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Adsorption Behavior of Iminodiacetic Acid Type of Chelating Gel Prepared from Waste Paper

Chaitanya Raj Adhikari, Durga Parajuli, Hidetaka Kawakita, Katsutoshi Inoue, Keisuke Ohto, and Daigo Fujiwara
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Abstract: Adsorption gel was prepared from waste recycled paper by immobilizing iminodiacetic acid (IDA) functional group by chemical modification. The gel exhibited good adsorption behavior for a number of metal ions viz. Cu(II), Pb(II), Fe(III), Ni(II), Cd(II), and Co(II) at acidic pH. The order of selectivity was found to be as follows: Cu(II) > Pb(II) > Fe(III) > Ni(II) ~ Cd(II) ~ Co(II). From the adsorption isotherms, the maximum adsorption capacity of the gel for both Cu(II) and Pb(II) was found to be 0.47 mol/kg whereas that for Cd(II) was 0.24 mol/kg. A continuous flow experiment for Cd(II) showed that the gel can be useful for pre-concentration and complete removal of Cd(II) from aqueous solution.

Keywords: Recycled paper, adsorption, metal ions, chelating gel, pre-concentration

INTRODUCTION

For a sustainable society in the near future, we should gradually reduce our dependence on the limited stock of fossil fuel resources and explore new alternatives based on the renewable biomass resources. That is, various biomass wastes generated in huge amounts in diverse fields like agriculture, forestry, and fishery at present should be much more effectively and largely utilized not only for biomass energy, composts and so on but also as feed

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materials for various advanced functional materials making use of their own original and excellent characteristics (1).

The major proportion of biomass waste consists of polysaccharides such as cellulose and, therefore, it is the most abundant natural resource in the world which is produced by plants through photosynthesis process (2). Commercial cellulose supplies an annual world consumption of about 150 million tonnes of fibrous raw materials. The greatest portion of this amount, derived mostly from pulped wood, is used for the production of paper (3).

Waste recycled paper is one of the various cellulosic biomass wastes generated in voluminous amount in various fields. It is an important fact that recycled paper cannot be recycled and reused for infinite times in the form of paper since its fibers are shortened at each stage of recycling and after a few cycles, falling short of the required fiber length, it becomes a waste. Consequently, it is necessary to find alternative applications for recycled paper not only to reduce the amount of waste and cut down the expenses of waste treatment but also, and more importantly, to prepare valuable materials by the effective use of its original good characteristics which have not been utilized yet.

In the present work, we have attempted to use the recycled paper as feed material for preparing adsorption gels for metal ions. To date, only little work has been reported on the adsorption of metal ions by waste recycled paper though a wide range of sorbents based on chemically modified cellulose have been developed for the concentration and selective separation of metal ions (4–11). Most of these adsorption gels are prepared by chemical modification of pure cellulose. Since waste paper, waste newspaper in particular, contains a high amount of lignin, the chemically modified waste paper has a possibility to exhibit different adsorption behavior from the gels prepared from pure cellulose. It is also noteworthy here that since the major component of recycled paper is wood cellulose, typical amorphous cellulose, its chemical modification, is easier in comparison to the other forms of cellulose composed mostly of crystalline parts. Although recycled paper itself has no ability to adsorb metal ions, it can be immobilized with a variety of functional groups by simple chemical modification to develop adsorption gels having high selectivity or high affinity to specific metal ions. Hence, in the present work, crushed recycled paper has been immobilized with the functional group of iminodiacetic acid, a typical chelating group, and tested for the adsorption of various heavy and base metals.

EXPERIMENTAL

Chemicals

The feed material of the gel was fiber material like cotton which was prepared by crushing waste newspaper by using the Dalton model P-3S power mill.

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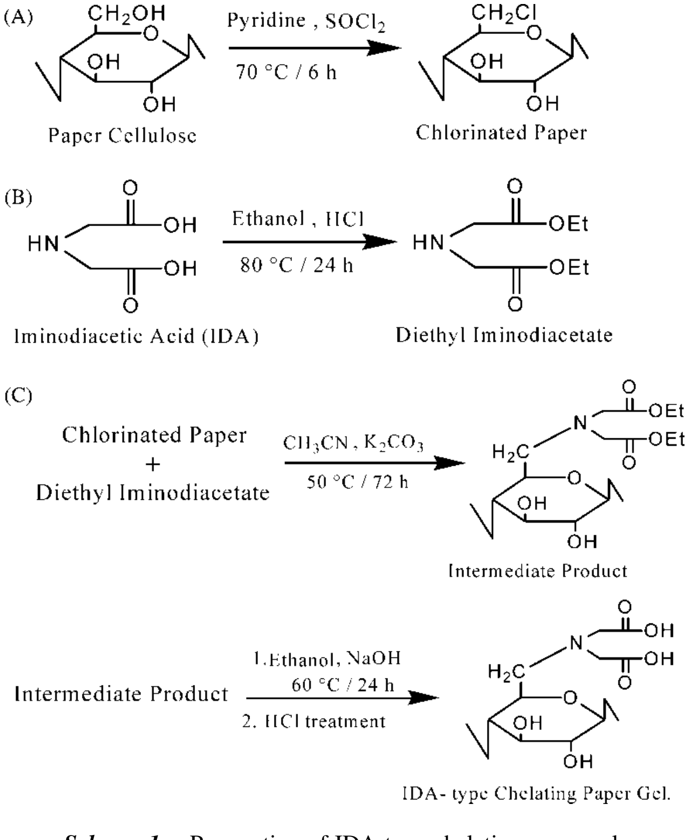
Analytical grade iminodiacetic acid was purchased from Dojindo, Japan and thionyl chloride from Sigma Aldrich, USA. All other chemicals used for the synthesis and for the adsorption tests were of analytical grade and were used without further purification.

Preparation of the Adsorption Gel

The required amount of crushed waste recycled paper was washed with soap and water many times to remove grease particles and treated with 20% sodium hydroxide solution for 5 h. It was washed again with water to remove excess NaOH till neutral pH. It was then dried in a convection oven at 50°C for 24 h. Thus pre-treated recycled paper was chemically modified with the iminodiacetic acid (IDA) group according to the reaction schemes shown in Scheme 1.



Scheme 1. Preparation of IDA-type chelating paper gel.

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At first, 0.5 g of the pretreated paper was chlorinated by mixing together with 25 mL of pyridine in ice bath to which 5 mL of thionyl chloride was added drop wise and the mixture was heated at 70°C for 6 h under N_2-atmosphere. The product obtained (0.5 g) was washed and dried overnight at 70°C in a convection oven. Diethyl iminodiacetate was prepared as follows. 400 mL of ethanol saturated with hydrochloric acid gas was prepared and mixed together with 20 g of IDA followed by heating at 80°C for 24 h. The product obtained (28 g) was neutralized with sodium bicarbonate and washed by chloroform.

Finally, 0.5 g chlorinated paper and 1.14 g of diethyl iminodiacetate were mixed together with 50 mL acetonitrile and 1.4 g potassium carbonate and stirred at 50°C for 72 h. The product obtained was filtered and washed with water. It was again dissolved in a mixture of 50 mL ethanol and 10 mL of 1 mol L^{-1} sodium hydroxide and stirred for 1 day at 60°C. The pH of the solution was adjusted to 2–3 for giving rise to precipitate. The precipitate was filtered and washed with 0.1 mol L^{-1} hydrochloric acid followed by distilled water and dried at 60°C in a convection oven to obtain 0.35 g chelating recycled paper gel.

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Characterization of the Adsorbent Gel

The quantity of the iminodiacetate group immobilized on the cellulose surface was determined by nitrogen elemental analysis. JASCO model 410 Fourier transform infrared (FTIR) spectrometer was also used to record the IR spectra of the gel.

Adsorption Tests

Metal Ion Uptake as a Function of pH

Batch wise adsorption tests were carried out to observe the pH dependence of the adsorption of various metal ions on the IDA–type chelating recycled paper gel. Test solutions containing 0.2 mmol L^{-1} of individual metal ions such as Cu(II), Fe(III), Cd(II), Co(II), and Ni(II) at pH 1–5 were prepared by dissolving corresponding analytical grade individual metal chlorides in 0.1 mol L^{-1} hydrochloric acid solution and in 0.1 mol L^{-1} HEPES (N-[2-Hydroxyethyl] piperazine-N′-[2-ethanesulfonic acid]) solution, a buffer reagent, followed by mixing these two solutions at an arbitrary volume ratio to adjust pH while dilute sodium hydroxide solution was used to prepare higher pH solution. In case of Pb(II), an analytical grade Pb(II) nitrate was used to prepare the test solution. 20 mg of the adsorbent was added to 20 mL of the above mentioned metal solutions at different pH. The pH of the test solution was measured by using a BECKMAN model ϕ-45 pH meter. The mixtures were shaken for 24 h in a thermostated shaker maintained at 30°C. The mixtures were filtered and the filtrate was taken as the sample solution for the metal ion concentration analysis. The concentrations of the corresponding metal ions before and after the adsorption were measured by using Shimadzu model AA-6650 atomic absorption spectrophotometer (AAS).

Adsorption Isotherm Test

Different concentration (0.2–2 mmol L^{-1}) of Cu(II), Pb(II), and Cd(II) individual ion solutions were prepared at pH 5, the optimum pH for the adsorption of metal ions. 15 mL of each of these solutions were shaken together with 20 mg of the adsorbent for 24 h in a thermostated shaker maintained at 30°C to attain equilibrium. The mixtures were filtered and the concentrations of metal ions were analyzed by AAS as mentioned above.

Breakthrough Followed by Elution Tests

About 0.1 g of the dry IDA-paper gel was weighed accurately and packed in a glass column (8 mm diameter, packing height 5.8 mm) and conditioned overnight to pH 5 by washing with water of pH 5 adjusted by 0.1 mol L^{-1} HEPES solution. A feed solution was prepared by mixing two solutions of 0.1 mol L^{-1} hydrochloric acid and 0.1 mol L^{-1} HEPES containing 2 mmol L^{-1} Cd(II) to adjust the pH to 5, which was fed to the column at 5.0 mL/h by using an Iwaki model PST-100 N peristaltic pump. The sample solutions from the outlet were collected using a Bio-Rad model 2110 fraction collector at time intervals of 1 h. After a complete breakthrough, the column was washed with distilled water to wash out all unadsorbed Cd(II). Then, an elution test was carried out using 1 mol L^{-1} hydrochloric acid fed at the same flow rate. The eluted solution was collected in a similar way at time intervals of 0.5 h. All the fractions collected were analyzed by using AAS.

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RESULTS AND DISCUSSION

Characterization of the Gel

IR Spectra

Figure 1 shows the IR spectra of various forms of recycled paper. As a result of chlorination, a sharp peak appeared at around 620 cm^{-1} in the spectra of chlorinated paper but it disappeared noticeably in the spectrum of IDA paper. Similarly, an intense but narrower peak corresponding to C=O stretch at 1600–1700 cm^{-1} region indicates the introduction of carboxyl group of IDA. Similarly, transformations along 3300–3600 cm^{-1} region from pretreated paper via chlorinated paper to IDA-type paper gel suggest the changes in hydroxyl groups and introduction of amine functionality onto the cellulose matrix.

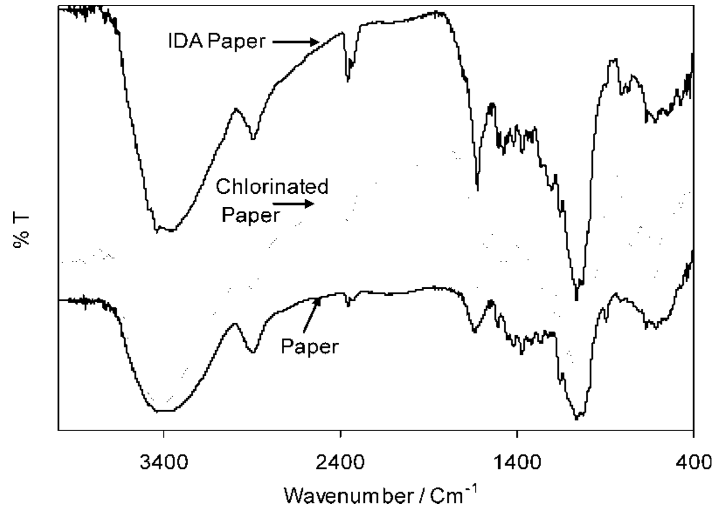

Figure 1. IR spectra of different forms of recycled paper.

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Elemental Analysis

The results of the elemental analysis are shown in Table 1. The chemical analysis of nitrogen in the IDA-type chelating adsorption gel shows that 2.17 mol/kg of the functional groups have been immobilized on the cellulose surface. Hence the degree of the immobilization of IDA groups or the extent of the conversion of hydroxyl groups at the 6th position of the cellulose unit was evaluated as 60%.

Effect of pH on the Adsorption Behavior of IDA-type Recycled Paper Gel

Figure 2(a) shows the results of the batch wise adsorption test of IDA-type recycled paper gel for various metal ions wherein the % adsorption of metal

Table 1. Elemental analysis of different forms of the recycled paper

Composition paper type	C (%) (observed/calculated)	H (%) (observed/calculated)	N (%) (observed/calculated)
Pretreated paper	46.29/44.40	5.70/6.17	—
Chlorinated paper	35.62/39.88	3.55/4.98	—
IDA-type paper	45.59/43.32	4.72/5.41	3.04/5.05

ions are plotted against equilibrium pH. The % adsorption of the metal ion onto the gel was calculated from the following equation:

$$\%\text{Adsorption} = \frac{(C_i - C_e)}{C_i} \times 100$$

where, C_i represents the initial concentration of the metal ion in the test solution and C_e represents the equilibrium concentration after adsorption.

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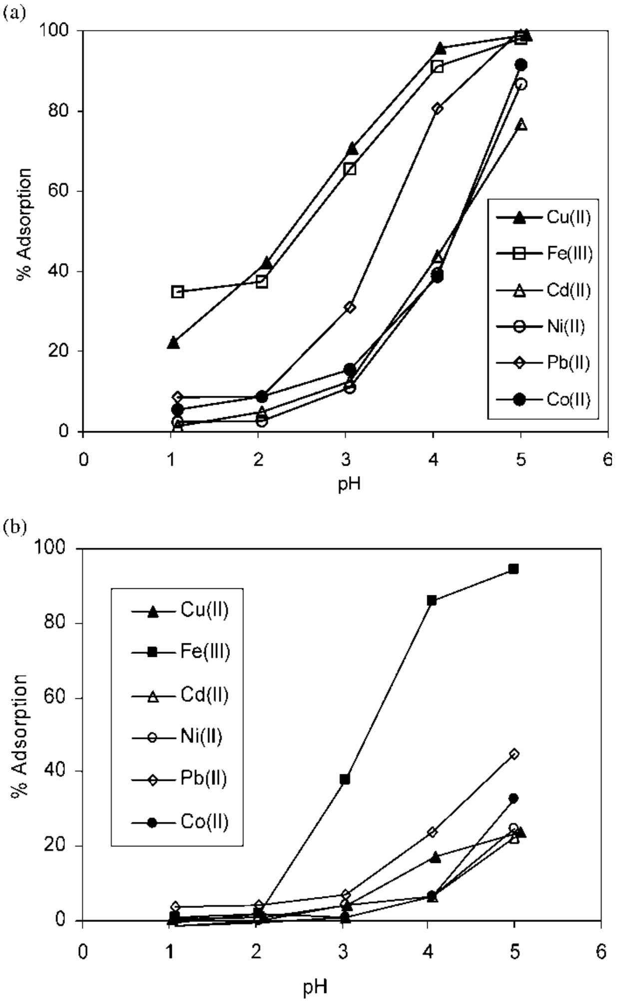

Figure 2. Variation of % adsorption of metal ions on (a) IDA-type chelating paper gel and (b) on original paper as a function of pH. Initial metal concentration = 0.2 mmol L^{-1}. Weight of gel = 20 mg. Shaking time = 24 h. Temperature = 30°C.

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From the figure, it can be observed that the percentage adsorption of metal ions on the chelating gel increases with increasing pH in acidic pH range which is a characteristic feature of cation exchange mechanism. The gel shows better adsorption for Cu(II) even at low pH. The % adsorption of Fe(III) is comparable to that of Cu(II). Pb(II) was effectively adsorbed at pH greater than 3. Adsorption behavior to Ni(II), Cd(II), and Co(II) were almost the same. The order of selectivity among the tested metal ions is as follows: Cu(II) > Fe(II) > Pb(II) > Co(II) ≈ Ni(II) ≈ Cd(II). The order of the stability constant (log K) of the corresponding metal-IDA chelates is: Cu(II), 10.63 > Fe(III), 10.42 > Ni(II), 8.19 > Pb(II), 7.45 > Co(II), 6.97 > Cd(II), 5.73 which is nearly the same with the selectivity order mentioned above except for Ni(II) (12).

Figure 2(b) shows the % adsorption of the metal ions on original recycled paper (i.e. before modification) under the same conditions as the IDA-type paper gel. It is clear from the figure that there is negligible adsorption of metal ions at pH lower than 3 except for Fe(III). Although the % adsorption increases gradually at pH greater than 3, it appears less impressive in comparison to the adsorption behavior of the IDA-type paper gel. However, in the case of Fe(III), precipitation of ferric hydroxide may have occurred at pH greater than 2 since stepwise hydrolysis of Fe^{3+} occurs at pH above 1 in the presence of complexing anions such as Cl^{-} (13).

Adsorption Isotherms

Figure 3(a) shows a plot of the adsorption isotherm for Cu(II), Cd(II), and Pb(II) on the IDA-type recycled paper gel i.e. the amount of adsorption against the equilibrium concentration of the metal ions at pH 5. From the figure, it appears that the adsorption of the metal ions took place according to the Langmuir type adsorption in which adsorption increases with increasing metal ion concentration at low concentration region while it tends to approach constant values corresponding to each metal ion at high concentration. From these constant values, the maximum adsorption capacities were evaluated as 0.47 mol/kg – dry gel for both Cu(II) and Pb(II) and 0.24 mol/kg – dry gel for Cd(II).

Figure 3(b) shows the linear plot of the adsorption data according to the Langmuir model equation which is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} \times C_e + \frac{1}{Q_{max} \times b}$$

where, C_e– equilibrium concentration of metal ion (mol L^{-1}); Q_e– amount of metal ion adsorbed per unit weight of the adsorbent (mol/kg); Q_{max}– maximum amount of metal ion adsorbed by the gel (mol/kg); b – langmuir constant.

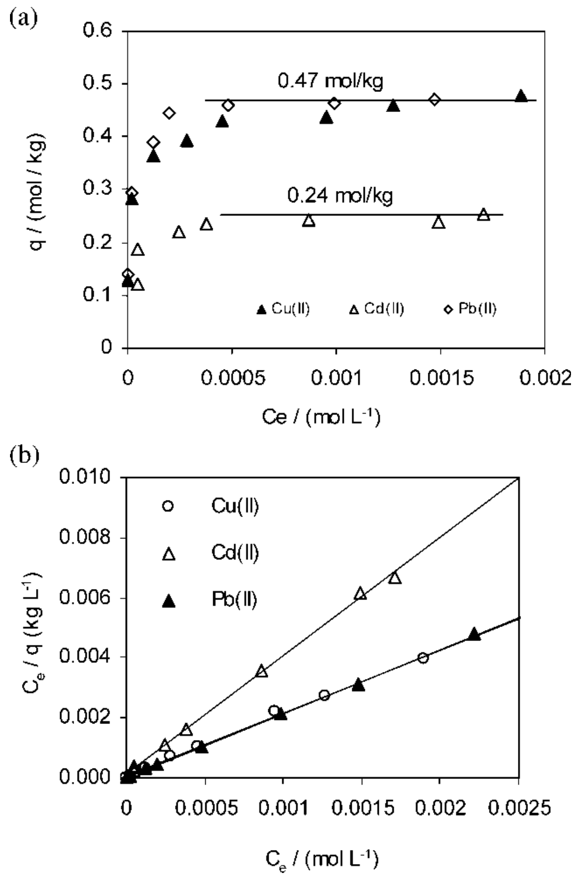

Figure 3. (a) Adsorption isotherm of some metal ions on IDA-type chelating paper gel at pH 5. Weight of gel = 20 mg. Shaking time = 24 h. Temperature = 30°C. (b) Langmuir plot.

Table 2 shows a comparison of the adsorption capacity of the present gel with those exhibited by some IDA immobilized cellulose based adsorbents prepared from cotton fiber, wood powder, or commercially available ordinary cellulose filter as starting material. Although direct comparison is difficult in some cases because of the different experimental conditions like pH and method of application, it is apparent from the table that the IDA-type recycled paper gel exhibits higher capacity than other types of gels.

Figure 4(a) shows the breakthrough profile of Cd(II) using a column packed with the IDA-type recycled paper gel under the conditions described in the figure legend. From the figure, it is clear that breakthrough occurred after 10 h (1500 bed volume). A total of 150 mL solution was passed to the column for complete saturation of the gel. Considering the amount of the gel

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Table 2. Comparison of the adsorption capacity of the present gel with some cellulose based gels

	Amount of metal adsorbed in g/kg of gel (equilibrium pH)			
Starting material	Cu(II)	Pb(II)	Cd (II)	References
Recycled paper gel	29 (5)	97.3 (5)	27 (5)	Present gel
Cotton fiber	27 (5)	70 (5)	47 (6)	(4)
Wood powder	20.5 (4)	45 (4)	–	(5)
Ordinary cellulose filter disc	12.83 (3)	45.17 (5)	19.2 (3)	(6)

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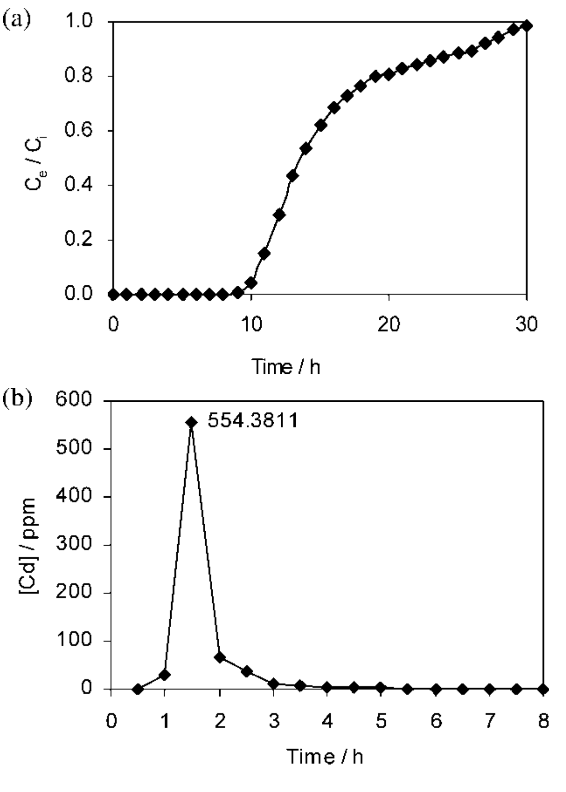

Figure 4. (a) Breakthrough and (b) elution profile of Cd(II) from the column packed with IDA-type chelating paper gel · [Cd] = 0.2 mmol L^{-1}. pH = 5. Weight of gel = 0.1 g. Eluent = 1 mol L^{-1} HCl. Feed rate = 5.00 ml/h.

packed in the column, the adsorption capacity of the gel (0.16 mol/kg) for Cd(II) looks quite reasonable in comparison to the adsorption capacity obtained from batch wise tests (0.24 mol/kg) because the column experiment differs from the batch wise adsorption test in some aspects i.e. less contact time between the metal ion and the gel and lack of agitation (by stirring). Figure 4(b) shows the elution profile of Cd(II) ions with 1 mol L^{-1} hydrochloric acid solution from the loaded column after complete saturation of the gel. It is clearly seen that Cd(II) is eluted at very high concentration, as high as 25 times compared to the feed concentration within the 2.5 mL fraction collected between 1–1.5 h. Also, nearly equal areas observed in both breakthrough and elution curves of Cd(II) indicated that almost complete recovery (~98%) of Cd(II) occurred within a small volume (15 mL) of the eluting solution. The high level of pre-concentration and the fast rate of elution can be very useful for the treatment of Cd(II) in industrial effluents.

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CONCLUSION

The IDA-type recycled paper gel prepared by immobilization of the IDA group onto waste paper exhibited good adsorption behavior for different base and heavy metals in a range of acidic pH. From the adsorption isotherms, the maximum adsorption capacity of the gel for both Cu(II) and Pb(II) was found to be 0.47 mol/kg whereas that for Cd(II) was 0.24 mol/kg. A continuous flow experiment carried out for Cd(II) showed that the gel can be useful for pre-concentration and complete removal of Cd(II) from aqueous solution. This presents a scope of the use of the gel for wastewater treatment and environmental remediation by removal of toxic heavy metal like cadmium.

REFERENCES

1. Parajuli, D., Inoue, K., Ohto, K., Oshima, T., Murota, A., Funaoka, M., and Makino, K. (2005) Adsorption of heavy metals on cross linked lignocatechol: a modified lignin gel. *React. Func. Polym.*, 62 (1): 129–139.
2. Klemm, D., Schmauder, H.-P., and Heinze, T. (2002) Cellulose. PP gel 375-319. In *Biopolymers—Polysaccharides II*; Vandamme, E.J., Baets, S.De, and Steinbuchel, A. (eds.); Wiley VCH: Weinheim.
3. Richardson, S. and Gorton, L. (2003) Characterisation of the substituent distribution in starch and cellulose derivatives. *Anal. Chim. Acta*, 497: 27–65.
4. Chan, W.H., Lam-leung, S.Y., Fong, W.S., and Kwan, F.W. (1992) Synthesis and characterization of iminodiacetic acid cellulose sorbent and its application in metal ion extraction. *J. Appl. Polym. Sci.*, 46 (5): 921–930.
5. Chan, W.H., Lam-leung, S.Y., Cheng, K.W., and Yip, Y.C. (1992) Synthesis and characterization of iminodiacetic acid cellulose sorbent and its analytical and environmental applications in metal ion extraction. *Anal. Lett.*, 25 (2): 305–320.

6. Gennaro, M.C., Baiocchi, C., Campi, E., Mentasti, E., and Aruga, R. (1983) Preparation and characterization of iminodiacetic acid—cellulose filters for concentration of trace metal cations. *Anal. Chim. Acta*, 151: 339–347.
7. Padilha, P.M., Rocha, J.C., Moreira, J.C., Campos, J.T.S., and Federici, C.C. (1997) Preconcentration of heavy metal ions from aqueous solutions by means of cellulose phosphate: an application in water analysis. *Talanta*, 45: 317–323.
8. Guclu, G., Gurdag, G., and Ozgumus, S. (2003) Competitive removal of heavy metal ions by cellulose graft copolymers. *J. Appl. Polym. Sci.*, 90: 2034–2039.
9. Gurnani, V., Singh, A.K., and Venkataramani, B. (2003) Cellulose based macromolecular chelator having pyrocatechol as an anchored ligand: synthesis and applications as metal extractant prior to determination by flame atomic adsorption spectrometry. *Talanta*, 61: 889–903.
10. Gurnani, V., Singh, A.K., and Venkataramani, B. (2003) Cellulose functionalized with 8-hydroxyquinoline: new method of synthesis and applications as a solid phase extractant in the determination of metal ions by flame atomic adsorption spectrometry. *Anal. Chim. Acta*, 485: 221–232.
11. Twu, Y.K., Huang, H.I., Chang, S.Y., and Wang, S.L. (2003) Preparation and sorption activity of chitosan/cellulose blend beads. *Carbohydr. Polym.*, 54: 425–430.
12. Cotton, F.A. and Wilkinson, G. (1988) *Advanced Inorganic Chemistry*, 5th Ed.; John Wiley and Sons: New York.
13. Hogfeldt, E. and Martell, A.E. (1971) *Stability Constants of Metal-Ion Complexes*; The Chemical Society: London, Supplement No. 1, Special Publication No. 25.

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