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Adsorption of methylene blue from aqueous solution by sol–gel silica doped with sec-octylphenoxyl acetic acid

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ABSTRACT

Sol–gel silica doped with different amount of sec-octylphenoxyl acetic acid (CA12) was prepared using sol–gel method and characterized by scanning electron microscopy and thermogravimetric analysis. The adsorption behavior of methylene blue (MB) from aqueous solution onto sol–gel silica doped with CA12 (SSC) was studied. Batch experiments were carried out to measure the adsorption as a function of equilibrium time, pH of the solution, initial MB concentration and temperature. The results showed that the contents of CA12 were 0, 4.4%, 5.1% and 7.5% for SSC-0, SSC-1, SSC-2 and SSC-3, respectively. The adsorption equilibrium was reached within 8 h for SSC-0, 5 h for SSC-1, 2 h for SSC-2 and SSC-3. With the increase of the content of CA12, the equilibrium time decreased, which may be due to their increased pore structure. Both the pseudo-first-order and pseudo-second-order kinetics models fitted the data well. The higher adsorption amount was found at neutral and basic conditions, and the lower adsorption amount was found at lower pH. The adsorption data for MB on SSC were consistent with the Langmuir isotherm equation. The maximum adsorption capacities of MB on SSC-0, SSC-1, SSC-2 and SSC-3 were 23.8, 32.4, 46.3 and 65.9 mg g^{-1}, respectively. The thermodynamics properties indicated that the adsorption processes were spontaneous and endothermic nature.

Keywords: Methylene blue; Sol–gel silica; Adsorption; Sec-octylphenoxyl acetic acid

1. Introduction

Numerous industries such as textile, leather, paper and dyestuff discharge a large amount of dye effluents into the environment [1,2]. Highly colored wastes may hinder light penetration and disturb the ecosystem. Furthermore, most organic dyes are harmful to human beings and hazardous to aquatic organisms [3]. The presence of very small amounts of dyes in water is highly visible and undesirable. Methylene blue (MB) is a commonly used cationic dye having various applications in chemistry, biology, medical science and dyeing industries. It can cause eye burns, nausea, vomiting, mental confusion and hypertension [4]. Therefore, it is important to treat effluent containing such dye [5,6].

Various techniques have been used to remove MB from wastewater, such as liquid–liquid extraction [7], oxidation [8], membrane separation [9], photocatalytic degradation [10] and electrochemical degradation [11]. But all these methods are difficult to completely remove the color from wastewater due to suffering from some limitations [12,13]. Adsorption has been found a very effective method for dye removal in terms of low initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [14–17]. Numerous adsorbents have been studied for the adsorption of MB, such as activated carbon [4], agricultural wastes [18], bioadsorbents [19], magnetic materials [20,21] and siliceous materials [14]. Siliceous material has well-modified surface property, excellent thermal and mechanical stability and good swelling resistance in solvents [22–25]. Various siliceous materials, such as modified mesoporous silica nanoparticle [26], nanoporous SBA-3 [27], chromatographic grade silica gel [28] and zeolite [29] have been studied for adsorption of MB.

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Siliceous material is negatively charged at higher pH due to the presence of Si–O and Si–OH groups, which can adsorb positively charged dyes [27,28].

In recent years, sol–gel silica functionalized with different organic reagents, such as Cyanex 272 [30,31], crown ether [32], 1,5-diphenylcarbazide [33] and ionic liquids [34,35] have been applied for recovery and separation of metal ions. Good results have been achieved. However, sol–gel silica doped with organic reagents has not been used for adsorption of MB. Moreover, the effects of different content of organic reagent to the structure and the adsorption of sol–gel silica have not been studied. Sec-octylphenoxyl acetic acid (CA12), a carboxylic acid extractant, was used in this study. In this study, sol–gel silica doped with CA12 (SSC) was prepared for adsorption of MB from aqueous solution. SSC prepared using simple sol–gel technique had high surface area and controllable particle size, which is useful for easy separation. CA12 doped in sol–gel silica may change the structure of SSC. And there may be interactions between CA12 and basic dye. The effect of equilibrium time, initial solution pH and temperature was studied. The adsorption isotherm, adsorption kinetics and thermodynamic were also evaluated.

2. Experimental section

2.1. Materials

MB was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and dissolved in distilled water in the adsorption tests. All chemicals used in this study were of commercially available analytical grade.

2.2. Methods

The morphology of the samples was observed using scanning electron microscope (SEM), JSF-5610LV (JEOL, Japan). Thermogravimetric analysis (TGA) was conducted by Thermal Analysis Instrument (NETZSCH STA409PC, NETZSCH, Germany). UV–visible spectra were measured with a Shimadzu UV-2550 spectrophotometer (Shimadzu, Japan).

2.3. Preparation of sol–gel silica doped with CA12

A certain amount of tetraethoxysilane (25 mL), formic acid (2.5 mL, 0.05 mol L^{-1}) and 10 mL of distilled water were mixed in a beaker. The mixture was stirred for 8 h at room temperature, and a homogeneous solution was obtained. Then, a certain amount of CA12 (0, 1, 2 or 3 g) was added and stirred continuously until the mixture coagulated. After aging for 2 h, the samples were dried at 40°C for 12 h [34]. Then, the sample was washed with distilled water to neutral pH and dried at 40°C for 12 h. The 50–100 μm particle size fraction was used in our experiments. The sol–gel silica doped with 0, 1, 2 or 3 g of CA12 are denoted as SSC-0, SSC-1, SSC-2 and SSC-3, respectively.

2.4. Determination of the content of CA12 in SSC

0.2 g of SSC-0, SSC-1, SSC-2 or SSC-3 was mixed with 20 mL of absolute ethanol and shaken for 12 h to remove CA12 doped in sol–gel material. The ethanol solution containing CA12 was separated by centrifuging. Then, the content of CA12 was titrated by 0.01 mol L^{-1} NaOH standard solution.

2.5. Adsorption studies using batch method

The sorption kinetics experiments were carried out by shaking 0.03 g of SSC-0, SSC-1, SSC-2 or SSC-3 and 20 mL of MB solution with initial concentration of 50 mg L^{-1} for different time intervals. The adsorption isotherm experiments were determined by placing 0.03 g of SSC-0, SSC-1, SSC-2 or SSC-3 and 20 mL of MB solution with desired initial concentrations (20–100 mg L^{-1}) and shaking to reach equilibrium. The effect of pH on the adsorption of MB was studied by shaking 0.03 g of SSC-0 or SSC-1 and 20 mL of MB solution (50 mg L^{-1}) at pH 1–12 to reach equilibrium. 1 mol L^{-1} HCl and 1 mol L^{-1} NaOH were used to adjust the pH. The effect of temperature on the adsorption of MB was studied by shaking 0.03 g of SSC-0, SSC-1 or SSC-2 with 20 mL of MB solution (50 mg L^{-1}) at different temperatures (293–313 K). The concentration of MB was determined by UV-2550 spectrophotometer at the maximum absorption wavelength of 664 nm. The amount of adsorbed MB was calculated by a mass balance between the initial and equilibrium concentrations. All experiments were conducted at room temperature and pH without adjustment except pH experiment.

3. Results and discussion

3.1. Characterization of SSC

The content of CA12 in SSC was determined by titration with NaOH standard solution. SSC-0 without CA12 was used as blank. The results showed that the CA12 contents were 4.4%, 5.1% and 7.5% for SSC-1, SSC-2 and SSC-3, respectively. The CA12 content increased with the increasing usage amount of CA12 in the preparation procedure. The morphology of SSC-0, SSC-1 and SSC-3 was characterized by SEM, as shown in Fig. 1. SSC is amorphous particle. The surface of SSC-0 hardly possesses visible macroporous structure. With the addition of CA12 in the synthesis process, the prepared SSC-1 and SSC-3 with CA12 content of 4.4% and 7.5% possesses macropores. Moreover, it can be seen from Fig. 1 that SSC-3 had more macropores than SSC-1, which indicated that the number of macropores increased with the content of CA12. SEM images revealed that the addition of CA12 in the synthesis process can improve the pore structure. However, CA12 cannot be added too much, otherwise the mixture will be hard to coagulate.

Fig. 2 shows the TGA plots of SSC-0, SSC-1, SSC-2 and SSC-3. SSC-0 presented a first weight loss until 192°C due to the loss of water and a second weight loss in the range of 192°C–800°C corresponding to the concentration of silanol groups. SSC-1, SSC-2 and SSC-3 with different content of CA12 decomposed in three steps. The first important weight loss occurred below 200°C, which was mainly attributed to the loss of water. The increased weight losses of the remaining two stages (from 200°C to 800°C) were 8.3%, 9.1% and 14.9% for SSC-1, SSC-2 and SSC-3, respectively, which may be due to the decomposition of doped CA12 and the concentration of silanol groups. The increased weight losses

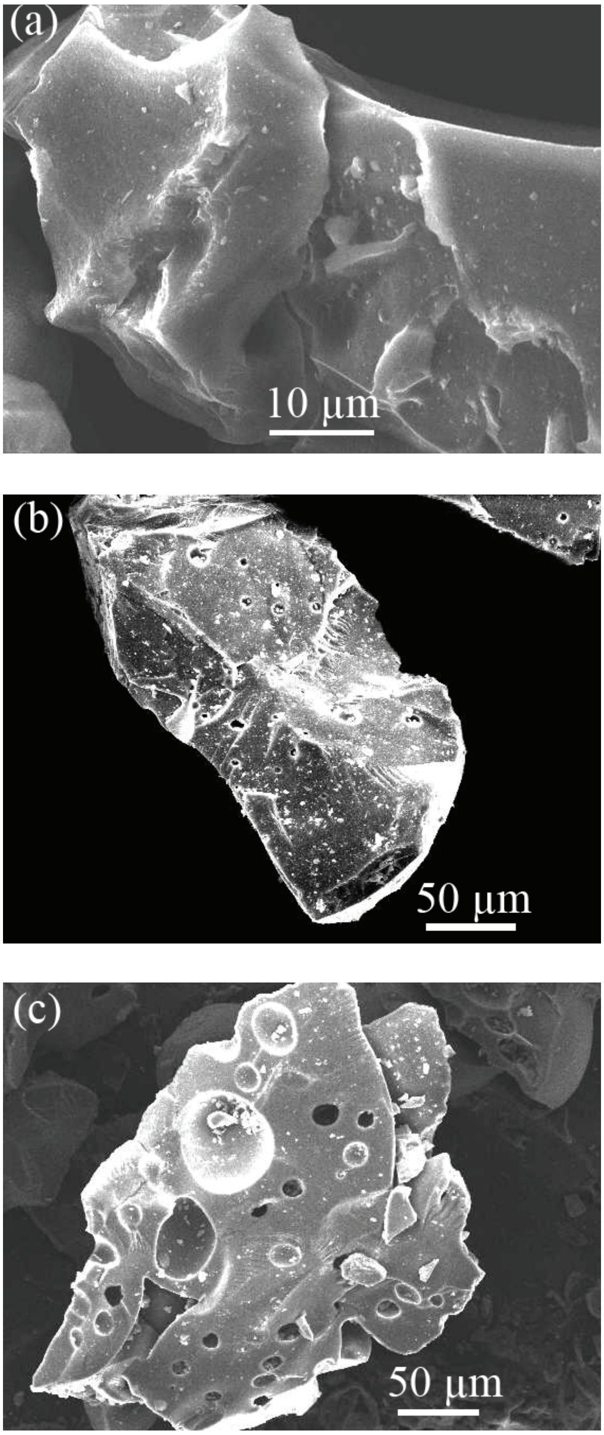

Fig. 1. SEM images of (a) SSC-0, (b) SSC-1 and (c) SSC-3.

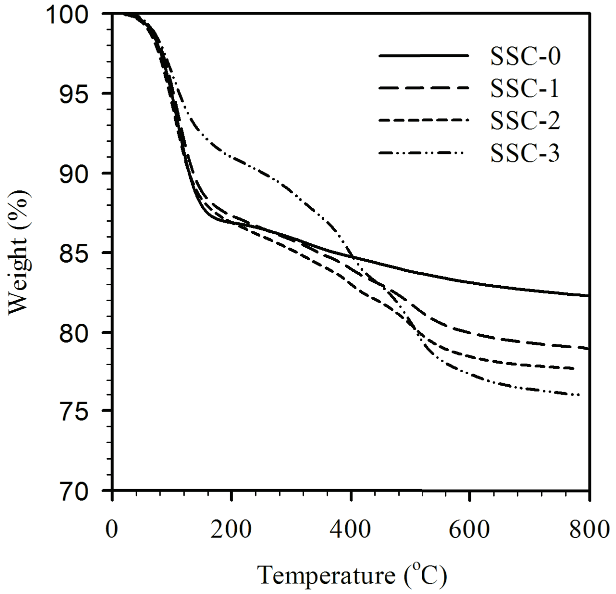

Fig. 2. TGA plots of SSC-0, SSC-1, SSC-2 and SSC-3.

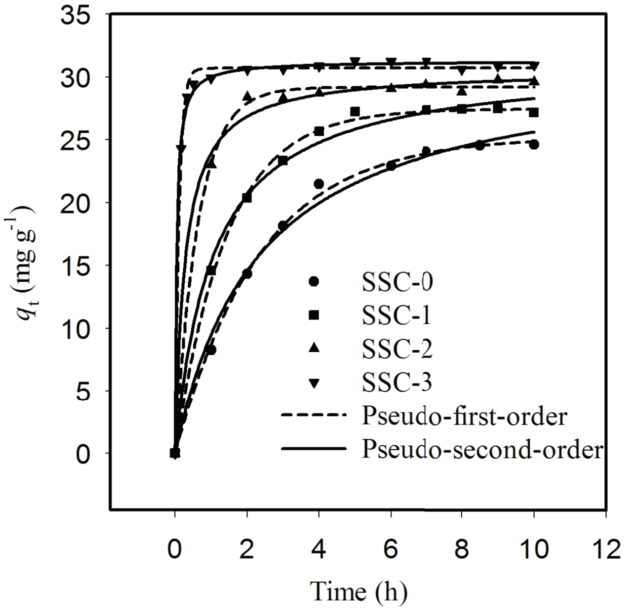

Fig. 3. Pseudo-first-order and pseudo-second-order kinetic model for MB adsorption on SSC.

from SSC-1 to SSC-3 also showed that the content of CA12 gradually increased.

3.2. Adsorption kinetics of MB on SSC

The solid points in Fig. 3 show the dynamic adsorption of MB on SSC-0, SSC-1, SSC-2 and SSC-3. The adsorption of MB was fast at initial times and then approached equilibrium at longer times. It took 8, 5, 2 and 2 h for SSC-0, SSC-1, SSC-2 and SSC-3 to reach adsorption equilibrium, respectively. With the increase of the content of CA12, the equilibrium time gradually decreased. The equilibrium time of SSC-2 and SSC-3 was much shorter than that of SSC-0 and SSC-1. That may be due to the increased pore structure of SSC-2 and SSC-3.

Pseudo-first-order and pseudo-second-order kinetic models were investigated by fitting the experimental data obtained from the batch method. The Lagergren pseudo-first-order equation [36] is expressed as Eq. (1).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

The pseudo-second-order model of Ho and McKay [37] is expressed as Eq. (2).

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

where q_t and q_e are the amounts of adsorbed MB at time t and equilibrium, respectively. k_1 is the rate constant of pseudo-first-order adsorption. k_2 is the rate constant of pseudo-second-order adsorption. The kinetics parameters of q_e, k_1 and k_2 can be calculated by plotting of q_t vs. t.

The fitted plots of the pseudo-first-order and pseudo-second-order kinetics models are shown in Fig. 3. Table 1 shows the values of k_1, k_2 and q_e for the adsorption of MB on SSC-0, SSC-1, SSC-2 and SSC-3. It can be seen that both the pseudo-first-order and pseudo-second-order kinetics models fitted the data well with high regression values.

3.3. Effect of pH on adsorption

As is known to all, the pH of the solution is recognized as an important parameter that influences the adsorption amount of adsorbents. Fig. 4 shows the effect of initial pH on the adsorption amount of MB on SSC-0, SSC-1 and SSC-2. The adsorption amount first increased with the pH increase and then decreased with the pH increase for all the three adsorbents. Maximum adsorption was observed at pH about 7 for the three adsorbents. The higher adsorption amount was found at neutral and basic conditions, and the lower adsorption amount was found at lower pH. That may be due to the nature of silica materials. Silanol groups were found to be the main functional group responsible for MB adsorption [38]. The surface of the SSC is positively charged at lower pH and negatively charged at higher pH. Therefore, the adsorption amount of cationic dye MB was lower at lower pH due to the positively charged surface. At higher pH the surface of SSC is negatively charged which can effectively adsorb cationic dye. For the adsorbents of different content of CA12, the adsorption amount of MB increased from SSC-0 to SSC-2. That may be due to the increased pore structure and the interactions between the doped CA12 and MB. The main reason may be the increased pore structure. Because at alkaline pH the negatively charged CA12 did not increase the adsorption amount of cationic dye MB further.

3.4. Adsorption isotherms

Different initial MB concentrations (20–100 mg L^{-1}) on the adsorption of MB on SSC-0, SSC-1, SSC-2 and SSC-3 were studied. The Langmuir and Freundlich isotherm models were used to evaluate the adsorption of MB on SSC. The Langmuir isotherm is frequently used single-component adsorption model [39]. Langmuir model assumes that the adsorption occurs on a homogeneous surface by monolayer adsorption without interaction between adsorbed molecules. The Langmuir equation is expressed as Eq. (3):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{3}$$

where C_e (mg L^{-1}) is the equilibrium concentration; q_e (mg g^{-1}) is the amount adsorbed at equilibrium; q_m (mg g^{-1}) is the maximum adsorption capacity and b (L mg^{-1}) is the Langmuir constant related to the energy of sorption.

The Freundlich equation (Eq. (4)) is based on heterogeneous surfaces suggesting that binding sites are not equivalent and/or independent [40].

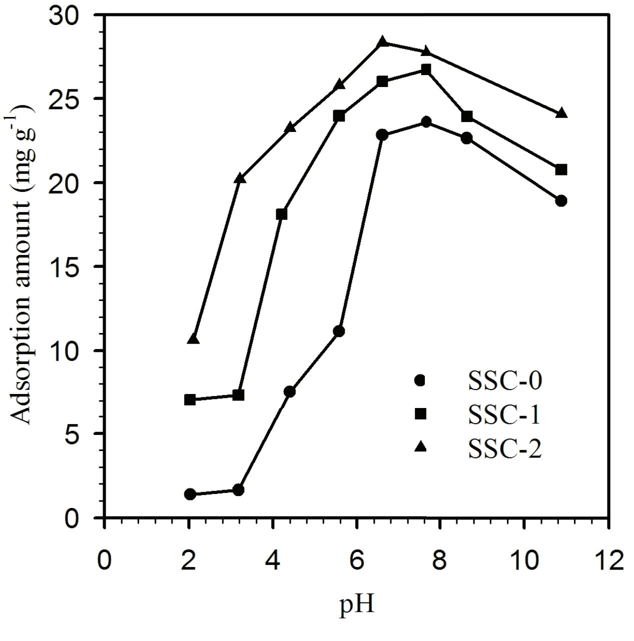

Fig. 4. The effect of initial pH on the adsorption amount of MB on SSC.

Table 1
Pseudo-first-order and pseudo-second-order kinetic parameters for MB adsorption on SSC

Adsorbents	Pseudo-first-order			Pseudo-second-order		
	q_e (mg g^{-1})	k_1 (h^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} h$^{-1/2}$)	R^2
SSC-0	25.2	0.43	0.998	31.6	0.014	0.991
SSC-1	27.4	0.70	0.997	31.2	0.031	0.993
SSC-2	29.2	1.57	0.998	30.6	0.118	0.995
SSC-3	30.7	8.97	0.996	31.3	0.758	0.998

$$q_e = K_f C_e^{1/n} \tag{4}$$

where q_e (mg g^{-1}) is the amount adsorbed at equilibrium; C_e (mg L^{-1}) is the equilibrium concentration; K_f [mg g^{-1}(L mg^{-1})$^{1/n}$] and n are Freundlich isotherm constants. The constant K_f is the measure of adsorption capacity and $1/n$ is the measure of adsorption intensity.

Fig. 5 shows the Langmuir and Freundlich adsorption isotherms of MB on SSC-0, SSC-1, SSC-2 and SSC-3. The adsorption of MB increased with the increase of equilibrium concentration. Table 2 shows the isotherm parameters and the regression values. From this result, all the regression values of Langmuir model were higher than that of the Freundlich model. It is indicated that the Langmuir model can give a better fit to the experimental data. The maximum adsorption capacities of MB on SSC-0, SSC-1, SSC-2 and SSC-3 were 23.8, 32.4, 46.3 and 65.9 mg g^{-1}, respectively. The maximum adsorption capacity was positively correlated with the content of CA12, which indicated that the addition of CA12 in sol–gel silica can improve its adsorption of MB. The adsorption capacity was higher than some other siliceous materials [28,29].

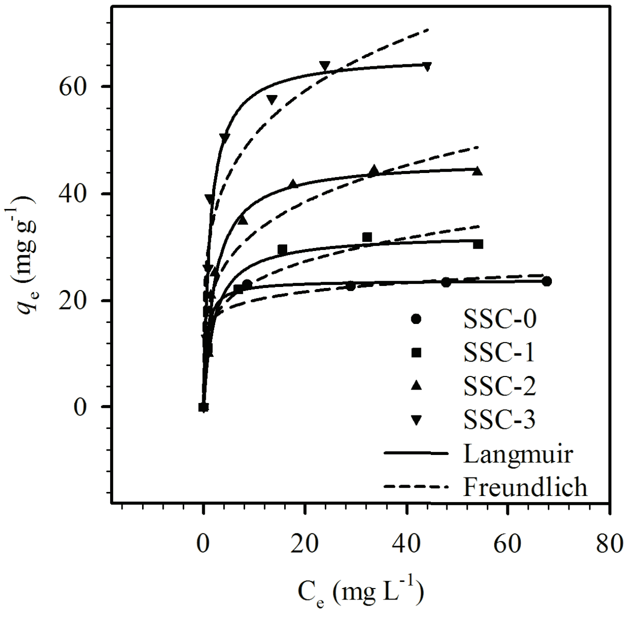

Fig. 5. The Langmuir and Freundlich adsorption isotherms of MB on SSC.

3.5. Adsorption thermodynamics

The effects of temperature on the adsorption of MB by SSC-0, SSC-1 and SSC-2 were studied in the temperature range of 298–313 K. The results are shown in Fig. 6. The adsorption amount of MB on SSC-0, SSC-1 and SSC-2 all increased with the rise of temperature, which indicated that the uptake of MB was favorable at higher temperature.

In order to better understand the effect of temperature on the adsorption of MB on SSC, the thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were determined. ΔG, ΔH and ΔS can be calculated from the following equations:

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

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

where T is absolute temperature (K), R is the gas constant (8.314 J mol^{-1} K^{-1}). K_c is the distribution coefficient, which is calculated as the ratio of MB equilibrium concentration in the adsorbents and aqueous phases.

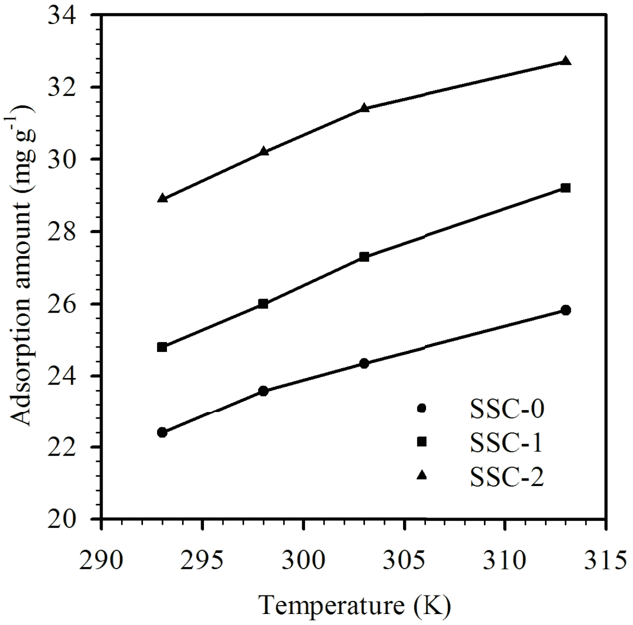

Fig. 6. The effect of temperature on the adsorption of MB by SSC.

Table 2
Adsorption isotherms constants for MB adsorption on SSC

Adsorbents	Langmuir model			Freundlich model		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_f [mg g^{-1}(L mg^{-1})$^{1/n}$]	$1/n$	R^2
SSC-0	23.8	1.669	0.998	15.6	0.11	0.965
SSC-1	32.4	0.48	0.983	14.4	0.21	0.956
SSC-2	46.3	0.47	0.988	19.0	0.24	0.930
SSC-3	65.9	0.79	0.974	30.6	0.22	0.905

Table 3
Thermodynamic parameters for the adsorption of MB on SSC

Adsorbents	Temperature (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
SSC-0	293	–1.79	19.22	71.69
	298	–2.14		
	303	–2.50		
	313	–3.21		
SSC-1	293	–2.56	34.22	125.54
	298	–3.19		
	303	–3.81		
	313	–5.07		
SSC-2	293	–4.35	80.06	288.08
	298	–5.79		
	303	–7.23		
	313	–10.11		

ΔH and ΔS can be obtained from the slope and intercept of the linear plot of $\ln K_c$ vs. $1/T$. ΔG can be calculated from Eq. (6). The thermodynamic parameters are given in Table 3. The positive values of ΔH indicated that the adsorption of MB on SSC was endothermic process. The negative values of ΔG indicated that the adsorption of MB on SSC was thermodynamically feasible and spontaneous. The positive values of ΔS corresponded to an increase in the degrees of randomness at the solid/liquid interface during the adsorption of MB on SSC. The absolute values of ΔG increased with the increase of temperature, which indicated that the adsorption becomes more feasible at high temperatures. At the same temperature, the absolute values of ΔG increased with the increase of the content of CA12 in SSC, which indicated that the adsorption becomes more feasible for SSC with high content of CA12.

4. Conclusions

A series of sol–gel silica doped with CA12 were prepared by sol–gel method with CA12 content of 0, 4.4%, 5.1% and 7.5% for SSC-0, SSC-1, SSC-2 and SSC-3, respectively. SSC was characterized by SEM and TGA and used for adsorption of MB from aqueous solution. With the increasing content of CA12, SSC has more pore structure, shorter equilibrium time and higher adsorption amount. The maximum adsorption capacities of MB on SSC-0, SSC-1, SSC-2 and SSC-3 were 23.8, 32.4, 46.3 and 65.9 mg g^{-1}, respectively. The Langmuir and Freundlich adsorption isotherm models were applied to the adsorption data of MB on SSC. The Langmuir isotherm was the best model to describe the experimental data. The adsorption kinetics of MB on SSC is well described by both the pseudo-first-order and pseudo-second-order kinetics models. The uptake of MB was favored at higher temperature. The thermodynamic parameters of negative values of ΔG and positive values of ΔH suggested the spontaneous and endothermic nature of the adsorption process.

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