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Adsorptive decolorization of methylene blue by crosslinked porous starch

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ABSTRACT

Crosslinked porous starch (CPS) was prepared by two steps. Native starch was crosslinked with epichlorohydrin and then CPS was prepared by hydrolyzing the crosslinked starch with α-amylase. As a biodegradable and safe adsorbent, CPS was used to remove methylene blue (MB) from the aqueous solution based on its characterizations, including surface area, pore volume and scanning electron microscopy (SEM). The results indicate that the adsorption capacity of CPS is much higher than native starch and relatively higher than porous starch. The effects of the initial concentration of MB, the time and temperature on the adsorption capacity were investigated. The pseudo-first-order kinetic model provides a better correlation of the experimental data in comparison with the pseudo-second-order model. The equilibrium adsorption data are well described by the Langmuir isotherm model with a maximum adsorption capacity of 9.46 mg g^{-1}. The adsorption of MB on CPS is endothermic and spontaneous in nature. The thermodynamics data are in good agreement with physical adsorption mechanism.

1. Introduction

Decolorization process is widely used in either wastewater treatment or manufacture of industrial products. Different technologies, such as biological treatments (An, Qian, Gu, & Tang, 1996; Kornaros & Lyberatos, 2006), advanced oxidation processes (Arslan & Balciolu, 1999; Galindo, Jacques, & Kalt, 2000), photocatalytic degradation (Konstantinou & Albanis, 2004; Sanghi & Bhattacharya, 2002), and adsorption (Annadurai, Juang, & Lee, 2002; Chiou & Li, 2003; Zacar & Sengil, 2005), can be used to decolor from aqueous solution. Among these techniques, adsorption is one of the techniques used to remove colorants from solution. Other technologies such as oxidation and degradation may cause secondary pollution. Adsorption technique for the removal of colorants has become more and more popular in the last few decades owing to its efficiency and the diversity of the adsorbents. Adsorptive decolorization is also widely used in food (Ozsoy & van Leeuwen, 2010; Qiu, Guo, & Chang, 2007), pharmaceuticals and cosmetics industries. More safe adsorbents are required to be used in these fields than in wastewater treatment. During recent years, starch-based adsorbents for dye removal focused particular attention on the development of biodegradable and safe adsorbents. Delval, Crini, Bertini, Filiatre, and Torri (2005) prepared crosslinked cationic starches using epichlorohydrin as a crosslinker in the presence of NH_4OH and found that these polymers exhibited interesting adsorption properties for dye. Ozmen, Sezgin, Yilmaz, and Yilmaz (2008) synthesized a starch-based polymer using hexamethylene diisocyanate as a crosslinker and found that the polymer presented high adsorption capacities toward Direct Violent 51. Guo, Li, Liu, Ma, and Zhang (2011) prepared water-insoluble starch sulfate to remove toluidine blue from aqueous solution and found that the maximum adsorption capacity from the Toth isotherm fitting is 26.56 mg g^{-1} and the adsorption process of toluidine blue on starch sulfate is exothermic in nature.

During the development of biodegradable and safe adsorbents, porous starch (PS) draws more and more interest due to its preparation without any toxic reagent. PS can be prepared by hydrolyzing raw starch with starch enzymes (α-amylase or amyloglucosidase) under the gelatinization temperature of starch (Yamada et al., 1995; Zhao, Madson, & Whistler, 1996). PS shows good adsorption performance for water, rape seed oil, ethanol and coffee oil due to its high surface area and porous structure (Yao & Yao, 2002). However, the structure of PS granules is not strong and stable, which is disadvantageous for PS to be used as an adsorbent.

With the aim to improve mechanical strength and the adsorption performance of PS granules, crosslinked porous starch (CPS) was prepared by two steps. Firstly, crosslinked starch was prepared by using epichlorohydrin as a crosslinker. Secondly, CPS was prepared by hydrolyzing the crosslinked starch with α-amylase. The porous morphology of CPS was observed with scanning electron microscope, and surface area and pore parameters of CPS were determined with surface area and porosity analyzer. Adsorptive decolorization performance of CPS was valued by using methylene

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blue (MB) as a model colorant. Investigations focused on adsorption mechanism, such as adsorption kinetics, adsorption equilibrium and adsorption thermodynamics.

2. Materials and methods

2.1. Materials

Corn starch (Zhucheng Xingmao Corn Developing Co., Ltd., food-grade) was dried at 105 °C before it was used. α-Amylase (Beijing Aoboxing Bio-Tech Co., Ltd.) was from *Bacillus subtilis* with a minimum activity of 4000 U g^{-1}. Methylene blue (MB) (analytic reagent grade) was obtained from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Epichlorohydrin, sodium sulfate, sodium dihydrogen phosphate, citric acid, and all other commercial chemicals were analytical reagent grade and used without further purification. All solutions and standards were prepared by using deionized water.

2.2. Preparation of crosslinked porous starch

Crosslinked starch was prepared by using epichlorohydrin as a crosslinker (Guo, Zhang, Ju, & Yang, 2006). Dried corn starch (40 g) was slurried in 250 mL water in a stirred glass kettle. Then, 0.8 g Na_2SO_4 and 0.2 g epichlorohydrin were added. The pH value of the slurry was adjusted to 10.5 with 0.1 mol L^{-1} NaOH, and the mixture was stirred for 3 h at 45 °C. Later on, the mixture was adjusted to pH 6 with 0.1 mol L^{-1} HCl. The slurry was subsequently washed with distilled water and 95% ethanol, and then filtered. The prepared crosslinked starch was dried and used for further chemical modification.

Crosslinked porous starch (CPS) was prepared by hydrolyzing the crosslinked corn starch with α-amylase (Yao & Yao, 2002). Dried crosslinked starch (40 g) and a certain amount of α-amylase were suspended in 80 mL buffer solution at pH 5.5 (0.2 M Na_2HPO_4, 0.1 M citric acid) and stirred at 60 °C for 24 h. Then the solution was adjusted to pH 7 with 0.1 mol L^{-1} NaOH, and subsequently filtered by suction. The precipitate was washed with distilled water three times, and then the product was dried in a vacuum-drier at 50 °C for 24 h. The cross-linking experiment itself was done once under the optimized conditions. Three crosslinked porous starches, named CPS1, CPS2 and CPS3, were prepared by using 0.2, 0.4 and 0.6 g α-amylase, respectively.

2.3. Characterization methods

A JEOL JSM-5610 LV scanning electron microscope (SEM) was used to investigate the morphology of CPS. The surface area of adsorbents was determined by using Surface Area and Porosity Analyzer (ASAP2020, USA).

2.4. Batch adsorption experiments

The adsorption experiments were carried out by the batch methods. The desired dose of CPS was added to 50 mL of aqueous MB solution in a series of 100 mL glass-stoppered Erlenmeyer flasks. The suspension was stirred on a magnetic stirrer at a uniform speed of 120 rpm in a constant temperature bath. After certain adsorption time, the suspension was filtered through 0.45 μm nylon membrane, and the concentration of MB in the supernatant solution was determined by using Shimadzu UV-VIS Spectrophotometer (UV-2550, Japan) at the maximum wavelength of 660 nm. The adsorption experiments for every adsorbent were repeated three times.

Table 1
Surface area and pore parameters (relative errors < 2%) for CPS samples.

Parameters	CPS1	CPS2	CPS3
Surface area			
Single point surface area at $p/p^0 = 0.20$ (m^2 g^{-1})	0.86	0.91	1.26
BET surface area (m^2 g^{-1})	0.91 ± 0.017	1.02 ± 0.014	1.74 ± 0.034
Pore volume			
Single point adsorption total pore volume of pores less than 80.95 nm diameter at $p/p^0 = 0.98$ (10^{-3} cm^3 g^{-1})	0.65	1.00	1.69
Pore size			
Adsorption average pore width (4V/A by BET) (nm)	2.87	3.42	3.89

The adsorption capacity was calculated from the following expression:

$$Q = \frac{(C_i - C_t)V}{m} \quad (1)$$

where Q is the adsorption capacity of the adsorbent (mg g^{-1}), C_i and C_t (mg L^{-1}) are the initial and terminal concentrations of MB in the adsorption solution, respectively, and V (mL) and m (mg) are the volume of the adsorption solution and the dose of the adsorbent, respectively.

3. Results and discussion

3.1. Characterizations of the adsorbents

The porous structure of crosslinked porous starch (CPS) granules can be observed from the SEM photographs. From Fig. 1, it can be seen that there are randomly distributed pores at the surface of CPS granules. The structure of starch granules was investigated by many people. Starch granules are part crystalline and part amorphous. As we all know, the amorphous regions of starch granules are preferentially degraded during the enzyme hydrolysis. The pores are formed when α-amylase degrades the amorphous regions of the starch granule. The more the α-amylase is, the more the pores in the starch granules are. So CPS3 granules contain the most pores among the three samples.

It should be noted that the results from SEM analysis were consistent with the results from surface area and pore size analysis, which are shown in Table 1. The BET surface area means needed gas quantity to cover the sample surface with a molecular layer and calculates surface area using Brunauer, Emmett and Teller (BET) theory. The surface area, pore volume and pore size of starch granules are increasing with the order of CPS1, CPS2 and CPS3. No active groups were introduced in the preparation process of CPS. The adsorption performance of CPS mainly depends on the porous structure. Generally speaking, the adsorption capacity is proportional to specific surface area. The adsorption performance of MB on CPS was thoroughly investigated in the following section.

3.2. Adsorption capacity comparison of starch, porous starch and CPS as adsorbents of MB

The starch molecules are crosslinked with epichlorohydrin via short-range interactions. The crosslinking effect can improve the mechanical properties and water stability of starch products (Reddy & Yang, 2010; Seker & Hanna, 2006). So crosslinking interaction can enhance mechanical strength of starch granules. But can the crosslinking interaction affect the adsorption capacity of porous starch? Experiments were carried out to study the effect. Every adsorption experiments were repeated three times. The relative errors of the repeated experiments' results were all less than 2.5%.

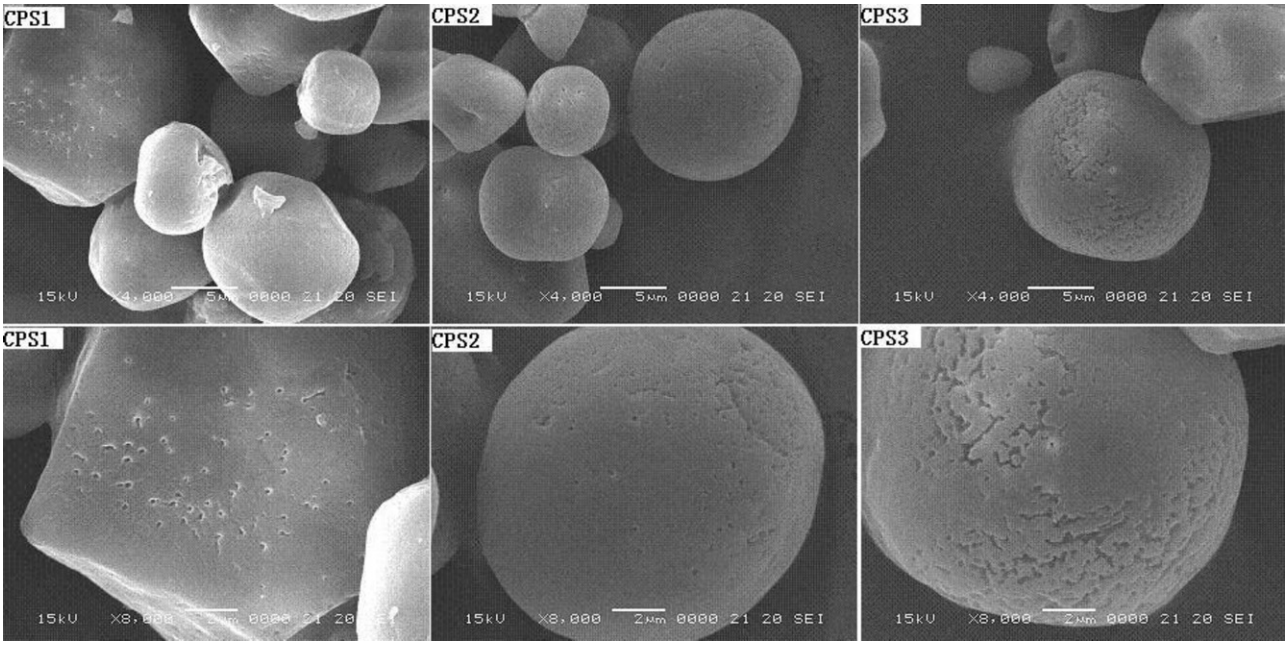

Fig. 1. SEM photographs of CPS samples.

The results showed that the adsorption capacities of MB on native starch, porous starch and CPS3 were 3.11, 7.26 and 8.33 mg g^{-1}, respectively, at the same conditions (C_i, 10 mg L^{-1}; temperature, 293 K; pH, 6.0; dose of adsorbents, 50 mg; adsorption time, 30 h). Porous starch and CPS were prepared at the same condition by using the same amount of starch and crosslinked starch as the materials respectively. It can be seen that CPS shows a much higher adsorption capacity than native starch and a relatively higher adsorption capacity than porous starch. The results indicate that crosslinking interaction may change into the structure of the starch granules and can improve the adsorption capacity of porous starch.

3.3. Adsorption kinetics of MB on CPS

Adsorption kinetic analysis is probably most important in adsorption system design. The adsorption kinetics relates to the change of adsorption capacity with time, so it is necessary to study the effect of contact time on the adsorption capacity of MB on CPS. As shown in Fig. 2, the adsorption capacity increased gradually with time, and the adsorption equilibrium was reached in about 30 h for three adsorbents. It is also indicated that the adsorption capacity of MB on CPS mainly depends on specific surface area. The adsorption capacity of MB increases with the increase in the specific surface area of CPS.

To investigate details of the adsorption processes of MB onto CPS, we analyzed the adsorption kinetics by using the pseudo-first-order equation (Lagergren, 1898) and pseudo-second-order rate equation (Ho, 1995), which are represented by Eqs. (2) and (3), respectively.

$$Q_t = Q_e(1 - e^{-K_1 t}) \quad (2)$$

$$Q_t = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t} \quad (3)$$

where Q_t (mg g^{-1}) is the adsorption capacity at any time t (h); K_1 and K_2, the pseudo-first-order rate constant (h^{-1}) and the pseudo-second-order rate constant (g mg^{-1} h^{-1}), respectively; Q_e, the equilibrium adsorption capacity (mg g^{-1}). The adsorption rate constant K_1 and K_2 can be determined by plotting of Q_t versus t by using the nonlinear regression analysis. Pseudo-first-order and pseudo-second-order plots are described in Fig. 2 as curves. The rate constants (K_1 and K_2), equilibrium adsorption capacities (Q_{e1} and Q_{e2}), the correlation coefficient (r^2), and root-mean-square error (RMSE) for each system were calculated and given in Table 2 along with equilibrium adsorption capacities from the experiments ($Q_{e\text{-exp}}$). The values of r^2 and RMSE indicate that both kinetic models well represent the adsorption of MB on CPS, and the pseudo-first-order model shows a little better fit of the experimental data compared with the pseudo-second-order model. Moreover, the equilibrium adsorption capacity calculated from the pseudo-first-order kinetic model fitting is nearer $Q_{e\text{-exp}}$ than it calculated from the pseudo-second-order kinetic model fitting.

Nonlinear fitting method is a more appropriate technique in predicting the adsorption kinetics than linear fitting method, especially involved in the pseudo-first-order kinetics (Kumar, 2006). Kumar and Sivanesan (2006) studied the adsorption of MB

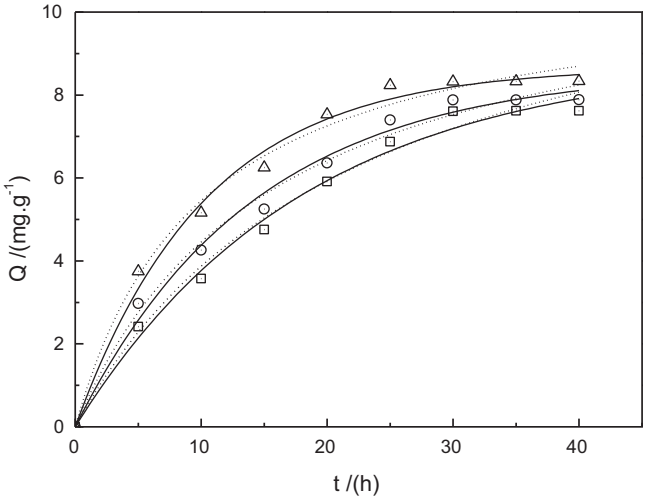

Fig. 2. Effect of the adsorption time on the adsorption capacities of MB on CPS and kinetic fitting curve (conditions: C_i, 10 mg L^{-1}; pH, 6.0; temperature, 293 K; dose of CPS, 50 mg): □, CPS1; ○, CPS2; △, CPS3; ––, pseudo-first-order; ……, pseudo-second-order.

Table 2
Pseudo first and second order kinetic parameters for the adsorption of MB on CPS.[a]

Sample	$Q_{e\text{-}exp}$ (mg g^{-1})	Pseudo first order				Pseudo second order			
		Q_{e1} (mg g^{-1})	K_1 (h^{-1})	r^2	RMSE	Q_{e2} (mg g^{-1})	K_2 (g mg^{-1} h^{-1})	r^2	RMSE
CPS1	7.63	8.90	0.055	0.9918	0.23	12.63	0.0035	0.9898	0.26
CPS2	7.90	8.61	0.071	0.9910	0.25	11.50	0.0055	0.9903	0.25
CPS3	8.35	8.67	0.097	0.9917	0.25	10.85	0.0093	0.9901	0.27

[a] Conditions: C_i, 2 mg L^{-1}; pH, 6.0; dose of CPS, 50 mg.

on activated carbon by using nonlinear fitting method and found that the adsorption process could be well represented by the pseudo first-order and pseudo second-order kinetics.

3.4. Adsorption equilibrium isotherm of MB on CPS

The adsorption isotherm is indispensable to reliably predict the adsorption capacities of different adsorbents. In the perspective, adsorption isotherms indicate how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Langmuir (1916) and Freundlich (1906) isotherms were widely used to examine the importance of different factors on dyes adsorption by a given adsorbent, and the two isotherms were used to describe the experimental data from the equilibrium adsorption of MB on CPS.

The nonlinear forms of Langmuir (1916) and Freundlich (1906) isotherms are generally expressed as:

$$Q_e = \frac{Q_m b C_e}{1 + bC_e} \quad (4)$$

$$Q_e = K_F {C_e}^{1/n} \quad (5)$$

where C_e and Q_e are equilibrium MB concentration (mg L^{-1}) and equilibrium adsorption capacity (mg g^{-1}), respectively; Q_m and b, the Langmuir constants representing the maximum adsorption capacity (mg g^{-1}) and adsorption energy (L mg^{-1}), respectively; K_F and $1/n$, the Freundlich constant (mg g^{-1}) and the Freundlich exponent, respectively. The parametric values of the respective isotherms were obtained by using nonlinear regression analysis, as shown in Table 3. The correlation coefficient (r^2) and root-mean-square error (RMSE) are also shown in Table 3. The plots for the Langmuir and Freundlich isotherms fitting of the experimental data are shown in Fig. 3 as curves.

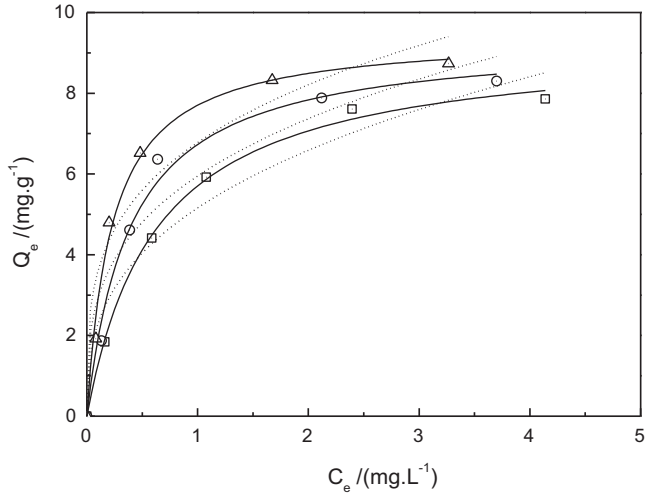

Fig. 3. Effect of the equilibrium concentration on the adsorption capacities of MB on CPS and adsorption equilibrium isotherms at 293 K (conditions: adsorption time, 40 h; pH, 6.0; dose of CPS, 50 mg): □, CPS1; ○, CPS2; △, CPS3; ––, Langmuir; . . . . ., Freundlich.

It is found that Langmuir equation represents a better fit than Freundlich equation according to the values of r^2 and RMSE under the experimental conditions. The maximum adsorption capacities of CPS1, CPS2 and CPS3 from Langmuir isotherm fitting are 9.29, 9.37 and 9.46 mg g^{-1}, respectively. The adsorption of MB on other adsorbents with high specific surface area and porous structure was also observed to obey the Langmuir equation well (Fernandes, Almeida, Debacher, & Sierra, 2010; Ma et al., 2010; Xiong et al., 2010; Yao, Xu, Chen, Xu, & Zhu, 2010).

3.5. Adsorption thermodynamic studies

The thermodynamics for the adsorption of MB on CPS3 was studied in the range of (293–313 K), and the influence of temperature on the adsorption under the optimized conditions is shown in Fig. 4(a). It can be found that there is a little increase for the equilibrium

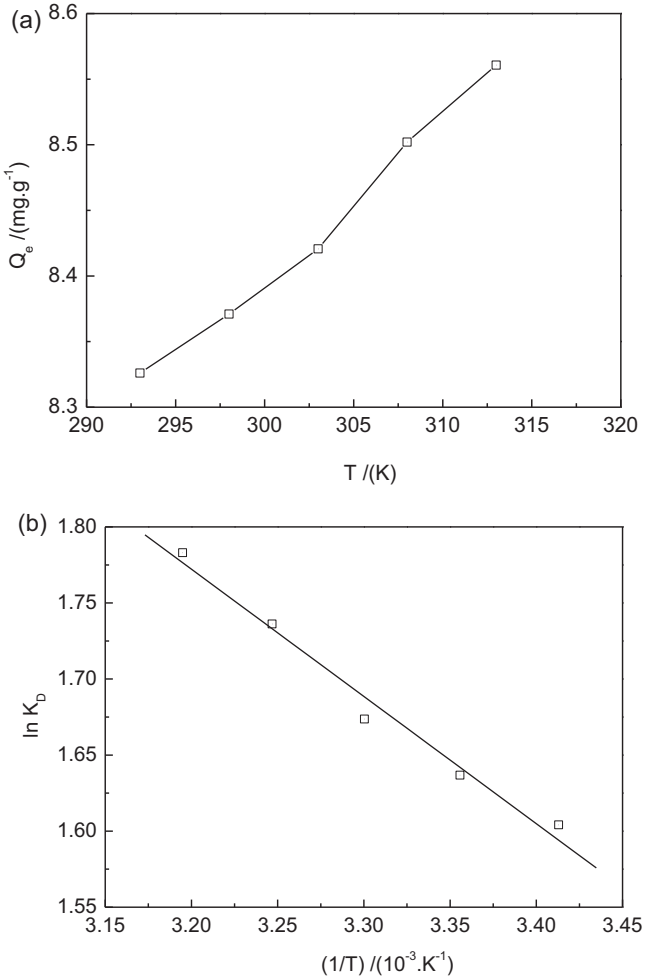

Fig. 4. (a) Effect of the temperature on the equilibrium adsorption capacity and (b) the plots of ln K_D versus $1/T$ for the adsorption of MB on CPS3 (conditions: C_i, 10 mg L^{-1}; adsorption time, 30 h; dose of CPS3, 50 mg; pH, 6.0).

Table 3
Langmuir and Freundlich parameters for the adsorption of MB on CPS at 293 K.[a]

Sample	Langmuir				Freundlich			
	Q_m (mg g^{-1})	b (L mg^{-1})	r^2	RMSE	K_F (mg g^{-1})	n	r^2	RMSE
CPS1	9.29	1.59	0.9977	0.14	5.16	2.84	0.9616	0.57
CPS2	9.37	2.55	0.9900	0.31	5.95	3.24	0.9346	0.78
CPS3	9.46	4.38	0.9929	0.28	6.78	3.62	0.9357	0.82

[a] Conditions: adsorption time, 40 h; pH, 6.0; dose of CPS, 50 mg.

Table 4
Thermodynamic parameters for the adsorption of MB on CPS3.[a]

T (K)	Q_e (mg g^{-1})	K_D (L g^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
293	8.33	4.97	−3.89		
298	8.37	5.14	−4.07		
303	8.42	5.33	−4.26	6.95	36.99
308	8.50	5.68	−4.44		
313	8.56	5.95	−4.63		

[a] Conditions: C_i, 10 mg L^{-1}; adsorption time, 30 h; dose of CPS3, 50 mg; pH, 6.0.

adsorption capacity with the temperature increase from 293 K to 313 K.

Thermodynamic parameters such as change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined by using the following equations (Reddy & Dunn, 1986):

$$K_D = \frac{Q_e}{C_e} \quad (6)$$

$$\ln K_D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

where K_D (L g^{-1}) is the distribution coefficient, Q_e (mg g^{-1}) and C_e (mg L^{-1}) are the adsorption capacity and MB concentration at equilibrium, respectively; T is the temperature in Kelvin, and R is the gas constant. ΔH and ΔS were obtained from the slope and intercept of the plot of ln K_D versus $1/T$ (Fig. 4(b)). Table 4 shows the calculated values of the thermodynamic parameters for the adsorption of MB on CPS3. The values of ΔG become more negative with increasing the temperature and the value of ΔH are positive, indicating that the adsorption process is more favorable at a higher temperature. The similar results were found in the adsorption studies of MB on peat (Fernandes et al., 2010) and carbon nanotube (Yao et al., 2010). The positive value of ΔS indicates that there is an increase in the randomness in the solid/solution interface during the adsorption process. In addition, the small values of ΔG are in the range of −20 to 0 kJ mol^{-1}, suggesting the adsorption of MB on CPS is a typically physical adsorption (Jaycock & Parfitt, 1981).

4. Conclusions

Crosslinked porous starch (CPS) was prepared via two steps. Crosslinked starch was prepared by using epichlorohydrin as a crosslinker and then α-amylase was used to hydrolyze the crosslinked starch. The results of surface area, porous volume and scanning electron microscopy (SEM) analysis show the porous structure of the CPS. As an adsorbent of methylene blue (MB), CPS shows a much higher adsorption capacity than native starch and a relatively higher adsorption capacity than porous starch. The adsorption kinetics of MB on CPS conforms to the pseudo-first-order model. The equilibrium adsorption data were well described by the Langmuir isotherm model with a maximum adsorption capacity of 9.46 mg g^{-1}. The ΔG values of the adsorption process become more negative with increasing temperature from 293 K to 313 K and all the values of ΔH are positive, which indicate that the adsorption process is endothermic in nature. The small values of ΔG within −20 to 0 kJ mol^{-1} reveal that the adsorption mechanism of MB on CPS is a typical physical adsorption. It is shown that CPS has the potential to act as a biodegradable and safe adsorbent of colorants in food, pharmaceuticals, cosmetics and pulp industries.

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