

Preparation and adsorption properties of dialdehyde 8-aminoquinoline starch

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ABSTRACT

Dialdehyde 8-aminoquinoline starch (DASQA) was synthesized by the reaction of dialdehyde starch (DAS) and 8-aminoquinoline and was used to adsorb various ions from aqueous solution. DASQA was characterized by Fourier transform infrared (FT-IR) spectra, thermogravimetric analysis, X-ray diffraction analysis. The adsorption properties of the polymer for Pb^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , and Zn^{2+} were investigated. The result of the experiment reveals that the adsorption for Cd^{2+} and Zn^{2+} were approximately 2.51 mmol/g, 2.17 mmol/g, followed by Pb^{2+} 1.93 mmol/g, Ni^{2+} 1.66 mmol/g, Cu^{2+} 1.19 mmol/g. Furthermore, the kinetic experiments indicated that the adsorption of DASQA for the above metal ions achieved equilibrium within 2 h. Therefore, DASQA is an effective adsorbent for the removal of different heavy metal ions from industrial waste solutions.

Key words | adsorption, dialdehyde 8-aminoquinoline starch, dialdehyde starch, heavy metals

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INTRODUCTION

Environmental pollution, especially water pollution dramatically influences our lives. Sewage and industrial waste-water which contain various heavy metal ions become huge barriers in water protection. Their acute toxicity, non-biodegradable nature and build-up of high concentrations in water bodies all over the world raise increasing concern in recent years. Therefore, to develop a low cost and efficient adsorbent material for the removal of heavy metals is still a priority (Sen Gupta & Bhattacharyya 2012).

Experts from all over the world pay great attention to adsorbent materials; among these, precipitation, ion exchange, solvent extraction, and synthetic polymers, biological treatment (Ishikawa *et al.* 2002), membrane processes, advanced oxidation processes, chemical and electrochemical techniques (el-Ashtouky & Amin 2010), and adsorption procedures are the most widely used techniques for removing metals from industrial wastewater (Eren & Afsin 2008; Liu & Bai 2010).

Among all the treatments proposed, adsorption is a commonly used technique for the separation and recovery of heavy metals (Dhodapkar *et al.* 2006; Demirbas 2008). Activated carbons (Mellah *et al.* 2006; Khaled *et al.* 2009; Zaini *et al.* 2010), zeolites, clays (Sari *et al.* 2007; Anirudhan *et al.* 2010), silica beads (Yantasee *et al.* 2010), industrial by-products, agricultural wastes, biomass, and polymeric materials

are examples of different adsorbents (Dong *et al.* 2010). Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers (Cui *et al.* 2010). Among these, polysaccharides such as alginic acid, starch and its derivatives, chitosan (Fujiwara *et al.* 2007; Elwakeel 2009; Repo *et al.* 2011) and cyclodextrin deserve particular attention.

These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards heavy metal ions, resulting from the presence of reactive chemical groups in polymer chains.

After incorporating various ligands, chelating polymers can form coordinating bonds with most of the toxic heavy metals, owing to the donor atoms such as N, S, O, and P. It is easy for Schiff bases ($\text{C}=\text{N}$) to form complexes with transition metal ions because of their multidentate coordination sites. Besides, the molecular structure of 8-aminoquinoline contains N atoms, which strengthen the ability to bridge with metals. Up to now, little is known about the comparative abilities of polymer materials containing Schiff bases to absorb different ions.

The present work briefly presents the synthesis of dialdehyde 8-aminoquinoline starch (DASQA). DASQA was used

to remove different ions from aqueous solution. Batch adsorption experiments were carried out as a function of pH and adsorption time.

EXPERIMENTAL

Materials and apparatus

Potato starch (food-grade) was dried at 105 °C before it was used. Zn(NO₃)₂ and Pb(NO₃)₂, Cu(NO₃)₂, Cd(NO₃)₂, Ni(NO₃)₂, NaOH were purchased from Xi'an Chemical Factory (Xi'an AR China). NaIO₄ and 8-aminoquinoline (AR) were obtained from Shanghai Guomao Chemical factory (Shanghai AR China). All the other commercial chemicals were of analytic reagent grade and used without further purification. Infrared spectra were characterized using the KBr disc technique and recorded on NEXUS670. The elemental analysis (C, H and N) was carried out using Vario EL. The morphology of samples was identified by a JSM-5600 LV scanning electron microscope (SEM) operated at 20 kV. Atomic adsorption spectra were confirmed by an AAnalyst 240 instrument (Varian American). XRD was confirmed by X-ray diffractometer (D/Max-2400).

Preparation of dialdehyde starch

Sodium periodate solutions 0.9 mol/L used as oxidant were added into 4.0 g potato starch suspension to prepare dialdehyde starch (DAS). The mixture was stirred slowly at 30 °C in the dark for 4 h and washed several times with distilled water and ethanol. The percentage of dialdehyde units was given by the equation:

$$\text{Da}\% = \left(\frac{V_1 C_1 - V_2 C_2 \times 100\%}{W/161} \right) \quad (1)$$

where V_1 , V_2 and W represent the total volumes (L) of H₂SO₄, NaOH and the dry weight (g) of the oxidized

starch, respectively. C_1 , C_2 (mol/L) represent the concentrations of H₂SO₄ and NaOH. One hundred and sixty-one is the average molecular weight of the repeated unit in DAS. The aldehyde group content was determined using the rapid quantitative alkali consumption method (Hofreiter *et al.* 1955). The Da of the adsorbent is 0.91.

Preparation of starch dialdehyde 8-aminoquinoline (DASQA)

A measure of 4.0 g DAS was suspended in 50 mL distilled water in a 100 mL two-necked flask, which was equipped with an electromagnetic stirrer and thermostat oil bath. As the melting point of 8-aminoquinoline is 62–65 °C, the mixture was in this temperature region. Afterwards, a certain amount of 8-aminoquinoline (the mole ratio of it to DAS is 2:1) was slowly put into the flask. Acetic acid was added into the flask to adjust the pH of the solution to 5.0. Under the protection of nitrogen for 4 h, the products of interest were separated by Buchner Filter Funnel, washed several times and then dried at 50 °C in vacuum.

The reaction process of dialdehyde 8-aminoquinoline is shown in Figure 1.

Adsorption properties of DASQA for heavy metal ions

Adsorption experiments were carried out by batch methods. A certain dose (0.15 g) of DASQA was added into a 100 mL Erlenmeyer flask with 50 mL 20.0 mmol/L ion solutions at 20 °C. Zn(NO₃)₂, Cu(NO₃)₂, Pb(NO₃)₂, Ni(NO₃)₂, Cd(NO₃)₂, were used respectively. The mixture was stirred on a magnetic stirrer at a proper speed in a constant temperature bath. A concentration of 0.1 mol/L HNO₃ or 0.1 mol/L NaOH was used before adding the adsorbent, the addition of HNO₃ and NaOH are to adjust the pH of the aqueous medium. Some time later, the mixture was filtered and the final concentration of ions was identified by atomic adsorption spectrophotometer.

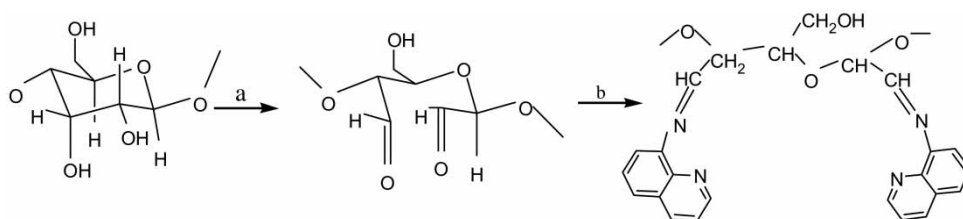


Figure 1 | Reagents and conditions; (a) NaIO₄ (b) 8-aminoquinoline.

The adsorption capacity was calculated by the following formula:

$$Q = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where Q is the adsorption capacity of the adsorbent (mmol/g), C_0 and C_t (mmol/L) are the initial and terminal concentrations of the ions in the adsorption solution, and V (mL) and m (g) are the volumes of the adsorption solution and the dose of the adsorbent, respectively.

RESULTS AND DISCUSSION

Characterization of DAS and DASQA

The FT-IR spectra of DAS and DASQA

The Fourier transform infrared (FT-IR) spectra of the products were stated in the $4,000\text{--}500\text{ cm}^{-1}$ on KBr pellet. Figure 2 shows the IR spectra of DAS and DASQA. It is evident that the characteristic bands are at $1,731$ and $2,922\text{ cm}^{-1}$. The former relate to the stretching vibrations of the $\nu(\text{C}=\text{O})$, while the peak at $2,922\text{ cm}^{-1}$ refers to $\nu(\text{C}-\text{H})$. Compared with DAS, the IR spectra of DASQA showed new bands at $1,622$ and $3,407\text{ cm}^{-1}$. The band at $1,622\text{ cm}^{-1}$ can be assigned to $\nu(\text{C}=\text{N})$, which is the identity of the connection between DAS and 8-aminoquinoline. The band observed at $3,407\text{ cm}^{-1}$ was the stretching vibrations of $\nu(\text{N}-\text{H})$.

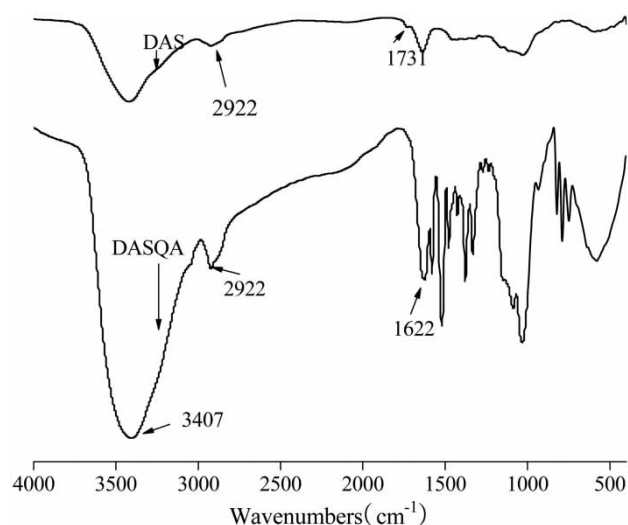


Figure 2 | FT-IR spectra of DAS and DASQA.

X-ray diffraction analysis

The effect of periodate oxidative and graft copolymerization on the crystallinity of starch, DAS and DASQA were studied by XRD. As we can see in Figure 3, the curves a, b and c refer to potato starch, DAS and DASQA, respectively. The original starch shows scattering at $2\theta = 15.5^\circ$, 17.2° , 24.2° , which are characteristic peaks of starch. The absence of the peak at $2\theta = 21.5^\circ$ in DAS indicates that the intensity and sharpness of the reflections decrease, confirming the decrease in the crystallinity. It is assumed that the aggregation phase of the original starch is changed from semicrystalline state to an amorphous aggregation state during the periodate oxidative and the chain breakage reactions. However, after DAS grafted 8-aminoquinoline, the peak further becomes weaker than DAS which indicates that its crystallinity is further reduced. In addition, the group $\text{C}=\text{N}$ replacing the $\text{C}=\text{O}$ would also probably causes the crystallinity of the DASQA to decrease.

Thermal stability analysis

The degradation process and thermal stability of DAS and DASQA were evaluated through thermogravimetric analysis (TGA). As observed from the Figure 4, the TGA of DAS and DASQA exhibit a weight loss in four main degradation stages. The first stage from 25 to 101°C shows 2.9% loss in weight, which is due to the loss of adsorbed and bound water. The maximum decomposition temperatures of DASQA were higher than DAS, as the water in DASQA was absorbed water, while the water in DAS was connected with the aldehyde group in hemiacetal. The second stage

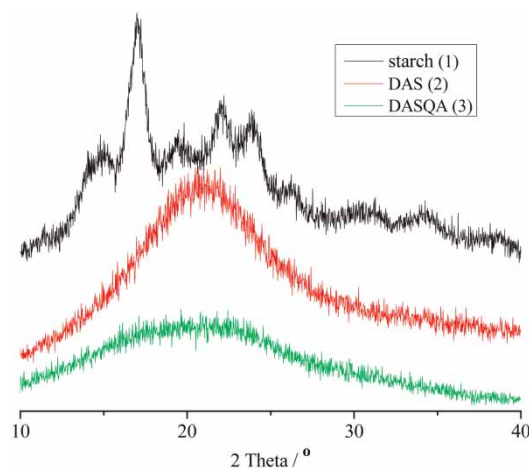


Figure 3 | XRD of starch, DAS and DASQA.

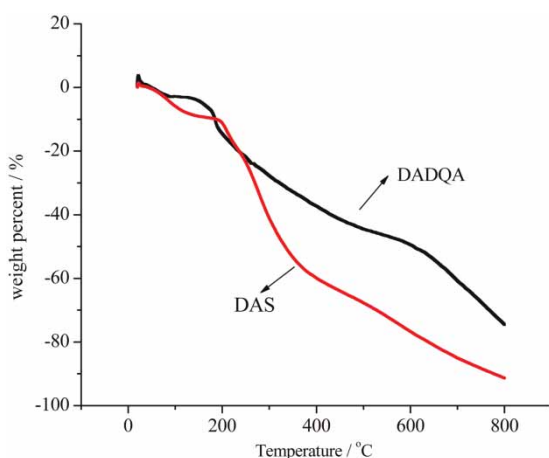


Figure 4 | TGA of DAS and DASQA.

was 101–175 °C, the weight loss of DASQA was about 7.1%, compared with DAS (10%). The maximum decomposition temperature of DASQA (175 °C) was also higher than of DAS (190 °C); in addition, the weight loss was even more. The reason is that the molecular chain was more degraded due to the eventual destruction of the polymer crystal structure. Meanwhile, the form of Schiff base generates more low energy unsaturated double bonds and nitrogen, therefore, those molecules are more likely to form volatile substances. The third step ranges from 175 to 534 °C, with the weight loss of 39.9%, in this pyrolysis stage, was less than DAS. The last stage was 534–792 °C, the hot polycondensation stage, and the weight loss was about 27.4%. The organic component hot polycondensation reaction had happened. The total loss was 73.6%, lower than the DAS, which was probably due to the more stable aromatic ring in the polymer.

Effect of the initial pH

Figure 5 shows the relationship between the pH value of metal ion solution and the adsorption capacity of DASQA for Pb^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} and Zn^{2+} . The experiments were conducted in the pH ranges of 2.0–6.0. The influences of $\text{pH} > 6.0$ were not studied to avoid the formation of precipitate. The adsorption uptake of DASQA for metal ion increased with the increase of the pH value up to a maximum value at $\text{pH} = 5$, and then decreased with further increase of pH. Underpinning the effect of iminodiacetate group forming stable complexes, adsorption took place even at $\text{pH} = 2$. During the chelation process, these ions form a coordinating bond with the electron pair of negatively charged oxygen and unshared electron pair of nitrogen in

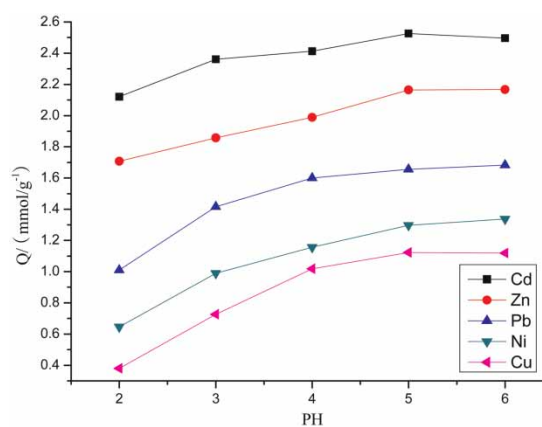


Figure 5 | Effect of pH on adsorption capacity of DASQA for metal ions. $[\text{M}(\text{NO}_3)_2] = 20 \text{ mmol/L}$; $t = 2 \text{ h}$; $T = 25 \text{ }^\circ\text{C}$; the dose of each DASQAs 0.15 g.

iminodiacetate which has nitrogen atoms linked to a short chain having carboxylic groups, making possible chelating metal ions at low pH. In this figure, as Zn and Cd are in a same group, 12 the adsorption of them is higher than the other ions. Probably because the numbers of the outermost electron are the same, making it easy to added into the adsorbent. Followed by Pb, Ni and Cu.

Effect of adsorption time

In order to explore the suitable reaction time, adsorption capacities of different ions were measured as a function of time. Response time varies from 30 to 180 min (Figure 6). The reaction reached a relatively stable position at approximately 2 h. After that, the optimum appeared and remained the same until 180 min. It is evident from the figure that the samples all attained equilibrium at 120 min or so. The tendency of the adsorption of the ions is the same as the pH figure.

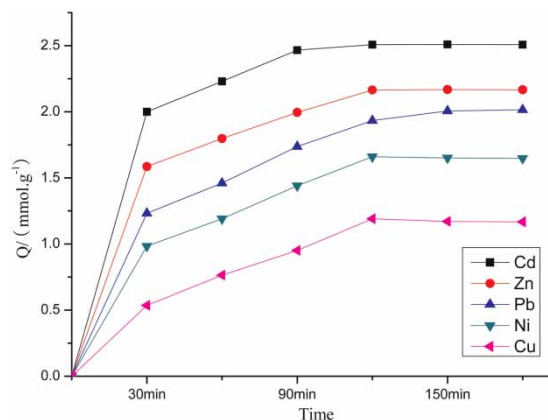


Figure 6 | Adsorption kinetics of DASQA for metal ions. $[\text{M}(\text{NO}_3)_2] = 20 \text{ mmol/L}$; $T = 25 \text{ }^\circ\text{C}$; the dose of each DASQAs 0.15 g.

CONCLUSIONS

In this paper, a novel method was used to adsorb the various ions from wastewater. DASQA was synthesized with 8-aminoquinoline and DAS. The adsorption properties of the polymer for Pb^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , and Zn^{2+} were different. The results of the experimental reveals that the adsorptions for Cd^{2+} and Zn^{2+} were approximately 2.51 mmol/g, 2.17 mmol/g, followed by Pb^{2+} 1.93 mmol/g, Ni^{2+} 1.66 mmol/g, Cu^{2+} 1.19 mmol/g. Furthermore, the kinetic experiments indicated that the adsorption of DASQA for the above metal ions achieved equilibrium within 2 h. Therefore, the effective and the inexpensive DASQA was bound to be an extensive adsorbent for the removal of different heavy metal ions from industrial waste solutions.

As an effective and biodegradable adsorbent, DASQA may have great potential application for the removal of different ions (II) from wastewater. Moreover, the product's selectivity was fine.

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