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Uptake behavior of titanium molybdophosphate for cesium and strontium

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Abstract This study investigates uptake of cesium and strontium from aqueous solution similar to nuclear waste on three samples of titanium molybdophosphate (TMP) synthesized under various conditions. Effects of concentration of sodium nitrate, pH and contact time on the uptake of cesium and strontium have been studied by bath method. The results showed that TMP has high affinity toward cesium and strontium at $\mathrm{pH} > 2$ and relatively low concentration of sodium nitrate. Kinetic data indicated that cesium uptake process to achieve equilibrium was faster than strontium. Cesium and strontium breakthrough curves were examined at 25 °C using column packed with H_3O^+ form of TMP and breakthrough curves showed symmetrical S-shaped profiles. At the same time, the calculated breakthrough capacity for cesium was higher than strontium. The results of desorption studies showed that over 99% of cesium and strontium was washed out of column by using 4 M NH_4Cl solution. This study suggests that TMP can have great potential applications for the removal of strontium and specially cesium from nuclear waste solution.

Keywords Cesium · Strontium · Titanium molybdophosphate · Uptake · Breakthrough

Introduction

During the past 50 years, nuclear power plants operation and consequently reprocessing of spent nuclear fuel have produced an enormous amount of nuclear waste containing fission product. Among them, strontium-90 and cesium-137 are considered as two major constituents of the fission products with regard to the contamination of the environment as well as their applications in industrial [1]. These ions with concentrations of $10^{-3} \sim 10^{-7}$ M in the waste solutions are the most hazardous and toxic radioisotopes to the environment in terms of their long-term effects. Their intermediate half-lives of about 30 years suggest that they are not only highly radioactive but also they have a relatively long half life to be around for hundreds of years [2–4]. Therefore, serious attention has been paid to manage the radioactive waste and improve the disposal of nuclear waste for environmental protection. Removing these radioactive nuclides from nuclear wastes in an economical and safe manner not only would result in a significant radioactivity and volume reduction but would also prepare the eligible elements to employ them in the field of medicine and industry.

Literature survey reveals that many different methods such as solvent extraction, ion exchange, precipitation, evaporation, bioaccumulation and adsorption have been studied for the removal and separation of these radiotoxic ions from aqueous solution [5–13]. Of the different methods, ion exchange method especially inorganic ion exchangers due to unique selectivity for certain elements, high thermal, chemical and radiation stability as compared

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to organic ion-exchange resins and carcinogenic solvent used in conventional liquid–liquid extraction have been found specific applications in the treatment and disposal of nuclear liquid wastes [14]. In this regard, many classes of inorganic ion exchangers have been studied to selective removal of cesium and strontium ions. Among these exchangers are zeolites, transition metal ferrocyanides, some polyoxometalates and metal oxide as selective to cesium or strontium [15–21]. However, polyoxometalates exhibit improved properties over the simple salt of the metals and other conventional inorganic ion exchanger due to their high selectivity, thermal and radiolytical stabilities [22].

In a continuation of our research work [22, 23], recently, an amorphous titanium molybdophosphate (TMP) as a new member of polyoxometalates family has been shown to have outstanding characteristics as an inorganic ion-exchanger on the basis of distribution coefficient studies of many metal ions and its ion exchange capacity [24]. It was also found to be high affinity toward cesium and strontium. This study, an extension of our previous work, deals with the investigation of adsorption behavior of TMP for cesium and strontium under various conditions of media.

Experimental work

Chemical and reagents

All the chemicals and reagents used were of Analytical Grade obtained from E. Merck or Fluka.

Apparatus

pH measurements were made with a Schott CG841 pH-meter (Germany). Quantitative determinations of strontium and cesium ions were carried out using an inductively coupled plasma (Varian Turbo Model 150-Axial Liberty) and atomic absorption spectrometer (Spectra AA-220 Varian, Australia), respectively. Waterbath shaker (model CH-4311, Infors AG) was used in determination of distribution coefficients of elements.

Synthesis of titanium molybdophosphate

The preparation of TMP was also performed as described elsewhere [24], Three samples of TMP were synthesized by adding gradually aqueous solution of molybdophosphoric acid (MPA) to alcoholic solution of titanium (IV) chloride under varying conditions given in Table 1. While the reaction mixture was thoroughly stirred with a magnetic stirrer at room temperature (25 °C), the pH of the system was increased slowly by adding NaOH for completion of the precipitation formation. Then the solution containing precipitate was stirred for 1 h and was refluxed at 75–80 °C for 24 h. The resulting precipitate was decanted and washed five times with demineralized water (DMW), filtered by suction and dried at 50 ± 2 °C for 24 h. It was further treated with excess of 0.1 mol L^{-1} nitric acid solutions for complete replacement of counter ions by H^+ ions. The excess of acid was removed by repeated washing with DMW. Finally the material was dried in an oven at 50 ± 2 °C.

Table 1 Conditions of synthesis of titanium molybdophosphate [22]

No	Sample code	Conditions of synthesis		
		Concn. of reagents $TiCl_4$, MPA (mol L^{-1})	Mixing volume ratio Ti:MPA	Final pH[a]
1	TMP-11	0.1, 0.05	1:1	0.8
2	TMP-21	0.1, 0.05	2:1	1.0
3	TMP-31	0.1, 0.05	3:1	1.3

[a] pH of the reaction mixture

Distribution coefficients

The distribution coefficients (K_d) for cesium and strontium ions were determined in aqueous solution by batch operation [25]. 200 mg of ion exchangers in H^+ form were kept in 20 mL of 1.2×10^{-4} M metal ion solution at 25 ± 1 °C for 5 h, with intermittent shaking to attain equilibrium. Blank solutions were prepared without ion exchanger, having the same concentration of metal ions. This solution was treated in the same way as above. The solution was then filtered and metal ions were determined using ICP or AAS methods [26]. The K_d values were calculated by the following equation;

$$K_d = [(I - F)/F] \times V/W \ (\mathrm{mL\,g^{-1}})$$

where I and F are the initial and final concentration (ppm) of metal ions in the solution phase, V is volume of initial solution in mL, and W is the dry mass of the ion exchanger in grams. Standard deviation for K_d values were checked by three determinations and were <10%.

Effect of hydronium ion concentration

To investigate the effect of hydronium ion concentration on the cesium and strontium uptake, the initial H_3O^+ concentration of Cs and Sr solutions were adjusted on 10^{-7}, 10^{-3}, 0.01, 0.1 and 0.5 M by using nitric acid solution. Other conditions for the determination of distribution coefficient such as the amount of ion exchanger, initial concentration of cesium and strontium, shaking time and temperature were the same as “Distribution coefficients”.

Effect of ionic strength

The solutions with initial concentration of 0, 0.001, 0.01, 0.1, 4 M $NaNO_3$ accompanied by cesium or strontium concentrations of 1.2×10^{-4} M in each of them, were chosen to investigate the effect of the ionic strength on cesium and strontium uptake. Other conditions for the determination of distribution coefficient were the same way as above.

Effect of contact time

The shaking time of 10, 30, 60, 150, 300 and 600 min were chosen to investigate the effect of contact time on the percentage of cesium and strontium uptake onto three samples of TMP. Other conditions were the same way as "Distribution coefficients".

Column experiments

For column breakthrough experiments, glass columns with internal diameter of 6 mm and glass wool at the lower end as a supporting surface for the exchanger were employed. Slurry of 0.4 g of an accurately weighed amount of the individual dried exchanger in H_3O^+ form was poured in a glass column. To avoid air bubbles, the loaded columns were carefully packed under water and then, the sorbent bed was washed with DMW. The loading process was carried out by passing a feed solution containing 0.005 M nitrate salt of each metal ion through the column at a constant flow rate of 0.3 mL min^{-1}. 2 mL fractions of the fluent were collected and the metal ion concentrations were determined by atomic absorption spectrometry or inductively coupled plasma. This was compared against the reference sample. The collection of the fractions was continued till the metal ion concentrations of the solution were roughly equal to that of the reference. The breakthrough capacities (meq g^{-1}) for cesium and strontium were measured directly in this technique and calculated from the following equation;

$$\text{Capacity} = (V50\% \times Z \times C_0)/W$$

where $V50\%$ is the volume, at which the element uptake is 50%; Z is the charge of the ion; C_0 is the initial concentration of each element (M) and W is the weight of the exchanging bed (g) [27].

For desorption study, the relevant ion was eluted with 4 M NH_4Cl solution from the above column containing saturated beds of TMP at flow rate of 0.3 mL min^{-1}.

Results and discussion

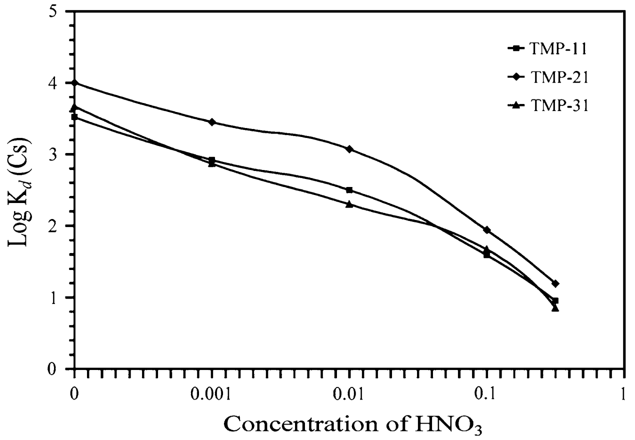

Fig. 1 The effect of H_3O^+ ion concentration on K_d values of cesium on synthetic TMP

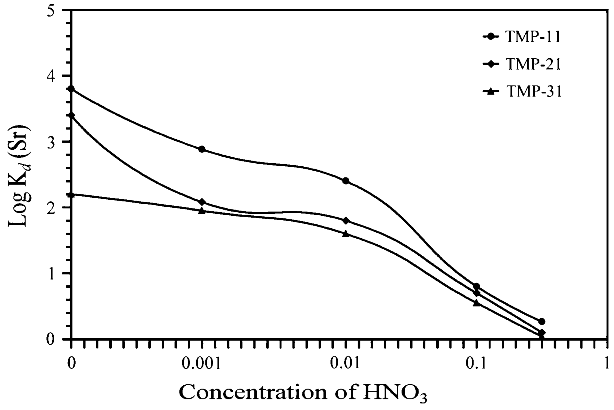

Fig. 2 The effect of H_3O^+ ion concentration on K_d values of strontium on synthetic TMP

Figures 1 and 2 show the effect of hydronium ion concentration on the distribution coefficient value of cesium and strontium. For both of metal ions, the uptake is seen to be strongly influenced by the pH of the solution. As it can be seen from both figures, the distribution coefficient of cesium and strontium decrease with the increase of hydronium ion concentration in all three samples. But this trend is observed to be less for the distribution coefficient of cesium. The decrease of distribution coefficient can be ascribed to the competition between the hydronium ion and cesium/strontium ions on the active sites of TMP. As shown in both figures, the high affinity of the sorbent towards strontium and cesium in the presence of relatively large concentration of hydronium ion ($[H_3O^+] \leq 0.01$) points to the possibility of its use for efficient removal of radiocesium and radiostrontium from acidic media loaded wastewater solutions. Also, According to these figures the high affinity sequences for cesium and strontium in three samples of TMP was TMP-21 > TMP-11 > TMP31 and TMP-11 > TMP-21 > TMP-31, respectively.

The effect of sodium ion concentration on the uptake behavior (distribution coefficient) of cesium and strontium

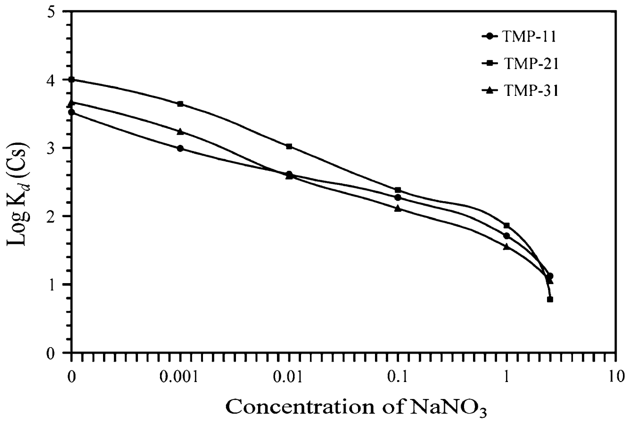

Fig. 3 Variation of K_d values of cesium on synthetic TMP as a function of Na^+ ion concentration

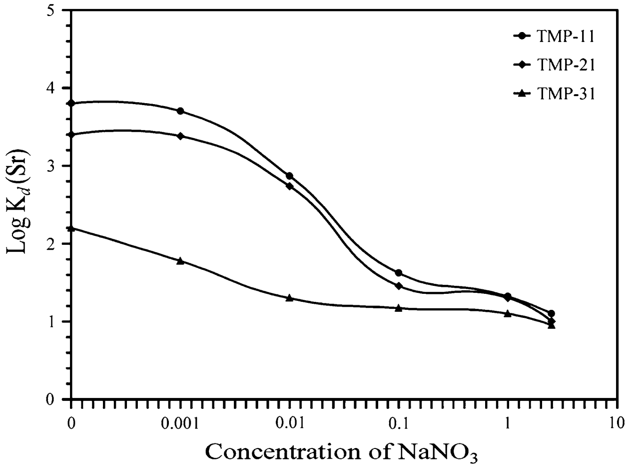

Fig. 4 Variation of K_d values of strontium on synthetic TMP as a function of Na^+ ion concentration

onto three samples of TMP is given in Figs. 3 and 4. As can be seen in both figures, with increasing in concentration of sodium ion, a decreasing pattern of the distribution coefficient of both Cs and Sr is observed. This phenomena can be explain by the fact that the increase of solution ionic strength decrease the activity coefficient of cesium and strontium ions, which limited their transfer to active site on the surfaces of TMP. At the same time, the competition between sodium ions and metal ions can be other important parameter to decrease of distribution coefficients of them. From both figures can be inferred that all the samples of TMP can remove cesium and strontium ions very well from aqueous solution with the concentration of below 1 M $NaNO_3$.

Adsorption kinetics, indicating the adsorption rate, is another important character for sorbents. Higher adsorption rate means shorter adsorption time and shorter equilibrium time is one of the most important parameters for economical wastewater treatment plant applications. The

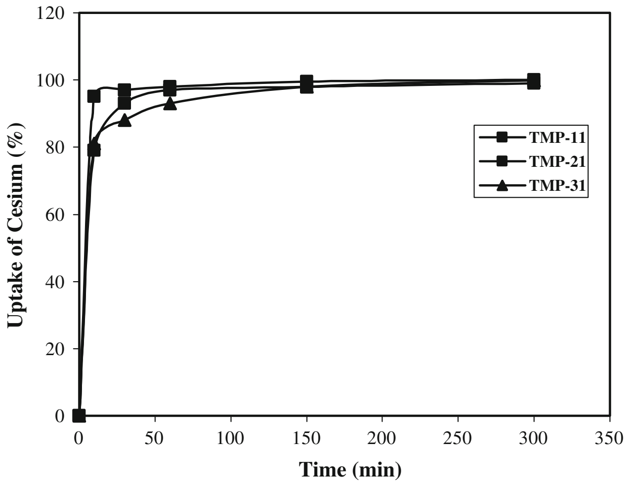

Fig. 5 Uptake of cesium on synthetic TMP as a function of time (minutes)

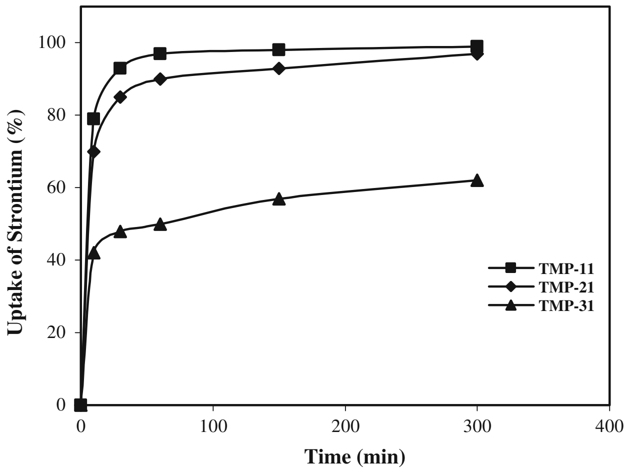

Fig. 6 Uptake of strontium on synthetic TMP as a function of time (minutes)

uptake percentage of cesium and strontium from aqueous solution by TMP at pH 6.5 as a functional of contact time is shown in Figs. 5 and 6. As shown in Fig. 5, the uptake rate of cesium on all the samples of TMP reached abruptly 80% within only 10 min of contact time and then slowly reached equilibrium within 80 min.

As it can be seen in Fig. 6, in the first 50 min the uptake rate of strontium for all samples reaches to the maximum. But the sorption of strontium on the sample TMP-31 is not complete and reaches to 60% after 5 h. From Fig. 6, the initial steep uptake suggests that strontium uptake occurs rapidly on TMP-11 and TMP-21 and then slowly reached equilibrium. For both of figures, this behavior may be explained by the fact that in the initial stage, the ion exchange on TMP occurs mainly on its external surface and the internal surface of its micropores. While in the later stage, because of the internal surface of the micropores is approximately saturated with the metal ions exchanged, the exchange reaction takes place mainly on the internal surface of micropores. So the exchange speed is relatively slow [18].

For evaluating the column efficiency of the investigated exchangers toward cesium and strontium, breakthrough curves were obtained for both cations by plotting the breakthrough ratio (C/C_0) against the effluent volume, where C_0 and C are the concentration of the initial solution and the effluent, respectively. Figures 7 and 8 show the breakthrough curves of cesium and strontium for three samples of TMP. Both breakthrough curves for sorbents exhibit rather symmetrical shapes that indicate the high selectivity of ion-exchanger toward cesium and strontium [28]. The breakthrough capacities for cesium and strontium on TMP were calculated from the corresponding curves and represented in Table 2. As it can be seen from Table 2, cesium has higher breakthrough capacity than strontium and it can be concluded that the divalent metal ions (Sr^{2+}) may be exchanged with two exchangeable sites on the surface of the column bed compared with one site in the case of monovalent Cs^+ ions [29]. Also, as shown in Table 2, TMP-21 and TMP-11 show highest breakthrough capacity for cesium and strontium, respectively.

Table 2 Breakthrough capacities of Cs^+ and Sr^{2+} ions on titanium molybdophosphate ion-exchanger at 25 ± 1 °C

Metal ions	Capacity (meq g^{-1})		
	TMP-11	TMP-21	TMP-31
Cs^+	0.2	0.24	0.08
Sr^{2+}	0.14	0.07	0.06

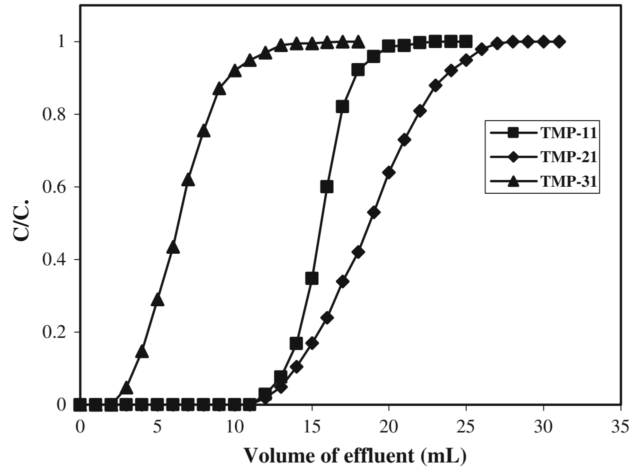

Fig. 7 Break-through curve of cesium ions on TMP, influent concentration 0.005 M, flow rate 0.3 mL min^{-1}, 0.4 g resin, at 25 ± 1 °C

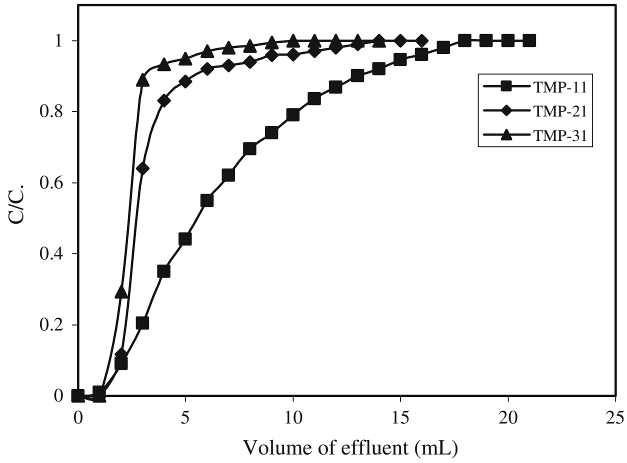

Fig. 8 Break-through curve of strontium ions on TMP, influent concentration 0.005 M, flow rate 0.3 mL min^{-1}, 0.4 g resin, at 25 ± 1 °C

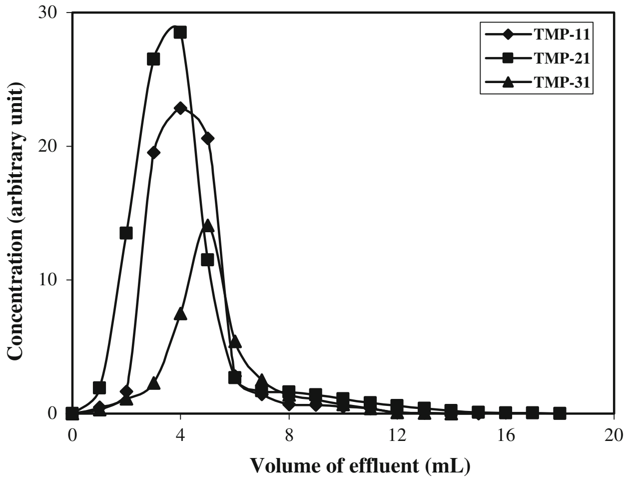

Fig. 9 Desorption of cesium from TMP using 4 M NH_4Cl, flow rate 0.3 mL min^{-1}

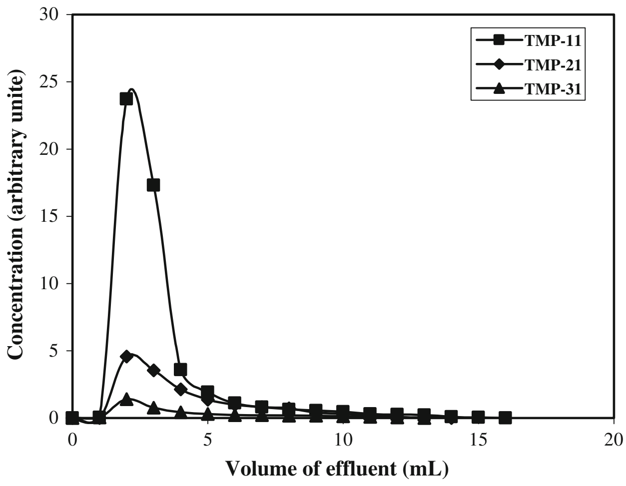

Fig. 10 Desorption of strontium from TMP using 4 M NH_4Cl, flow rate 0.3 mL min^{-1}

Cesium and strontium desorption from the cesium and strontium saturated bed of all the samples of TMP using 4 M ammonium chloride are shown in Figs. 9 and 10. As shown in both figures, by using 15 and 11 mL of 4 M NH_4Cl, over 99% of cesium and strontium was washed out from the column, respectively. In both figures, the Gaussian type peaks are the reasons for the reversible interaction of ions with the exchanger [28].

Conclusions

TMP, as an inorganic ion exchanger was used to investigate the uptake behavior of cesium and strontium from aqueous solution by bath and column methods. In batch studies, the uptake of cesium and strontium is dependent on the concentration of hydronium and sodium ions. At the same time, experimental results indicate that the uptake of cesium and strontium is favorable at $pH > 2$ and relatively lower ionic strength. The maximum uptake of cesium and strontium is observed on TMP-21 and TMP-11, respectively. In column studies, the breakthrough capacity for cesium on all samples of TMP is higher than strontium and elution curves indicate that desorption of cesium and strontium is done completely by using 4 M NH_4Cl.

The short equilibrium time accompany by the high uptake of cesium and strontium at solution containing relatively high concentration of hydronium and sodium ions reveal that TMP can be a very useful ion exchanger in treatment with nuclear waste solution for removal of them.

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