Column Behaviour of Resorcinol-Formaldehyde Polycondensate Resin for Radiocesium Removal from Simulated Radwaste Solution

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The selective removal of radiocesium was studied using a column filled with resorcinol-formaldehyde polycondensate resin (RFPR) prepared in the laboratory. The feed to the column was a simulated alkaline radioactive waste solution with high salt load of spent fuel reprocessing plant origin. Repeated loading-elution-regeneration cycles were conducted to determine reproducibility of breakthrough behaviour. The breakthrough data were correlated with batch equilibration data on cesium uptake. The quantitative elution of sorbed radiocesium was also confirmed.

KEYWORDS: cesium, removal, cesium isotopes, resorcinol formaldehyde polycondensate resin, ion exchange, columns, breakthrough curve, elution, distribution coefficient, radioactive wastes

I. INTRODUCTION

The major radioactivity in alkaline intermediate level aqueous radwastes generated at spent fuel reprocessing plants in India is due to the presence of radiocesium. In our studies on the uptake of cesium by phenolic resins, we have found that a resorcinol-formaldehyde polycondensate resin (RFPR) made in the laboratory is highly selective towards cesium in alkaline solutions even in the presence of large quantities of sodium ions. The synthesis and characterization of this phenolic resin as well as batch equilibration results on the uptake of cesium from solutions of different compositions have already been reported by us⁴. We have also demonstrated the usefulness of this resin for the effective removal of radiocesium from actual alkaline intermediate level radwaste stored at a spent fuel reprocessing plant site⁵. In the present communication, we report the results of experiments carried out using a simulated radwaste solution to understand the column breakthrough and elution behaviour of this resin in greater detail.

II. EXPERIMENTAL

1. Synthesis of the Resin

The RFPR was synthesized using polycondensation reaction between resorcinol and formaldehyde in the presence of sodium hydroxide as catalyst. The details of synthesis and conditioning procedure have been described in an earlier publication⁴. The final product, air-dried and in H⁺-form, was obtained in the form of 0.3-0.85 mm size particles.

2. Ion-Exchange Capacity

About 0.5 g of the H⁺-form, air-dry resin was equilibrated with 100 cm³ of 0.1 M (mol·dm⁻³) NaOH solution containing 5% NaCl. From the amount of NaOH consumed, the total H⁺-Na⁺ ion-exchange capacity was calculated and expressed as milliequivalents/g of air-dry, H⁺-form resin.

3. Moisture Content

The moisture content was determined by...
measuring the loss in weight of a known weight of resin on heating in an air-oven at 100°C for 24 h.

4. Simulated Waste Solution
The intermediate level waste under investigation is a mixture of decladding wastes and neutralised evaporator condensates from a plant reprocessing aluminium-clad fuels from a research reactor. A solution was prepared to simulate the composition of this alkaline salt-loaded waste solution. The composition of the simulated waste solution is shown in Table 1. The total dissolved solid content was 28.3% and as can be seen in Table 1, this was due to the presence of sodium salts in the solution (\([Na^+] = 4.0 M\)). The only radioisotope added was \(^{134}Cs\) as the tracer for cesium. The concentration of inactive cesium salt added was equivalent to a \(^{137}Cs\) activity of about 3.7 GBq·dm\(^{-3}\) in the waste solution.

Table 1 Composition of simulated waste

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1.0 M</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>2.5 M</td>
</tr>
<tr>
<td>NaNO(_2)</td>
<td>0.1 M</td>
</tr>
<tr>
<td>Na(_2)CO(_3)</td>
<td>0.1 M</td>
</tr>
<tr>
<td>NaAI(_2)O(_5)</td>
<td>0.15 M</td>
</tr>
<tr>
<td>Na(_2)PO(_4)</td>
<td>0.003 M</td>
</tr>
<tr>
<td>CsNO(_3)</td>
<td>8.7 × 10(^{-3}) M</td>
</tr>
<tr>
<td>(^{134}Cs)</td>
<td>Tracer</td>
</tr>
<tr>
<td>TDS</td>
<td>28.3%</td>
</tr>
</tbody>
</table>

5. Batch Distribution Coefficient \((D_M)\)

The batch distribution coefficient \((D_M)\) was determined by equilibrating 0.1 g of the air-dried H\(^+\)-form resin with 50 cm\(^3\) of the simulated waste solution in stoppered polyethylene containers. All equilibrations were done in duplicate. The mixtures were shaken for 6 h at the room temperature of 27 ± 1°C and left overnight. From the activities of the solution before and after equilibration measured using a well-type NaI(Tl) gamma scintillation counter, the \(D_M\) value was calculated according to the following general equation:

\[
D_M = \frac{\text{Milliequivalents of trace ion per g of resin}}{\text{Milliequivalents of trace ion per cm}^3\text{ of solution}},
\]

\[
= \frac{C_i - C_f}{C_f} \times \frac{V}{W} \text{ (cm}^3\text{·g}^{-1}),
\]

where \(C_i\) and \(C_f\) are the initial and final activities in cpm·cm\(^{-3}\), \(V\) the volume of equilibrating solution (50 cm\(^3\)) and \(W\) the mass of resin taken (0.1 g).

6. Column Loading and Elution

The ion-exchange column was a small glass tube (i. D. = 1.06 cm) with a sintered disc to support the resin and a PTFE stopcock at the bottom. The experimental setup is shown schematically in Fig. 1. A Watson-Marlow peristaltic pump (Model 501U, 10 rpm) was used for metering the solutions through the resin bed, either upflow or downflow as required, by suitably operating a series of pinchcocks on flexible polymeric tubings.

To start with, 1.25 g of air-dry, H\(^+\)-form RFPR was soaked in distilled water for 4 h and then transferred to the column. The bed height was about 30 mm. The resin was then regenerated, i. e. converted to Na\(^+\)-form, by passing sufficient excess of 1.0 M NaOH solution upflow through the bed. On settling, the bed height of RFPR(Na\(^+\)) in 1.0 M NaOH was found to be 65 mm, i. e. a bed volume of 5.73 cm\(^3\).

The next step was loading of simulated waste solution. This was done downflow through the bed at a flow rate of about 0.57
cm$^3$·min$^{-1}$ which amounts to 6 bed volumes per hour (bv·h$^{-1}$). Samples of the column effluent were taken periodically and the gamma activity monitored with a single-channel NaI(T1) gamma scintillation counter assembly. The first loading run was continued for 66 h (396 bed volumes) when the dose rate at the surface of the column due to sorbed $^{134}$Cs was found to be about 50 mR·h$^{-1}$.

Loading was followed by upflow rinsing with 0.1 M NaOH solution. The final stage of column run was elution of the sorbed cesium with 0.5 M formic acid (HCOOH) in the upflow mode at a flow rate of about 10 bv·h$^{-1}$. Eluate samples were collected from the side tube at the top of the column. The elution run was over after passing about 30 bed volumes of eluent. The resin bed was finally rinsed with about 100 cm$^3$ of distilled water upflow.

Two more complete ion-exchange cycles were run with the same bed as described above. The loading, however, was limited to less than 300 bed volumes. All the effluent and eluate samples were collected and their activity measured. The cumulative effluent and eluate volumes were also sampled for activity determination.

### III. RESULTS AND DISCUSSION

The results of characterization of the RFPR product are shown in Table 2. The distribution coefficient, $D_M$, is calculated from batch equilibration data and relates to unit mass of the resin. The value obtained, 2,970 cm$^3$·g$^{-1}$, though lower than values $>10^4$ cm$^3$·g$^{-1}$ measured in solutions having lower sodium concentrations$^{11}$, is still sufficiently high and shows the extraordinary selectivity of RFPR for cesium even in the presence of large concentrations of sodium ions. It is also possible to calculate a volumetric distribution coefficient, $D_V$, which relates to unit volume of the resin in column and is defined as follows:

$$D_V = \frac{\text{Milliequivalents of trace ion per cm}^3 \text{ of resin bed}}{\text{Milliequivalents of trace ion per cm}^3 \text{ of solution}}.$$ (3)

The two distribution coefficients can be related by the following equation:

$$D_V = D_M \delta_r,$$ (4)

where $\delta_r$ is the mass of the resin per cm$^3$ of resin bed in the column. As mentioned earlier, a bed of 5.73 cm$^3$ volume was finally obtained from 1.25 g of the resin initially loaded in the column. This enormous swelling in alkaline solutions is not found in conventional ion-exchange resins based on a polystyrene-divinylbenzene matrix and seems to be a characteristic feature of phenolic resins like RFPR. From the above data we have, $\delta_r = 1.25/5.73 = 0.218$ g·cm$^{-3}$. Substituting the value of $D_M$ and $\delta_r$ in Eq. (4) we get, $D_V = 2,970$ cm$^3$·g$^{-1}$·cm$^3$·g$^{-1} = 647$.

The significance of the volumetric distribution coefficient, $D_V$, lies in the fact that it can be ideally related to the performance of the column.

<table>
<thead>
<tr>
<th>Nature of resin</th>
<th>Resorcinol-formaldehyde polycondensate resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin form</td>
<td>H$^+$-form, air-dry</td>
</tr>
<tr>
<td>Particle size</td>
<td>0.3~0.85 mm</td>
</tr>
<tr>
<td>Ion-exchange capacity (H$^+$-Na$^+$)</td>
<td>4.90 meq·g$^{-1}$</td>
</tr>
<tr>
<td>Moisture content</td>
<td>23.3 wt.%</td>
</tr>
<tr>
<td>Cs distribution coefficient ($D_M$)</td>
<td>2,970 cm$^3$·g$^{-1}$</td>
</tr>
</tbody>
</table>

For establishing such a relation, let us consider an ideal breakthrough curve (BTC), as shown in Fig. 2. At the break point "a", the bed is not fully saturated and hence the breakthrough capacity is always less than the equilibrium saturation capacity ($q_s$) which is realised after an effluent volume corresponding to point "c" on the X-axis, has passed. The quantity $q_s$ is given by the following equation:

$$q_s = (1/V_r)C_0 \int_0^V (1 - C/C_0) dV \text{ (meq·cm}^{-3}),$$ (5)

where $C$ is the concentration of the ion of interest in the effluent at any time (meq·cm$^{-3}$), $C_0$ is its concentration in the influent solution (meq·cm$^{-3}$), $V_c$ the volume (cm$^3$) corresponding
to point "c" on the BTC and \( V_r \), the volume (cm\(^3\)) of the resin bed.

Since \( q_s \) is the saturation capacity of the resin bed in equilibrium with the feed concentration \( C_0 \), we can write Eq. (3) as follows:

\[
D_V = \frac{q_s}{C_0}. \quad (6)
\]

The quantity \( q_s \) can be found by performing the integration given in Eq. (5) if the complete BTC is experimentally measured. However, a simpler method is possible by considering the geometry of the BTC in Fig. 2. Assuming that the BTC is symmetrical about point "d", the point for 50% breakthrough (\( C/C_0 = 0.5 \)), it is clear that portions shaded doubly above and below point "d" are of equal area. Hence the total area to the left of the BTC is equal to the area between Y-axis and the line "bdf" corresponding to \( C/C_0 = 0.5 \) or 50% breakthrough. Therefore we have the following relation:

\[
\text{Total uptake} = q_s V_r = C_0 V_{0.5}, \quad (7)
\]

where \( V_{0.5} \) is the volume corresponding to 50% breakthrough. Combining Eqs. (6) and (7), we get

\[
D_V = \frac{V_{0.5}}{V_r} = N_{bv}, \quad (8)
\]

where \( N_{bv} \) is the number of bed volumes passed till 50% breakthrough. Therefore, in an ideal case, the number of bed volumes that can be treated till 50% breakthrough is equal to the volumetric distribution coefficient. If the results of a column experiment satisfy the above relation, it can be said that the column is behaving normally. In many cases, however, a column may not be run till saturation and hence the complete BTC is not available. For such cases, a useful property of the BTC helps in finding the value of \( N_{bv} \) from data generated for only the initial portion of the BTC. According to this property, symmetrical S-shaped breakthrough curves, like the one shown in Fig. 2, become straight lines when plotted on probability-logarithmic graph paper\(^{(4)}\). This helps in extrapolation of data generated for the initial part of the BTC and hence calculation of \( N_{bv} \).

The loading results in this experiment are plotted in Fig. 3 as breakthrough curves for all the three runs. It is seen that all three runs showed nearly identical breakthrough behaviour. Even after 120 bed volumes, the breakthrough was <0.1%, i.e., a decontamination factor (DF) of >1,000. Thereafter the curves rise slowly.

Figure 4 shows the breakthrough data for all the three runs plotted on probability-logarithmic graph paper. It is seen that the results for all the three runs fall satisfactorily on a single straight line indicating thereby that the column was behaving normally. By extrapolation of the straight line, the number of bed volumes corresponding to 50% breakthrough, \( N_{bv} \), is found to be about 600. The agreement between this value and that of \( D_V \)
mentioned above, though not exact, may be considered to be satisfactory and thus proves the validity of the simplified treatment outlined above for fixed-bed ion-exchange column operation based on well-known principles.

Phenolic resins being weakly acidic in nature, they have a strong affinity for H\(^+\) ions. Hence it is possible to easily elute sorbed ions from such resins with the help of weak acids like formic acid. The results of elution showed that in each of the above three cases, 100\% of the loaded activity could be eluted with about 20 bed volumes of 0.5 M HCOOH. The distribution of eluted activity vs. bed volumes of eluent can be seen in Table 3, compiled from the results for the second run. Another important observation, not unexpected, made during elution was the marked reduction in resin volume with the progress of elution. The resin volume in H\(^+\)-form was about 43\% of its volume in Na\(^+\)-form. This is possibly due to the weak acid nature of RFPR which remains largely un-ionized in the acid form whereas the salt form produced in alkaline solution is ionized, leading to hydration of the ions and consequent swelling of the resin matrix.

### IV. CONCLUSIONS

Resorcinol-formaldehyde polycondensate resin (RFPR) prepared in the laboratory was found to be suitable for use in packed columns for the selective removal of radiocesium from radwaste solutions. The breakthrough data were reproducible for three repeated loading-elution-regeneration cycles. The number of bed volumes that could be passed till 50\% breakthrough was determined by extrapolation of initial breakthrough data plotted on probability-logarithmic graph paper. This number was found to satisfactorily agree with the volumetric distribution coefficient determined from batch equilibration data. Complete elution was achieved with about 20 bed volumes of 0.5 M formic acid. The resin bed showed large difference in volume in alkaline and acidic solutions.

### ACKNOWLEDGMENT

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### REFERENCES