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Acyclic polyamine modified starch for amido black 10B removal in basic solution

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ABSTRACT

Four acyclic polyamine modified starches, CAS1, CAS2, CAS3 and CAS4 were synthesized by using ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine, respectively. Their interactions with amido black 10B in aqueous solution at pH value of 10 were investigated. It was found that the adsorption was predominantly governed by hydrogen bonding. The removal process of AB10B increased smoothly and followed the pseudo-second-order equation. The Langmuir isotherm gave satisfying fits to equilibrium data and the capacities followed the order CAS2 > CAS1 > CAS3 > CAS4. The thermogravimetric analyses indicated the fact that the interaction of CAS2 with amido black 10B was strongest, bringing on the highest adsorption capacity. In the presence of NaCl, the capacties increased slightly.

Keywords: Acylic polyamine; Modifed starch; Amido black 10B; Adsorption; Thermogravimetry

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1. Introduction

With the development of textile and related industries, dyeing effluents cause serious environmental problem [1]. As a consequence, the treatment of dyeing effluents is of major concern. Several treatment technologies for dye removal have been investigated extensively, such as chemical oxidation [2], photodegradation processes [3], and activated sludge [4]. Such methods often suffer from high cost and low effect because many dye contaminants are stable to light, heat and oxidizing agents. By using techniques that change or destroy the dye chromophore, fragments (i. e. primary aromatic amine and phenol) are always produced remaining in effluents. Comparatively, adsorption of dye molecules onto a sorbent can be a very effective and low-cost method [5,6]. Adsorption processes have long been studied and recognized as one of the most important techniques [7]. Proper selection of adsorbent used in the adsorption procedure will produce high-quality treated effluents. In 2004, natural polysaccharides are employed to remove acid dyes from aqueous solutions [8]. Amongst numerous polysaccharides starch is an abundant, inexpensive, renewable and fully biodegradable natural raw material [9]. However, its application in environmental engineering is limited due to its poor physical properties (mechanical properties, dimensional stability and so on). To improve it, crosslinking reaction is applied to acquire insoluble, high surface and stable modified starch [10]. Furthermore functional group such as citrate or quaternary ammonium, is grafted onto the cross-linked starch, which enhances affinity with dyes [11,12]. But the acyclic polyamine modified cross-linked starch for adsorption of dye molecules is neglected, particularly the mechanism of interaction is unclear. Additionally, many experiments were carried out in acidic solutions. However, many dyeing effluents are typically basic [13]. Studies concerning the adsorption of dyes in acidic conditions could not well meet the requirements of treatment of basic dyeing effluents. It deserves to study the interaction of dyes with various sorbents in basic

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solution. In this paper, ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine are grafted onto cross-linked starch, respectively. The purpose is to investigate their interactions with acid dye (amido black 10B) in basic solutions, in an attempt to find out the relation between adsorption ability and properties of acyclic polyamine.

2. Experimental Section

2.1. Materials

Commercial maize starch, of food grade quality, was used in this research. Amido black 10B (AB10B) was purchased from Sigma chemical company and used as received. It is a widely used azo dye (Fig. 1) and regarded as a typical contaminant in the discharged effluent [14,15]. Epichlorohydrin, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine and other routine reagents were analytical grade. They were used without any further purification process.

2.2. Preparation of cross-linked amino-starch (CAS)

The synthesis of cross-linked amino-starch was according to literature [16]. First the cross-linked starch (CS) was synthesized by reacting 100 g maize starch with 8.0 mL epichlorohydrin (ECH) in 200 mL dilute NaOH solution (0.16 mol L^{-1}) under 25°C. After 18 h, the pH was adjusted to 6–7 and the CS was separated from solution. Then the intermediate, 3-chloro-2-hydroxypropyl cross-linked starch (CHCS) was prepared from 25 g of dried CS with ECH in the presence of $HClO_4$ (the molar ratio was CS: ECH:$HClO_4$= 1:2.5:0.03). The dried CHCS further reacted with acyclic polyamine to produce cross-linked amino-starch (CAS) in basic solution under 60°C for 8 h. The product was washed with deionized water, dilute HCl solution, dilute NaOH solution and acetone in sequence. The acquired CAS was kept in a vacuum oven for 1 day and stored in desiccators. CAS1, CAS2, CAS3 and CAS4 were synthesized using ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine, respectively. The nitrogen content was measured on a Vario EL III elemental analyzer. The proportions of nitrogen are 0.81, 0.96, 1.27, 1.51% for CAS1, CAS2, CAS3 and CAS4, respectively.

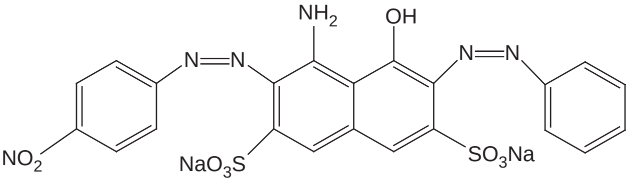

Fig. 1. Chemical structure of amido black 10B (C. I. 20470).

2.3. Equipment

The concentration of AB10B in aqueous solution was determined using a Agilent 8453 UV-Vis spectrophotometer. The absorbance was measured over a range from 300 to 800 nm. Absorbance values at the wavelength of maximum absorbance (λ_{max}= 620 nm) were recorded, and AB10B solution was initially calibrated for concentration in terms of absorbance units. Thermogravimetric analysis was performed with STA 409 PC/4/H Luxx at a heating rate of 10°C per minute under N_2 atmosphere.

2.4. Sorption experiments

Sorption experiments were performed by the batch technique. The amount of CAS used in each flask is 0.0500 g. The solution pH was monitored and kept constant by using dilute NaOH. For kinetic studies, a series of 100 mL conical flasks were employed. The concentration of AB10B was fixed at 0.6488 mmol L^{-1} and the volume of solution was 75 mL. The pH of the solution was adjust to 10. Then the flasks were agitated in the thermostatic shaker bath at 25±1°C. The concentration of each dye was measured at different time intervals up to 200 minutes. Each data point was obtained from an individual flask, therefore no correction due to withdrawn sampling volume was necessary. The results were then used to determine each dye loading on CAS applying equation (1):

$$q_t m=(c_0-c_0)V \tag{1}$$

where q_t is the dye concentration in solid phase at time t (mmol g^{-1}), m is the mass of CAS used (g), c_0 is the initial dye concentration in the liquid phase (mmol L^{-1}), c_t is the dye concentration in the liquid phase at time t (mmol L^{-1}), and V is the total volume of solution used (L).

For equilibrium sorption studies, a fixed mass of CAS (0.0500 g) was weighed into flasks and contacted with 50 mL of AB10B solutions with predetermined initial concentrations (varied from 0.4866 mmol L^{-1} to 1.6221 mmol L^{-1}). The pH of the solutions was 10. Then the flasks were sealed and agitated for 6 h at 200 rpm in the thermostatic shaker bath. The temperature was maintained at 25±1°C. After filtration, the concentrations of AB10B solutions were determined, and the amounts of dye sorbed were calculated using the mass balance. The models of kinetics and isotherms were fitted by employing a nonlinear method, using the nonlinear fitting facilities of the software Microcal Origin 7.0.

Usually, a certain amount of inorganic salt is used in the dyeing processes [17]. To understand the effect of inorganic salts on adsorption efficiency of sorbents, further experiments were conducted in the presence of 0.001 mol L^{-1} NaCl as the background electrolyte. For these experiments, a fixed mass of 0.050 g CAS was added into a 0.6488 mmol L^{-1} AB10B solution (V = 75 mL) at pH 10. After shaking for 6 h, the concentration of AB10B left in solution was measured.

3. Results and discussion

3.1. Sorption kinetics

To evaluate the effectiveness of the adsorbate, studies on kinetics of adsorption processes are necessary. A simple kinetic analysis of adsorption is the pseudo-first-order equation [18] in the form

$$q_t = q_e(1-e^{-k_1 t}) \quad (2)$$

A pseudo-second-order equation [19] was also tested on the experimental data. The kinetic rate equation is

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

and the initial sorption rate h (mmol·g^{-1}·min^{-1}) is

$$h = k_2 q_e^2 \quad (4)$$

where q_t is the amount of dye on the sorbent (mmol·g^{-1}) at any time t (min), q_e is the amount of dye absorbed at equilibrium (mmol·g^{-1}), k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and k_2 is the rate constant of pseudo-second-order adsorption (g·mmol^{-1}·min^{-1}).

The applications of the two models fitting to experimental data are shown in Figs. 2 and 3, respectivley. The constants determined from the experimental data and the correlation coefficients (R^2) are list in Table 1. As can be seen from the kinetic curves that the AB10B removals smoothly increase with time and the equilibria are achieved after 150 minutes. Compared to pseudo-first-order equation, the pseudo-second-order equation gives well fits to experimental results. The sorption rate follows the sequence CAS1 > CAS2 > CAS3 > CAS4. The rates of adsorption of AB10B on CAS1 and CAS2 are rapid in the beginning and over 80% of the ultimate adsorption occurs within 30 minutes. CAS4 shows a slowest adsorption rate for AB10B uptake and a lower removal efficiency than the others.

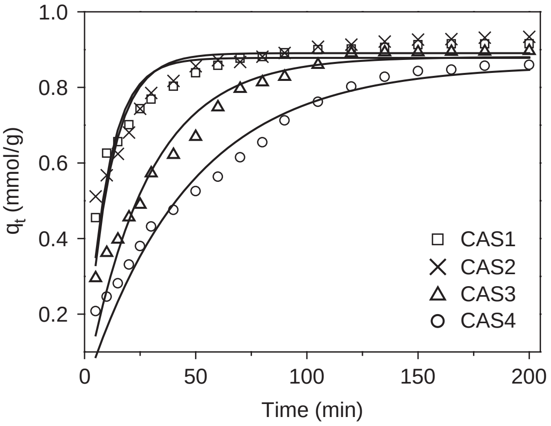

Fig. 2. Kinetics of AB10B adsorption onto various CAS for an initial concentration of 0.6488 mmol L^{-1}. Lines represent modeled results using the pseudo-first-order equation.

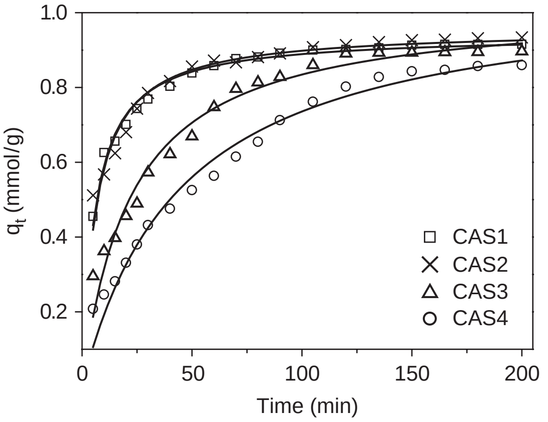

Fig. 3. Adsorption kinetic data fitted to the pseudo-second-order equation. Lines represent modeled results using the pseudo-second-order equation.

Table 1
Parameters of kinetic models for AB10B adsorption onto various CAS.

Sorbent	Pseudo-first-order k_1(min $^{-1}$)	R^2	Pseudo-second-order k_2 (g·mmol^{-1} min^{-1})	h(mmol g^{-1} min^{-1})	R^2
CAS1	0.102	0.857	0.180	0.160	0.986
CAS2	0.092	0.813	0.164	0.149	0.956
CAS3	0.036	0.933	0.044	0.046	0.971
CAS4	0.021	0.956	0.020	0.023	0.977

3.2. Sorption isotherm and mechanism

Adsorption isotherms describe how adsorbates interact with adsorbents. It is of importance in understanding the adsorption mechanism and optimizing the use of adsorbents. The Langmuir isotherm was used to fit the experimental data. The well-known Langmuir isotherm was originally proposed to describe the adsorption of gas molecules onto metal surfaces [20]. The model assumes uniform energies of adsorption onto the surface and no migration of adsorbate in the plane of surface. Moreover the Langmuir adsorption isotherm has successfully applied to many other real sorption courses of monolayer sorption [21], and it is written as

$$q_e = \frac{abc_e}{1 + bc_e} \tag{5}$$

where q_e is the adsorbed amount of the dye at equilibrium (mmol g^{-1}), c_e is the adsorbate concentration at equilibrium in aqueous solution (mmol L^{-1}). The Langmuir isotherm parameters are a and b. The capacity of the adsorbent can be evaluated by a, and the parameter b includes various physical constants [22].

The results show that the Langmuir isotherm gives satisfying fits to the experimental data (Fig. 4). It can be seen from Table 2 that the adsorption capacities of different CAS are in the order CAS2 > CAS1 > CAS3 > CAS4. In the case of basic solution at pH 10, the equilibrium would favor the unprotonated form of CAS and AB10B with almost complete exclusion of the protonated form, suggesting that additional mechanisms of interaction were in operation other than electrostatic attraction. Both CAS and AB10B have multi functional groups like amines and hydroxyls, resulting in strong tendency to form hydrogen bonds. Some researchers have reported the formations of hydrogen bonding between chitosan/cellulose and acid dyes in basic solutions [8,23]. Therefore, the interaction mechanism is predominantly based on hydrogen bonding, and the dye adsorption efficiency is related to the total number of active sites available on the polymer surface. It can be observed that the four macromolecules have very similar structure, but difference in the content of nitrogen. The CAS2 has a higher adsorption efficiency than CAS1 mostly due to more amines available, which can form much firmer hydrogen bonds with AB10B. However, the capacity decreases with the order CAS2 > CAS3 > CAS4 although the nitrogen content increases in the sequence CAS2 < CAS3 < CAS4. The chain length of polyamine is considerable. The molecular chain of tetraethylenepentamine is longest amongst the polyamines used. After it was grafted to starch to obtain CAS4, the branch chains of cross-linked starch elongate and the molecule becomes curled resulting in strong intra-molecular hydrogen bonding and shielding of amine groups. It weakens the interaction between CAS4 and AB10B. Therefore the capacity of CAS4 is lowest.

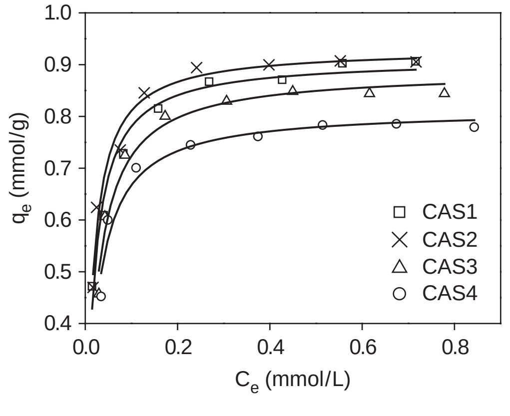

Fig. 4. Langmuir isotherms (real lines) fitting to equilibrium data.

Table 2
Parameters of Langmuir isotherm for AB10B adsorption onto various CAS.

Sorbent	a (mmol g^{-1})	b(L $mmol^{-1}$)	R^2
CAS1	0.911	59.93	0.973
CAS2	0.931	67.51	0.975
CAS3	0.888	44.02	0.971
CAS4	0.813	45.64	0.957

3.3. Thermogravimetric analysis (TGA)

Thermal analysis is a very useful technique for evaluating a range of different samples of the same material [24]. The CAS before and after adsorption of AB10B were studied by thermogravimetry. As shown in Fig. 5, the first weight loss stage is in the temperature range of about 50–110°C due to the loss of adsorbed water. The CAS is stable

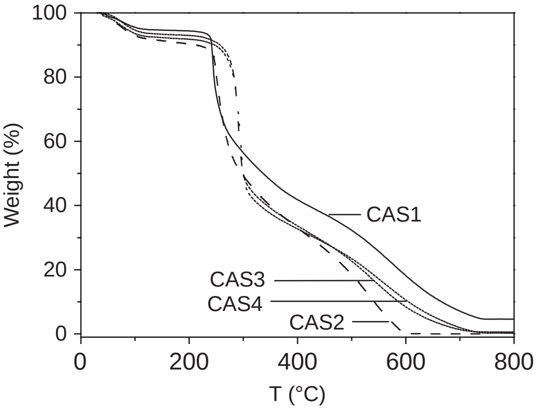

Fig. 5. TGA curves of various CAS.

up to 220°C, and then a continuous weight loss occurs above the temperature. It can be assigned to the decomposition of the polymer. For CAS3 and CAS4, the decomposition rate at the beginning is smaller than those of CAS1 and CAS2. It may be attributed by the intra-molecular hydrogen bonding formed by amines. After adsorption occurred, complexes of AB10B with different CAS are formed (AB10B-CAS). The samples of AB10B-CAS show lower decomposition rates (Fig. 6) indicating the formation of more stable complexes. Comparatively, the complex of CAS2 with AB10B has a much smooth weight loss curve and a higher final temperature of decomposition. The facts indicate that the interaction of CAS2 with AB10B is stronger than the others, bringing on the highest adsorption capacity. According to the above observations, a proposal mechanism was depicted in Fig. 7.

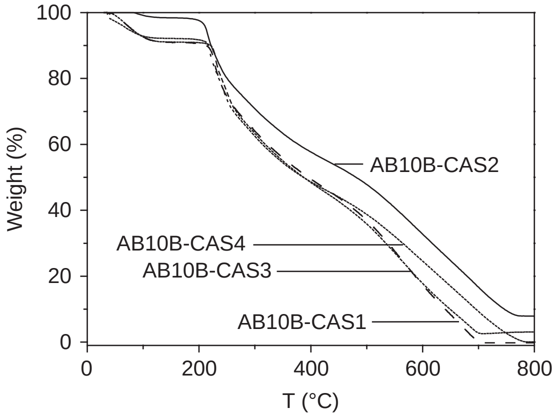

Fig. 6. TGA curves of complexes of various CAS with AB10B (AB10B-CAS).

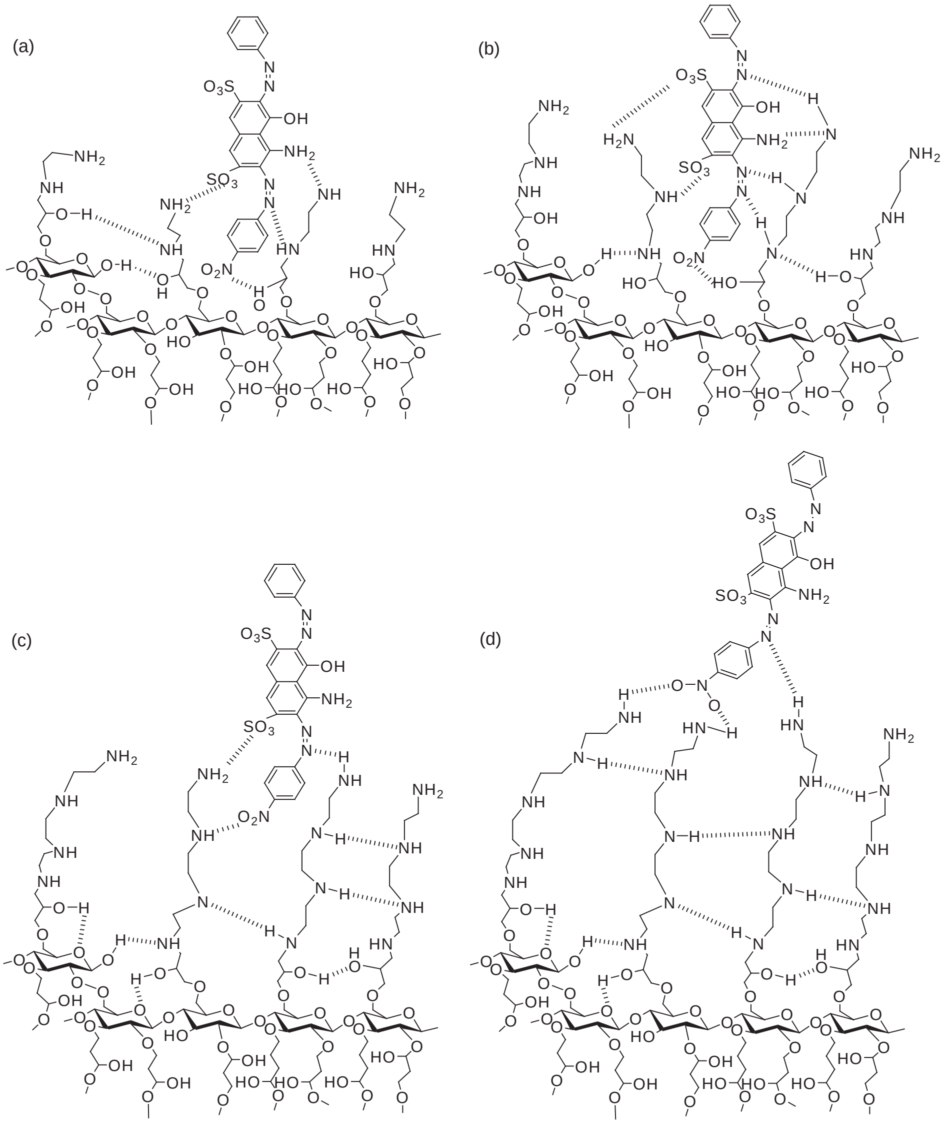

Fig. 7. A proposal interaction mechansim between AB10B and different CAS. (a) CAS1 with AB10B; (b) CAS2 with AB10B; (c) CAS3 with AB10B; (d) CAS4 with AB10B.

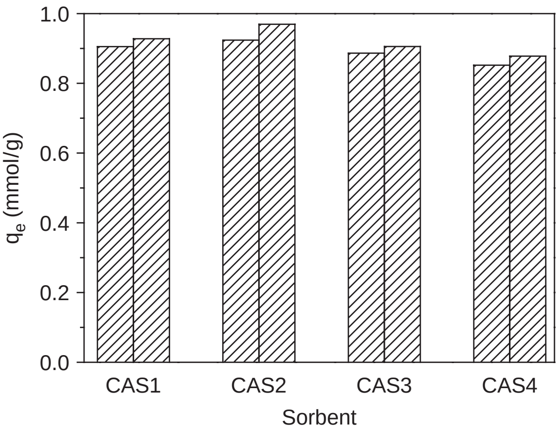

Fig. 8. Comparisons of capacities of various CAS. The lower column: in 0.6488 mmol L^{-1} AB10B solution; the upper column: 0.6488 mmol L^{-1} AB10B solution using 0.001mol·L^{-1} NaCl as background electrolyte.

3.4. Dye removal in the presence of NaCl

Apart from dyes, the wastewaters from textile-manufacturing or dye-producing industries also contain certain amounts of electrolytes. In particular, NaCl is widely used. Fig. 8 presents the adsorption capacities of various CAS for AB10B removal. In the presence of NaCl, the capacities increase slightly. The utmost increase in capacity of CAS2 is 4.92%. Such facts can be explained by that the electrolyte screens the electrostatic repulsion between sorbents and dye molecules. Also it reduces the degree of dissociation of the dye molecules and facilitate the amount of dye sorbed via hydrogen bonding [25].

4. Conclusions

This study concerning the adsorption performance of the acyclic polyamine modified starch (CAS) indicates great potential for the removal of acid dyes from aqueous solutions in basic conditions. The adsorption kinetics, equilibrium uptake and effect of NaCl were investigated. The results indicated that the interaction mechanism was based on hydrogen bonding. The adsorption kinetics followed the pseudo-second-order equation and the Langmuir isotherm gave satisfying fits to equilibrium data. The adsorption capacities of different CAS was in the order CAS2 > CAS1 > CAS3 > CAS4. The thermogravimetry demonstrated that the complex of CAS2 with amido black 10B was stablest amongst all complexes of different CAS with amido black 10B, bringing on the highest adsorption capacity of CAS2. The inorganic electrolyte, NaCl, had slightly effect on the capacities.

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