Microwave Preparation and Adsorption Properties of EDTA-Modified Cross-Linked Chitosan

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ABSTRACT: A novel chitosan-based adsorbent (CCTE) was synthesized by the reaction between epichlorohydrin O-cross-linked chitosan and EDTA dianhydride under microwave irradiation (MW). The chemical structure of this new polymer was characterized by infrared spectra analysis, thermogravimetric analysis, and X-ray diffraction analysis. The results were in agreement with the expectations. The static adsorption properties of the polymer for Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Co^{2+} were investigated. Experimental results demonstrated that the CCTE had higher adsorption capacity for the same metal ion than the parent chitosan and cross-linked chitosan. In particular, the adsorption capacities for Pb^{2+} and Cd^{2+} were 1.28 mmol/g and 1.29 mmol/g, respectively, in contrast to only 0.372 mmol/g for Pb^{2+} and 0.503 mmol/g for Cd^{2+} on chitosan. Kinetic experiments indicated that the adsorption of CCTE for the above metal ions achieved the equilibrium within 4 h. The desorption efficiencies of the metal ions on CCTE were over 93%. Therefore, CCTE is an effective adsorbent for the removal and recovery of heavy metal ions from industrial waste solutions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 514–519, 2010

Key words: chitosan; chemical modification; microwave irradiation; metal ions; adsorption

INTRODUCTION

Heavy metal ions in wastewater can bring harmful effects to human beings, as well as to animals and plants. As a result, efficient removal of heavy metal ions from various water resources has been a crucial issue by employing appropriate treatment methods. Several conventional technologies have been used to remove these toxic metal ions from aqueous solutions such as chemical precipitation, ion exchange, coagulation, membrane process, and adsorption using different kinds of adsorbents.[1–3] Among these developed methods, adsorption is generally considered to be an effective and economic one. Activated-carbon has been undoubtedly regarded as one of the most popularly used adsorbents in wastewater treatment application.[4] However, the regeneration of activated-carbon is quite difficult after being used, which makes it too expensive for use in the widespread removal of metal ions from wastewaters. With the increasing demand for economical process of wastewater treatment, the development of novel, low-cost, and efficient adsorbent is of great significance.[5] Therefore, in recent years, researchers have extensively focused on research into biosorbent such as chitosan, chitin, and sodium alginate because of their desirable properties like nontoxic, inexpensive, biocompatible, and efficient.[3,6]

Chitosan (CTS) is a biocompatible polysaccharide obtained from deacetylation of chitin, which has been found to be capable of chemically or physically entrapping various metal ions due to the presence of amine and hydroxyl groups that can serve as the chelating and reaction sites.[7,8] This has, therefore, attracted great research and application interest in using biopolymer chitosan as an adsorbent to remove metal ions from various industrial or municipal wastewaters.[9,10] However, it is difficult to directly apply the raw chitosan for removal of metal ions in wastewater treatment because of its disadvantage such as swelling, solubility in acidic conditions, and unsatisfying mechanical property. To overcome these problems, CTS was chemically modified with different cross-linking reagents such as glutaraldehyde, epichorohydrin, and ethylene glycol diglycidyl ether.[11–14] However, it has been reported that the adsorption capacity of cross-linked chitosan is largely reduced due to consumption of amino groups and hydroxyl groups after chemical modification.[10] Hence, it is very desirable to modify chitosan by grafting new functional groups on the cross-linked chitosan to preserve or enhance the

adsorption capacity. Some chemicals such as crown ethers, amino acids, and amino compounds were used to prepare the modified cross-linked chitosan compounds, which can greatly improve adsorption capacity and broaden the fields of potential application of them.[15–17]

Recently, microwave chemistry has received much attention due to higher conversion and shorter reaction times under microwave irradiation than those of conventional heating.[18] Therefore, microwave irradiation as a means of chemical reaction has been widely applied in various synthetic fields of chemistry such as organic synthesis, polymer synthesis, and so on.[19–23] In this work, we will attempt to apply microwave technology to prepare a new chitosan-based adsorbent. This work is to serve as not only an expansion of microwave irradiation in application of reaction system, but also an expansion of chitosan as an adsorbent for heavy metal removal. This novel chitosan derivative (CCTE) was synthesized by the reaction of an intermediate of epichlorohydrin O-cross-linked chitosan with EDTA dianhydride under microwave irradiation. The choice of EDTA is because the introduction of EDTA residues into chitosan could significantly enhance the adsorption ability compared with the parent CTS.[24,25] Therefore, it is possible that this derivative of CTS can show its promising application in water treatment.

EXPERIMENTAL

Materials and apparatus

Chitosan (degree of deacetylation : 90%) was purchased from Qingdao Lizhong chitin factory (Qingdao, China). The chosen metal salts $Pb(NO_3)_2$, $CuSO_4 \cdot 5H_2O$, $3CdSO_4 \cdot 8H_2O$, $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$ were analytical-grade reagents and were obtained from Guangzhou Chemical Reagent Co. (Guangzhou, China). All other reagents and solvents were used on analytical grade without further purification. All solutions were prepared with distilled deionized water.

A Galanz microwave oven (WP700L17) produced by Shunde Galanz Electric Appliance Factory, China, was employed and the temperature of microwave reaction system could be controlled in these studies after modification.[21,22] FTIR spectra of the solid products were recorded on a Bruker Fourier transform infrared spectrometer (Teser27) using KBr pellets. Wide-angle X-ray diffraction patterns (WAXD) were determined with a Rigaku diffractometer (D/max-IIIA). Thermogravimetric analysis was carried out on a Universal V4.1 DTA instrument (SDTQ600) under N_2 atmosphere at a heating rate of $10°C/min$. Measurements of solution pH were performed on a pH meter (PHS-25) produced by Shanghai Weiye
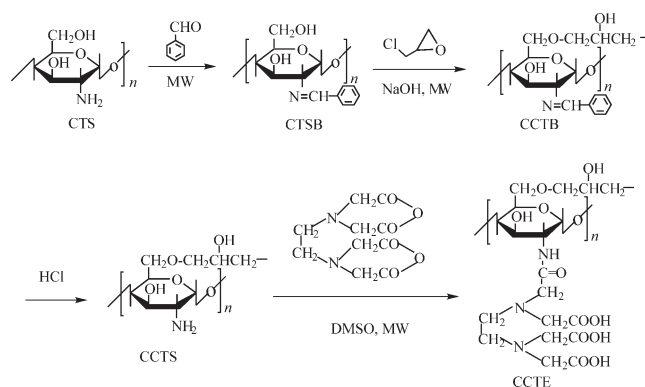

Figure 1 The reaction scheme for the preparation of CCTE.

Instrument Plant, China. The carbon and nitrogen contents in a sample were measured with a CHNS Elemental Analyzer (Elementar Vario EL).

Preparation of CCTE

To improve the mechanical and chemical stability of CTS, a cross-linked structure of CTS was synthesized with epichlorohydrin as crosslinker. However, C_2 amino groups in CTS are more reactive than C_6 hydroxyl groups. To make the reaction of CTS with epichlorodydrin take place in the position of C_6 hydroxyl groups, therefore, the amino groups must be protected firstly. The protection of amino groups can be successfully performed by employing the reaction of benzaldehyde with CTS to form N-benzylidene chitosan.[26] A schematic representation for the preparation of CCTE is illustrated in Figure 1.

Preparation of Schiff base chitosan-benzaldehyde (CTSB)

Powdered CTS (1 g) was dissolved in 30 mL of 2% acetic acid. The solution was diluted with 20 mL ethanol, and then 5 mL of benzaldehyde was added slowly. The mixture was stirred at 65°C under microwave irradiation for 14 min to obtain a transparent gel. After the reaction, the mixture was neutralized with 0.1 mol/L NaOH solution and the massive deposit was obtained. The deposit was washed with ethanol several times to remove the unreacted benzaldehyde, and then dried in vacuum at 60°C. CTSB (1.35 g) was obtained.

Preparation of O-cross-linked chitosan-benzaldhyde (CCTB)

Powdered CTSB (1 g) was swollen in 50 mL of 4% sodium hydroxide solution, and then 2 mL epichlorohydrin was slowly dropped into the solution. The mixture was agitated at 60°C under microwave irradiation for 30 min. After filtering, the filter residue

was washed with distilled deionized water, acetone, and ether in sequence and dried in vacuum. CCTB powder (1.12 g) was obtained.

Preparation of O-cross-linked chitosan (CCTS)

CCTB (1 g) was dipped into 2% hydrochloride aqueous solution at room temperature for 24 h to remove the Schiff base. After filtering, the filter residue was washed with distilled water, ethanol, and dried in vacuum at 60°C. White powdered CCTS (0.84 g) was obtained.

Preparation of CCTE

EDTA dianhydride (1.5 g) was dissolved in 50 mL of dimethyl sulfoxide. Then, CCTS (0.8 g) was added into the solution, and the mixture was agitated at 60°C under microwave irradiation for 30 min. Next, the resulting cross-linked chitosan was stirred in ethanol at 60°C under microwave irradiation for 30 min. After filtering, the precipitate was washed with water and dried in vacuum. Light yellow powder CCTE was obtained. The degree of substition of EDTA in CCTE was determined from the C/N ratio,[25] which is 41.7%.

Adsorption experiment

Aqueous solutions of metal ions were prepared from Pb(NO$_3$)$_2$, CuSO$_4$·5H$_2$O, 3CdSO$_4$·8H$_2$O, NiSO$_4$·6H$_2$O, CoSO$_4$·7H$_2$O. 0.1 g of CTS or its derivate was added into a reagent bottle containing 25 mL of metal ion solution (0.02 mol/L). The pH of the solution was adjusted to the desired value with 0.1 mol/L hydrochloric acid or an acetate buffer solution. The mixture was stirred at 25°C for 12 h for adsorption, and then the mixture was filtered. The concentrations of the metal ions in the original solution and in the filtrate were determined by the titration with 0.01 mol/L EDTA solution.[27] The amounts of adsorbed-metal ions were calculated as follows:

$$q = (C_0 - C)V/m$$

where q is the adsorption capacity of adsorbent (mmol metal ion/g adsorbent), C_0 and C are the concentrations of metal ion before and after adsorption (mol/L), V is the volume of solution (mL), and m is the mass of adsorbent (g).

Adsorption kinetics was obtained by determining the adsorption capacity at different time intervals.

Desorption of metal ions

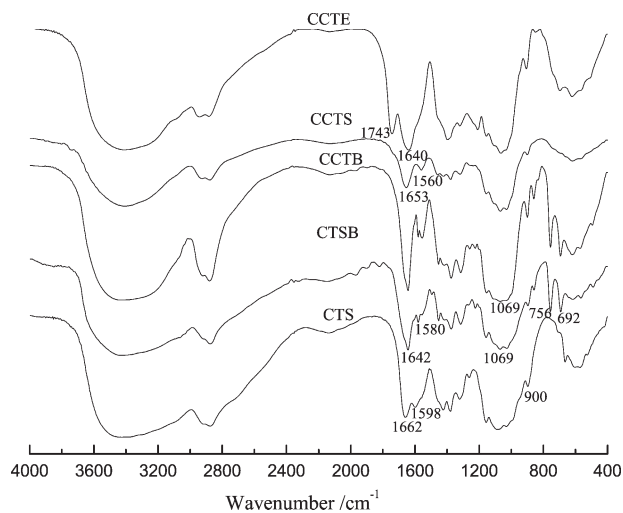CCTE adsorbed Cu^{2+} was agitated in 20 mL of 2.0 mol/L hydrochloric acid solution at room tempera-

Figure 2 FTIR spectra of CTS, CTSB, CCTB, CCTS, and CCTE.

ture for 8 h, and CCTE adsorbed other metal ion was stirred in 20 mL of 1.0 mol/L thiourea and 2.0 mol/L hydrochloric acid solution at room temperature for 8 h. The solution was then filtered to remove the filtrate residue. The metal ion in the filtrate was determined by the titration method and desorption efficiency of metal ion was calculated.

RESULTS AND DISCUSSION

Characterization of chitosan and modified-chitosan

Infrared spectroscopy

The products from each synthesis step were confirmed by FTIR analysis. Figure 2 displays the FTIR spectra of CTS and its derivatives. It was observed in Figure 2 that the characteristic peak of β-D-pyranoid near 900 cm^{-1} kept unchanged, indicating that pyranoid ring of CTS did not break up during the reaction.[28] In comparison with the FTIR spectra of CTS, CTSB, and CCTB, it was found that the characteristic peak of —C=N group stretch vibration appears at 1642 cm^{-1}, the characteristic peak of benzene ring backbone vibration appears at 1580 cm^{-1}, the intense peaks for the aromatic —CH— out of plane deformation appears at 756 cm^{-1} and 692 cm^{-1} for the existence of the phenyl group on CTSB and CCTB. However, these characteristic peaks disappear in CCTS due to removal of the Schiff base after the treatment of CCTB with hydrochloride acid solution, which can effectively protect the amino groups in CTS. By comparing the FTIR spectra of CCTE with CCTS, it can be clearly seen that a new and strong peak at 1743 cm^{-1} appears in CCTE, which was assigned to the stretching vibration of C=O in the carboxyl groups of reacted EDTA. Furthermore, a sharp peak at 1560 cm^{-1} (N—H

scissoring of the primary amine) disappears. The above analysis clearly indicates that the amino groups of CCTS were involved in the reaction with EDTA dianhydride.

X-ray diffraction analysis

The change of CTS structure before and after chemical modification was investigated by means of powder X-ray diffraction. Figure 3 depicts WAXD patterns of CTS and chitosan derivatives. The WAXD pattern of CTS represents the distinct crystalline peaks at $2\theta = 10°$ and $20°$.This is due to plenty of hydroxyl and amino groups exist in the chitosan structure, which can form stronger intermolecular and intramolecular hydrogen bonds. In addition, the structure of chitosan molecules has certain regularity. As a result, chitosan molecules can form crystalline regions very easily.[29] However, as regards CCTS, the characteristic peak at $2\theta = 10°$ disappears, and the characteristic peak at $2\theta = 20°$ decreases obviously. The X-ray diffraction pattern of CCTE is similar to that of CCTS. The decrease in crystallinity of the chitosan derivatives should be attributed to the deformation of the strong hydrogen bond in original chitosan due to the substitution of amino and hydroxyl groups by epichlorohydrin or EDTA group. This implies that the modified-chitosan is substantially more amorphous than chitosan. This may be very favorable for improving the adsorption capacities of CCTE for metal ions.[30]

Thermal stability analysis

The degradation process and thermal stability of CTS and CCTE were evaluated through thermogravimetric analysis (Fig. 4). As can be seen from Figure 4, TGA of CTS exhibits a weight loss in three main
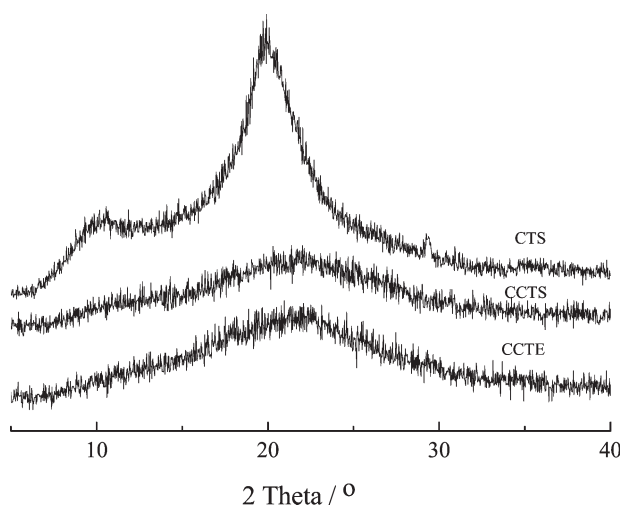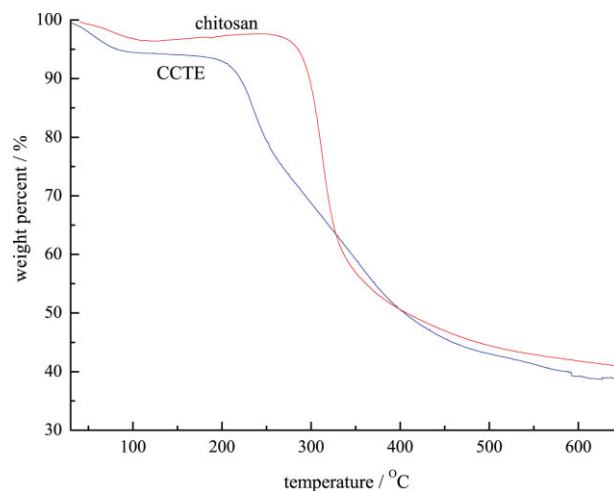

Figure 4 TGA of chitosan and CCTE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

degradation stages. The first stage ranges from 40°C to 150°C and shows about 3% loss in weight, which corresponded to the loss of adsorbed and bound water. The second stage of weight loss occurs in the range of 250 to 400°C and weight loss is about 47%, which was responsible for the scission of the ether linkage in CTS backbone. The third stage shows a weight loss of 10% in the range of 400 to 650°C, which was attributed to the thermal decomposition of glucosamine residues. However, CCTE has different course of the thermal degradation compared with CTS. The first thermal decomposition process starts at 30°C and continues upto 120°C with the loss of adsorbed and bound water of about 6%. The second stage ranges from 160 to 450°C and weight loss shows about 49%, corresponding to the scission of the ether linkage in CCTE backbone and the thermal decomposition of the EDTA residues. The third stage from 450 to 650°C shows a weight loss of about 7%, which is ascribed to the thermal decomposition of glucosamine residues. The onset temperature of both the dehydration and the thermal degradation is lower than that of the CTS. These mean that the thermal stability of CCTE decreases slightly.

Adsorption properties of CCTE for heavy metal ions

Adsorption capacities of CTS, CCTS, and CCTE

Table I displays the adsorption capacities of CTS, CCTS, and CCTE at pH = 5 for heavy metal ions such as Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Co^{2+}. It can be seen that the adsorption capacities of the same metal ion on the three adsorbents follows the order CCTE > CTS > CCTS. The adsorption capacities of CCTE for Pb^{2+} and Cd^{2+} are significantly improved

Figure 3 X-ray diffraction patterns of CTS, CCTS, and CCTE.

TABLE I
Adsorption Capacities of CTS, CCTS, and CCTE for Some Metal Ions

Adsorbent	Adsorption capacities/(mmol·g^{-1})				
	Pb^{2+}	Cu^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
CTS	0.372	1.97	0.503	1.33	1.01
CCTS	0.155	0.710	0.332	0.595	0.172
CCTE	1.28	2.13	1.29	1.34	1.28

compared with CTS, and its adsorption capacities for metal ions decrease in following order: $Cu^{2+} > Ni^{2+} > Cd^{2+} > Pb^{2+} \approx Co^{2+}$. The decrease of adsorption capacity of CCTS is mainly due to hydroxyl groups as the chelating sites are consumed after cross-linking modification.[11] The significant increase of adsorption uptake of CCTE may be attributed to the presence of the high content of carboxyl groups in the structure and the existence of coordination sites that form chelates with metal ions. With the addition of EDTA residues, it provides plenty of functional carboxyl groups in CCTE, resulting in that the adsorption power of CCTE can be dramatically enhanced over that of CCTS. This phenomenon should suggest that the adsorption mechanism is concluded to be adsorption within the porous and reactive polymer, rather than the adsorption on the polymer surface. Several studies have also reported that the introduction of carboxyl groups into chitosan backbone gives rise to enhancement of adsorption capacity toward metal ions.[10,31,32] As regards the adsorption of Ni^{2+}, however, CCTE has the similar adsorption capacity with CTS, which may mainly result from the chelation power of EDTA residue with metal ion. For some

different metal ions, CCTE represents the different adsorption capacities, which is possibly caused by different electrostatic interaction, covalent contribution, and properties of metal ions.

Effect of pH

Figure 5 exhibits the relationship between the pH value of metal ion solution and the adsorption capacity of CCTE for Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Co^{2+}. The experiments were conducted in the pH ranges of 2.0–6.0. The influences of pH > 6.0 were not studied to avoid the formation of precipitate. From Figure 5, it can be observed that the pH value of the solution strongly affects the adsorption performance of this adsorbent. The adsorption uptake of CCTE for metal ion increased with the increase of the pH value till a maximum value at pH = 5, and then decreased with further increase of pH. The adsorption capacities for metal ions were enhanced sharply in weakly acidic condition, which is mainly attributed to electrostatic interaction for adsorption mechanism. At lower pH, the amino groups get protonated and the —COOH groups on CCTE retain their protons; whereas at higher pH, many of the —COOH groups on CCTE are easily dissociated into the —COO⁻ groups. This makes the electrostatic interaction between CCTE and metal ion very active and favorable, thereby, resulting in the remarkable advance on adsorption capacity for metal ion at pH = 5. However, when pH increases too higher, the decreased adsorption for metal ion may be due to the electrostatic repulsion between surface sites of adsorbent and metal ion. A similar effect of pH on adsorbent was also observed on the literatures.[6,8,10]
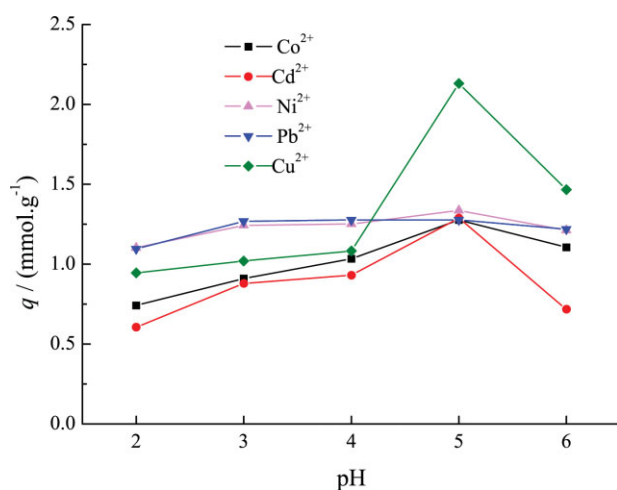
Figure 5 Effect of pH on adsorption capacity of CCTE for metal ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
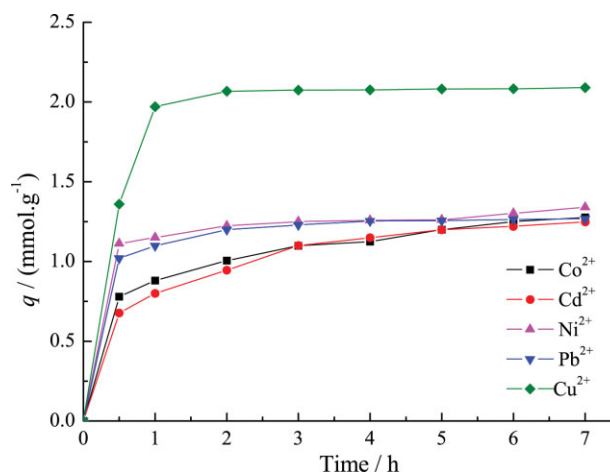
Figure 6 Adsorption kinetics of CCTE for metal ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Desorption Efficiency of CCTE for Some Metal Ions

Metal ion	Pb^{2+}	Cu^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
Desorption efficiency/%	95.8	93.3	95.9	94.3	98.7

Adsorption kinetics

Rapid interaction of the metal ion with adsorbent is desirable and beneficial for the practical adsorption application. The uptake kinetics of metal ions adsorption (pH = 5) on CCTE was investigated, as shown in Figure 6. It can be seen that metal ions uptake on CCTE is a fast process. The amount of adsorption increased rapidly in the first 1 h, contributing to about 70% of the ultimate adsorption amount, and then augmented gradually. Under our experimental conditions, the adsorption equilibrium was achieved within about 4 h for metal ions.

Desorption of metal ions

The desorption studies are of great importance since the economic success of the adsorption process depends on the regeneration of adsorbent. Hence, the metal ions should be quantitatively eluted from the adsorbent after adsorption. Desorption percentages of metal ions adsorbed by CCTE are showed in Table II. From Table II, it can be concluded that CCTE has the higher desorption percent of metal ions. The desorption efficiencies of metal ions were beyond 93%, indicating that the adsorbed-metal ions get easily removed and CCTE can be reused. However, the parent CTS is not suitable for regeneration after being used because of its solubility in strong acidic solution. Therefore, CCTE has potential to be used as an effective material in wastewater treatment.

CONCLUSIONS

Under microwave irradiation, a novel chemically modified-chitosan polymer (CCTE) was successfully prepared by the reaction of epichlorohydrin O-cross-linked chitosan with EDTA dianhydride. This biosorbent was confirmed by FTIR, XRD, and TGA analysis. Adsorption experiments showed that CCTE had highly enhanced adsorption capacity for some metal ions in comparison with CTS, being attributed to EDTA residues grafted on CCTE. The adsorption capacity depended on pH of the metal ion solution and the maximum adsorption of metal ions on CCTE was at pH = 5.0. Adsorption kinetics experiments demonstrated that the adsorption of CCTE for metal ions was reasonably successful and fast. Desorption experiments indicated that CCTE was easily

regenerated after being used. Therefore, the EDTA-as a new adsorbent showed obviously comparative competitive advantages over CTS. This novel derivative of chitosan may be used for the separation and recovery of some metal ions from wastewaters.

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