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Synthesis and adsorption performance of dithiocarbamate-modified glycidyl methacrylate starch

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ABSTRACT

The design of chelating polymers with fast complexation of the metal ions is particularly interest. In this work, the dithiocarbamate-modified glycidyl methacrylate starch was synthesized and characterized by FT-IR, ^{13}C NMR and XRD spectra. Its sorption performance for heavy metals fixation was studied. It was found that the removal process of metal ions involved a fast increase stage followed by a slower stage. There was a higher match between the pseudo-second-order equation and the experimental data. The sorption rate constants were related to the substitution rates of hydrated metal ions in aqueous solutions, showing typical chemisorption. The Langmuir isotherm gave satisfying fits to equilibrium data of metals adsorption. And the capacities followed the sequence $Cu^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$, which could be well demonstrated with chelating interaction caused by sulfur atoms. Such understanding provides new insights as how to synthesize and use the dithiocarbamate-based polysaccharides.

1. Introduction

Water pollution due to toxic heavy metals has caused a serious environmental and public problem (Quintelas et al., 2009). The removal of heavy metals from river water, lake water, and wastewater is a crucial issue of concern to health (Qu, 2008). Several techniques that have been used to reduce the heavy metal content of effluents include chemical precipitation (Azetsu-Scott et al., 2007), ion exchange (Oehmen, Viegas, Velizarov, Reis, & Crespo, 2006), membrane filtration (Bloche et al., 2003), and adsorption (Mata, Blázquez, Ballester, González, & Muñoz, 2009). Among these techniques, adsorption is generally preferred for the removal of heavy metal ions because of its high efficiency, ease of handling, and availability of a wide range of adsorbents (Ngomsik et al., 2009; Shukla, Pai, & Shendarkar, 2006). The search for effective adsorbents has also become the focus of attention of many researchers (Pimentel et al., 2007; Sud, Mahajan, & Kaur, 2008). Heavy-metal removal by using the chelating polymers would be of great importance in environmental applications (Beatty, Fischer, Hagers, & Rosenberg, 1999; Liu, Hu, Fang, Zhang, & Zhang, 2009). The main criterion in the design of chelating polymers with substantial stability is fast complexation of the metal ions. Also it is much popular that the polymers are abundant and easily modified. The dithiocarbamate functionalized resins have attracted much attention due to potential application in analysis, separation and catalysis (McClain & Hsieh, 2004; Roy, Rawat, & Rai, 2003). The synthesis of dithiocarbamate functionalized materials is of particularly interest still today (Jing et al., 2009; Ünlü & Ersoz, 2007). However, the dithiocarbamate-modified glycidyl methacrylate starch was not studied. Also, many metal ions (such as the Zn^{2+} and Mn^{2+}) adsorbing to dithiocarbamated functionalized polysaccharides were not well understood. It is very important to clarify the chelating mechanism for various heavy metals.

In the present work, the dithiocarbamate-modified glycidyl methacrylate starch (DMGS) was synthesized and characterized by elemental analysis, FT-IR, solid state ^{13}C NMR, and X-ray diffraction spectra. The adsorption kinetics and equilibrium of frequently observed heavy metal ions (Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Mn^{2+}) on DMGS were investigated. The kinetics and equilibrium parameters were correlated with the properties of metal ions.

2. Materials and methods

2.1. Materials and equipments

Food grade corn starch was used in this research. The other reagents used were analytical pure and purchase from Shanghai Reagents Company. The chloride salts of metal ions were used.

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The concentrations of metal ions in aqueous solutions were measured by using an atomic absorption spectrophotometer (Z5000 AA spectrometer; Hitachi, Osaka, Japan). The elemental analysis was carried on a Vario EL III elemental analyzer. Fourier Transform Infrared spectra (FT-IR) were recorded on PE Spectrum One spectrometer with KBr pellets in the 4000–450 cm^{-1} regions. The solid state ^{13}C NMR was acquired on a 400 MHz Bruker DMX spectrometer. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max 2550 V instrument with Cu Kα radiation (λ = 1.5406 Å).

2.2. Preparation of dithiocarbamate modified glycidyl methacrylate starch (DMGS)

The DMGS was synthesized by three steps and the process is shown in Fig. 1. Firstly, glycidyl methacrylate starch (GS) was prepared according to reference (Abo-Shosha & Ibrahim, 1992). The dried GS (20 g) further reacted with ethylenediamine to produce ethylenediamine-modified glycidyl methacrylate starch (EGS) in basic solution under 60 °C for 12 h. The mixture was warmed up to 40 °C. After 12 h, the precipitation dithiocarbamate-modified glycidyl methacrylate starch (DMGS) was separated and washed with deionized water, dilute HCl solution, dilute NaOH solution and acetone in sequence. The acquired DMGS was kept in a vacuum oven for 1 day and stored in desiccators. Elemental analysis: C 35.71, H 8.32, N 3.23, S 2.62%.

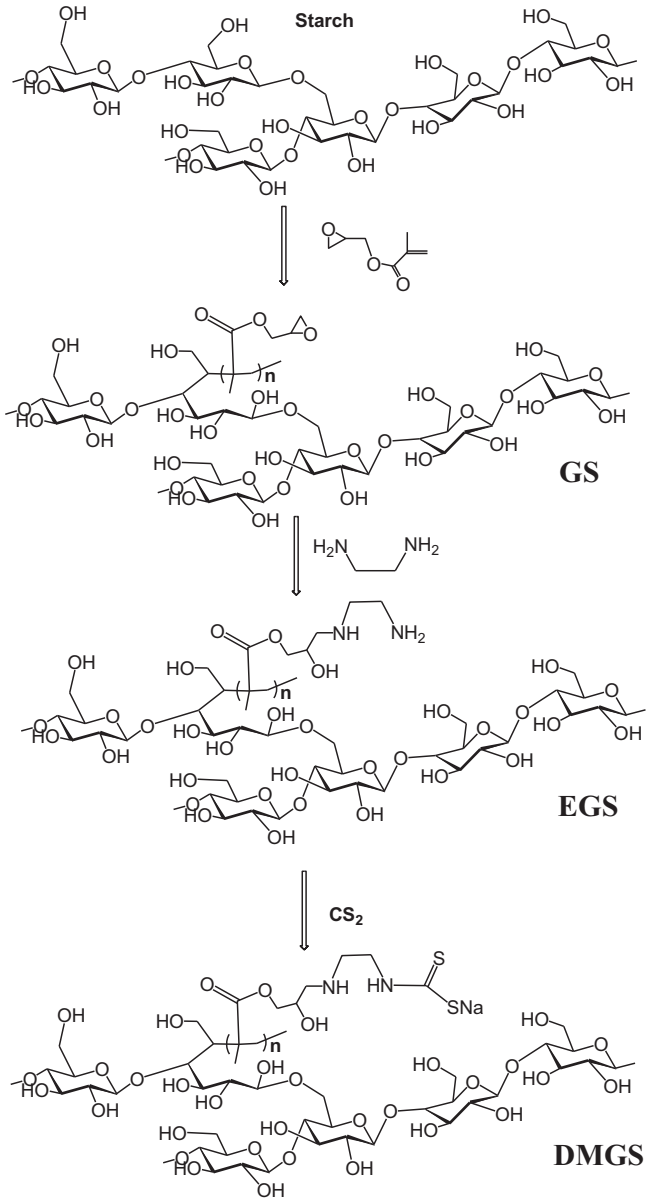

Fig. 1. Synthesis of DMGS.

2.3. Sorption experiments

Sorption studies were performed by the batch technique. The temperature of all experiments was maintained at 25 ± 1 °C. The solution pH was buffered at 5.5 because the metal ions tended to hydrolyze at higher pH and the capacity decreased in lower pH solutions. For all adsorption tests, blank experiments were performed and the same experimental procedure was carried out to check the extent of adsorption by the glass flasks and the membrane filters. The amount of DMGS used in each flask is 0.100 g. The adsorption kinetics was studied with the initial concentration of metal ion fixed at 1.0×10^{-3} mol/L and the volume of solution was 50 mL. The concentration of metal was measured at different time intervals up to equilibrium. Each data point was obtained from an individual flask; therefore no correction due to withdrawn sampling volume was necessary. The amount of metal adsorbed at time t, q_t (mmol/g), was deduced from the mass balance between initial concentration and concentration at time t in solution.

For equilibrium sorption studies, a fixed mass of DMGS (0.100 g) was weighed into flasks and contacted with a 50 mL solution containing a known amount of the respective metal (varied from 5.0×10^{-5} mol/L to 1.8×10^{-3} mol/L). The flasks were agitated for 12 h in the thermostatic shaker bath. After filtration, the concentrations of metal solutions were determined. The results were then used to determine metal loading on DMGS applying Eq. (1):

$$q_e m = (c_0 - c_e) V \quad (1)$$

where q_e is the metal concentration in the solid phase (sorbent) at equilibrium (mmol/g), m is the mass of DMGS used (g), c_0 is the initial metal concentration in the liquid phase (mmol/L), c_e is the metal concentration in the liquid phase at equilibrium (mmol/L), and V is the total volume of solution used (L). The models of the kinetics and isotherms were fitted using a nonlinear method, with the nonlinear fitting facilities of the Microcal Origin 7.0 software.

3. Results and discussion

3.1. Synthesis and characterization of DMGS

The most important functional group of DMGS is the dithiocarbamate. In the synthesis course, it is easy to be oxidized at high temperatures. Therefore, the reaction temperature was below 40 °C in the last synthesis step. Generally, the reactions were mild. The obtained product, DMGS is almost insoluble in commonly used solvents, such as water, alcohol, acetone, chloroform, and dimethyl sulfoxide. It cannot characterized by solution NMR. So the solid state NMR is better to identify the chemical structure of DMGS. As can be seen from Fig. 2, the solid state ^{13}C NMR spectrum of DMGS shows the —NCS_2 signal at 208 ppm and the —C═O signal at 181 ppm. Two broad peaks at 102 ppm are the ethylenediamine signals adjacent to the dithiocarbamate, and the left peaks are carbons of starch.

3.2. Application in heavy metal removal and mechanism

To evaluate the metal fixation ability of DMGS, its adsorption behaviors were investigated. Firstly, the kinetics of adsorption processes was studied. A simple kinetics analysis of adsorption is the

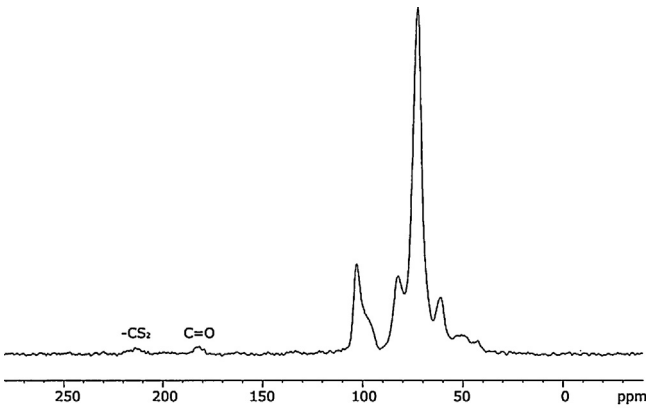

Fig. 2. Solid state ^{13}C NMR spectrum of DMGS.

pseudo-first-order equation (Wu, Tseng, & Juang, 2001) in the form

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

A pseudo-second-order equation (Ho, Ng, & McKay, 2000) was also tested on the experimental data. The kinetic rate equation is

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and k_2 is the rate constant of pseudo-second-order adsorption (g/mmol/min).

The applications of the models fitting to experimental data are shown in Fig. 3(a). The constants determined from the experimental data and correlation coefficients (R^2) are list in Table 1. As can be seen from the Fig. 3(a), the adsorption of metal ions was very fast. The process had two stages. The first was a fast increase stage, which lasted for 10 min. The majority of cations were removed in the stage. Then a slower stage extended to 30 min, when equilibrium was reached. However, the equilibrium time of Ni^{2+} adsorption was slightly different. It was achieved after 50 min of contact time. Compared with the pseudo-first-order equation, there was a higher match between the pseudo-second-order equation and the experimental data. The sorption rate constants followed the sequence $Cu^{2+} > Cd^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+}$, which was related to the substitution rates of hydrated metal cations in aqueous solutions (Dai, 1987). It can be seen from Fig. 3(b) that the relation between the pseudo-second-order constants k_2 and the substitution rate constants ($\log k_{hs}$) of hydrated metal ions is linear. The observations suggest that the adsorption of heavy metal onto DMGS is typical chemisorption. Previous studies have clearly found that the pseudo-second-order equation was able to better describe the metal ions adsorption on polysaccharides (Benguella & Benaissa, 2002; Sun & Wang, 2006). The rate controlling mechanism is chemisorption. The very fast sorption kinetics represents an advantageous aspect when water treatment system is designed.

Adsorption isotherms describe how adsorbates interact with adsorbents, and are important in optimizing the use of adsorbents. Two isotherms (Langmuir and Freundlich isotherms) were used to fit the equilibrium data. The well-known Langmuir isotherm was originally proposed to describe the adsorption of gas molecules onto metal surfaces (Langmuir, 1918). The model assumes uniform energy of the adsorption onto the surface and no migration of the adsorbate in the plane of the surface. The Langmuir adsorption isotherm has been applied successfully to many other real situations of monolayer adsorption (Basha, Murthy, & Jha, 2009; Dupont & Guillon, 2003) and can be expressed as

$$q_e = \frac{q_m b c_e}{1 + b c_e}, \quad (4)$$

where q_e is the amount of metal adsorbed at equilibrium (mmol/g), and c_e is the adsorbate concentration at equilibrium in aqueous solution (mmol/L). The Langmuir isotherm parameters are q_m and b. The capacity of the adsorbent can be evaluated by q_m, and the

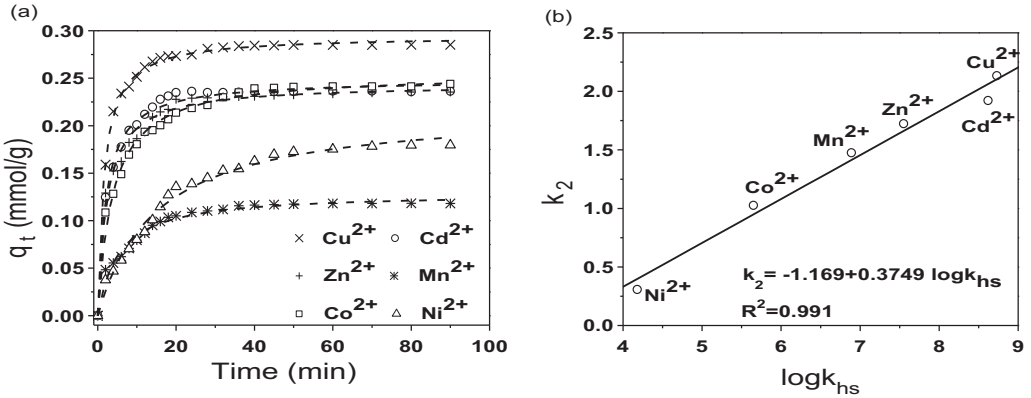

Fig. 3. (a) Kinetics of metal adsorption onto DMGS for an initial concentration of 1.0×10^{-3} mol/L. The dash lines represent modeled results using the pseudo-second-order equation. (b) Plots of k_2 versus the substitution rate constant of hydrated metal ion.

Table 1
Parameters of kinetic models for metal adsorption on DMGS.

Metal ion	Pseudo-first-order		Pseudo-second-order		
	k_1(min^{-1})	R^2	k_2 (g/mmol/min)	q_e (mmol/g)	R^2
Cu^{2+}	0.349	0.977	2.133	0.295	0.998
Cd^{2+}	0.267	0.976	1.922	0.249	0.991
Zn^{2+}	0.244	0.942	1.724	0.244	0.985
Mn^{2+}	0.129	0.966	1.475	0.129	0.981
Co^{2+}	0.167	0.949	1.026	0.255	0.990
Ni^{2+}	0.063	0.989	0.308	0.219	0.988

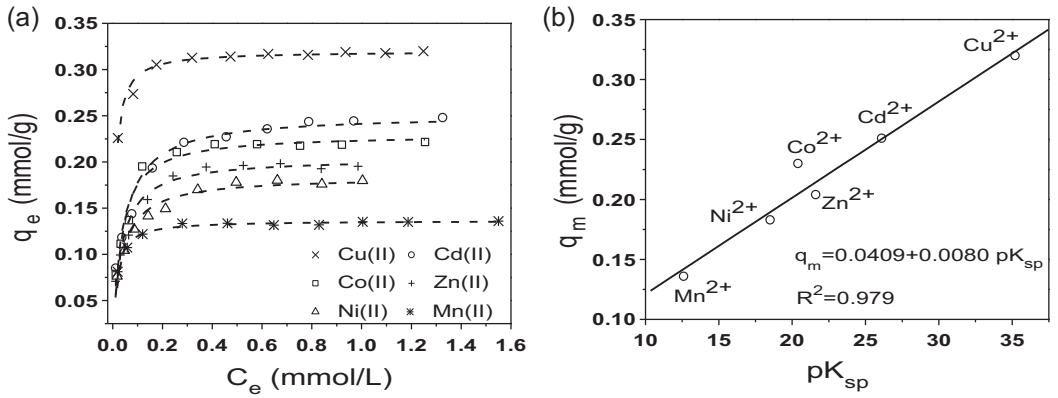

Fig. 4. (a) Langmuir isotherm (dash line) fitting to experimental data. (b) Plots of q_m versus the solubility product of metal sulfide.

Table 2
Parameters of Langmuir and Freundlich isotherms for metal ions adsorption onto DMGS.

Metal ion	Langmuir isotherm			Freundlich isotherm		
	q_m (mmol/g)	b (L/mmol)	R^2	K_f (mmol$^{1-1/n}$ L$^{1/n}$/g)	$1/n$	R^2
Cu^{2+}	0.320	109.37	0.967	0.325	0.072	0.855
Cd^{2+}	0.251	24.19	0.960	0.253	0.203	0.933
Co^{2+}	0.230	31.98	0.968	0.234	0.178	0.839
Zn^{2+}	0.204	30.92	0.966	0.214	0.196	0.898
Ni^{2+}	0.183	29.40	0.966	0.192	0.183	0.926
Mn^{2+}	0.136	71.53	0.988	0.137	0.091	0.811

parameter b includes various physical constants (Giles, Smith, & Huitson, 1974).

Eq. (5) is the well-known Freundlich isotherm, which describes heterogeneous systems (Freundlich, 1906). It is an empirical equation, and can be written as follows:

$$q_e = K_f c_e^{1/n}, \quad (5)$$

where K_f is the Freundlich constant, which is indicative of the extent of adsorption, and $1/n$ is the heterogeneity factor, an indicator of adsorption effectiveness.

The Langmuir isotherms fitting to experimental data are shown in Fig. 4(a). Parameters of nonlinear form of isotherms are listed in Table 2. As a result, the Langmuir isotherms are represented, and the good agreement with the experimental data suggests that the metal ions adsorbed form a monolayer coverage on the adsorbent surface. Many thiol functionalized adsorbents also followed the Langmuir isotherm (Yantasee et al., 2007). The correlation coefficients fitted to Freundlich isotherm are relatively lower. The adsorption capacity for metal ion follows the sequence $Cu^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$. It can be seen that the adsorption affinity is related to the solubility product (K_{sp}) of metal sulfide (Dean, 1973). The relationship between the maximum capacity and K_{sp} corresponding to different metal ions was demonstrated in Fig. 4(b). The linear-curve with a satisfying correlative parameter of $R^2 = 0.979$, indicating that the chelating interaction between dithiocarbamate and metal ion did play an important role during the adsorption process. The correlation provides insights into the factors governing the complexation formation on DMGS surface and may allow for prediction of unknown formation. Many linear relationships can be found between the capacity or complex formation and a variety of properties of the metals such as the ionic radius or the first hydrolysis constant $\log K_1$ (OH^-) (Martell & Hancock, 1996; Reddad, Gerente, Andres, & Le Cloirec, 2002). In our case, the ionic radius did not appear to reflect the adsorption capacities.

FT-IR spectra were used to evaluate the heavy metal adsorption onto DMGS. The different FT-IR spectra of DMGS and heavy metal loaded DMGS are shown in Fig. 5 in the region of 1800–500 cm^{-1}. It can be observed that the sharp peaks for DMGS at 1208 and 1081 cm^{-1} are attributed to the ν(—CS_2) vibrations of dithiocarbamate (Kaul & Pandeya, 1978; Nakamoto, Fujita, Condrate, & Morimoto, 1963). The νC—N (—N—CS_2) vibration (Macías, Villa, & Rodriguez-Gallego, 1995) is seen at 1470 cm^{-1}, whereas the νC—N (CH—N—CH_2CH_2) vibration (Zhang, Gao, Zhai, Liu, & Gao, 2008) appears at 1158 cm^{-1}. The strong and broad peak at 1020 cm^{-1} is caused by the coupling vibrations of νC—O and νC—O—C. Another significant peak at 932 cm^{-1} showed the δC_1—H vibration of pyranose ring. After adsorption of the metal ions, the peak at 1208 cm^{-1} shifted to about 1233 cm^{-1} indicating the —CS_2 binding to metals (Jian et al., 1999). Also, a new peak appeared at 1106 cm^{-1}, which suggested the coordination of sulfur atoms. Interestingly, the coordination of metal ions to —CS_2 resulted in the hypsochromic shift

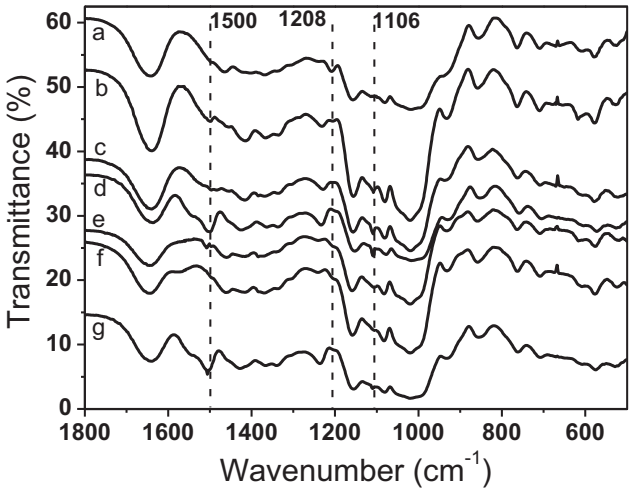

Fig. 5. FT-IR spectra of DMGS before and after adsorption of metals. (a) DMGS; (b) DMGSCu; (c) DMGSZn; (d) DMGSMn; (e) DMGSCd; (f) DMGSCo; and (g) DMGSNi.

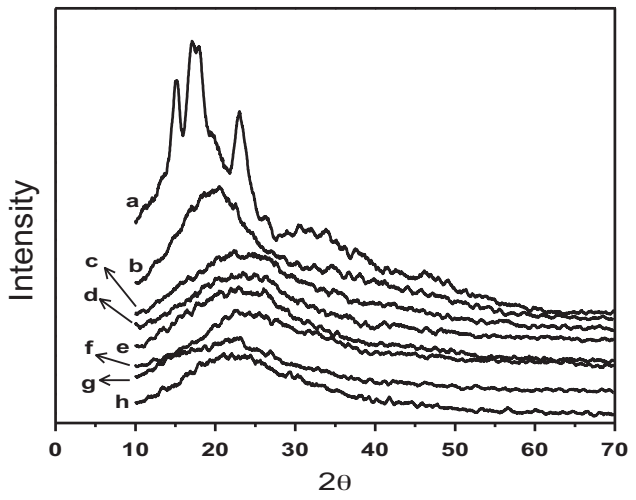

Fig. 6. XRD spectra of corn starch, DMGS, and DMGS after adsorption of metals. (a) Corn starch; (b) DMGS; (c) DMGSCu; (d) DMGSZn; (e) DMGSMn; (f) DMGSCd; (g) DMGSCo; and (h) DMGSNi.

of $\nu(-N-CS_2)$ vibration, whereas the $\nu C=O$ vibration of methacrylate did not significantly change. These data demonstrate that the dithiocarbamate groups chelate the metal ions and the DMGS effectively adsorbs the metal ions. Furthermore, X-ray diffraction measurements (Fig. 6) were performed to check if the chemical modification altered the crystallinity of starch. Typically, corn starch, as described earlier, showed an A-type XRD pattern. It gives strong reflection at15°, 17°, and 23° (Zobel, 1988). But the DMGS only shows a broad peak over the region 15–23°. It can be explained that the crystalline structure has been destroyed and the crystallinity has been reduced due to the incorporation of grafted copolymer. It can, therefore, be inferred that along with the amorphous region, the crystalline region of the granular starch is also involved in grafting (Gao, Tian, Yu, & Duan, 1994). After DMGS adsorbed metal ions, the peak further becomes weaker and broader rather than DMGS. It indicates that its crystallinity is further reduced. This is because the metal ions enter the inner of DMGS, which destroy assignment and movement of the chain of DMGS. Also, the coordination of metal ions with dithiocarbamate would break down the intermolecular hydrogen bonds.

4. Conclusions

In this work, the dithiocarbamate-modified glycidyl methacrylate starch (DMGS) was synthesized and characterized by spectroscopic methods. Further studies concerning the adsorption performance of the DMGS indicate great potential for the removal of heavy metal from aqueous solutions. DMGS displayed quick adsorption performance within 1 h and the kinetics process was found to follow the pseudo-second-order equation. The equilibrium data fit well with Langmuir isotherm and the capacities follow the order $Cu^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$. The mechanism concluded from experimental results is based on chelating adsorption. The FT-IR and XRD spectra demonstrate that the dithiocarbamates chelate the metals and the DMGS effectively adsorbs the metal ions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.04.001.

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