Solid phase extraction of lead using modified cellulose in natural, wastewater and egg samples

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Received 23 July 2004; revised received 15 April 2005; accepted 2 May 2005

2-Pyridyliminosalicylcellulose has been used for the sorption and estimation of lead(II) by column and batch techniques. The distribution coefficient (D) was found to be $4.3 \times 10^2$ for the lead ion. The detection limit was found to be 3.82 ng mL$^{-1}$ and the breakthrough volume was 20 mL. The present matrix coupled with FAAS has been used to enrich and determine the lead ions in natural and wastewater (RSD ~ 2.52-3.50%) and egg samples (RSD ~ 2.73%). The method is simple, rapid and relatively free from interference and satisfactorily applied for the estimation of lead (~98% recovery) in natural, wastewater and egg samples.

**Keywords:** Lead(II), extraction, 2-pyridyliminosalicylcellulose, preconcentration, FAAS

**IPC Code:** C22B13/00; B01D; C02F1/00

Lead poisoning occurs in human beings and in all domestic animals and is a significant clinical problem. In humans, lead can affect blood, renal, neuromuscular, gastrointestinal, central nervous and reproductive systems. Lead can be found in paint, dust, soil, drinking water and food (rarely). Children may be exposed to lead from lead printed toys and newsprint. The determination of low concentrations of lead in water samples requires powerful techniques and only a few techniques have sufficient sensitivity.

Solid phase extractors for metal ions are considered to be superior to the liquid-liquid extraction due to their simplicity, rapidity and the ability to provide a high enrichment factor. The macromolecular chelators are found more selective for solid phase extraction in comparison to ion exchangers. Among different kinds of support materials used to design them such as organic polymer like Amberlite XAD series resin, silica gel and cellulose, the last one appears attractive as kinetics of sorption and desorption on it may be fast due to good porosity and hydrophilicity of the support. The low swelling, good chemical resistance, and ease of availability in nature also make it an attractive support for designing macromolecular chelators. The cellulose sorbents containing iminodiacetic acid, ethylenediaminetriacetic acid and diethylene-triaminetetraacetic acid functionality have been reported for multi-element preconcentration. It was therefore, thought worthwhile to immobilize 2-pyridyl iminosalicylaldehyde (schiff base) onto cellulose which influences the sorption capacity and the resin are found promising for lead enrichment.

The present paper describes a novel approach to synthesize modified cellulose and the preconcentration coupled with FAAS determination method has been applied to determine lead in natural, wastewater and egg samples.

**Experimental Procedure**

**Materials and methods**

All chemicals and solvents used were of analytical reagent grade. Double distilled water was used throughout the investigation. Microcrystalline cellulose, 2-hydroxy-5-bromobenzaldehyde and 2-aminopyridine were procured from Aldrich. The stock solution of lead ions (1000 μg/mL) was prepared by dissolving lead(II) acetate in an appropriate amount of deionized water acidified with 5 mL of the acetic acid. Acetate buffer solutions were prepared by mixing 0.2 M acetic acid and 0.2 M sodium acetate in suitable proportions. A digital (ECIL model) pH-meter 5651A and a Shimadzu AA-640-13 flame atomic absorption spectrophotometer were used. A tube of 100 mm length and 7 mm i.d. was used as a column.

**Preparation of immobilized cellulose**

2-Aminopyridine was immobilized onto cellulose in two separate steps:
Step 1: Cellulose (10 g) was suspended in a 100 mL, 1 M solution of 2-hydroxy-5-bromobenzaldehyde (HBB) in dry ether. The mixture was refluxed on water bath for 2 h in the presence of base (triethylamine), the resulting product HBB-cellulose (HBBC) was filtered, washed consecutively with ether, ethanol, acetone and then heated at 60°C for 8 h in a vacuum line (Scheme 1).

Step 2: HBBC (5 g) was reacted with 50 mL of 1 M 2-aminopyridine in dry diethylether with constant stirring in the presence of an acid. The solid product 2-pyridyliminosalicylcellulose (PISC) was filtered, washed and dried by heating in a vacuum line (Scheme 2).

The model compounds (scheme 1 & 2) were synthesized and the matrix is reproducible. IR spectral data were used to authenticate the immobilization of 2-pyridyliminosalicylaldehyde onto cellulose. The IR spectrum of modified cellulose does not differ markedly from that of unmodified cellulose. The infrared spectrum confirmed the occurrence of the coupling reaction. The band at 1640 cm$^{-1}$ is due to C–N stretching frequency of the imino group. There is no appreciable change in $\sim$OH frequency (~ 3480 cm$^{-1}$) in modified cellulose.

Recommended methods for preconcentration and determination of lead(II) ion

The column and batch methods both were standardized for preconcentration and determination of Pb(II) ions. The recommended procedures used are as follows:

**Batch method**

Immobilized cellulose (0.08 g) was equilibrated with 10 mL (10 ppm) solution of Pb(II) for 20 min in 100 mL flask. The pH of Pb(II) solution was maintained between 6.0-8.0 by sodium acetate-acetic acid buffer or with sodium acetate. The total volume of the solution was made to 20 mL. The solution was then maintained at 40°C for 20 min in a thermostat. Immobilized cellulose was allowed to settle. Supernatant solution was separated and Pb(II) in supernatant solution was determined by FAAS.

**Column method**

Glass columns were packed with 0.08 g of modified cellulose to a height of about 10 mm. A 10 mL (10 ppm) solution of Pb(II) maintained between 6.0-8.0 pH, with sodium acetate-acetic acid buffer, was passed through the column at a flow rate of 2mL/min. Sorbed Pb(II) was eluted from the column using 20 mL of 0.1 N HNO$_3$ and was then determined by FAAS.

**Tolerance limit measurement**

A set of solution containing 50 μg of lead ion was taken and spiked with varying amount of electrolyte or a cation. After making the volume to 100 mL the solution was passed through the modified cellulose column and Pb(II) was eluted with acid of optimum concentration as given in the recommended column method. Each reported tolerance is in the preconcentration and not in the determination by FAAS, as checked with the help of reagent matched standard solutions.

**Determination of lead in water samples**

200 mL of natural or wastewater (collected from different areas of Delhi, India) was evaporated to reduce the volume to approximately 15 mL. 3 mL of
concentrated HNO₃ and H₂SO₄ (1:1) was added to it and evaporated nearly to dryness. This process was repeated thrice and finally, after filtration, was made up to 100 mL with double distilled water. Aliquots (10 mL) of the sample solution were added into five conical flasks which contained 2 mL stock solution, buffer solution (5 mL) and distilled water (8 mL). This solution was then passed through the column filled with immobilized cellulose. The lead ions were then eluted from the column using 0.1 N HCL/HNO₃ and determined using FAAS.

**Determination of lead in egg**

Grinded egg (0.5 g) was put into a 250 mL beaker, 5.0 mL of concentrated H₂SO₄ and 15 mL HNO₃ were added to it and carefully heated under a cover on hot plate, and then treated with 1 M HCl, evaporated to near dryness. The digested sample was diluted to 100 mL with double distilled water. Aliquots (10 mL) of the sample solution were added into five conical flasks which contained 2 mL stock solution, buffer solution (5 mL) and distilled water (8 mL). This solution was then passed through the column filled with immobilized cellulose. The lead ions were then eluted from the column using 0.1 N HCl/HNO₃ and determined using FAAS.

**Results and Discussion**

**Effect of time**

The time required for the solid-liquid system to attain the equilibrium condition was determined at a definite temperature by placing 10 mL (10 ppm) of Pb(II) solution in a conical flask and shaking it with 0.08 g of immobilized cellulose. The supernatant solution was separated off at different time intervals. Fig. 1 shows the plot of percentage of lead sorbed verses time. It was found that the time required to reach the equilibrium is ~15 min. The percentage extraction of 10 ppm Pb(II) by immobilized cellulose was found to be maximum when 0.08 g of immobilized cellulose was used.

**Effect of pH**

Retention of Pb(II) on a column packed with immobilized cellulose was studied as a function of pH. Lead ion solution was adjusted to different pH values and passed at a rate of 2 mL/min through the column. The sorbed Pb(II) was eluted from the column with 0.1 N HNO₃ and determined by FAAS. It was found that the maximum sorption occurred in the pH range 6.0-8.0 (Fig. 2).

**Effect of temperature**

Sorption of lead ion is affected by temperature. The equilibrium constant of the complexation reaction has been found to decrease with decrease in temperature. It has been observed that sorption increased with increase in temperature up to 35 °C and practically remained constant after that (Fig. 3).

**Effect of flow rate**

The dependency of uptake of Pb(II) (10 ppm) on the flow rate was studied with the pH of the lead ion solution being chosen for maximum sorption. The flow rate was varied from 0.5 to 5 mL/min. Sorption was quantitative and reproducible in the above given range. The flow rate of 2 mL/min, was found to be the most suitable one.
Effect of electrolytes

Chloride, nitrate, sulphate and phosphate ions present in natural water have the capability to complex with many metal ions. Therefore, in their presence the efficiency of the immobilized ligand to bind metal ions may be hampered resulting in the reduction of overall extraction. Thus the effect of NaCl, NaBr, Na3PO4, NaNO3, citric acid, ascorbic acid, sodium tartarate and EDTA on the efficiency of functionalized cellulose to sorb Pb(II) was studied. The effect of bivalent cations such as Ca(II) and Mg(II) (added as chloride and sulphate respectively) was also investigated. The electrolytes have no effect on the sorption of lead ion by the immobilized cellulose. The tolerance limit of various electrolytes and cations Ca(II) and Mg(II) in the sorption of lead(II) ions are given in Table 1.

Sorption isotherm

The amount of lead ion sorbed by solid phase was calculated using equation

\[ N_f = \frac{[X - Y]}{Z} \]

where \( X \) is the initial amount of lead ions, \( Y \) is the amount of lead ions in the supernatant, \( N_f \) is the amount of lead ion sorbed and \( Z \) is the mass of modified cellulose (g).

For sorption isotherms, the distribution coefficient \( D \) defined as \( D = \frac{N_f}{C} \) and expressing the value of \( N_f \) in mmol/g and \( C \) in mmol/mL, the average value of \( D \) was calculated for lead (mL/g) in the concentration range 2.0×10^{-5} -2.5×10^{-3} M. The average value of \( D \) for lead ion was found to be 4.2×10^{2}.

Optimum conditions for sorption and desorption

The multivariant approach was used to optimize the working conditions. Each optimum condition was, however, rechecked after standardizing the remaining ones. Each of the repeated optimum conditions was established (by repeated trials) when others were kept at the optimum value. The column method was optimized for quantitative sorption (pH and flow rate) and desorption (concentration and volume of eluent) for Pb(II). The various optimum condition for Pb(II) are summarized in Table 2.

Detection/determination limit

The detection for Pb(II) was determined by passing a blank solution (3L) through columns of the modified cellulose. The metal contents was desorbed from the column using 20 mL of 0.1 N HNO3. The elute was aspirated into the flame of AAS for metal ion monitoring. The detection limits (blank +3\( \sigma \), where \( \sigma \) is standard deviation of blank estimation) for resin is 3.82 ngmL^{-1}. On increasing the volume of blank solution, the limits remain unchanged.
Breakthrough volume of acid for elution
The efficacy of the eluent (0.1 N HNO₃) was studied by taking its different volumes (5-25 mL). It was found that 20 mL of acid was sufficient for quantitative recovery of the Pb(II) from the resins. Therefore 20 mL of 0.1 N HNO₃ was used for the elution in all the further studies. The desorption was virtually instantaneous.

Stability and reusability of modified cellulose
The stability of the present modified resin was studied in acid (0.05-0.2 M HNO₃). The modified cellulose was shaken with acid solutions of varying concentrations for 6 h and filtered. The solid was washed with distilled water until free from acid, dried under vacuum and its sorption capacity was determined. The sorption capacity of chelating resin treated with 0.1 M acid was found to be similar to that of the untreated one. The present modified cellulose on treatment with HNO₃ of concentration > 2.0 M showed sign of degradation. The sorption capacity of 2-pyridyliminosalicylaldehyde anchored cellulose stored for more than six months has been found to be practically unchanged.

Using the same matrix bed for sorption-desorption of Pb(II) ions for 40 times tested the reusability of the matrix. The maximum change in the performance of the matrix after the repeated use was < 2.5%, indicating that its repeated use is feasible.

Preconcentration and recovery of metal ions
The column method was used for the preconcentration and recovery of lead ion. The concentration of lead ions was taken 10 μg/mL and the recovery was in the range 9.89-9.92 μg/mL. The percentage recovery was found in the range 98-99% depending on the concentration of lead ions used, when the volume of eluent was kept 20 mL.

Applications of the method

Determination of lead in water samples
The results given in Table 3(i) indicate the suitability of the present resin for the preconcentration of lead from various water samples, collected from the different sites. The high percentage recovery of lead (98%) and consistent percentage RSD values for five determinations indicate the present matrix can be used to enrich and determine lead ions in water samples.

Determination of lead in egg
The results given in Table 3(ii) show that the percentage recovery of lead in egg samples was found to be 98% with percentage RSD 2.7 for five determinations. This indicates the present matrix is suitable for preconcentration and recovery of lead ion from egg samples.

Conclusion
The studies presented in this paper proved that 2-pyridyliminosalicylaldehyde immobilized on cellulose can be applied for the determination of lead in water and egg samples by the column and batch methods. It has been found that there is no effect of electrolytes on the sorption of Pb(II) ion by the matrix used. The

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of lead (μg/mL)</th>
<th>Recovery (%)</th>
<th>RSD* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural water (1)</td>
<td>Present: 22.0</td>
<td>98.2</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>Found: 21.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural water (2)</td>
<td>Present: 23.0</td>
<td>97.8</td>
<td>3.02</td>
</tr>
<tr>
<td></td>
<td>Found: 22.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wastewater (1) (Wazirabad Drain, Delhi)</td>
<td>Present: 55.0</td>
<td>98.0</td>
<td>3.48</td>
</tr>
<tr>
<td></td>
<td>Found: 53.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wastewater (2) Kirtinagar Industrial Area, Delhi</td>
<td>Present: 56.0</td>
<td>98.4</td>
<td>2.96</td>
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<tr>
<td></td>
<td>Found: 55.01</td>
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</table>
*For five determination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of lead (μg/mL)</th>
<th>Recovery (%)</th>
<th>RSD* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh egg</td>
<td>Present: 11.0</td>
<td>98.18</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>Found: 10.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Preserved egg</td>
<td>Present: 11.2</td>
<td>98.21</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td>Found: 11.0</td>
<td></td>
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</tbody>
</table>
*For five determination.
method is simple, rapid and effective for the estimation of lead (98% recovery).

Acknowledgements
B K Singh acknowledges University Grants Commission (New Delhi) for financial support under research award scheme.

References