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Separation of strontium from low level radioactive waste solutions using hydrous manganese dioxide composite materials

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ABSTRACT

^{90}Sr is one of the major isotopes present in the low level radioactive liquid waste (LLW) generated during operation of nuclear reactors and spent fuel reprocessing plants. A composite ion exchange material consisting of hydrous manganese oxide and poly methyl methacrylate (PMMA) was developed for removal of strontium from aqueous radioactive waste. The prepared composite material showed very good strontium adsorption properties in aqueous solutions. Sorption of strontium on the composite material as a function of pH, equilibration time and strontium ion concentrations were studied. The process of sorption of strontium from solution was analysed using different isotherm models like Langmuir, D–R and Freundlich. Four different error functions were employed to find out the most suitable isotherm model to represent the experimental data and it was found that Freundlich model best fits the sorption of strontium on the composite material. Analysis of the data obtained from the sorption kinetics studies showed that the data fitted better to the pseudo-second order kinetic model. Lab scale column performance study of the composite material revealed that the material could be effectively used in column operations to remove strontium from LLW solutions.

1. Introduction

Radioactive ^{90}Sr is one of the important fission products with a long half life and high fission yield. The major radioactive isotopes of the low-level radio active liquid waste (LLW) generated during operation of nuclear reactor and spent fuel reprocessing plants are ^{137}Cs and ^{90}Sr. The processes adopted for the treatment of LLW are evaporation, chemical precipitation and ion exchange and sorption [1]. The efficiency of a treatment scheme is judged by the values of decontamination factor (DF) obtained. The ion exchange and sorption methods offer better volume reduction factor (VRF), which is the ratio of initial volume to final volume, compared to that of chemical treatment and are more economical than evaporation methods.

There are various processes for separation of strontium from radioactive waste streams. Lead sulphate precipitation has been reported for separation of strontium from HLW [2,3]. Bis-2-ethyl hexyl phosphene acid diluted with tri butyl phosphate (TBP) and aliphatic hydrocarbon is a well known extractant for strontium from dilute acid solutions in the pH range of 4–6 [4,5]. Extraction of strontium from acidic and alkaline waste solutions using tetra alkyl cobalt dicarbolides in mesityline, diethyl benzene and nitro benzene were also studied extensively [6,7]. Many reports are available in literature about the use of various synthetic crown ethers for selective removal of alkali and alkaline earth elements [8–10]. All the above methods are based on solvent extraction techniques and are not suitable for very low concentration levels of strontium. Inorganic ion exchangers like titanosilicate are highly selective for caesium and strontium [11–13]. The hydrous antimony peroxide of pyrochlore structure has very high affinity for strontium in acidic solutions [14,15].

Hydrous manganese dioxide exists in nanocrystalline powder form and cannot be used as such in column mode operation. Some workers have tried composite ion exchanger of hydrous manganese oxide with polyurethane foam as base material for removal of strontium from LLW solutions [16]. Kirillov et al. have reported the preparation and characterization of a composite material of hydrous manganese oxide/titanium oxide (AMTO composite) for the removal of strontium from Savannah River Site high level waste supernatants [17].

The studies reported in this paper include preparation of hydrous manganese dioxide–poly methyl methacrylate (MnO_2–PMMA) composite material and its evaluation with respect to strontium sorption as a function of pH, equilibration time and strontium ion concentrations. The present study is also aimed to generate data on the equilibrium isotherm parameters and kinetics of the material with reference to strontium sorption at

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low concentrations in aqueous medium. The data obtained from the equilibrium isotherm studies were analysed using different isotherm equations. The data obtained from monitoring the time concentration profile of the sorption of strontium on the composite material were tested with different kinetic models. Lab scale column study of the composite material was carried out to reveal the performance of it in column mode operations.

2. Experimental

2.1. Materials

All the chemicals listed in this study were of analytical grade, and they were used as received. PMMA beads having 0.3–0.5 mm size was procured and used as such for coating manganese dioxide. The adhesive used for coating was methyl methacrylate monomer (MMA).

Simulated LLW having 20 g/l of sodium and inactive strontium in nitrate forms spiked with ^{90}Sr tracer at pH 9 was prepared for the studies.

2.2. Preparation of hydrous manganese dioxide composite material

Hydrous manganese oxide was prepare by mixing solutions of potassium permanganate and manganese sulphate in 1:1.4 molar ratio and the pH was adjusted to 7.5–8 [16]. The precipitate formed was washed, dried and powdered to get particle size below 2 μm. Weighed quantity of manganese dioxide powder was mixed with MMA to get a thick paste. Weighed amount of PMMA beads was then added to the paste and stirred mechanically to get a uniform coating of manganese oxide on the surface of PMMA beads. The product was then dried at 50 °C for overnight in an electrical oven to polymerize the MMA. MnO_2–PMMA composite materials having 10 and 15 wt.% of MnO_2 were thus prepared.

2.3. Determination of distribution coefficient

For the determination of distribution coefficient (K_d) about 0.1 g of the composite material was equilibrated with 10 ml of solution containing inactive strontium (25 ppm) spiked with ^{90}Sr tracer at pH 9 for 1 h. The supernatant solution was filtered and analysed for ^{90}Sr activity using GM counter supplied by Nuclionics India Limited. The K_d value in ml/g was calculated using the following equation:

$$K_d = \frac{(A_i - A_f)}{A_f} \times \frac{V}{m} \tag{1}$$

where A_i and A_f are the initial and final specific activity respectively of the equilibrating solution. V and m are the volume of equilibrating solution (ml) and the mass of the composite sorbent (g) respectively taken for equilibration.

2.4. Effect of pH on strontium removal efficiency

Sorption of strontium as a function of equilibrium pH was studied by equilibrating 10 ml of solution containing 25 ppm inactive Sr^{2+} ions in the form of strontium nitrate and ^{90}Sr tracer with 0.1 g of sorbent. Precipitation of strontium was not observed at this strontium concentration through out the pH range studied. The pH of the solution was adjusted, using dilute nitric acid or sodium hydroxide as applicable, to the required pH (2–12). After 1 h equilibration, the solution was filtered and the activity in the supernatant was measured using GM counter. The K_d value was calculated using Eq. (1). K_d of the material in simulated waste solution was also determined.

2.5. Kinetics of sorption

Sorption of strontium as a function of time was studied at room temperature by equilibrating 0.5 g of the sorbent with 50 ml of the solution containing 0.1 ppm Sr^{2+} ions in the form of strontium nitrate spiked with ^{90}Sr tracer at pH 9. The equilibrium was stopped at various intervals of time and the percentage of strontium sorbed by the sorbent was determined.

2.6. Sorption isotherms

In order to determine the sorption isotherm, 0.1 g of the sorbent was brought into contact with 10 ml of solutions containing varied concentrations of inactive Sr^{2+} ions and ^{90}Sr tracer at pH 9. The experiment was conducted at ambient temperature and the contact time was 3 h. The strontium concentration in the solution was varied from 25 ppm to 400 ppm. The amount of strontium sorbed by the sorbent was calculated from the activity measurements.

2.7. Column performance evaluation

To study the performance of MnO_2–PMMA composite material in column mode operations for removal of strontium from LLW, lab scale column experiment was carried out. Characteristics of LLW are given in Table 1. Details of the column used for the study are given in Table 2.

Simulated LLW solution having 0.1 ppm inactive strontium was passed through the column with a flow rate of 3 bed volumes per hour. The column effluent samples were collected periodically and monitored for ^{90}Sr activity using GM counter. The ratio of strontium concentrations in the effluent and loading solution (C/C_0) at each interval was calculated for plotting the break through curve, C/C_0 versus volume.

3. Result and discussion

Visual observation of MnO_2–PMMA composite material beads indicated a uniform coating of MnO_2 particles on the surface of the PMMA beads. When viewed under SEM, the 10 wt.% material showed a uniform coating of MnO_2 particles, where as the 15 wt.% material was having agglomeration of MnO_2 on the PMMA bead surface. So the former composite material was selected for further studies. The size of the composite material beads was in the range of 0.3–0.5 mm. Bulk density of MnO_2–PMMA composite material was 0.63 g cm^3. The bulk density value is promising from the viewpoint of column performance.

The polymer substrate PMMA was found to be stable in the acidic and alkaline pH ranges. Also the material does not have any pick up for strontium.

Table 1
Characteristics of LLW.

Property	Value
pH	8–9
Density (g cm^{-3})	1.102
Total solid (%W/V)	15
Gross β (mCi l^{-1})	0.2–0.5
Gross α (mCi l^{-1})	BDL
^{137}Cs (mCi l^{-1})	0.1–0.4
^{134}Cs (mCi l^{-1})	2×10^{-4}
^{106}Ru (mCi l^{-1})	5×10^{-3}
^{90}Sr–^{90}Y (mCi l^{-1})	0.05–0.07

Table 2
Details of MnO_2–PMMA composite column.

Column	Glass column
Column diameter	0.8 cm
Exchange material	MnO_2–PMMA
Loading solution	Simulated LLW having 20 g/l sodium nitrate and 0.1 ppm Sr spiked with ^{90}Sr at pH 9
Bed volume	1.6 ml
Bed height	3.1 cm
Flow rate	5–6 bv/h

3.1. Distribution coefficient in different media

The distribution coefficient (K_d) of MnO_2–PMMA composite material for strontium in solution containing 25 ppm inactive strontium spiked with ^{90}Sr as well as in simulated LLW having 25 ppm inactive strontium was estimated. The values are 946 and 312 ml/g, respectively. The K_d value was observed to be low in simulated LLW having high concentration of Na ions.

3.2. Effect of pH on strontium removal efficiency

The percentage sorption of strontium on the composite materials as a function of pH of equilibrating solution is presented in Fig. 1. The figure clearly demonstrates that for an increase in pH from 2 to 4 a sharp increase in sorption of strontium was observed and then got stabilized up to pH 10. Then the sorption slightly decreased. The metal oxide surface can exist as negative, positive or neutral charge state in an aqueous solution depending on the pH of the solution. It is also reported that hydrous manganese dioxide exhibits a negative charged surface in the pH range from 2.3 to 3 [18], which clearly explains the sharp increase in the sorption of strontium at this pH range. Since the LLW to be treated with the composite material has pH in the range 8–9, present studies were conducted at pH 9.

3.3. Kinetics of sorption process

Fig. 2 shows the amount of strontium sorbed by the composite materials as a function of time at room temperature. The uptake of strontium was rapid in the first 30 min and then gave way to a much slower adsorption, which became constant at 3 h. The initial rapid uptake can be attributed to the concentration gradient at the start of the adsorption process.

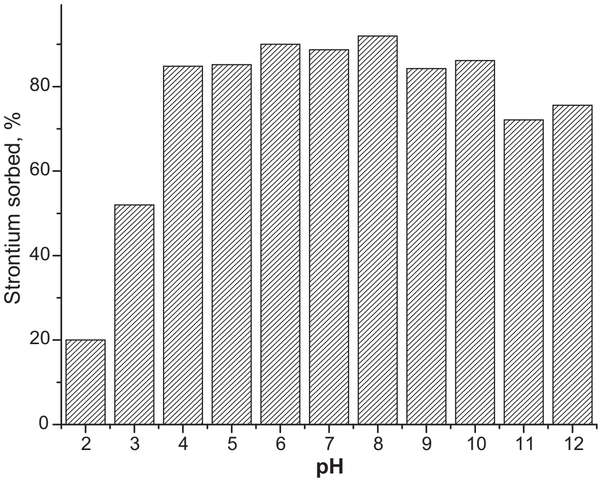

Fig. 1. Variation of percentage sorption of Sr as a function of pH.

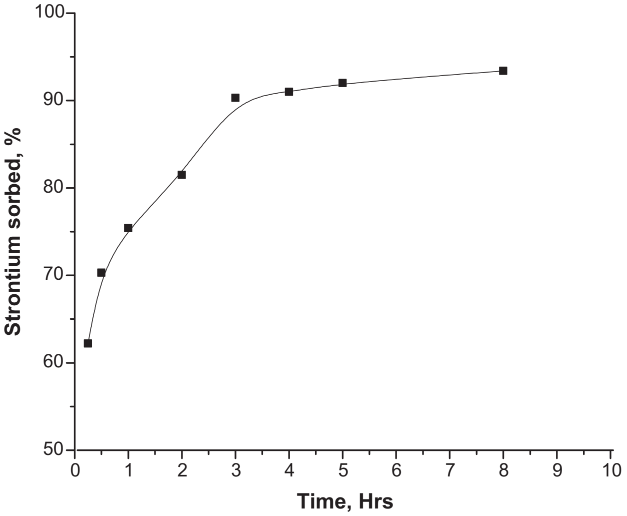

Fig. 2. Variation of percentage sorption of Sr as a function of time.

The kinetic studiers of sorption process are important because the data obtained from such studies are necessary to understand the variables that influence the sorption process. In order to define the sorption kinetics of strontium on MnO_2–PMMA composite material, Langergren first order, pseudo-second order and the intra particle diffusion models were studied.

3.3.1. Langergren first order model

The linearised form of the Langergren first order equation is generally expressed as [19]

$$\log(q_e - q_t) = \log q_e - \frac{K_L}{2.303}t \tag{2}$$

where q_e and q_t are the amount of sorbate sorbed at equilibrium and at time t respectively (mg g^{-1}) and K_L is the rate constant for the first order sorption (min^{-1}).

If first order kinetic model is applicable, the plot of $\log(q_e - q_t)$ versus t should give a linear relationship from which the first order parameters can be determined. The Langergren first order plot for the sorption of strontium on MnO_2–PMMA composite materials was constructed (Fig. 3). The linearity of the plot is not very good ($R^2 = 0.9802$). The first order rate constant obtained is 0.0083 min^{-1}.

3.3.2. Pseudo-second order model

Owing to the low linearity of the plot obtained from first order study, the pseudo-second order kinetic model was also used to test the data obtained. The pseudo-second order kinetic model considers the rate determining step as the formation of a chemisorption bond [20]. The pseudo-second order model equation is expressed as [21]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

where q_e and q_t are the amount of Sr sorbed at equilibrium and at time t respectively (mg g^{-1}) and K_2 is the rate constant for pseudo-second order sorption (g mg^{-1} min^{-1}).

If the pseudo-second order kinetics is applicable, the plot of t/q_t against t should give a linear relationship, from which q_t and K_2 can be determined. The plot of t/q_t against t (Fig. 4) yields a very good straight line ($R^2 = 0.9984$), which shows the applicability of pseudo-second order kinetics for sorption of strontium on MnO_2–PMMA composite material. The rate constant obtained for pseudo-second order sorption is 0.0929 g mg^{-1} min^{-1}. Therefore the

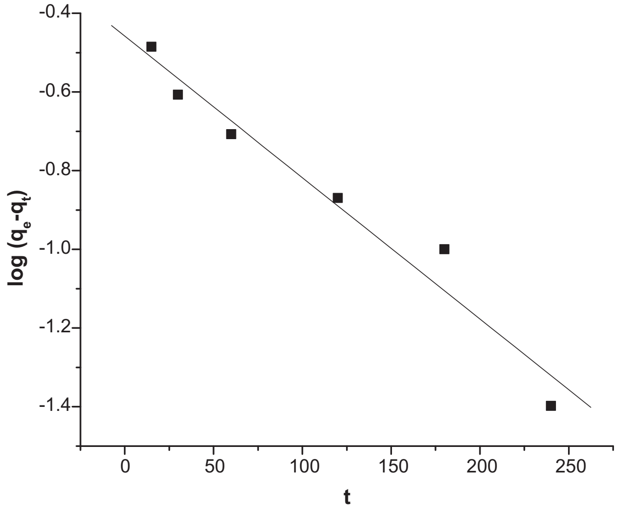

Fig. 3. Langergren first order plot for Sr sorption.

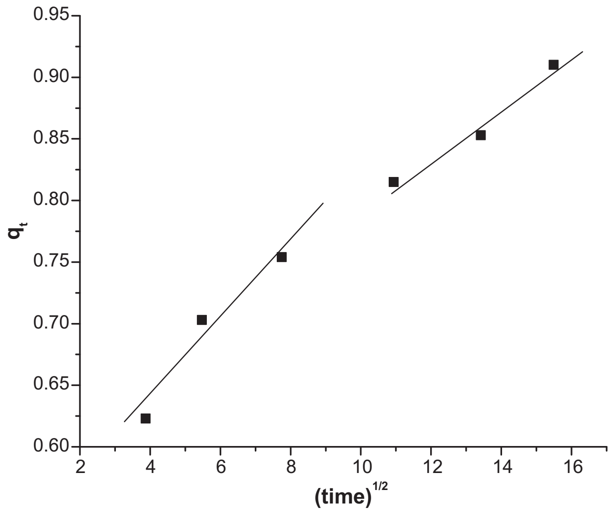

Fig. 5. Weber–Morris plot for Sr sorption.

pseudo-second order kinetic model described the sorption of strontium on MnO_2–PMMA composite material.

3.4. Intra particle diffusion

To see whether the sorption kinetics of strontium on the MnO_2 composite material is having intra particle diffusion mechanism, Weber–Morris intra particle diffusion model was applied to the equilibrium time data. This model is expressed by the equation [22]:

$$q_t = K_{id}t^{1/2} + I \tag{4}$$

where q_t is the amount adsorbed at time t (mg g^{-1}), K_{id} is the intra particle diffusion rate constant (mg g^{-1} min$^{-1/2}$) and I is a constant, the value of which gives an idea about the thickness of the boundary layer.

Plot of q_t versus $t^{1/2}$ for adsorption of strontium ions on the MnO_2–PMMA composite materials is given in Fig. 5. From the figure it may be seen that the intra particle diffusion of strontium with in the composite materials occurred in two steps. The first straight portion is attributed to the boundary layer diffusion (phase I) and the second linear portion to intra particle diffusion (phase II) [23]. The intra particle diffusion parameters for the two steps are 0.0330 and 0.0207 mg g^{-1} min$^{-1/2}$ respectively. The results indicate that the Sr ions diffused quickly into the MnO_2 in the beginning of the adsorption process and then slowed down and stabilized. The multi linearity curve indicates that intra particle diffusion is not a fully operative mechanism in the sorption of strontium by MnO_2 composite materials [20].

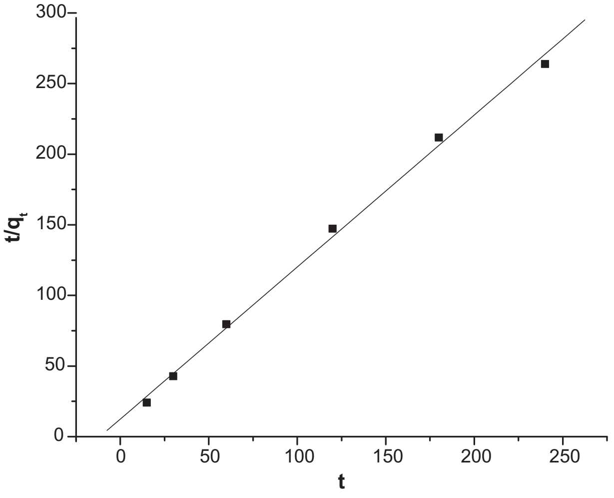

Fig. 4. Pseudo-second order plot for Sr sorption.

3.5. Equilibrium isotherm studies

The equilibrium relationship between the concentrations of strontium in the aqueous phase and that in the composite material at a given temperature was studied. The data obtained were interpreted using Langmuir, Dubenin–Rodushkevich and Freundlich adsorption isotherm models.

Langmuir isotherm represents the monolayer coverage of the sorbate on a sorbent surface at constant temperature. It hints towards the surface homogeneity. The Langmuir adsorption isotherm in the liquid phase can be represented by the equation [24]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{5}$$

where C_e is the equilibrium concentration of metal ions in aqueous phase, mg l^{-1}, q_e is the amount of metal ions sorbed on the solid phase at equilibrium, mg g^{-1} and q_0 and b are the Langmuir constant related to the sorption capacity of the metal ions and energy of adsorption respectively.

A plot of C_e/q_e versus C_e gives a straight line, if the sorption process is described by the Langmuir isotherm equation. The values of q_0 and b are obtained from the slope and intercepts of the straight line.

Dubenin–Rodushkevich (D–R) isotherm is postulated within an adsorption ‘space’ close to sorbent surface [25]. If the surface is heterogeneous and an approximation to a Langmuir isotherm is chosen as a local isotherm for all sites that are energetically equivalent then the quantity $\beta^{1/2}$ can be related to the mean sorption energy, E, which is the free energy of the transfer of ions from infinity to the surface of sorbent. The difference in the free energy between the adsorbed phase and saturated liquid sorbate is referred as adsorption potential, which was first, put forward by Polanyi [26] and later developed by Dubinin and his coworkers. The linearised form of D–R isotherm is given by following equation.

$$\ln q_e = \ln q_0 - \beta\varepsilon^2 \tag{6}$$

where q_0 is the maximum sorption capacity, mmol g^{-1}, β is the activity coefficient related to mean sorption energy, mol^2 J^{-2} and ε is Polanyi potential, J^2 mol^{-2}; it is given by the equation

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{7}$$

where R is gas constant in J K^{-1} mol^{-1}, T is temperature in Kelvin and C_e is the equilibrium concentration of metal ions in aqueous phase, mmol l^{-1}.

The plot of $\ln q_e$ versus ε^2 gives a straight line, if the sorption process is described by the D–R isotherm equation. From the slope and intercepts of the plot the values of β and q_0 can be calculated.

Freundlich sorption isotherm, one of the most widely used mathematical descriptions usually fits the experimental data over a wide range of concentration. The Freundlich sorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich adsorption isotherm in liquid phase is given by the equation [27,28]:

$$\log q_e = \log q_0 + \frac{1}{n}\log C_e \tag{8}$$

where q_e is the metal ions concentration in the solid phase at equilibrium, mg g^{-1}, C_e is the metal concentration in solution at equilibrium, mg l^{-1} and q_0 and n are Freundlich parameters related to the adsorption capacity and adsorption intensity.

The plot of $\log q_e$ versus $\log C_e$ gives a straight line, if the sorption process is described by the Freundlich isotherm equation. From the slope and intercepts of the plot the values of n and q_0 can be calculated.

In order to understand the mechanism of adsorption of strontium on MnO$_2$–PMMA composite material, the adsorption experimental data were fitted to the aforementioned isotherm equations and the isotherm parameters obtained from the different plots are presented in Table 3.

An error function is required to evaluate the fitness of each isotherm equation to the experimental data obtained from the optimization process employed. Four different error functions were employed in this study to find out the most suitable isotherm model to represent the experimental data. The error functions used are R^2, SSE, SAE and ARE. R^2 is the linear correlation coefficient of determination. The sum of the squares of the errors (SSE) is given as [29]:

$$\text{SSE} = \sum_{i=1}^{n}(q_{e,cal} - q_{e,\exp})_i^2 \tag{9}$$

where $q_{e,cal}$ and $q_{e,\exp}$ are the calculated and experimental values of the adsorbate concentration on the sorbent at equilibrium (mg m^{-1}) and n is the number of data points.

The sum of absolute errors (SAE) is given as [29]:

$$\text{SAE} = \sum_{i=1}^{n}|q_{e,cal} - q_{e,\exp}|_i \tag{10}$$

The average relative error (ARE) is given as [29]:

$$\text{ARE} = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{q_{e,\exp} - q_{e,cal}}{q_{e,\exp}}\right| \tag{11}$$

Table 4
Isotherm error analysis for strontium sorption on the composite material.

Isotherm	R^2	SSE	SAE	ARE
Langmuir	0.8722	12.35	6.84	12.33
D–R	0.9022	112.89	22.07	32.34
Freundlich	0.9938	3.34	3.86	8.27

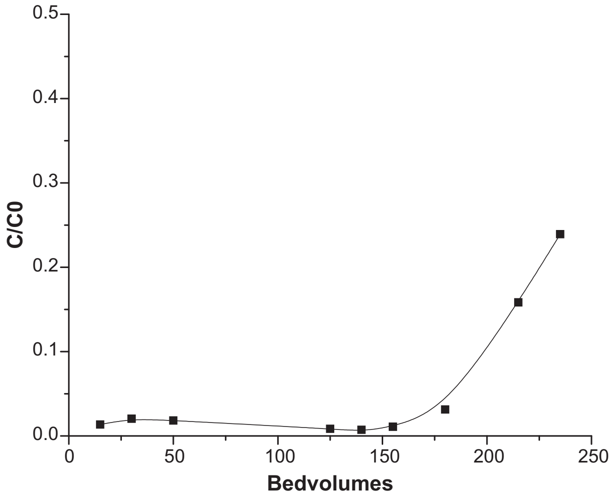

Fig. 6. Breakthrough curve for strontium sorption.

The values of the four error functions for all the three isotherm plots are presented in Table 4. By comparing the values of error functions, it is found that Freundlich model best fits the sorption of strontium on the composite material. Better fitting of the sorption data to the Freundlich model than Langmuir and D–R model is an evidence for the presence of multilayer sorption nature of strontium on MnO$_2$–PMMA composite material [20].

3.6. Column performance

The breakthrough curve for strontium on the composite material is given in Fig. 6. It can be seen that the 5% break through of strontium occurred at about 180 bed volumes. Considering the higher concentration of strontium in the feed solution (0.1 ppm = 14.4 mCi/l) than that present in the actual LLW (0.05–0.07 mCi/l), this bed volume is much higher. Higher concentration of strontium in the test solution was preferred to avoid handling of large volumes of active solution. Also the loading was stopped after obtaining the breakthrough to avoid handling of large volumes of active solution. The flow rate remained constant till the end of the experiment.

3.7. Disposal of activity loaded composite material

Since the concentration of radioactive strontium in LLW is very low (mCi l^{-1}), the radioactive dose on the spent composite material will be of the order of few rads. This permits a shallow land disposal of the same after converting it into a monolithic solid form. By using methyl methacrylate monomer, the spent composite material along

Table 3
Isotherm parameters of Langmuir, D–R and Freundlich isotherms for strontium sorption on the composite material.

Langmuir isotherm		D–R isotherm		Freundlich isotherm	
q_0 (mmol g^{-1})	b (l mg^{-1})	β (mol^2 (K J)$^{-2}$)	q_0 (mmol g^{-1})	q_0 (mmol g^{-1})	n
0.5603	0.006	-4.13×10^{-2}	0.1752	0.0078	1.4732

with radioactivity can be converted into a monolithic polymer form having good mechanical strength and leach resistance.

4. Conclusion

The above studies indicate that the MnO_2–PMMA composite material can be used for the treatment of low level radioactive waste for removal of radioactive strontium in column operations. The K_d values obtained are good enough for column mode operation of the material. The material has a wide pH range (4–10) for operation. Freundlich adsorption equation gave the best fit amongst all the adsorption equations studied. The sorption process was found to follow pseudo-second order mechanism more than any other kinetic models studied. For the disposal of the spent composite material, the material along with radioactivity can be converted into a monolithic polymer form having good mechanical strength and leach resistance.

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