Synthesis, Characterization and Sorption Behavior of Some Radionuclides on Zirconium Tungstate Ion Exchanger

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ABSTRACT

Zirconium tungstate as an inorganic ion exchange material has been synthesized at different conditions. The materials were characterized by means infrared spectroscopy, thermo gravimetric analysis, and X-ray diffraction techniques. The stability of the ion exchangers was investigated in acidic and alkaline media. Ion exchange properties of synthesized materials were studied by measuring the distribution coefficient for ^{134}Cs, ^{85}Sr, ^{57}Co, and ^{152}Eu radionuclides. In acidic medium, zirconium tungstate shows a high affinity for ^{134}Cs. This result could be helpful for nuclear waste management, for waste water effluents containing ^{134}Cs, ^{85}Sr, ^{57}Co, and ^{152}Eu. The adsorption isotherm models of sorption process were calculated for ^{134}Cs.

Keywords: Synthesis; characterization; inorganic ion exchanger; zirconium tungstate, Radionuclides

1-INTRODUCTION

A highly efficient treatment concept is the removal of radionuclides from the bulk waste solution. The method for removal of trace radionuclides from effluents, which contain large amounts of inactive metal ions, must be highly selective for the radioactive component. This requirement can be met with the use of inorganic ion exchangers. Ion exchange as a separation process is relatively facile and energy-efficient compared to other traditional waste treatment techniques used in nuclear industry (e.g. solvent extraction, precipitation, evaporation) (1-3).

Inorganic materials lend themselves to this challenging task extremely well, because of their good tolerance against ionizing radiation and thermal stability, as well as their compatibility with the final waste forms (4) Very high selectivity can be obtained in inorganic ion exchangers and thus good separation efficiencies for trace ions in complex radioactive solutions of high concentrations of interfering salts, acidity and alkalinity. Until now, however, most of these synthetic ion exchange materials have shown poor ion exchange capacity and poor selectivity for metal ions and low thermal and chemical stability (5–9)

Acid salts of tetravalent metal ions with the general formula M(IV) $(HXO_4)_2 \cdot nH_2O$, where M represents Zr(IV), Ti(IV), Sn(IV), etc. and X represents P, W, Si, Mo, Se, As, etc., have been extensively studied. Both single and double salts have been synthesized, but the double salts have better ion exchange capacity, better thermal and chemical stability and high resistance toward radioactivity. Ti(IV) tungstate has a negligible adsorption of trivalent ions such as Fe^{3+}, Al^{3+} and In^{3+} (10-11), in contrast to Zr(IV) tungstate, uranium tungstate, and stannic tungstate, which adsorb them completely (12). A number of synthetic inorganic ion exchange materials have been found to act as electron exchange material (13-15).

Tungstates of chromium, thorium, titanium, tin, and zirconium exhibit low capacity (varying from 0.02 to 0.05 meq/g), poor selectivity, and poor stability (16-17). In contrast, stannic(IV) tungstoselenate and stannic(IV) tungstoarsenate have exhibited higher capacities of 0.88 and 1.06 meq/g, respectively (18-19). Removal of radio Cs from low level wastes can be achieved with use of highly selective ion exchange materials. It is well known that transition metal ferrocyanides are selective for Cs uptake and a great number of them have been studied for their prospective use in the

separation of radioactive Cs from nuclear waste streams. One of the most promising Cs-selective ferrocyanides is potassium cobalt ferrocyanide (20-22).

Natural zeolites have been used for the removal of ^{137}Cs from low and intermediate level radioactive waste effluents (23-24). A major disadvantage, however, is the competitive interactions of other monovalent cations present in waste effluents, in particular Na and K (20). Over 97% and 85% removal of ^{137}Cs and ^{60}Co, respectively, has been achieved from the waste effluents. Dyer et al. (25) studied the uptake of ^{137}Cs and ^{90}Sr on natural zeolites (clinoptilolites) from Mongolia in the presence of competing cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+}. A reasonable order of removal of the cations was $Cs^+ > K^+ > Sr^{2+} > Ca^{2+} > Na^+ > Mg^{2+}$. Another limitation of zeolites is their poor stability in acidic solutions due to dissolution of Al from the framework. Paterson-Beedle et al. (26) used hydrogen uranyl phosphate as an inorganic ion exchanger for the removal of ^{60}Co, ^{137}Cs, and ^{90}Sr and demonstrated that ~100% removal each from aqueous solution. The findings were confirmed in experiments with test nuclides ^{60}Co, ^{137}Cs, and ^{90}Sr in a wastewater pool where spent fuels were stored and cooled, sited at a post-irradiation examination facility at the Korea Atomic Energy Research Institute.

Kotvitskyy et al. (27) investigated the selective removal of Cs^+ ions by electro-deionization, using a combined inorganic ion exchanger containing zirconium hydro-phosphate and phosphomolybdic acid prepared by sol-gel method. The adsorption and migration of Na^+ and Cs^+ ions adsorbed on the ion exchanger were investigated. High selectivity toward Cs^+ ions was found. The selective removal of Cs^+ ions was also studied using a combined inorganic ion exchanger and organic ion exchanger Dowex-50WX2 as transport medium. As much as 98% cesium removal from sodium-containing solution with simultaneous 8-fold concentration in the cathode compartment was demonstrated.

Rathore et al. (28) tested an inorganic exchangers, namely hydrated iron oxide (HFeO) and a mixture of hydrated titanium oxide (HTiO) and hydrated thorium oxide (HThO), for the removal of actinides such as Pu and Am and fission products such as ^{137}Cs, ^{90}Sr, and [106]Ru. They observed that HFeO can be used for the removal of Pu and Am, while the mixture of HTiO and HThO is suitable for the removal of Cs, Ru, and Sr from alkaline intermediate level liquid wastes.

In the present work, an inorganic zirconium tungstate ion exchanger was synthesized and characterized, and its selectivity toward some radionuclides was investigated.

2-EXPRIMENTAL

Chemicals and reagents:

All chemicals and reagents were of analytical grade and used without further purification. Zirconium oxychloride and sodium tungstate were obtained from Alfa Aesar (Germany) and Fluka (Switzerland), respectively. Hydrochloric acid was from J.T. Baker (Holland) and nitric acid from Prolabo (England). The suppliers of the radiotracers were Perkin Elmer for Sr-85, Eckert&Ziegler for Co-57and Cs-134, and Amersham Laboratories for Eu-152.

Preparation of reagents and synthesis of ion exchange material;

A 0.1 M solution of zirconium oxychloride was prepared in 2 M HCl, and solution of 0.1 M sodium tungstate was prepared in deionized water. Ion exchanger samples of zirconium tungstate (ZrW) were prepared by mixing aqueous solutions of 0.1 M sodium tungstate and 0.1 M solution of zirconium oxychloride (HCl medium) under various reaction conditions. Fine white precipitate was formed after complete mixing of reagents. The mixture was then stirred for 1 hr at room temperature and allowed to stand in the mother liquor at room temperature for different aging times (one, two, or three days). The supernatant was filtered under suction and the excess acid in precipitates was removed by washing several times with deionized water. The products were dried at 55±2 ?C in an oven, then crushed and sieved to obtain particles of size less than 500 μm. Three ZrW products with the same molar ratio (1:1) were obtained at the different aging times (one, two, or three days) and are referred to below as ZrW-1, ZrW-2, and ZrW-3.

FT-IR, TGA, and XRD analyses:

The ion exchangers were characterized by FT-IR, TGA and XRD techniques . Infrared absorption spectra of the synthesized ZrW cation exchange materials were recorded with an FT-IR spectrophotometer (Perkin-Elmer, USA). Thermogravimetric analyses (TGA) were carried out with a Mettler-Toledo TA800 instrument by heating the samples up to 800 ?C at a constant rate of 10 ?C min^{-1} in nitrogen atmosphere. Powder X-ray diffraction (XRD) patterns were collected with a Phillips PW 1710 powder diffractometer (operating at 30 kV and 50 mA) with Cu Ka (1.54 A°) radiation.

Chemical stability:

The extent of dissolution of the exchange material in different media (deionized water, mineral acids, and alkaline solutions), was studied by equilibrating 0.50 g of ZrW-2 material with 50.0 ml of the solution of interest for 24 h at room temperature. The amounts of zirconium and tungsten were determined by inductively coupled plasma (ICP).

Sorption studies:

Batch adsorption experiments were performed to clarify selectivity of the exchange material for some radionuclides. The distribution coefficients (K_d) for radionuclides were determined radiometrically. A weighed amount of the prepared materials (0.05 g) was mixed with 10.0 ml of deionized water that had been spiked with a trace amount of each radionuclide under study: ^{134}Cs, ^{85}Sr, ^{152}Eu, and ^{57}Co. The resultant mixture was shaken mechanically at the appropriate pH until equilibrium was achieved. The pH was adjusted by either dilute nitric acid solution or ammonia solution. The mixture was centrifuged until the supernatant was free from suspended prepared materials and then filtered through 0.2 mm ion chromatography filter. Aliquots (5.0 ml) of the liquid were sampled and analyzed with a gamma-ray spectrometer with single-channel NaI detector (Wallac, Wizard analyzer).

The distribution coefficients (K_d), the percentage removal (% R) and the amount of radionuclides adsorption at equilibrium (q_e), (mg/g) were calculated from the following equations:

$$K_d = \frac{C_S}{C_L} = \frac{A_o - A_e}{A_e} \times \frac{V}{m} \qquad (1)$$

$$\% \ R = \frac{A_o - A_e}{A_o} \times 100 \qquad (2)$$

$$q_e = \frac{(A_o - A_e)C_0}{A_o} \times \frac{V}{m} \qquad (3)$$

where C_S and C_L are the equilibrium concentrations of radionuclide in the solid exchanger and solution, respectively; A_o and A_e are the initial and equilibrium activities per unit volume of solution for the radionuclide; V is the volume of the solution (ml); and m is the weight of ion exchange material (g). Care was taken during the measurements to ensure that the counting rate was generally at least 8000 CPM to maintain the statistical error of individual measurements at less than 1%.

3-RESULTS &DISCUSSION

Characterization of ion exchange material:

The FTIR spectra of the exchangers (Fig. 1) show a broad but strong peak in the region 3600–3000 cm^{-1}, which represents the O–H stretching of lattice water molecules ([29-30). The strong and sharp peak at 1620 cm^{-1} may be due to H–O–H bending. The broad and weak bands in the regions 830–780 and 900–825 cm^{-1} can be assigned to $(WO_4)^{2-}$ and metal oxide groups, respectively [30–32]. As can be seen in Fig. 1, aging time affects the appearance and intensity of the characteristic peaks. In general, ZrW-1 produces much weaker adsorption peaks than ZrW-2 or ZrW-3. The ZrW-2 material produces the strongest peaks, indicating greatest coverage of OH groups, which may be reflected in its ion exchange properties.

The thermograms (TGA) of zirconium(IV) tungstate (Fig.2) reveal weight losses of ~3.9%, ~24%, and ~5% for ZrW-1, ZrW-2, and ZrW-3, respectively, up to 220 ^{o}C. The losses are due to the removal of external water molecules. The larger weight loss in ZrW-2 is attributed to the loss of an internal water molecule due to the condensation of hydroxyl groups (15). Evidently, too, the original water content was greater than in the other ZrW materials. The further loss in weight observed beyond 600 ^{o}C is attributed to the formation of metal oxide. Thereafter the weight becomes constant (13).
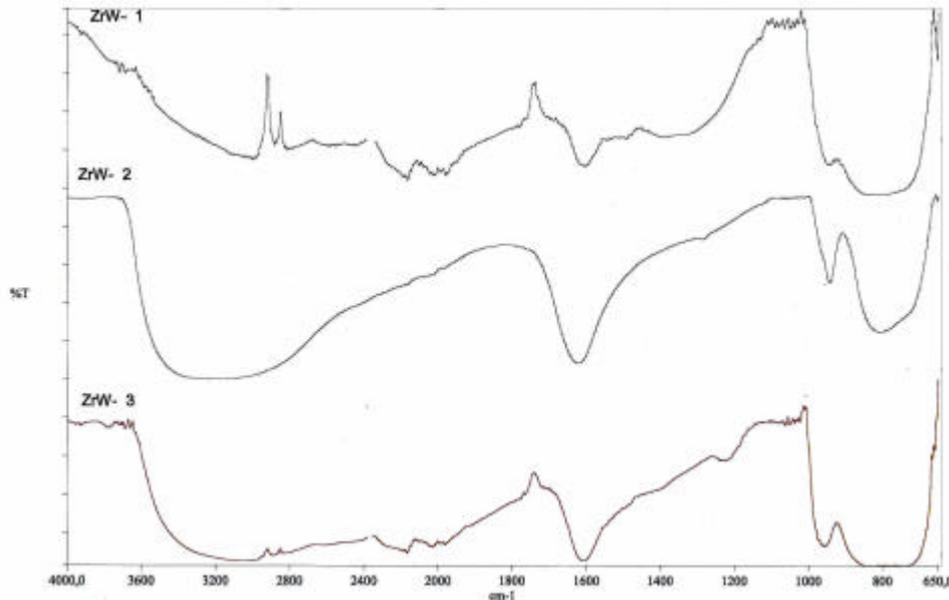

Fig. 1: IR spectra of zirconium tungstate (ZrW-1, ZrW-2, and ZrW-3) **ion exchange materials.**

Finally the materials were characterized by XRD study. The X-ray diffraction pattern of ZrW-2 material shows the exchanger to be amorphous in nature. This is in agreement with a number of prepared and characterized inorganic cation exchangers, such as zirconium (IV) molybdo tungsto vanado silicate [33], zirconium(IV) iodotungstate (34), Ti(IV) iodovanadate (15), zirconium(IV) iodovanadate (13), and cerium(IV)iodotungstate (35).
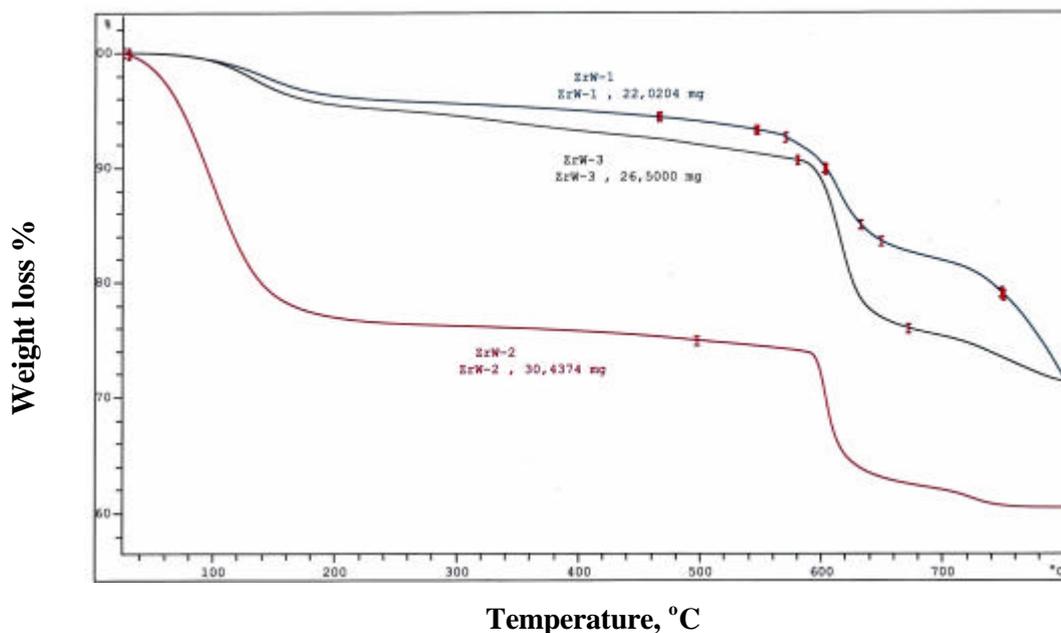

Temperature, ^{o}C

Fig. 2: TGA thermograms of zirconium tungstate ion exchange materials.

   The chemical stability of the ZrW ion exchange materials in different chemical media was determined by investigating the effect of HNO_3 and NaOH on dissolution of ZrW material. Table 1 summarizes the dissolution (%) of zirconium and tungsten ions from ZrW-2. The material was found to be fairly stable in low concentration of NaOH and quite-stable in HNO_3 and water.

Table 1: Dissolution (%) of ZrW-2 ion exchange material in different chemical media

Medium	Zr	W
H_2O	6.80566E-06	2.06486E-05
0.1 M NaOH	4.02676E-05	4.380006646
0.001 M HNO_3	6.85189E-06	0.001683543
0.1 M HNO_3	0.158028201	0.45972785

Effect of pH and aging time on distribution coefficient:

   The pH of the aqueous solution is an important controlling parameter in adsorption and ion exchange processes. The effect of pH on the distribution coefficient of ^{134}Cs on the three synthesized ZRW cation exchangers was investigated at different pH values. As can be seen in Fig. 3, the initial distribution coefficient of ^{134}Cs is higher for Zr-2. For all three exchangers the rate of increase of the distribution coefficient is fastest between pH 0.5 and 4, after which the rate declines slightly up to about pH 6. The lower distribution coefficient at acidic pH is due to the presence of excess H^+ ions competing for the adsorption sites with exchange cation and/or adsorbed cation. Moreover, as the pH of the system decreases, the number of negatively charged adsorbent sites decreases, while the number of positively charged surface sites increases. The adsorption of positively charged cations is less favored, therefore, owing to electrostatic repulsion.

   From the pattern of the distribution coefficients, it is clear that the aging time is an essential factor for the efficiency of the exchanger. The distribution coefficient (K_d) values of ^{134}Cs vary widely with the aging time of the ZrW material, with the maximum value obtained for ZrW-2 and lowest for ZrW-3. The aging time considerably affects the degree of hydration and the composition of the exchanger and thereby the particle size of the cavities inside the exchanger as well as other properties. (20, 27). The results show the distribution coefficient of ^{134}Cs to be maximum (~ 2000 ml/g) when ZrW-2 is used at pH 6.

Selectivity for radionuclides and effect of nitric acid concentration :

   Distribution coefficient (K_d) values were used as a measure of the selectivity of the material for metal (Cs, Co, Sr, and Eu) ions. The selectivity determines how efficiently the element of interest is separated from other elements. In the case of radioactive waste treatment, these other elements are usually present in vast concentrations and compete for the ion exchange sites of the exchanger. Because of this, the selectivity of the exchanger for a specific radionuclide (i.e., the K_d value) must be high for meaningful separation to occur.
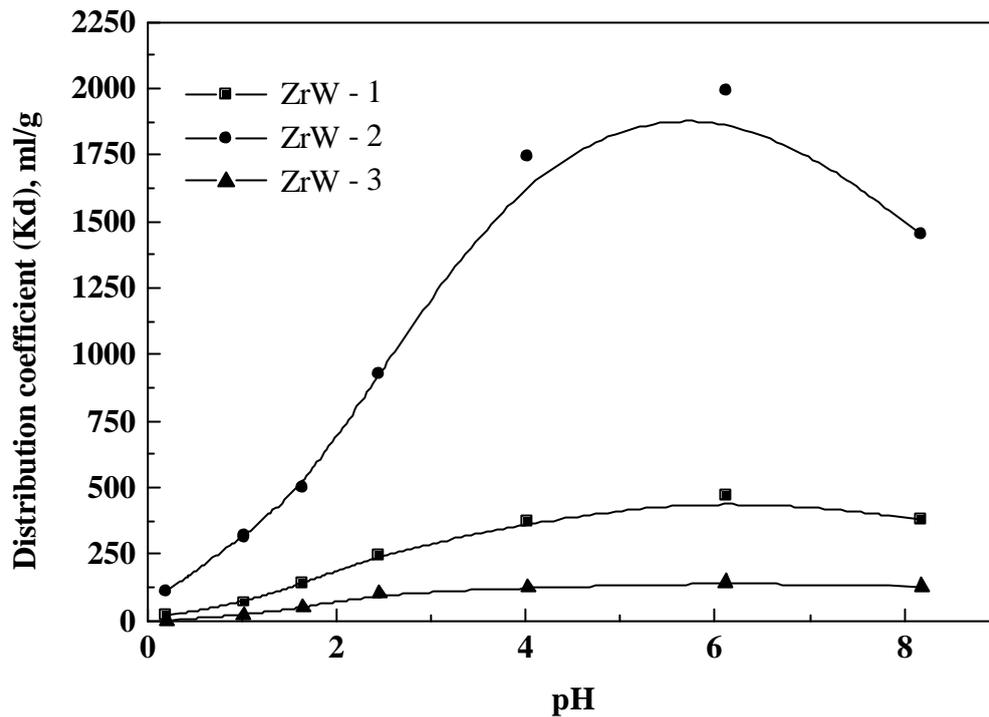
Fig. 3: Effect of pH on the distribution coefficient (K_d) of cesium with different zirconium tungstate ion exchange materials.

The distribution coefficients of ^{134}Cs, ^{57}Co, ^{85}Sr, ^{152}Eu on the ZrW inorganic ion exchangers were investigated at different concentrations of nitric acid medium and in double distilled water. It is clear from the results presented in Table 2, the distribution coefficients are in all cases larger with the exchanger aged for two days than with the exchanger aged just for one day, and they are small with the exchanger aged for three days. At the same time, the sorption capability of ZrW-2 is significantly higher for ^{134}Cs than for the other radionuclides studied (^{57}Co, ^{85}Sr, ^{152}Eu), as shown in Fig. 4. The difference is most pronounced at low nitric acid concentration (0.001 M), where ion exchange is dominant over physical adsorption. As presented in Table 2, the distribution coefficient of ^{134}Cs increases drastically for all three exchange materials as the nitric acid concentration decreases from 3.0 to 0.001 M, and the distribution coefficient of ^{134}Cs is maximum at 0.001 M nitric acid. With increase in the nitric acid concentration, deprotonation on the surface of the exchanger decreases and thus also the electrostatic interaction with cesium metal ion.

Clearfield ([3], Lehto and Harjula (37) have described the latest developments in inorganic adsorbents and their applications in the treatment of nuclear wastes. They also indicate that few inorganic adsorbents effectively execute the separation of fission products from acidic liquid wastes and suggest the need for new inorganic adsorbents able to show function under these conditions. The results of the present investigation show the prepared exchanger ZrW-2 to have promising capability for the sorption of cesium from acidic wastes solutions. On Zr-2, the distribution coefficient of ^{134}Cs is much higher than the distribution coefficients of the other radionuclides, making it a highly selective sorbent material for cesium.
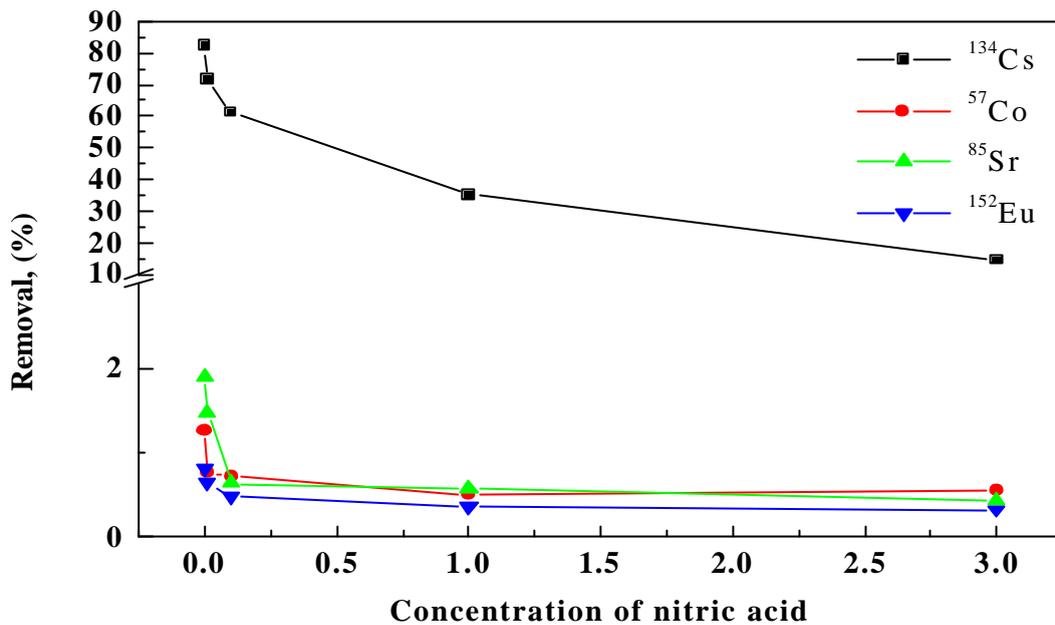
Fig. 4: Effect of concentration of nitric acid on removal efficiency (%) of ^{134}Cs, ^{57}Co, ^{85}Sr, and ^{152}Eu with use of ZrW-2 ion exchange material.

Effect of contact time :

Sorption experiments were carried out on ZrW-2 material with a fixed adsorbent dosage of 50 mg at pH 6 of deionized water. As the results in Fig. 5 show, the uptake of Cs ion increases with the contact time. Also, the rate of uptake is maximum at 360 min, and thereafter the adsorption proceeds at slower rate until equilibrium is achieved. After equilibrium the rate of adsorption is constant. The equilibrium time for the removal of cesium was taken as 1440 min (i.e., 24 hr).

Table 2: Distribution coefficients (K_d, ml/g) of ^{134}Cs, ^{57}Co, ^{85}Sr, and ^{152}Eu partitioned onto ZrW inorganic cation exchange materials from nitric acid medium and in double distilled water (DW).

| Material	Radionuclides	Concentration of nitric acid					DW
		0.001M	0.01M	0.1M	1.0M	3.0M	
ZrW-1	^{134}Cs	247.01	138.55	68.63	16.64	9.35	466.45
	^{57}Co	1.62	0.35	2.97	0.54	0.52	8.94
	^{85}Sr	0.91	0.11	0.20	1.12	0	2.4
	^{152}Eu	0.032	0	0	0	0	2.69
ZrW-2	^{134}Cs	**926.03**	502.22	316.81	108.52	34.01	**1993.96**
	^{57}Co	2.48	0.002	1.42	0.98	1.10	9.88
	^{85}Sr	2.63	3.44	1.25	1.03	0	1.17
	^{152}Eu	1.59	1.29	0.90	0	0	13.15
ZrW-3	^{134}Cs	99.21	48.32	20.44	0.64	3.06	141.7
	^{57}Co	2.41	0.91	2.25	0.71	0.23	13.52
	^{85}Sr	1.29	1.18	0.25	0.43	0	2.73
	^{152}Eu	0.24	0	0	0	0	8.21
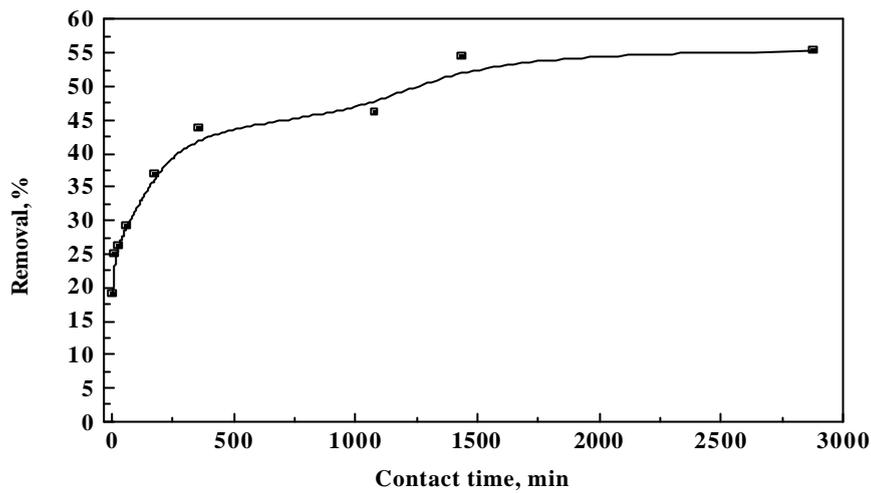
Fig. 5: Removal (%) of cesium with ZrW-2 ion exchange material as function of contact time.

Effect of volume to mass ratio:

The ratio of solution volume to exchanger mass was investigated to determine the minimum weight of ZrW-2 cation exchange material able to provide a reasonable uptake percentage of ^{134}Cs at pH 6 of deionized water. The weight of the ZrW-2 material was increased from 0.025 to 2 g, while the volume of the aqueous solution was kept constant at 10.0 ml. Fig. 6 shows how the removal percentage of ^{134}Cs is affected by the weight of ZrW-2 material. The removal percentage of ^{134}Cs was ~ 80% at V/m ratios between 40 and 5 (ml/g). Hence, V/m ratio = 40 (ml/g) is recommended for maximum removal percentage of ^{134}Cs.
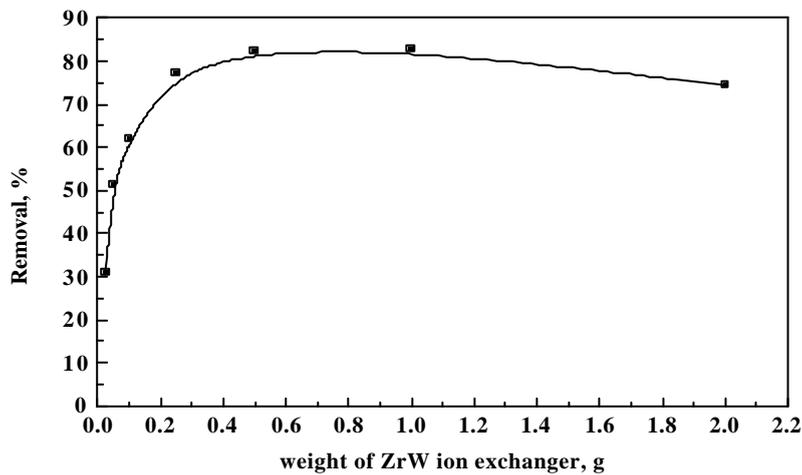

Fig. 6: Effect of volume (10 ml) to mass ratio on removal (%) of cesium with ZrW-2 ion exchange material.

Effect of initial concentration of cesium:

Adsorption isotherms were measured by a well-known method: by gradually increasing the concentration of sorbate ions in solution and measuring the amount adsorbed at each equilibrium concentration. The degree of sorption should be a function of the concentration of sorbate ions only.

The adsorption isotherms were investigated for Cs$^+$ on ZrW-2 in concentration range from 1 to 25 mg/L at a constant volume to mass ratio of 40 ml/g.

As shown in Fig. 7, the efficiency of cesium removal decreased from 76% to 22% as the initial concentration of Cs ions was increased from 1 mg/L to ~ 25 mg/L. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and as the metal concentration increases, these sites become saturated. That is, for a given mass of exchanger, removal percent is maximum for a particular metal concentration, and beyond that concentration no more metal ions are adsorbed because all sites are occupied (38).

Analysis of Data using Various Adsorption Models:

Adsorption isotherms are used to express the surface properties and affinity of the adsorbent and can also be used to compare the adsorption capacities of the sorbents for pollutants in aqueous solutions. These isotherms are useful for estimating the total amount of adsorbent needed to adsorb a required amount of adsorbate from solution..

In this regard the adsorption data were analyzed by fitting them to different equations. These included the Langmuir, Freundlich and Tempkin equations. In the present work the models were used to describe the relationship between the amount of ^{134}Cs adsorbed and its equilibrium concentration for ZrW-2.

The basic assumption of the Langmuir isotherm model is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and no further adsorption thereafter. The Langmuir isotherm is represented by the following linear equation (39-41):
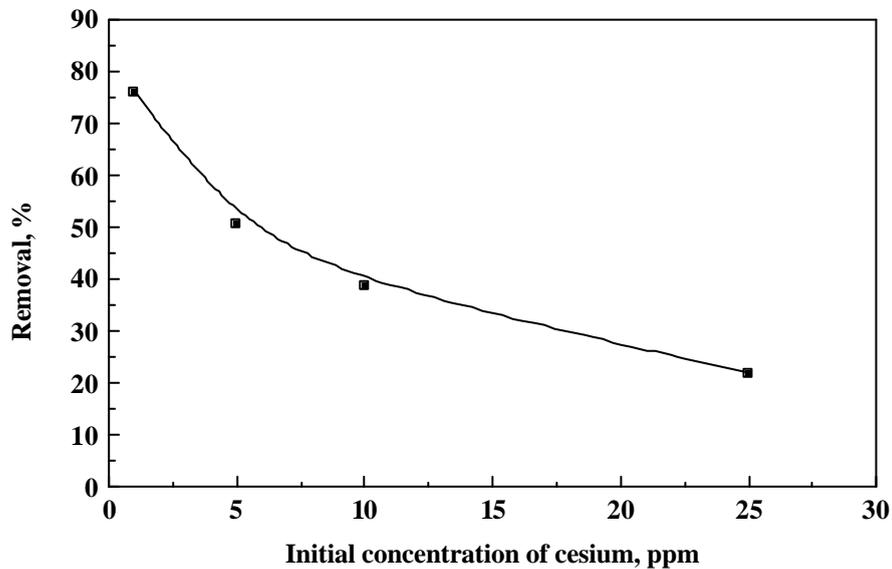

Fig. 7: Effect of initial concentration on removal (%) of cesium using ZrW-2 ion exchange material.

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (4)$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g) and C_e is the equilibrium concentration of the adsorbate (mg/L). The constants Q and b are Langmuir constants. When C_e/q_e was plotted against C_e, a straight line with a slope of **b/Q** was obtained.

The relationship between the ^{134}Cs uptake capacity q_e (mg/g) of adsorbent and the residual ^{134}Cs concentration C_e (mg/L) at equilibrium is given by Freundlich isotherm. The linear form of the Freundlich equation is given by (39, 40):

$$\ln q_e = \ln k + \frac{1}{n}\ln C_e \qquad (5)$$

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of the ^{134}Cs . K and n are Freundlich constants, n giving an indication of how favorable the adsorption process is, and K (mg/g $(L/mg)^{1/n}$) is the adsorption capacity of the adsorbent. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to 0 [39-41]. The plot of ln q_e versus ln C_e gives a straight lines with a slope of 1/n.

Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in Freundlich equation. Temkin model [39-41] can be shown as:

$$q_e = (\frac{RT}{b})\ln(K_t C_e) \qquad (6)$$

This equation in its linear form can also be written as:
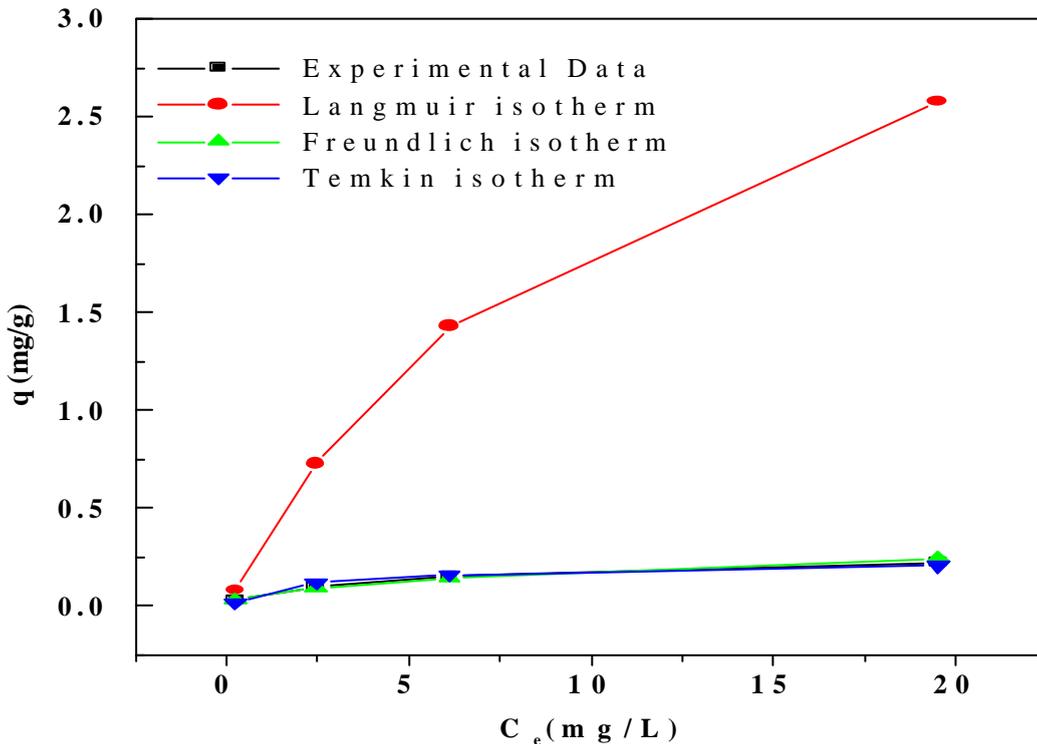
$$q_e = B\ \ln K_t + B\ \ln C_e \qquad (7)$$

Fig. 8: Comparison of the fit of various isotherm equations for the adsorption of ^{134}Cs onto ZrW-2 exchanger.

$$B = \frac{RT}{b} \qquad (8)$$

The adsorption data were analyzed with the help of equation (7). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants K_t and B. K_t is the equilibrium binding constant (L/mg) and corresponds to the maximum binding energy, whereas, constant B is related to the heat of adsorption.

The sorption isotherms for [134]Cs binding on ZrW-2 in acidic medium are shown in Fig. 8. The isotherm model parameters were obtained by non-linear least square fitting of the experimental data using Microcal Origin 5.0 program. The values of constants or binding parameters obtained by fitting Langmuir, Freundlich and Tempkin models to the experimental adsorption data obtained during adsorption of [134]Cs on ZrW-2,as well as the values of correlation coefficients are given in Table 3.

From Fig. 8, the Freundlich and Tempkin models fits well the experimental isotherm data and suggests that favorable sorption and multilayer sorption is the prevalent mechanism on ZrW-2 exchanger.

Table 3: Langmuir, Freundlich and Tempkin isotherm model constants
and correlation coefficients for the adsorption of [134]Cs on ZrW-2

Isotherm Parameters	Parameters
Langmuir	
Q (mg/g)	4.0640
b (L/mg)	0.0888
R^2	0.9942
Freundlich	
k	0.06220
$1/n$	0.45913
R^2	0.99410
Tempkin	
K_t	6.8510
B	0.0425
R^2	0.9845

4-CONCLUSIONS

An amorphous zirconium (IV) tungstate cation exchanger was synthesized at different conditions. The materials were characterized by FTIR, TGA, and X-ray diffraction techniques. Both thermal and chemical stability of the exchanger were acceptable. Two days aging time was found to be optimum for the ZrW material. Sorption studies showed the material to be selective for [134]Cs, which is a major polluting radionuclide in many nuclear industry effluents. The Zr(IV)W exchanger effectively separates Cs^+ ions from other fission and activation products (Sr, Co, and Eu). A special feature is that is has potential for decontaminating acidic waste solutions, which cause severe environmental problems. The isotherm data showed that the adsorption is multilayer mechanism on ZrW-2 exchanger.

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