Removal of heavy metal ions from aqueous solutions using cellulose tetraethylene-pentamine [CTEPA] resin

A V Singh*, R S Sindal & Pradeep Sharma
Department of Chemistry, JNV University
Jodhpur 342 005, India
Email: areshvikram04@rediffmail.com

Received 27 November 2002; revised 18 February 2004

Cellulose tetraethylene-pentamine [CTEPA] resin is synthesized. The distribution coefficient of Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ on CTEPA resin at different pHs have been systematically studied.

**IPC Code:** Int. Cl. C08L 1/08; B01D 15/04

The removal of metal ions from sewage and industries waste is attracting the attention of researchers due to limitations of conventional waste treatment processes. Ion exchangers find tremendous applications in waste water treatment because of greater selectivity and higher exchange properties.

Application of chelating cellulose ion exchanger with the functional group of diethylenetriamine acetic acid has been reported for the determination of lead and cadmium in soils, plants and fertilizers. Sulphoxime cellulose (8-hydroxy quinoline-5-sulphonic acid cellulose) prepared by Mannich reaction from amino ethyl cellulose or via chloroethoxy and ethylene diamine cellulose was used in FI-GFAAS system for the preconcentration of trace metals like Cd, Co, Ni, Pb, and V from water and mineralized water.

Lewatit OC-1026 ion exchange resin was used for the recovery of zinc, in a relatively pure form, from a zinc rich industrial waste liquor and from model zinc rich solution. The chelating resin Puzolit S-930, metal fix chelamine and metal fix chelosolve showed greater selectivity for Cu, Cd, Pb ions from zinc rich waste liquors. Amongst all the natural polymers, cellulose is of special interest due to its easy availability and wide application both in natural as well as modified form. Chemical modification of cellulose can be used to have earlier reported use of variety of cellulose graft copolymers for sorption of Cu$^{2+}$ ions from its aqueous solution.

The styrene - DVB based chelating resin containing 4-(2-thiazolylazo) resorcinol (TAR) functional group have been investigated for the sorption behaviour of thirteen metal ions including U (VI) by batch and column experiments. This chelating resin is highly selective for Cu (II) and U (VI) in the pH range of 1-2. Vinyl graft copolymers of some important carbohydrates including cellulose have been reported earlier for the removal of metal ions from aqueous solution by Khalil et al. Linkov et al. also reported the adsorption of heavy metal ions, i.e., Ni, Cu, Zn, Cd by amino carboxyl ion exchanger ANKB-35 and parameters of ion adsorption from highly concentrated solution were established in order to determine regeneration condition of the resins.

Similar experiment was carried by Matsumura et al. in which an adsorbent for heavy metal, i.e., mercury, was synthesized by introducing polyethyleneimine (PEI) into porous cellulose carrier. At low concentration ranges, mercury adsorption by cell-PEI can be interpreted by the Langmuir isotherm.

**Experimental**

Cellulose tetraethylene-pentamine resin (CTEPA) was synthesized by the method of functionalisation of the polysaccharides described by Porath, in which cellulose was treated with epoxychloropropane followed by tetraethylenepentamine in strongly alkaline medium.

All other reagents and chemicals used were high purity commercial products and were used as such.

Perkin-Elmer Model 460 Atomic Absorption Spectrophotometer was used for quantitative determination of trace metals. For different metals, standard wavelengths of main resonance line and an air - acetylene flame were used.

**Anion - exchange capacity determination**

CTEPA resin (10.0 g) was completely converted into chloride form by treatment with liberal excess of 0.1N hydrochloric acid. Then the resin was washed with distilled water. Washings were collected in the same volumetric flask, the contents were neutralized with dilute nitric acid and the volume made up to 250 ml. Aliquots (25 ml) of the effluent was titrated against 0.1N silver nitrate solution using potassium chromate (10% aqueous solution) as indicator. Mois-
ture content was also determined by drying known amount of the resin in the oven. Scientific weight capacity (Q weight) was calculated using the formula:

\[
Q_{\text{weight}} = \frac{\text{Effluent volume} \times \text{milliequivalents of titrant used}}{\text{Volume of aliquot} \times \text{Weight of dried resin}}
\]

It was found to be 1.50 meq/g of the dry CTEPA resin, and the moisture content was 20.0%.

**Chelation chromatography on CTEPA resin**

Standard stock solution of Cu²⁺ of the strength 0.1M and those of Co²⁺, Ni²⁺, Cd²⁺, Zn²⁺ and Pb²⁺ of the strength 0.01M were prepared by dissolving the appropriate salts into solutions. These were diluted so as to give 0.60 mg/ml of Ni²⁺, 0.10 mg/ml of Cd²⁺, 0.65 mg/ml of Zn²⁺, 0.10 mg/ml of Pb²⁺ and 6.30 mg/ml of Cu²⁺ in individual solutions.

The molal distribution coefficient \((K_d)\) of metals showing pronounced adsorption on chelating resin were determined by the batch equilibrium method. Portions of CTEPA resin (1.0 g) in the chloride form placed in glass stoppered conical flasks containing a known volume of an appropriate buffer and 1 ml portions of a metal solution was added. The mixtures were shaken mechanically for 24 hr at 25°C. After equilibrium, the two phases were separated by filtration and aliquot of the filtrate was analysed for the metal concerned using the atomic absorption spectrometer. For this determination, standard solutions of metals were analysed atomic absorption spectrometrically. For different metals standard wavelengths of main resonance line and an air acetylene flame were used. The corresponding calibration curves were plotted for different metals. The concentration of the filtrates of metals were determined with the help of calibration curves, and the distribution coefficients \((K_d)\) calculated.

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe²⁺</th>
<th>Co²⁺</th>
<th>Ni²⁺</th>
<th>Zn²⁺</th>
<th>Cu²⁺</th>
<th>Cd²⁺</th>
<th>Pb²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>272.8</td>
<td>468.2</td>
<td>875.5</td>
<td>228.4</td>
<td>326.8</td>
<td>133.9</td>
<td>102.4</td>
</tr>
<tr>
<td>5</td>
<td>308.3</td>
<td>540.6</td>
<td>947.0</td>
<td>342.6</td>
<td>410.6</td>
<td>204.2</td>
<td>294.0</td>
</tr>
<tr>
<td>6</td>
<td>384.5</td>
<td>849.1</td>
<td>1504.6</td>
<td>490.0</td>
<td>672.5</td>
<td>378.0</td>
<td>390.5</td>
</tr>
<tr>
<td>7</td>
<td>1012.8</td>
<td>412.5</td>
<td>1112.3</td>
<td>564.8</td>
<td>795.9</td>
<td>588.3</td>
<td>696.1</td>
</tr>
<tr>
<td>8</td>
<td>879.3</td>
<td>386.1</td>
<td>886.7</td>
<td>642.2</td>
<td>1108.3</td>
<td>817.6</td>
<td>750.0</td>
</tr>
<tr>
<td>9</td>
<td>612.0</td>
<td>347.8</td>
<td>715.4</td>
<td>865.0</td>
<td>1697.6</td>
<td>1100.3</td>
<td>1207.4</td>
</tr>
<tr>
<td>10</td>
<td>313.8</td>
<td>288.2</td>
<td>685.1</td>
<td>717.5</td>
<td>546.9</td>
<td>872.4</td>
<td>692.6</td>
</tr>
</tbody>
</table>

**Results and discussion**

The resins prepared with DVB-styrene backbone are hydrophobic and this affects their efficiency in metal ion separation and concentration from solution. Also these resins are prepared from petrochemicals, which are very costly. The scarce supply and cost limit their use.

The naturally occurring polysaccharides give hydrophilic backbone for preparation of chelating resins. The fibrous nature of naturally occurring polysaccharide cellulose imparts the ease of accessibility of ion to the functional group in the macromolecules from the surrounding solution. A new range of chelating ion-exchangers having polyamine groups and based on cellulose matrix can be used as hydrophilic, renewable and selective ion-exchangers. Cellulose dihydroximate has been reported earlier for the separation of Cu²⁺, Ni²⁺, Co²⁺, Ca²⁺, and Fe²⁺ by Mae kawa et al. The CTEPA resin is more selective than cation exchangers and finds applications in preconcentration, isolation and separation of free metal ions (aquo or solvated) due to binding dissociation equilibria. The relative preference for various metal ions in CTEPA is pH dependent. The distribution coefficients of various metal ions are given in Table 1.

The perusal of the results shows that the distribution coefficient value first increases and then decreases with increasing pH. The order of the \(K_d\) values for metal ions at the pH of their maximum adsorption follows the sequence: Cu > Ni > Pb > Fe > Cd > Zn > Co. Pb, Cd, Cu and Zn show strong adsorption in high pH range, i.e., 9. Fe shows maximum adsorption at pH 7, whereas Co and Ni show an appreciably high adsorption at pH 6. Difference in distribution coefficients at the same pH for different metal ions suggests a possible strategy for separation of these ions from their mixtures.

The metal ions were eluted quantitatively with different strength of acids. Zn²⁺ was eluted with 0.05N
HCl; Fe$^{2+}$ with 0.5$\text{N}$ HCl; Cu$^{2+}$ with 2.5$\text{N}$ HCl; Cd$^{2+}$ with 0.5$\text{N}$ HNO$_3$ and Pb$^{2+}$ was eluted with 1$\text{N}$ HNO$_3$. Co$^{2+}$ and Ni$^{2+}$ were eluted with 0.5$\text{N}$ HCl and 1.0$\text{N}$ HCl respectively. Then the resin column was washed thoroughly with demineralized water. It could be reused up to five cycles with recovery better than 95%. After elution the resin can be finally disposed off either by burning it or by incineration as it is based on biopolymer.

**References**

11. Maekawa et al., Cellulose Hydroximate Derivatives (Wood Research Institute, Japan), 611(1983) 68.