



Adsorbent grafted on cellulose by in situ synthesis of EDTA-like groups and its properties of metal ion adsorption from aqueous solution

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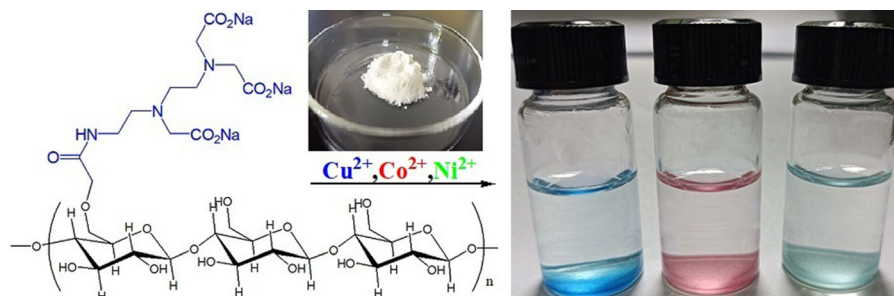
Abstract This paper describes the synthesis of a novel chelating material derived from cellulose, and its heavy metal ion adsorption properties from aqueous solution. The first section of this paper reports the chemical grafting of cellulose, that amino acetic acid groups were grafted onto the cellulose by in situ synthesis, a novel yet unreported modified cellulose derivative N,N-(dicarboxymethylaminoethyl, carboxymethyl)aminoethylamine carboxymethyl cellulose amide was synthesized. 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, the adsorption of Cu^{2+} and Pb^{2+} from single metal ion aqueous solutions onto this adsorbent were evaluated and analyzed by the Freundlich and Langmuir models. Further more, 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. The results indicated that this modified cellulose exhibited adsorption properties similar to those of EDTA, and showed good adsorption capacity for a wide range of metal ions.

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Graphical abstract



Keywords Modified cellulose · Amino acetic acid group · Adsorption · Metal ions

Introduction

Environmental issues have always been an important research topic. Among all of the pollutant species, heavy metal ion pollution has a large proportion, and it is related to everyone's health. For example, Cu^{2+} , Hg^{2+} , Ag^{+} and other trace amounts of heavy metals enter human body through food and drinking water and then accumulated, resulting in heavy metal poisoning (Bhalla et al. 2007; Pereira et al. 2016). The Cu^{2+} content in drinking water must not exceed $20 \mu\text{M}$, the normal concentration of copper ion in blood is $15.7\text{--}23.6 \mu\text{M}$ ($100\text{--}150 \mu\text{g/dL}$) (Carver 2013; Kirsipuu et al. 2020; Lim et al. 2007). Therefore, heavy metal ion removal from water with low cost and high efficiency has been an important endeavor.

At present, the removal methods of heavy metal ions mainly include chemical precipitation, electrolysis, ion exchange, reverse osmosis, and membrane separation etc. (Barakat 2011; Chauhan et al. 2005; Xu 2014). Among them, electrolysis and chemical precipitation are not suitable for the treatment of trace heavy metal wastewater, 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 sources, and are cheap and renewable have been paid more and more attention in the field of heavy metal removal (Barakat 2011).

Cellulose meets the above demands. It has a wide range of sources and biodegradability, and there is a large number of easily reactive chemical groups in the molecules, which are widely used as modified matrix of various metal ion pollutant adsorbents (Cao et al. 2017; Chauhan et al. 2005; Gao et al. 2018; Lin et al. 2021; Mengxuan et al. 2016; Nongbe et al. 2018). Cellulose-based adsorbents have great potential for the adsorption and removal of heavy metal ions in water.

Many studies have been reported 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 ion removal in aqueous solution by cellulose EDTA solid phase extractant reported by Satoshi Tsukinoki (Tsukinoki et al. 2008), and 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 Martin d'Halluin (d'Halluin et al. 2017). In other reports (Singh et al. 2012; Huang et al. 2015), EDTA analogue of amino triacetic acid was grafted onto cellulose. These materials have good adsorption properties for metal ions.

These reported adsorption materials based on cellulose matrix (such as microcrystalline cellulose, bagasse, cotton), EDTA, as well as its analogues, were grafted onto cellulose by ester bond. By using microcrystalline cellulose as raw material, we report the feasibility of a new strategy for in situ synthesis groups of similar structure to EDTA on cellulose and the complete synthesis process. This method might also be used for the synthesis of other amino carboxymethyl adsorbent based on matrix such as bagasse, cotton etc..

The first section of this work describes the chemical grafting of cellulose by amino acetic 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 adsorption competition of this adsorbent between ions was 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 (Ardiyanita et al. 2020; Wilpizewska 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, acidified, filtrated 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 h. After the reaction completed, a white small granular solid was 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 was added respectively into a 100 mL round bottom flask, and sealed in 75 °C water bath for about 48 h. After cooled to room temperature, filtered, and washed with anhydrous ethanol to neutral, dried, a white solid was obtained, 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, 4.9 g diethylenetriamine carboxymethyl cellulose amide were added, and the reactant was stirred for 72 h at room temperature. The pH value was detected and adjusted with anhydrous Na_2CO_3 during the reaction and maintained between 9–10. After filtering, it was washed with ethanol and dried; a white solid was obtained.

Kinetic study of metal ion adsorption of 4

Adsorption equilibrium time of adsorbent with metal ions were 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 absorption process were carried out at pHs 5.0 for Cu^{2+} and Pb^{2+} , optimal contact time to get the best adsorption. During the process, pH values should be adjusted and maintained at 5.0, and NaOH solution (0.01 mol/L) could be added. 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 (Cu^{2+} and Pb^{2+}) adsorption was performed by experiments. 10 mg of adsorbent 4 was added into a 50 mL 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 was 30 min. After filtered, the remaining metal ion concentration of the solution was determined by the ICP spectroscopy. No significant change in the pH values in the solution were observed in the course of experiments.

Saturated adsorption and ion adsorption competition experiments

According to the conditions obtained from adsorption for Pb^{2+} and Cu^{2+} , the contact time was 30 min, 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 ion adsorption competition experiments, a lower pH was selected for preventing the hydrolysis of the easily hydrolyzed metal ion, for example, ion adsorption competition between Mg^{2+} and Zn^{2+} , pH 4.0 was chosen. Initial concentration of all metal ions were 300 ppm.

Saturated adsorption for ions. 10 mg of adsorbent **4** was added into a 50 mL 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 solution (0.1–1.0 mol/L). The contact time in experiments was 30 min. After filtered, the remaining metal ion concentration of the solution was determined by the ICP spectroscopy.

Ion adsorption competition. 20 mg of adsorbent **4** was added into a 50 mL 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 solution (0.1–1.0 mol/L). The contact time in experiments were 30 min. After filtered, the remained metal ion concentration of the solution was determined by the ICP spectroscopy. No significant change in the pH values in the solution were 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) ^{13}C NMR spectroscopy was recorded by a Bruker AVANCE III 600 M 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** is presented in Fig. 1.

Carboxymethyl cellulose **1** was synthesized by conventional method reported in the literature.

The esterification of carboxymethyl cellulose has not been reported before. The esterification reaction is a solid–liquid heterogeneous reaction, in this paper, $\text{SOCl}_2/\text{CH}_3\text{OH}/\text{DMF}$ (Hosangadi et al. 1996) were used as reagents. The optimized reaction conditions were obtained through many experiments. Initially, for a higher conversion rate and accelerating the reaction speed, heating was carried out as described in the literature, thus leading to the degradation of cellulose. Satisfactory results were obtained when reaction conditions (temperature, time) were controlled. The optimized reaction conditions were that, SOCl_2 was added very slowly and ice bath was used to keep low temperature, during the next stage, the reaction was carried out at room temperature.

Ammonolysis of methyl carboxymethyl cellulose ester **2**, and then, carboxymethylation of amino groups with chloroacetic acid for the terminal product **4** are also solid–liquid heterogeneous reactions. A large excess of diethylenetriamine and chloroacetic acid was added to increase the conversion ratio of groups.

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

Carboxymethyl cellulose **1** was characterized by IR spectroscopy. The spectrum of **1** and unmodified cellulose is displayed in Fig. 2. Compared with unmodified cellulose, a strong band at 1733 cm^{-1} in

Table 1 Main IR 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

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, indicate the successful esterification.

In IR spectrum of material **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 appears at 1419 cm⁻¹ was assigned to C–N bond in the amide (Karnitz et al. 2007).

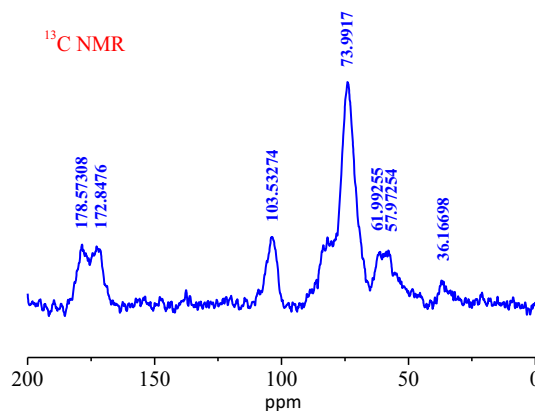
Terminal material **4** was got by carboxymethylation from **3**, one band found at 1748 cm⁻¹ assigned to C = O for stretch vibration is much stronger than material **3** for the increase of carbonyl groups, and bands of axial deformation of C = O in the amide and the N–H bond angular deformation in amine appear 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.

Solid State Nuclear Magnetic Resonance (SSNMR) ¹³C NMR spectrum of material **4** is presented in Fig. 4, and the chemical shift and its assignments are listed in Table 2.

The elemental analysis data of material **4** is listed in Table 3. A larger percentage of nitrogen was found for the introduction of amino carboxylic group onto cellulose. A minor portion of sulfur was found remained for result of the esterification process.

According to the infrared spectrum analysis, Solid State Nuclear Magnetic Resonance (SSNMR) ¹³C 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. 4** SSNMR ¹³C NMR spectrum of 4

Adsorption study of 4 to Cu²⁺ and Pb²⁺

Cu²⁺ and Pb²⁺, as common heavy metal pollutant ions, were always used as target adsorbed ions (Jilal et al. 2018; Júnior et al. 2009; Tsukinoki et al. 2008; Vaughan et al. 2001). Started with Cu²⁺ and Pb²⁺, the conditions and adsorption capacity of adsorbent **4** obtained could compare with literature, and the adsorption properties of adsorbent **4** could be evaluated. Conditions of the solution effect on adsorption were first carried out as functions of time and pH.

Contact time effect on absorption

Contact time effect (kinetic study) of adsorbent **4** on adsorption to Cu²⁺ and Pb²⁺ are shown in Fig. 6. Time to reach the equilibrium was within 30 min for adsorption Cu²⁺ and Pb²⁺. So, 30 min was used as contact time to study the absorption effect of adsorbent **4** with ions.

pH Effect

Solution pH is a very important factor that affect on adsorbent for the removing metal ions in water by adsorption, because it affects the protonation of amino acetic acid groups, the ionization degree of chelating group and the type of adsorption functional group. In general, with a higher pH value, the adsorption capacity is greater, but, it can not exceed the limit pH value of hydrolysis of metal ion, so pH range of 2–5 was chosen, and adsorption capacity was carried out as function of pH. Of course, a pH range

Table 2 Chemical shift and assignments in ^{13}C NMR spectrum of 4

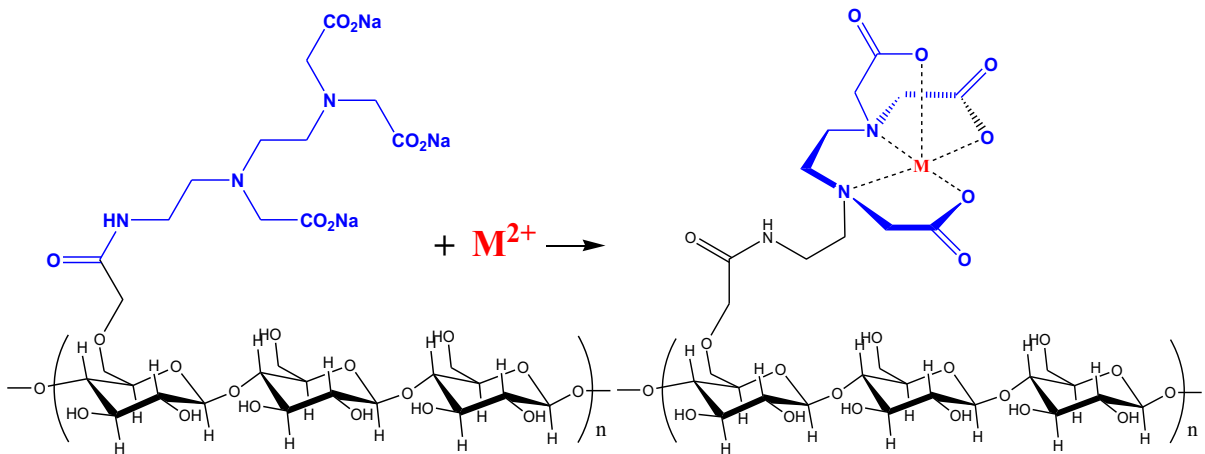
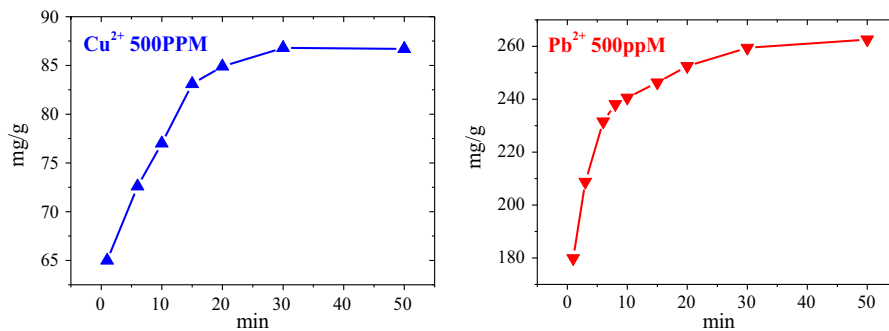
Chemical shift (ppm)	Assignment
178,172	$-\text{CO}_2\text{H}$, $-\text{CON}-$
103	$\text{O}-\text{C}-\text{O}$ of cellulose
65–85	Carbons in cellulose, $\text{O}-\text{CH}_2-\text{CON}$
50–65	$\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$, $\text{CON}-\text{CH}_2-\text{CH}_2-\text{N}$, $\text{N}-\text{CH}_2-\text{CO}_2\text{H}$
36	$\text{CON}-\text{CH}_2-\text{CH}_2-\text{N}$

Table 3 Elemental analysis data of material 4

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

of 2–5, is also the expected range of polluted acid water.

Under the condition of contact time 30 min, the influence of the pH value on the adsorption of metal ions were studied. As shown in Fig. 7, when the pH value increases, the adsorption amount of metal ion by adsorbent 4 has a greater value. When the solution pH was 5, the adsorbent observed a maximum adsorption

**Fig. 5** Proposed structure of the material 4 and its chelating center with ion**Fig. 6** Contact time effect in adsorption of adsorbent 4 to metal ion

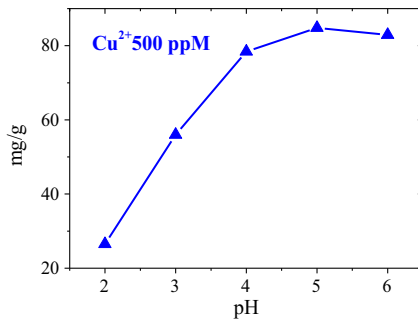


Fig. 7 pH Effect on adsorbent 4 in adsorption of metal ion

amount to Cu²⁺ and Pb²⁺, and pH 5, does not exceed the limit value of hydrolysis of metal ions.

Adsorption isotherms

Under optimal conditions (equilibrium time 30 min and pH 5.0), adsorption experiments were carried out for evaluation with Langmuir (Eq. (1)) and Freundlich (Eq. (2)) isotherms (Ho et al. 2005; Karnitz et al. 2007), that manifests function relationship between adsorption effect and the initial concentration of metal ion. The results are displayed in Fig. 8 and Fig. 9, and the data is listed in Table 4.

$$\frac{c}{q} = \frac{1}{Q_{\max} \times b} + \frac{c}{Q_{\max}} \tag{1}$$

$$\ln q = \ln k + \frac{1}{n} \ln c \tag{2}$$

In Eqs. (1) and (2), *q*(mg/g) is an amount of metal ion adsorbed by the unit adsorbent, *c*(mg/L) is the concentration of the remaining metal ion in the solution when adsorption reaches equilibrium, *Q*_{max}

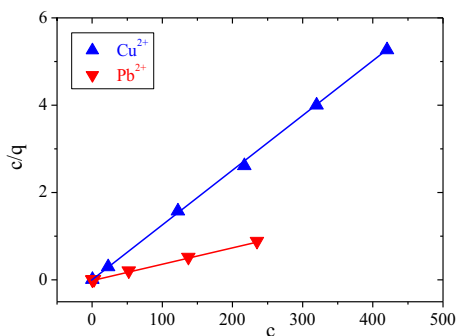


Fig. 8 The Langmuir isotherms of adsorbent 4

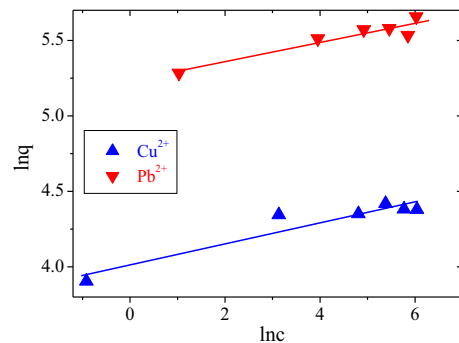
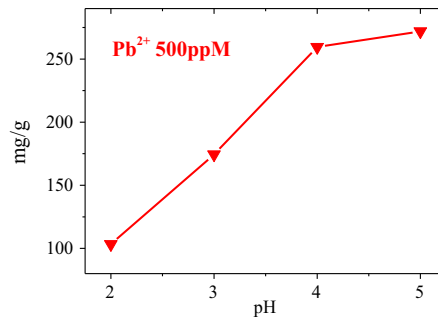


Fig. 9 The Freundlich isotherms of adsorbent 4

and *b* are parameters unique in Langmuir equation, and *k* and *n* are parameters unique in Freundlich equation.

In Figs. 8 and 9, 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 well be used to explain the adsorption properties 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 Cu²⁺ was 80.3 mg/g (1.264 mmol/g), while for Pb²⁺ was 266.7 mg/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 in Table 4, It can be concluded that adsorbent 4 shows a larger bond energy with Cu²⁺ than Pb²⁺, the possible

Table 4 The parameters in Langmuir and Freundlich equations

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

Table 5 Some Q_{\max} for Cu^{2+} and Pb^{2+} of adsorbents reported in literature

	Cu^{2+}	Pb^{2+}	Adsorbent	Literature
Q_{\max} (mg/g)	62	122	Duolite GT-73	Vaughan et al. (2001)
Q_{\max} (mmol/g)	0.25	–	EDTA-CELL	Tsukinoki et al. (2008)
Q_{\max} (mg/g)	66.7	232.0	EMC	Júnior et al. (2009)
Q_{\max} (mg/g)	77.1	109.65	HEC-EDTA	Jilal et al. (2018)
Q_{\max} (mg/g)	80.3	266.7		This paper

explanation is that Cu belongs to transition metal and nitrogen atom have a stronger bond with copper ion.

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, feature closer to the industrial wastewater. So that the parameter k could be used for adsorption capacity assessment of metal ion in diluted contaminated solution. The value 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 ion in solution at very low concentration.

These results were compared with some Q_{\max} for Cu^{2+} and Pb^{2+} of adsorbents reported in literature, data is listed in Table 5. Duolite GT-73, a purchasable macroreticular adsorbent which having thiol groups, reported by Vaughan (Vaughan et al. 2001), 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. Compared with other adsorbents, which contain EDTA group connected to cellulose by ester bond, the Q_{\max} for Cu^{2+} and Pb^{2+} of adsorbent **4** were far more larger.

Saturated adsorption and ion adsorption competition

Adsorbent **4** exhibited fast visible color change when adsorbed ions were Cu^{2+} , Co^{2+} and Ni^{2+} , this is

shown in Fig. 10. 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 is 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 differ each other at a rather low level, it could be concluded that there is fixed binding sites in adsorbent **4** and through which metal ion were adsorbed, proposed chelating center is presented in Fig. 5. In the adsorbent **4**, the adsorption binding site was amino acetic acid functions, It has similar feature to the EDTA, and the results indicated that, the adsorbent **4** showed a good adsorption capacity to a wide range of metal ions.

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

In Fig. 12, adsorption competition was carried out between Mg^{2+} and other ions. In the competition between Mg^{2+} and Ba^{2+} , the adsorbent **4** showed a greater adsorption amount for Mg^{2+} . Adsorption competition 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 the competition with Cu^{2+} .

In Fig. 13, adsorption competition was conducted between Co^{2+} and other ions. The adsorbent **4** showed

Fig. 10 Adsorbent 4 and color change after adsorption of Cu^{2+} , Co^{2+} and Ni^{2+}

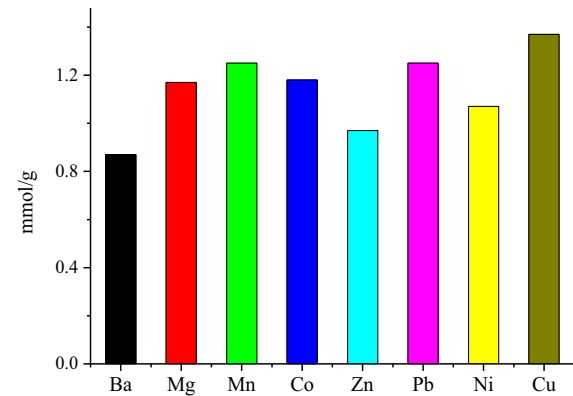
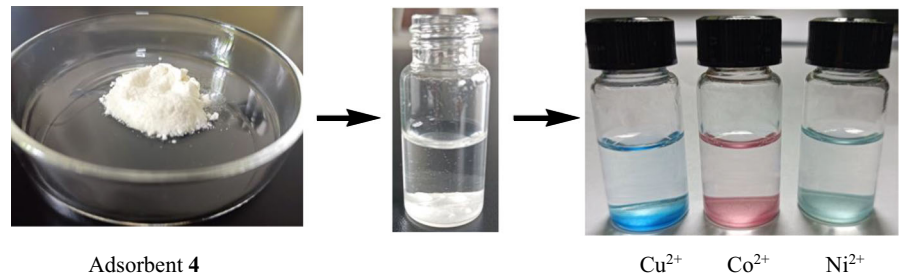


Fig. 11 Adsorption capacity for Ba^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} and Cu^{2+}

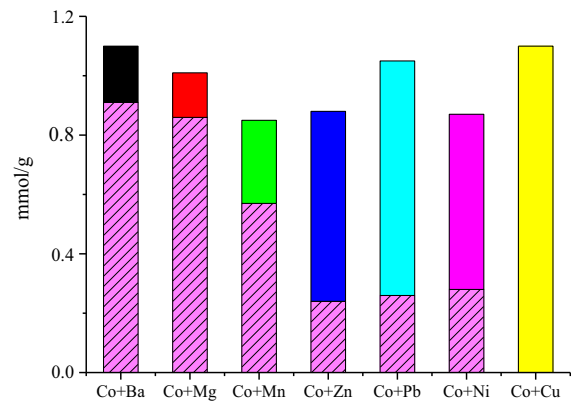


Fig. 13 Ion adsorption competition: Co^{2+} + ions

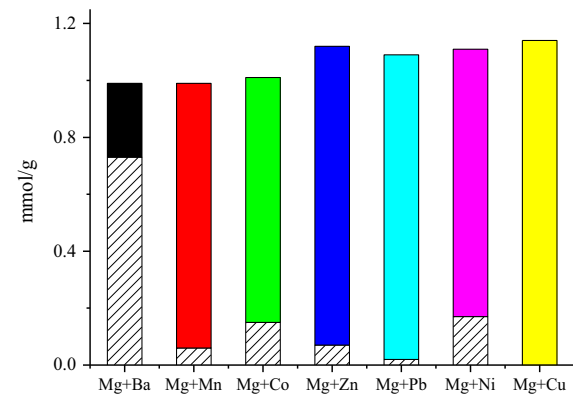


Fig. 12 Ion adsorption competition: Mg^{2+} + ions

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 solution of Co^{2+} mixed with Zn^{2+} , Pb^{2+} , Ni^{2+} respectively, the adsorbent 4 was more inclined to adsorb Zn^{2+} , Pb^{2+} and Ni^{2+} . Few Co^{2+} was absorbed in competition with Cu^{2+} .

In Fig. 14, adsorption competition was conducted between Pb^{2+} and other ions. The amount of metal ion adsorbed by adsorbent 4 vast majority was Pb^{2+} in the

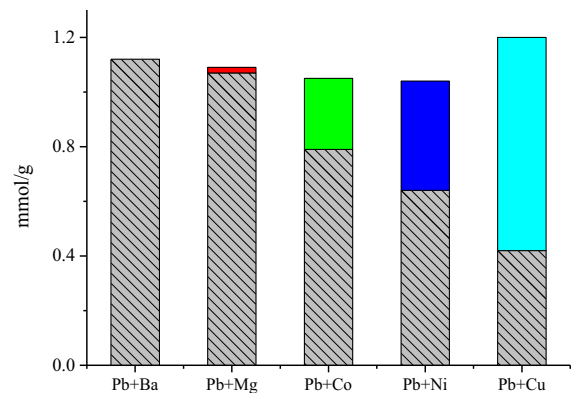


Fig. 14 Ion adsorption competition: Pb^{2+} + ions

mixed solution of Pb^{2+} with Ba^{2+} , Mg^{2+} respectively. In the adsorption competition between Pb^{2+} and Co^{2+} , Ni^{2+} , the adsorbent 4 was inclined to adsorb Pb^{2+} . In the adsorption competition between Pb^{2+} and Cu^{2+} , adsorbent 4 exhibited a larger adsorption amount for Cu^{2+} , and it was the evidence that adsorbent 4 shows a larger bond energy with Cu^{2+} than Pb^{2+} manifested by Parameter b in Langmuir isotherm equation.

According to the results presented in Figs. 12, 13 and 14, it could be concluded that the adsorption

Table 6 The formation constant $\lg K$ (ML) of EDTA with metal ions

Ion	Ba ²⁺	Mg ²⁺	Mn ²⁺	Co ²⁺	Zn ²⁺	Pb ²⁺	Ni ²⁺	Cu ²⁺
$\lg K$ (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

properties of the adsorbent **4** is similar to that of EDTA, and the formation constant $\lg K$ (ML) of EDTA with ions were used to explain the adsorption properties of adsorbent **4**. From data listed in Table 6, it could be seen that, among all metal ions, formation constant $\lg K$ (ML) of EDTA with Ba²⁺ and Mg²⁺ are much smaller, so in ion adsorption competition experiments, the adsorbent **4** prefer to absorb other metal ions than Ba²⁺ and Mg²⁺. Formation constant $\lg K$ (ML) of EDTA with Co²⁺ is bigger than Ba²⁺, Mg²⁺ and Mn²⁺, thus the adsorbent **4** tends to adsorb Co²⁺ in competition experiments. Zn²⁺, Pb²⁺, Ni²⁺ and Cu²⁺ have bigger $\lg K$ (ML) with EDTA than Co²⁺, so the adsorbent **4** tends to absorb these metal ions. $\lg K$ (ML) of Ba²⁺ and Mg²⁺ with EDTA are much smaller than Pb²⁺, so the metal adsorbed mainly was Pb²⁺. When Pb²⁺ competition with Co²⁺, the amount of Pb²⁺ adsorbed was bigger because its larger $\lg K$ (ML) with EDTA. The $\lg K$ (ML) of EDTA with Cu²⁺ is slightly bigger than Pb²⁺, and therefore the amount of Cu²⁺ adsorbed is slightly greater than Pb²⁺.

Conclusions

A novel chelating material modified from cellulose was synthesized in situ for the first time, it was a new possible strategy for introducing chelating groups (amino acetic acid) onto the cellulose. Modified cellulose exhibited good adsorption capacity for a wide range of metal ions, such as Ba²⁺, Mg²⁺, Mn²⁺, Co²⁺, Zn²⁺, Pb²⁺, Ni²⁺ and Cu²⁺, ion adsorption competition experiments reveal its similar feature to EDTA, and it has potential use in the removal of heavy metal ions and recovery of useful ions from aqueous solution.

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Availability of data and materials Data listed in this paper are available once you send a request e-mail to the communications contacts at 441430968@qq.com.

Declarations

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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