Adsorption of Zn(II) on dialdehyde *m*-phenylenediamine starch

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ABSTRACT

A new chelating material dialdehyde *m*-phenylenediamine starch (DASMPA) was synthesized by reacting *m*-phenylenediamine with dialdehyde starch. The obtained material was characterized by element analysis and Fourier transform infrared (FT-IR) spectra. The FT-IR of DASMPA showed an absorption peak at 1605.95 cm^{-1} indicating the formation of a Schiff base (C=N). Adsorption activity of DASMPA for Zn^{2+} was also investigated in terms of contact time, pH, the initial Zn(II) concentration and temperature, the results revealed that pH = 5, t = 1 h were the optimal conditions. With the degree of substitution (DS) of the DASMPA increased, the adsorption capacity increased gradually. The adsorption equilibrium data correlated well with Freundlich isotherm. Moreover, lower temperature was preferable for the process as it was exothermic.

Key words | adsorption, dialdehyde *m*-phenylenediamine starch, dialdehyde starch, Zn(II)

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INTRODUCTION

In recent years, heavy metal ions from sewage and industrial wastewater have affected our lives and are going to get worse over the coming decades, so water pollution has been given considerable attention (Zhang *et al.* 2011). The problems of Zn-containing wastewater are of environmental concern due to Zn^{2+} ions having the characteristics of persistence, toxicity and non-biodegradability (Gupta *et al.* 1997; Gupta & Sharma 2002, 2003). Therefore, it is urgent to find an effective way to remove Zn^{2+} from the wastewater. Several methods have been utilized to remove toxic metal ions from industrial wastewater, such as precipitation (Trainor *et al.* 2000; Ha *et al.* 2006), filtration (Nakatsuka *et al.* 2007), reverse osmosis (Ipek 2005), evaporative recovery (Bisio *et al.* 2002), and adsorption (Gupta & Ali 2004; Gupta & Rastogi 2009). Among them, adsorption is a commonly used method for the separation and recovery of heavy metal ions (Gupta *et al.* 2003, 2004, 2005; Ali & Gupta 2006; Gupta *et al.* 2006, 2007a, b; Gupta & Rastogi 2008d). Adsorption on activated carbon (Gupta *et al.* 2011) is a well known method for the separation of heavy metals, but the cost restricts its large-scale usage. Therefore, development of a low-cost, efficient adsorbent material is still necessary (Gupta & Rastogi 2008b; Gupta *et al.* 2009).

Compared with synthetic polymers, biopolymers attract more and more attention due to their lower cost, lower toxicity nature (Gupta *et al.* 2003; Gupta & Rastogi 2008a, c; Gupta *et al.* 2010). Starch, as a kind of biodegradable and environment-friendly material, is called a green material. In the past few years, several methods have been used to modify starch to adsorb heavy metal ions. Various chemicals have been used, such as carboxylate (Khalil & Abdel-Halim 2001), xanthate (Bose *et al.* 2002), phosphate (Guo *et al.* 2006), acrylamide (Chauhan *et al.* 2006) and acrylonitrile (Abdel-Aal 2006). At present, a widely used method is oxidation (Yu *et al.* 2010); aldehyde groups could form hemiacetals and acetals, glyoxal and glutaraldehyde, which have been successfully used in cross-linking acetalation of cellulose derivatives.

Dialdehyde groups of dialdehyde starch (DAS) are gained through periodate oxidative cleavage of the C (2)–C (3) bond of starch (Zhao *et al.* 2010); they can be further modified, for example, reacting with dithiosemicarbazone, disemicarbazone (Ropek & Para 2002) or dihydrazone (Para *et al.* 2004) could form complexes to absorb metal ions – these molecules usually contain electron donor atoms such as N, S, O, and P (Zhang, S. F. *et al.* 2008; Zhang, Y. J. *et al.* 2008; Zhao *et al.* 2010; Ding *et al.* 2011).

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In the present work, we have prepared a new chelating material, dialdehyde *m*-phenylenediamine starch (DASMPA). On the one hand, the structure of *m*-phenylenediamine contains N atoms which are coordination sites for Zn(II). On the other hand, the Schiff base (C=N) can form complexes with transition metal ions. DASMPA was used to adsorb Zn(II) from aqueous solutions. Adsorption studies were carried out at different adsorption times, pH, initial Zn(II) concentration and temperature to determine the optimal conditions. The adsorption isotherm and thermodynamics parameters of the adsorption were also studied.

EXPERIMENTAL

Materials and apparatus

Potato starch (food-grade). $Zn(NO_3)_2$ and NaOH were obtained from Shanghai Chemical Factory (Shanghai AR China). $NaIO_4$, *m*-phenylenediamine and H_2SO_4 were purchased from Tianjing Chemical Factory (Tianjing AR China). All the 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 NEXUS670. The element analyses for C, H and N were performed on a VarioEL. Atomic adsorption spectrometry was carried out using an AAnalyst 240 instrument (Varian American). The λ max for Zn(II) in AAS analysis is 213.9 nm. The BET was studied by Chemisorb 2750.

Preparation of dialdehyde starch

DAS was prepared by adding 4.0 g potato starch into sodium periodate solution in a 100 mL flask. The pH of the mixture was adjusted to 5.0. The reaction was maintained at 35 °C for 5 h in the dark under stirring. Then the products were filtered and washed with distilled water and ethanol. In order to study the influences of oxidation degrees on the adsorption, three DASs with different oxidations were prepared and defined as DAS_1, DAS_2, and DAS_3 (Zhao *et al.* 2010). The aldehyde group content was determined by the rapid quantitative alkali consumption method (Hofreiter *et al.* 1955). The aldehyde group contents were 28, 53 and 70% for DAS_1, DAS_2 and DAS_3, respectively.

The percentage of dialdehyde units were given by Equation (1):

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

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 DAS.

Preparation of dialdehyde *m*-phenylenediamine starch

An amount of 4.0 g of DAS and *m*-phenylenediamine (molar ratio was 1:2) were stirred in 50 mL distilled water in a 100 mL flask. The pH of the mixture was adjusted to weak acid. The reaction was stirred for 4 h at 55 °C under nitrogen protection. The product was separated and washed several times with distilled water and then dried at 50 °C in a vacuum.

The reaction process is showed as Figure 1.

Adsorption experiments

A certain dose (150 mg) of DASMPA and 50 mL Zn^{2+} solution were added into a 100 mL flask under stirring. The pH of the solution was adjusted with 0.1 mol/L HNO_3 and 0.1 mol/L NaOH. Several hours later, the mixture was filtered and the final concentration of Zn^{2+} was identified by atomic adsorption spectrophotometer.

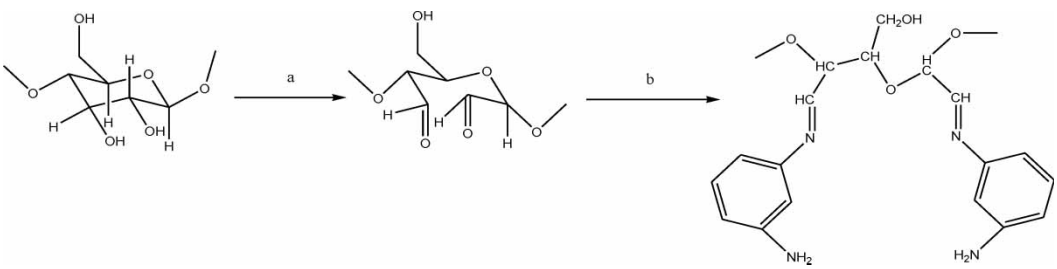

Figure 1 | Reagents and conditions: (a) $NaIO_4$; (b) *m*-phenylenediamine.

The adsorption capacity of DASMPA was calculated by the expression (2):

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

Q is the adsorption capacity of the adsorbent (mmol/g), C_i 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 (mg) are the volumes of the adsorption solution and the dose of the adsorbent, respectively.

RESULTS AND DISCUSSION

Characterization of the prepared DASMPA

The FT-IR of the DAS and DASMPA

Fourier transform infrared spectra of the products were recorded on KBr pellets using NEXUS670. As shown in Figure 2, bands of DAS at 1732.31 and 2930.15 correspond to the stretching vibrations of the C=O and C–H bonds. Compared with DAS, the absorption peak of C=O at 1,732.31 cm^{-1} disappeared in the spectrum of DASMPA, but a new strong absorption peak appeared at 1,605.95 cm^{-1}, which indicated the generation of C=N. The band observed at 3,340.50 cm^{-1} was the stretching vibration of N–H.

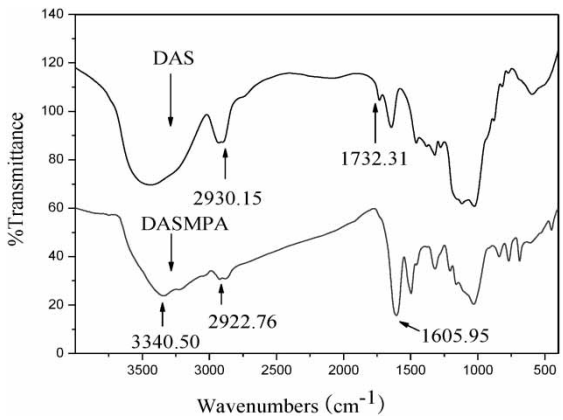

Figure 2 | FT-IR spectra of DAS and DASMPA.

Elemental characterization

$DASMPA_1$, $DASMPA_2$ and $DASMPA_3$ were characterized by elemental analysis. The substitution degree (DS) of DASMPA was calculated according to Equation (3):

$$DS = \frac{161 \times N\%}{2{,}800 - 90.14 \times N\%} \quad (3)$$

DS and N% represent the substitution degree of DASMPA and the nitrogen content in DASMPA, respectively. Table 1 indicates the results of the element analyses. The DS of $DASMPA_1$, $DASMPA_2$ and $DASMPA_3$ were 0.29, 0.48, and 1.10, correspondingly.

BET specific surface area

The BET surface area (S_{BET}) of $DASMPA_1$, $DASMPA_2$ and $DASMPA_3$ are given in Table 1. The S_{BET} increased with the increase in DS.

Adsorption of Zn^{2+} ions

Effect of initial pH

An important factor affecting the adsorption capacity of DASMPA was the pH of solution, pH affected adsorbent surface charge, degree of ionization of the functional groups, and metal ion speciation (Ding *et al.* 2011). Figure 3 shows the relationship between pH and adsorption capacity. To avoid the formation of precipitation, the influence of pH > 6.0 was not studied. At lower pH, the adsorption of Zn^{2+} was weakened because of the competition between H^+ and Zn^{2+} ions. With the increase of pH, the protonated sites were deprotonated. The maximal adsorption of Zn^{2+} was observed at pH = 5.0. When pH > 5.0. The decreased adsorption for Zn^{2+} may be due to the electrostatic

Table 1 | Element analysis and the BET surface area of DASMPA

			Element analysis				
Product	**Reactant**	**Color**	***N*(%)**	***C*(%)**	***H*(%)**	**DS**	**BET(m^2/g)**
$DASMPA_1$	DAS_1	Grey	4.40	43.45	6.25	0.29	25.1
$DASMPA_2$	DAS_2	Grey	6.60	38.92	5.20	0.48	28.3
$DASMPA_3$	DAS_3	Grey	11.85	53.30	5.91	1.10	30.5

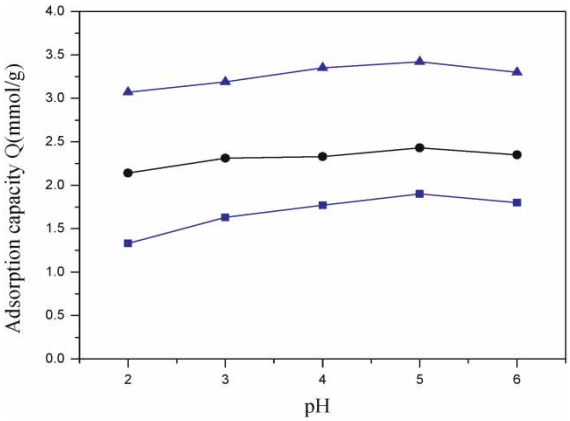

Figure 3 | Effect of the initial pH of Zn^{2+} on adsorption capacity. (■) $DASMPA_1$; (•) $DASMPA_2$; (▲) $DASMPA_3$; $[Zn(NO_3)_2] = 20$ mmol/L; $t = 1$ h; $T = 25$ °C; the dose of DASMPA is 150 mg.

repulsion between surface sites of adsorbent and metal ion (Zhang, Y. J. *et al.* 2008). At the same pH, the adsorption capacity of DASMPA was augmented with the increase of DS ($DASMPA_3 > DASMPA_2 > DASMPA_1$).

Effect of adsorption time

In order to establish a suitable adsorption time, adsorption capacity of Zn(II) ions was measured as a function of time (Ding *et al.* 2011). Figure 4 illustrated that the adsorption time ranged from 0.5 to 2.5 h. It can be inferred that the adsorption progress became constant after 60 min, so the optimal adsorption time was chosen to be 60 min. The adsorption of Zn(II) onto DASMPA was very rapid during the initial 30 min, From 30 to 60 min, the sorption rate became slow. Thus we can conclude that the initial rapid step, adsorption, may be attributed to the physical and surface reactive sorption from a facile immediate interaction between Zn(II) and the active groups based on the surface of DASMPA. However, the subsequent slow step, the occupation of the remaining vacant sites would be difficult due to the repulsive forces between the metal ions. After 60 min, the metal ions should achieve equilibrium. At the same time, the adsorption capacity is augmented with the increase of DS ($DASMPA_3 > DASMPA_2 > DASMPA_1$).

Effect of the initial Zn(II) concentrations

Adsorption capacity of DASMPA was investigated by varying initial Zn(II) concentrations. In Figure 5, Q of $DASMPA_1$, $DASMPA_2$ and $DASMPA_3$ increased from 0.23 to 1.9 mmol/g, 0.31 to 2.43 mmol/g and 0.42 to 3.42 mmol/g as the Zn(II) concentrations increased from 2.5 to 20 mmol/L. Q increasing significantly when initial Zn(II) concentrations increased meant abundant active groups on the surface of DASMPA. At the same Zn(II) concentration, the adsorption capacity was augmented with the increase of DS ($DASMPA_3 > DASMPA_2 > DASMPA_1$). That the adsorption trends were similar indicated that the sorts of adsorption isotherms were similar (Yin *et al.* 2008).

Adsorption isotherm

The Freundlich isotherm has been widely used to study the adsorption behavior (Ma *et al.* 2008), which could be expressed as follows:

$$Q_e = K_f C_e^{1/n} \tag{4}$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

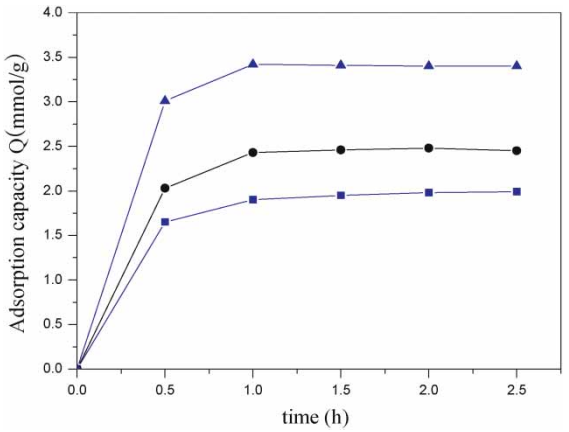

Figure 4 | Effect of adsorption time: (■) $DASMPA_1$; (•) $DASMPA_2$; (▲) $DASMPA_3$; $[Zn(NO_3)_2] = 20$ mmol/L; pH = 5; $T = 25$ °C; the dose of each DASMPA is 150 mg.

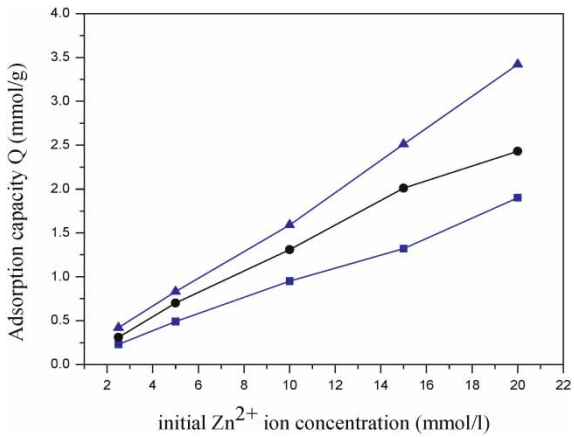

Figure 5 | Effect of initial concentrations of Zn(II) on (■) $DASMPA_1$; (•) $DASMPA_2$; (▲) $DASMPA_3$; $t = 1$ h; pH = 5.0; $T = 25$ °C; the dose of DASMPA is 150 mg.

C_e and Q_e are equilibrium Zn(II) ion concentration (mmol/L) and equilibrium adsorption capacity (mmol/g), respectively. K_f and n are Freundlich constants, which affect the adsorption processes such as adsorption capacity and intensity of adsorption, The model is based on the assumption that adsorption occurs on a heterogeneous adsorption surface having unequally available sites with different energies of adsorption (Zhao *et al.* 2010). In Figure 6, three good linearized plots of log Q_e versus log C_e were obtained. K_f and n were calculated from the slopes and interceptions. The Freundlich constants are presented in Table 2.

Thermodynamic studies

The adsorption behavior of $DASMPA_3$ at different temperatures was also investigated from 25 to 65 °C (Ding *et al.* 2011). Log (Q/C_e) versus $1/T$ for $DASMPA_3$ is shown in Figure 8. Enthalpy and entropy were determined by the following equations:

$$\log\frac{Q}{C_e} = -\frac{\Delta H^\theta}{2.303RT} + \frac{\Delta S^\theta}{2.303R} \quad (6)$$

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta \quad (7)$$

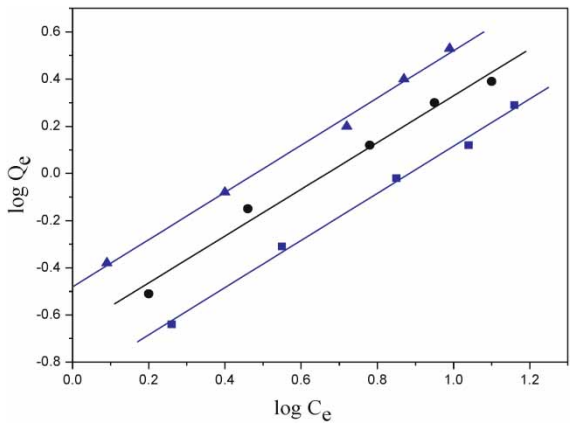

Figure 6 | Freundlich isotherm for the adsorption of Zn(II) ions on (■) $DASMPA_1$; (•) $DASMPA_2$; (▲) $DASMPA_3$; pH = 5.0; t = 1 h; T = 25 °C; the dose of DASMPA is 150 mg.

Table 2 | Freundlich parameters for three kinds of DASMPA

Sample	K_f (mmol/g)	n(1)	R(1)
$DASMPA_1$	7.5858	1.0031	0.9991
$DASMPA_2$	4.5709	1.0051	0.9864
$DASMPA_3$	3.0200	1.0052	0.9919

ΔG^θ, ΔH^θ and ΔS^θ represent Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (kJ $K^{-1}mol^{-1}$) respectively. ΔH^θ and ΔS^θ can be calculated according to the slope and interception of the linear plot. ΔG^θ was acquired from Equation (7). In Figure 7, with the temperature increased, adsorption capacity of $DASMPA_3$ reduced significantly: we can conclude that the adsorption process was

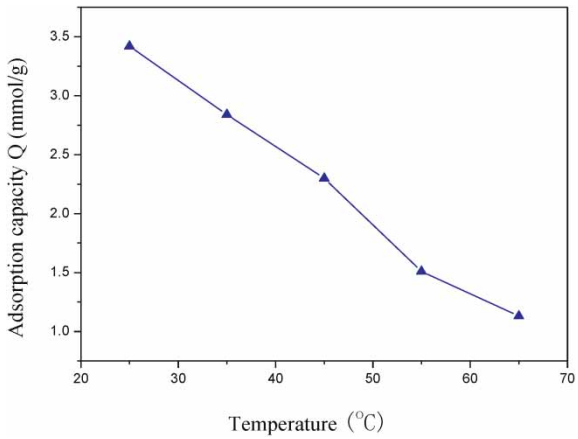

Figure 7 | Effect of adsorption temperature on (▲) $DASMPA_3$. $[Zn(NO_3)_2]$ = 20 mmol/L; pH = 5.0; t = 1 h; the dose of $DASMPA_3$ is 150 mg.

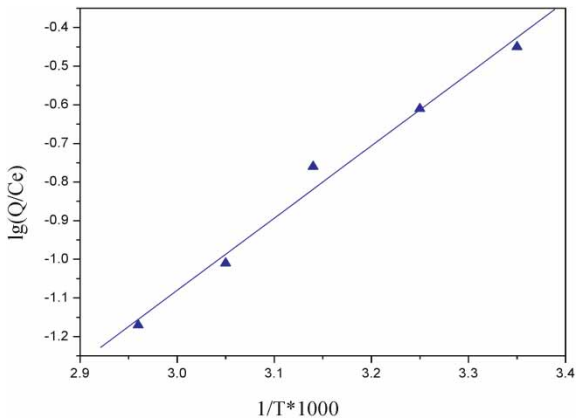

Figure 8 | lg $(Q/C_e) \sim 1/T*1{,}000$ for (▲) $DASMPA_3$. $[Zn(NO_3)_2]$ = 20 mmol/L; pH = 5.0; t = 1 h; the dose of $DASMPA_3$ is 150 mg.

Table 3 | Thermodynamic parameters for $DASMPA_3$

Temperature (°C)	ΔG^θ (kJ/mol)	ΔH^θ (kJ/mol)	ΔS^θ (kJ $K^{-1}mol^{-1}$)
25	−6.01		
35	−5.01		
45	−4.01	−35.82	−0.10
55	−3.01		
65	−2.01		

exothermic. Figure 7 shows a good linear between log (Q/C_e) and 1,000/T for $DASMPA_3$. Thermodynamic parameters are listed in Table 3. Lower temperature is beneficial for adsorption due to ΔH^θ being negative. In addition, the values of ΔS^θ and ΔG^θ demonstrated a decrease in entropy and an increase in the feasibility of adsorption at lower temperatures.

CONCLUSION

The chelating material (DASMPA) can remove the zinc ions from aqueous solution effectively and it was relatively cheap. DASMPA was prepared by reacting *m*-phenylenediamine with DAS. From batch experiments, we concluded that adsorption capacity was greatly affected by DS of DASMPA, and the DS was determined by the oxidation of starch. So oxidation was a most important factor affecting adsorption capacity. The adsorption of Zn(II) achieved its maximum when $pH = 5$, $t = 60$ min. The maximal adsorption capacities of $DASMPA_1$, $DASMPA_2$ and $DASMPA_3$ in this study were 1.9, 2.43, and 3.42 mmol/g, respectively. In addition, the adsorption equilibrium data fitted well with the Freundlich model. It was exothermic; lower temperature was preferable for adsorption.

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