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Effect of degree of substitution on adsorption behavior of Basic Green 4 by highly crosslinked amphoteric starch with quaternary ammonium and carboxyl groups

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Abstract

A series of crosslinked amphoteric starches with different degrees of substitution (DS) of carboxymethyl groups synthesized by a semi-dry process are investigated as an absorbent for removal of basic dye. Basic Green 4 is used to study the absorption behavior under various conditions, including initial pH of solution, dose of amphoteric starches, and dye initial concentration, adsorption time, adsorption temperature, and DS of carboxymethyl groups. The results show that adsorption amount of amphoteric starch is dependent of initial pH of dye solution, dose of absorbents and adsorption time. The adsorption capacity is affected strongly by the DS of carboxymethyl groups in the absorbents. 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.
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Keywords: Amphoteric starch; Basic dyes; Adsorption; Crosslinked

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. Attempts to find inexpensive and effective absorbents result in wide application of naturally occurring materials (Bilgic, 2005; Garg, Amita, Kumar, & Gupta, 2004; Inthorn, Singhtho, Thiravetyan, & Khan, 2004; Janos, Buchtova, & Ryznarova, 2003; Tsai, Chang, Lai, & Lo, 2005). As a low-cost, renewable and biodegradable biomass, starch has attracted considerable attention since it can be modified to remove heavy metal ions and dyes (Chan & Wu, 2001; Chan & Ferng, 1999; Kweon, Choi, Kim, & Lim, 2001). Cationic starches are reported as effective adsorbents for handling the dyes in wastewater (Ju, 2000). The result shows that the presence of cationic groups and the nature of the dye could influence the adsorption capacity.

In previous work, we have indicated that crosslinked amphoteric starches containing carboxymethyl and the quaternary ammonium groups can remove heavy metal anion Cr(VI) and cation Pb(II) from aqueous solution effectively (Xu et al., 2003; Xu, Feng, Peng, Wang, & Alayiding, 2005). These studies showed that amphoteric starch can quickly remove pollutants containing cationic or anionic groups, and hence lower the cost of disposal. Until now there are only limited data on the adsorption of dyes onto amphoteric starch (Wang, Xu, Wu, Wang, & Li, 2006), so it is important to investigate different types of dyes using amphoteric starch as an adsorbent.

In the present study, the adsorption behavior of basic dye Basic Green 4 is investigated in solution using highly crosslinked amphoteric starch containing quaternary

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ammonium and carboxymethyl groups as absorbents. The effects of DS of carboxymethyl groups are evaluated.

2. Experimental

2.1. Materials

Corn starch, food grade quality, from Hutubi factory (Xinjiang), was dried at 105 °C before use. 3-Chloro-2-hydroxypropyltrimethylammonium chloride (65% aqueous solution), epichlorohydrin (A.R), chloroacetic acid (A.R), and Basic Green 4 (indicator grade, its structure shown in Fig. 1) were used as received.

2.2. Synthesis of crosslinked amphoteric starch

The processes for preparing crosslinked amphoteric starch by semi-dry reaction were described in previous work (Xu, 2002). Nitrogen content and the DS of quaternary ammonium groups in the amphoteric starch were measured with the Kjeldahl method; the amount and DS of carboxymethyl group was measured with acid-wash method (Zhang, 1999).

2.3. Adsorption procedure

The adsorption experiments of this study were carried out in a series of Erlenmeyer flasks containing the desired dose of the crosslinked amphoteric starch and the 50 mL Basic Green 4 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 certain time, the tubes were removed and the concentration of dyes after the adsorption was analyzed by Spectrophotometer (Model 722, Shang Hai).

The amount absorbed was calculated using the following equation:

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

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

3. Results and discussion

The above reaction process can be proposed as the following Scheme 1.

Where $C_6H_7(OH)_3$ is anhydro glucose unit (AGU) on starch; x is DS of cationic groups; y is DS of carboxymethyl groups; z is the amount of the crosslinker per AGU. The structural parameters for three samples (denoted as CAS1, CAS2, and CAS3, respectively) are shown in Table 1 and structure of crosslinked amphoteric starch is proposed in Fig. 2.

3.1. The effect of pH

Fig. 3 shows the dye residual concentration varies with different DS of carboxymethyl group from pH 2 to 10. Contrary to the adsorption behaviors of acid dyes (Wang et al., 2006), the residual concentration decreases with the increasing pH value. Under acidic condition, carboxyl group is protoned as COOH since its pK is about 4.7, which weakens the electrostatic attraction between the

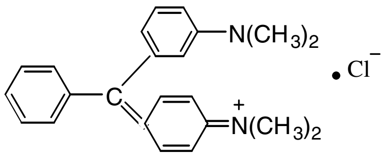
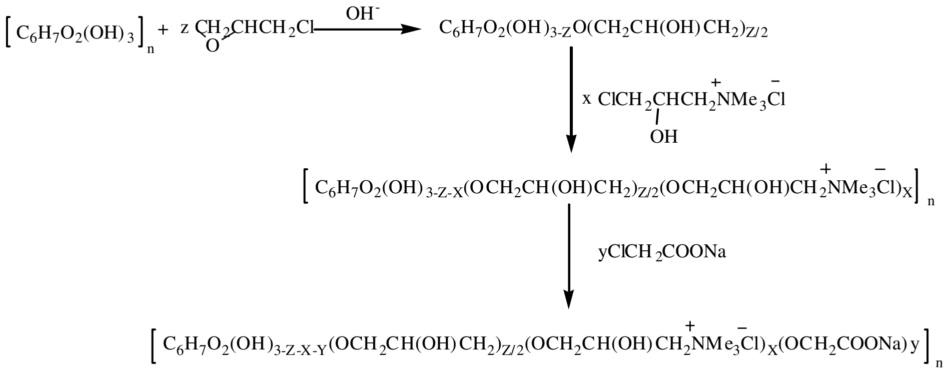


Fig. 1. The structure of Basic Green 4.

Table 1
Structural parameters for three amphoteric starches

Sample	x	y	z
CAS1	0.30	0.12	0.14
CAS2	0.30	0.20	0.14
CAS3	0.30	0.33	0.14



$$[C_6H_7O_2(OH)_3]_n + z\,\underset{O}{CH_2CHCH_2Cl} \xrightarrow{OH^-} C_6H_7O_2(OH)_{3\text{-}Z}O(CH_2CH(OH)CH_2)_{Z/2}$$

$$\downarrow x\,ClCH_2\underset{OH}{CH}CH_2\overset{+}{N}Me_3\overset{-}{Cl}$$

$$[C_6H_7O_2(OH)_{3\text{-}Z\text{-}X}(OCH_2CH(OH)CH_2)_{Z/2}(OCH_2CH(OH)CH_2\overset{+}{N}Me_3\overset{-}{Cl})_X]_n$$

$$\downarrow y\,ClCH_2COONa$$

$$[C_6H_7O_2(OH)_{3\text{-}Z\text{-}X\text{-}Y}(OCH_2CH(OH)CH_2)_{Z/2}(OCH_2CH(OH)CH_2\overset{+}{N}Me_3\overset{-}{Cl})_X(OCH_2COONa)_Y]_n$$

Scheme 1. The reaction process for crosslinked amphoteric starch.

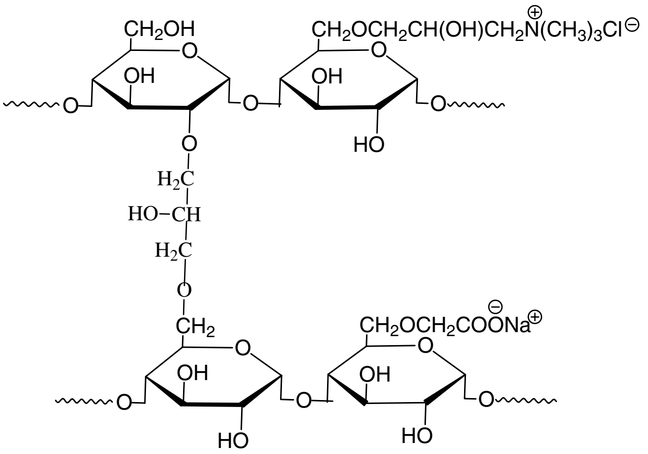


Fig. 2. The proposed structure of crosslinked amphoteric starch.

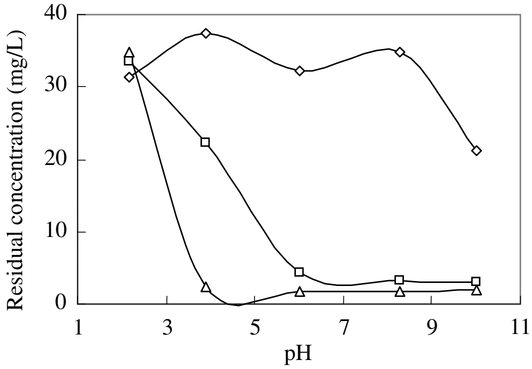


Fig. 3. Effect of pH on dye adsorption. (◇) CAS1; (□) CAS2; (△) CAS3. ($C_0 = 40$ mg/L; $T = 293$ K; $t = 2$ h; $m_{\mathrm{CAS1}} = m_{\mathrm{CAS2}} = m_{\mathrm{CAS3}} = 20$ mg).

ammonium groups of dyes and carboxymethyl groups in absorbents. Besides, the amount of adsorption shows a large difference among three absorbents with different DS of carboxymethyl groups. At pH 10, the residual concentration for CAS1, CAS2, and CAS3 are 21.1, 3.1, and 2.0 mg/L, respectively, thus the higher DS leads to higher amount of adsorption.

3.2. Effect of dose of absorbents

The residual concentration of the dye after treatment of doses of absorbent ranging from 10 to 50 mg to an initial concentration of 40 mg/L Basic Green 4 at 20 °C are shown in Fig. 4. It is clearly observed that the adsorption proceeds effectively at a larger dose. The increase in dose appears to promote more active sites, which facilitates the adsorption of dyes. However, with increasing dose, more ammonium groups as repulsive sites are introduced, hence interfering with the adsorption process. When the dose is 20 mg, the absorbents CAS2 and CAS3 show effective adsorption with residual concentrations of 4.6 and 1.9 mg/L, respectively.

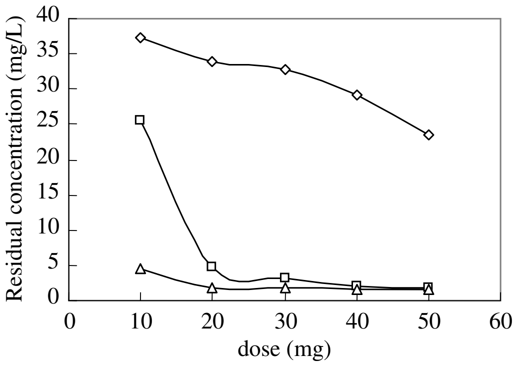


Fig. 4. Effect of the dose of absorbents on dye adsorption. (◇) CAS1; (□) CAS2; (△) CAS3. ($C_0 = 40$ mg/L; $T = 293$ K; $t = 2$ h; pH 2.10.)

3.3. Effect of dyes initial concentration

Fig. 5 shows the dependence of the residual concentration on the dyes initial concentration. The adsorption capacities of CAS2, CAS3 in experiment are calculated and give a value of 101.7, 141.9 mg/g, respectively, which is less than the theoretical values (225.0, 337.5 mg/g correspondingly) at 60 mg/L dye initial concentration. It could be interpreted that, under a lower initial concentration, some active adsorbed sites remain unoccupied, thus leading to an unsaturated adsorption. However, for CAS1, the adsorption capacity is only 17.8 mg/g at 12 mg/L initial concentration, far less than the theoretical value 135.0 mg/g. An explanation is that surplus positive charges in CAS1 shield the attraction between carboxymethyl groups in the amphoteric starch and ammonium groups in the dyes. Unlike the adsorption behavior of Pb(II) (Xu et al., 2005), the big gap between experimental and theoretical capacity for Basic Green 4 is found partly due to the large size of dye molecule.

3.4. Adsorption isotherm and kinetics

CAS3 is chosen to investigate the adsorption isotherm and kinetics concerning its good adsorption ability. Langmuir isotherm and Freundlich isotherm model are tested to

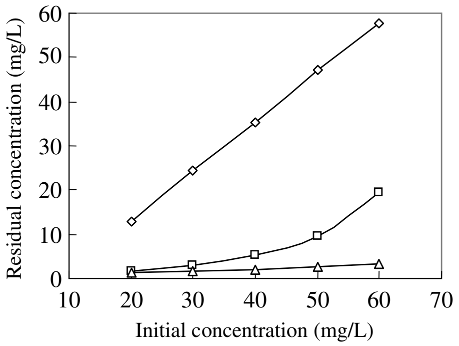


Fig. 5. Effect of dye initial concentration on dye adsorption. (◇) CAS1; (□) CAS2; (△) CAS3. (pH 2.10; $T = 293$ K; $t = 2$ h; $m_{\mathrm{CAS1}} = m_{\mathrm{CAS2}} = m_{\mathrm{CAS3}} = 20$ mg.)

fit the experimental data. They can be described as follows, respectively:

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

$$\ln Q = n \ln C_e + \ln K,$$

where 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 best fit for CAS3 is achieved using the Freundlich isotherm model (seen in Table 2).

The residual concentration of the dyes onto CAS3 for adsorption times ranging from 0.5 to 120 min at 20 °C is shown in Fig. 6. Two different models are used to investigate kinetic parameters for the adsorption process (seen in Table 3). The pseudo-first-order model and pseudo-second-order model are described as follows, respectively (McKay & Ho, 1998):

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t,$$

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

The rate parameter of intraparticle diffusion (Nassar & Magdy, 1997) can be defined as

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

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

Table 2
Freundlich isotherm parameters

Sample	Freundlich isotherm equation	K	n	r
CAS3	$y = 1.1369x + 3.6842$	39.8	1.1369	0.9867

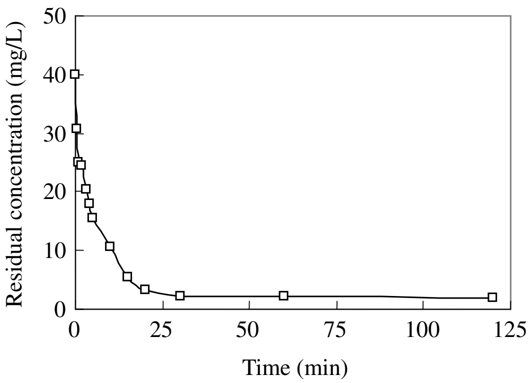


Fig. 6. Effect of adsorption time on dye adsorption. (pH 2.10; $T = 293$ K; $C_0 = 40$ mg/L; $m_{CAS3} = 20$ mg.)

Both linear plots of the t/Q_t against t and $\ln(Q_e - Q_t)$ against t shown in Table 3 have a linear correlation coefficients higher than 0.99. But the experimental adsorption capacity is not equal to the theoretical value when the pseudo-first-order is used, while it is almost equal in the pseudo-second-order model. Thus this reveals the applicability of this kinetic equation and the pseudo-second-order nature of the adsorption of Basic Green 4 on CAS3.

3.5. Effect of temperature

Fig. 7 is given by plotting the residual concentrations against adsorption temperature (20–50 °C). An upward-shape curve is shown, which implies that the adsorption process is exothermic. To certify the conclusion, Q/C_e is plotted against $1/T$ (Fig. 8) to give ΔH^θ, ΔS^θ according to the equation as follows:

$$\lg \frac{Q}{C_e} = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{2.303R}.$$

The change of apparent enthalpy (ΔH^θ), free energy (ΔG^θ), and entropy (ΔS^θ) are calculated using the relationship below and listed in Table 4:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta.$$

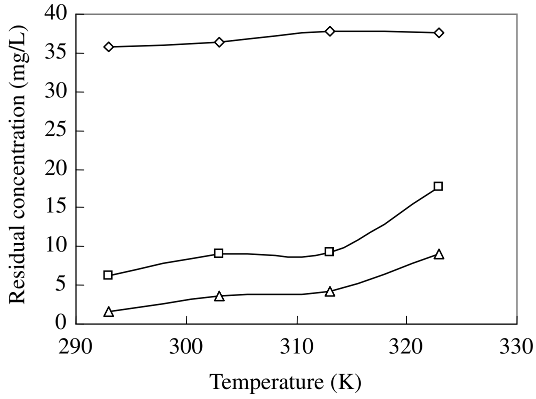


Fig. 7. Effect of adsorption temperature on dye adsorption. (◇) CAS1; (□) CAS2; (△) CAS3. (pH 2.10; $t = 1$ h; $m_{CAS1} = m_{CAS2} = m_{CAS3} =$ 20 mg; $C_0 = 40$ mg/L.)

Table 3
Kinetic parameters for Basic Green 4

Sample	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion	
	K_1 (min^{-1})	R_1	ΔQ_1 (mg/g)	K_2 (g mg^{-1} min^{-1})	R_2	ΔQ_2 (mg/g)	K_{int}	R_{int}
CAS3	0.1319	0.9926	23.21	4.24×10^{-3}	0.9903	1.70	20.01	0.9787

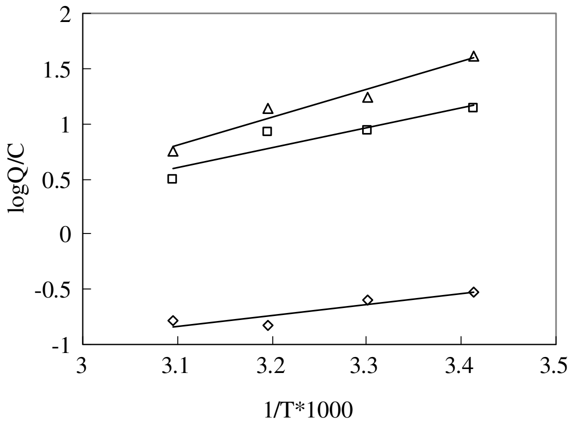


Fig. 8. Logarithm of absorption capacity to equilibrium concentration as a function of adsorption time.

Table 4
Thermodynamic parameters of crosslinked amphoteric starches for Basic Green 4

Absorbents	Temperature (°C)	Capacity *Q* (mg/g)	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
CAS1	20	104.75	2.99	−18.25	−72.50
	30	104.52	3.71		
	40	100.73	4.44		
	50	98.32	5.17		
CAS2	20	103.60	−6.55	−34.85	−96.60
	30	102.99	−5.58		
	40	98.78	−4.61		
	50	94.75	−3.64		
CAS3	20	99.80	−8.95	−48.48	−134.91
	30	98.88	−7.60		
	40	95.45	−6.25		
	50	90.36	−4.90		

It can be observed that the residual concentration increases as the temperature increases. The negative values of ΔH^0 indicate that the adsorption of Basic Green 4 is an exothermic process, which is facilitated at lower temperature. The negative ΔG^0 for CAS2 and CAS3 shows the spontaneous nature of the process.

4. Conclusions

The crosslinked amphoteric starches with ammonium groups (DS = 0.30) and carboxymethyl groups with different DS (0.12, 0.20, and 0.33 for CAS1, CAS2, and CAS3, respectively) are prepared for the adsorption of Basic Green 4. The adsorption capacity is affected strongly by the DS of carboxymethyl groups in the absorbents. The adsorption capacity for CAS3 achieves 141.9 mg/g at pH 2.1, the dose of 40 mg, and the dye initial concentration of 60 mg/L. The adsorption follows Freundlich isotherm and pseudo-second-order kinetic model. The thermodynamics data shows the process is exothermic, and spontaneous at room temperature.

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