Solid phase extraction and estimation of cadmium using glycine immobilized cellulose chelating resin

Parul Singh*, S Mittal** & R K Sharma
Department of Chemistry, University of Delhi
Delhi 110 007, India

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A simple and rapid method of preconcentration and determination of cadmium by both batch and column techniques using glycine immobilized cellulose is presented. Cadmium ion is quantitatively retained on the column packed with immobilized cellulose in the pH range of 6.6-7.8. The distribution coefficient for cadmium is found to be $2.32 \times 10^2$ mL g$^{-1}$. The method is successfully applied to the determination of cadmium content in water and cigarette samples.

Keywords: Solid phase extraction, Chelating resin, Cellulose, Glycine, Preconcentration

IPC Codes: C22B17/00, A61K

Cadmium is a highly toxic element$^{1,2}$. It is considered as cumulative poison in mammals causing renal failure and hypertension. International Agency for Research on Cancer classified cadmium as a human carcinogen$^3$. It can also cause destabilization of genome$^4$. Cadmium enters in the environment through the wastewater of electroplating and battery industries using cadmium and from the discharge of the iron, steel, pigments and metal coating industries. Cadmium gets incorporated through food into liver and kidneys of slaughter animals hence enter in the human system. Even wild mushrooms are also particularly rich in this element. Cadmium absorption is especially effective via tobacco smoke, the cadmium content in the blood of smokers being much higher than that of non-smokers.

Due to its toxic effects, the separation and determination of cadmium is becoming increasingly important. Different procedures for the preconcentration and separation of cadmium have been proposed, such as coprecipitation$^5$, ion exchange$^6$, liquid-liquid extraction$^7$. These conventional methods are usually time-consuming, labor and cost intensive and use large amount of solvents, which creates environmental problems. An effective method for the preconcentration and separation of metal ions is solid phase extraction$^8-15$. The technique reduces solvent usage and exposures, disposal costs and extraction time$^{16}$. Furthermore, high preconcentration factor can be achieved by using solid phase extraction. A number of solid supports such as chelating resins$^{17}$, activated carbon$^{18,19}$, activated alumina$^{20}$, bagasse fly ash$^{21}$, red mud$^{22}$, polymeric supports$^{23,24}$ and C-bonded silica$^{25}$ have been used for the preconcentration and determination of cadmium. Among these, chelating resins have widely been used for the selective trace metal analysis in solid phase extraction$^{26,27}$ as they provide good stability, high concentrating ability, easy regeneration and high capacity for metal ions. Various materials such as amberlite XAD functionalized with 4-(2-pyridylazo) resorcinol$^{28}$, xylene orange$^{29}$, 1-(2-pyridylazo) 2-naphthol$^{30}$ and 2,2-dithiobisaniline$^{31}$, chromosorb$^{32}$, microcrystalline naphthalene functionalized with 1-benzyl-piperazinedithiocarbamate$^{33}$, chromosorb 108 as bathocuproinedisulphonic acid chelates$^{34}$, cellulose-sodium sulphide/thiourea mixture$^{35}$, aminocarboxylic acid cellulose filter paper$^{36}$ and oxycellulose$^{37}$ have been used as chelating solid supports for the preconcentration and determination of cadmium. Among these cellulose is superior to other solid supports as immobilization reaction on cellulose is relatively simple and it shows fast metal ion exchange kinetics. Glycine is an important chelating agent, it forms stable complexes with transition metal ions$^{38,39}$.

In view of the strong chelation behaviour of glycine and advantages of cellulose as solid support in the present study glycine is immobilized on cellulose and resulting glycine immobilized cellulose is used as a chelating resin for the preconcentration and separation of cadmium. The method is applied for the determination of cadmium content in water and cigarette samples.

*Present address: Optical Radiation Standards, National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi 110 012, India
**Present address: Department of Chemistry, Deen Dayal Upadhyaya College, Karampura, New Delhi 110 015, India
Experimental Procedure

Apparatus

The pH measurements were made on ECIL digital pH meter model 5651. For the estimation of cadmium ion ECIL 4136 atomic absorption spectrophotometer was used. A glass column of 100 mm length and 7 mm internal diameter has been used as a chromatographic column. Batch experiments were carried out at constant temperature (25°C) maintained by Julabo F-20 thermostat.

Reagents

All the chemicals used were of analytical regent grade and used without further purification. Double distilled water was used throughout the study. Microcrystalline cellulose, glycine, cadmium sulphate was procured from Aldrich. The stock solution of cadmium was prepared by dissolving an appropriate amount of CdSO$_4$.8H$_2$O in double distilled water. Working solutions were prepared by appropriate dilution of the stock solution. The pH was maintained with acetate buffers (prepared by mixing 0.2 M acetic acid and 0.2 M sodium acetate) in the pH range of 3.8-6.0. The pH below 3.8 was maintained by dil. HCl whilst pH above 6.0 was maintained by dil. NaOH solution.

Synthesis of immobilized cellulose

Glycine was immobilized on cellulose through ester linkage. It was performed in two steps

(i) Preparation of acid chloride of glycine

Ten grams of glycine were suspended in 30 mL of freshly distilled thionyl chloride in a round bottom flask. The mixture was refluxed on a water bath for 2 h. The unreacted thionyl chloride was distilled off and resulting solid was collected (Scheme 1).

(ii) Immobilization of glycine on cellulose

A mixture of glycinyl chloride (5 g), pyridine (50 mL) and cellulose (10 g) was refluxed for 4 h with constant stirring. The resulting solid, glycine immobilized cellulose was filtered and washed consecutively with pyridine, nitrobenzene and ethanol till the washings were colourless (Scheme 2).

The resin was dried and characterized by infrared spectroscopy. Two bands at 3272 and 2421 cm$^{-1}$ show the presence of free – NH$_2$ group. The band at 1650 cm$^{-1}$ is attributed to the ester linkage.

Method for preconcentration and determination of cadmium

Batch technique

Immobilized cellulose was stirred with 10 mL solution of cadmium ion maintained at required pH value (between 3.0-8.0) at 25°C in a constant temperature bath for 20 min. The supernatant solution was then separated and subjected to determination of cadmium by atomic absorption spectroscopy (AAS).

Column technique

In the column technique, dried sample of immobilized cellulose was packed in the glass column and cadmium ion solution at definite pH (between 3.0-3.8) was passed through this column at a flow rate of 2 mL min$^{-1}$. After the process is over, the adsorbed cadmium ion was eluted from the column with 10 mL of 0.1 N HCL and determined by AAS.

Effect of electrolytes and interfering cations

The effect of various electrolytes and commonly occurring cations such as Co(II), Ni(II), Mn(II), Fe(II), Fe(III), Na(I), K(I), Mg(II), Ca(II) on the sorption of cadmium by glycine immobilized cellulose was studied. A set of solutions containing 20 ppm of cadmium ion and varying amount of electrolytes and cations were prepared. After making the volume to 100 mL the solution was passed through the immobilized cellulose column and the cadmium ion was determined by recommended column technique.

Optimization of adsorption time

The time required for the solid-liquid system to attain the equilibrium condition was determined by batch technique. 10 mL solution of the cadmium ion (2 ppm) maintained at pH 7.5 was taken in various conical flasks and shaken with 0.05 g of cellulose.
The supernatant from each flask was separated off at different time intervals and the cadmium ion was determined by AAS. The time interval studied was between 3-40 min. The amount of cadmium ion adsorbed by the solid phase was determined using Eq. (1).

\[ N_f = \frac{(x - y)}{z} \]  

where \( x \) is the initial amount of the cadmium ion taken (in mmol L\(^{-1}\)), \( y \) is the amount of cadmium ion in supernatant (in mmol L\(^{-1}\)), \( z \) is the mass of immobilized cellulose (g) taken and \( N_f \) is amount of cadmium ion adsorbed per gram of modified cellulose (in mmol g\(^{-1}\)).

Results and Discussion

The effects of following parameters were investigated for optimizing the condition for preconcentration of cadmium (II) ion.

Adsorption study by column technique

Effect of pH

The sorption of metal ions on chelating resin is dependent on the pH of the sample solution due to competitive reaction between chelate forming groups and hydrogen ions in the solution. The effect of pH on the retention of Cd(II) ion on immobilized cellulose was studied by column technique. The pH of the solutions was varied from 3.0-8.0 using acetate-acetic acid buffer. It was observed that the adsorption of Cd(II) increases with pH. Below pH 5.0, the adsorption is very low since the functional groups were protonated. The maximum adsorption of cadmium occurred in the pH range of 6.6-7.8 with a recovery of 97.0%. Above pH 7.8 the adsorption decreases.

Effect of amount of immobilized cellulose

The amount of the resin is another important parameter for obtaining quantitative recovery. The percentage retention of Cd(II) ion on immobilized cellulose was determined by column method by using 25 mL (0.8 ppm) solution of Cd(II) ion with different amounts of immobilized cellulose (between 0.01-0.10 g). The results show that the percentage retention of cadmium on different amount of immobilized cellulose was found to be maximum and constant when 0.02 g of immobilized cellulose was employed. In subsequent studies, however for simplicity 0.05 g of modified cellulose was used.

Effect of flow rate

The effect of flow rate on the adsorption of Cd(II) ion was studied under optimum condition using solid phase extraction. The flow rate was varied from 0.5 to 5 mL min\(^{-1}\). Adsorption was quantitative and reproducible in the studied range. In order to avoid too high and too low flow rate the flow rate was maintained at 2 mL min\(^{-1}\) throughout the experiment.

Effect of electrolytes and interfering cations

The effect of various electrolytes, such as NaCl, NaF, NaNO\(_2\), NaNO\(_3\), Na\(_2\)SO\(_4\) and Na\(_3\)PO\(_4\) on the adsorption of cadmium on modified cellulose was investigated. It was found that all the electrolytes were tolerated in the concentration range 0.4-0.9 M except Na\(_3\)PO\(_4\) in which case the tolerance limit was found 0.02 M. It was found that in the sorption of 10 ppm of Cd(II), Co(II) 30 ppm, Ni(II) 20 ppm, Fe(III) 25 ppm and Mn(II) 35 ppm did not show any interference. Fe(II) did not show any affinity for resin used. The alkali and alkaline earth metal ions do not effect the recovery of cadmium ion up to 200 fold-excess, however, the recovery is not compatible above this concentration ratio.

Preconcentration and recovery of the metal ion

The column method was used for the preconcentration and recovery of cadmium ion. The concentration of the cadmium ion was taken 2 ppm and the recovery was found to be 1.93 ppm. The percentage recovery was found 96.5%, when the volume of the eluent was kept 10 mL. The experiment was carried out in triplicate.

Adsorption study by batch technique

Optimization of adsorption time

It was observed that the percentage of cadmium adsorbed increases up to 5 min and then remained constant up to 40 min. It shows that the time taken by the system to reach the equilibrium was 5 min.

Effect of temperature

The influence of temperature on the adsorption of Cd(II) ion, by immobilized cellulose was studied by batch technique. Solutions of the cadmium ion and immobilized cellulose were equilibrated at different temperatures (15-55°C). It was observed that adsorption of cadmium remained constant up to 35°C and decreased after that. The decrease in adsorption at higher temperature may be due to the possibility of desorption of metal ion from the resin sites.
**Adsorption isotherm**

The adsorption isotherm was obtained by batch technique at 25°C. Solutions of Cd(II) ion in the concentration range of $4.4 \times 10^{-5} - 5.3 \times 10^{-4}$ M (maintained at pH 7.5) were shaken for 45 min with 0.05 g of immobilized cellulose. The cadmium content in supernatant solution was determined by AAS technique after appropriate dilution. The amount of Cd(II) ion adsorbed was calculated with the help of Eq. (1). The average value of distribution coefficient, $D (N_f / C)$ calculated for cadmium has been found to be $2.32 \times 10^2$ mL/g (Fig. 1).

**Applications of the method**

**Determination of cadmium in water samples**

This study was carried out with glass column packed with immobilized cellulose. 100 ml of water was adjusted to pH 7.5 and passed through the column packed with immobilized cellulose. The adsorbed cadmium ion was eluted from the column with 10 mL of 0.1 N HCl and determined by AAS. The amount of cadmium in the eluent (10 mL 0.1 N HCl) is 0.14 ppm. The method is very precise as standard deviation is found to be 0.03 for three samples studied. The accuracy of the described preconcentration method was tested in the recovery studies by adding known amount (0.2 ppm) of the cadmium to the water samples. The results obtained from standard addition are depicted in Table 1.

**Determination of cadmium in cigarette sample**

The tobacco (1.5 g) of a cigarette was taken in 100 mL conical flask, and then 5 mL of concentrated HNO$_3$ was added to it. This solution was digested and evaporated to dryness. This process was repeated 3-4 times. The solution was filtered and transferred to a 100 mL calibrated flask. This solution was then adjusted to required pH and final volume made up to 100 mL. 10 mL aliquot of the solution was passed through the column packed with immobilized cellulose. The adsorbed cadmium ion was then eluted from the column with 10 mL of 0.1 N HCl and determined by AAS. The results of determination of cadmium in cigarette sample are given in Table 1. The standard deviation is found to be about 0.02 for the three samples studied. The described method is verified by adding known amount of cadmium (0.2 ppm) in the sample solution. The results given in Table 1 show that the percentage recovery of Cd(II) ion on standard addition is 96.8% with a standard deviation of 0.02. This indicates that present method is suitable for preconcentration and determination of cadmium from cigarette samples.

**Conclusion**

A simple, rapid and effective method based on the quantitative adsorption of cadmium on glycine immobilized cellulose has been developed. The results show that method can be used successfully for the treatment of cadmium containing water. It has

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**Table 1—Determination of cadmium in various samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume of eluent (mL)</th>
<th>Amount of cadmium added (ppm)</th>
<th>Amount of cadmium found* (ppm)</th>
<th>Recovery (%)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water sample</td>
<td>10.0</td>
<td>0.0</td>
<td>0.14</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>0.2</td>
<td>0.33</td>
<td>97.1</td>
<td>0.04</td>
</tr>
<tr>
<td>Cigarette sample</td>
<td>10.0</td>
<td>0.0</td>
<td>0.11</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>0.2</td>
<td>0.30</td>
<td>96.8</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Mean of three experiments*
been found that there is no effect of common electrolytes on the sorption of Cd(II) ion by the chelating resin used.

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References