Synthesis and Characterization of Iminodiacetate Cellulosic Sorbent and Its Application in Metal Ion Extraction

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SYNOPSIS

Iminodiacetate cellulosic chelating sorbent, derived from cotton fabric, was synthesized in a two-step reaction sequence. The pH dependence of the metal ion extraction for Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) was studied. Under optimum conditions, the average sorptive capacity of the sorbent was found to be 0.38 mmol metal ion/sorbent. The viability of using this sorbent for recycling, preconcentration of metal ion, and selective metal ion extraction was demonstrated.

INTRODUCTION

The importance of chelating sorbents in chemical applications has been evident for a long period of time. During recent years, we have witnessed a substantial growth in interest and uses of chelating sorbents in the field of water treatment,[1] pollution control,[2] and analytical chemistry.[3-5] Among many sorptive materials, various forms of cellulose which are abundantly available at low cost have emerged as one of the most important polymeric matrices for the synthesis of new sorbents. In addition to their ready availability, chelating sorbents based on cellulosic materials have several appealing advantages for aqueous separation processes.[6] They have outstanding sorptive capacity, high hydrophilicity, and favorable kinetic properties.[4] A wide range of sorbents based on chemically modified cellulose have been developed, and some of them demonstrated superiority to sorbents derived from synthetic polymers in water treatment. In particular, the iminodiacetate group confers desirable chelating properties on sorbents, and are widely used to bond on the cellulose matrix.[7,8]

Heavy metal pollution from industrial effluents are an urgent problem of many industrialized cities. Under current trends of worldwide environmental regulations, chemical industry has the obligation to control the wastewater and hazardous wastes they generate.[9] The electroplating industry, one of the major chemical industries in Hong Kong, produces a great number of metal ions which may contaminate the industrial effluents. Making the situation unique, the majority of electroplating factories are small in size and most of them are located in multistory buildings. As a consequence, there is a great local demand for the design of cost-effective waste control devices to fit unique local situations. With the objective of synthesizing a new chelating sorbent and exploration of its potential in industrial wastewater treatment, we report the functionalization and characterization of a cellulose based sorbent. Also, the viability of using this sorbent in the recycling and preconcentration of metal ions becomes evident during the discussion.

EXPERIMENTAL

Apparatus

Metal ion determinations were performed with a Varian Spectra AA-20 atomic absorption spectrophotometer (AAS). The chloride concentration and pH of solutions were determined with a pH meter (Orion Model 611), using a chloride ion electrode (Orion 4210-N88) and a Sensonex combined pH electrode (Model S200C).

Reagent

Pure cotton fabric was purchased from local stores and was used as the starting material. All solvents and reagents for the synthesis were reagent grade and were used without further purification. Standard solutions of Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) was prepared by dissolving an appropriate amount of pure metal in minimum amount of concentrated nitric acid and then diluted to 1000 ppm with deionized water (DI).

Preparation of Cellulose Chloride[1]

Pure cotton fabric was stirred with 95% ethanol for 30 min, and was then air-dried. This pretreated fabric was stored in a desiccator for later use.

Method A (Phase Transfer Catalysis Method)[10]

Under vigorous stirring, a piece of pretreated cotton fabric (about 0.5 g) was refluxed in a mixture of 20 mL chloroform, 20 mL 50% (w/v) NaOH solution, and 10% (w/w to the fabric) tetrabutylammonium hydrogensulfate for 3 h. After cooling, the fabric was taken out, washed with DI, and then allowed to air-dry. The chlorine content in the fabric, which reflected the degree of substitution, was determined by sodium fusion followed by chloride ion determination.

Method B (POCl₃ as Chlorination Agent)[8]

Under vigorous stirring, a piece of pretreated cotton fabric (about 0.5 g) was refluxed in a mixture of 2 mL $POCl_3$ and 20 mL dried dimethyl formamide (DMF) for 0.5 h. After cooling, the fabric was washed with DI and air-dried. Finally, the chlorine content of the fabric was determined as before.

Preparation of Cellulose–Iminodiacetate (CIDA) Sorbent 2

About 0.5 g of chlorinated fabric was immersed in 10 mL of DMF and water mixture in a volume ratio of 12:5. Five equivalent amounts of sodium iminodiacetate was then added. The mixture was heated at 100°C under vigorous stirring for 8 h. After cooling, the fabric was taken out and washed thoroughly with DI and air dried. Together with the blank of cotton fabric, the nitrogen content of CIDA sorbent was determined by the Kjedahl method.

Estimation of the Degree of Functionalization (DF) of Cellulose-Derived Materials

Chlorine Content

About 0.05 g of chlorinated fabric was subjected to the sodium fusion treatment.[11] The chloride content of the fabric after decomposition was determined by a chloride selective electrode.

Nitrogen Content

About 0.04 g of cellulose sorbent (2) was digested in 98% sulfuric acid, according to the standard Kjedahl method.[12] To speed up the digestion, the mixture was refluxed until a clear solution was obtained. The digested solution was then neutralized with 30% sodium hydroxide solution. Ammonia evolved was steamed distilled, collected, and absorbed in a boric acid solution containing an acid–base indicator. The absorbed boric acid was then titrated with standardized hydrochloric acid for its ammonium content.

Metal Ion Uptake as a Function of pH

Batch equilibrium technique was used to determine the pH dependence of CIDA sorbent towards the sorption of different metal ions. Metal ion solutions containing 20–50 ppm cadimum(II), cobalt(II), copper(II), lead(II), and nickel(II) at pH 2–7 were prepared. About 30 mg of the sorbent was added to 20 mL of the above metal ion solutions at different pHs. The mixtures were vigorously stirred for 1 h, and the sorbent was taken out and was washed with DI. The solution and rinse water were subjected to metal ion determinations. The metal ion uptake at various pH by the underivatized cotton fabric was also determined as the blank.

Sorption Capacity

Different concentrations (from 10 to 250 ppm) of Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) ion at optimum pH for metal ion removal were prepared. Twenty milliliters of each of these solution were equilibrated with about 30 mg of the sorbent for 1 h. The sorbent was then taken out and rinsed with a small portion of DI. The metal ion solution and the rinse water after proper dilution was analyzed for metal ion remaining by the AAS method.

Kinetic Characteristics of the Sorbent

Four pieces of the sorbent (about 30 mg each) were equilibrated separately in 20 mL of 20 ppm Cu(II) ion solution at pH 5 for 15, 30, 45, and 60 min, respectively. A series of blanks were run with the underivatized cellulosic fabric under the same conditions. The mixtures were filtered and the recovered sorbents were washed with DI. The copper content of the filtrate and the rinse water was determined as usual. Similar studies were carried out for Cd(II), Co(II), Pb(II), and Ni(II) ion solutions.

Recovery of Metal Ions from the Sorbent

These experiments were performed after conditions for maximum uptake of metal ions by the sorbent had been found. Five pieces of CIDA sorbent (about 30 mg each) were first allowed to take up the maximum amount of copper(II) ion under optimum conditions. These five pieces of sorbent were then put into five beakers containing 20 mL nitric acid with the concentration range $0.1 M$ to $3 M$. Each solution was allowed to stir for 0.5 h at room temperature. The final solutions were filtered, and the filtrates collected. The concentration of metal ion released after the acid treatment was determined by AAS. Similar studies were carried out for cadium(II), cobalt(II), lead(II), and nickel(II) ion solutions.

Sorption Characteristics of the Sorbent in Dynamic Mode

Sorption of Pb(II) Ion

About 0.25 g of the air-dried CIDA sorbent was weighed accurately and packed in a 50 mL buret to 1 in. below the rim of the buret. Ten portions of 20 mL each of 200 ppm Pb(II) solution at pH 5 were allowed to flow down the buret by gravity through the sorbent. The flow rate of the Pb(II) solution was adjusted to 4 mL/min. After passing through the packed sorbent, each of the 20 mL portions of the Pb(II) solution was collected successively. The amount of Pb(II) remaining in each portion of solution was determined by the AAS method.

Desorption of Pb(II) Ion by Acid Treatment

After the sorption was completed, five portions of 10 mL each of $3 M$ nitric acid were allowed to flow down the buret in the same manner. The amount of Pb(II) ion released from the sorbent in each portion was determined. The whole experiment was re-

peated by changing the elution rate of the sorption and desorption process to 8 mL/min.

Preconcentration of Metal Ion Solution

About 1 g air dried sorbent was accurately weighed and packed in a buret as described above. One liter of 2 ppm Pb(II) solution at pH 5 was allowed to flow down the column continuously by gravity through the packed sorbent at an elution rate of 10 mL/min. After sorption was complete, five portions of 5 mL each of $3 M$ nitric acid were eluted through the sorbent. The concentration of Pb(II) in each portion of nitric acid was determined. Another set of data was obtained by repeating the above experiments with a 0.2 ppm Pb(II) solution.

Selective Extraction of Metal Ion Solution

About 0.34 g air-dried sorbent was accurately weighed and packed in a buret as mentioned above. Two hundred milliliters of metal ions solution each containing 50 ppm Ni(II) and Co(II) ions at pH 6 was continuously passed through the sorbent at an elution rate of 3 mL/min. A total of 180 mL eluate was collected in nine equal portions. The concentration of nickel and cobalt in each portion of the eluate was determined by AAS.

Stability of the Sorbent

About 0.21 g sorbent was cut into six pieces of nearly equal weight, and these were put into 100 mL 100 ppm Ni(II) solution. Sorption and desorption experiments were carried out as above. Then two out of the six pieces of fabric sorbent were taken out and their nitrogen content determined. The remaining four pieces of fabric sorbent were again subjected to the sorption and desorption experiment; and two out of the four pieces of fabric were taken out and their nitrogen contents determined. The remaining two pieces of fabric was treated for the third time by the same procedure. Three sorption filtrates and three acid recovery filtrates were thus obtained and their metal contents were compared.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cotton-Fabric-Based Sorbent

A cellulose-based iminodiacetate sorbent (CIDA sorbent) derived from cotton fabric was synthesized, using the following two step reaction sequence (Scheme 1):
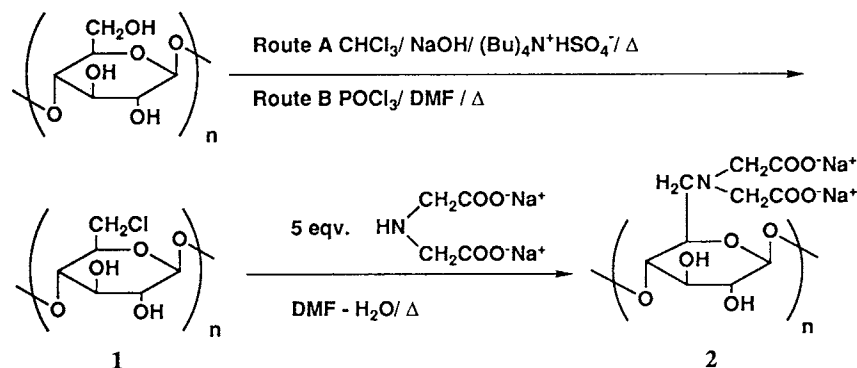
Scheme 1 Synthetic scheme for the synthesis of CIDA sorbent

Due to its intrinsic strength and availability at low cost, cotton fabric provides an ideal backbone as a cellulose-based matrix for chemical functionalization. Since the chelating characteristics of the iminodiacetate group have been well documented,[8] facile transformation of cellulose hydroxyl groups into iminodiacetate groups was the primary goal of this study. To establish the efficiency of each step in the synthesis, the intermediate cellulose chloride (1) and the chelating sorbent (2) were characterized by chlorine and nitrogen content determination, respectively. Two different approaches were employed to synthesize cellulose chloride (1). By systematic variation of the parameters of the two reactions, optimum conditions for the synthesis of cellulose chloride were found. The preparation of 1 by the phosphoryl chloride route (route B) appeared to be the method of choice, and a product containing more than 10% chlorine, corresponding to a 0.4926 degree

of substitution, could be obtained. This route was very much superior to route A, which gave a product containing less than 4% chlorine. Although prolonged heating in route B could produce a product with still greater chlorine content, the texture of the fabric deteriorated. It was concluded that 0.5 h refluxing may be the desired reaction time, since half of the primary hydroxyl groups of cellulose are converted to chloride. Subsequent introduction of the chelating iminodiacetate group into the cellulose backbone produces the sorbent. After varying the amount of sodium iminodiacetate, composition of the solvent and the reaction time, we were able to prepare 2 smoothly by refluxing 1 with five equivalents of sodium iminodiacetate in a 5:12 water/ DMF mixture for 8 h. Based on chlorine and nitrogen analyse, the efficiency of each step in the synthesis of the chelating sorbent 2 is summarized in Table I.

Table I Optimization of the Synthesis of Cellulose Chloride 1 and CIDA Sorbent 2

| Substrate | Optimum Conditions | mg Heteroatom/g of the Product | | Degree of Substitution | Product of the Reaction |
		Cl	N		
Cotton-fabric-based cellulose	Method A 10% PTC[a]/50% NaOH/ reflux 3 h	34.0	—	0.1580	Cellulose chloride 1
	Method B 2 ml POCl$_3$/20 ml DMF/ reflux 30 min	102.2	—	0.4926	Cellulose chloride 1
Cellulose chloride 1 (from method B)	5 eq IDA[b]/DMF–H$_2$O/ 100°C for 8 h	—	30.3	0.4667	CIDA sorbent 2

[a] Tetrabutylammonium hydrogen sulfate was used as the PTC in method A.
[b] IDA = sodium iminodiacetate.
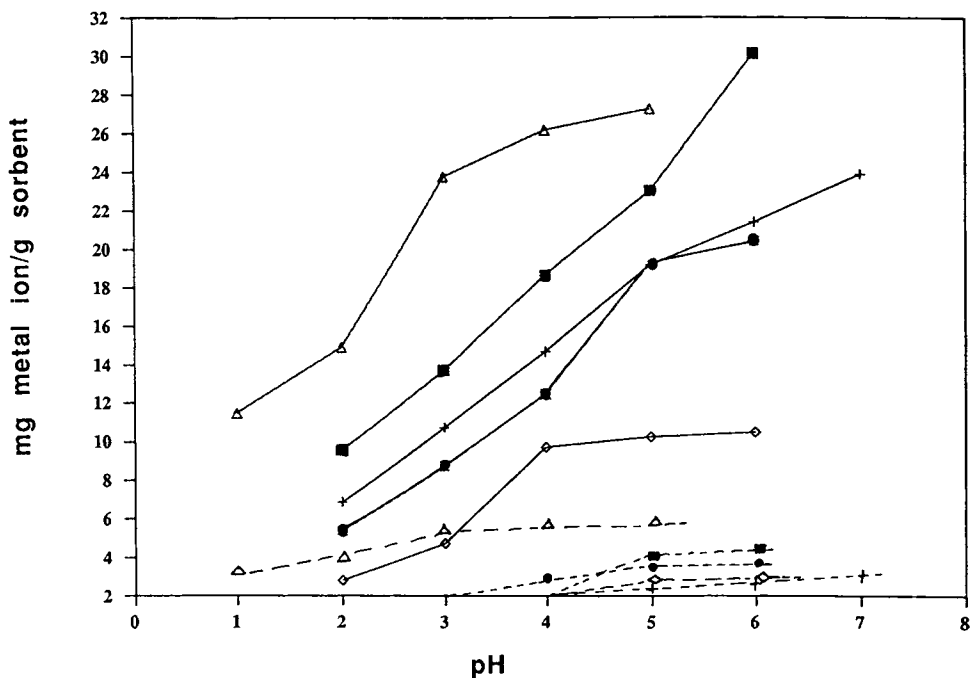
Figure 1   Metal ion uptake as a function of pH: (– – –) blank; (———) CIDA sorbent: (■)
50 ppm Cd(II); (+) 50 ppm Co(II); (◇) 20 ppm Cu(II); (△) 50 ppm Pb(II); (●) 50 ppm
Ni(II) solution.
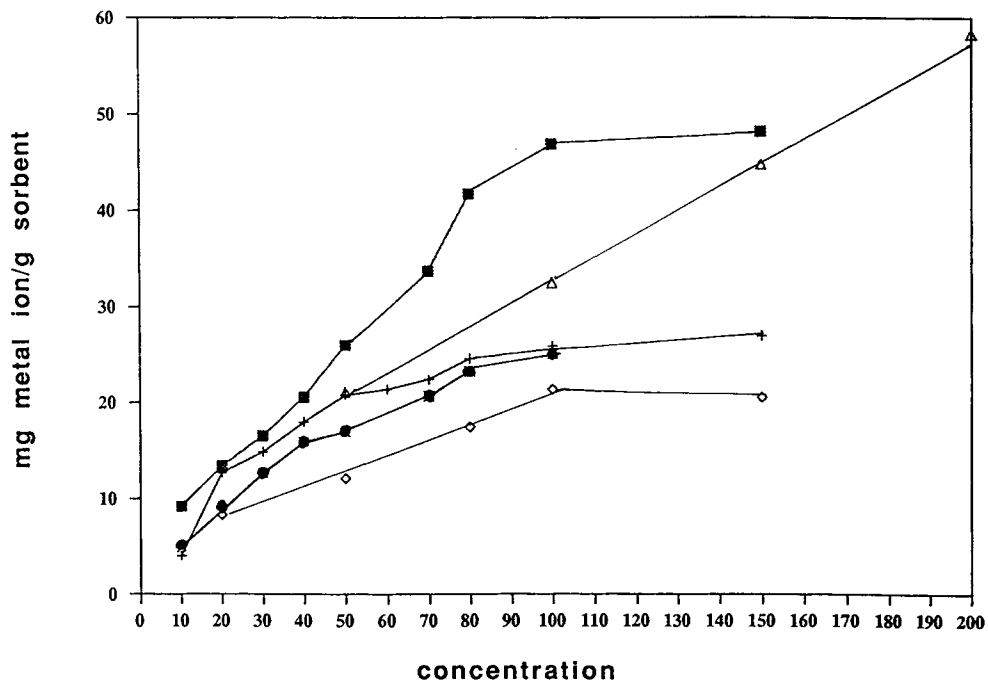
Figure 2   Metal ion uptake (corrected for the physical sorption by the blank) as a function
of metal ion concentration: (■) Cd(II); (+) Co(II); (◇) Cu(II); (△) Pb(II); (●) Ni(II)
solution.

Table II Sorption Capacity of CIDA Sorbent towards Various Metal Ions

Metal Ion	pH	Chemical Sorption		Total Capacity[d] Metal Ion[a] (mg)
		Metal Ion[a] (mg)	Metal Ion[a] (mmol)	
Cd(II)	6	47	0.42	59[b]
Co(II)	7	26	0.44	35[b]
Cu(II)	5	22	0.35	27[b]
Pb(II)	5	58	0.28	70[c]
Ni(II)	6	25	0.43	32[b]

[a] Per gram of sorbent.
[b] Equilibrated with 100 ppm metal ion solution.
[c] Equilibrated with 200 ppm metal ion solution.
[d] Represents the total sorption before subtraction of the blank.

Metal Ion Uptake as a Function of pH

To differentiate physical adsorption from chemical sorption, the metal ion uptake of unmodified cotton fabric was first determined and was taken as the blank of reference. Metal ion sorption in excess of that of the blank can be attributed to the chemical sorption by the sorbent. The availability of chelating carboxylates group for metal ion complexation is pH dependent. The sorption characteristics of the sorbent towards five metal ions (i.e., Cd, Co, Cu, Pb, and Ni) were investigated in an aqueous solution over pH range 2–7, using a batch equilibrium tech-nique. The sorption affinity of the sorbent, together with the adsorption by the blank is plotted as a function of pH (Fig. 1). The extent of physical adsorption towards different metal ions is similar and appears to be unimportant as compared with the total sorption. In general, the amount of metal ion uptake by the sorbent increases significantly as the pH increases. To prevent the formation of metal hydroxide, the optimum operational pH for Cu(II), Pb(II), Ni(II), Cd(II), and Co(II) ion sorption was chosen at 5, 5, 6, 6, and 7, respectively, for subsequent investigations. At the optimum pH, less than 25% of total metal ions sorption is due to physical adsorption by the fabric. In other words, the introduction of the chelating group into cotton fabric gives a four- to fivefold enhancement of metal ion uptake.

Sorption Capacity

To explore the applications of the sorbent, it was informative to obtain knowledge on the sorption capacity of the sorbent towards different metal ions. Studies on the sorption capacity of the sorbent towards various metal ions were carried out by equilibrating a fixed amount of the sorbent with a series of metal ion solutions of gradually increasing concentration. A maximum amount of metal ion can be removed from the solution when the chelating sites of the sorbent are saturated. As depicted in Figure

Table III Sorption and Desorption Characterstics of CIDA Sorbent by the Column Method

Sorption (Eluate: 200 ppm Pb(II) Ion Solution)			Desorption (Eluate: 3M Nitric Acid)		
Fraction (20 mL each)	Mass of Pb(II) Adsorbed (mg)		Fraction (10 mL each)	Mass of Pb(II) Released (mg)	
	4 mL/min[a]	8 mL/min[a]		4 mL/min[a]	8 mL/min[a]
1	3.74	2.67	1	9.40	8.20
2	3.21	2.38	2	1.72	1.42
3	2.65	1.92	3	0.07	0.32
4	1.98	1.64	4	0.00	0.17
5	1.22	1.32	5	0.00	0.09
6	0.59	0.98			
7	0.39	0.74	Total recovery	11.19	10.20
8	0.21	0.61	% recovery	78.6	77.2
9	0.16	0.52			
10	0.09	0.41			
Total sorp.	14.24	13.19			
Max. exp. sorption	17.28[b]	18.01[b]			

[a] Rate of elution.
[b] Sorption capacity defined by the batch equilibrium method × mass of the sorbent used.
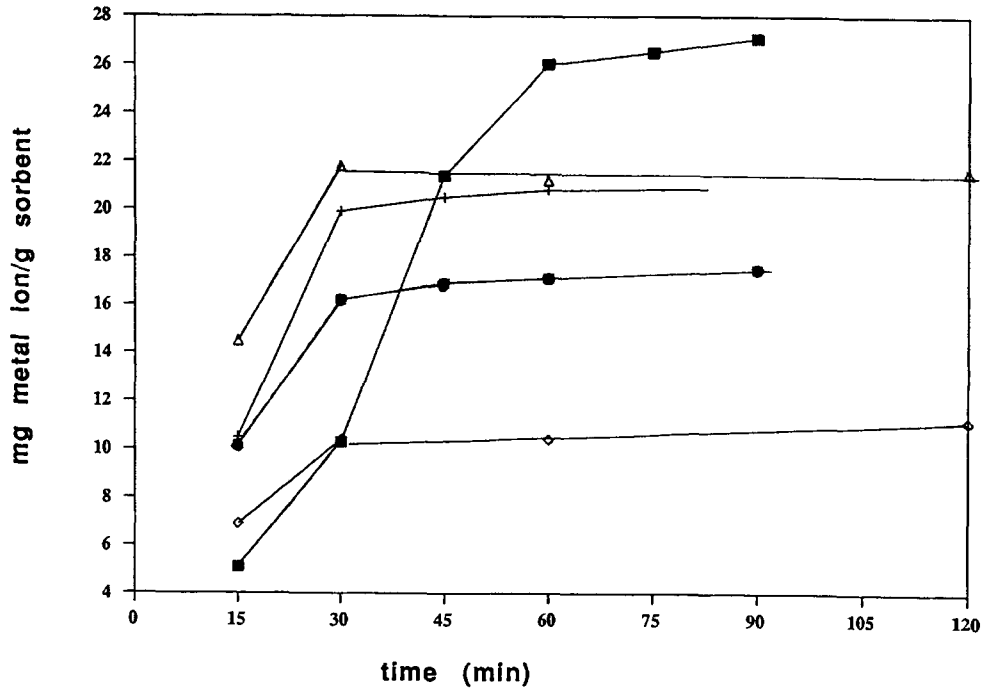
Figure 3   Kinetic characteristics of the sorbent towards various metal ions in chemical sorption: (■) 50 ppm Cd(II); (+) 50 ppm Co(II); (◇) 20 ppm Cu(II); (△) 50 ppm Pb(II); (●) 50 ppm Ni(II) solution.
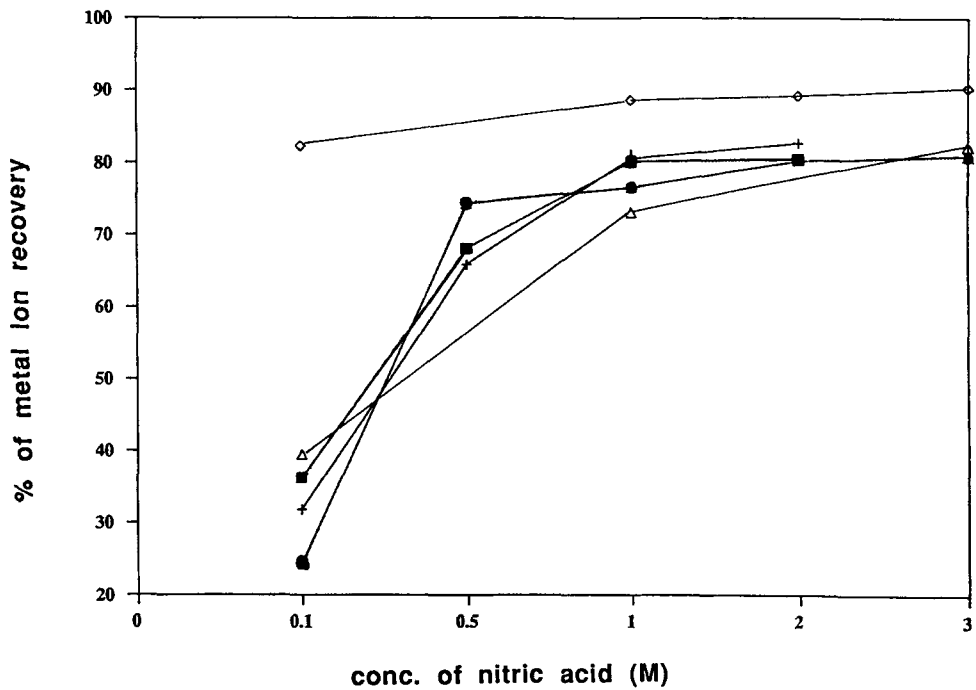
Figure 4   Removal of metal ion by various concentrations of nitric acid treatment: (■) Cd(II); (+) Co(II); (◇) Cu(II); (△) Pb(II); (●) Ni(II); the elution volume of the acid is 20 mL.

Table IV   Preconcentration Recovery of Pb(II) by 3M Nitric Acid Elution

	Before Preconcentration		After Preconcentration	
Original concn (ppm)	0.2	2	0.2	2
Volume (mL)	1000	1000	5	5
Concn found (ppm)	0.2	2	15.2	253
Total mass of Pb (mg)	0.2	2	0.076	1.42
% recovery	—	—	38	71
Preconcn factor	—	—	76[a]	127[a]

[a] Preconcentration factor = (concn found)/(original concn).

2, the chemisorption capacities (i.e., after correction for the physical sorption by the blank) of the sorbent towards Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) were found to be different. However, when the chemical sorption capacities of the sorbent towards various kinds of metal ion were expressed in mmol/g dry sorbent, most of them appear close enough to be a constant (column 4 of Table II). According to the nitrogen content of the modified cotton fabric, each gram of the sorbent on the average contains 2.16 mmol of the imimodiacetate group. The studies thus reveal that about 20% of the available chelating groups are utilized for metal ion chelation.

Sorption Characteristics of the Sorbent in Dynamic Mode

For real world application of the sorbent, such as preconcentration in an analytical manipulation or recycling of metal ions from an industrial process, the batch equilibrium technique is inapplicable. Hence we turned our attention to the sorption characteristics of the sorbent in a dynamic mode via a column method. To evaluate the performance of the sorbent, Pb(II) ion solutions were eluted through a column of the sorbent at a controled elution rate. The metal ions remaining in the eluent, and thus the amount of metal ions absorbed, could be used as the indicator of the efficiency of metal ion removal by the column. It was demonstrated by Table III that the column could absorb lead ion very well at the beginning of the elution, but the efficiency gradually decreased as chelating sites became relatively unavailable. A slower elution rate might improve absorption of metal ions. The total lead ion absorbed by the column method compared favorably with the batch equilibrium method. With respect to metal desorption experiments, about 80% of the metal ion absorbed can be removed simply by elution with 3M

nitric acid. Because the majority of the metal ion absorbed was released in the first one or two 10-mL elution fractions (within two bed volume), metal desorption results in Table III also demonstrate that the column method is a viable way to concentrate metal ion solutions.

Kinetic Characteristics of the Sorbent

Cellulosic sorbents, because of the hydrophilicity of the hydroxyl groups, should exhibit outstanding kinetic properties in removing metal ions from aqueous solution. As shown in Figure 3, over 90% of the sorption capacity of the sorbent for most of the metal ions studied was utilized within the first 0.5 h. This observation demonstrates the viability of using the sorbent in water treatment.

Table V   Selective Extraction of CIDA Sorbent towards a Mixture of Ni(II)–Co(II)

Fraction[a,b]	Metal Adsorbed (mg)		Selectivity Ratio Ni/Co
	Ni(II)	Co(II)	
1	0.904	0.775	1.17
2	0.775	0.453	1.70
3	0.774	0.370	2.09
4	0.759	0.335	2.27
5	0.758	0.280	2.71
6	0.756	0.265	2.85
7	0.745	0.258	2.89
8	0.738	0.240	3.08
9	0.728	0.225	3.24
Total	8.937	3.201	

[a] 20 mL of eluate was collected in each fraction.
[b] Total 200 mL of metal ions solution, consisted of 50 ppm each of Ni(II) and Co(II) ion, was used.

Table VI Reusability of CIDA Sorbent

Trial	Sorption[a] (mg) Metal Ion/g Sorbent	Desorption[b] % of Metal Ion Recovery	State of Sorbent	
			% Material Loss	N Content Wt. %
1	26.22	80.90	20.30[c]	3.06
2	25.37	78.60	3.05	2.89
3	23.88	71.15	0.81	2.71

[a] Batch equibrated with 100 mL of 100 ppm Ni(II) solution.
[b] Desorbed by 50 mL of 1M nitric acid.
[c] It was observed that upon vigorous stirring some fibers of the cellulosic sorbent was torn off in the first metal adsorption experiment.

Recovery of Metal Ions from the Sorbent

To be useful in metal ion recycling processes, metal ions absorbed by the sorbent should be easily released under appropriate conditions. Since the sorbent contains carboxylate as the chelating group, metal ions absorbed can be liberated by washing with concentrated acid. After some experimentation, nitric acid, in contrast to acetic acid and sulfuric acid, emerged as the most effective one for recovery of metal ions from the sorbent. In fact, for all metal ions studied, over 80% of the chelated metal ions could be released by treatment with 3M nitric acid for a short period of time (Fig. 4). Moreover, the sorbent is able to withstand the strong acidic conditions, and its chelating properties are retained after repeated acid treatment (vide infra).

Preconcentration of Metal Ion Solution

The obvious analytical application of the chelating sorbent was preconcentration of trace metal ions. Diluted Pb(II) ion solutions were first absorbed on the sorbent via the column method. Then a small amount of 3 M nitric acid was eluted through the column to remove the metal ion. For 200 ppb lead (II) ion solution, over a 76-fold preconcentration factor can be achieved, with 38% metal ion recovery. Even a higher preconcentration factor and greater metal ion recovery can be accomplished for 2 ppm lead (II) ion solution (Table IV).

Selective Extraction of Metal Ion Solution

The chelating sorbent should demonstrate some selectivity towards different metal ions. Since nickel and cobalt ions have different stability constants in complexing with EDTA (i.e., 3.98×10^{18} vs 1.99×10^{16} for Ni and Co, respectively),[13] it was hoped that in the presence of cobalt, nickel ion could be selectively extracted by the sorbent. When the concentration of chelating sites is much higher than that of the metal ions, the preference of the sorbent for nickel ion over cobalt ion is not manifested. However, under competitive conditions, a selectivity factor of over 3 could be observed in the preferential extraction of nickel over cobalt ion by the sorbent (Table V). It is expected that a greater selectivity factor could be achieved for metal ions which have a larger difference in their stability constant with EDTA.

Stability of the Sorbent

To be a viable material used in laboratory or industry, the sorbent must be chemically stable and have a reasonably long working lifetime. We were gratified to find that the synthesized sorbent could be stored for at least 2 months without any special precaution and yet remain stable and active, as indicated by the constancy of the nitrogen content of the sorbent and its metal ion extraction ability. In addition, upon repeated sorption and desorption experiments, the sorbent compared favorably with a freshly prepared one in metal ion sorption (Table VI).

From the results mentioned above, it is evident that CIDA sorbent is of practical value in analytical and environmental applications. Scale-up of the preparation of the sorbent for treatment of real industrial wastewater from local industry is now being active pursued.

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