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Chemical Engineering Journal 117 (2006) 161–167

Chemical Engineering Journal

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Adsorption behaviors of acid and basic dyes on crosslinked amphoteric starch

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Received 29 April 2005; received in revised form 2 December 2005; accepted 13 December 2005

Abstract

Crosslinked amphoteric starch with carboxymethyl and quaternary ammonium groups is investigated as an adsorbent for removal of both acid and basic dyes in solution. Acid Light Yellow 2G, Acid Red G, Methyl Green and Methyl Violet were used to study the adsorption behaviors under various parameters such as pH, dose of amphoteric starches, initial dye concentration, adsorption time and adsorption temperature. At the preset pH value, the relationship between adsorption amount and the initial dye concentrations is given. The adsorption isotherm is discussed by modeling Langmuir and Freundlich isotherm. The kinetic study shows that the pseudo-second-order model fits the experimental data better. Also, the thermodynamic parameters are shown.

Keywords: Amphoteric starch; Acid dyes; Basic dyes; Adsorption

1. Introduction

Synthetic dyes in an effluent, even in a small amount, are highly visible and have undesired effects not only on the environment, but also on living creatures. In addition, most dyestuffs are stable to light and oxidizer, thus making physical adsorption a quite effective method for the removal of dyes from wastewater. Activated carbon, as an adsorbent has been widely investigated for the adsorption of basic dyes [1,2], but its high cost limits its commercial application. In recent years, there has been growing interest in finding inexpensive and effective alternatives to carbon. Such alternatives include clay minerals [3–5], weeds [6], fly ash [7,8] and Indian rosewood sawdust [9].

As a low-cost renewable, biodegradable biomass, starch has attracted considerable attention since it can be modified to remove heavy metal ions and dyes [10–13]. Cationic starches are reported as effective adsorbents for handling the dyes in wastewater. Ju studied the discoloration of cationic starch with a high degree of substitution (DS) for different kinds of negatively charged dye systems [14]. It was found that cationic starch with a higher DS had high adsorption capacity. Delvala et al. used crosslinked polysaccharides derivatives containing tertiary amine groups to recover various textile dyes in aqueous solutions [15]. The result shows that the presence of amino groups and the nature of the dye could influence the adsorption capacity.

In the previous work of our group, highly crosslinked amphoteric starches with a high degree of substituted cationic and anionic groups were synthesized by a semi-dry process. Also it has been indicated by us that crosslinked amphoteric starches, which contain carboxymethyl and quaternary ammonium groups can effectively remove the heavy metal anion Cr(VI) and the cations Cu(II), Pb(II) in aqueous solution [16–18]. These studies showed that amphoteric starch has a wide application perspective. It can quickly remove pollutants containing cationic or anionic groups, and hence lower the cost of disposal. Furthermore, amphoteric starch can be used across a wide pH range due to its peculiar electrical character. Until now there are only limited data on the adsorption of dyes onto amphoteric starch [19], so it is important to investigate different types of dyes using amphoteric starch as an adsorbent.

In this study, crosslinked amphoteric starch was used for removing anionic and cationic dyes in a range of systems (Scheme 1). The effects of various parameters such as pH,

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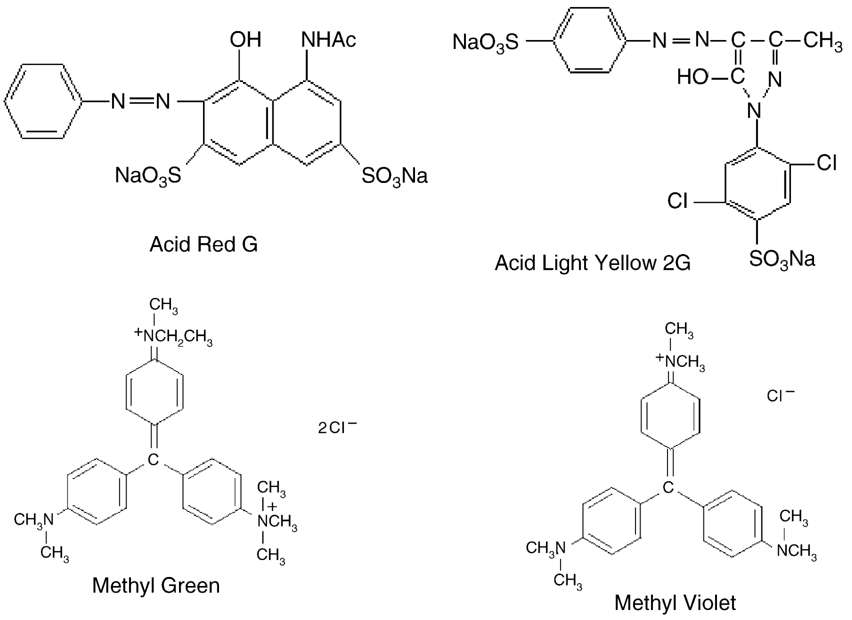
doi:10.1016/j.cej.2005.12.012



Scheme 1. The structures of acid and basic dyes used in this study.

adsorption time, the initial dye concentration and dose of adsorbents were investigated. The adsorption isotherms, as well as kinetic parameters were determined.

2. Experimental

2.1. Materials

Corn starch, food grade quality, from Hutubi factory (Xinjiang), dried at 105 °C before use. 3-Chloro-2-hydroxypropyltrimethylammonium chloride (prepared according to the previous work [20]), epichlorohydrin (Hubei University Chemical Co.), chloroacetic acid (Dianjin Yongda Chemical Co.), Acid Red G and Acid Light Yellow 2G (Rosi Chemical Co. Ltd.), Methyl Green (Model Factory, Shanghai) and Methyl Violet (Beijing Chemical Co.) were used as received.

2.2. Synthesis of crosslinked amphoteric starch

The method to prepare crosslinked amphoteric starch by semi-dry reaction was described in our previous work [14]. Ten grams of the crosslinked starch was first etherified by reacting with 7.2 g 65% 3-chloro-2-hydroxypropyltrimethylammonium chloride in a cylindrically shaped reactor with a mechanical stirrer. The percentage of water in the whole system was maintained at 25% and mixed evenly. The mixture was then reacted at 80 °C for 2.5 h. The resulting product was rinsed and neutralized with 80% ethanol solution containing hydrochloric acid and then dried. The dried product was carboxymethylated using a fixed dose of chloroacetic acid with 30% water in the whole reaction system at 45 °C. Nitrogen content and the DS of quaternary ammonium groups in the amphoteric starch were measured using the Kjeldahl method; the amounts and DS of carboxymethyl group were measured using the acid-wash method [21] and values calculated using Eqs. (1)–(3):

$$\mathrm{DS_{cation}} = \frac{162\mathrm{N\%}}{1400 - 152\mathrm{N\%}} \tag{1}$$

$$\mathrm{DS_{anion}} = \frac{162A}{1000 - 58A} \tag{2}$$

$$A = \frac{V_1C_1 - V_2C_2}{M} \tag{3}$$

N% is the nitrogen content, V_1 and V_2 are the volumes of NaOH solution and HCl solution (mL), respectively; C_1 and C_2 are the concentrations of NaOH solution and HCl solution (mol/L), respectively, and M is the weight of the sample (g).

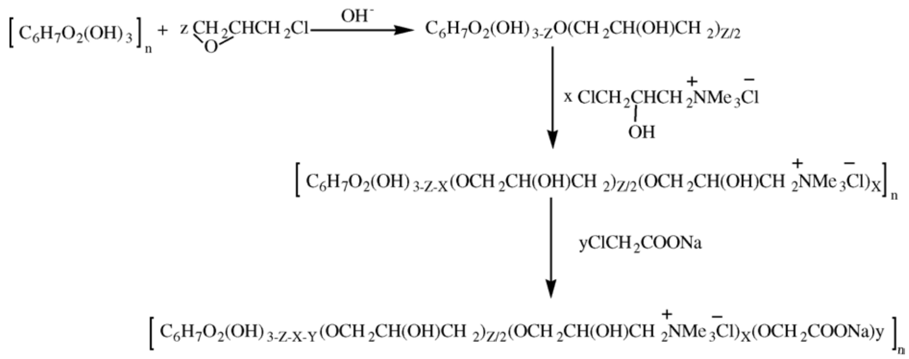
2.3. Adsorption procedure

The adsorption experiments were carried out in a series of Erlenmeyer flasks containing the desired dose of the crosslinked amphoteric starch and the 50 mL dyes aqueous solution at the desired concentration and initial pH (adjusted with dilute hydrochloric acid or 0.1 N NaOH, measured by LP115-pH meter) in a constant temperature bath. After shaking for a fixed time, the flasks were removed and the concentration of dyes after the adsorption was analyzed by spectrophotometer (Model 722, Shang Hai).

The amount of adsorbed dyes was calculated using the following equation:

$$Q = \frac{(C_0 - C_1) \times V}{m} \tag{4}$$

where Q is the amount of absorbed dyes (mg/g); C_0 and C_1 are the initial and residual concentration (mg/L), respectively; V is the volume of dyes aqueous solution (L); m is the dose of crosslinked amphoteric starch (g).



Scheme 2. The proposed reaction process for crosslinked amphoteric starch.

3. Results and discussion

The proposed reaction process is shown in Scheme 2, where $C_6H_7(OH)_3$ is anhydro glucose unit (AGU) in starch matrix; x is DS of cationic groups; y is DS of carboxymethyl groups; z is the amount of the crosslinker per AGU. The DS of cationic group in amphoteric starch is 0.3, and carboxymethyl group is 0.20 (denoted as CAS).

3.1. Effect of initial pH

Fig. 1 shows the effect of pH value on the adsorption of acid dyes by CAS. It is observed that the effective adsorption for two acid dyes took place under acidic condition. The adsorption process happens mainly because of static attractions between the sulfonate groups in the dye and ammonium groups in the adsorbents. Under acidic conditions, the carboxymethyl group exists mainly in the form of COOH, which screens static repulsion. Upon further increasing the pH value, the amount of adsorption can be maintained at relatively stable level over a wide range of pH due to coexistence of COOH and COO^-. However, it is noticed that the residual concentration of the Acid Red G decreases abruptly when the pH value is above 10. In a strongly basic condition, the negatively charged phenolic hydroxyl groups become potentially active sites and could be attracted by the ammonium groups in the absorbents. According to the investigation above, the following experiments for acidic dyes were carried out at pH 2.16. The adsorption behavior of basic dyes were investigated at pH 7.

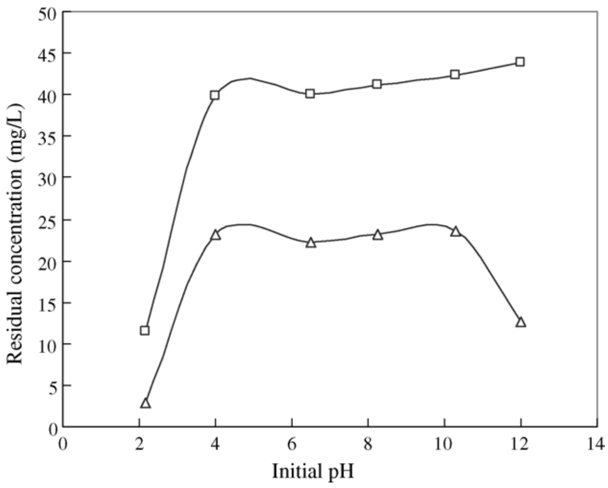


Fig. 1. Effect of initial pH on dye adsorption by crosslinked amphoteric starch. (□) Acid Light Yellow 2G; (△) Acid Red G ($C_{\text{Acid Light Yellow 2G}} = 65.2$ mg/L; $C_{\text{Acid Red G}} = 49$ mg/L; $T = 293$ K; $t = 2$ h; $m_{\text{CAS}} = 20$ mg).

3.2. Effect of the dose of absorbents

The residual concentrations obtained for various doses of adsorbent from 10 to 50 mg are shown in Fig. 2. The results show that the adsorption amount of four dyes, either acid or basic, decreased with the increasing dose of absorbents, until a level degree of adsorption was observed. The increase in dose appeared to promote more active sites, which facilitates the adsorption of dyes. However, along with the increase of dose, more repulsive groups are introduced to the system, which will interfere with the adsorption process. So the adsorption reaches equilibrium in a considerable dosage.

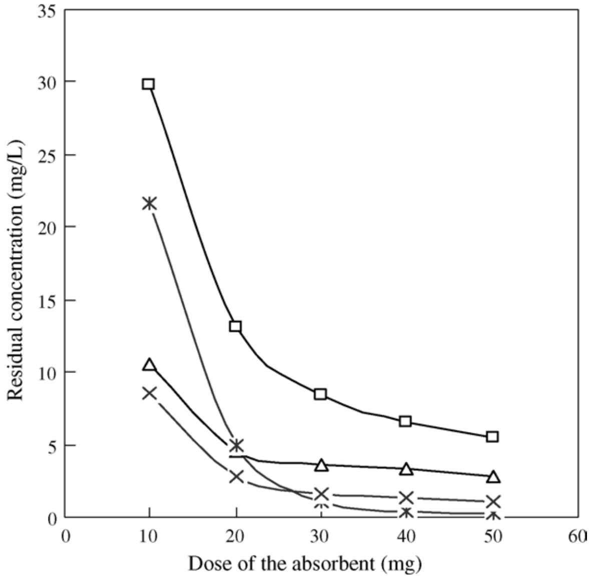


Fig. 2. Effect of dose of the absorbent on dye adsorption by crosslinked amphoteric starch. (□) Acid Light Yellow 2G; (△) Acid Red G; (✱) Methyl Green; (×) Methyl Violet ($C_{\text{Acid Light Yellow 2G}} = 65.2$ mg/L; $C_{\text{Acid Red G}} = 49$ mg/L; $C_{\text{Methyl Green}} = C_{\text{Methyl Violet}} = 50$ mg/L; $T = 293$ K; $t = 2$ h).

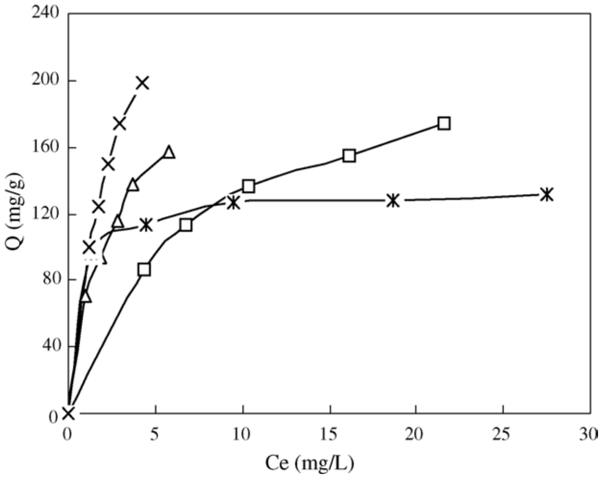


Fig. 3. Effect of initial dye concentration on dye adsorption by crosslinked amphoteric starch. (□) Acid Light Yellow 2G; (△) Acid Red G; (✱) Methyl Green; (×) Methyl Violet ($m_{\text{Acid Light Yellow 2G}} = m_{\text{Acid Red G}} = C_{\text{Methyl Green}} = C_{\text{Methyl Violet}} = 20$ mg; $T = 293$ K; $t = 2$ h).

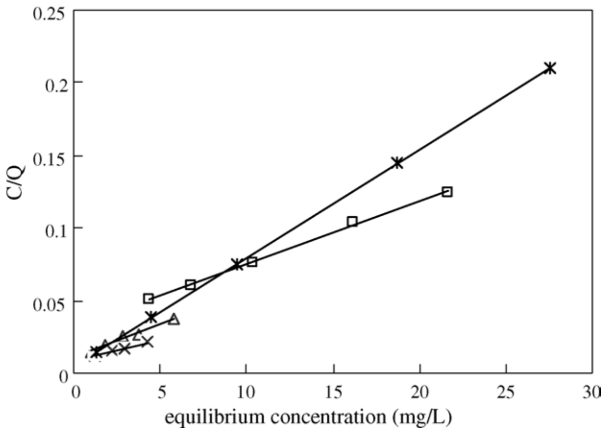


Fig. 4. Langmuir isotherm.

3.3. *Effect of initial dye concentration*

Fig. 3 shows the effect of the initial dye concentration on the adsorption. The Langmuir and Freundlich isotherm models [22] were used to study the adsorption isotherm.

The Langmuir adsorption isotherm can be expressed as a simple model (5) in which the attachment of adsorbate to the surface is represented:

$$\frac{C_e}{Q} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{5}$$

Freundlich adsorption isotherm (6) is also used to fit the experimental data:

$$\ln Q = n \ln C_e + \ln K \tag{6}$$

C_e is the equilibrium concentration of dye in the solution (mol/L), Q is the adsorption capacity (mg/g), Q_0 is the maximum capacity (mg/g) and b is the Langmuir constant (mg/L). K and n are the Freundlich constants. The Langmuir and Freundlich parameters are shown in Table 1. It is found that the adsorption isotherm can be explained using both the Langmuir and Freundlich models for low initial concentrations (Figs. 4 and 5). The adsorption amount reaches 174.1, 157.0, 131.2 and 198.9 mg/g, when the initial dye concentrations of Acid Light Yellow 2G, Acid Red G, Methyl Green and Methyl Violet are 91.3, 68.6, 80 and 80 mg/L, respectively. The experimental adsorption capacity is less than the maximum adsorption capacities. This is probably due to some unoccupied active adsorption sites left under the experimental concentration. The results show that the values of n for all four dyes are between 0.1 and 1, confirming that the adsorption process is favorable.

Table 1
Langmuir and Freundlich isotherm parameters for four dyes

Sample	Langmuir			Freundlich		
	b (L/g)	Q_0 (mg/g)	R_1	K	n	R_2
Acid Red G	0.43	217.39	0.9951	70.69	0.47	0.9960
Acid Light Yellow 2G	0.14	227.27	0.9989	48.47	0.42	0.9891
Methyl Green	1.56	133.33	0.9999	96.10	0.10	0.9708
Methyl Violet	0.35	333.33	0.9946	91.99	0.56	0.9927

3.4. *Effect of adsorption time*

As shown in Fig. 6, the residual concentrations level off over a short time scale, which implies that there are strong statistic interactions between sulfonate anion and positively charged ammonium groups in the amphoteric starch for acid dyes, or between ammonium cation and negatively charged carboxymethyl groups in the amphoteric starch for the basic dyes. Almost all the adsorptions reached equilibrium within 20 min.

To further analyze the experimental data two different models were used to investigate kinetic parameters for the adsorption process. The pseudo-first-order model (7) and pseudo-second-order model (8) are described as follows [23]:

$$\ln (Q_e - Q_t) = \ln Q_e - K_1 t \tag{7}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \tag{8}$$

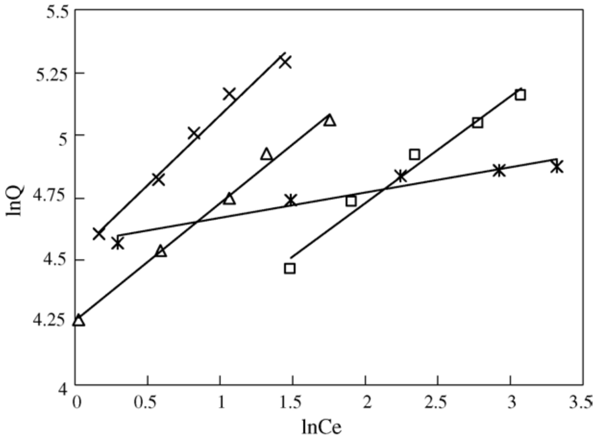


Fig. 5. Freundlich isotherm.

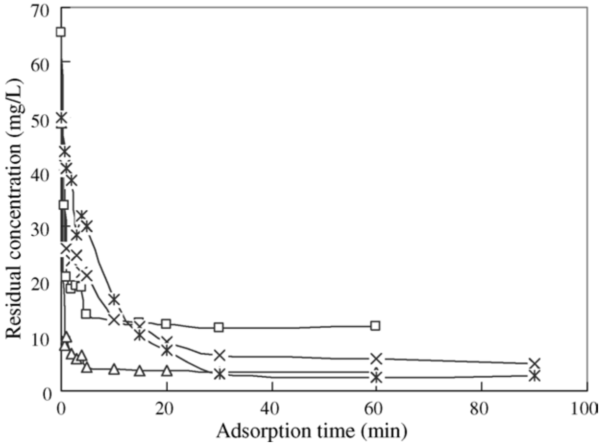


Fig. 6. Effect of adsorption time on dye adsorption by crosslinked amphoteric starch. (□) Acid Light Yellow 2G; (△) Acid Red G; (✱) Methyl Green; (×) Methyl Violet ($C_{\text{Acid Light Yellow 2G}} = 65.2$ mg/L; $C_{\text{Acid Red G}} = 49$ mg/L; $C_{\text{Methyl Green}} = C_{\text{Methyl Violet}} = 50$ mg/L; $m_{\text{Acid Light Yellow 2G}} = m_{\text{Acid Red G}} = C_{\text{Methyl Green}} = C_{\text{Methyl Violet}} = 20$ mg; $T = 293$ K; $t = 2$ h).

The intraparticle diffusion model [24] can be defined as:

$$Q_t = K_{\text{int}} t^{1/2}$$

where Q_e and Q_t (mg g^{-1}) are the adsorbed amounts at equilibrium and at time t, respectively; K_1 (min^{-1}), K_2 (g mg^{-1} min^{-1}) and K_{int} (mg g^{-1} min$^{-1/2}$) are the equilibrium rate constants for pseudo-first-order, pseudo-second-order and intraparticle diffusion.

The results show that both models have decent correlation coefficients ($R > 0.9$) and might be used to describe the experimental data. However, for the pseudo-first-order model, the adsorption capacity has an obvious gap between the experimental values and the calculated ones. Comparing to the pseudo-first-order model, the gap for the pseudo-second-order one is smaller. Furthermore, the higher correlation coefficient for the pseudo-second-order model suggests that the adsorption process can be better explained by a pseudo-second-order mechanism, indicating that the rate-limiting step is chemical adsorption [25]. The K_2 values for two acid dyes are higher than the ones for two basic dyes. This might be attributed to the special rigid structure caused by triphenylmethane groups in the dye molecules (Table 2).

3.5. *Effect of adsorption temperature*

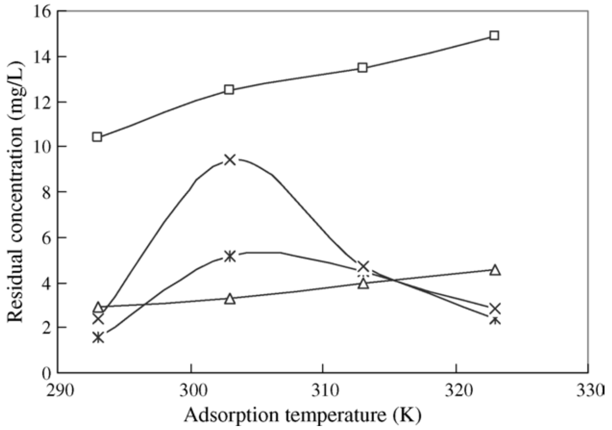


Fig. 7. Effect of adsorption temperature on dye adsorption by crosslinked amphoteric starch. (□) Acid Light Yellow 2G; (△) Acid Red G; (✱) Methyl Green; (×) Methyl Violet ($C_{\text{Acid Light Yellow 2G}} = 65.2$ mg/L; $C_{\text{Acid Red G}} = 49$ mg/L; $C_{\text{Methyl Green}} = C_{\text{Methyl Violet}} = 60$ mg/L; $m_{\text{Acid Light Yellow 2G}} = m_{\text{Acid Red G}} = 20$ mg; $C_{\text{Methyl Green}} = C_{\text{Methyl Violet}} = 30$ mg; $t = 2$ h).

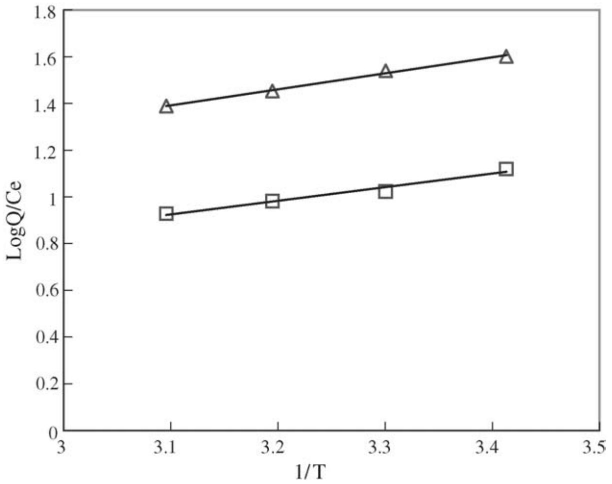


Fig. 8. Log(Q/C_e)–$1/T$ for Acid Light Yellow 2G and Acid Red G. (□) Acid Light Yellow 2G; (△) Acid Red G.

The adsorption behaviors of dyes on the adsorbents at different temperatures (varied from 293 to 323 K) are investigated (Fig. 7). The results show that the adsorption behaviors of acid dyes are different to the basic dyes. For acid dyes, the adsorption capacity at 293 K is higher than that of 323 K, which implies the adsorption process would be exothermic. To verify the conclusion, the curves of log(Q/C_e) versus $1/T$ for Acid Red G and Acid Light Yellow 2G are shown in Fig. 8. Since the relation between log(Q/C_e) and $1/T$ is linear, the changes of apparent enthalpy (ΔH^{θ}), entropy (ΔS^{θ}) are calculated using the Van't

Table 2
Kinetic parameters for four dyes

Sample	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion	
	K_1 (min^{-1})	Q_e (mg/g)	R_1	K_2 (mg mg^{-1} min^{-1})	Q_e (mg/g)	R_2	K_{int}	R_{int}
Acid Red G	0.14	12.79	0.9327	55.31	113.64	0.9999	4.53	0.9291
Acid Light Yellow 2G	0.16	25.28	0.9333	19.56	135.14	0.9996	7.62	0.9676
Methyl Green	0.10	66.61	0.9409	5.90	105.26	0.9952	14.96	0.9580
Methyl Violet	0.11	108.02	0.9886	1.41	128.21	0.9493	26.54	0.9888

Table 3
Thermodynamic values at various temperatures for Acid Red G and Acid Light Yellow 2G

Sample	Temperature (K)	ΔG^θ (kJ/mol)	ΔH^θ (kJ/mol)	ΔS^θ (J/mol K)
Acid Red G	293	−10.82	−12.59	−6.03
	303	−10.76		
	313	−10.70		
	323	−10.64		
Acid Light Yellow 2G	293	−7.41	−10.34	−9.99
	303	−7.31		
	313	−7.21		
	323	−7.11		

Hoff equation:

$$\log\left(\frac{Q}{C_e}\right) = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{2.303R} \tag{9}$$

The changes in free energy (ΔG^θ) are calculated using the thermodynamic equation:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \tag{10}$$

The values of ΔH^θ, ΔS^θ and ΔG^θ are shown in Table 3. The results indicate that along with the increase of temperature, the value of Q will increase. The adsorption process is exothermic because of the negative value of ΔH^θ. In addition, the negative values of ΔS^θ and ΔG^θ demonstrate that the adsorption process is a spontaneous process.

Unlike the two acid dyes no consistent trend was found for the two basic dyes, According to Fig. 7 the adsorptions for two basic dyes are exothermic below 303 K, and endothermic above 303 K. An explanation for this would be that exothermic static interaction is dominant below 303 K, while the endothermic hydrophobic interactions become dominant above 303 K. Three hundred and three Kelvin is the equilibrium point for these two interactions [26].

4. Conclusions

Crosslinked amphoteric starch containing quaternary ammonium and carboxymethyl groups was studied as a low-cost alternative adsorbent for removal of dyes. The results show that this adsorbent can be applied on both acid and basic dyes. For acid dyes, the active site are the quaternary ammonium groups, while for basic dyes, they are carboxymethyl groups. The adsorption processes are exothermic for acid dyes, which mean that low temperature will facilitate the adsorption, while the basic dyes have the highest adsorption capacity at 303 K. The relationship between adsorption amount and the initial dye concentrations are given. Both Langmuir isotherm and Freundlich isotherm models can be applied well in the experimental concentration. The kinetic study shows that the pseudo-second-order model fits the experimental data better.

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