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Preparation and characteristics of novel dialdehyde aminothiazole starch and its adsorption properties for Cu (II) ions from aqueous solution

Qiang-Feng Yin, Ben-Zhi Ju, Shu-Fen Zhang *, Xin-Bo Wang, Jin-Zong Yang

State key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, PR China

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Abstract

Novel Schiff base type starch dialdehyde aminothiazole (DASAT) was synthesized by the reaction of aminothiazole and dialdehyde starch (DAS) from periodate oxidized corn starch. The DASAT was characterized by element analysis, FT-IR spectra and SEM. DASATs with different DS (0.29, 0.46 and 0.78) of aminothiazole were prepared and their adsorption properties for Cu (II) ions from aqueous solution were investigated. Batch adsorption experiments were carried out as a function of adsorption time, pH, initial Cu (II) ions concentration and temperature. The adsorption follows the Langmuir isotherm and the adsorption capacity increases with the increasing DS of the DASAT. Moreover, the adsorption process is endothermic, and higher temperature is favorable to the adsorption of Cu (II) ions.

Keywords: Dialdehyde starch; Dialdehyde starch aminothiazole; Cu (II); Adsorption

1. Introduction

Heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain and hence in the human body (Malik, 2004). The removal of heavy metal ions from aqueous solution has been traditionally carried out by several techniques such as ion exchange, reverse osmosis, adsorption, complexation/sequestration and precipitation–neutralization. Among these methods, adsorption is considered as a powerful technique that was extensively used for removal of heavy metal ions from domestic and industrial effluents. Activated carbon, metal oxides, clay minerals, microbial biomasses and polymeric materials have been used as adsorbents for removal of heavy metal ions from aqueous solutions (Babel & Kurniawan, 2003; Huang, Peng, & Li, 2006). Among the absorbents investigated polymers have attracted the most attention as carrier matrices because they are easily and effectively produced in a wide variety of compositions, and can be modified into specific sorbents with various functional groups by introducing a variety of metal-complexing ligand (Birlik, Ersoz, Acikkalp, Denizli, & Say, 2007; El-Hag Ali, Shawky, Abd El Rehim, & Hegazy, 2003). However, the synthetic polymers are usually non-renewable and non-biodegradable and these processes often result in secondary environmental pollution (Kweon, Choi, Kim, & Lin, 2001).

Starch is renewable and biodegradable. In recent years, many approaches have been made to utilize starch as a metal absorbent (Crini, 2005), by introducing the activity substituents, such as carboxylate (Khalil & Abdel-Halim, 2001; Xu, Feng, Peng, Wang, & Yushan, 2005), xanthate (Bose, Bose, & Kumar, 2002), acrylamide (Chauhan, Singh, Sharma, et al., 2006), acrylonitrile (Abdel-Aal, Gad, & Dessouki, 2006), tertiary amine (Xu, Feng, Yue, & Wang, 2004) and phosphate (Guo, Zhang, Ju, & Yang, 2006). Dialdehyde starch (DAS) has highly reactive dialdehyde groups which is obtained from the periodate oxidative cleavage of the C(2)–C(3) bond of the anhydroglucose units of starch

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* Corresponding author. Tel./fax: +86 411 88993621.
E-mail address: zhangshf@chem.dlut.edu.cn (S.-F. Zhang).

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polysaccharide chains. Since aldehyde groups form hemiacetals and acetals, DAS has been used as cross-linking agents in several visible industrial applications, such as wet-strength additive for tissue-paper (Veelaert, Wit, Gotlieb, & Verhe, 1997). Recently, Para investigated some derivatives of starch dialdehyde such as dihydrazone, semicarbazone, dithiosemicarbazone, and dioxime (Para & Karolczyk-Kostuch, 2002a, 2002b; Para, Karolczyk-Kostuch, & Fiedorowicz, 2004; Para, 2004) which were used to form water-insoluble complexes with heavy metal ions.

Chelating Polymers, in general, incorporate with a variety of metal-chelating ligands which contain one or more electron donor atoms (Lewis base) such as N, S, O, and P that can form coordinating bonds with most of the toxic heavy metals (Lewis acid). It is well known that Schiff bases (C=N) having multidentate coordination sites are easy to form complexes with transition metal ions. In the other hand, the molecular structure of thiazoles contains N and S atoms, which are easily able to bridge with other molecules or metals too. Recently, many polymer matrixes containing Schiff base (Liu, Tokura, Haruki, et al., 2002; Samal, Acharya, Dey, et al., 2002) or thiazole (Filho, 1999; Roldan, Alcantara, Castro, & Rocha, 2003) ligands were investigated to adsorb Cu (II) ions.

The present work describes the preparation of chemically modified dialdehyde starch with 2-aminothiazole. The result macromolecular product is water insoluble and has the characteristic properties of hydroxy, thiazole and Schiff base. These novel starch dialdehyde aminothiazoles (DASATs) with different DS were used to remove Cu (II) ions from aqueous solution. Batch adsorption experiments were carried out as a function of adsorption time, pH, initial Cu (II) ions concentration and temperature. The adsorption isotherm and thermodynamics were also investigated.

2. Experimental

2.1. Materials and apparatus

Corn starch (food-grade) was dried at 105 °C before use. $NaIO_4$, Cu $(Ac)_2$ and NaOH were obtained from Shantou Xilong chemical factory (Guangzhou, PR China). Aminothiazole (AR) was purchased from Beijing chemistry factory (Beijing, PR China). All other commercial chemicals were of analytic reagent grade and used without further purification. Infrared spectra were obtained by the KBr disc technique and were recorded on a FT/IR-430 spectrometer. The elemental analyses (C, H, N) were performed on a VarioEL. III apparatus. The morphology of samples was observed with a JSM-5600LV scanning electron microscopy (SEM) operated at 30 kV.

2.2. Preparation of dialdehyde starch

Corn starch (dry base) (16.2 g) suspended in 50 mL water was mixed with 100 mL various concentrations of sodium periodate solutions (0.3, 0.5 and 0.7 mol/L). The pH of the suspension was adjusted to 3.5 by adding 0.2 mol/L sulfuric acid. The mixture was stirred gently at 20 °C in the dark for 6 h. The reaction mixture was filtered and washed three times with distilled water (3× 100 mL), and then dried at 50 °C to a constant weight.

2.3. Determination of aldehyde content

The aldehyde group content was determined using the rapid quantitative alkali consumption method (Hofreiter, Alexander, & Wolff, 1955). Dried DAS (0.2 g) was weighed into a 125-mL Erlenmeyer flask and 10 mL of standardized 0.2 mol/L sodium hydroxide was added. The flask was swirled in a water bath at 70 °C for 2 min, then cooled immediately under running tap water with rapid swirling for 1 min. Ten mililiter of standardized 0.2 mol/L sulfuric acid, 50 mL of water and 1 mL of neutral 0.2% phenolphthalein was added in turn. Titration of the acid solution was carried out using 0.2 mol/L sodium hydroxide. The percentage of dialdehyde units was given by the equation:

$$Da\% = \frac{(V_1C_1 - 2V_2C_2) \times 100\%}{W/161}$$

where V_1, V_2 and W represent the volumes (L) of total H_2SO_4, total NaOH and the dry weight (g) of the oxidized starch, respectively. C_1, C_2 (mol/L) represent the concentrations of H_2SO_4 and NaOH, respectively; 161 is the average molecular weight of the repeat unit in dialdehyde starch.

2.4. Preparation of starch dialdehyde aminothiazole (DASAT)

The DAS slurry was prepared from 12.9 g dry DAS and 100 mL distilled water in a 500 mL three-necked flask, which was equipped with a mechanical stirrer and thermostat water bath. One hundred mililiter solution of aminothiazole with respect to the stoichiometric amount was slowly dropped into the flask under nitrogen. The pH of reaction solution was adjusted to 5.0 by adding acetate. The reaction was carried out at 50 °C and 4 h duration. The resulting solid was separated from solution by filtration and washed three times with distilled water (3× 100 mL), then dried at 50 °C to a constant weight.

The degree of substitution of aminothiazole for DASAT was theoretically calculated from the nitrogen content with the following equation:$\mathrm{DS} = 161 \times \mathrm{N}\%/(28 - 82.14 \times \mathrm{N}\%)$.

2.5. Adsorption experiments

The adsorption experiments were carried out in a series of 100 mL Erlenmeyer flasks containing the desired dose of DASAT and 50 mL of $Cu(Ac)_2$ solution at the desired concentration in a shaking bath. The initial pH was adjusted with acetic acid or ammonia before adding the adsorbent. After shaking for a certain time, the mixture was centrifuged and filtered. The concentration of Cu (II) was determined by chemical titrimetric analysis.

The adsorption capacity was calculated from the following expressions:

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

where Q is the adsorption capacity of the adsorbent (mmol/g), C_i and C_t (mol/L) are the initial and terminal concentrations of the Cu (II) ions in the adsorption solution, respectively, and V (mL) and m (g) are the volume of the adsorption solution and the dose of the adsorbent, respectively.

3. Results and discussion

The reaction process of dialdehyde aminothiazole starch can be proposed as Scheme 1. Firstly, three kinds of DAS were designated as DAS1, DAS2 and DAS3, of which the degree of oxidation could be controlled by the addition of $NaIO_4$ (0.03, 0.05 or 0.07 mol), respectively. Their percentage of dialdehyde units was determined using the rapid quantitative alkali consumption method and was 29%, 51% and 72%, respectively. Then, these DASs reacted with the stoichiometric amount aminothiazole with mole ratio of it to dialdehyde of 2:1 to form novel starch aminothiazole derivatives (DASATs). The results of the elemental analyses and the reaction yields of the condensation products are listed in Table 1. It can be seen that the nitrogen content in DASAT increased obviously with increasing of the dialdehyde percentage of DAS. The DS of aminothiazole which represented the average molecular number of the repeat unit in dialdehyde starch aminothiazole for DASAT1, DASAT2 and DASAT3 was 0.29, 0.46 and 0.78, respectively.

3.1. The FT-IR spectra of DAS and DASAT

The infrared spectra of the compounds under investigation were recorded in the 4000–400 cm^{-1} region with KBr pellets. As shown in Fig. 1, the characteristic bands of DAS appeared in the 1730 and 780 cm^{-1} regions. The peak at 1734 cm^{-1} is a characteristic band of carbonyl groups. The band observed at 780 cm^{-1} can be assigned to the hemiacetal form. However, these characteristic bands of DAS did not appear as shown in the spectra of DASAT. In comparison with DAS, the IR spectra of DASAT appeared new bands which can confirm the presence of aminothiazole groups bound to the DAS. The band at 1629 cm^{-1} can be assigned to the ν(C=N) stretching vibrations of the imine group, confirming the formation of Schiff bases between aminothiazole and dialdehyde starch. The band at 1519 can be assigned to ν(C=N) of the thiazole ring and that at 1480 to the vibrationally coupled modes of the heterocycle (Bolos, Fanourgakis, Christidis, & Nikolov, 1999; Filho, 1999).

3.2. Morphological studies of DASAT

Scanning electron microscopy (SEM) was used to study the granule morphology before and after adsorp-

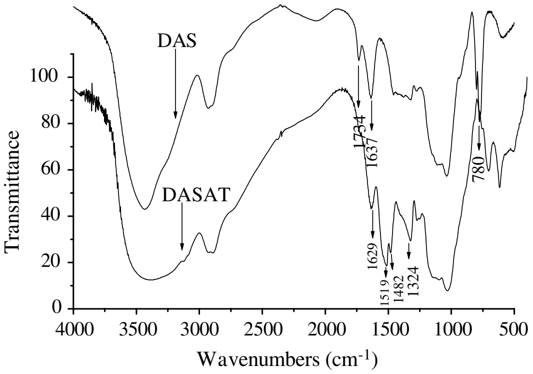
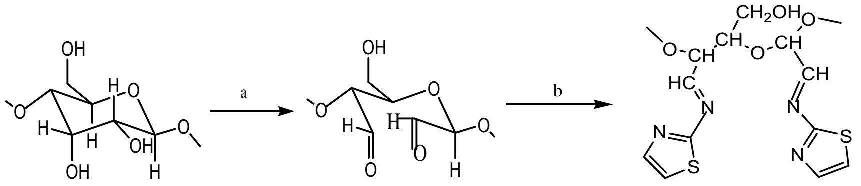


Fig. 1. FT-IR spectra of DAS and DASAT.



Scheme 1. Reagents and conditions: (a) $NaIO_4$; (b) aminothiazole.

Table 1
Degree of substitution for DASAT

Product	Reactant	Color	Yield (%)	Elemental analysis			DS
				N (%)	C (%)	H (%)	
DASAT1	DAS1	Yellow	62.4	4.37	44.99	6.24	0.29
DASAT2	DAS2	Yellow	65.5	6.37	44.27	6.02	0.46
DASAT3	DAS3	Yellow	84.0	9.34	42.98	5.34	0.78

tion. Photographs of representative areas of the samples were taken at 100 (Fig. 2a, c, e and g) and 1000 (Fig. 2b, d, f and h) magnifications. Fig. 2 illustrates SEM of corn starch, DAS3, DASAT3 and DASAT3 adsorbed Cu (II) ions. The original corn starch particles (Fig. 2a and b) show dispersed and smooth, but after oxidization by periodate, the particles (Fig. 2c and d) appeared obviously diverse. Clearly, the cleavage of glucoside rings leads to an altered uneven surface, creating pore on the particles. Also notable was that the particles were conglomerated closely, and the granules became much bigger in contrast to the original. DASAT (Fig. 2e and f) after reacting with aminothiazole showed particle fragments and irregular structure due to cross-linking disappearance. Fig. 2g and h shows micrographs of the DASAT after adsorbed Cu (II) ions, which had no obviously diversification in comparison to DASAT.

3.3. Adsorption of Cu^{2+} ions

Among the numerous techniques of heavy metals removal, adsorption gives the best results as it can be

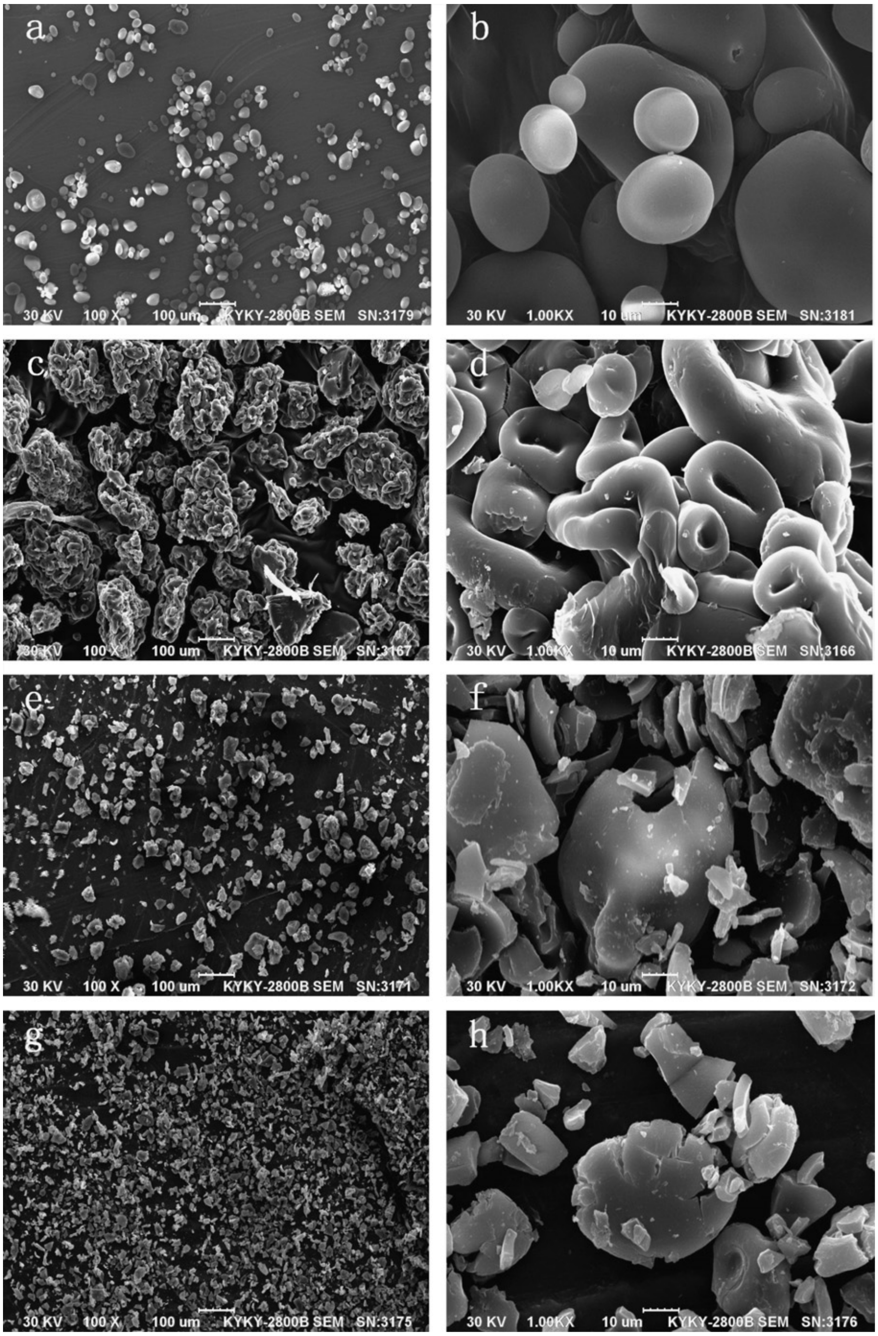


Fig. 2. SEM pictures of different starch granules (a and b) corn starch; (c and d) DAS3; (e and f) DASAT3; (g and h) DASAT3 adsorbed Cu (II) ions. The scale bar is 100 μm for (a, c, e and g) and 10 μm for (b, d, f and h).

used to remove different types of heavy metals effectively. However, sufficient effectivity of an absorbent is closely related to the application conditions. Here, as a new absorbent, DASAT was investigated on various adsorption conditions to achieve a satisfied performance. Besides, in consideration of the possible chelation adsorption mechanism rather than electrostatic attraction, adsorption processes were discussed in detail to reveal the difference.

3.3.1. Effect of initial pH

The metal adsorption capacity of DASAT was compared at different pH of the Cu^{2+} solutions. In Fig. 3 it can be seen that below pH 3 or so, the binding of Cu^{2+} was very low, then increased gradually with pH increasing from 3 to 6. This was due to the fact that the adsorbents were highly protonated in an acid medium, and can not effectively interact with the metal ions because of the loss of negative charge. Thus, the increased proton concentration in the medium inhibited the metal-chelate complex of the adsorbent (Kweon et al., 2001). In the medium pH range of 6–7 the adsorbent has a stable maximum binding capacity, which involves competitive reactions of protonation and complex binding (Juang & Chen, 1996). At alkaline pH, in order to avoid the precipitation of copper hydroxide the ammonia was used to adjust pH and can form water-soluble ammoniacal copper (II) solution ($[Cu(NH_3)_4]^{2+}$) with Cu (II) ion. Above pH 7.0, the adsorption capacity decreased sharply, which was likely due to competition reaction of OH^-, ammonia and DASAT with metal chelates. Justi et al., in studying the adsorption capacities of Chitosan functionalized with 2[-bis-(pyridylmethyl)aminomethyl]4-methyl-6-formyl-phenol for Cu (II) ion (Justi, Laranjeira, Neves, Mangrich, & Favere, 2004), observed the similar phenomenon in the same pH range. All three kinds of DASAT had the same trends, and their adsorption capacity increased with the increase of DS of the aminothiazole groups in the same pH, i.e. $Q_{DASAT1} < Q_{DASAT2} < Q_{DASAT3}$.

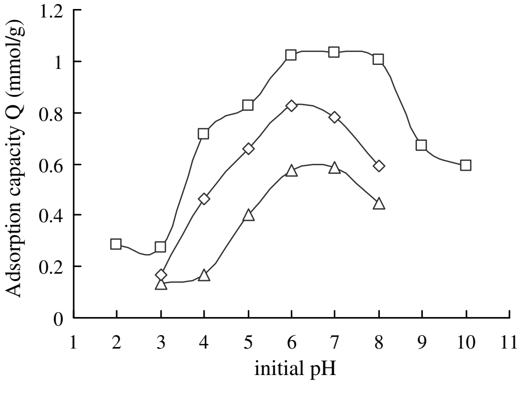


Fig. 3. Effect of initial pH value of solution on adsorption capacity: (Δ) DASAT1; (◇) DASAT2; (□) DASAT3. ($[Cu\,(Ac)_2] = 0.02$ mol/L; $t = 4$ h; $T = 20$ °C; the dose of each DASAT is 0.15 g.)

3.3.2. Effect of adsorption time

Fig. 4 illustrates the adsorption of Cu^{2+} in the solution at $T = 20$ °C and pH = 5.3 as a function of contact time. The adsorption time of starch in the metal solution was changed from 20 to 240 min. As seen, the capacity of adsorption increased with increase of the treatment time during the first 120 min and reached the maximum at that time. However, the adsorption capacity decreased little as the adsorption time increased. The reduced metal-adsorption was caused by the increased amount of dissolved starch possibly. The result indicated that although the DS of DASAT was different, their equilibrium time was almost 2 h.

3.3.3. Effect of the initial Cu (II) ions concentration

The adsorption capacity of DASAT for Cu (II) ions was dependent on the initial concentration of Cu (II) ions solution. As shown in Fig. 5, when the initial Cu (II) ions concentration was 2 mmol/L, the adsorption capacity of DASAT1, DASAT2 and DASAT3 was 0.29, 0.43 and 0.59 mmol/g, which was equivalent to 53.7, 85.1 and 131.6 mmol/AGU, respectively. However up to 14 mmol/L, the adsorption capacity was raised

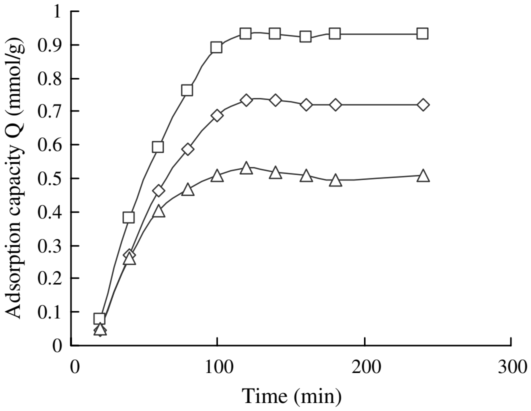


Fig. 4. Effect of adsorption time: (Δ) DASAT1; (◇) DASAT2; (□) DASAT3. ($[Cu\,(Ac)_2] = 0.02$ mol/L; pH = 5.3; $T = 20$ °C; the dose of each DASAT is 0.15 g.)

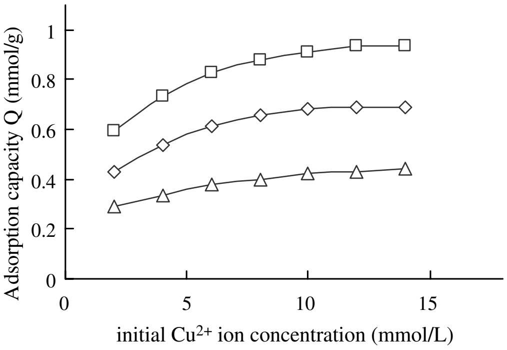


Fig. 5. Effect of initial concentration of Cu (II) on (Δ) DASAT1; (◇) DASAT2; (□) DASAT3. ($t = 4$ h; pH = 5.3; $T = 20$ °C; the dose of each DASAT is 0.15 g.)

to 0.44, 0.69 and 0.93 mmol/g, which was equivalent to 81.5, 136.6 and 207.4 mmol/AGU under 14 mmol/L of Cu (II), respectively. Moreover, the three curves showed a common trend, which implied the type of the adsorption isotherm for the three absorbents may be the same.

3.3.4. Adsorption isotherm

To design adsorption process effectively, it is useful to employ mathematical models to predict the metal adsorption. Langmuir equation was applied to quantify adsorption capacity and given as follows:

$$\frac{C_e}{Q} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$

where C_e and Q are equilibrium Cu (II) ions concentration (mmol/L) and equilibrium adsorption capacity (mmol/g), respectively; Q_m and b are the Langmuir constants representing maximal adsorption capacity (mmol/g) and energy of adsorption (L/mmol), respectively. The straight lines were given by plotting C_e/Q versus C_e, as shown in Fig. 6, which gave the values of b and Q_m in Table 2 according to the intercept and slope of these lines, respectively. Notice the fit of data to linearity was very good. The maximal adsorption capacity of DASAT1, DASAT2 and DASAT3 was 0.44, 0.69 and 0.95 mmol/g, respectively. These results agree with the previous experimental data. On the other hand, the conclusion that the adsorption capacity increases with increasing DS of aminothiazole group can be drawn from the Langmuir constant b: b increases from 0.361 to 0.447 to 0.529 L/mmol, when the DS of the aminothiazole group increases from 0.29 to 0.49 to 0.78.

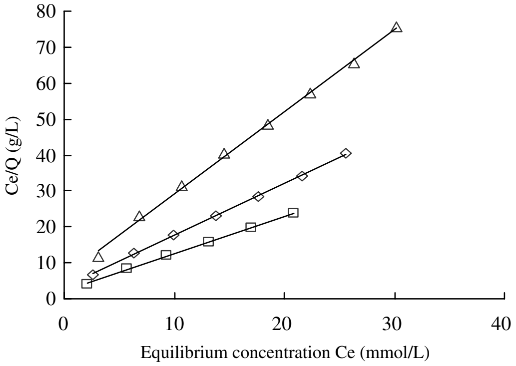


Fig. 6. Langmuir adsorption isotherm. (Δ) DASAT1; (◇) DASAT2; (□) DASAT3. (pH = 5.3; t = 4 h; T = 20 °C; the dose of each DASAT is 0.15 g.)

Table 2
Langmuir parameters for three kinds of DASAT

Sample	Q_m (mmol/g)	b (L/mmol)	R^2
DASAT1	0.44	0.361	0.9985
DASAT2	0.69	0.447	0.9993
DASAT3	0.95	0.529	0.9988

A wide variety of polymers containing similar structure with DAS used to adsorb Cu^{2+} ions have been reported. Ngah et al. achieved 59.7 mg/g Cu (II) adsorption capacity with cross-linked chitosan with glutaraldehyde (Ngah, Endud, & Mayanar, 2002). Baraka et al. reported 29.7 mg of Cu (II)/g melamine–formaldehyde resin modified with nitrilotriacetic acid (Baraka, Hall, & Heslop, 2007). Filho et al. reported less than 0.2 mmol of Cu (II)/g as the adsorption capacity for 2-aminothiazole-modified silica gel (Filho, Carmoa, & Rosa, 2006). Comparing these data, we may conclude that the DASAT is a promising biodegradable adsorbent for the removal of Cu^{2+} ions.

3.3.5. Thermodynamic studies

Fig. 7 shows the effect of temperature (20–60 °C) on the adsorption process. It is obvious that the adsorption capacity increases with increasing temperature, which applies that the adsorption process is endothermic. Thermodynamic parameters such as change in enthalpy (ΔH^θ) and entropy (ΔS^θ) were determined using the following equations:

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

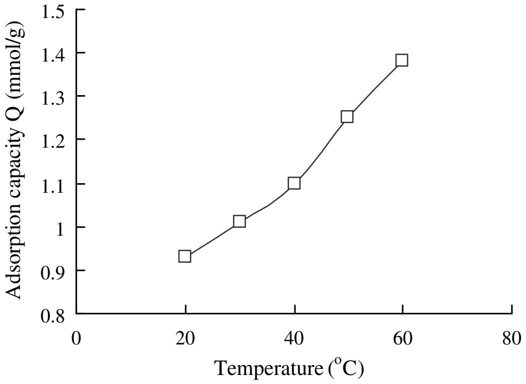


Fig. 7. Effect of adsorption temperature for DASAT3. ([Cu (Ac)$_2$] = 12 mmol/L; pH = 5.3; t = 4 h; the dose of DASA3 is 0.15 g).

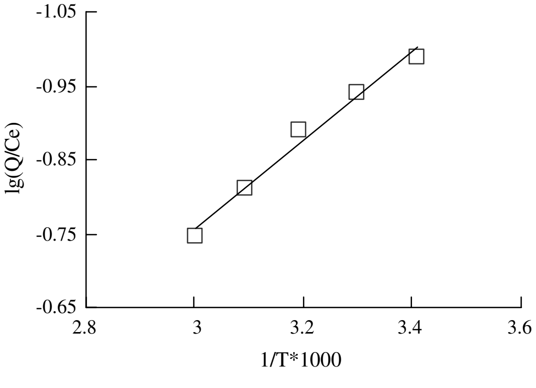


Fig. 8. $\log(Q/C_e) \sim 1/T * 1000$ for DASAT3. ([Cu (Ac)$_2$] = 12 mmol/L; pH = 5.3; t = 4 h; the dose of DASAT3 is 0.15 g.)

Table 3
Thermodynamic parameters for DASAT3

Temperature (°C)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)
20	5.61		
30	5.41		
40	5.21	11.41	19.78
50	5.02		
60	4.82		

ΔH^0 and ΔS^0 were obtained from the slope and intercept of the plot of $\log Q/C_e$ versus $1/T$ (Fig. 8). The change of adsorption free energy (ΔG^0) was calculated from the thermodynamic equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0.$$

Table 3 shows the calculated values of the thermodynamic parameters. The decrease in ΔG^0 with the increase temperature shows that the adsorption is more favorable at high temperatures. The positive value of ΔS^0 indicates that there is an increase in the randomness in the system solid/solution interface during the adsorption process. In addition, the positive value of ΔH^0 indicates that the adsorption is endothermic and higher temperature makes the adsorption easier.

4. Conclusions

A novel neutral starch chelating agent DASAT was prepared by reacting dialdehyde starch with aminothiazole. The adsorption between Cu (II) ion and dialdehyde aminothiazole starches (DASATs) is found to be dependent on the pH of the solution, the initial concentration of Cu^{2+} ion, as well as the adsorption temperature. The adsorption follows the Langmuir isotherm. The adsorption capacity increases with the increasing DS of the DASAT, and reaches 0.44, 0.69 and 0.95 mmol/g at 20 °C, respectively, for DASAT1, DASTA2 and DASAT3. The adsorption process of DASAT3 is endothermic, and the apparent enthalpy (ΔH^0) is 11.41 kJ/mol. For effectual metal removal, the metal solution should be in a bearable neutral pH range. By raising the DS of the DASAT, the metal removal could reach the level required for distinguished adsorption capacity, thus, DASAT gave a potential application as a low-cost and effective absorbent.

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