3.1 Introduction

Resorcinol formaldehyde (RF) resin is the most widely used organic ion exchanger for removal/recovery of cesium from alkaline nuclear wastes. RF resin was developed in Savannah River National Lab, for its use in nuclear industry. Since then, it has been considered as a satisfying option for removal of Cs\(^+\) ions from highly alkaline media because of low-cost, safety, availability, profitability, easy operation and efficiency considerations.\(^\text{150}\) RF resin has exceptionally high affinity for Cs\(^+\) ions, which can be attributed to the presence of -OH groups, which ionize under high alkaline condition. Conventionally, RF resin is prepared by bulk polymerization reaction between resorcinol and formaldehyde in alkaline medium, to get big chunks of the polymeric
resin, and then, these chunks are ground and sieved, to get desirable mesh size.\textsuperscript{104} But, these ground gel particles are of irregular shape, have broad particle size distribution, and exhibit poor column hydraulic behavior. These problems can be solved by using spherical resin material. The literature survey suggests that, the earlier research in the synthesis of RF resin involves specific inventory, such as vibrating column, laminar flow, supercritical drying, etc. Some inventors have used oil as a stabilizing media, to produce beads, with control over size, but washing out of the oil is a tedious step, and, moreover, it also generates secondary waste in considerable amount. We have developed new and simple methods for the synthesis of resorcinol formaldehyde beads, with good control over size. Two approaches have been used for the synthesis of spherical RF resin beads:

- **Suspension polymerization:** Synthesis of spherical RF resin beads by suspension polymerization, involves use of a suitable stabilizing polymer solution as a suspension medium, in which the aqueous droplets of required size, containing precursor of RF resin, are stabilized.

- **Templating method:** In this method, a suitable pre-formed spherical template, such as beads of XAD-4, or calcium alginate, is used as base material which is equilibrated with the precursors of RF resin, to synthesize spherical RF resin beads. Depending upon the nature of the template, it may be retained in the final beads or removed by a suitable treatment, to incorporate porosity, and hence, increase the surface area for efficient sorption.

The methods do not require any sophisticated equipment, and the beads can be made free of unwanted contaminants by easy washing. The synthesis, characterization and sorption studies, carried out with these beads, are described in this chapter.
3.2 Materials

Resorcinol, formaldehyde (37% in methanol) and sodium hydroxides were obtained from Merck. Amberlite XAD-4, sodium alginate and calcium chloride were procured from S. D. Fine chemicals, India. All the other solvents and the chemicals used were of analytical grade. Water obtained from Millipore-Q water purification system, with conductivity < 0.3 µS/cm, was used in all the experiments. $^{134}$Cs and $^{137}$Cs radiotracers were procured from the Board of Radiation and Isotope Technology (BRIT), Mumbai, India.

3.3 Synthesis
3.3.1 Synthesis of pure RF resin beads

The resorcinol-formaldehyde pre-condensate was prepared, by reacting resorcinol with formaldehyde in a suitable proportion under alkaline conditions. The pre-condensate was allowed to polymerize until it attained appropriate viscosity, and then, it was added to the stabilizing polymer solution, with optimum stirring. After stirring for certain time, the reaction mixture was kept undisturbed, for complete curing of the RF polymer. The cured RF beads were recovered from the reaction vessel, by washing out the polymer with a suitable solvent for the stabilizing polymer and then washing the beads with distilled water, and drying at room temperature. The cured beads of specific size were separated, using test sieves. Fig. 3.1 represents the schematic diagram of the steps involved in the synthesis of RF beads. Patent for the detail method of the synthesis of RF resin beads is in process.
3.3.2 Synthesis of RF-XAD resin beads

Resorcinol formaldehyde pre-condensate was prepared by reacting resorcinol and formaldehyde in aqueous media, using NaOH as a catalyst. An aqueous solution, with resorcinol : formaldehyde : catalyst in the molar ratios of 1 : 3 : 6, was prepared, and allowed to react for some time. Then, the XAD beads were equilibrated with this RF pre-condensate solution, for 2 hours. The equilibrated beads were separated from the rest of the RF pre-condensate solution, and the solution sorbed onto the beads was allowed to cure completely. After complete curing at 105 °C, for 4 hours, brown-colored RF-coated XAD beads were obtained. The synthesized beads were in the sodium form, and hence, were dark-colored. These resin beads were converted into the hydrogen form, by mixing these with 0.5 M HNO₃ in a 3:1 ratio of liquid-to-resin volumes, for 1 hour, with
occasional gentle shaking. After that, the resin beads were separated, and washed with water thoroughly, to remove any residual acid, till pH of the washing became near neutral. This acid treatment turned the resin into a light-colored hydrogen form. This hydrogen form of the resin was air-dried, and stored. It was used as such, without any further pre-treatment, in all the sorption experiments.

### 3.3.3 Synthesis of alginate assisted RF (RF^A) beads

In order to synthesize RF^A beads, template alginate beads were first synthesized. For that, 2.0% (w/v) aqueous solution of sodium alginate was obtained, by dissolving 2.0 g of sodium alginate in 100 ml of water, which was then, dropped into a calcium chloride solution (4%) through a syringe needle of 0.8 mm internal diameter, forming gelified calcium alginate microspheres. These beads were kept overnight in the calcium chloride solution, for complete curing, and then, washed with water. Resorcinol formaldehyde pre-condensate was prepared by reacting resorcinol and formaldehyde in aqueous media, using NaCO₃ as a catalyst. An aqueous solution, with resorcinol: formaldehyde: catalyst in the molar ratios of 1: 2: 0.05, was prepared, and was allowed to react for ~15 min. The pre-formed water-swollen alginate beads were equilibrated with this RF pre-condensate solution, for 3 hours, and then, separated from the rest of the RF pre-condensate solution. The solution adsorbed on the beads was allowed to cure completely. After complete curing at 105 °C, for 4 hours, the brown-coloured RF^A beads were obtained. These dark-coloured beads were in sodium form, and were converted into hydrogen form, by the method mentioned earlier for the RF-XAD beads, before carrying out the sorption experiments.
3.4 Sorption Studies

The solutions of the radiotracers, $^{134}$Cs and $^{137}$Cs, were further diluted to the required concentrations, as and when required. The sorption experiments on RF resin beads were carried out, by equilibrating 0.05g of RF resins beads with 5 mL of the CsNO$_3$ solution of appropriate concentration, containing $^{137}$Cs as a radiotracer. The solutions were stirred, using a mechanical shaker, for 6 hours. The sorption experiments with RF-XAD and RF$^A$ resin beads were carried out, using $^{134}$Cs as a radiotracer, for 4 hours of contact time, keeping the sample volume to the resin mass ratio same, as mentioned earlier. The contact time was found to be sufficient for attaining equilibrium. However, for studying the kinetics of sorption, the equilibration time was varied from 0 to 4 hours. All the test solutions, containing cesium ions, were prepared in 0.1 N NaOH solution, to maintain similar alkalinity of the solutions. After the equilibration, a small portion of the aqueous phase (1 ml) was separated, and taken for counting gamma activity. The gamma activity measurements were carried out in a well-type NaI (T1) [ECIL] detector, connected to a single-channel analyzer. The sorption capacity at equilibrium, $q_e$, was calculated by the equation (3.1)

$$q_e = \frac{(C_0 - C_e)V}{m}$$

(3.1)

where $C_0$ and $C_e$ are, respectively, the initial and the equilibrium concentrations of cesium ions, $V$ is the volume of the solution, and $m$ is the mass of the sorbent used.
3.5 Results and Discussion

3.5.1 RF resin beads

3.5.1.1 Characterization

3.5.1.1.1 Optical microscopy and SEM studies

Fig. 3.2(a) and (b) show the optical microscope image of RF ground gel and RF beads of size 20-40 mesh (0.8-0.4 mm), respectively. Fig. 3.2(c) depicts the SEM image of the outer surface of a RF bead. There are some big pores on the outer surface of the bead, which might have formed due to water loss during curing. These pores will offer higher surface area to the sorbate during sorption process, and hence, will increase its capacity.

![Fig. 3.2: Optical microscope image of (a) the RF ground gel, and (b) the RF resin beads, and (c) SEM image of a RF bead](image)

3.5.1.1.2 Mechanical strength

Mechanical strength of the synthesized RF beads was tested, and compared with that of the conventional ground RF gel particles, using a universal testing machine. The measurement was carried out, by applying the load in the range of 0-250 N, using a 500 N load cell. The spherical RF beads showed the first break at a load of 12-14 N, for the different samples. Under similar experimental conditions, the first breakage for the ground RF gel was observed at 2.5-5 N, and different breakages were seen in the range of 2.5-15 N, depending on the shape and the size of the granular RF particles. The irregular-sized ground gel particles have some sharp and weak edges, which are the most
susceptible for breaking under pressure, and result in generation of fine powder that leads to choking of column. These results suggest that the synthesized RF resin beads offer better mechanical strength, and are expected to work better in column mode of operation.

3.5.1.1.3 Water content and surface area analysis

The moisture content of the synthesized RF beads was determined by thermogravimetry technique. For this measurement, a pre-weighed amount of the RF beads was heated isothermally at 100°C, under N₂ atmosphere, for 2 hours, and the loss in the weight was determined. The water content of these beads was found to be 18% of the total weight. The specific surface area and the pore volume of the beads were determined by BET N₂ adsorption method. The nitrogen adsorption-desorption isotherms were measured at 77 K, at a relative partial pressure (i.e. P/Pₒ) of N₂ of 0.98, after degassing the samples at 100 °C, for 5 hours. The surface area of the beads was determined to be 273.6 m²/g. The higher surface area of the beads, along with 18 % moisture content, indicates towards its better sorption efficiency for removal of cesium ions.

3.5.1.1.4 Ion-exchange capacity

About 0.5 g of the H⁺-form, air-dried RF resin beads were equilibrated with 100 ml of 0.1 M NaOH solution, containing 5% NaCl. From the amount of NaOH consumed, the total H⁺-Na⁺ ion-exchange capacity was determined to be 6.15 milliequivalents/g of air-dried, H⁺-form RF resin beads.

3.5.1.2 Sorption studies

3.5.1.2.1 Effect of the size of the resin

The effect of the size of the synthesized RF resin on the sorption of cesium was determined, by agitating 0.05 g of the RF resin beads of different sizes, ranging from less than 20 to more than 80 mesh, with 5 mL of 0.005 mmol/L cesium ion solution in 0.1 M
NaOH in separate equilibration tubes, using a shaker, at 20 °C. Agitation was provided at a constant speed of 150 rpm, for 6 hours, which is sufficient to reach equilibrium. The percentage removal of cesium ions can be calculated as follows

\[
\text{% Removal} = \left(1 - \frac{c_e}{c_o}\right) \times 100
\]  

(3.2)

Fig. 3.3: Effect of the mesh size of the RF resin beads on % removal of cesium ions

Fig 3.3 shows the effect of the size of the RF resin beads on % removal of cesium ions from alkaline solution (0.1 M NaOH). With increase in the mesh size, i.e., decrease in the particle size, of the RF resin beads, the % removal of cesium ions increases gradually. In the case of bigger size RF resin beads (less than 20 mesh), 80% cesium is removed, whereas under similar experimental condition, ~ 91 to 96% cesium is removed, in the case of higher mesh size resin beads. The increase in percentage removal of cesium ions with the decrease in particle size (from 20-40 mesh to more than 80 mesh) of the sorbent is very small ~ 5.0%. Hence, a reduction of the particle size, from less than 20 mesh to 20-40 mesh size, leads to increased removal of cesium due to increased
availability of the sorption sites, but further decrease in the resin size does not show much improvement. So, the optimum particle size for the sorbent may be considered as 0.4–0.8 mm, corresponding to 20-40 mesh size, which was selected for all the further sorption experiments. Particle size of this range has been also reported in literature for removal of cesium from alkaline waste.104

3.5.1.2.2 Effect of Na\textsuperscript{+} ion concentration

The effect of the presence of the Na\textsuperscript{+} ions on equilibrium uptake capacity of the RF resin beads, for Cs\textsuperscript{+} ions, was studied at 0.02 mM initial cesium ion concentration, at 20 °C. Fig. 3.4 shows that the sorption of cesium ions decreases with increase in sodium ion concentration up to the studied concentration of 3.0 M. These results indicate that the $q_e$ value for cesium ion is significantly affected by the presence of Na\textsuperscript{+} ions in the solution, due to the competition offered by Na\textsuperscript{+} ions for the available exchange sites. But, the observed $q_e$ value of ~0.4 mmol/g at 2 M Na\textsuperscript{+} ion concentration is sufficient, to remove the amount of cesium usually present in the low-level alkaline waste.

![Fig. 3.4: Effect of Na\textsuperscript{+} ion concentration on the sorption of cesium ions](image-url)
3.5.1.2.3 Effect of cesium ion concentration

The sorption of cesium ions by the beads at different initial concentrations, ranging from 0.5 to 50 mM, at 20 °C, is illustrated in Fig 3.5. It is evident that the amount of cesium ions sorbed increases with the increase in the concentration of cesium ions in the solution, but the percentage sorption decreases (Fig. 3.5 (b)). When the initial cesium concentration increases from 0.5 to 50 mM, the sorption uptake of cesium ions increases from 0.04 to 1.79 mmol/g, i.e., 5.3 to 238 mg/g (Fig. 3.5(a)).

A higher initial concentration provides an important driving force, to overcome all resistances to the cesium ions between the aqueous and solid phase, and thus, increasing the uptake. Moreover, with increase in the initial cesium ion concentration, there is an increase in the number of collisions between the cesium ions and the active sites of the RF resin, which results in both increase in the rate of sorption and enhanced equilibrium sorption capacity. While the percentage removal of cesium ions decreases from 99.3 to 35.9%, as the initial concentration increases from 0.5 to 50 mM (Fig. 3.5(b)). This is because the total number of active sites are finite due to the fixed amount of the resin taken for sorption studies.

![Fig. 3.5: Effect of the initial cesium concentration on (a) equilibrium sorption capacity and (b) percentage removal of cesium ions by the RF resin](image)
3.5.1.3 Sorption isotherms

The sorption data were analyzed, using the Langmuir and the Freundlich sorption isotherm models. The Langmuir sorption isotherm is the simplest model for the sorption of a solute from a liquid solution.\textsuperscript{154} The Langmuir sorption model is based on the assumption that maximum sorption corresponds to a saturated monolayer of the solute molecules on the sorbent surface.\textsuperscript{130, 154} The linearized expression of the Langmuir model is

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e}
\]  

(3.3)

Where \(q_m\) is the maximum monolayer loading capacity, and \(K_L\) is a constant related to the affinity of the binding sites.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig3_6.png}
\caption{Langmuir plot for sorption of Cs\(^+\) ions onto the RF resin beads at 293 K}
\end{figure}

The linear plot of \(1/q_e\) verses \(1/C_e\), with \(R^2\) value of 0.9794 (Fig. 3.6), shows that the sorption seems to obey the Langmuir model. The Langmuir constants \(q_m\) and \(K_L\) are
determined from the intercept and slope of the plot, respectively, and are given in Table 3.1.

The Freundlich model is an empirical equation that assumes heterogeneous sorption due to the diversity of the sorption sites. The Freundlich equation is expressed as

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

(3.4)

where \( K_F \) is related to the sorption capacity and \( 1/n \) is the sorption intensity. The magnitude of the exponent, \( 1/n \), gives an indication of the favorability of the sorption. The values of \( K_F \) and \( n \) are calculated from the intercept and slope, respectively, of the linear plot of \( \log q_e \) vs. \( \log C_e \) (Fig. 3.7), and are listed in Table 3.1.

![Freundlich isotherm plot](image)

**Fig. 3.7:** Freundlich isotherm plot for sorption of \( \text{Cs}^+ \) onto RF resin beads at 293 K

The regression correlation coefficients obtained for both the Langmuir and the Freundlich models are almost similar, but the maximum monolayer capacity determined from the Langmuir model is less than the experimentally determined equilibrium.
capacity. Therefore, the Langmuir model is not the best model, to describe the sorption of cesium ions onto the synthesized beads. From Table 3.1, it can be seen that the value of Freundlich isotherm parameter ‘n’ lies between 1 and 10, which indicates favorable sorption. From the high $R^2$ value for Freundlich model, and fractional value of $1/n$, it can be concluded that Freundlich isotherm explains sorption process well. The predicted expressions for the $q_e$, corresponding to the Langmuir and the Freundlich models, for sorption of ions onto the RF resin beads, useful for design calculations, can be given by equations (3.6) and (3.7), respectively.

\[
\text{Langmuir: } q_e = \frac{0.7158C_e}{1+9.3835C_e} \quad (3.6)
\]

\[
\text{Freundlich: } q_e = 0.50066C_e^{0.43123} \quad (3.7)
\]

**Table 3.1:** Langmuir and Freundlich isotherm parameters for sorption of cesium ions onto the RF resin beads

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$</td>
<td>0.715 mmol/g</td>
</tr>
<tr>
<td></td>
<td>$K_L$</td>
<td>0.852 L/mmol</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9793</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>0.481 mmol/g</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.431</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9754</td>
</tr>
</tbody>
</table>

**3.5.1.4 Sorption kinetics**

The effect of contact time on the removal of cesium ions by the RF resin, studied at three different initial concentrations, in the range 0.5–10 mM, at 20 °C, shows rapid sorption of cesium ions in the initial period of 2 hours (Fig. 3.8(a)). About 96 % and 64 % removal of cesium ions is observed for the initial concentrations of 0.5 and 10 mM, respectively, during this time period (Fig. 3.8(b)). Such short times, coupled with high % removals, indicate a high degree of affinity of the RF beads for the cesium ions, pointing
towards chemisorption. The decrease in sorption rate is observed with increase in contact time, and gradually, sorption reaches equilibrium value in about 3 to 6 hours, depending on the initial cesium ion concentration. For cesium ion solution, with initial concentrations of 5 mM, the contact time of 5 hours is sufficient to attain equilibrium. The time required to attain the state of equilibrium is termed as the equilibrium time, and the amount of cesium ions sorbed at the equilibrium time reflects the maximum cesium sorption capacity of the sorbent, under these particular conditions.

Fig. 3.8: Effect of contact time on (a) the sorption capacity, and (b) the percentage removal of cesium ions by RF resin beads, at different cesium ion concentrations

Various kinetic models have been proposed, to determine the mechanism of the sorption process, which provides useful data, to improve the efficiency of the sorption and feasibility of scale-up of the process. In order to analyze the sorption kinetics of cesium ions onto RF resin, the pseudo first-order, pseudo second-order, and intraparticle diffusion models, given by equations (3.8), (3.9) and (3.10), respectively, were used.

\[
\log (q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \\
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \\
q_t = k_{id} t^{1/2} + I
\]

(3.8) (3.9) (3.10)
where \( q_t \) is the amount of the cesium ions sorbed at time \( t \), \( k_1 \), \( k_2 \) and \( k_{id} \) are the rate constants of the pseudo first-order, the pseudo second-order sorption and the intraparticle diffusion model, respectively, and \( I \) gives an idea about the boundary layer thickness.\textsuperscript{156}

Fig. 3.9: Pseudo first-order kinetic plots for sorption of cesium ions onto the RF resin

Fig. 3.9 shows the plots of log \((q_e - q_t)\) vs \( t \), for sorption of cesium ions onto the RF resin, along with the fitted straight lines. The values of the pseudo first-order sorption rate constant \( (k_1) \) for the sorption of cesium ions onto RF resin, and the sorption capacity \( (q_e) \) were determined from the slopes and the intercepts, respectively, of the corresponding straight lines of the Fig. 3.9. The parameters of the pseudo first-order model are summarized in Table 3.2. Although the correlation coefficient, \( R^2 \), for the application of the pseudo first-order model is reasonably high in some cases, the calculated \( q_e \) values do not match with the experimental \( q_e \) values, suggesting that the sorption of cesium ions onto the RF resin does not follow the pseudo first-order kinetics, at the studied initial concentrations of cesium ions.
The kinetic data were further analyzed, using the pseudo second-order relation proposed by Ho and McKay,\textsuperscript{156} equation (3.9). Fig. 3.10 shows the plots of \( t/q_t \) vs \( t \), for the sorption of cesium ions onto the RF resin beads, along with the fitted straight lines. From the slope of the straight line, the corresponding value of the sorption capacity, \((q_e)\) can be determined. Once the value of \( q_e \) is known, the rate coefficient \( k_2 \) can be determined from the intercept of the straight line.

**Table 3.2:** Comparison of the kinetic constants and the calculated and the experimental \( q_e \) values for the sorption of cesium ions onto the RF resin beads at different initial concentrations

<table>
<thead>
<tr>
<th>( C_0 ) (mM)</th>
<th>Pseudo first-order kinetic model</th>
<th>Pseudo second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{e,\text{exp}} ) (mmol/g)</td>
<td>( k_1 ) (/h)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.049</td>
<td>0.901</td>
</tr>
<tr>
<td>5.0</td>
<td>0.461</td>
<td>0.736</td>
</tr>
<tr>
<td>10.0</td>
<td>0.805</td>
<td>0.652</td>
</tr>
</tbody>
</table>

**Fig. 3.10:** Pseudo second-order kinetic plots for sorption of cesium ions onto the RF resin

It is evident from these results that the correlation coefficients for the pseudo first-order kinetics model, obtained at all the studied concentrations, are a bit lower than those
for the pseudo second-order model. Moreover, the theoretical q_e values calculated from the pseudo second-order kinetic model are closer to the experimentally determined q_e values, whereas the theoretical q_e values obtained from the pseudo first-order model do not seem to be reasonable. These results indicate that the sorption of cesium ions onto the RF resin beads is chemisorption, and follows pseudo second-order kinetics. From Table 3.2, it is observed that the pseudo-second-order rate constant (k_2) decreases significantly with the increase in the initial cesium concentration.

### 3.5.1.5 Mechanism

In order to identify the sorption mechanism, the intraparticle diffusion model, equation 3.10, proposed by Weber and Morris, was applied to the kinetic data. According to this theory, if the intraparticle diffusion is followed, then, the plot of q_t vs t^{1/2} plot will be linear, and if this straight line passes through origin, then, only the intraparticle diffusion can be considered as the rate limiting step, otherwise, some other mechanism may also be involved. Fig. 3.11 shows the plots of q_t vs. t^{1/2}, for various initial cesium ion concentrations. These plots are multilinear. The value of k_id and I can be determined from the slope and intercept, respectively, of the second linear portion of the corresponding plot. The values of intraparticle diffusion rate constant and I values are given in Table 3.3, for the different initial concentrations of cesium ions.

It can be seen from Table 3.3 that the R^2 values are >0.92, but the plots do not pass through the origin, suggesting that sorption involves intraparticle diffusion, though that is not the only rate-controlling step. Other kinetic steps also may govern the sorption rate. The value of the intraparticle diffusion rate constant, k_id, for the studied system, is observed to increase with increase in the initial cesium ion concentration, from 0.5 to 10
mmol/L. The boundary layer thickness also increases with increase in the initial cesium ion concentration.

Table 3.3: Intraparticle diffusion parameters at different initial cesium ion concentrations, for its sorption onto the RF resin beads

<table>
<thead>
<tr>
<th>Initial conc. (mg/L)</th>
<th>k_{id} (mmol/g h^{1/2})</th>
<th>I (mmol/g)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.001</td>
<td>0.048</td>
<td>0.93885</td>
</tr>
<tr>
<td>5.0</td>
<td>0.039</td>
<td>0.368</td>
<td>0.91901</td>
</tr>
<tr>
<td>10.0</td>
<td>0.137</td>
<td>0.475</td>
<td>0.97996</td>
</tr>
</tbody>
</table>

In order to predict whether the sorption proceeds via film diffusion or intraparticle diffusion mechanism, the kinetic data were further analyzed, using the kinetic expression given by Boyd et al.\textsuperscript{146}

\[
Bt = 2\pi - \frac{\pi^2 F}{3} - 2\pi(1 - \frac{\pi F}{3})^{1/2} \quad (3.11)
\]

\[
Bt = -0.4977 - \ln (1 - F) \quad (3.12)
\]

The value of Bt was calculated for each value of F, using equation (3.11), for F values upto 0.85, and equation (3.12), for F values higher than 0.85.\textsuperscript{147} The calculated Bt values
are plotted against time (Fig. 3.12). The linearity of this plot provides useful information to distinguish between the film diffusion and the intraparticle-diffusion rates of sorption. A straight line passing through the origin is indicative of sorption process governed by intraparticle diffusion mechanism. In the present case, all the plots are linear, with $R^2$ value >0.98, in the whole studied initial concentration range, but do not pass through the origin, indicating that the sorption process is of complex nature, consisting of both film diffusion and intraparticle diffusion steps, with film diffusion mainly governing the rate-limiting process in the studied solute concentration range.

![Fig. 3.12: Boyd’s plots for sorption of cesium ions onto the RF resin beads](image)

**3.5.2 RF-XAD Resin beads**

**3.5.2.1 Characterization**

**3.5.2.1.1 Optical microscopy and SEM studies**

Figs. 3.13 and 3.14 represent the optical microscope and SEM images of the XAD and RF-XAD beads, respectively, and confirm the coating of RF on the pre-formed XAD beads. The SEM image (Fig. 3.14 (a)) of the outer surface of a RF-XAD bead shows
porosity. This porous nature of the beads, which is also corroborated from the results of the TGA study discussed ahead, is a desirable feature, as it will contribute to better sorption behavior. The SEM image of a cross-section of the RF-XAD bead does not show any distinct boundary, or contact between the RF coating and the XAD template, indicating that the RF has penetrated inside the XAD-4 beads (Fig. 3.14 (b)). This supports the observations from the studies on the testing of the mechanical strength of the beads.

![Fig. 3.13: Optical microscope image of (a) XAD beads and (b) RF-XAD beads (10X magnification)](image)

![Fig. 3.14: SEM image of (a) the surface and (b) the cross-section of RF-XAD bead (scale bar 500 nm)](image)

**3.5.2.1.2 Mechanical strength testing**

Mechanical strength of the synthesized RF-XAD beads was tested, and compared with that of the conventional ground RF gel particles and the blank XAD beads, using
universal testing machine. The XAD blank beads showed the first breakage at an applied load of 2 N, and second breakage at 4 N; at this stage, the XAD bead was completely compressed, and no machine extension was observed for even higher applied load. Spherical RF-XAD beads showed the first break at a load of 13-15 N, for the different samples tested, while the same for the ground RF gel was observed at 2.5-5 N. The increase in the mechanical strength of RF-XAD beads suggests that, the RF is present not only on the surface of the XAD template beads, but it has also penetrated in the pores of the XAD beads, and solidified. This observation supports the results from BET surface area analysis discussed subsequently. The synthesized RF-XAD beads are spherical in size, and have better mechanical strength as compared to that of the currently used ground RF resin gel particles, making these more suitable for column operation.

3.5.2.1.3 Thermogravimetric analysis

Thermo gravimetric analysis (TGA) of the synthesized RF-XAD beads was performed at a heating rate of 10°C/min, in nitrogen atmosphere, from ambient conditions to 900 °C. Fig. 3.15 shows typical TGA profiles of the granular RF gel, XAD and RF-XAD beads. The thermal decomposition profile of pure granular RF particles is continuous, and unlike that of XAD and RF-XAD beads, it does not show well-defined decomposition steps (trace a, Fig. 3.15). After heating upto 110 °C, a weight loss of about 8% is observed, which could be due to the absorbed water. Additional 7% weight loss is observed upto 216 °C, which could be due to decomposition of RF. With further increase in temperature, a continuous decrease in the weight takes place, and at the end of the heating cycle, a charred mass is obtained, which is about 37% of the initial weight taken. The thermal decomposition of XAD beads takes place in two major steps (trace b, Fig. 3.15). In the first step, (30 to 86 °C), there is a weight loss of 8.7 %, corresponding to
evaporation of the sorbed water. Then, the second step starts at 343 °C, in which degradation of XAD matrix takes place, and additional weight loss of ~72 % is observed at the end of this step at 560 °C. The TGA profile of RF-XAD beads (trace c, Fig. 3.15) also can be divided into two main stages. The first stage is from 30 to 118 °C, over which a weight loss of about 36% is observed, due to dehydration. The weight loss in the same range of 343-560 °C, as that in the case of XAD beads, is of about 38 %, due to simultaneous degradation of RF and XAD. The TGA profiles of XAD and RF-XAD appear similar, but the extent of thermal degradation of the composite beads is much lower than that of the XAD beads, and the water content in the blank XAD is less than that in the RF-XAD beads.

![TGA profiles of (a) granular RF gel, (b) XAD beads and (c) RF-XAD beads](image)

**Fig. 3.15:** TGA profiles of (a) granular RF gel, (b) XAD beads and (c) RF-XAD beads

The enhanced thermal stability of the composite beads can be attributed to the presence of RF, which is more thermally stable than XAD. In addition, the factors, such as the RF coating affecting the release of the gases from the XAD core, and the
difference in the heat transfer behavior due to the new surface, may also be contributing, to some extent. The higher water content indicates hydrophilic and porous nature of the RF coating. These characteristics of the RF-XAD beads improve efficiency of Cs$^+$ ion sorption, from alkaline aqueous waste.

### 3.5.2.1.4 BET surface area

The specific surface area and the pore volume of the beads were determined by BET N$_2$ sorption method, as described earlier. The surface area was found to be 170 m$^2$/g, and the pore volume was found to be 0.19 cc/g. The pore radius was determined to be ~20 Å, confirming mesoporous nature of the synthesized beads. The surface area of the blank Amberlite XAD-4 beads, as per specifications, is 750 m$^2$/g, with an average pore diameter of 100 Å. The reduction in the surface area and the pore diameter of the template beads in the RF-XAD beads suggest the presence of the RF inside the pores also.

### 3.5.2.1.5 Ion-Exchange Capacity

The ion exchange capacity of the RF-XAD beads was determined by the method described in section 3.5.1.1.4. From the amount of NaOH consumed, the total H$^+$-Na$^+$ ion-exchange capacity was found to be 2.35 milliequivalents/g, i.e., 2.35 mmol/g of air-dried, H$^+$-form RF-XAD resin. The capacity of the template XAD-4 beads was also tested, using $^{134}$Cs radiotracer, and it was confirmed that blank XAD-4 beads do no pick up cesium ions from aqueous solution.

### 3.5.2.2 Sorption studies

#### 3.5.2.2.1 Effect of Na$^+$ ion concentration

The competitive effect of Na$^+$ ions on the sorption of Cs$^+$ ions onto the RF-XAD beads was investigated, by varying Na$^+$ ion concentration, at a constant Cs$^+$ ion
concentration of 0.02 M, at 300 K. The solutions were prepared in aqueous 0.1 M NaOH, and the concentration of Na\(^+\) ions was varied, using NaNO\(_3\), as a source of Na\(^+\) ions. The batch distribution coefficient (K\(_d\)) was calculated, using equation (3.13)

\[ K_d = \frac{A_0 - A}{A} \times \frac{V}{m} \]  

(3.13)

where \(A_0\) and \(A\) are the initial and the final activities, respectively, of the solution, \(V\) is the volume of equilibrating solution (10 ml), and \(m\) is the weight of the resin beads taken (0.1 g).

**Fig. 3.16:** Effect of the Na\(^+\) ion concentration on the sorption of Cs\(^+\) ions (at 0.02 M) onto the RF-XAD beads at 300 K

### 3.5.2.2.2 Effect of Cs\(^+\) ion concentration

The sorption capacity of the RF-XAD beads for cesium ions was determined, by studying the sorption as a function of cesium ion concentration, at 300 K, in a batch experiment. The concentration of inactive cesium ions in the aqueous solution was increased from 0.1 to 250 mM, and the \(q_e\) was determined. It is observed that, \(q_e\)
increases gradually with increase in cesium ion concentration, and reaches a saturation value of ~1.5 mmol/g at 250 mM, as shown in Fig. 3.17. The initial concentration provides an important driving force, to overcome all the mass transfer resistances to the Cs\(^+\) ions between the aqueous and the solid phases. Therefore, a higher initial Cs\(^+\) ion concentration will enhance the sorption process. The observed results can be explained by the fact that, with increase in concentration, the incremental increase in cesium ion uptake by sorbent will be more initially, as a large number of active sites are available, but, with further increase in concentration it decreases, as the number of the available active sites decreases, and finally, it becomes zero.

![Graph](image.png)

**Fig. 3.17:** Effect of the initial metal ion concentration on the sorption of Cs\(^+\) ions onto the RF-XAD beads at 300 K

### 3.5.2.3 Sorption isotherms

To evaluate the nature of the sorption, the data were fitted to the Langmuir and the Freundlich isotherm models, equations (3.6) and (3.7), respectively. The plot of \(1/q_e\) vs \(1/C_e\) for sorption of cesium ions onto the RF-XAD beads is a straight line (Fig. 3.18).
The value of correlation coefficient $R^2$ is 0.9981, which indicates a good agreement between the experimental data and the Langmuir sorption model. The maximum sorbing capacity of the RF-XAD beads, for Cs$^+$ ions, is determined to be 2.17 mmol/g, i.e., 287 mg/g of the resin. The sorption coefficient, $K_L$, which is related to apparent energy of sorption of Cs$^+$ ions onto the RF-XAD, is determined to be 0.66 L/mmol. The high sorption capacity of the synthesized beads can be attributed to the high surface area of the RF-XAD beads.

![Langmuir isotherm plot for sorption of Cs$^+$ ions onto the RF-XAD beads, at 300 K](image)

**Fig. 3.18:** Langmuir isotherm plot for sorption of Cs$^+$ ions onto the RF-XAD beads, at 300 K

The favorability of sorption of Cs$^+$ ions onto the RF-XAD beads can be expressed in terms of a dimensionless constant, ($R_L$), called separation factor, using the essential features of the Langmuir isotherm, as given below

$$R_L = \frac{1}{1 + K_L C_0}$$  \hspace{1cm} (3.14)
The calculated values of $R_L$ are less than one (in the range of 0.94 to 0.15), indicating that the RF-XAD beads are good sorbent for $\text{Cs}^+$ ions, and the sorption process is favorable for efficient removal of $\text{Cs}^+$ ions from alkaline aqueous waste solutions.

The data were also analyzed, using the Freundlich isotherm, and from the slope and the intercept of $\log (q_e)$ vs $\log (C_e)$ straight line, the values of $1/n$ and $K_F$, respectively, were determined (Fig. 3.19). The correlation function value $R^2$ for this plot is 0.9302, which suggests that the correlation between the experimental data and the Freundlich isotherm model is not as good as that of the Langmuir sorption model. The different sorption parameters, obtained by fitting the experimental data to both the models, are given in Table 3.4.

![Fig. 3.19: Freundlich isotherm plot for the sorption of $\text{Cs}^+$ ions onto the RF-XAD beads at 300 K](image-url)
Table 3.4: Langmuir and Freundlich isotherm parameters, for sorption of cesium ions onto the RF XAD beads

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$</td>
<td>2.17 mmol/g</td>
</tr>
<tr>
<td></td>
<td>$K_L$</td>
<td>0.66 L/mmol.</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.99815</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>136 mmol/g</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.93023</td>
</tr>
</tbody>
</table>

3.5.2.4 Sorption kinetics

The kinetics of sorption describes the law governing the rate of the sorbate uptake by the sorbent, and this rate governs the equilibrium time. The kinetics of an sorbate uptake is required for selecting optimum operating conditions for the full-scale batch process. Therefore, the effect of equilibration time on the sorption of cesium ions, from aqueous solutions, was also studied. The sorption increases with increase in contact time (Fig. 3.20).

The uptake of Cs$^+$ ions is rapid in the initial 2 hours, and the equilibrium is reached in ~4 hours, indicating a quite fast sorption rate. The initial rapid sorption can be related to the abundant availability of the active sites in the initial stage. Later on, as both the availability of the sites and the concentration of the solute decrease, the process becomes relatively slower, and equilibrium conditions are reached in about 4 hours. At this point, the amount of the cesium ions being sorbed onto the sorbent is in dynamic equilibrium with the amount of the cesium ions desorbing from the sorbent. The time required to attain this equilibrium is termed as the equilibrium time, and the amount of cesium ions sorbed at the equilibrium time is the equilibrium sorption capacity of the sorbent under those operating conditions. As the equilibrium stage is attained in 4 hours, further batch experiments, for uptake determination, were carried out at 4 hours of
equilibration time. The experimental $q_e$ values, at the three studied concentrations of 100, 500 and 1000 $\mu$M, were found to be 6.7, 23.8 and 36.8 $\mu$mol/g, respectively.

![Figure 3.20](image)

**Fig. 3.20:** The effect of equilibration time on the sorption of $\text{Cs}^+$ ions onto the RF-XAD beads, at three different initial concentrations

In order to investigate the sorption process of cesium ions onto the RF-XAD beads, three kinetic models, namely, pseudo-first-order (equation (3.8)), pseudo-second-order (equation (3.9)), and intraparticle diffusion models (equation (3.10)), were used. Fig. 3.21 depicts the pseudo first-order plots for the sorption of cesium ions onto the RF-XAD beads. The data were fitted, with correlation coefficient values in the range of 0.81 to 0.98, depending on the initial concentration, which indicates that the rate of sorption of cesium ions onto the RF-XAD beads cannot be explained by the pseudo first-order kinetic model, for the entire studied range of the initial cesium ion concentration. The $q_e$ values obtained from this model, 3.33, 12.54 and 12.08 $\mu$mol/g, respectively, at the three studied initial concentrations of 100, 500 and 1000 $\mu$M, are significantly lower than the
corresponding experimental $q_e$ values of 6.7, 23.8 and 36.8 μmol/g. the results are listed in Table 3.5.

![Graph showing pseudo first-order plots for sorption of Cs$^+$ ions onto the RF-XAD beads, at three different initial Cs$^+$ ion concentrations.](image1)

**Fig. 3.21:** Pseudo first-order plots for sorption of Cs$^+$ ions onto the RF-XAD beads, at three different initial Cs$^+$ ion concentrations.

![Graph showing pseudo second-order plots for the Cs$^+$ ion sorption onto the RF-XAD beads at three different initial concentrations of Cs$^+$ ions](image2)

**Fig. 3.22:** Pseudo second-order plots for the Cs$^+$ ion sorption onto the RF-XAD beads at three different initial concentrations of Cs$^+$ ions
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Pseudo second-order plots for the Cs$^+$ ion sorption are shown in Fig. 3.22. The parameters obtained from the plots are given in Table 3.5. It is clear that $k_2$ decreases with increase in the initial Cs$^+$ ion concentration. The values of $R^2$ for the pseudo second-order kinetic model are higher than that for the pseudo first-order kinetic model, for all the studied concentrations of cesium ions. And, the values of $q_e$ calculated, using this model, are also in good agreement with the actual experimental values. Therefore, this model can be applied to the sorption process in the entire studied concentration range, and it can be concluded that the sorption process obeys pseudo second-order kinetics.\textsuperscript{152}

3.5.2.5 Mechanism

The experimental data were further analyzed using the intraparticle diffusion model, equation (3.10). Fig. 3.23 shows that the plots of $q_t$ vs $t^{1/2}$ are multilinear, and hence, intraparticle diffusion is also involved in the sorption process. The value of $K_{id}$ is calculated from the slope of the second stage, and its value, for the studied system, is found to increase with increase in the initial concentration, from 100 to 1000 $\mu$mol /L. The boundary layer also increases with increase in the initial cesium ion concentration. In order to predict whether sorption proceeds via film diffusion or intraparticle diffusion mechanism, the kinetic data were further analyzed, using the solutions, equations (3.11 and 3.12), of the kinetic expression given by Boyd et al. On plotting the calculated values of $B_t$ vs $t$, as per Boyd’s equation, it is found that the fitted lines, for all the concentrations studied, do not pass through origin, indicating that the sorption process is mainly governed by the film diffusion (Fig. 3.24).
**Fig. 3.23:** Intraparticle diffusion plots for sorption of Cs\(^+\) ions onto the RF-XAD beads at three different initial concentrations of Cs\(^+\) ions

**Fig. 3.24:** Boyd’s plots for sorption of Cs\(^+\) ions onto the RF-XAD beads at three different initial concentrations of Cs\(^+\) ions
### Table 3.5: Kinetic parameters of the different models for the sorption of cesium ions onto the RF-XAD resin beads at different initial cesium ion concentrations

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Parameters</th>
<th>100 μM</th>
<th>500 μM</th>
<th>1000 μM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>experimental</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>q&lt;sub&gt;e&lt;/sub&gt; (μmol/g)</td>
<td>6.7</td>
<td>23.8</td>
<td>36.8</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;1&lt;/sub&gt; (hr&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.51</td>
<td>0.44</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>0.9777</td>
<td>0.8084</td>
</tr>
<tr>
<td>Pseudo-2&lt;sup&gt;nd&lt;/sup&gt; order</td>
<td>q&lt;sub&gt;e&lt;/sub&gt; (μmol/g)</td>
<td>3.33</td>
<td>12.54</td>
<td>12.08</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;2&lt;/sub&gt; (g μmol&lt;sup&gt;-1&lt;/sup&gt; hr&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.27</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.9989</td>
<td>0.9973</td>
<td>0.9982</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>k&lt;sub&gt;id&lt;/sub&gt; (g μmol&lt;sup&gt;-1&lt;/sup&gt; hr&lt;sup&gt;-1/2&lt;/sup&gt;)</td>
<td>2.2</td>
<td>8.09</td>
<td>10.68</td>
</tr>
<tr>
<td></td>
<td>I (μmol/g)</td>
<td>2.36</td>
<td>7.13</td>
<td>16.90</td>
</tr>
<tr>
<td></td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.9876</td>
<td>0.9995</td>
<td>0.9818</td>
</tr>
</tbody>
</table>

### 3.5.3 RF<sup>A</sup> resin beads

#### 3.5.3.1 Characterization

#### 3.5.3.1.1 Optical microscope and SEM studies

Figs. 3.25(a) and (b) represent the optical microscope images of the alginate and RF<sup>A</sup> beads, respectively, confirming the loading of RF on the pre-formed alginate beads. Fig. 3.25(c) shows the SEM image of the outer surface of the RF<sup>A</sup> beads. On the surface itself, long connecting channel-like features are visible. These channels may provide better accessibility to the exchangeable sites, which will ultimately lead to better sorption properties.
3.5.3.1.2 Mechanical strength testing

Mechanical strength of the synthesized RF\textsuperscript{A} beads was analyzed, employing universal testing machine, and it was observed that spherical RF\textsuperscript{A} beads showed first break at a load of 24-29 N, for the different samples tested. Thus, the mechanical strength of the RF\textsuperscript{A} beads is much better as compared to the ground gel particles currently in use, having first break at much lower load of 4-5 N, as mentioned earlier. From the mechanical strength studies, it can be concluded that the RF\textsuperscript{A} beads are more appropriate for column operation.

3.5.3.1.3 Thermogravimetric analysis

Thermo gravimetric analysis (TGA) of the synthesized beads was performed at a heating rate of 10 °C/min, in nitrogen atmosphere, from ambient conditions upto 700 °C. TGAs of the RF ground gel and the synthesized RF\textsuperscript{A} beads were carried out, using the
prepared material as it is, without any pre-treatment, whereas that of the alginate beads was carried out, after just removing the surface water present on the swollen beads, using a filter paper. Fig. 3.26 shows typical TGA profiles of the alginate beads, RF ground gel and RF\textsuperscript{A} beads. The thermal degradation of the blank alginate beads occurs in two steps (Fig. 3.26, trace a). In the first step, (30 °C to 110 °C), there is a weight loss of ~62 %, which is due to the loss of the absorbed water. Then, an additional weight loss of 3.7 %, due to thermal degradation of alginate, is observed in the temperature range 200-700°C. Fig. 3.26, trace b shows degradation of the RF ground gel. The thermal decomposition of RF ground gel does not have clear degradation steps, but only a gradual degradation profile. The weight loss (~9 %) observed upto 110 °C may be due to the absorbed water. Then, a continuous weight loss is observed till the highest temperature investigated. TGA profile of the RF\textsuperscript{A} beads (Fig. 3.26, trace c), too, has the same features as that of the RF ground gel, and does not show any well-defined degradation steps. After heating upto 110 °C, a weight loss of ~ 9 % is observed, which could be due to the absorbed water. The TGA profiles of the RF ground gel and the RF\textsuperscript{A} beads are overlapping till 200 °C, and after that, a slightly more % weight loss is observed for the RF\textsuperscript{A} beads, as compared to that for the RF ground gel in the temperature range of 200 to 473 °C. This could be due to the simultaneous decomposition of the remaining alginate, along with that of RF. But, at the end of 700°C, about 46% of the total weight is left as charred residue, in the case of RF, as compared to 41 %, in the case of RF ground gel. Similar nature of the TGA profiles of the RF ground gel particles and the synthesized RF\textsuperscript{A} beads indicates the presence of negligible amount of alginate in the synthesized beads.
Ion-exchange capacity and BET surface area

The total H\(^+\)-Na\(^+\) ion-exchange capacity of the beads was determined to be 2.84 milliequivalents/g, i.e., 2.84 mmol/g of air-dried H\(^+\) form of the RF\(^A\) resin. The specific surface area and the pore volume of the beads were determined by BET N\(_2\) sorption method. The surface area was found to be 568.45 m\(^2\)/g, and the pore volume was found to be 0.19 cc/g. The observed high surface area of the synthesized beads supports the observations from SEM studies.

Sorption studies

Effect of Na\(^+\) ion concentration

From Fig. 3.27, it is observed that, in the studied concentration range 0.1-3.0 M, q\(_e\) decreases abruptly with increase in the Na\(^+\) ion concentration upto 1 M. After that, the q\(_e\) value remains almost unaffected upto 2.0 M Na\(^+\) ion concentration. Thereafter, further decrease of q\(_e\) value to 46.47 mg/g is observed. These results indicates that the q\(_e\) value for cesium ion is affected by presence of Na\(^+\) ion in the solution due to the competitive
sorption of Na\textsuperscript{+} ions onto the available exchange sites. The capacity of the RF\textsuperscript{A} beads, even at 3.0 M NaOH is enough to remove/extract cesium ions from aqueous solution.

![Graph showing the effect of Na\textsuperscript{+} ion concentration on the removal of cesium ions](image)

**Fig. 3.27:** Effect of the Na\textsuperscript{+} ion concentration on the removal of cesium ions

### 3.5.3.2.2 Effect of cesium ion concentration

The sorption capacity of the RF\textsuperscript{A} beads for cesium ions was determined, by studying the sorption as a function of cesium ion concentration, at 300 K, in a batch experiment. The concentration of inactive cesium ions in the aqueous solution was increased from 5 to 400 mM, and the q\textsubscript{e} was determined. It is observed that, initially, q\textsubscript{e} increases almost linearly, with increase in Cs\textsuperscript{+} ion concentration, because the available active sites on the sorbent are sufficient, and the amount of cesium ions sorbed depends on the number of cesium ions transported from bulk to the sorbent. But, with further increase in the cesium ion concentration, the number of available active sites decreases, and consequently, the incremental increase in q\textsubscript{e} drops exhibiting deviation from linearity in the q\textsubscript{e} vs C\textsubscript{o} plot. An equilibration value of \(~326\) mg/g is obtained at 400 mM, as shown in Fig. 3.28. The initial concentration provides an important driving force, to
overcome all the mass transfer resistances to the Cs\(^+\) ions between the aqueous and the solid phases. Therefore, a higher initial Cs\(^+\) ion concentration will enhance the sorption process.

![Figure 3.28](image.png)

**Fig. 3.28:** Effect of the initial metal ion concentration on sorption of Cs\(^+\) ions onto the RF\(^A\) beads at 300 K

### 3.5.3.3 Sorption isotherms

The sorption isotherm data were further analysed, using the Langmuir and the Freundlich isotherm models, equations (3.3) and (3.4), respectively. Figs. 3.29 (a) and (b) show the Freundlich and the Langmuir isotherm plots, respectively, along with the fitted straight lines. From these figures, it is observed that the equilibrium data fit to the Freundlich and Langmuir expressions, with a correlation coefficient values of 0.631 and 0.994, respectively. The higher correlation coefficient of 0.994 for the Langmuir isotherm shows that the sorption process conforms to the Langmuir isotherm, which predicts monolayer coverage of cesium ions onto the RF\(^A\) resin. Table 3.6 gives the results of the fitting of the sorption data to the Langmuir and the Freundlich isotherm models, after 4
hours of equilibration. Based on the Langmuir model, the maximum sorption capacity $q_m$ (mg/g) of the RF$^A$ beads for sorption of cesium is 490.2 mg/g.$^{153}$

![Graph](image)

**Fig. 3.29:** (a) Freundlich and (b) Langmuir isotherm plots for sorption of Cs$^+$ ions onto the RF$^A$ beads at 300 K

The predicted Langmuir isotherm equation, for sorption of cesium onto the RF$^A$ at 300 K, useful for design calculations, is given by

$$\text{Langmuir: } q_e = \frac{23.04C_e}{1+0.047C_e}$$

(3.13)

| Table 3.6: Sorption isotherm constants for sorption of cesium ions onto the RF$^A$ beads |
|-----------------|-----------------|----------------|----------------|
| $K_F$ (mmol/g)  | $1/n$           | $R^2_{\text{(Freundlich)}}$ | $K_L$ (L/mmol) |
| 5.46            | 0.3902          | 0.631            | 0.047          |
|                 |                 |                  | 490.2 mg/g    | 0.994          |

**3.5.3.4 Sorption kinetics**

Fig. 3.30 shows the effect of contact time on the removal of cesium ions at different initial cesium ion concentrations. It is observed that the % removal of cesium ions decreases with increase in the initial cesium ion concentration. For a contact time of 4 hours, the % cesium ion removal decreases from 87.7% to 15.4%, for an increase in the initial Cs$^+$ ion concentration from 0.5 to 5 mM. Also, from the figure, it is observed that, at all the studied initial cesium ion concentrations, the rate of removal of Cs$^+$ ions is very rapid for the initial period of about 90 min, and thereafter, the sorption rate decreases, and
finally, becomes negligible after about 240 min. This is due to the combined effect of the decrease in flux (concentration gradient) with time due to transfer of the solute onto the solid phase, and availability of lesser vacant sorption sites.

![Lagrenge kinetic plots](image)

**Fig. 3.30:** The effect of equilibration time on the sorption of Cs\(^+\) ions onto the RF\(^A\) beads at different initial Cs\(^+\) ion concentrations

Fig. 3.31 shows the Lagergren pseudo first-order kinetic plots, equation (3.8), at two initial cesium ion concentrations of 0.5 and 5 mM. It is observed that Lagergren first-order kinetic model describes the sorption process well only for the first 90 min, at both the initial cesium ion concentrations, and thereafter, the sorption deviates from the model, more so, at the lower studied concentration. In other words, the sorption data are well represented by the model only in the region where rapid sorption takes place, i.e., for the first 90 min. Ho and McKay\(^{143}\) too, reported that the sorption data were represented well by the Lagergren first-order kinetic model only for the rapid initial time period. This confirms that it may not be appropriate to use only the Lagergren first-order kinetic model, to describe sorption of cesium ions onto the RF\(^A\) resins over the entire sorption
period and at all the initial concentrations. The parameters and the coefficients obtained, by applying the pseudo first-order kinetic model to the experimental data, are given in Table 3.7.

![Fig. 3.31: Pseudo first-order kinetic plots for the sorption of Cs\(^+\) ions onto the RF\(^A\) beads, at two different initial Cs\(^+\) ion concentrations](image-url)

Fig. 3.32 shows the pseudo second-order kinetic plots, equation (3.9), for the sorption of cesium ions onto the RF\(^A\) beads at the two different initial concentrations of cesium ions. The results show that, at lower initial cesium ion concentration, i.e., 0.5 mM, \(R_2^2\) value is found to be higher than that for the pseudo first-order kinetic plot, whereas the \(R_2^2\) value for the higher concentration (5 mM) is less than that for pseudo first-order kinetic plot. Moreover, the value of \(q_e\) calculated from the pseudo second-order plot is in agreement with the experimental \(q_e\) value of 7.93 mg/g at 0.5 mM initial cesium ion concentration. But, the \(q_e\) value calculated from the pseudo first-order plot is closer to that determined experimentally (45.3 mg/g) for 5 mM initial cesium ion concentration (Table 3.7). These observations suggest that the sorption process is
explained best by pseudo second-order kinetics at the lower initial cesium ion concentration, whereas at the higher initial cesium ion concentration, pseudo first-order kinetics is followed\textsuperscript{153, 157}.

![Graph showing pseudo second-order kinetic plot for sorption of cesium ions onto the RF\textsuperscript{A} beads, at two different initial Cs\textsuperscript{+} ion concentrations](image)

**Fig. 3.32:** Pseudo second-order kinetic plot for sorption of cesium ions onto the RF\textsuperscript{A} beads, at two different initial Cs\textsuperscript{+} ion concentrations

### 3.5.3.5 Mechanism

The intraparticle diffusion plots for the sorption of cesium onto the RF\textsuperscript{A} beads, as given in Fig. 3.33, for the different initial concentrations of cesium ions, show multilinearity. The first linear portion is followed by a second linear portion, representing the different stages in the sorption, followed by the intraparticle diffusion of the cesium ions onto the RF\textsuperscript{A} beads. The intraparticle diffusion parameter, K\textsubscript{id}, at the two studied initial concentrations, is determined from the slope of the corresponding second linear region of the Fig. 3.33, whereas the intercept of this second linear portion gives an idea about the boundary layer thickness. The calculated K\textsubscript{id} and I values at different cesium ion concentrations are given in Table 3.7.
Table 3.7: Kinetic constants for the sorption of cesium ions onto the RF\textsuperscript{A} beads

<table>
<thead>
<tr>
<th>$C_0$, (mM)</th>
<th>Pseudo first-order model</th>
<th>Pseudo second-order model</th>
<th>Intraparticle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$, min(^{-1})</td>
<td>$R_1^2$</td>
<td>$q_{e,cal}$ (mg/g)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.024</td>
<td>0.7172</td>
<td>5.21</td>
</tr>
<tr>
<td>5.0</td>
<td>0.013</td>
<td>0.9634</td>
<td>50.00</td>
</tr>
</tbody>
</table>

As can be seen from Fig. 3.33, the plots of $q_t$ vs $t^{1/2}$, for both the concentrations, are neither straight line nor pass through origin. This indicates some degree of boundary layer control, and also that, the intraparticle diffusion is not the only rate-limiting step, but other kinetic processes also may govern the rate of sorption, all of which may be operating simultaneously. Therefore, in order to find what the actual rate-controlling step, involved in the cesium ion sorption process, is, the sorption data were further analyzed by the kinetic expression given by Boyd et al., the solutions of which are given by equations (3.11 and 3.12). The calculated values of $B_t$ were plotted against time.
(Fig. 3.34). In the present case, the plots are non linear, and do not pass through the origin, indicating that, the sorption process is of complex nature, consisting of both film diffusion and intraparticle diffusion steps, and film diffusion being mainly the rate-limiting process for the studied solute concentration range.

![Graph](image)

**Fig. 3.34**: Boyd’s plots for the sorption of cesium ions onto the RF$^A$ beads at two different initial cesium ion concentrations

### 3.5.3.6 Desorption studies

Desorption experiments of the sorbed cesium ions were carried out, using 0.5M HNO$_3$. First, 0.5 mM alkaline solution of cesium ions was equilibrated with the synthesized resin beads, for 4 hours, keeping V/m ratio same as in the other experiments. The sorbed cesium ions were then eluted, by equilibrating the resin with 5 ml of 0.5 M HNO$_3$ solution, and suitable aliquots of this solution were counted at different intervals of time. It was observed that, in ~ 10 min of elution time, 100% desorption of the sorbed
cesium from the RF\textsuperscript{A} beads was achieved. This indicates that the beads can be regenerated, and complete recovery of the sorbed cesium is possible.

### 3.6 Comparison of the Resin Beads

Three different methods have been developed for the synthesis of RF resin directly in the spherical beads form. In the first method, spherical RF beads have been synthesized by suspension polymerization, using a suitable polymer solution, both as a suspension media and a protective polymer. In the other two methods, pre-formed beads of XAD-4 and calcium alginate were used as templates. The difference in the use of the two templates is that, in the case of alginate template, a negligible amount of alginate is retained in the final product, and the RF resin beads obtained are almost pure. From the TGA profile of the RF\textsuperscript{A} beads also, it is clear that the TGA profile of RF\textsuperscript{A} is almost similar to that of the RF particles, and hence, the effective presence of alginate in the final product is negligible. On the other hand, RF-XAD beads are actually composite beads, in which RF is present only on the surface, and in the pores of the XAD beads.

The surface area of the different resin beads increases in the order RF-XAD < RF< RF\textsuperscript{A}. During the synthesis of the RF-XAD beads, the RF pre-condensate penetrates in the pores inside, in addition to that on the surface of the template, and gets solidified on curing. This clogs the pores of XAD beads, and results in the drop of the surface area. While in the case of the alginate-assisted synthesis of the RF beads, the leaching of the alginate from the matrix during the synthesis generates connected pores, leading to high surface area. Probably, due to this high surface area, the cesium ion capacity of the RF\textsuperscript{A} is also the highest among the three types of the synthesized beads. The mechanical strength of all the resin beads is higher than that of the conventional RF granules. The sorption capacity of the RF\textsuperscript{A} is highest among all of the synthesized RF resins. Kinetics of
sorption is fast, in the case of all the three resin beads, and follows pseudo second-order kinetics. Only RF\(^A\) beads are observed to follow pseudo first-order kinetics at higher cesium ion concentration. The mechanism of the sorption of cesium ions onto these beads is complex, and involves both film diffusion and intraparticle diffusion, with the former as the rate determining step.

### 3.7 Conclusions

The results described in the present studies show that the RF resin beads can be synthesized directly into spherical form, with good control over the size, by varying the various synthesis parameters, using three different methods. The methods of synthesis described here are new, novel and simple, and do not require any intricate machinery. The beads can be made free of unwanted contaminants by easy washing. The mechanical strength, water content and the surface area of the beads are quite high. The cesium ion sorption capacity of the beads is also very high, and even in the presence of high sodium ion concentration, all the resin beads showed good sorption capacity. The \( q_e \) values for RF resin, RF-XAD and RF\(^A\) resin beads are 238 mg/g, 287 mg/g and 326 mg/g, respectively. Kinetics of the sorption of cesium onto these beads is quite fast, and almost completes in ~4 hours, depending on the system and the initial cesium ion concentration. Analysis of mechanistic steps, involved in the sorption process, confirms that the sorption process involves multiple steps, including film diffusion and intraparticle diffusion, with the film diffusion as the rate governing step. The results from the different sorption studies suggest that these synthesized sorbent beads have good potential for sorption of cesium ions from alkaline waste, and can be used in both batch and column modes.