Selective Separation of Uranium(VI) on a Chelating Styrene-DVB Based Resin Containing Quinaldinic Acid Amide Group

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A new chelating styrene-DVB based resin containing quinaldinic acid amide functional group, has been synthesised and characterised. The sorption patterns of Na(I), K(I), Be(II), Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), Pb(II), Ni(II), Bi(III), Fe(III), Ti(IV) and U(VI) have been studied as a function of pH. The resin sorbs U(VI) over a wide range of pH (1.0 to 4.0) with a maximum sorption of 0.32 mmol/g at pH 3.5 to 4.0. Zn(II), Cd(II), Cu(II), Ni(II), Pb(II), Fe(III) and Ti(IV) are also sorbed to different extents by the resin while Na(I), K(I), Be(II), Ca(II), Mg(II) and Bi(III) are not sorbed. Conditions for separation of U(VI) from these metal ions have been identified. The eluting agent used for U(VI) is 3 N HNO₃ and the recovery recorded is about 99.9%.

Very few chelating ion exchangers¹⁻³ have been used for the separation and preconcentration of U(VI), among which N-phenyl and N-methyl substituted hydroxamic acid resins⁴ are worth special mention. The aim of the present investigation was to develop a chelating ion-exchanger for the selective and rapid separation of the trace amounts of U(VI) from other metal ions. In this work a new styrene-DVB (8%) based chelating resin containing quinaldinic acid amide as a functional group has been synthesised and used for the preconcentration and separation of U(VI) from various metal ions.

The resin reported in this work has a much higher sorption capacity for uranyl ion compared with those of the other resins developed so far, exhibits a smooth peak of sorbance and does not require any gradient elution.

Materials and Methods

An atomic absorption spectrophotometer (Shimadzu AA-646) and a double beam UV-visible spectrophotometer (Shimadzu Acculab 20) were used for measurement of the concentrations of the metal ions. A digital pH meter (Sambros-335) was used for adjustment of pH. Infrared spectrum was recorded in KBr matrix on a Beckmann Acculab-10 IR spectrophotometer. Nitrogen was determined by a standard Micro-Duma's apparatus. A gravity-flow column with an appropriate reservoir was used as holder of the ion exchange resin.

Uranium solution was prepared from uranyl nitrate (E. Merck) and the metal content was determined by the standard method⁵. The stock solutions of various metal ions were prepared from their salts or oxides and estimated following standard methods.

Buffer solutions were prepared by mixing different proportions of standard solutions of sodium chloride and hydrochloric acid (pH 0.5 to 3.5), acetic acid and sodium acetate (pH 3.5 to 5.9) and Na₂HPO₄ and KH₂PO₄ (pH 5.9 to 8.0). During studies on separation from lead, HNO₃ and NaOH were used to control the pH.

Synthesis of the resin

Styrene-DVB polymer beads (80-100 mesh size) containing 8% DVB (Thermax Private Ltd., Poona, India) was nitrated using a mixture of H₂SO₄ and HNO₃. After washing the nitrated product with water, it was reduced to aminopolystyrene by tin (E. Merck) and cone. hydrochloric acid. The aminated product was then condensed with quinaldinyl chloride⁶ by refluxing the mixture in toluene medium on a waterbath for 24 hr. A schematic diagram of the synthesis of the resin is given below:

\[
\text{HN03/H2SO4} \rightarrow \text{NO2Sn/HCl} \rightarrow \text{NH2}
\]

\[
\text{C10H8ONCl} \rightarrow \text{NH-C-Cl}
\]

Schematic Diagram

Determination of sorption capacity of the resin for U(VI) and other metal ions

The sorption capacity of the resin for different metal ions was determined by batch and column
Fig. 1—Sorption capacity of the resin for different metal ions as a function of pH [(a) U(VI), (b) Pb(II), (c) Cu(II), (d) Cd(II), (e) Fe(III), (f) Ti(IV), (g) Ni(II) and (h) Zn(II)]

In batch operation, ~0.5 g of the air-dried resin was stirred on a magnetic stirrer for 24 hr with an excess of the desired metal ion solution of known strength (0.1 M) and volume (10 ml); the pH was controlled by a suitable buffer. The sorbed metal ions were eluted by using appropriate eluting agents [2N H₂SO₄ for Na(I), K(I), Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), Ni(II) and Fe(III)]; 4N H₂SO₄ for Ti(IV); 3N HNO₃ for Be(II), Pb(II), Bi(III) and U(VI)]. The whole process was repeated for different pH values. The eluted metal ions and also the metal ions left in the wash solution were determined following standard methods. The sorption capacity of each of these metal ions against pH has been shown in Fig. 1.

In column operation, a glass column (1 cm i.d., 30 cm length) was packed with ~22 g resin. The resin was initially swollen with 2N HCl and then washed with deionised water. The packed column was washed with appropriate buffer. The flow rate was adjusted at 0.5-1.5 ml/min. Calculated excess amount of the desired metal ion (150 ml, 0.1 M), at desired pH, was passed through the column, washed with appropriate buffer and eluted with suitable eluting agents as stated earlier. The sorption capacity in column operation was slightly lower than the capacity in batch operation. The sorption capacity of uranium(VI) studied by both batch and column operations are given in Table 1.

Separation and determination of uranium in uraninite ore

A weighed amount of the ore (200-400 mg) was treated first with dil. HNO₃ and then with 5 ml of conc. H₂SO₄ following a standard procedure. Finally, the volume was made upto 250 ml. The solution was adjusted to pH ~1.0, and 10 ml EDTA (~1 M) was added. The pH of the solution was raised to ~4.0. Excess of EDTA did not affect the sorption capacity of U(VI) around pH ~4.0 but suppressed the exchange of other metal ions present in the solution and also prevented precipitation due to hydrolysis. The solution was then percolated through the resin column and uranium was eluted with 3N HNO₃, as described earlier.

Results and Discussion

Characterisation of the resin

The resin being a new one, was characterised by its water regain value, infrared spectrum, its stability towards acids and alkali, elemental analysis and metal exchange capacity.

Water regain value was observed to be 0.37 g/g, indicating appreciable sorption capacity of the resin. Infrared spectrum of the resin showed a band at 1500 cm⁻¹ indicating the presence of –CONH– grouping. In addition to this sharp band, the IR spectrum exhibited medium bands at 1615, 1600 and 1438 cm⁻¹ which are very close to the ring breathing bands of quinaldinic acid.
Table 2—Separation of Uranium(VI) from Diverse Ions

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Amount (mg)</th>
<th>U(VI) recovered (mg)</th>
<th>Average (mg)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(I)</td>
<td>0.65</td>
<td>0.227</td>
<td>0.227</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>0.227</td>
<td>0.229</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>1.95</td>
<td>0.229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(II)*</td>
<td>0.60</td>
<td>0.228</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.228</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(III)b</td>
<td>1.45</td>
<td>0.227</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.80</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>0.229</td>
<td>0.228</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>4.34</td>
<td>0.229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(III)*</td>
<td>0.75</td>
<td>0.229</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.666</td>
<td>0.229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti(IV)c</td>
<td>1.50</td>
<td>0.229</td>
<td>0.229</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>2.25</td>
<td>0.228</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In presence of (a) EDTA (b) thiourea (c) fluoride

The resin was found to be stable for at least 7 days in 4 N H₂SO₄, 4 N HNO₃, 4 N HCl, 4 N HClO₄ and 2 N NaOH because no appreciable changes in nitrogen content and sorption capacity were found after treatment with the above mentioned reagents.

The thermogravimetric analysis (TGA) showed that the dried resin started decomposing at 260°C and loss in weight (20.2%) was attributed to the loss of quinaldinic acid group.

The resin was also found to be quite stable to γ-radiation. There was no loss of activity on exposure to a 3.12 or 9.36 M rad source for 24-72 hr. However, on exposure to 18.72 M rad source for 144 hr, the activity decreased by 12%. The activity of the resin was measured by the sorption capacity of U(VI) before and after exposing the resin to radiation.

The nitrogen content of the nitrated polymer was found to be 11.31%. After reduction, the resin contained 11.46% nitrogen. Amino group was estimated by titration in nonaqueous medium which indicated about 68% conversion of nitro-resin to amino-resin. The nitrogen content of the final chelating resin was found to be 9.22%. The conversion of amino group to quinaldinic acid amide group was calculated as 85%. Thus, the final resin contained about 21.5% of quinaldinic acid amide group and this value agrees with TGA result which is slightly lower as the TGA experiment was carried out in presence of air. The metal exchange capacity of both nitrated and aminated polymer was found to be negligible; hence, the free amino and nitro groups present in the final resin are not the active sites of the resin.

Metal absorption capacity and separation

Conditions for separation of U(VI) from the metal ions Na(I), K(I), Be(II), Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), Pb(II), Ni(II), Bi(III), Fe(III) and Ti(IV) were studied.

Among the above metal ions, Cd(II), Ni(II) and Zn(II) showed different sorption patterns in the pH region ~2.0-5.0, but at pH ~1.0 they were not sorbed by the resin and instead U(VI) was sorbed by the resin in the pH region ~1.0 to 4.0. So, for the separation of U(VI) from these metal ions the mixture was maintained at pH ~1.0, the resin column was washed with the same buffer and the mixture was passed through the column when only U(VI) was sorbed by the resin.

Separation of Zn(II), Cd(II) and Ni(II) from U(VI) was also achieved between pH 3.5 and 4.0. But, as the resin sorbs Zn(II), Cd(II) and Ni(II) in small amounts, EDTA was used to suppress the chelation of these metal ions. At pH ~1.0 sorption capacity of U(VI) is small. Hence, when urani-
When uranium present in uraninite ore was separated and determined using this resin; uranium found was 0.157% against the reported value of 0.16%.

A few other separations, e.g., Fe(III) from Cu(II), Zn(II) or Cd(II) can also be effected using this resin. However, these separations are not reported as they are of limited practical utility due to low sorption capacities of the metal ions.

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