A novel adsorbent features like EDTA synthesized in situ by chemically modified cellulose and its behavior in metal ions adsorption from aqueous solution

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A novel adsorbent features like EDTA synthesized in situ by chemically modified cellulose and its behavior in metal ions adsorption from aqueous solution

Tao Hu · Xiaoli Hu · Cheng Tang · Dan Liu

Abstract This paper describes the synthesis of a novel chelating material derived from cellulose, and its heavy metal ions adsorption behavior from aqueous solution. The first section of this paper reports the chemical grafting of cellulose, that aminoacetic acid groups were grafted into the cellulose, resulted a novel yet unreported modified cellulose derivative N,N-(dicarboxymethylaminoethyl, carboxymethyl) aminoethylamine carboxymethyl cellulose amide. This obtained adsorbent was characterized by elemental analysis, infrared spectroscopy (IR) and Solid State Nuclear Magnetic Resonance (SSNMR) ^{13}C NMR spectroscopy. In the second section, adsorption behaviors such as kinetic study, adsorption isotherms of the adsorbent for Cu^{2+} and Pb^{2+} single metal ions from aqueous solution, and adsorption capacity for Ba^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} and Cu^{2+} , and the competitive adsorption of this adsorbent between ions were evaluated by ICP spectroscopy.

Keywords Modified cellulose · Aminoacetic acid group · Adsorption · Metal ions

Introduction

Environmental problems is always one of the focus that people concerned about. Heavy metal pollution accounts for a large proportion of all pollutant species, as a main pollution source, heavy metal ion pollution in water is related to everyone's health. For example, Cu^{2+} , Hg^{2+} , Ag^{+} and other trace amounts of heavy metals enter

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human body through food and drinking water and then enriched, resulting in heavy metal poisoning, caused great harm to human health (Pereira. 2016 and Bhalla et al. 2007). The Cu^{2+} content in drinking water must not exceed 20 μM , the normal concentration of copper ions in blood is 15.7-23.6 μM (100-150 $\mu\text{g/dL}$) (Mi et al. 2007; Carver. 2013 and Kirsipuu et al. 2020). Therefore, heavy metal ions removal from water with low cost and high efficiency has been a hot topic.

At present, the removal methods of heavy metal ions mainly include chemical precipitation, electrolysis, ion exchange, reverse osmosis, and membrane separation etc (Hu et al. 2016; Barakat. 2011 and Xu C. 2014). Among them, electrolysis and chemical precipitation are not suitable for the treatment of trace heavy metal waste water, ion exchange and membrane separation have better effect on the treatment of trace heavy metal ions, but the treatment capacity is limited and the maintenance cost is relatively high. Therefore, the materials with large adsorption capacity, high selectivity, wide range of source, cheap and renewable have been paid more and more attention in the field of heavy metal removal (Barakat. 2011).

Cellulose is the most abundant natural biomass resource in nature, meets the above conditions. It has a wide range of sources and biodegradability, and there are a large number of easily reactive chemical groups in the molecules, which are widely used in the modified matrix of various metal ion pollutant adsorbents (Ghanshyam. 2005; Hu et al. 2016; Cao et al. 2017; Gao et al. 2018; Nongbe et al. 2018; Lin et al. 2021). Cellulose-based heavy metal ion adsorbents have great potential for the adsorption and removal of heavy metal ions in water because of their good adsorption properties, good mechanical properties and renewable.

Many studies have been published around the world about cellulose chemically modified by esterification with EDTA for metal ion recovery, such as adsorption and removal of Cu^{2+} 、 Co^{2+} 、 Ni^{2+} ; metal ions in aqueous solution by cellulose EDTA solid phase extractant reported by Satoshi Tsukinoki (Tsukinoki et al. 2008), the preparation of hydrophilic filter paper which can filter and remove heavy metal ions, and the preparation of metal ion adsorption materials which connect EDTA to cellulose derivatives by Issam Jilal (Jilal et al. 2018) and Halluin MD (Halluin et al.

2017); In other reports (Singh et al. 2012; Huang et al. 2015), EDTA analogues of amino triacetic acid were grafted to cellulose. These materials have good adsorption properties for metal ions.

This work describes the preparation a novel chelating adsorbent by chemically modified cellulose, that aminoacetic acid groups was introduced into cellulose, and the evaluation its adsorbtion heavy metal ions in water. The first section of this work describes the chemically grafting of cellulose by introduced with aminoacetic acid functions. The second section of this work evaluates the conditions of adsorption of Cu^{2+} and Pb^{2+} by this grafted cellulose from aqueous solutions, and adsorption capacity for Ba^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} and Cu^{2+} , and the competitive adsorption of this adsorbent between ions were also evaluated by ICP spectroscopy.

Experimental

Materials

Microcrystalline cellulose was purchased from Huzhou Linghu Xinwang Chemical Co., Ltd. Polyamine diethylenetriamine was from Shanghai Aladdin Biochemical Technology Co., Ltd. Chloroacetic acid was bought from Sinopharm Chemical Reagent Co., Ltd. Dichlorosulfoxide (SOCl_2), methanol, ethanol , N,N-Dimethyl formamide (DMF), Na_2CO_3 were purchased from ChengDu Chron Chemicals Co.,Ltd, and were used without further purification.

Synthesis of carboxymethyl cellulose 1

According to literature method (Wilpiszewska et al. 2020; Ardiyanita et al. 2020), the microcrystalline cellulose was suspended in 25% NaOH (mass fraction) and etherified with chloroacetic acid at 65°C. After the reaction completed, a solid particles were obtained by cooling, acidification, filtration and washed with ethanol.

Synthesis of Methyl carboxymethyl cellulose ester **2**

In a 250 mL bottom flask, 10 g of carboxymethyl cellulose, 100 mL anhydrous methanol, 1 mL DMF were added, cooled by ice bath, with magnetic stirring, 12 mL of SOCl_2 was added slowly with a drop funnel and reaction temperature was controlled below 5°C . And then the reaction was continued at room temperature for another 24 hours. After reaction complete, a white small granular solid were obtained by Vacuum filtration, washed with anhydrous ethanol until no HCl was detected, and dried with vacuum.

Synthesis of diethylenetriamine carboxymethyl cellulose amide **3**

Methyl Carboxymethyl cellulose ester 5 g, anhydrous ethanol 50 mL, 5 mL (0.0465 mol) diethylenetriamine were added respectively into a 100 mL round bottom flask, and sealed in 75°C water bath for about 48 hours. After cool to room temperature, filter, washed with anhydrous ethanol to neutral, dried, get a white solid, which has weak ammonia smell.

Synthesis of N,N-(dicarboxymethylaminoethyl, carboxymethyl) aminoethylamine carboxymethyl cellulose amide **4**

9.0 g chloroacetic acid (about 0.1 mol) was dissolved in 20 mL distilled water in a 250 mL round bottom flask, with stirring, Na_2CO_3 powder was added to adjust the pH value to 9-10. And then 100 mL anhydrous ethanol, 4.9g diethylenetriamine carboxymethyl cellulose amide were added, and the reactant was stirred for 72 hours at room temperature. The pH value was detected and adjusted with anhydrous Na_2CO_3 during the reaction and maintained between 9-10. Stand still, Filter, Washed with ethanol, dried, a white solid was obtained.

Kinetic study of metal ion adsorption of **4**

Adsorption equilibrium time of adsorbent with metal ions was determined within 50 min in several min intervals. 10 mg of adsorbent was placed in a 50 mL round bottom flask, and then 10.0 mL of 500 ppm metal ion solution was added with continuous stirring. The adsorption process were carried out at pHs 5.0 for Cu^{2+} and Pb^{2+} , optimal contact time to get the best adsorption. Along with process, pH values should be adjusted and maintained at 5.0, and NaOH solution (0.01 mol/L) could be added into the solutions. After filtration, the concentration of metal ion remained in aqueous solution was determined by ICP spectroscopy.

pH study of metal ion adsorption of **4**

The effect of pHs on metal ion adsorption were performed by experiments with adsorbent and metal ion Cu^{2+} and Pb^{2+} . 10 mg of adsorbent **4** was added into a 50mL round bottom flask, and then under continuous stirring 10.0 mL of 500 ppm metal ion solution was added. pH was adjusted when needed with NaOH or HCl solutions (0.1–1.0 mol/L). The contact time in experiments were 30 min. After filtration, the remaining metal ion concentration of the solution was determined by the ICP spectroscopy. No significant change in the pH values in the solution was observed in the course of experiments.

Saturated adsorption for ions and competitive ions adsorption experiments

According to the conditions obtained from adsorption for Pb^{2+} and Cu^{2+} , the contact time was 30 minutes, a maximum pHs value before ion hydrolysis was chosen, pHs 7.0 for Ba^{2+} , Mg^{2+} and Mn^{2+} , pHs 6.0 for Co^{2+} and Ni^{2+} , pH 4.0 for Zn^{2+} . In the competitive ions adsorption experiments, a lower pHs of the ion was selected for preventing the hydrolysis of the easily hydrolyzed metal ion, for example, competitive ions adsorption between Mg^{2+} and Zn^{2+} , pH 4.0 was chosen. Initial concentration of all metal ions was 300 ppm.

Saturated adsorption for ions. 10 mg of adsorbent **4** was added into a 50mL round bottom flask, and then under continuous stirring 10.0 mL of 300 ppm metal ion solution was added. pH was adjusted when needed with NaOH or HCl solutions (0.1–1.0 mol/L). The contact time in experiments were 30 min. After filtration, the remaining metal ion concentration of the solution was determined by the ICP spectroscopy.

Competitive ions adsorption. 20 mg of adsorbent **4** was added into a 50mL round bottom flask, and then under continuous stirring 20.0 mL of mixed solution (300 ppm metal ion 1 and 300 ppm metal ion 2) was added. pH was adjusted when needed with NaOH or HCl solutions (0.1–1.0 mol/L). The contact time in experiments were 30 min. After filtration, the remaining metal ions concentration of the solution were determined by the ICP spectroscopy. No significant change in the pH values in the solution was observed in the course of experiments.

Characterization for materials obtained

The characterization of materials **1**, **2** and **3** were carried out by IR spectroscopy in a iS10 FT-IR spectrometer from Thermo Nicolet Corporation equipment with KBr. And the terminal adsorbent **4** was characterized by IR spectroscopy, Elemental analyses were accomplished in Vario EL cube from Elementar Trading (shanghai) Co.,Ltd, and Solid State Nuclear Magnetic Resonance (SSNMR) ¹³C NMR spectroscopy was recorded by a Bruker AVANCE III 600M equipment. Metal ion concentration was determined by ICP spectroscopy with an ICP-OES 5110 spectrometer produced by Agilent Technologies Inc.

Results and discussion

Synthesis of N,N-(dicarboxymethylaminoethyl, carboxymethyl) aminoethylamine carboxymethyl cellulose amide **4**

The route used to synthesize terminal adsorbent **4** was presented in Fig.1.

Carboxymethyl cellulose is the largest production of cellulose ether, the most widely used, and the most convenient product, commonly known as “industrial condiments”. Its synthesis method is mature and the product quality is stable. We used the conventional method reported in the literature to synthesize.

The esterification of carboxymethyl cellulose has not been reported in literature. The esterification reaction is a solid and liquid heterogeneous reaction, for a better esterification effect, we use $\text{SOCl}_2/\text{DMF}/\text{CH}_3\text{OH}$ (Hosangadi et al. 1996) as reagents. And during the procedure, SOCl_2 was added very slowly and ice bath was used to keep low temperature. When addition was completed, the reaction was carried out at room temperature to avoid heating, and avoid a large amount of HCl released in a short time, which will lead to the fracture of cellulose ether bond, and caused the decomposition of cellulose into small molecular products.

Ammonolysis is also a solid and liquid heterogeneous reaction. In order to obtain satisfactory ammonolysis effect, we use a large amount of excess one of the reactants to increase the yield of ammonolysis. The ratio of reaction material is as follows: diethylenetriamine: cellulose structure unit = 1.5:1. The reaction system is alkaline and the ether bond does not be broken. The reaction temperature was 75°C , heating can accelerate the reaction. After the reaction time is for about 48 hours, cooled, filtered by vacuum to remove the unreacted amine, a white solid product obtained, with a faint smell of ammonia.

The terminal product was obtained by carboxymethylation of amino groups with chloroacetic acid under alkaline conditions. The final product was obtained in the form of sodium salt, filtered, dried to obtain small white granular solids.

The intermediate products were identified by infrared spectrum, and the final product was verified by infrared spectrum, elemental analysis and Solid State Nuclear Magnetic Resonance (SSNMR) ^{13}C NMR spectroscopy.

Fig.1. Synthesis route for the terminal adsorbent **4**

Characterization of **1**, **2**, **3** and **4**

Carboxymethyl cellulose **1** was characterized by IR spectroscopy. The spectrum of **1** and unmodified cellulose was displayed in Fig.2. Compared with unmodified cellulose, a strong band at 1733 cm^{-1} in **1** was found, and it is the evidence that carbonyl functions was introduced into cellulose.

Fig. 2. IR spectrum of cellulose and carboxymethyl cellulose **1**

Fig. 3. IR spectrum of **2**, **3** and **4**

The IR spectra of **2**, **3**, and **4** showed in Fig.3. Product of esterification of carboxymethyl cellulose **2** showed a very wide and strong new band at 1630 cm⁻¹, Here is the stretching vibration of C=O of the carbonyl in ester. Accompanied by the disappearance of C=O double bonds stretching vibration in carboxylic acid at 1733 cm⁻¹, indicating the successful esterification.

IR spectrum of Material **3** presented In Fig.3. One band found at 1747 cm⁻¹ was assigned to C=O for stretch vibration. A very strong band found at 1615 cm⁻¹ was assigned for the presence of axial deformation vibration of C=O in the amide and angular deformation vibration of N-H in amine. The band appear at 1419 cm⁻¹ was assigned to C-N bond in the amide (Osvaldo et al. 2007).

Terminal material **4** was got by carboxymethylation from **3**, one band found at 1748 cm⁻¹ assigned to C=O for stretch vibration is much stronger than material **3** for the increase of acid groups, and bands of axial deformation of C=O in the amide and the N-H bond angular deformation in amine appears at 1635 cm⁻¹, which became weaker for the substitution of N-H by chloroacetic acid.

The main bands observed in **1**, **2**, **3** and **4** are presented in Table 1.

236 Table 1

237 Main IR absorption peaks found in **1**, **2**, **3** and **4**

materials	Bands found (cm ⁻¹)
1	1733,1421,1373,1058
2	1630,1409, 1057
3	1747, 1615, 1419, 1326,1058
4	1748,1635,1434,1059

238 Solid State Nuclear Magnetic Resonance (SSNMR) ¹³C NMR spectrum of
239 material **4** was represented in Fig.4, and the chemical shift and its assignments were
240 list in Table 2.

241 Table 2

242 Chemical shift and assignment ¹³C NMR spectrum of **4**

Chemical shift (ppm)	Assignment
178,171	-CO ₂ H, -CON-
103	O-C-O of cellulose
65-85	Carbons in cellulose, O-CH ₂ -CON
50-65	N-CH ₂ -CH ₂ -N, CON-CH ₂ -CH ₂ -N, N-CH ₂ -CO ₂ H
36	CON-CH ₂ -CH ₂ -N

243

244

245 Fig. 4. SSNMR ¹³C NMR of **4**

The Elemental Analysis data of adsorbent **4** was listed in Table 3. A larger percentage of nitrogen was found for the introduction of amino carboxylic group into cellulose. A minor portion of sulfur was found remained for result of the esterification process.

Table 3

Elemental analysis data of adsorbent **4**

Element	Found (%)	Proposed structure (%)
N	4.67	4.54
C	38.54	38.97
H	5.924	5.78
S	0.466	

According to the infrared spectrum analysis, Solid State Nuclear Magnetic Resonance (SSNMR) ^{13}C NMR spectrum analysis, and the results of elemental analysis, A possible structure of material **4** was given in Fig.5. Its calculated values of the elemental analysis are listed in Table 3.

Fig.5. Proposed structure of the material **4**

263 Fig.6. Adsorbent 4 and color change after adsorption of Cu^{2+} , Co^{2+} and Ni^{2+}

264

265 Adsorption study of **4** to Cu^{2+} and Pb^{2+}

266

267 Adsorption properties of the adsorbent **4** to target metal ions was studied. Conditions

268 (Contact time and pH) of the solution effect on adsorption were first carried out as

269 functions of time and pH.

270

271 Contact time effect on absorption

272

273 Contact time effect (kinetic study) of adsorbent **4** on adsorption Cu^{2+} and Pb^{2+} ions

274 was showed in Fig.7. Time to reach the equilibrium was within 30 min for adsorption

275 Cu^{2+} and Pb^{2+} ions. So, 30 min was used as contact time to study the effect of material

276 **4** absorption with ions.

Solution pH is a very important factor that affect on adsorbent for the removing metal ions in water by adsorption, because it affects the proprotization of aminoacetic acid groups, the ionization degree of chelating group and the type of adsorption functional group. The influence of the pH value on the adsorbent **4** for adsorption of metal ions was studied, and the contact time was 30min. As shown in Fig.8, when the pH value increases, the adsorption amount of metal ions by adsorbent **4** has a greater value. When the solution pH was 5, the adsorbent observed a maximum adsorption amount on Cu^{2+} and Pb^{2+} ions, and pH 5, not exceed the limit of hydrolysis of metal ions.

Fig.8. pH Effect of adsorbent **4** in adsorption of metal ion

Adsorption isotherms

Under optimal conditions included equilibrium time 30 min and pH 5.0 for Cu^{2+} and Pb^{2+} , adsorption experiments were carried out for evaluation of Langmuir (Eq. (1)) and Freundlich (Eq. (2)) isotherms (Ho et al. 2005; Osvaldo et al. 2007), that manifests function relationship between adsorption effect and the initial concentration of metal ions. The results are displayed in Fig.9 and Fig.10, and the data were listed in Table 4.

$$\frac{c}{q} = \frac{1}{Q_{\max} \times b} + \frac{c}{Q_{\max}} \quad (1)$$

$$\ln q = \ln k + \frac{1}{n} \ln c \quad (2)$$

Fig. 9. The Langmuir isotherms of adsorbent 4

Fig. 10. The Freundlich isotherms of adsorbent 4

Table 4

The parameters in Langmuir and Freundlich equation

Metal ion	Langmuir			Freundlich		
	$Q_{\max}$ (mg/g)	b (L/mg)	R^2	k (mg/g)	n	R^2
Cu ²⁺	80.3	3.894	0.99946	55.45	14.351	0.89493
Pb ²⁺	266.7	0.509	0.99982	187.06	15.55	0.89834

In Equation (1) and (2), $q(\text{mg/g})$ is an amount of metal ions adsorbed by the unit adsorbent, $c(\text{mg/L})$ is the concentration of the remaining metal ion in the solution when adsorption reaches equilibrium, $Q_{\max}$ and b are parameters unique in Langmuir equation, and k and n are parameters unique in Freundlich equation.

In Fig.9 and Fig.10, it can be seen that the data in the diagram are fitted by using Langmuir and Freundlich equations with good linear relations and high correlation coefficients, and thus the equations can be well used to explain the adsorption behavior of this adsorbent to metal ions

$Q_{\max}$ in Langmuir isotherm equation is a parameter that manifests the largest adsorption capacity of adsorbent when the target metal ion in higher concentrated solution. In Table 4, It is clear that adsorbent 4 exhibits the maximum adsorption capacity for Cu^{2+} was 80.3mg/g (1.264 mmol/g), while adsorbs Pb^{2+} was 266.7mg/g (1.287 mmol/g), and the maximum adsorption capacity of the two ions were almost the same in molar per gram. Parameter b manifests the bond energy in the coordination reaction between adsorbent and metal ion. Through the results listed Table 4, It can be concluded that adsorbent 4 shows a larger bond energy with Cu^{2+} than Pb^{2+} , the possible explanation is that Cu belongs to transition metal and nitrogen atoms have a stronger bond with copper ions.

In Freundlich equation, parameter k is a index for adsorption capacity at the condition when metal ion concentration in equilibrium is unitary, and the case is 1 mg/L, features closer to the industrial wastewater. So that the parameter k could be used for adsorption capacity assessment of metal ions in contaminated solutions diluted. The values of k for Cu^{2+} was 55.45 mg/g (0.873 mmol/g), and 187.06 mg/g (0.903 mmol/g) for Pb^{2+} , the values were almost the same when calculated into molar per gram. This indicates the adsorption superiority of adsorbent 4 when target metal ions in solution at very low concentrations.

These results were compared with a purchantable macroreticular adsorbent Duolite GT-73, which having thiol groups, reported by Vaughan et al (Vaughan et al, 2001). Duolite GT-73, the $Q_{\max}$ of Cu^{2+} was 62 mg/g and Pb^{2+} was 122 mg/g, respectively. The adsorbent 4 described in this paper exhibited double Pb^{2+} $Q_{\max}$ and higher Cu^{2+} $Q_{\max}$ than those of Duolite GT-73.

Saturated adsorption for ions and competitive ions adsorption

Adsorbent **4** exhibited fast visible color change when adsorbed ions were Cu^{2+} , Co^{2+} and Ni^{2+} et al, this was showed in Fig.6. According to the conditions obtained from Pb^{2+} and Cu^{2+} , saturated adsorption capacity (mmol/g) were determined for Ba^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} and Cu^{2+} . The data was presented in Fig.11. The minimum adsorption capacity among them was 0.87 mmol/g for Ba^{2+} . By comparing saturated adsorption capacity (mmol/g) of metal ions, the values differs each other at a rather low level, it could be concluded that there is fixed binding sites in adsorbent **4** and through which metal ions were adsorbed. In the adsorbent **4**, the adsorption binding site was aminoacetic acid functions, It has similar features to the EDTA, and the results indicated that, the adsorbent **4** showed a good adsorption capacity to a wide range of metal ions.

Fig.11. Adsorption capacity for Ba^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} and Cu^{2+} .

For a further comparing the adsorption properties of adsorbent **4** and EDTA, three different metal ions Mg^{2+} , Co^{2+} and Pb^{2+} were selected as reference ions, and competitive ions adsorption experiments were conducted firstly. The data were presented in Fig.12, Fig.13 and Fig.14.

Fig.12. Competitive ions adsorption: Mg^{2+} + ions

In Fig.12, competitive ions adsorption was carried out between Mg^{2+} and other ions. In the competitive adsorption between Mg^{2+} and Ba^{2+} , the adsorbent 4 showed a greater adsorption amount for Mg^{2+} . Competitive ions adsorption between Mg^{2+} and other metal ions, the adsorbent 4 was more inclined to adsorb other metal ions, such as Mn^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} and Ni^{2+} . Few Mg^{2+} was absorbed in competitive adsorption with Cu^{2+} .

Fig.13. Competitive ions adsorption: Co^{2+} + ions

In Fig.13, competitive ions adsorption was conducted between Co^{2+} and other ions. In the competitive adsorption between Co^{2+} and Ba^{2+} , Mg^{2+} and Mn^{2+} , the

adsorbent **4** showed a much larger adsorption amount for Co^{2+} in competition with Ba^{2+} and Mg^{2+} , and a small larger amount than Mn^{2+} . In the mixed solution of Co^{2+} with Zn^{2+} , Pb^{2+} and Ni^{2+} respectively, the adsorbent **4** was more inclined to adsorb Zn^{2+} , Pb^{2+} and Ni^{2+} . Few Co^{2+} was absorbed in competitive adsorption with Cu^{2+} .

Fig.14. Competitive ions adsorption: Pb^{2+} + ions

In Fig.14, competitive ions adsorption was conducted between Pb^{2+} and other ions. The amount of metal ion adsorbed by adsorbent **4** vast majority was Pb^{2+} in the mixed solution of Pb^{2+} with Ba^{2+} , Mg^{2+} . In competitive ion adsorption between Pb^{2+} and Co^{2+} and Ni^{2+} , the adsorbent **4** was inclined to adsorb Pb^{2+} . Between Pb^{2+} and Cu^{2+} , adsorbent **4** exhibited a larger adsorption amount for Cu^{2+} , it was the evidence that adsorbent **4** shows a greater adsorption capacity for copper.

Table 5

The formation constant $\lg K$ (ML) of EDTA with metal ions

ion	Ba	Mg	Mn	Co	Zn	Pb	Ni	Cu
$\lg K$ (ML) with EDTA	7.86	8.70	14.05	16.31	16.50	18.04	18.66	18.83

Data from Ringbom A, Complexation in Analytical Chemistry, Interscience Publishers, NewYork,1963.

According to the results presented in Fig.12, Fig.13 and Fig.14, it could concluded that the adsorption behavior of the adsorbent **4** is similar to that of the EDTA, and the formation constant $\lg K$ (ML) of EDTA with ions were used to explain

the adsorption behavior of adsorbent 4. From data listed in table 5, it could be seen that, among all metal ions, formation constant $\lg K(\text{ML})$ of EDTA with Ba^{2+} , Mg^{2+} are the much smaller, so in competitive ions adsorption experiments, the adsorbent 4 prefer to absorb other metal ions than Ba^{2+} and Mg^{2+} . Formation constant $\lg K(\text{ML})$ of EDTA with Co^{2+} is bigger than Ba^{2+} , Mg^{2+} and Mn^{2+} , thus the adsorbent 4 tends to adsorb Co^{2+} in competitive experiments. Zn^{2+} , Pb^{2+} , Ni^{2+} and Cu^{2+} have bigger $\lg K(\text{ML})$ with EDTA than Co^{2+} , so the adsorbent 4 tend to absorb these metal ions in competition adsorption. $\lg K(\text{ML})$ of EDTA with Ba^{2+} and Mg^{2+} are much smaller than Pb^{2+} , so the metal adsorbed mainly was Pb^{2+} in competitive ions adsorption. In the competition with Co^{2+} and Ni^{2+} , the amount of Pb^{2+} adsorpted by adsorbent 4 were bigger. The $\lg K(\text{ML})$ of EDTA with Cu^{2+} is slightly bigger than Pb^{2+} , and therefore the amount of Cu^{2+} adsorpted is slightly greater than Pb^{2+} .

Conclusions

A novel chelating material features like EDTA modified from cellulose was synthesized in situ for the first time, and thus, it was a new possible strategy for introducing chelating groups (aminoacetic acid) into the cellulose. Modified cellulose exhibited good adsorption capacity for a wide range of metal ions, such as Ba^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} and Cu^{2+} . Competitive ions adsorption experiments reveal its similar features of this adsorbent to EDTA, and it has potential use in the removal of heavy metal ion and recovery of useful ions from aqueous solution.

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Data listed in this paper are available in the mailbox of <https://mail.126.com/> :

User Name: xiaoli_hu_sasu

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Compliance with ethical standards

Conflict of Interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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