FIXATION OF ^{90}STRONTIUM ONTO STYRENE-DIVINYLBENZENE CATION EXCHANGE RESINS

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Abstract

Radioactive tracer batch equilibration ion exchange experiments were employed to investigate the uptake of ^{90}Strontium radioisotope, under different conditions i.e., carrier free radioisotope traced in deionized water and with 0.005M $SrCl_2$ carrier solution. The exchanger used was a highly cross-linked (30%) macroporous styrene-divinylbenzene cation exchange resin, which was also converted to its cation exchanged forms. The other characteristics of the resin were calculated as; 0.406 ml/g pore volume, 110 Å pore diameter and 150 m^2/g surface area. The uptake of ^{90}Strontium was determined by taking liquid aliquotes at various time intervals from solutions over various cationic forms of the resin. The liquid to solid ratio was kept at 200. The results of kinetics and distribution coefficients for the uptake of carrier free ^{90}Strontium radioisotope were evident in all cationic forms of the resins. In case of carrier (0.005M $SrCl_2$) solution, the percent uptake and K_d values were also determined and best results were obtained from the H^+-form of the resin. All the experiments were made at room temperature.

Introduction

From the beginning of the nuclear industry and especially with the operation of nuclear reactors much attention has been paid to the separation of ^{90}Strontium radioisotope from nuclear waste streams (which is produced in abundance), because of its health hazard nature and biotoxicity in the environment. Several factors contribute to this interest; chemically it behaves similar to calcium, hence accumulates in the bones . It has a relatively long half-life $t_{1/2}$ = 29.1 years and consequently upon its high ^{235}U or ^{239}Pu fission yield its bio-availability is high and hence remain in the environment for a very long time. This makes it radio-logically an important and a relevant radioisotope to be dealt with.

One of the best available technologies for the separation of ^{90}Strontium from the waste streams is the ion exchange, which has developed significantly in recent years due to the availability of various types of organic and inorganic ion exchange materials. Faced with the removal of the radionuclides in the nuclear industry and the difficulty of fully removing them, research efforts for higher performance of exchanger have been carried out towards improving properties of ion exchange resins. The prime objective of ion exchange resin is satisfied by a sufficiently high capacity and selectivity. But in dynamic situations the question of a rapid attainment of equilibrium and a satisfactory rate of exchange must also taken into consideration because these determine the length and the shape of the ion exchange reaction zone-hence the exchange capacity and leakage. The kinetics of the resins depend on a number of criteria including the internal porosity (gel structure) and the surface area of the beads (which influences the ion exchange rates at the solid/liquid boundary). The degree of cross-linking determines the lattice width, swelling characteristics, ease of ion movement, hardness and resistance to mechanical break down.

By employing different methods for the synthesis of ion-exchange resin, they can have specific values for parameters like pore volume, pore size and pore size distribution, surface area, capacity, mechanical strength, and more importantly the diffusion coefficient.

The advantages of ion exchange resins are as:

- The resins can be synthesized as spherical beads of fairly uniform size having less resistance to the flow of solution when used in column operations.
- Their exchange capacities, measured either in milliequivalents per gram (meq/g) or in milliequivalents per millilitre (meq/ml) are relatively high and can be improved up to the requirements.
- Their rate of exchange is usually much faster and can be enhanced.
- They are chemically stable at very high acidic pH.

Although styrene-divinylbenzene resins and particularly the ion exchangers derived from them, have been widely used in the nuclear industry, their further development, improvement, characterization and exploitation continues unabated in a number of fields. Their demand has been further stimulated in particular by the drive to produce cleaner industrial processes, in order to meet increasingly strict environmental demands[1-6].

In this research paper, the performance of this highly cross-linked (30%) macro-porous styrene-divinylbenzene cation exchange resin was assessed by some radioactive tracer batch equilibration ion

exchange experiments for the removal of ^{90}Strontium radioisotope both in carrier free and with carrier concentrations.

Experimental

Materials and chemicals

Styrene and divinylbenzene (50% isomers, 45% ethylvinylbenzene) were supplied by Reidel-de-H'en, Germany and were used without further purification. Diethylphthalate, Petroleum ether (b.p. 130^0) and Benzoylperoxide were obtained from Fluka Chemicals, Switzerland.

The ^{90}Strontium was obtained from Amersham Life Science, U.K. and its characteristics can be found from the literature. All the other reagents used were of AnalR grade.

Synthesis of styrene-divinylbenzene cation exchange resin

By using the conventional suspension polymerization technique, macroporous, 30% cross-linked styrene-divinylbenzene, resin was synthesized. Benzoyl peroxide was used as initiator. The diluents used were diethyl pthalate and Petroleum ether (b.p. 130 °C) in 60 % amount with (1:1 ratio). The synthesized copolymer was converted into cation exchange resin by its sulfonation with H_2SO_4 (98%) at 80 ^{0}C for 3 hours time. The synthesis procedure and other details can be found from the literature.[11]

Cation exchanged forms of styrene-divinylbenzene resin

The cation exchanged forms of styrene-divinylbenzene resin were obtained by treating the original synthesized form with respective metal chloride and ammonium chloride salt solution in excess. A typical procedure was: 5 to 10 g of styrene-divinylbenzene was treated with one litre of metal chloride or ammonium chloride salt solution in a plastic bottle, respectively. The bottle was sealed and rolled on a mechanical roller at room temperature. The salt solution was decanted and a fresh lot of salt solution was added. The procedure was repeated three times to ensure the cation exchanged form of the resin. The resin was filtered and washed with deionized water to ensure the excess salts had been removed and kept in an oven at 40 °C for drying. The dried resins were then kept in desiccator to equilibrate with water vapours and for future use.

Kinetic experiments

Batch contact ion exchange experiments were carried out to find out the percent uptake of ^{90}Sr with and without "carrier" solution. A typical procedure was: 20 ml solution of carrier free or with 0.005M $SrCl_2$ salt solution traced with ^{90}Sr radioisotope in each case was equilibrated with 0.1 g of various cationic forms of styrene-divinylbenzene resin in separate polythene vials at room temperature. The volume to solid ratio was kept at 200. The vials were shaken by rotating on a mechanical roller and at various time intervals, 10 ml of the supernatant solution in each case was withdrawn and counted for ^{90}Sr radioisotope by the Cerenkov counting in the tritium channel of a Packard Model A-2700TR Liquid Scintillation Analyzer. The samples were counted several times so as to count the maximum β^- rays emitting from ^{90}Sr radioisotope remaining in the liquid phase for achieving reproducible results.

Radioisotope measurement: Percent uptake of ^{90}Sr isotope as a function of time for various cationic forms of styrene-divinylbenzene resins were determined from Eq. (1).

$$\% \text{ Uptake} = \frac{A_i - A_f}{A_i} \times 100 \qquad (1)$$

where A_i is the initial and A_f is the final activity of the solution (cpm. ml^{-1}), respectively. All the radioactive samples were corrected for backgrounds.

Distribution coefficient measurements

The distribution coefficient measures partitioning of ions between solid and liquid phase. It gives an idea of the affinity of ions to the ion exchanger. The distribution coefficient (K_d ml g^{-1}) values (milli-equivalents of ion per gram of the exchanger/milli-equivalents of ion per ml of solution) for carrier free ^{90}Sr and with carrier concentrations were determined at equilibrium. In these experiments 0.1 g of vacuum dried styrene-divinylebenzene resin in different cationic forms were equilibrated with 20 ml each of the reference solution of either carrier free ^{90}Sr radioisotope or with 0.005M carrier solution. The vials were rotated in a mineralogical roller for 24 hours to attain complete equilibrium. the vials were centrifuged and 10 ml of the supernatant solution was pipetted out into separate plastic vials for Cerenkov counting as before. The distribution coefficients were calculated from Eq. (2).

$$K_d = \frac{(A_i - A_f)V}{A_f . W} \text{ ml . g}^{-1} \qquad (2)$$

where, A_i and A_f are same as in Eq. (1) at equilibrium, V is the volume of solution (ml) and W is the weight of styrene-divinylebenzene resin (g).

Results and discussion

Removal of ^{90}Sr in carrier free (CF) conditions

The kinetic experiments at room temperature of carrier free ^{90}Sr showed that the rate of exchange was very fast in various cationic forms of styrene-divinylebenzene resins and 100% uptake of ^{90}Sr was achieved within minutes. This reflected the fast exchange reaction which would be due to the large surface area and selectivity of the exchanger towards the counter ion i.e. Sr^{2+} cation in carrier free condition.

Removal of ^{90}Sr with 0.005M carrier solutions

The kinetic experiments of ^{90}Sr with 0.005M carrier solution (Table 1) showed that the uptake was observed in almost all the cationic forms of the ion exchange resins as was in carrier free condition. However, the rate of uptake of ^{90}Sr with 0.005M strontium chloride solution for various cationic forms was in the order of:

$$H^+ < Li^+ < Na^+ < NH_4^+ < K^+$$

and ranged from 82-99% uptake. This also indicated that the maximum cation exchange capacity for strontium obtained was equivalent to 2 milli-equivalents per gram (meq . g^{-1}) of H^+-form (H_3O^+) of styrene-divinylbenzene resin. This gives an idea that in future we may be able to further increase the cation exchange capacity for the same Sr^{2+} ion by change in the cross-linking of the resin.

Table 1: Percent uptake of ^{90}Sr with 0.005M carrier solution onto various cationic forms of styrene-divinylbenzene resins

Time (Hours)	H^+-form	Li^+-form	Na^+-form	K^+-form	NH_4^+-form
1	95.0	93.0	92.5	82.0	89.0
2	96.0	94.0	93.0	85.0	90.0
5	98.0	95.6	95.0	89.0	93.5
24	98.99	98.0	97.0	91.5	95.75

Distribution coefficients values in the presence of carrier solutions

The kinetic experiments for carrier free ^{90}Sr radioisotope showed that the uptake was achieved within minutes due to the fast exchange reaction of the resin, but nevertheless 24 hours equilibration time was given to all the experiments to establish equilibrium. The distribution coefficients (K_d) values for ^{90}Sr onto various cationic forms of styrene-divinylbenzene resins were determined at room temperature. In all these experiments as both the ingoing cation e.g., Sr^{2+} and concentration of carrier solution were the same, the differences in the K_d values for ^{90}Sr obtained may be due to the differences in selectivity of ^{90}Sr for various cationic forms of the resins. The K_d values for ^{90}Sr in H^+ (H_3O^+), Li^+ and Na^+ forms of the resins were higher compared to K^+ and NH_4^+ form of the resin. This may be due to the differences in the ionic sizes (Table 2) of more hydrated ions e.g. Li^+ and Na^+ ion compared to the least hydrated ions e.g., K^+ and NH_4^+ ion. Horvath[7] states that least hyderated ammonium and potassium ions are identical in size (1.33 Å), so the position of ammonium in the selectivity series qouted above is sensible. Similar data on the hydronium ion are lacking. The better results of K_d values obtained in the H^+-form of the resin are unexplained.

Table 2: K_d values for ^{90}Sr onto homoionic forms of styrene-divinylbenzene resins in deionized water (carrier free)

Cationic forms of resins	Ionic size (Å)	K_d values (ml/g)
H^+	1.41	19600
Li^+	0.60	16389
Na^+	0.95	15900
K^+	1.33	10060
NH_4^+	1.33	12005

Table 3: K_d values for strontium onto homoionic forms of styrene-divinylbenzene resins with 0.005M $SrCl_2$ solution

Cationic forms of resins	Ionic size (Å)	K_d values (ml/g)
H^+	1.41	9600
Li^+	0.60	6269
Na^+	0.95	5930
K^+	1.33	2060
NH_4^+	1.33	4515

The ionic radius of the ingoing cation Sr^{++} is 1.13 Å.

Conclusions

It may be concluded that H^+-form and Li^+-form of styrene-divinylbenzene resins were more effective in removing ^{90}Sr in comparison to the other cationic forms both in carrier free and with carrier concentrations. In our previous study for the uptake of ^{137}Caesium[8] of this series the best results were also obtained by the same cationic forms of the resin.

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