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Technical paper

Adsorption of Strontium from Acidic Solutions Using an Inorganic Exchanger – Uranium Antimonate

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Abstract

The applicability of uranium antimonate (USb) for the efficient removal of strontium from aqueous acidic solutions by adsorption has been investigated. The adsorption data analysis was carried out using the Freundlich and Langmuir isotherms for the uptake of Sr in the initial concentrations range 1.14×10^{-4} to 1.14×10^{-2} mol L^{-1} on USb from nitric acid medium. The adsorption process is heterogeneous in nature as evident from the fractional value (0.48) of β. The sorption capacity '*b'* was found to be 18.81 mg g^{-1} from 0.5 mol L^{-1} nitric acid medium. Equilibrium adsorption values at different temperatures have been utilized to evaluate the change in enthalpy, entropy and free energy. The adsorption of strontium on USb was found to be endothermic.

Keywords: Strontium, uranium antimonate, adsorption, inorganic exchanger, adsorption isotherms.

1. Introduction

Recovery of radioisotopes from nuclear waste is a subject of growing interest in recent years all over the world because of their potential applications[1–3] in the field of medicine, food irradiation, and sewage treatment technologies. The removal of fission products like ^{137}Cs and ^{90}Sr from the bulk of these wastes will considerably reduce the controlled storage time. The potential application of these radioisotopes have made everyone to reconsider the existing disposal options and examine the possibility of recovering these useful radioisotopes from high level liquid waste for real applications. Further, the stringent safety regulations also demand the separation of these long-lived radiotoxic and hazardous metal ions from a large volume of the waste and concentrate into small volumes by a suitable technology.

Isolation of these radioisotopes on an inorganic ion exchanger is an emerging field of research. Inorganic compounds are extremely proven candidates for the separation and recovery of cesium and strontium from aqueous wastes[4–9] owing to their specific selectivity, exceptional stability and resistance to temperature and irradiation.[10] The inorganic ion exchangers have rigid structures and do not undergo any appreciable dimensional change during the ion exchange process which is a key factor for its specific selectivity. Composite type of sorbents such as zirconium molybdoarsenate,[11,12] ammonium molybdophosphate-polyacrylonitrile[13] for Cs and zirconium molybdate – zirconium tungstate for the removal of Cs and Sr from nitric acid solutions were reported earlier.[14] In this sequence and in search of promising sorbent for Sr from acidic solutions, we prepared uranium antimonate (USb) in nitric acid medium and the results on effect of time and temperature on the sorption of Sr are presented.

2. Experimental

2. 1. Materials

All the reagents used were procured from Merck and were of analytical AR grade.$^{(85+89)}$ Sr radioisotope with a specific activity of 18.5MBq was obtained from the Board of Radiation and Isotope Technology (BRIT), Mumbai, India.

2. 2. Preparation of the Sorbent

The sorbent was prepared by mixing 1.0 L of 0.1 mol L^{-1} potassium pyroantimonate and 1.0 L of 0.025 mol L^{-1} uranyl nitrate in 2.0 mol L^{-1} nitric acid. The resultant precipitate was heated to 80–90 °C for about 1 h and further heated for 14 h at 60 °C. The precipitate after allowing to settle overnight was filtered, washed several times with distilled water to eliminate acid and dried at 60 °C. The dried product was sieved to –30 +52 BSS size and converted to H^+ form by passing 4.0 mol L^{-1} nitric acid.

2. 3. Determination of Cation Exchange Capacity

0.5 g of the sorbent was taken in a glass column and converted to H^+ form by passing 1.0 mol L^{-1} nitric acid. The column was then washed thoroughly with distilled water. Nearly 100 mL of 0.5 mol L^{-1} sodium chloride solution was passed through the column at a flow rate of 0.5 mL per minute. The effluent was collected and titrated with sodium hydroxide. From the amount of sodium hydroxide consumed the cation exchange capacity was calculated.

2.4. Sorption Studies

The rate of sorption of strontium on USb was studied by equilibrating 0.05 g of the sorbent with 10 mL of test solution containing strontium ion spiked with $^{(85+89)}$Sr tracer ($t_{1/2}$ = 64.84 days) of activity 4×10^3 Bq at different nitric acid concentrations at 299 K. The temperature controlled mechanical shaker was used to ensure good mixing. The equilibration was stopped at various intervals of time and the percentage of strontium sorbed was calculated by the radioactivity measurements of the supernatant using Eqn.(1). The radioassay of strontium was performed by counting the gamma radiation emitted from the isotope (Eγ = 514Kev) using NaI(Tl) detector coupled to a single channel analyzer. The percentage sorption or the distribution coefficient (K_d) was calculated from the radioactive measurements by

$$\%\ \text{Sorption} = \frac{A_i - A_f}{A_i} \times 100$$

or (1)

$$K_d\ (\text{mL/g}) = \frac{A_i - A_f}{A_f} \times \left(\frac{V}{m}\right)$$

where A_i and A_f are the initial and final activity of the supernatant in dpm/mL and *V* and *m* are the volume of the solution (mL) and weight of the sorbent (g) taken for equilibration.

3. Results and Discussion

The sorbent was found to be stable in nitric acid medium and the sodium ion exchange capacity was found to be 2.03 mmol per gram. The sorption of strontium on USb was studied at different initial concentrations of Sr in 0.5 and 1.0 mol L^{-1} nitric acid medium at 299 K. Figure 1 shows the sorption of strontium as a function of time. It is seen that there is a rapid increase in sorption of strontium with time in the initial stages of equilibration followed by saturation. Equilibrium was established within 14 h of contact between sorbent and solution. At a given time the percentage sorption was found to decrease with increasing concentration of nitric acid and strontium.

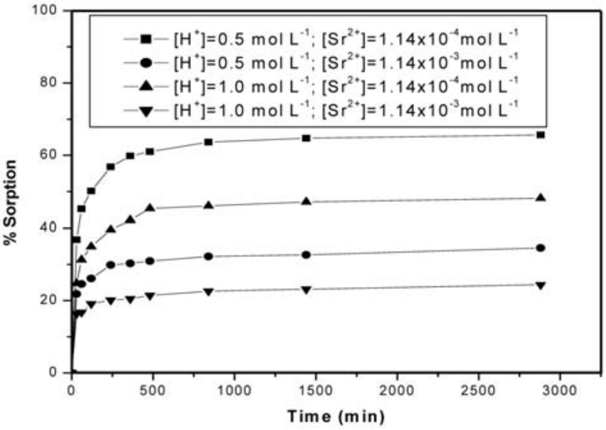

Figure 1: Variation of % sorption of strontium with time

3. 1. Adsorption Isotherms

Adsorption data for a wide range of adsorbate concentrations are most conveniently described by adsorption isotherms such as Freundlich and Langmuir, which relates equilibrium adsorbate concentration in the sorbent phase and bulk fluid phase. The Freundlich model assumes that the surface of adsorbent is heterogeneous in nature. The adsorption data for wide range of $[Sr^{2+}]$ (1.14×10^{-4} to 1.14×10^{-2} mol L^{-1}) in 0.5 mol L^{-1} nitric acid were analysed by applying the Freundlich adsorption isotherm[15] in its logarithmic form

$$\log\,[Cs]_E = \log k + \beta \log\,[Cs]_S \qquad (2)$$

where $[Cs]_E$ is the amount of Sr adsorbed on the exchanger (mg g^{-1}) at equilibrium and $[Cs]_S$ is the adsorptive equilibrium concentration in solution (mg L^{-1}). β and k are the empirical parameters of positive values indicating energetic heterogeneity of the sorbent and average adsorption affinity respectively. The physical significance of Freundlich constants can be explained by assuming that each class of exchanger site adsorbs individually. According to Freundlich equation, the plot of log $[Cs]_E$ *vs* log $[Cs]_S$ was found to be linear (R^2 = 0.998) (Fig.2) suggesting that the adsorption of strontium on USb obeys Freundlich adsorption isotherm over entire range of adsorptive concentrations studied. The fractional value of β (0.48) calculated from the slope of plot shows that the process is heterogeneous in nature.[16]

The Langmuir isotherm[17] is the simplest theoretical model for monolayer sorption. The model assumes that the surface of the adsorbent contains a finite number of identical sites with uniform energies and no transmigration of adsorbate in the plane of the surface. The Langmuir equation relating the strontium ion concentration in the solid and liquid phase is given by

$$\frac{C_f}{C_s} = \frac{1}{K^* b} + \frac{C_f}{b} \tag{3}$$

where C_f and C_s are the concentrations of Sr in the liquid (mg L^{-1}) and solid (mg g^{-1}) phases respectively. The magnitude of *'b'* gives the experimental sorption capacity and K^* is a constant. The plot of C_f / C_s *vs* C_f is linear (R^2 = 0.995) (Fig. 2) and the value of *'b'* was determined from the slope of the plot. The maximum sorption capacity was found to be 18.81 mg g^{-1}.

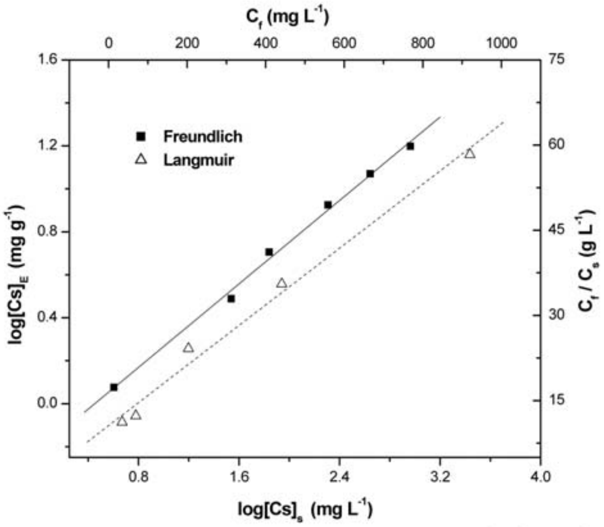

Figure 2: Freundlich and Langmuir adsrption isotherms for Sr on USb

3. 2. Effect of Temperature

The adsorption of strontium on USb has been studied as a function of temperature in the range of 299 to 323 K, keeping the Sr initial concentration as 1.14×10^{-3} mol L^{-1} in 0.5 mol L^{-1} nitric acid. It was observed that the uptake of strontium increases with increasing temperature. The standard enthalpy (ΔH°) is calculated from the van't Hoff equation:

$$\log K_d = \left(\frac{-\Delta H^o}{2.303R}\right)\frac{1}{T} + \text{constant} \tag{4}$$

The ΔH° for the process was evaluated from the slope (R^2 = 0.997) of the plot (Fig.3) of log K_d *vs* 1/T. The positive enthalpy value of 15.26 kJ mol^{-1} for Sr adsoption on this exchanger from 0.5 mol L^{-1} nitric acid indicates that the adsorption process is endothermic and the value is within the range of an ideal ion exchange system (8–42 kJ mol^{-1}).[18]

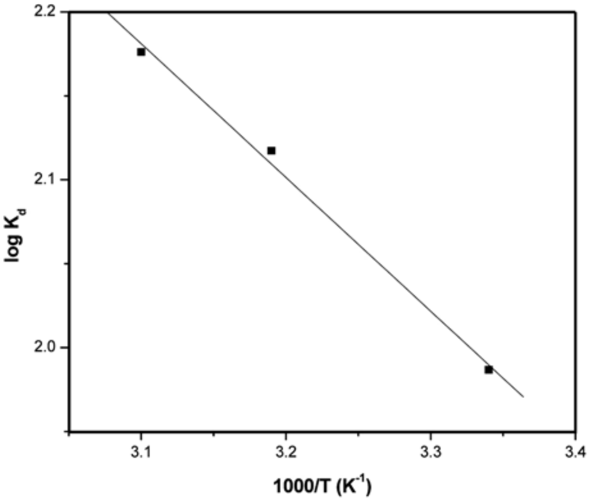

Figure 3: Effect of Temperature on adsorption of Sr on USb

The change in standard free energy (ΔG°) values for adsorption of Sr on this exchanger had been evaluated by

$$\Delta G^o = -RT \ln K_d \tag{5}$$

and the standard entropy changes (ΔS°) are calculated from

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{6}$$

A negative value of standard free energy –11.37 kJ mol^{-1} and the positive value of the entropy change 89.06 J K^{-1} mol^{-1} at 299 K indicate the spontaneity of the process. The –ΔG° values are found to be higher (Table 1) at higher temperatures indicating the favourable adsorption of Sr at elevated temperatures.

Table 1. Thermodynamic parameters for adsorption of strontium on USb

Temp. K	ΔH° kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}	–ΔG° kJ mol^{-1}
299	15.26	89.06	11.37
313		89.64	12.80
323		88.88	13.45

4. Conclusions

The present study indicates that the uranium antimonate prepared in nitric acid medium is a good candidate for the selective sorption of Sr from nitric acid solutions.

The adsorption data analysis by Freundlich and Langmuir isotherm models shows a better agreement for the range of Sr concentrations studied. The favourable adsorption of Sr at higher temperatures indicates that USb can be efficiently used for the removal of Sr from the acidic radioactive wastes.

5. Acknowledgement

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6. References

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Povzetek

Proučevali smo primernost uranovega antimonata (USb) kot sorbenta za adsorpcijo stroncija (Sr) iz kislih vodnih raztopin. Ugotovili smo, da proces v območju začetne koncentracije Sr med 1.14×10^{-4} in 1.14×10^{-2} mol L^{-1} pri različnih koncentracijah dušikove(V) kisline lahko opišemo s Freundlichovo in Langmuirjevo adsorpcijsko izotermo. Vrednost Freundlichovega adsorpcijskega koeficienta $\beta = 0.48$ kaže, da gre za heterogen proces. Kapaciteta adsorpcije »*b*«, dobljena iz Langmurjeve adsorpcijske izoterme znaša 18.81 mg g^{-1} pri 0.5 mol L^{-1} HNO_3. Raziskave adsorpcije pri različnih temperaturah kažejo, da gre za endotermen proces, ki ga spremlja povečanje entropije.