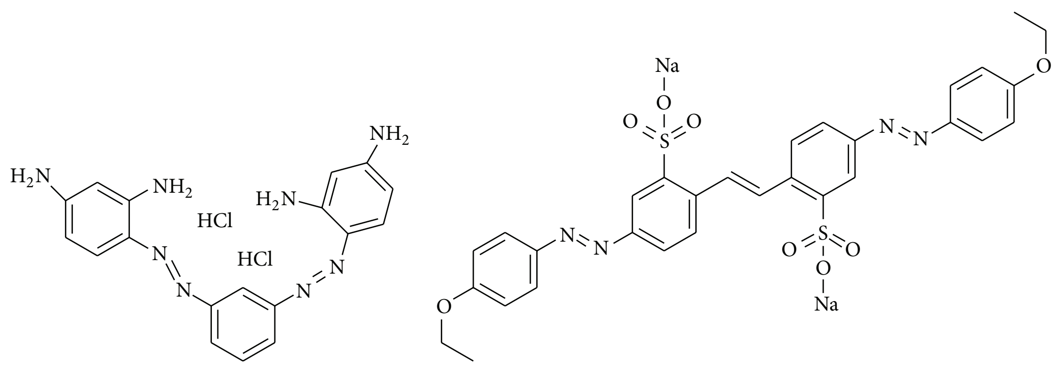

Figure 1: Molecular structure of Basic Brown (a) and Chrysophenine (b).

2. Experimental

2.1. Materials and Instruments. All chemical reagents were of analytical grade purity and used as received without further purification. All dyes were dried at 110°C for 2 h before using. All solutions were prepared with distilled water.

Basic Brown, industrial grade, is a dark brown-red powder with Color Index number 1 (21000) and CAS 8052-76-4. Its structure is shown in Figure 1(a), and the structural formula is $C_{18}H_{18}N_8 \cdot 2HCl$. Chrysophenine, industrial grade, is a dark yellow powder with Color Index number 12 (24895) and CAS 2465-27-2. Its structure is shown in Figure 1(b), and its structural formula is $C_{30}H_{26}N_4Na_2O_8S_2$. The structures of the two dyes are given in Figure 1.

The surface area and pore-size distribution of magnesium silicate gel were determined by N_2 adsorption/desorption analysis using ASAP 2020, Micromeritics. The surface area was evaluated by Brunauer-Emmett-Teller (BET) equation, and the pore-size distribution was determined by Barrett-Joyner-Halenda (BJH) equation. The finial equilibrium concentration was measured by 722 UV-Vis spectrophotometer. Solution pH was determined through pHS-3C meter equipped with a combined pH electrode.

2.2. Synthesis of Magnesium Silicate Gel. Magnesium chloride hexahydrate and sodium silicate nonahydrate (Na_2O/SiO_2 module = 1) were mixed with the mole ratio of 2 : 1 at room temperature. The resultant white precipitate appeared immediately. Keeping the precipitate stirring for 5 h at room temperature, then the turbid liquid was transited into reaction kettle for 24 h reaction at 120°C. Finally, the reaction was cooled to room temperature, and the resultant samples were washed using heat water until without Cl^-. The prepared adsorbent was dried in an air oven at 110°C for 10 h and allowed to cool naturally.

2.3. Adsorption Test. Adsorption experiments of Basic Brown and Chrysophenine on magnesium silicate gel were carried out through changing dyes initial concentration, adsorbent dosage, solution pH, contact time, and temperatures. Solution pH was adjusted by adding 0.1 mol·L^{-1} NaOH or HCl solution and determined by using a pHS-3C meter equipped with a combined pH electrode. The pH-meter was standardized with normal buffer solution (NBS) before measurement. After adsorption equilibrium was established, the residual concentration was measured by using a 722 UV-Vis spectrophotometer at the corresponding maximum wavelength. The percent of removal and adsorption capacity of the two dyes on magnesium silicate gel were calculated as the following equations:

$$E\% = \frac{C_0 - C_e}{C_0} \times 100, \qquad q_e = \frac{C_0 - C_e}{m} \times V, \tag{1}$$

where $E\%$ is the percent of removal after adsorption equilibrium; C_0 and C_e are dyes initial concentration and equilibrium concentration, mg·L^{-1}; q_e is the equilibrium adsorption capacity, mg·g^{-1}; V is the volume of the solution, L; m is the mass of adsorbent, g.

3. Results and Discussion

3.1. Characterization of Adsorbent

3.1.1. Analysis of Surface Area and Pore-Size Distribution. N_2 adsorption/desorption isotherms and pore-size distribution are shown in Figure 2. The isotherms can be recognized as the classical IV type with a hysteresis loop in the relative pressure range of 0.85–1.0, which indicates that the prepared magnesium gel possesses mesoporous structure. The N_2 adsorption quantity fast increases under the low relative pressure and gradually increases as the relative pressure reaches 0.8 and then sharply increases when the relative pressure is between 0.8 and 1. The maximum adsorption reaches 330 cm^3·g^{-1} when the relative pressure approaches 1. The special surface area calculated from BET is 576.4 m^2·g^{-1}, and the average pore width is 2.76 nm. The pore-size distribution obtained from the desorption isotherm displayed a narrow distribution centering the range of 2 nm–4 nm.

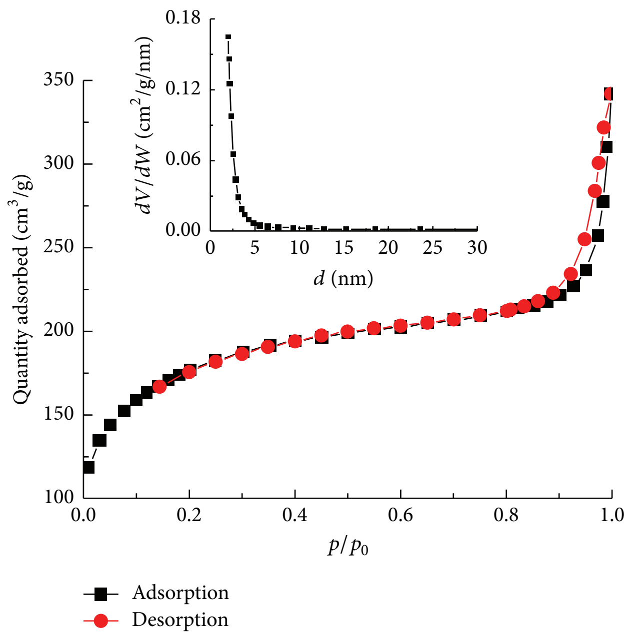

FIGURE 2: N_2 adsorption/desorption isotherms and pore-size distribution (inset).

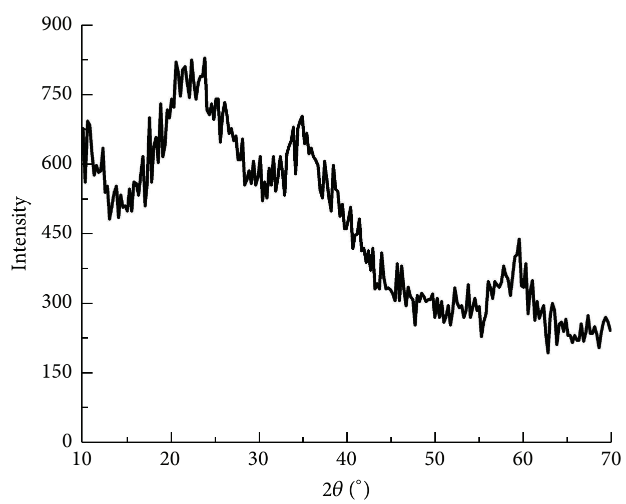

FIGURE 3: The X-ray powder diffraction (XRD) of magnesium silicate gel.

3.1.2. X-Ray Powder Diffraction (XRD) Analysis. The X-ray powder diffraction (XRD) of magnesium silicate gel is shown in Figure 3. The figure shows that the prepared sample is amorphous. The diffraction curve possesses three classical diffraction peaks, such as 20–30, 32–38, and 56–61°, which was consistent with the literature result [18, 19].

3.2. Effect of Initial Concentration. The effect of initial concentration of the two dyes on magnesium silicate gel can be investigated when the mass of adsorbent used was $2\,g{\cdot}L^{-1}$. The removal ratio of the two dyes on magnesium silicate gel as a function of dyes initial concentration was given in Figure 4 at 298 K. As can be seen from the plot, the removal

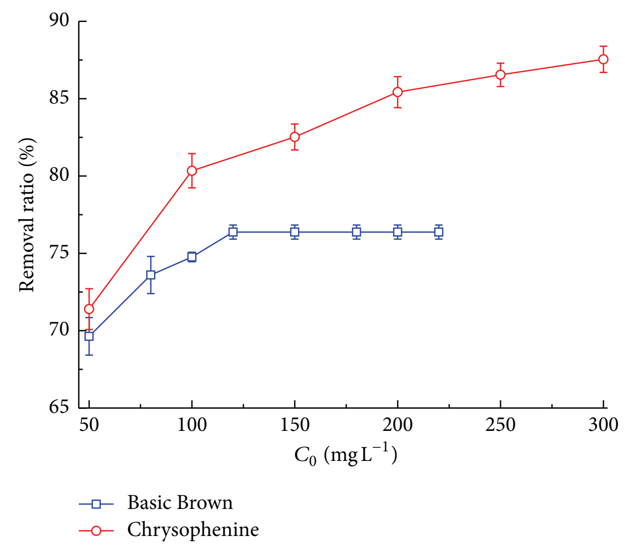

FIGURE 4: The adsorption effect of the two dyes on magnesium silicate gel as a function of initial concentration (mass of magnesium silicate gel: $2\,g{\cdot}L^{-1}$; adsorption time: 2 h for Basic Brown and 7 h for Chrysophenine; pH: 7.1).

ratio gradually increases with the increase of initial concentration; then the adsorption reached equilibrium. When the initial concentration of Basic Brown was $120\,mg{\cdot}L^{-1}$, the removal ratio was 75%. When the initial concentration of Chrysophenine was $200\,mg{\cdot}L^{-1}$, the removal ratio was 85%. Thus, the adsorption results of the two dyes illustrated that the adsorption processes were favorable. The performance also showed that the initial concentration provided an important driving force to overcome the mass transfer resistance of dye between the solution and adsorbents surface.

3.3. Effect of Mass of Adsorbent. The mass of magnesium silicate gel was in the range of $0.5–5\,mg{\cdot}L^{-1}$, and the concentration of dyes was $200\,mg{\cdot}L^{-1}$. The removal ratio of the two dyes on magnesium silicate gel was shown in Figure 4. As shown in Figure 5, the removal ratio of the two dyes gradually increases with the increase of mass of magnesium silicate gel. When the mass of magnesium silicate gel was lower than $2\,g{\cdot}L^{-1}$, the removal ratio of Chrysophenine sharply increases, and the removal coefficient of Basic Brown performed better than that of Chrysophenine. When the mass of magnesium silicate gel was higher, the removal of Chrysophenine displayed better adsorption coefficient than that of Basic Brown. When the mass was $5\,g{\cdot}L^{-1}$, the removal ratio of Chrysophenine was 90%, and that of Basic Brown was 80%.

3.4. Effect of Solution pH. The removal effect of Basic Brown and Chrysophenine on magnesium silicate gel as a function of solution pH was shown in Figure 6. As can be seen from the figure, there is no obvious effect on the removal of Chrysophenine, and the removal ratio keeps constant at 85%. However, the solution pH has a significant effect on the removal of Basic Brown. At low pH (pH < 5), the adsorption

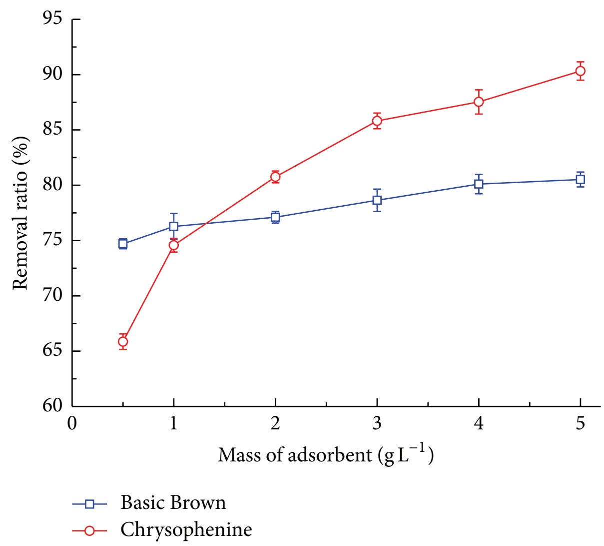

FIGURE 5: The effect of mass of magnesium silicate gel on the removal of Basic Brown and Chrysophenine (concentration of dyes: 200 mg·L^{-1}; adsorption time: 2 h for Basic Brown and 7 h for Chrysophenine; pH: 7.1).

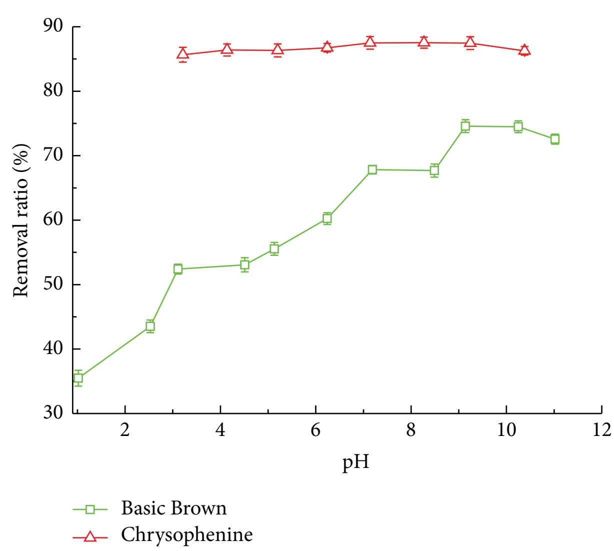

FIGURE 6: The effect of solution pH on the removal of the two dyes on magnesium silicate gel (concentration of dyes: 100 mg·L^{-1}; mass of adsorbent: 2 g·L^{-1}; adsorption time: 2 h for Basic Brown and 7 h for Chrysophenine; pH: 7.1).

efficiency was low. As the pH increased, the removal ratio gradually increased and reached the maximum value of 75%. When pH continued to increase, the removal ratio began to decrease. Therefore, the best adsorption efficiency was obtained with the solution pH of 9.

3.5. Effect of Contact Time. At 298 K, the adsorption effect of Basic Brown and Chrysophenine on magnesium silicate gel as a function of different contact time was shown in Figure 7. As can be seen, the adsorption of Basic Brown was

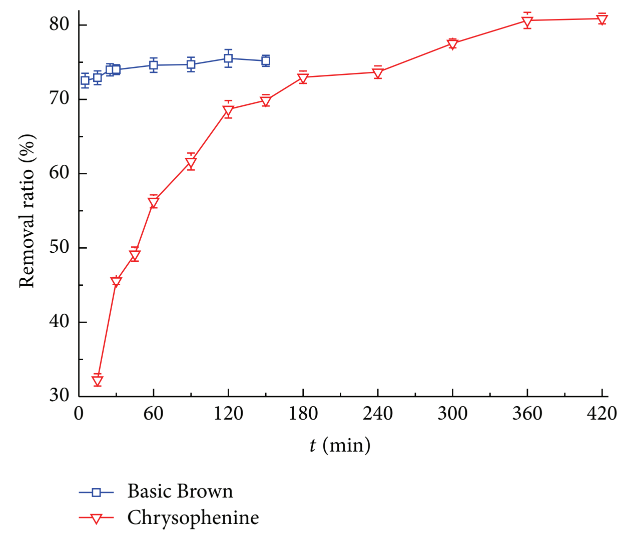

FIGURE 7: The effect of contact time on the removal of the two dyes on magnesium silicate gel (concentration of dyes: 100 mg·L^{-1}; mass of adsorbent: 2 g·L^{-1}; pH: 7.1).

a fast adsorption process, and the adsorption equilibrium was finished in a relative short time with the removal ration of 73%. The adsorption of Chrysophenine on magnesium silicate gel exhibited three different stages: the fast adsorption process, the slow adsorption course, and the final adsorption equilibrium.

3.6. Adsorption Isotherms. The effect of adsorption temperature on the removal of Basic Brown and Chrysophenine is shown in Figure 8. As shown in the figure, there is no obvious change for the removal of the two dyes on magnesium silicate gel at the different temperatures. The equilibrium adsorption quantity gradually increased with the increase of the concentration. The adsorption quantity of Basic Brown was 76.6 mg·g^{-1}, when the initial concentration was 200 mg·L^{-1}, while the adsorption quantity of Chrysophenine was 57.8 mg·g^{-1} with the same initial concentration.

The Langmuir and Freundlich adsorption models have been used to fit the experimental data at different adsorption temperatures:

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m},$$
$$\text{Freundlich: } \lg q_e = \lg K_F + \frac{1}{n}\lg C_e, \qquad (2)$$

where C_e is equilibrium concentration, mg·L^{-1}; q_e is the equilibrium adsorption capacity, mg·g^{-1}; q_m is the maximum adsorption quantity, mg·g^{-1}; K_L, K_F, and n are adsorption constants.

The analysis revealed that the adsorption isotherms did not meet the Langmuir adsorption model, which indicated the adsorption of Basic Brown and Chrysophenine on magnesium silicate gel was not simple single-molecule adsorption. The Freundlich adsorption model can describe the

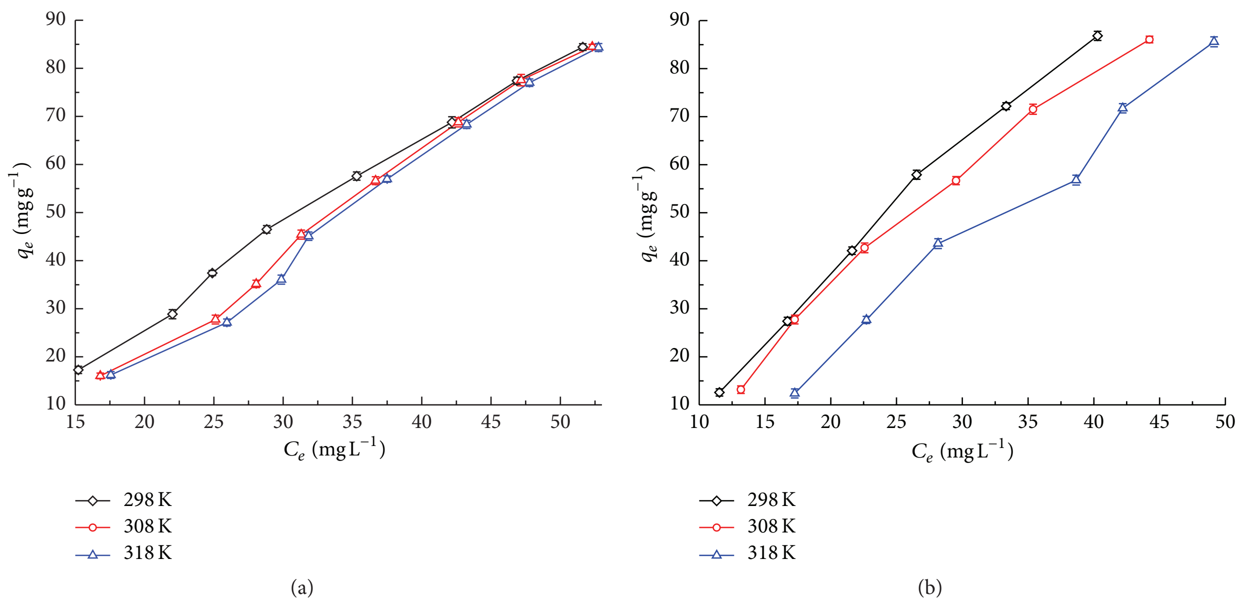

FIGURE 8: Adsorption isotherms of Basic Brown (a) and Chrysophenine (b) at different adsorption temperatures.

TABLE 1: The relative parameters of Freundlich adsorption isotherm model.

Dyes	C_0 mg·L^{-1}	T/K	Freundlich model K_F	$1/n$	R^2
Basic Brown	200	298	0.5629	1.2849	0.9888
	200	308	0.2473	1.49	0.9895
	200	318	0.1802	1.565	0.9876
Chrysophenine	200	298	0.3574	1.5201	0.9742
	200	308	0.2998	1.5327	0.9450
	200	318	0.0738	1.8268	0.9556

adsorption process of the two dyes very well, and the square correlation coefficient value of Basic Brown approached 0.97, while the coefficient value of Chrysophenine was 0.94. The corresponding parameters are given in Table 1.

3.7. Adsorption Kinetics. At different adsorption temperatures, the removal of Basic Brown and Chrysophenine on magnesium silicate gel at different adsorption time was shown in Figure 9. As can be seen from the figure, the adsorption quantity gradually increased with the extension of contact time, while, at the same contact time, the adsorption quantity slowly decreased with the temperature increasing.

In order to investigate the adsorption kinetics behavior, the first-order kinetic and second-order kinetic models were used to discuss the adsorption mechanism.

The first-order kinetics equation is presented as

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t, \tag{3}$$

where q_e is the amount adsorbed at equilibrium, mg/g; q_t is the amount adsorbed at time t, min; k_1 is the first-order rate constant of adsorption, min^{-1}, which can be determined from the slopes of the plots $\ln(q_e - q_t)$ versus t.

The second-order kinetics equation is given as

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

where k_2 is the second-order rate constant of adsorption, g/mg/min, which can be obtained from the slopes and intercepts of plots t/q_t versus t.

The experimental data was analyzed through the first-order kinetics model and second-order kinetics model, respectively. The corresponding kinetics parameters were obtained from (3)-(4) and given in Table 2. It can be seen that the calculated equilibrium adsorption quantity and experimental adsorption quantity were close and that the correlation coefficient values approached 1 ($R_2 \; > 0.99$). Therefore, the obtained parameters showed that the second-order kinetics model could describe the adsorption process very well.

4. Conclusions

A kind of high special surface area adsorbent, magnesium silicate gel, was prepared through hydrothermal synthesis. The calculated special surface area was 576.4 m^2·g^{-1}, and the average pore width was 2.76 nm. The adsorption experiments showed that the removal ratio gradually increased with the increase of initial concentration, mass of adsorbent, solution pH, and contact time as well as the decrease of the temperature. The adsorption quantity of Basic Brown was 76.5 mg·g^{-1} and the adsorption quantity of Chrysophenine was 57.8 mg·g^{-1} with the initial concentration of 200 mg·L^{-1} for both dyes, respectively. The adsorption equilibriums were finished in a short time for removal of Basic Brown, and the adsorption process of the two dyes performed physical

Table 2: Second-order kinetics values calculated for the adsorption of the two dyes on magnesium silicate gel.

Dyes	C_0 mg·g^{-1}	T/K	First-order k_1/min^{-1}	First-order R^2	$q_{e,\exp}$/mg·g^{-1}	Second-order $q_{e,\mathrm{cal}}$/mg·g^{-1}	Second-order k_2/g·mg^{-1}·min^{-1}	Second-order R^2
Basic Brown		298	0.0187	0.951	76.6	76.92	0.0180	1.000
		308	0.0377	0.973	76.4	76.92	0.0133	1.000
		318	0.0043	0.944	76.1	74.07	0.0190	1.000
Chrysophenine		298	0.0092	0.972	56.8	60.61	5.44×10^{-4}	0.9975
		308	0.0079	0.994	76.4	58.82	5.47×10^{-4}	0.9980
		318	0.009	0.993	76.1	57.47	4.90×10^{-4}	0.9974

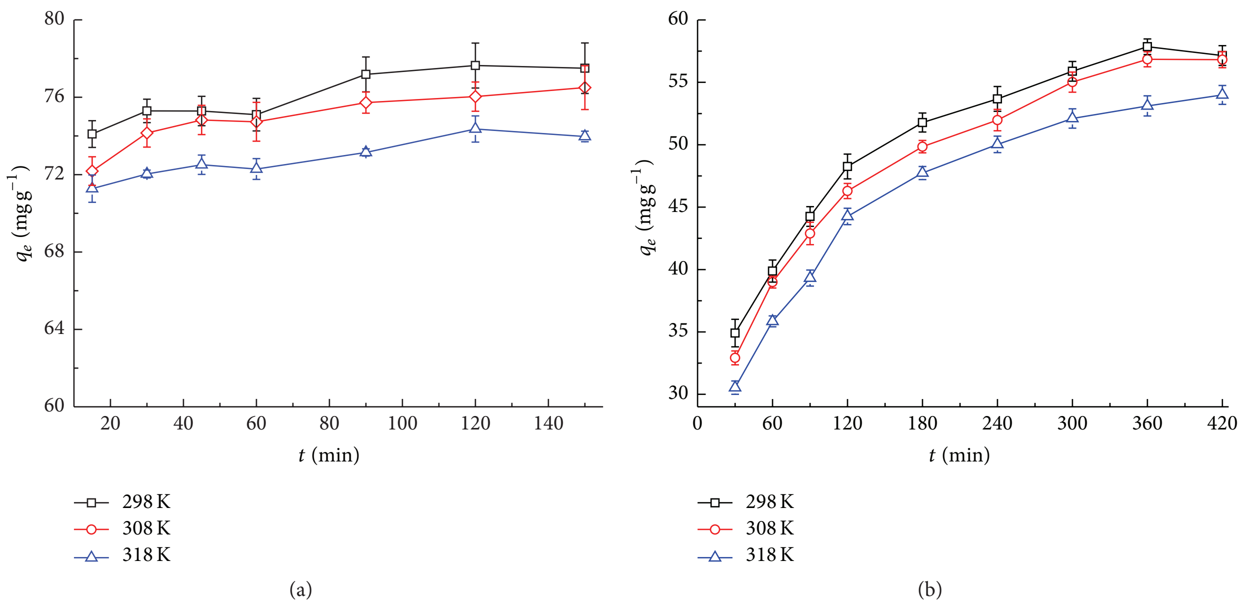

Figure 9: The adsorption kinetics of Basic Brown (a) and Chrysophenine (b) at different adsorption time.

adsorption. Freundlich adsorption isotherm and second-order kinetics models well described the adsorption behavior of the two dyes on magnesium silicate gel.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors' Contribution

Zhenhua Li and Zhun Zhao contributed equally to this study.

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