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Removal of Zn (II) ions by dialdehyde 8-aminoquinoline starch from aqueous solution

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ABSTRACT

Dialdehyde 8-aminoquinoline starch (DASQA) was synthesized by the reaction of dialdehyde starch (DAS) and 8-aminoquinoline. It was used to adsorb Zn (II) ions from aqueous solution. DASQA was characterized by element analysis, FT-IR spectra, SEM and BET. The results of FT-IR showed the difference between DAS and DASQA in the spectrum. The adsorption study revealed that 120 min and pH 5.0 were the optimal conditions for adsorption of Zn^{2+}. Maximum adsorption capacity was found to be 1.915 mmol/g. The adsorption equilibrium data correlated well with the Langmuir isotherm model. With the degree of substitution (DS) of the DASQA increased, the adsorption capacity increased gradually, which can also be reflected in the results of BET. Moreover, higher temperature was preferable to the adsorption since it was endothermic.

1. Introduction

Environment protection has been given considerable attention over recent years. Heavy metal ions from sewage and industrial waste water are of environmental concern due to their acute toxicity, non-biodegradable nature and build-up of high concentration in water bodies all over the world (Mark et al., 2008). In the past few years, various technologies have appeared to remove toxic metal ions from waste water. Precipitation, ion exchange (Gupta & Mohan, 1999; Huang, Si, & Li, 1997; Karakisla, 2003), solvent extraction, and adsorption on activated carbon, as well as synthetic polymers (Egawas, Nonaka, Abe, & Nakayama, 1992; Lee & Hong, 1995; Piskin, Keenci, & Satiroglu, 1996; Rivas, Pereira, Gallegos, & Geckeler, 2002) are available for removing the heavy metal ions from aqueous solutions. Among them, adsorption is a common used technique for the separation and recovery of heavy metal ions (Guo, Zhang, & Yang, 2006; Gupta, Saini, & Jain, 2005). Therefore, to develop a low-cost and efficient adsorbent material for the removal of heavy metals is still in urgent need.

As sorbents, biopolymers attract more and more attentions from chemists because of its economical and effective characteristics (Gupta & Sharma, 2002, 2003; Gupta, Ali, Suhas, & Saini, 2006; Gupta, Carrott, Ribeiro Carrott, & Suhas, 2009; Gupta & Rastogi, 2008a, 2008b, 2008c, 2008d; Gupta, Rastogi, & Nayak, 2010a). Among these biopolymers, polysaccharides deserve particular attentions. While as a natural polysaccharide, starch is renewable and biodegradable. Furthermore, the low-cost modified starch is capable of adsorbing heavy metal ions. It is previously reported that various approaches have been used to modify starch as a metal absorbent (Crini, 2005; Gupta, Rastogi, & Nayak, 2010b). Carboxylate (Khalil & Abdel-Halim, 2001; Xu, Feng, Peng, Wang, & Yushan, 2005; Xu, Zhang, Lu, Yang, & Cui, 2003), xanthate (Bose, Bose, & Kumar, 2002), phosphate (Guo, Zhang, Ju, & Yang, 2006), acrylamide (Chauhan, Singh, & Sharma, 2006) and acrylonitrile (Abdel-Aal, Gad, & Dessouki, 2006) can be used in the chemical modification (including esterification, etherization and oxidation). Since aldehyde groups could form hemiacetals and acetals, glyoxal and glutaraldehyde have been successfully used in cross-linking acetalation of cellulose derivatives (Maurer, 1969). Industrial applications of dialdehyde starch are also based on its cross-linking ability. As an example, majority of DAS productions were consumed by the paper industry as wet-strength improver (Gupta & Suhas, 2009; Jetten, Timmmerman, Besemer, VandenDool, & Boumans, 2003; Schneider & Riella, 1980; Thornton, VanBrussel-Verraest, Besemer, & Sandberg, 2001).

Previous studies revealed that dialdehyde starch with dithiosemicarbazone (Para & Ropek, 2000), disemicarbazone (Ropek & Para, 2002) or even dihydrazone (Para, Karolczyk-Kostuch, & Fiedorowicz, 2004) could form stable complexes to absorb heavy metal ions (Yin, Ju, Zhang, Wang, & Yang, 2008). After incorporated with various ligands, chelating polymers (Moniera, Ayadb, & Sarhanb, 2010) can form coordinate with most of the toxic heavy metals owning to the donor atoms such as N, S, O, and P. It is easy for Schiff bases (C=N) to form complexes with transition metal ions because of its multidentate coordination sites. Besides, the molecular structure of 8-aminoquinoline contains N atoms,

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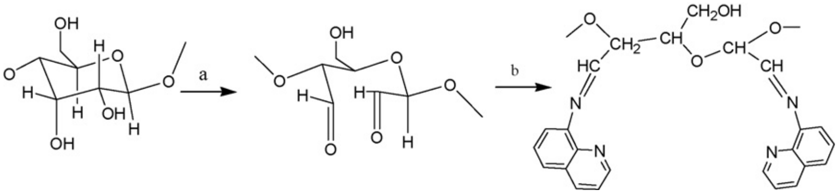

Scheme 1. Reagents and conditions: (a) $NaIO_4$ and (b) 8-aminoquinoline.

which strengthened the ability to bridge with metals. Up to now, few work about polymer matrixes containing Schiff base to absorb Zn (II) ions has been reported.

This work briefly presented the synthesis of dialdehyde 8-aminoquinoline starch (DASQA), which was used to remove Zn (II) ions from aqueous solution. Batch adsorption experiments were carried out as a function of pH, adsorption time, initial Zn (II) ions concentration and temperature. The adsorption isotherm and thermodynamics parameters of the adsorption were also studied.

2. Experimental

2.1. Materials and apparatus

Potato starch (food-grade) was dried at 105 °C before it was used. Zn $(NO_3)_2$ and NaOH were purchased from Xi'an Chemical Factory (Xi'an AR China). $NaIO_4$ 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. An infrared spectrum was characterized by the KBr disc technique and was recorded on NEXUS670. The elemental analysis (C, H and N) was carried out using VarioEL. The morphology of sample was identified by a JSM-5600 LV scanning electron microscopy (SEM) operated at 20 kV. Atomic adsorption spectrometry was confirmed by an Analyst 240 instrument (Varian American). The BET was studied by Chemisorb 2750.

2.2. Preparation of dialdehyde starch and determination of aldehyde content

Dialdehyde starch was prepared according to the method described in the paper (Yin et al., 2008). Sodium periodate solutions (0.3 mol/L, 0.5 mol/L and 0.9 mol/L) used as oxidant were added into 4.0 g potato starch suspension to prepare dialdehyde starch. The mixture was stirred slowly at 30 °C in the dark for 4 h and washed several times with distilled water and ethanol. Three samples with different degrees of oxidation were defined as DAS1, DAS2 and DAS3, respectively. The aldehyde group content was determined using the rapid quantitative alkali consumption method (Hofreiter, Alexander, & Wolff, 1955) and the results were 28%, 45% and 88% for DAS1, DAS2 and DAS3, respectively.

The percentage of dialdehyde units was given by the equation:

$$Da\% = \frac{(V_1C_1 - V_2C_2) \times 100\%}{W/161} \qquad (1)$$

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

2.3. Preparation of starch dialdehyde 8-aminoquinoline

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. Since the melting point of 8-aminoquinoline ranged between 62 °C and 65 °C, the mixture was also at that temperature regime. Afterwards, 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 Filter Funnel Buchner and washed for several times and then dried at 50 °C in vacuum.

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

2.4. Analysis of adsorbents

The substitution degree of 8-aminoquinoline for DASQA was theoretically calculated from the nitrogen content using the following equation:

$$DS = \frac{161 \times N\%}{2800 - 126.18 \times N\%} \times 100\% \qquad (2)$$

DS and N% represent the substitution degree of DASQA and the nitrogen content in DASPDA, respectively.

Table 1 indicates the results of the element analyses. The DS of $DASQA_1$, $DASQA_2$ and $DASQA_3$ were 0.29, 0.46, and 0.91, correspondingly.

2.5. Adsorption experiments

Adsorption experiments were carried out by batch methods. Certain dose (0.15 g) of DASQA was added into a 100 mL Erlenmeyer flask with 50 mL 20.0 mmol/L Zn $(NO_3)_2$ solution at 20 °C. The suspension was stirred on a magnetic stirrer at a proper speed in a constant temperature bath. 0.1 M HNO_3 or 0.1 M NaOH was used before adding the adsorbent. Some time later, the mixture was filtered and the final concentration of zinc (II) ions was identified by atomic adsorption spectrophotometer.

The adsorption capacity was calculated by the following formula:

$$Q = \frac{(C_0 - C_t)V}{m} \qquad (3)$$

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 Zn (II) 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.

Table 1
Degree of substitution of DASQA.

Product	Reactant	Color	Elemental analysis			DS	BET (m^2/g)
			N (%)	C (%)	H (%)		
DASQA1	DAS1	Yellow	4.16	49.38	5.86	0.29	24.8
DASQA2	DAS2	Yellow	5.85	52.03	5.81	0.46	26.2
DASQA3	DAS3	Yellow	9.24	60.73	5.43	0.91	29.0

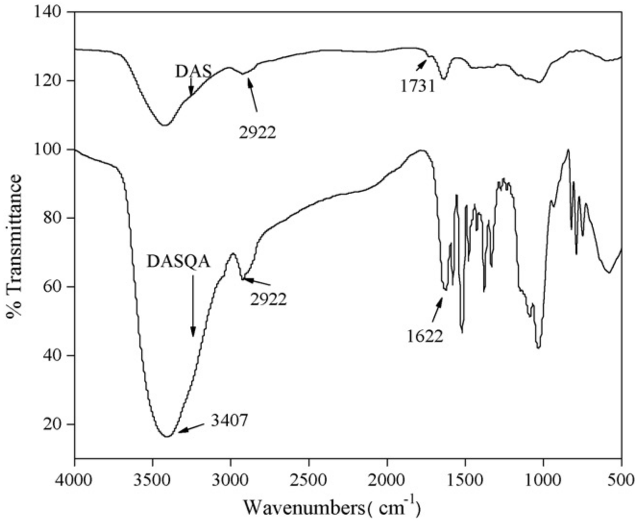

Fig. 1. FT-IR spectra of DAS and DASQA.

3. Results and discussion

3.1. Characterization of the prepared DASQA

3.1.1. The FT-IR spectra of DAS and DASQA

The FT-IR spectra of the products were stated in the 4000–500 cm^{-1} on KBr pellet. Fig. 1 shows the IR spectra of DAS and DASQA. It was evident that the characteristic bands at 1731 cm^{-1} related to the stretching vibrations of the ν(C=O), while the peak at 2922 cm^{-1} referred to ν(C–H). Compared with DAS, the IR spectra DASQA appeared new bands at 1622 cm^{-1} and 3407 cm^{-1}. The band at 1622 cm^{-1} could be assigned to ν(C=N), which was the identity of the connection between DAS and 8-aminoquinoline. The band observed at 3407 cm^{-1} was the stretching vibrations of ν(N–H).

3.1.2. Surface morphology of DASQA

SEM photographs clearly showed the structure of different samples (original potato starch, DAS$_3$, DASQA$_3$ and DASQA$_3$ with Zn^{2+}) in Fig. 2. Generally, Fig. 2a, c, e and g are taken at 500 magnifications while Fig. 2b, d, f and h at 1000 magnifications. It can be seen that the surfaces of original potato starch particles (Fig. 2a and b) were smooth, however, the cleavage of glucosidal rings for particles oxidized by periodate produced and led to uneven surface, and created pores on the particles (Fig. 2c and d). Furthermore, the particles were conglomerated closely, and the granules became much bigger than the original starch. Connecting with 8-aminoquinoline, the particles (Fig. 2e and f) fragments and the irregular structure appeared due to reduction or loss of cross-linking. After the absorption of Zn^{2+}, the fragments (Fig. 2g and h) became much smaller. The photos were similar with the paper revealed before (Yin et al., 2008; Zhao et al., 2010).

3.1.3. BET specific surface area

The BET surface area (S_{BET}) of DASQA$_1$, DASQA$_2$ and DASQA$_3$ are given in Table 1. The S_{BET} increased with the raise of DS. Besides, the specific surface area of DAS was smaller than the others, because of its high degree of cross-linking.

3.2. Adsorption of Zn^{2+}ions

3.2.1. Effect of initial pH

The removal of metal ions from aqueous solution by adsorption was depended on the pH of the solution, since it affected adsorbent surface charge, degree of ionization of the functional groups, and metal ion speciation (Flaviane, Leandro, & Laurent, 2010). Most researchers agreed that the optimal pH vary with diverse metal ions. DASQA adsorption capacity of metal ions enhanced with the increase of PH.

Table 2
Langmuir parameters for three kinds of DASQAs.

Sample	Q_m (mmol/g)	b (L/mmol)	R^2
DASQA1	1.9734	0.5241	0.9980
DASQA2	2.0201	0.7114	0.9994
DASQA3	2.0788	0.8306	0.9997

Fig. 3 exhibits the relationship between the pH value of metal ion solution and the adsorption capacity of DASQA for Zn^{2+}. The experiments were conducted in the pH ranges of 2.0–6.0. The phenomenon can probably be explained like this: underpinning the effect of iminodiacetate group forming stable complexes, adsorption took place even at pH 2. During the chelation process, zinc ions formed a coordinating bond with the electron pair of negatively charged oxygen and unshared electron pair of nitrogen in iminodiacetate which has nitrogen atoms linked to a short chain having carboxylic groups, making possible chelating metal ions at low pH values (Flaviane et al., 2010). As for the following experiments, pH 5 was chosen owing to the little difference between the adsorption ability of pH 5 and pH 6, and to avoid the possibility of the error caused by precipitation as well. The adsorption ability of the three samples rose with the increase of PH. Adsorption ability of DASQA$_2$ was lower than DASQA$_3$ but higher than DASQA$_1$, which just met the DS of 8-aminoquinoline (DS$_1$ < DS$_2$ < DS$_3$) groups.

3.2.2. Effect of adsorption time

In order to explore the suitable adsorption time, adsorption capacity of Zn (II) ions was measured as a function of time. Time ranged from 30 min to 180 min. Fig. 4 exhibits the adsorption progress became constant after 120 min, so the optimal adsorption time was 120 min. It was evident from Fig. 4 that all the samples attain equilibrium at 120 min.

3.2.3. Effect of the initial Zn (II) ions concentration

Initial Zn (II) concentrations had a direct effect on the adsorption capacity of DASQAs. In Fig. 5, the adsorption capacity of DASQA$_1$, DASQA$_2$, and DASQA$_3$ increased from 1.544 mmol/g to 1.746 mmol/g, 1.694 mmol/g to 1.848 mmol/g and 1.753 mmol/g to 1.915 mmol/g correspondingly when the initial Zn (II) ions changed from 12.0 mmol/L to 20.0 mmol/L. The adsorption trends among three samples were similar, which implied that the types of adsorption isotherms of them were alike. The DASQA$_3$ adsorption capacity was much better than others.

3.2.4. The Langmuir isotherm

Langmuir isotherm was widely used to study the adsorption behavior. It could be expressed as follows:

$$\frac{C_e}{Q} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (4)$$

As stated above, Q (mmol/g) is the equilibrium adsorption capacity while Q_m (mmol/g) is the maximum amount of metal ion per unit weight of the material; C_e (mmol/L) and b (L/mmol) are the equilibrium Zn (II) ions concentration and Langmuir constant related to the binding sites affinity, respectively.

A pretty good linearized plot of C_e/Q versus C_e can be seen in Fig. 6. Q_m, b and R^2 were obtained from the slopes and interceptions of different lines. Table 2 shows the calculated results. Also, the Langmuir constant b (0.5241 L/mmol, 0.7114 L/mmol and 0.8306 L/mmol) shared same trend with DS (0.29, 0.46 and 0.91) of the aminothiazole group.

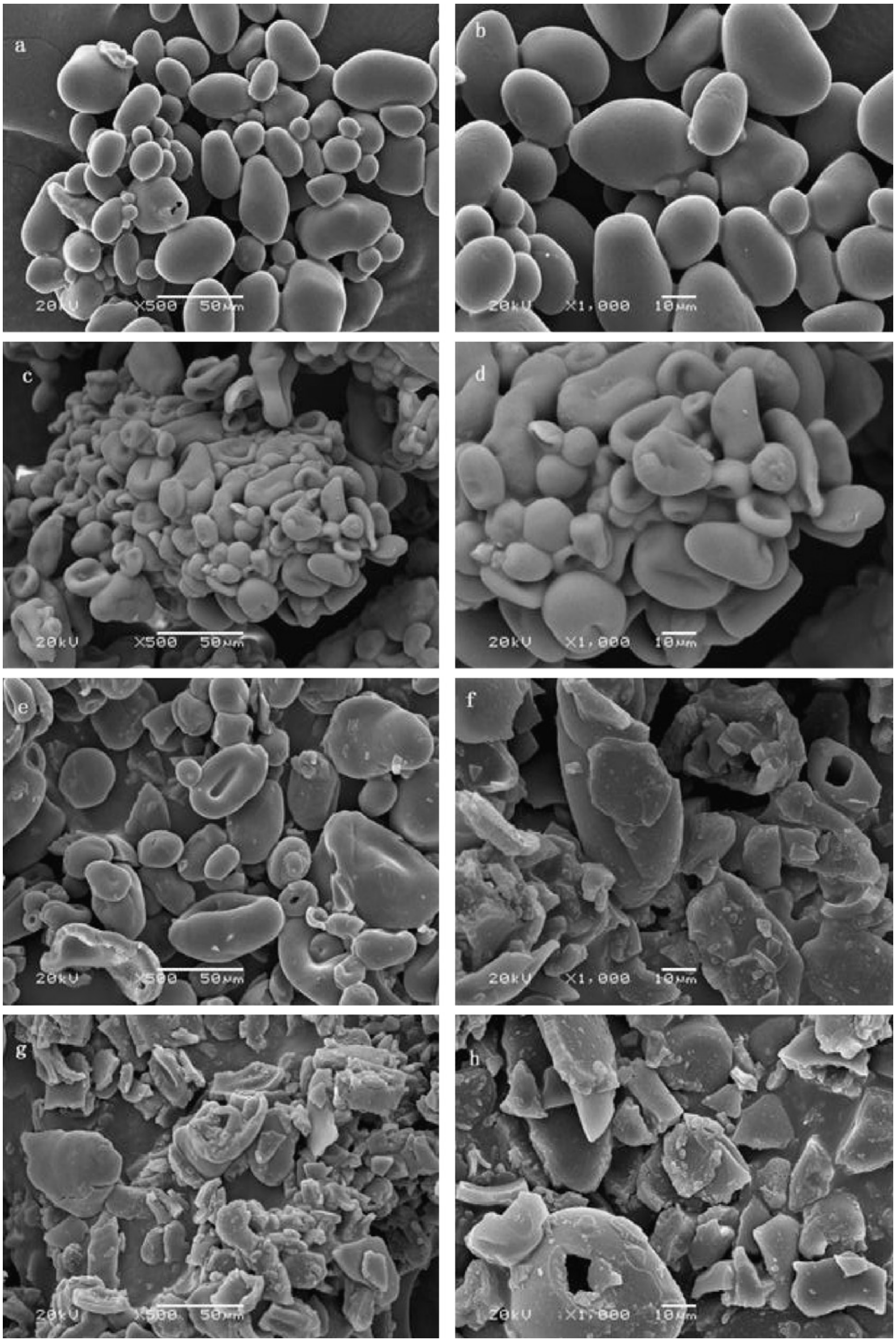

Fig. 2. SEM images of different starch granules. (a and b) Potato starch; (c and d) DAS_3; (e and f) DASQA; (g and h) DASQA adsorbed Zn (II) ions. The scale bar is 50 µm for (a), (c), (e) and (g) and 10 µm for (b), (d), (f) and (h).

3.3. *Adsorption isotherm*

3.3.1. *Thermodynamic studies*

The thermodynamics for the adsorption of Zn (II) on $DASQA_3$ was investigated in the range of 20–60 °C. Fig. 7 shows that, value Q raised with the increase of temperature in this scope. Therefore, thermodynamic expression was prone to get rid of this problem. The equations were as follows:

$$\log \frac{Q}{C_e} = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{2.303R} \tag{5}$$

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \tag{6}$$

Above the formulas, ΔG^θ, ΔH^θ and ΔS^θ represent Gibbs free energy, enthalpy and entropy. In more detail, Fig. 8 displays the plot of $\log(Q/C_e)$ versus $1/T$, ΔH^θ and ΔS^θ can be acquired according to the slopes and interceptions of the former Eq. (5). Besides, ΔG^θ can be acquired from the latter (6). Thermodynamic parameters (ΔH^θ, ΔS^θ and ΔG^θ) are listed in Table 3. So from the analysis, we can draw a conclusion that high temperatures would be beneficial for adsorption, since ΔG^θ decreased with the increase of temperature. While the positive value of ΔS^θ indicates that there was an increase

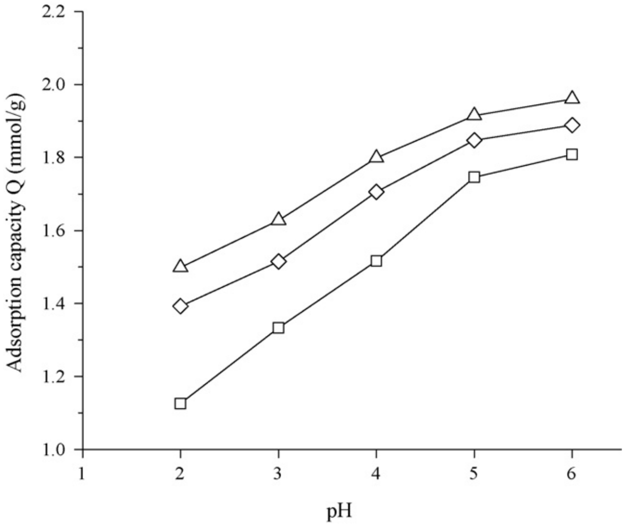

Fig. 3. Effect of initial pH value of the solutions on adsorption capacity: (△) DASQA$_1$; (◊) DASQA$_2$; (□) DASQA$_3$ $[Zn(NO_3)_2] = 20$ mmol/L; $t = 2$ h; $T = 25\,^{\circ}C$. The dose of each DASQA is 0.15 g.

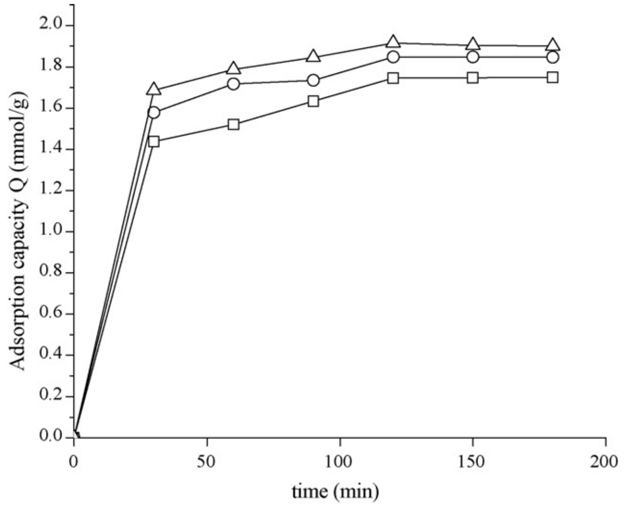

Fig. 4. Effect of adsorption time: (△) DASQA$_1$; (◯) DASQA$_2$; (□) DASQA$_3$ $[Zn(NO_3)_2] = 20$ mmol/L; $t = 2$ h; $T = 25\,^{\circ}C$. The dose of each DASQA is 0.15 g.

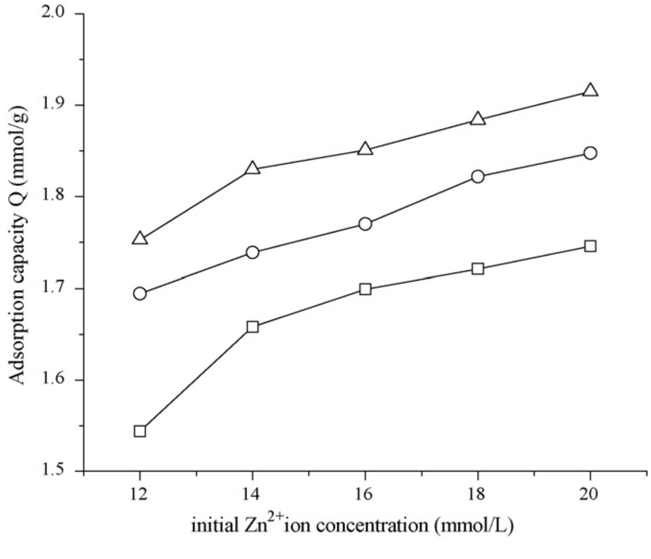

Fig. 5. Effect of initial concentration of Zn (II) on (△) DASQA$_1$; (◯) DASQA$_2$; (□) DASQA$_3$; $t = 2$ h; $T = 25\,^{\circ}C$. The dose of each DASQA is 0.15 g.

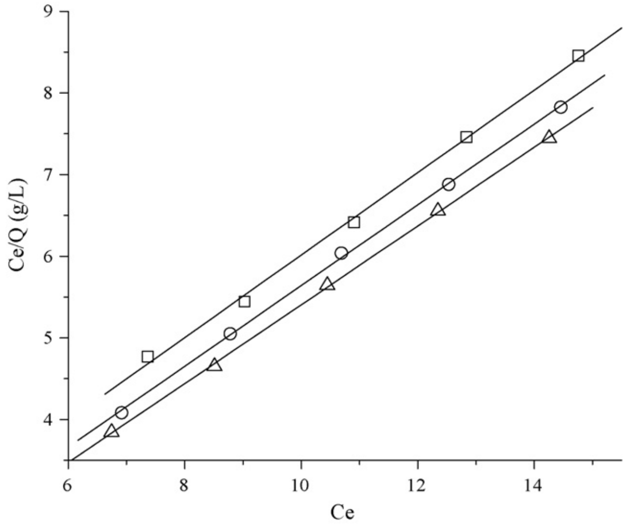

Fig. 6. Langmuir isotherm for the adsorption of Zn (II) ion: (△) DASQA$_1$; (◯) DASQA$_2$; (□) DASQA$_3$ $[Zn(NO_3)_2] = 20$ mmol/L; $t = 2$ h; $T = 25\,^{\circ}C$. The dose of each DASQA is 0.15 g.

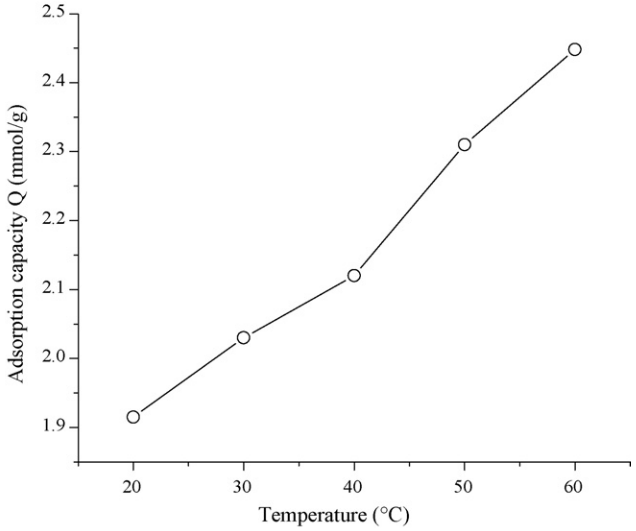

Fig. 7. Effect of adsorption temperature (◯) DASQA$_3$ $[Zn(NO_3)_2] = 20$ mmol/L; $t = 2$ h; $T = 25\,^{\circ}C$. The dose of each DASQA is 0.15 g.

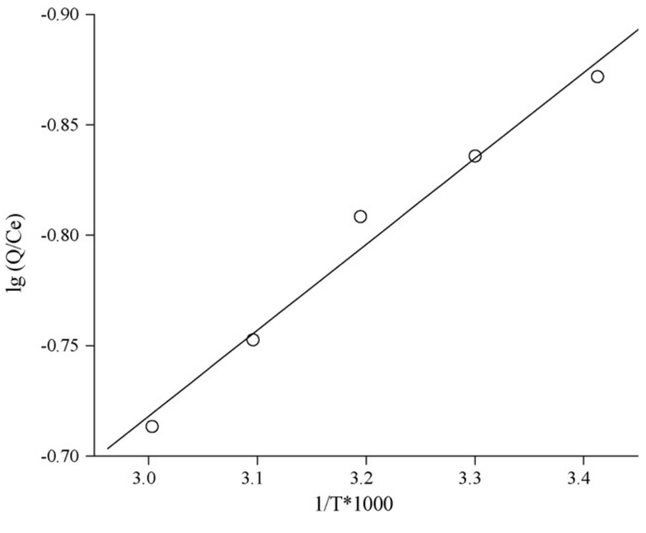

Fig. 8. $\log(Q/C_e) \sim 1/T^{*}1000$ for DASQA$_3$ $[Zn(NO_3)_2] = 20$ mmol/L; $t = 2$ h; $T = 25\,^{\circ}C$. The dose of each DASQA is 0.15 g.

Table 3
Thermodynamic parameters for DASQA3.

Temperature (°C)	ΔG^θ (kJ/mol)	ΔH^θ (kJ/mol)	ΔS^θ (kJ/mol K^{-1})
20	4.930	7.442	8.574
30	4.845		
40	4.759		
50	4.674		
60	4.587		

in the randomness at the solid/solution interface during the adsorption process. The small values of ΔH^θ were likely to be on account of the weak ionic bond interactions of Zn (II) ions (Guo, Sun, Li, Liu, & Ji, 2009). Moreover, the positive value of ΔH^θ indicated that high temperature was preferable for adsorption.

4. Conclusions

The adsorbent (dialdehyde 8-aminoquinoline starch) can remove the zinc ions from aqueous effectively and it was relatively cheap as well. DASQA was synthesized by 8-aminoquinoline and dialdehyde starch (DAS). During the experiment, we can see that the pH of the solution, the initial concentrations of Zn (II) ions, and the adsorption temperature had important effect on the adsorption ability. The optimal adsorption and pH were 120 min and 5.0. The maximal adsorption capacities of $DASQA_1$, $DASQA_2$ and $DASQA_3$ in this study were 1.746 mmol/g, 1.848 mmol/g, and 1.915 mmol/g, respectively. The adsorption process can be well described by Langmuir isotherm. The adsorption capacity increased with the DS of the DASQA increasing. The adsorption process of $DASQA_3$ was endothermic, and the apparent enthalpy (ΔH^θ) was 7.442 kJ/mol. As effective and biodegradable adsorbents, DASQA may have great potential application for the removal of Zn (II) ions from waste water.

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