A novel method for amino starch preparation and its adsorption for Cu(II) and Cr(VI)

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ABSTRACT

A novel method was proposed to prepare amino starch by reacting ethylenediamine with previously synthesized dialdehyde starch. Different factors affecting the preparation, i.e., ethylenediamine concentration, ethylenediamine:dialdehyde starch molar ratio, pH, duration and temperature have been studied. The modified starch was characterized by IR spectroscopy, elemental analysis, X-ray diffraction and differential scanning calorimetry. The amino starch derivatives were evaluated as adsorbents. The adsorption activity for heavy metals such as Cu(II) and Cr(VI) by crosslinked amino starch was studied in terms of adsorption amount, kinetics and isotherm; and adsorbent reuse were also studied. Adsorption processes for Cu(II) and Cr(VI) on crosslinked amino starch fit a Langmuir isotherm, and adsorption for Cu(II) and Cr(VI) from aqueous solution was endothermic reactions. Crosslinked amino starch was very effective for the adsorption of Cu(II) and Cr(VI), and efficient in capacity, recycled.

1. Introduction

Removal of toxic heavy metal ions from industrial and mining wastewaters has received much attention in recent years because they cause health problems in human beings and animals [1,2]. Various traditional and advanced technologies have been utilized for the removal of heavy metals from water, such as ion-exchange, precipitation, flotation, solvent extraction, adsorption, and electrolytic methods [3,4].

Among these techniques, adsorption is generally preferred for the removal of heavy metal ions because of its high efficiency, easy handling, and availability of different adsorbents [5]. So the search for cost-effective adsorbents and economic method of removing toxic heavy metal ions has also become the focus of attention of many studies [6,7].

In this respect, many natural polysaccharides and their derivatives containing various functional groups may have some potential. Recently, chitin and its derivatives, modified cellulose, and modified starch ethers have been studied with respect to their ability to remove heavy metal ions from aqueous solutions [8–10].

As low-cost, renewable, biodegradable polymers, starch-based products have been proposed as chelating agents to remove heavy metal ions from electroplate metallurgy wastewater. Xu et al. [11] studied the adsorption process of Pb(II) by crosslinked amphoteric starch with quaternary ammonium and carboxymethyl groups. Khalil and Abdel-Halim [12] prepared anionic starches containing carboxyl groups and used them as chelating agents for removal of some divalent metal ions. Kweon and Choi [13] investigated the adsorption of divalent metal ions by succinylated and oxidized corn starches. Zhang and Chen [14] investigated crosslinked starch graft copolymers containing amine groups as the adsorbents for Pb(II) and Cu(II). Kim and Lim [15] reported the removal of heavy metal ions from water by crosslinked carboxymethyl corn starch. Amino Starch is also developed for heavy metal removal. Xiang and Li [16] found amino starch has high adsorption capacity for Cu(II). But the preparation of amino starch is processing etherification reactions which is affecting by many factors and the reaction condition is difficult to control.

Dialdehyde starch (DASt) has highly reactive dialdehyde groups which is obtained from periodate oxidative cleavage of the C(2)–C(3) bond of the anhydroglucose units of starch [17]. In general, incorporate with some metal-chelating ligands which contain 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.

The present work describes the preparation of amino starch by chemically modified dialdehyde starch (DASt) with ethylenediamine (EDA), and the removal of Cu(II) and Cr(VI) from aqueous solution by amino starch was also investigated. There are many factors affecting the preparation, including EDA concentration and solvent pH, duration and temperature. Also different factors affecting the removal efficiency for Cu(II) and Cr(VI) ions were thoroughly investigated by batch experiments, encompassing effect of treatment time, medium pH and molar mass dose. The crosslinked amino starch (CASt) samples were chelated with different metal ions such as Cu(II) and Cr(VI), which supplied as $CuSO_4$ and $K_2Cr_2O_7$. Further, the adsorption rate, adsorption isotherm and the reusability of the adsorbents were also investigated.

2. Experimental

2.1. Materials

Corn starch (food grade, Wuhan Yifeng Food Factory, Wuhan, China) was dried 2 h at 105 °C before use. Epichlorohydrin (ECH),

$NaIO_4$ and ethylenediamine (EDA) (AR, Shanghai Chemical Reagent Factory, Shanghai, China) were used as crosslinking agent, oxidize agent and amino agent respectively. $CuSO_4$ and $K_2Cr_2O_7$ (AR, Shanghai Chemical Reagent Factory, Shanghai, China) were used for the removal of heavy ions. Acetone, sodium chloride (AR, Tianjin Chemical Reagent Factory, Tianjin, China) and other compounds were used as purchased. All aqueous solutions and standards were prepared using deionized water.

2.2. Preparation of crosslinked starch (CSt)

Corn starch (100 g), 1% (w/w) sodium chloride solution (150 mL) was slurred in a 250 mL three-necked glass reaction kettle equipped with a stirrer and a thermometer. The slurry was heated to 30 °C and kept at the constant temperature in water bath. Fifteen percentage (w/w) NaOH solutions (20 mL) was added to this slurry, then ECH added drop wise for about 15 min, and the mixture was stirred for 5 h at 30 °C.

Upon completion of the reaction, CSt suspension slurry was adjusted to pH 6–7 with HCl (0.1 M), and then the reaction mixture was filtered and washed with deionized water.

Then CSt production was dried at 80 °C under vacuum for 2 h.

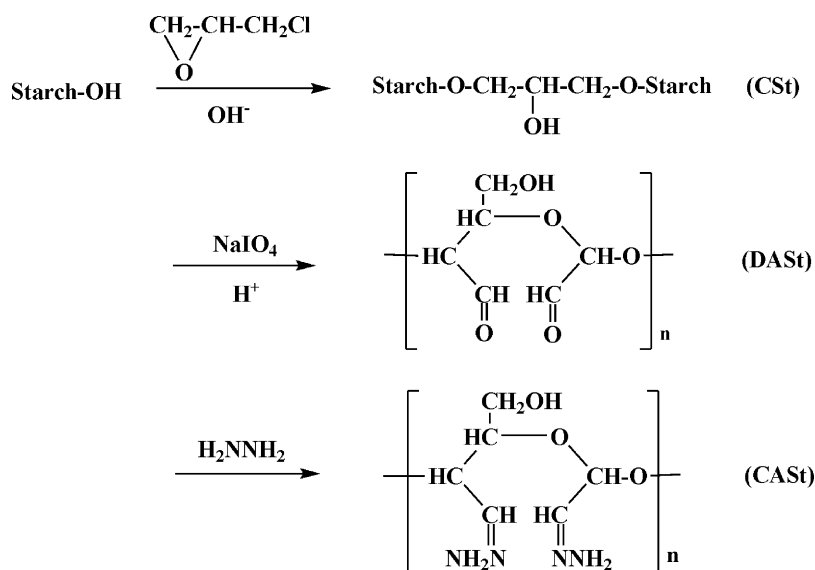### 2.3. Preparation of dialdehyde starch (DASt)

The DASt samples were prepared by reacting CSt with $NaIO_4$ in presence of HCl in a 250 mL three-necked flask equipped with a stirrer and a thermometer. And this reaction equipment is in dark to prevent light. The mixture was heated to 35 °C for 2 h under stirring. Then the reaction mixture was filtered, washed with deionized water, and dried at 60 °C under vacuum.

2.4. Preparation of crosslinked amino starch (CASt)

DASt, EDA, and deionized water were mixed under stirring at 40 °C for 3 h, and then CASt was obtained. The reaction mixture was then filtered; washed with HCl (1%, w/w), NaOH (1%, w/w), and deionized water successively; and the solid CASt was dried at 60 °C under vacuum for 8 h. Nitrogen content was measured with the Kjeldahl method.

The total reaction process.

The proposed reactions involved in the above process can be represented as shown in the following scheme:

2.5. Adsorption procedure

The adsorption experiments in this study were carried out in a series of 100 mL Erlenmeyer flasks containing the desired dose of CASt and 50 mL $CuSO_4$, $K_2Cr_2O_7$ aqueous at the desired concentration and initial pH (adjusted with 0.1N hydrochloric acid and 0.1N NaOH) in a shaking bath. After shaking for a certain time, the supernatant was removed and the concentration of Cu(II), Cr(VI) was analyzed by atomic adsorption spectrophotometer.

All results were performed in triplicate and the data were recorded as a mean. The adsorption amounts of CASt and ion removal were calculated by the following expression:

$$Q = \frac{(C_0 - C_t)V}{m}$$

$$P = \frac{C_0 - C_t}{C_0} \times 100\%$$

where Q is the adsorption amount of the CASt on metal ions (mg/g), P is ion removal of Cu(II), Cr(VI) ions (%); C_0 and C_t (mg/L) are the concentration of Cu(II), Cr(VI) ions at the initial time and time t,
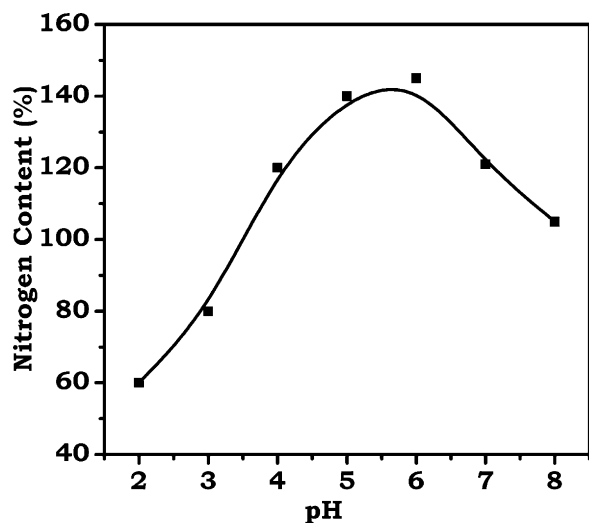
Fig. 1. Effects of pH on nitrogen content.

Fig. 2. Effects of reaction temperature on nitrogen content.

respectively, V is the total volume of the aqueous solution (L) and m is the dose weight of CASt (g).

2.6. Characterization

Infrared (IR) spectra was recorded on a NEXUS 670SX (Nicole Instrument Corporation, USA) with KBr dispersion method. The FTIR spectra were in the range of 4000–400 cm^{-1}.

Elemental analysis studies of dry samples were performed on a Vario EL elemental analyzer (Elemental Instrument Corporation, Germany). Three elements, i.e., carbon, hydrogen, and nitrogen were conformed.

The X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX-3B powder X-ray diffract meter using the Cu radiation, over a 2θ range of 3–70° at a scanning speed of 5° min^{-1}.

The thermal stability of the starch samples was examined using NETZSH DSC 209C from room temperature to 400 °C under an inert nitrogen atmosphere and a heating rate of 10 °C min^{-1}.

The concentrations of Cu(II) and Cr(VI) in aqueous solutions were measured using an atomic adsorb spectrophotometer (Z5000 AA spectrometer, Hitachi, Osaka, Japan).

3. Results and discussion

3.1. Preparation of CASt

3.1.1. Effect of initial pH
Fig. 1 shows effect of pH on the reaction extent of DASt with the EDA (expressed as Nitrogen content). The reaction was carried out at 35 °C for 2 h, pH 5.5, using 10 mmol DASt, an EDA:DASt molar ratio 4:1, and varying pH (2–8).

As the increasing of pH, the reaction extent increased obviously at pH < 5 and deceased sharply at pH > 6. It can be termed that ethylenediamine reacting with DASt was nucleophilic addition reaction. The pro-nuclear capability of EDA was improved in system high pH. But in system pH > 6 DASt molecules undergo disproportionate changes to alcohol hydroxyl and carboxyl which were soluble in water. So the higher pH was disadvantage to the main reaction, and we should control the pH at 5.5.

3.1.2. Effect of reaction temperature
Fig. 2 shows effect of temperature on reaction extent occurring between DASt and EDA. The DASt (10 mmol) was reacted with EDA (4 mmol) at varying temperatures (20–40 °C) for 2 h.

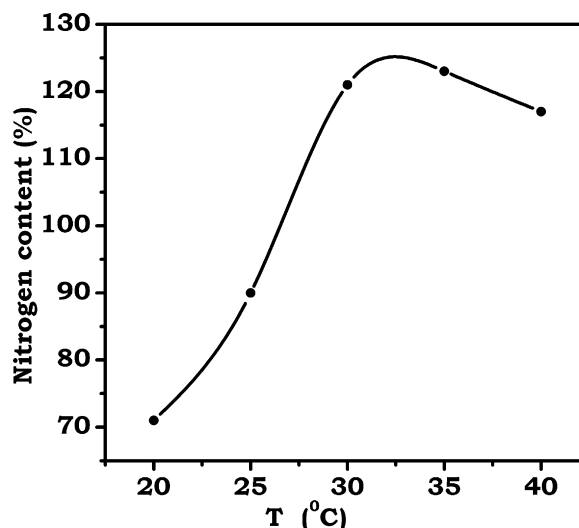As can be seen from Fig. 2, the reaction extent increased obviously when the reaction temperature was heightened. Because, the higher temperature did favor to the expansion of DASt granules and the mobility of reaction reagents, which made EDA permeated to DASt granules easily, thus improved the reaction efficiency. But when the temperature was higher than 35 °C, DASt would decompose to small molecules under acidic condition. So the reaction extent decreased at higher temperature than 35 °C. Experiments showed that the reaction solution at 40 °C was a uniform system of deep yellow which cannot leaching.

3.1.3. Effect of reaction duration time
Fig. 3 shows effect of duration time on reaction extent occurring between DASt and EDA. The starch (10 mmol) was reacted with EDA (4 mmol) for varying duration time (0.5–3) h.

As can be seen from Fig. 3, as the increasing of duration time, nitrogen content was also increased and reached the maximum at 2 h. The longer reaction time made DASt reaction with EDA fully. But, as the reaction time continued increase, nitrogen content had a slight decline. This could be explained that, hydrogen ions concentration increases while the occurring of reaction, which can result in the fracture of C=N (product of DASt reaction with ethylenedi-
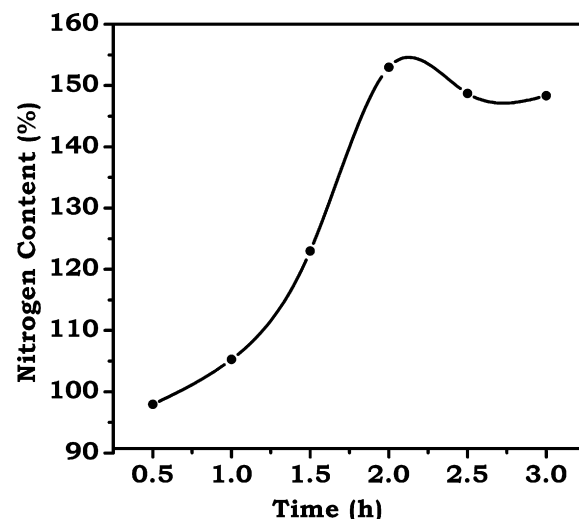

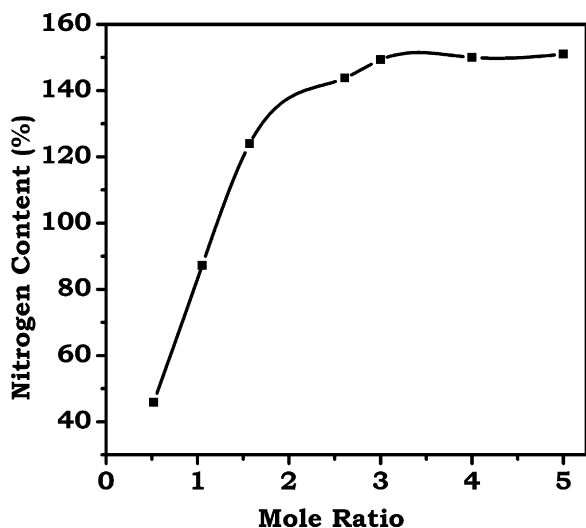**Fig. 3.** Effects of duration time on nitrogen content.

Fig. 4. Effect of EDA:DASt molar ratio on nitrogen content.

Fig. 5. Effects of EDA concentration on nitrogen content.

amine). The leave of amino groups decreased the reaction extent of DASt with EDA.

3.1.4. Effect of molar ratio

Fig. 4 shows effect of EDA:DASt molar ratio on the reaction extent occurring between DASt and EDA. The DASt was reacted with ethylenediamine at 35 °C for 2 h, varying EDA: DASt molar ratio (0.5–5).

As can be seen from Fig. 4, the reaction extent increased sharply as the EDA: DASt molar ratio increasing up to 3.0, but at higher ratios the nitrogen content had a slightly decrease. This could be interpreted in terms that, a high EDA: DASt molar ratio providing a large number of accessible amino groups which are available for reaction with starch. But a higher EDA:DASt molar ratio will raise pH of reaction system which could lead starch granular into degradation. It was also possible that the DASt molecules undergo disproportionate changes that diminish their reaction activity. Although the smaller molecular DASt can still react with EDA, but the product with smaller molecular weight is soluble and difficult to separate.

All these reactions would balance the sharp increase observed upon using EDA:DASt molar ratio to 4:1.

3.1.5. Effect of EDA concentration

Fig. 5 shows the effect of EDA concentration on reaction extent occurring between DASt and EDA. The reaction was carried out at 35 °C for 2 h, pH 5.5, using 10 mmol starch, an EDA: DASt molar ratio 4:1, and varying EDA concentration (0.4–1.2) mol/L.

As can be seen that, an increasing EDA concentration up to a molar concentration of 0.6 caused significant enhancement in the reaction extent. Thereafter, further increase in EDA concentration decreased the reaction yield. That is, a maximum yield was obtained at an EDA molar concentration of 0.6. It is logical that EDA concentrations are sufficient to drive the reaction to its maximum when EDA concentration is not high enough. The effect of EDA concentration on reaction yield basing on the valid collision between amino group and aldehyde group. However, higher EDA concentration favor overdose free amino group and which can make the reaction system has a high pH. When meeting higher pH system, DASt granules will swell and some of DASt breaks down into small molecules soluble in water. Simultaneously, the DASt molecular will reaction in disproportionation in higher alkaline concentration, and the loss of aldehyde will decrease the reaction ability of DASt.
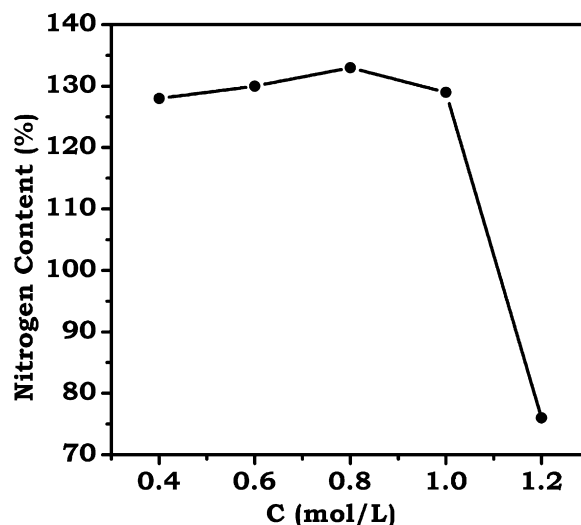
3.1.6. Characterization of CASt

Starch, DASt and CASt samples were characterized by infrared (IR) spectroscopy (Fig. 6).

Comparing the IR results of these three samples, we found that in the curve of DASt there was a sharp absorption peak at $1732.12\,cm^{-1}$, which was the characteristic absorption peak of aldehyde group. In the curve of CASt, a broad absorption band at $3394\,cm^{-1}$ is for the –N–H stretching wavenumber of the $-NH_2$ group; the characteristic absorption peak of aldehyde group at $1732.12\,cm^{-1}$ was disappeared, but there was s new strong absorption peak at $1654.48\,m^{-1}$ which indicated the new generation of carbon–nitrogen double bond. Meanwhile, there was weak adsorption at 1560^{-1} was found in the IR results of the amino starch.

These new peaks were characteristic absorption of amino group (I) and (II). These results showed that, amino group was grafted on starch through C=N successfully.

The elemental analysis studies of dry samples showed that CASt contains 36.03% carbon, 7.82% hydrogen, and 19.26% nitrogen, respectively.

The XRD results of the modified starch and starch unmodified were showed in Fig. 7. As shown in Fig. 7, the XRD curves of modified starch express traditional "A" style, and the XRD peeks of starch at 2θ were 14.9°, 17.4°,19.7° and 23.6°, which were the hydroxy diffraction peek. But the modified starch after crosslink only have
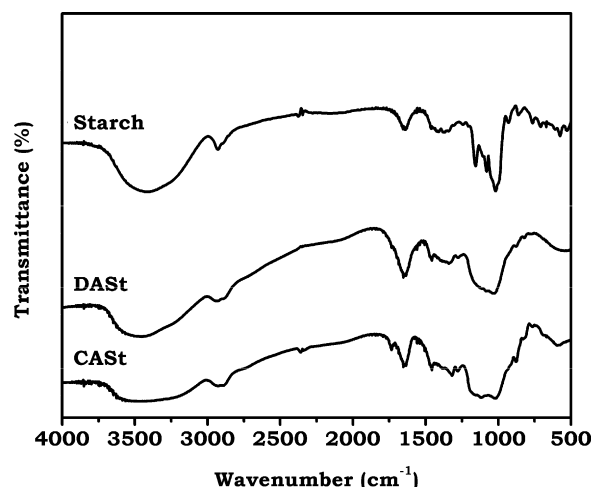

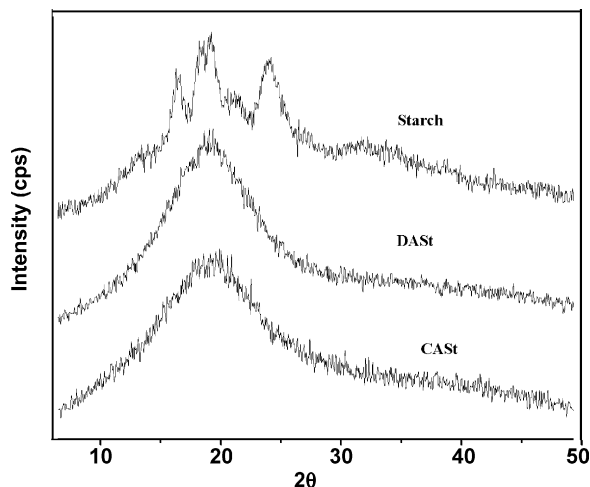**Fig. 6.** IR spectras of modified starch.

Fig. 7. XRD spectras of modified starch.

Fig. 9. Effect of treatment time on ions adsorption amount.

a wide amorphous diffraction peek at 21.28°, which mean that the crystallinity of DASt and CASt decreased crazily than native starch. And so EDA was not only the nitrogen supplier, but also act as a crosslink agent who made the starch has larger molecular.

DSC curves of starch and CASt are presented in Fig. 8. The DSC curve of starch recorded after heating of the sample clearly presents two changes of heat capacity: two increase of heat capacity at 87 and 325 °C. These events could be attributed to water evaporation for the lower temperature and to the decomposition of the starch for the higher temperature. Comparing DSC curves of starch and CASt we found that, sample of CASt only have one increase of heat capacity at 87 °C which was the water evaporation, but did not has the increase of heat capacity at 325 °C. This result showed that CASt did not decomposition at 325 °C and has a better stability.

These above analysis results prove that CASt has been successfully synthesized and has a well stability.

3.2. Evaluation of CASt adsorbent

3.2.1. Effect of treatment time

Fig. 9 gives the effect of treatment time on the adsorption of Cu(II) and Cr(VI) ions on amino starch from aqueous solutions, respectively.
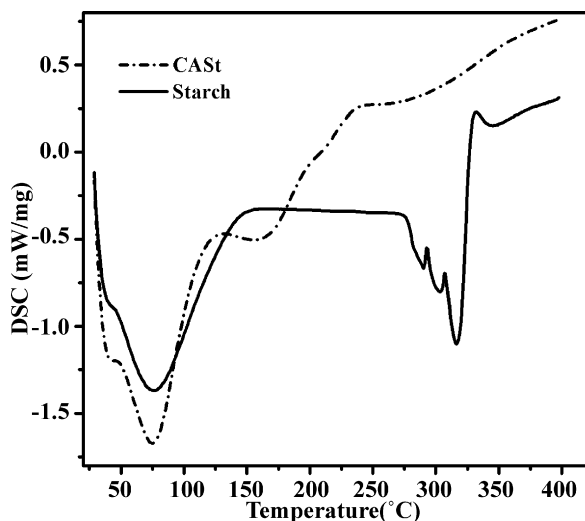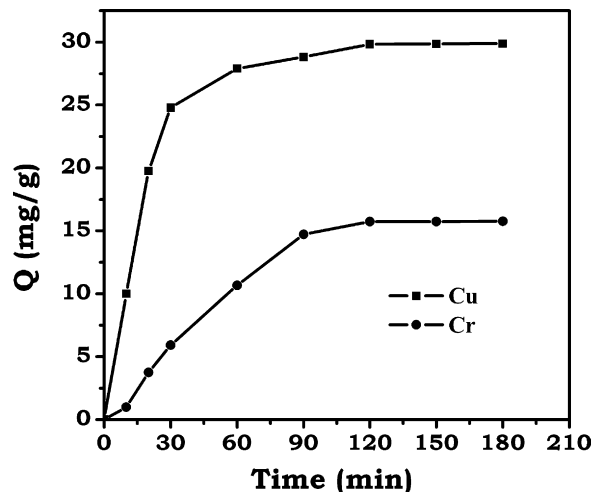
The removal of these two ions increased with increasing time and attained saturation at about 120 min. The rate of metal removal is higher at the beginning owing to many active groups of the CASt being available for the adsorption. The rate of removal becomes almost insignificant owing to a quick exhaustion of the adsorption sites.

CASt was prepared using a solid-state technique, so most of the active groups are on the particle surface, which makes the adsorption process rapid. This is important in likely industrial applications. For the following experiments, the treatment time was maintained at 120 min to ensure that equilibrium was really achieved.

In contrast, the adsorption rate of Cu(II) ions is higher than that of Cr(VI) ions. This may be due to the higher complex formation rate between Cu(II) ions and Cr(VI).

3.2.2. Effect of pH

The effect of pH is shown in Fig. 10. The pH has big influent on the morphology of Cu(II) and Cr(VI) ions and CASt adsorbent. Below pH 2.0 or so, there is little adsorption of Cu(II) and Cr(VI). The greatest increase in the removal percentage is observed for pH changes from 3.0 to 4.0, but then there is big decrease for pH changes from 5 to 7.
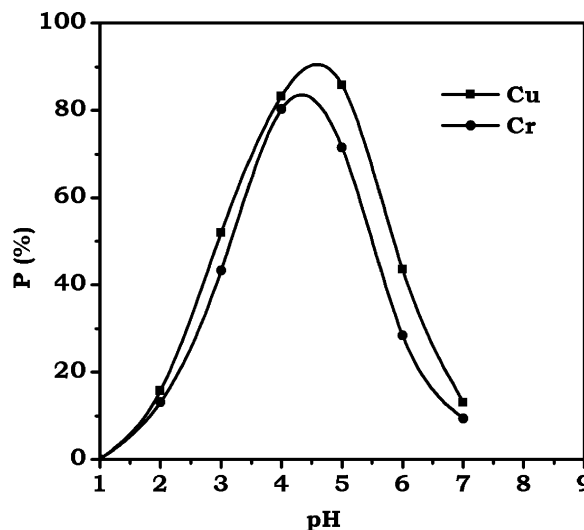

Fig. 8. DSC spectras of modified starch.

Fig. 10. Effect of pH on ions removal.

Table 1
Kinetics parameters for CASt.

T (K)	K_1 (min^{-1})		R^{2a}	
	Cu(II)	Cr(VI)	Cu(II)	Cr(VI)
303.15	0.02632	0.00454	0.97361	0.97884
303.15	0.03467	0.00907	0.97301	0.99585
303.15	0.05259	0.00973	0.99057	0.9929

[a] The relative coefficient.

In an acidic medium, the active groups responsible for the adsorption process mainly exist in the form Cu^{2+} and NH^{3+}, and they prevent the adsorption of Cu(II) ions onto CASt. As the pH increases from 3.0 to 4.0, the active site of CASt becomes free NH_2 which can chelation on Cu^{2+} easily. Beyond pH 5.0, the removal percentages become deceasing because the presence of Cu(II) was $Cu(OH)_2$ precipitation.

Similarly, in the solution pH < 3, the existence patterns of Cr(VI) mainly $HCrO_4^{-}$; and in solution pH around 4, the existence patterns of Cr(VI) mainly $Cr_2O_7^{2-}$ which can be adsorbed on NH_2 easily. While beyond pH > 6, the increasing of OH-concentration weakened the affinity between starch–OH and $Cr_2O_7^{2-}$ resulting in lower adsorption. Therefore, the adsorption reaction pH controlled at 3.0–5.0 is appropriate.

3.2.3. Adsorption kinetics study

The adsorption rate can be described by the first-order kinetic model, and which expressed:

$$-\ln\left(1 - \frac{Q_t}{Q}\right) = k_1 t$$

where k_1 is the first-order equilibrium constant, and where Q_t and Q (all in mg/g) represent adsorption value of Cu(II) and Cr(VI) ions in aqueous solutions at any time t and at equilibrium, respectively.

The relationship between $-\ln(1 - Q_t/Q)$ and t is observed in Fig. 11, and the nearly straight line observed indicates that the adsorption reactions can be approximated to a first-order kinetics.

Adsorption rate constants k_1 and R^2 for CASt were calculated and are shown in Table 1. It can be seen that the adsorption rate of CASt for Cu(II) was higher than that for Cr(VI) at any temperature. A reasonable explanation is that the functional group of CASt binds Cu(II) ions more easily than Cr(VI).

3.2.4. Adsorption isotherm

The adsorption isotherm for Cu(II) and Cr(VI) ions on the adsorbent CASt can be analyzed by the Langmuir adsorption isotherm which is expressed as

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e}$$

where C_e is the equilibrium concentration of the metal ions in solution, mg/L; Q_e is the equilibrium adsorption amount of adsorbent, mg/g; Q_0 is the maximum adsorption amount of adsorbent, mg/g; and b is the Langmuir constant, l/mg. Thus, a plot of $1/Q_e$ versus $1/C_e$ should yield a straight line having a slope $1/bQ_0$ and an intercept of $1/Q_0$ from which the values of Q_0 and b may be readily attained.

The Langmuir plot of the data of adsorbed Cu(II) and Cr(VI) ions on the absorbent at 30 °C are shown in Fig. 12. The relationship between $1/Q_e$ and $1/C_e$ is linear which exhibits that the adsorption behavior follows the Langmuir adsorption isotherm. The values of Q_0 and b are listed in Table 2.

The results indicate that the adsorbent has largest adsorption capacity in the case of Cu(II) and Cr(VI). So we got a conclusion that the adsorption of Cu(II) and Cr(VI) on CASt was monolayer adsorption which belonged to chemisorption.
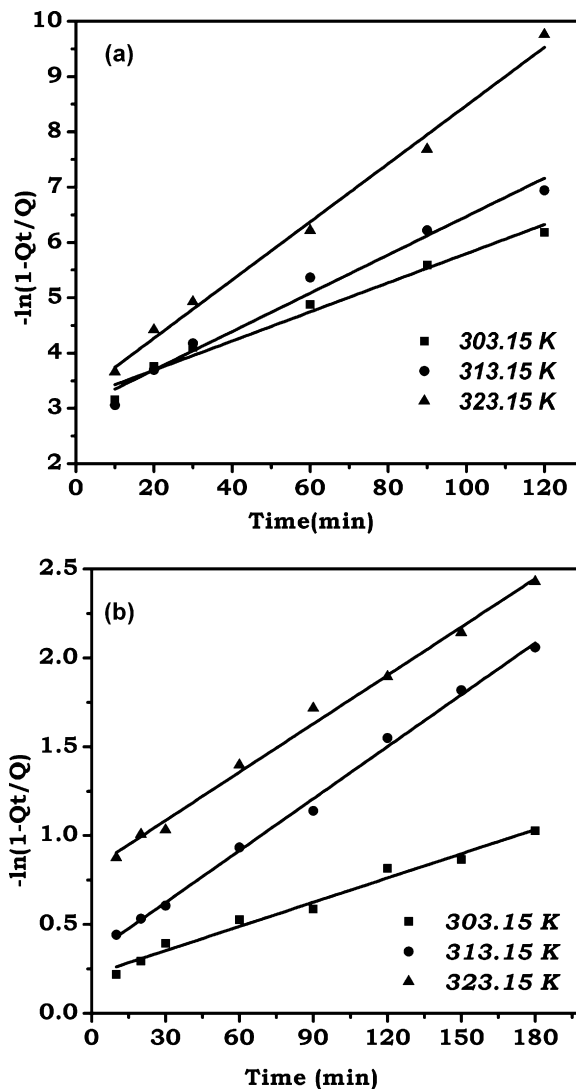

Fig. 11. Adsorption rate curves of CASt: (a) Cu(II); (b) Cr(VI).

Table 2
Langmuir parameters for CASt.

Metal ion	R^{2a}	Q_0	b
Cu(II)	0.9965	8.134	2.05
Cr(VI)	0.99932	12.12	0.06

[a] The relative coefficient.

3.2.5. Adsorbent reuse

The adsorption amount of Cu(II) on CASt regeneration or not were showed in Table 3.

As shown, there is little decrease on the adsorption amount regeneration or before. The regeneration experiment was processed in acid medium, and CASt would decompose. From the data we found that regeneration adsorbent can be reused.

Table 3
Two cycles of adsorption of CASt.

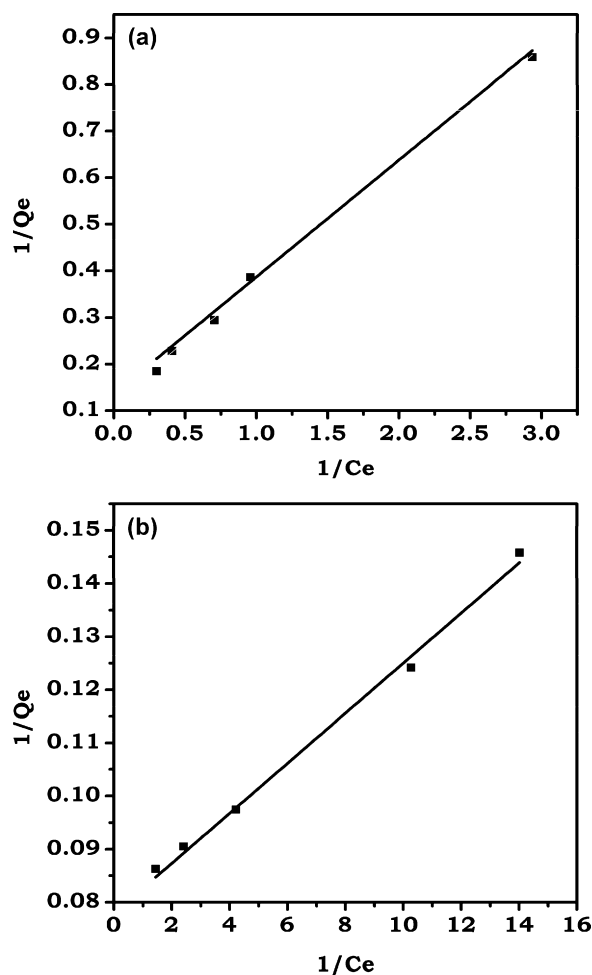| Metal ion	Q (mg/g)	
	1st cycle	2nd cycle
Cu(II)	29.4	28.3
Cr(VI)	12.5	11.4

Fig. 12. Langmiur isothermal adsorption curves of CASt: (a) Cu(II); (b) Cr(VI).

4. Conclusion

In this paper, a novel method was proposed to prepare CASt. CASt was prepared using corn starch as raw materials, through DASt reacting with EDA. The preparation was affected by pH, reaction time and temperature, EDA concentration and EDA:DASt molar ratio. The optimization synthesis condition of CASt was determined: EDA:DASt molar ratio 4:1, EDA concentration 0.6 mol/L,

pH 5.5, at 35 °C for 2 h. And under these conditions, the nitrogen content of CASt obtained to 150%, which was nearly twice of the traditional ether method. The CASt was characterized by IR, elemental analysis, XRD, and DSC. These analysis results prove that CASt has been successfully synthesized and has a well stability.

The adsorption activity of CASt for heavy metals such as Cu(II) and Cr(VI) was studied in terms of adsorption amount, kinetics and isotherm, adsorbent reuse was also studied. Adsorption processes for Cu(II) and Cr(VI) on CASt both fit langmiur isotherm model, and adsorption for Cu(II) and Cr(VI) from aqueous solution were endothermal reactions. CASt was very effective for the adsorption of Cu(II) and Cr(VI), and efficient in capacity, stability.

References

[1] J.S. Yang, T.S. Kwon, J.W. Yang, Cationic starch-enhanced ultrafiltration for Cr (VI) removal, Desalination 206 (2007) 245–250.
[2] U.C. Ghosh, Studies on adsorption behavior of Cr (VI) onto synthetic hydroxs-tannic oxide, Water Resour. 31 (2005) 597–602.
[3] N.N. Mamdouth, T.E. Kamar, E.E. Ebrahiem, Adsorption of iron and manganese ions using low cost materials as adsorbents, Adsorpt. Sci. Technol. 22 (2004) 25–37.
[4] M. Kobya, Adsorption, kinetic and equilibrium studies of chromium (VI) by hazenut shell activated carbon, Adsorpt. Sci. Technol. 22 (2004) 54–63.
[5] H.M. Kneg, Adsorption of Cu (II) and Cr (VI) ions by chitosan kinetic and equilibrium studies, Water Resour. 27 (2001) 1–5.
[6] Q. Yin, A.Q. Dong, Y.P. Yin, Rheological and thermal behavior of starch/LDPE blends containing EAA, Polym. Compos. 29 (2008) 45–749.
[7] M.I. Khalil, A.A. Aly, Preparation and evaluation of some cationic starch derivatives as flocculants, Starch/Staerke 53 (2001) 84–89.
[8] S.F. Zhang, B.Z. Ju, J.Z. Yang, X. Quan, Removal of Pb (II) from aqueous solution by cross-linked starch phosphate carbamate, J. Polym. Res. 13 (2006) 213–217.
[9] A.Q. Dong, Q. Yin, J. Xie, Y.P. Yin, Rheological and thermal behavior of CaCO₃/LDPE blends containing EAA, Polym. Compos. 30 (2009) 1212–1217.
[10] J. Xie, X.S. Zheng, A.Q. Dong, Biont shell catalyst for biodiesel production, Green Chem. 11 (2009) 355–364.
[11] S.M. Xu, S. Feng, G. Peng, J.D. Wang, Adsorption of Zn (II) ion onto crosslinked amphoteric starch in aqueous solutions, J. Polym. Res. 11 (2004) 105–108.
[12] M.I. Khalil, M.G. Abdel-Halim, Preparation of some starch-based neutral chelating agents, Carbohydr. Res. 324 (2000) 189–199.
[13] D.K. Kweon, J.K. Choi, Adsorption of divalent metal ions by succinylated and oxidized corn starches, Carbohydr. Polym. 46 (2001) 171–177.
[14] L.M. Zhang, D.Q. Chen, An investigation of adsorption of lead (II) and copper (II) ions by water-insoluble starch graft copolymers, Colloids Surf. A 205 (2002) 231–236.
[15] B.S. Kim, S.T. Lim, Removal of heavy metal ions from water by cross-linked carboxymethyl corn starch, Carbohydr. Polym. 39 (1999) 217–223.
[16] B. Xiang, Y.J. Li, Removal of Cu (II) from aqueous solutions by chelating starch derivatives, J. Appl. Polym. Sci. 92 (2004) 3881–3885.
[17] Q. Yin, B. Ju, Sh. Zhang, X. Wang, J. Yang, Preparation and characteristics of novel dialdehyde aminothiazole starch and its adsorption properties for Cu(II) ions from aqueous solution, Carbohydr. Polym. 72 (2008) 326–333.