Desalination and Water Treatment
www.deswater.com

13 (2010) 418–426
January

1944-3994/1944-3986 © 2010 Desalination Publications. All rights reserved
doi: 10.5004/dwt.2010.999

Removal of ^{60}Co and ^{134}Cs radionuclides from aqueous solution using titanium tungstate ion exchanger

G. M. Ibrahim*

Hot Laboratories Center, Atomic Energy Authority, P.O. No. 13759, Cairo, Egypt
Tel. +20222060107; Fax +20222059240; email: gehanmohamed71@yahoo.com

Received 19 April 2009; accepted 22 October 2009

ABSTRACT

A weakly crystalline titanium tungstate with Ti:W ratio of 1:1.3 has been prepared and evaluated as a novel inorganic ion exchange resin for the separation of some radioactive isotopes. The product was characterized using X-ray diffraction, FTIR-spectra, thermal analysis and finally X-ray fluorescence. The selectivity behavior of the exchanger was determined for cesium and cobalt ions at concentration range 10^{-2} to $10^{-}4$ M. The distribution coefficients for both ions were also, evaluated at different nitric acid concentrations. The adsorption results obey Freundlich isotherm and the values of adsorption capacity and intensity were computed for both ions. The different thermodynamic parameters, ΔH (4.45, 13.7 kJ/mol), ΔS (46.5, 68.66 J/mol/deg) and ΔG (−9.61, −7.1 kJ/mol) for the adsorption of cesium and cobalt ions have been reported, respectively.

Keywords: Ion exchange; Titanium tungstate; Characterization; Capacity; Distribution coefficients; Adsorption isotherm; Column

1. Introduction

As one of the requirements in environmental protection, radioactive waste management strategies, including treatment and disposal are considered as challenging areas of interest. The separation of long-lived radionuclides such as ^{134}Cs, ^{60}Co from the nuclear waste is an essential step in this regard. It may reduce the volume of the treated waste as well as its reclassification as lower level category. Ion exchange technique is one of the most important methods that used in radioactive waste treatment [1,2].

The use of inorganic sorbents for the treatment of radioactive waste was originally made on the basis of their resistance to radiation, good resistance to chemical attack, their compatibility with potential immobilization materials and selectivity towards certain metal ions [3]. A wide range of acidic salts of multivalent metals was synthesized. Poorly crystalline and amorphous forms of different compounds have been reported earlier, amongst which zirconium phosphate is the most widely studied [4–6]. Beside, compounds like antimonate, molybdate, tungstate, vanadate and silicate salts of zirconium, titanium, cerium, iron and thorium have been reported also [7–10].we have reported some inorganic ion exchangers and some composites and showed their utility in the nuclear field [11,12].

Clearfield et. Al. prepared some ion exchange resins that can be used in different applications [13–15]. They include the hydrothermal syntheses, characterizations and crystal structures of lead(II) carboxylate-phosphonate with a double layer structure and nickel(II) carboxylate-phosphonate containing a hydrogen-bonded 2D layer with intercalation of ethylenediamines [16]. Also, they prepared α-zirconium phosphate (α-ZrP)

---

*Corresponding author

by using two α-ZrP samples with different levels of crystallinity and two structurally different intercalating molecules to study the effect of guest molecular architecture and host crystallinity upon the mechanism of the intercalation reaction [17]. In the same context, they prepared a series of porous TiO_2–SiO_2 mixed metal oxides which clearly synthesized via sol–gel route using *n*-alkyl amine as pore directing templates [18]. The mixed oxides were characterized by nitrogen physisorption for surface area, pore volume and pore size distribution, as well as by FTIR, TGA, SEM, and TEM for the dispersion of titanium.

However, little work had been done on titanium tungstate and its application in the nuclear fields where, the effect of variation of the amount of tungsten in titanium tungstate exchanger on the distribution coefficients of cesium and strontium were studied by T. Moller et-al [19]. The distribution coefficients of some ions have been determined and some separations such as HF^{4+} from Zr^{4+} and La^{3+} from Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}, were also, obtained on the same exchanger [20], as well as its comparison to other exchangers [21].

Titanium (IV) based exchangers were known to be chemically and thermally stable in under identical conditions of synthesis [22]. However, the titanium ratio would reflect the chemical interaction within the exchanger; titanium tungstate exchanger with specific molar ratio (W: Ti = 1.5) was optimized. Further Increasing the tungsten content retards the distribution coefficient values for^{137}Cs ions [19].

Therefore, the tested titanium to tungstate ratio was kept at 1.3 under various preparation conditions so that crystalline structure was obtained. Then, the distribution coefficients of both cesium and cobalt ions on the exchanger was measured at different conditions, finally, testing the suitable isotherm. The applicability of this material in the separation of both ions was studied via the column technique.

2. Experimental

All the reagents and chemicals used were of analytical grade and were obtained from Merck, Germany.^{134}Cs and ^{60}Co radioisotopes were supplied by irradiating the nitrate salt of both ions in the ERR2 research reactor at Inshas site irradiated in with thermal neutron flux of 10^{14} n cm^{-2} s^{-1} for about 4 h.

2.1. Preparation of Titanium tungstate

Titanium tungstate ion exchanger was prepared by dropwise addition of 100 mL of 1 M titanium tetrachloride and 50 mL 1 M hydrated sodium tungstate in a water bath at 70 °C with a constant stirring using magnetic stirrer for 2 h. A yellow precipitate was obtained which left in the mother liquor for overnight standing, the slurry was filtered and washed with deionized water for several times until chloride free and the pH of the supernatant solution had a constant value 4.30 ± 0.02. The precipitate was then filtered again using centrifuge (10^4 rpm), dried at 50 °C for 6 days, then ground and sieved to obtain different mesh sizes and stored at room temperature.

2.2. Chemical stability

The chemical stability for the prepared samples was determined by dissolving about 0.1 g of the exchanger in 100 mL water and different concentrations from hydrochloric and nitric acids for a period of 48 h, followed by the determination of the weight loss of the exchanger.

2.3. Characterization

X-ray powder diffraction techniques, XRD, was performed by means of Shimadzu X-ray diffractometer, XD610 Model, with a nickel filter and Cu–K_α radiation (1.54A°) operating at high voltage of about 30 kV and 30 mA AC current.

Thermal stability of the prepared exchanger was carried out using simultaneous Differential thermal analysis–Thermogravimetric analysis system, Shimadzu DTA-TGA-60H thermal analyzer obtained from Shimadzu Inc., Kyoto, Japan. The samples measured from the ambient temperature up to 600 °C with a heating rate of 10 deg./min. under N_2 atmosphere.

The FTIR spectrum of the prepared exchanger was obtained using FTIR spectrometer, applying KBr disc technique. A compressed KBr pellet containing 6wt-% of the sample was used for this purpose in the range between 4,000 and 400 cm^{-1} with a resolution of 4 cm^{-1} and wave number accuracy of 1 cm^{-1}.

The X-ray fluorescence (XRF) was carried out using Phillips X-ray Fluorescence, Model PW 2400 spectrometer, by applying the fusion disc technique, Philips, Germany.

2.4. Batch equilibrations

Both distribution coefficient determinations and capacity measurements were performed by batch technique at constant volume (*V*) to mass (*m*) ratio of 100 mL/g. A mixture of the exchanger (0.05 g) and the solution (5 mL) of either separate cobalt nitrate or

Table 1
Chemical stability of titanium tungstate ion exchangers in different mineral acids.

HCl			HNO_3		H_2SO_4	
Concentration	Ti	W	Ti	W	Ti	W
0.01 M	UD	UD	UD	UD	UD	UD
0.05 M	UD	UD	UD	UD	UD	UD
0.1 M	UD	UD	UD	UD	UD	UD
0.5 M	UD	UD	UD	UD	UD	UD
1 M	2.1 ppm	1.7 ppm	3.2 ppm	2.9 ppm	3.1 ppm	2.9 ppm
2 M	8.3 ppm	6.2 ppm	9.5 ppm	5.6 ppm	8.4 ppm	4.2 ppm

cesium nitrate traced with the radioactive isotope (^{60}Co, ^{134}Cs) was allowed to stand overnight in a shaker thermostat adjusted at 30 ± 1 °C with shaking to ensure establishment of equilibrium. The solid was then separated from its solution by filtration, then 1 mL from the aliquots of the filtrate was measured for the ^{60}Co and^{134}Cs activities.

The distribution coefficient (K_d mL/g) values for the individual cations Co^{2+} and Cs^+ were determined at different acidities and different metal ion concentrations(10^{-4} to 10^{-2} M) using the equation

$$K_d = \frac{A_o - A_f}{A_f} * \frac{V}{m} \tag{1}$$

Where A_o and A_f are the initial and final counting rates in 1mL of the solution before adding the adsorbent and after equilibrium.

The adsorption isotherms of cobalt and cesium were determined by employing the same general protocol and analysis procedure as above at the same concentration range at 30, 45 and 60 °C.

2.5. Quantitative separation of Co^{2+} and Cs^+ ions

Quantitative separations of cobalt and cesium ions were achieved on titanium tungstate column. The exchanger in H^+ form was packed in an open glass column (20 cm height and 0.5 m diameter) and conditioned for subsequent operations; after washing the column thoroughly with deionized water, the mixture of cesium and cobalt ions of 0.01 M each, at natural pH was allowed to pass with a flow rate of 2 mL/min. The elution was achieved by passing different concentrations from nitric acid as eluent at a flow rate of 1 mL/min. through the column.

2.6. Radiometric analysis

The radioactive nuclides of ^{60}Co, ^{134}Cs used in this study were assayed by measuring their gamma ray activities using NaI (Tl) scintillation detector connected to a scalar of SR7 type obtained from Enterprises, USA and using a multichannel analyzer Genie-2000 Spectroscopy, Canberra Industries INC, USA.

3. Results and discussion

3.1. Characterization

The solublities of titanium tungstate in different mineral acid concentarions were used as a measure for chemical stability of the exchanger and represented as Ti and W concentrations as shown in Table 1. The concentrations of both ions were measured using ICP technique. measurements showed that titanium tungstate is stable in water, dilute mineral acids up to 0.5 M solution while, it partially decomposes at concentrations ≥ 1 M acid solutions.

X-ray powder diffraction pattern of titanium tungstate clearly exhibited the presence of two sharp to medium peaks with *d*-values 2.8206 and 1.8127 A° at angles(2θ) 31.697 and 47.497A°, respectively, that suggesting a low crystalline structure of the material (Fig. 1).

Infrared spectrum was shown in Fig. 2.The broad band appeared at about 3170 cm^{-1} is characteristic to the stretching mode of free water and OH^- groups while, the small peak at ~ 1,527 cm^{-1} represents the bending mode of vibration. The other peaks represented in the chart at about 1,000 cm^{-1} and smaller than this value may be due to the formation of metal oxides [23].

Fig. 3 Shows TGA and DTA curves for titanium tungstate exchanger. The DTA curve shows an endothermic peak at 163.21 °C due to loss of free water, another endothermic peak at 334.81 ° was represented due to the loss of chemical bond water [24]. The last one appears in the figure at 459.97 °C due to the phase transformation. The TG curve shows a total weight loss of 12.84% (w/w) at nearly 480 °C. This results support

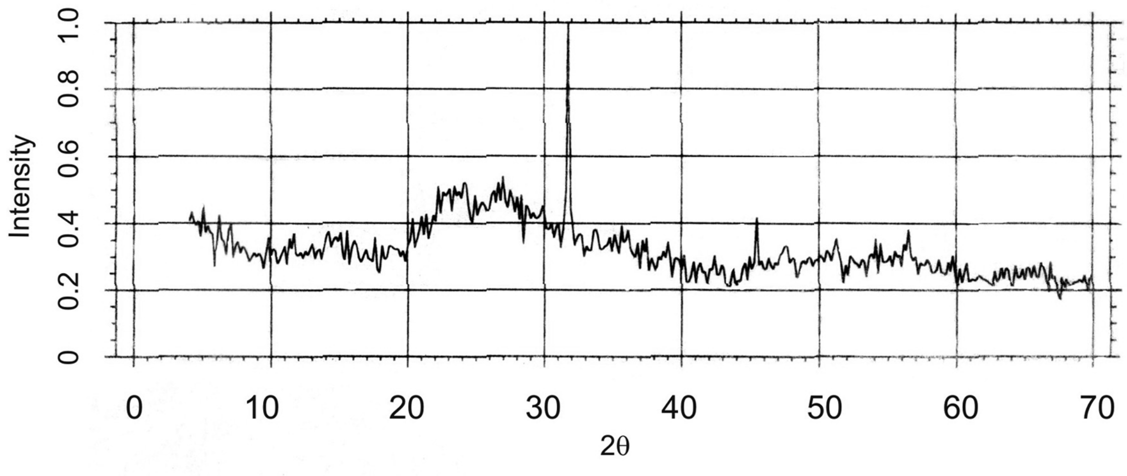

Fig. 1. XRD of titanium tungstate.

the fact that inorganic exchangers show high stability than the organic resins.

3.2. Distribution and capacity measurements

Fig. 4 Shows the effect of cesium and cobalt concentrations on their distribution between aqueous and solid phases in the concentration range 10^{-2} to 10^{-4}M, at constant pH $= 3 \pm 0.02$. A sharp decrease in the K_d values was observed in case of cesium ions while for cobalt a stepwise decrease occurred in the studied concentration range. This figure shows also that, the distribution coefficients for Cs^+ ions much higher than that for Co^{2+} upon the studied concentration range.

The theory of an ideal binary ion exchange system has been previously discussed [25]. According to this theory, if an ion exchanger containing exchangeable cations B^{Zb} is contacted with a solution containing cations A^{Za} which then exchanges with the cations of the exchanger, the ideal ion exchange process can be expressed as

$$Z_bA^{Z_a} + Z_a\overline{B}^{Z_b} \rightleftarrows Z_b\overline{A}^{Z_a} + Z_aB^{Z_b} \tag{2}$$

Where, Z_a and Z_b are the charges of the respective exchanging ions; $\overline{A}^{Z_a}$ the exchanged cations on the ion exchanger; B^{Zb} the exchanged cations in the solution. To test the ability of the prepared material in the

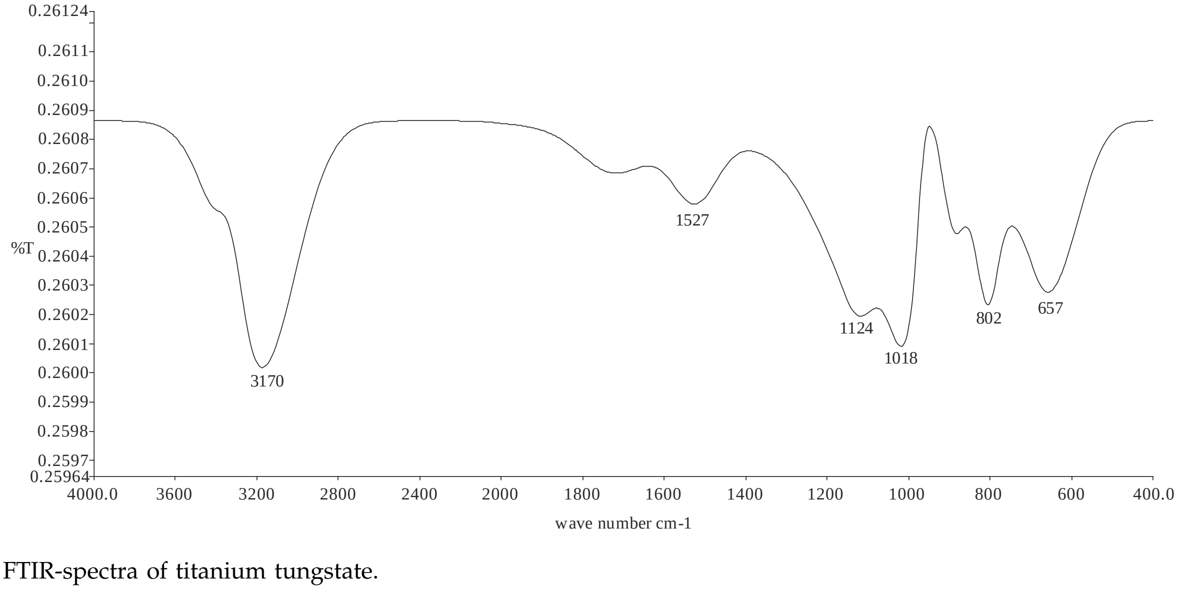

Fig. 2. FTIR-spectra of titanium tungstate.

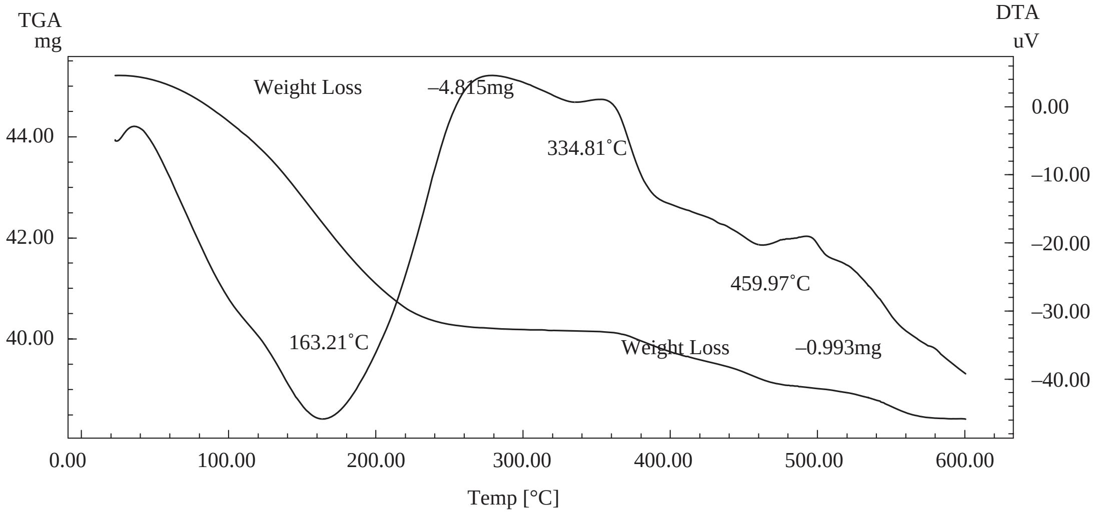

Fig. 3. DTA and TG for titanium tungstate exchanger.

recovery of cesium and cobalt ions, the distribution coefficients (K_d)were determined at different hydrogen ion concentrations,the selectivity coefficient ($K_{A/B}$) is also employed as it measures the selectivity of an ion exchanger for a given cation with respect to the other competing cation. The selectivity coefficient is given by

$$K_{A/B} = \overline{C}_A^{Z_b} C_B^{Z_a} \Big/ \overline{C}_B^{Z_a} C_A^{Z_b} \tag{3}$$

Where, $\overline{C}_A$ and $\overline{C}_B$ are the concentrations of the exchangeable cations in the ion exchanger; C_A and C_B are the concentrations of the exchangeable cations in the solution.The final equation after substitution of the above expression in the that for K_d given as

$$\log K_d = \frac{1}{Z_b}\log(K_{A/B}\overline{C}_B^{Za}) - \frac{Z_a}{Z_b}\log C_B \tag{4}$$

So, according to the above equation a plot of log K_d against Log C_B must give a straight line with slope equal to –(Z_a/Z_b). Plotting of log K_d vs. log [HNO_3] for cobalt and cesium ion on titanium tungstate was linear with a slop of −0.312 and −0.281 for each ion respectively Fig. 5. The slopes of the straight lines were of value less than the charge of cobalt and cesium ions which confirm that the ion exchange was not the main mechanism that control the adsorption of cesium and cobalt ions on titanium tungstate from nitrate medium. The adsorption of these ions may be due to complexation, chelation, and formation of physical bonding between the surface of the sorbent and the ions or through a combination of these interactions.

The capacity of titanium tungstate for cesium and cobalt was measured at different metal ion concentrations and the results were tabulated as shown in Table 2.

From the given data, it is evident that titanium tungstate has high capacity for cesium ions than cobalt ions at the different conditions. The same behavior was observed for titanium vanadate exchanger when used for the removal of cesium, strontium and cobalt ions from nitrate medium [11].

3.3. Isotherm studies

At equilibrium, a certain relationship prevails between the solute concentration in solution and the

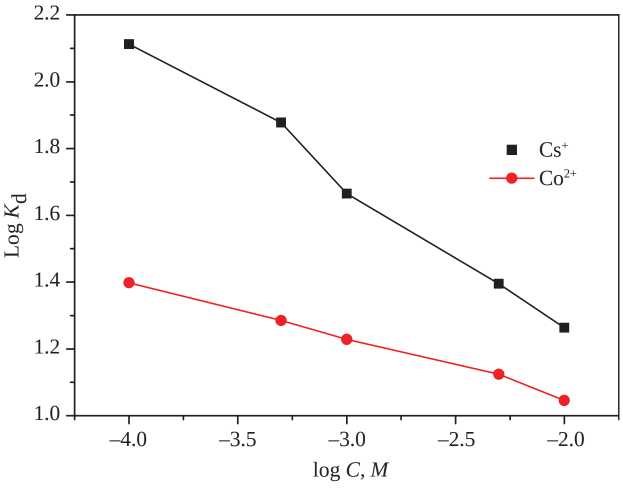

Fig. 4. The effect of ion concentration on the distribution coefficients of Cs^+ and Co^{2+}ions on titanium tungstate.

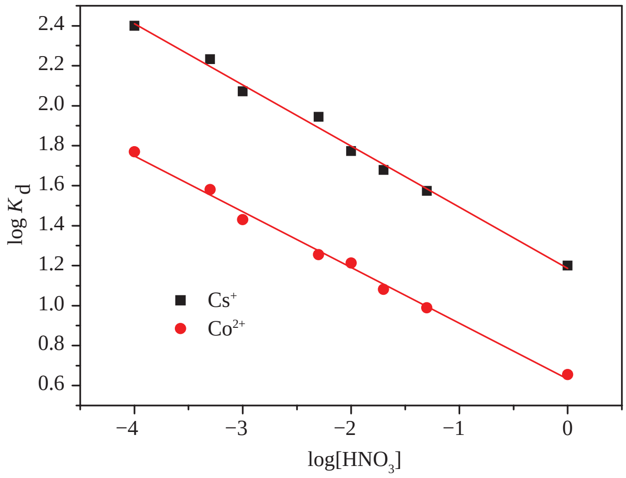

Fig. 5. Log K_d vs. log $[H^+]$ for $Cs^+$and Co^{2+} ions on titanium tungstate.

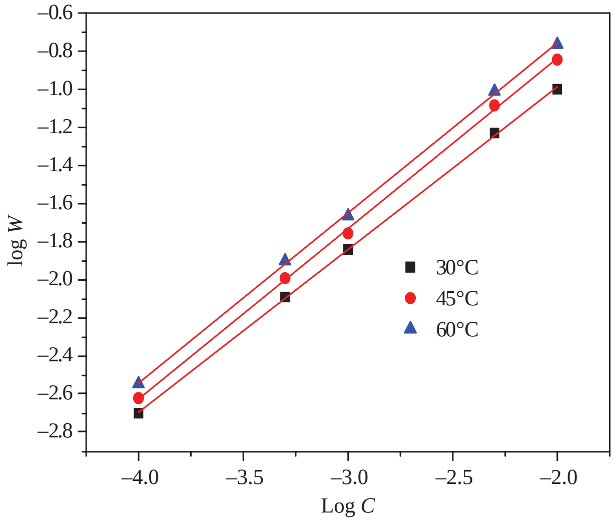

Fig. 6. Relation between log C and log W for Co^{2+} ions at different reaction temperatures.

amount of solute adsorbed per unit mass of adsorbent. Their equilibrium concentrations are a function of temperature. Therefore, the adsorption equilibrium relationship at a given temperature is referred as adsorption isotherm. Several models were used to describe the adsorption in liquid–solid systems but the most common are Freundlich and Langmuir models. For the adsorption of cesium and cobalt ions on titanium tungstate, the results show a better fitting with the Freundlich than Langmuir isotherm. Freundlich isotherm in its linear form represented by the following equation

$$\mathrm{Log}W = \mathrm{Log}K + 1/n\log C_{eq} \qquad (5)$$

Where, W is the amount adsorbed at equilibrium; C_{eq} is the bulk concentration of the adsorbate at equilibrium; $1/n$ and K are Freundlich constants (calculated from the slopes and the intercepts of the linear plots of log W versus log C_{eq}. Log K is equivalent to log W when C_{eq} equals unity. However, when $1/n \neq 1$, the K value depends on the units upon which W and C_{eq} are expressed. A favorable adsorption tends to have Freundlich constant n between 1 and 10. Larger value of n implies stronger interaction between the adsorbent and the adsorbate while $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites [26]. When the value of n is less than 1 this suggests the presence of a concave/ curved upward isotherm, which known sometimes as solvent-affinity isotherm [27]. In this type of isotherm, strong adsorption of solvent as a result of strong intermolecular attraction within the adsorbent layers occurs. In the studied systems Figs. 6 and 7), the calculated values of n at 30 °C were, 1.1719 and 1.388 for cobalt and cesium respectively which indicate a favorable adsorption of both ions on titanium tungstate while, the tendency for ^{134}Cs higher than for ^{60}Co. these results augment the results obtained from thermodynamics, in which physical adsorption is preferred.

Table 2
Loading capacities (mmol/g) of cesium and cobalt ions on titanium tungstate ion exchangers at different concentrations

Conc.(M) ions	0.0001	0.0005	0.001	0.005	0.01
Cs^+	0.0158	0.0427	0.0806	0.1155	0.1857
Co^{2+}	0.0076	0.0098	0.0289	0.0644	0.1452

On the other hand adsorption capacity (K) is characteristic of an adsorbent. This constant is governed by a series of properties, such as pore and particle size distribution, specific surface area, pH, cation exchange capacity, and temperature. The values of K were found to be 5.239 and 4.472 for cobalt and cesium ions respectively.

Different thermodynamic parameters can be calculated from the following equations

$$\Delta G = -\mathrm{R}T\ln K_d \qquad (6)$$

$$\Delta H = \frac{-\mathrm{R}d\ln K_d}{d(1/T)} \qquad (7)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (8)$$

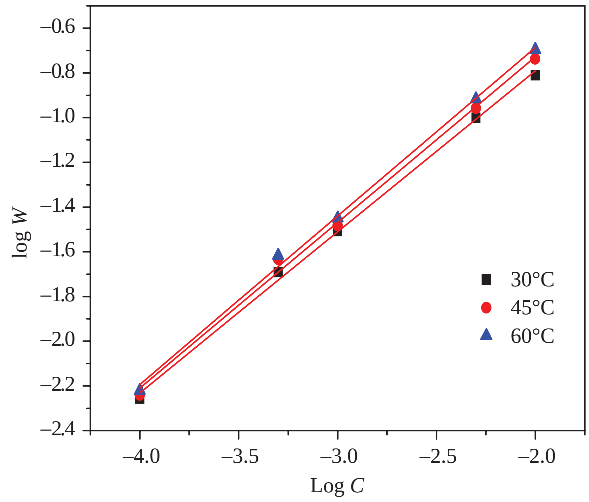

Fig. 7. Relation between Log *C* and Log *W* for Cs^+ ions at different reaction temperatures.

Where, R is the general gas constant, *T* is the absolute temperature, ΔG is the free energy, ΔH is the enthalpy change and ΔS is the entropy of activation.

Plotting $1/T$ against log K_d for the exchange of10^{-3} M cesium and cobalt on titanium tungstate gives a straight line from which the enthalpy changes and entropy changes can be calculated Fig. 8. The calculated thermodynamic parameters were represented in Table 3. Analysis of the data reveals that, positive values of enthalpy changes for the exchange of both Cs^+ and Co^{2+} ions on titanium tungstate indicates that this exchange is an endothermic process. A positive value of the entropy changes related to the disorder that occurs in both systems beside it gives an indication that the ions adsorbed in the hydrated form. Negative values of the free energy (ΔG) were observed for the studied systems which indicate the spontaneity of the adsorption process. In addition, it support the fact that cobalt ions were more bounded to the exchanger than cesium ions although the material preferred Cs^+ ions than $Co^{2+}$and this result supported experimentally from the column studies as will see latter. The negative free energy was observed for the exchange of Cs^+ ions on tin (IV) antimonate in different media [28].

Table 3. Thermodynamic parameters for the exchange of Cs^+ and Co^{2+} ions on titanium tungstate.

Co^{2+}	Cs^+	Ion Thermodynamic parameters
13.703	4.4517	ΔH(KJ/mol)
68.66	46.501	ΔS(J/mol)
−7.101	−9.613	ΔG(KJ/mol)

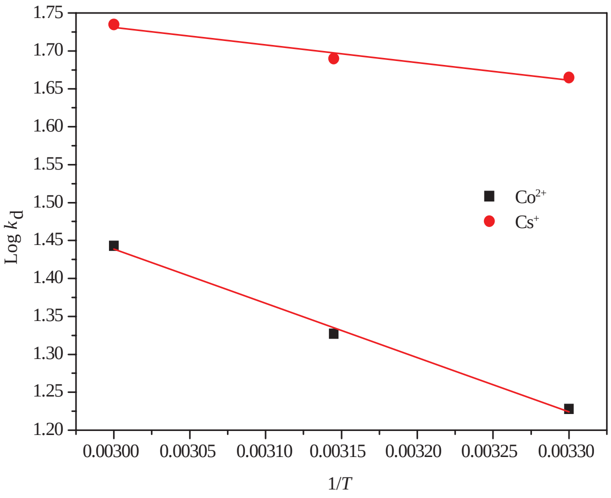

Fig. 8. Plots of Log K_d against $1/T$ for the exchange reaction of 10^{-3} M Cs^+ and Co^{2+} on titanium tungstate at pH 2.

3.4. Column operation

Prior to elution of the aforementioned ions, loading of these radionuclides was achieved. Generally, the obtained breakthrough capacities are less than those obtained from batch experiments. This behavior could be attributed to the insufficient time required for equilibrium in case of column operation. The breakthrough capcities reached was about 1.13 and 1.85 mmol/g for ^{134}Cs and ^{60}Co, respectively. These values are also less than those obtained Freundlich equilibrium parameters under isothermal conditions as shown in Table 2. This could be attributed to multilayer adsorption postulation in Freundlich model.

Fig. 9 shows the elution profiles of ^{134}Cs and ^{60}Co radionuclides from zirconium titanium tungstate ion exchanger surface using bidistilled water, hydrochloric acid and nitric acid with different concentrations as eluting agents. On using bidistilled water, 0.01 M HCl and 0.01 M HNO_3 as eluents, no release of any of the isotopes was observed. However, ^{134}Cs and ^{60}Co were released when 0.1 M HCl is used. This may be assigned to the cationic nature of the both exchangers having hydroxyl groups that act as week acidic centers similar to the snake structure of carboxylic groups in a cage like structure of amphoteric retardion11A8 [29] used for the separation of cadmium and zinc in geological and environmental materials using neutron activation analysis technique. In this case, the release of ^{134}Cs is maximum, and the remaining part of the loaded cesium ions was finally eluted using 0.5 M HCl. However, ^{60}Co radionuclides elution could be achieved using 0.1 M HNO3, which may be explained according the

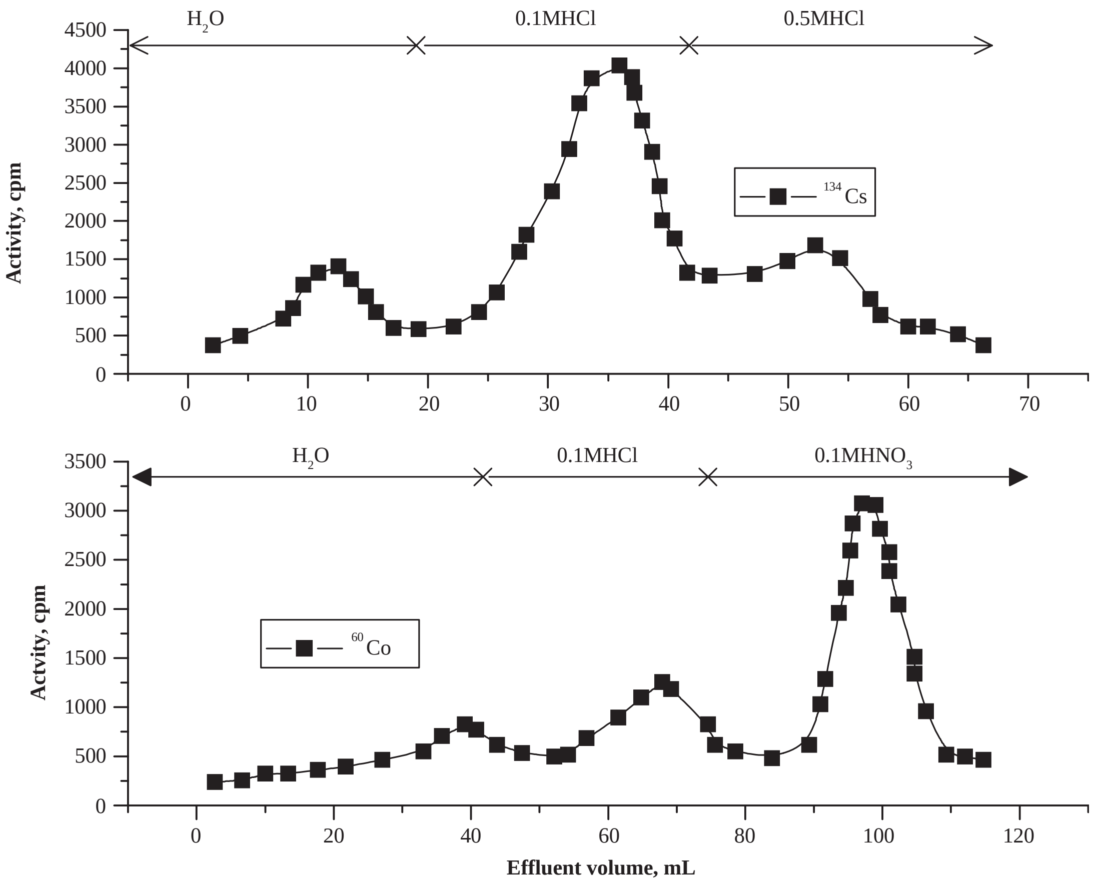

Fig. 9. Elution profile of ^{134}Cs and ^{60}Co from titanium tungstate.

selectivity order of both exchangers towards the different radionuclides. ^{134}Cs and ^{60}Co elution profiles are slightly interfered when separated on titanium tungstate cation exchanger when using 0.1 M HCl, as they have closer values of distribution coefficients at these conditions. However complete separation could be achieved by using different acid media as shown in Fig. 9. The separation process was found to be independent of acid concentration, but most likely acid type dependent. This interpreted by the low complex formation in case of cesium ions. However, the separation process was found to be slightly complicated when the loading process was carried out at high pH values, due to formation of new species of cobalt complexes [30].

4. Conclusion

Titanium tungstate which was prepared and characterized using different technique had higher capacity for cesium than cobalt ions. The adsorption isotherms were described by Freundlich model. The adsorption of Cs^+ and Co^{2+} ions on the prepared exchanger is an endothermic process and the numerical value of the enthalpy change, free energy change and entropy change were computed for both ions from which we concluded that cobalt ions are more strongly bound to the exchanger than cesium ions. Complete separation for cesium ions from cobalt ions was obtained using 0.1 and 0.5 M HCl as eluent.

References

[1] A. I. Bortun, S. A. Khainakov, L. N. Bortuun, E. Jaimez, J. R. Garcia, and A. Clearfield, Synthesis and characterization of a novel tin(IV) phosphate with ion exchange properties, Mater. Res. Bull., 34(6) (1999) 921.

[2] S. Lahiri, K. Roy, S. Bhaacharya, S. Maji and S. Basu, Separation of ^{134}Cs and ^{152}Eu using inorganic ion exchanger zirconium vanadate and ceric vanadate, Appl. Rad. Isotopes, 63 (2005) 293-297.

[3] M. M. Abou Mesalam, I. M. El-Naggar, Diffusion mechanism of Cs^+, Zn^{2+} and Eu^{3+} ions in the particles of zirconium titanate ion exchanger using radioactive tracers, Colloids Surf. A, 215 (2003) 205-211.

[4] A. Clearfield, Inorganic Ion Exchange Materials, CRC Press Inc. Boca Raton, FL (1982).

[5] Ma Xuebing, Fu Xiangkai, Synthesis of the novel layered amorphous and crystalline zirconiumphosphate–phosphonates

$Zr(HPO_4)[O_3PCH_2N(CH_2CH_2)_2O]\cdot nH_2O$, $Zr(HPO_4)[O_3PCH_2N(CH_2CO_2H)_2]\cdot nH_2O$, zirconium phosphonates $Zr[(O_3PCH_2)NCH_2CO_2H]\cdot nH_2O$ and the catalytic activities of their palladium complexes in hydrogenation, J. Mol. Catal. Chem., 208 (2004) 129-133.

[6] K. M. Parida, B. B. Sahu and D. P. Das, A comparative study on textural characterization: cation-exchange and sorption properties of crystalline α-zirconium(IV), tin(IV), and titanium(IV)phosphates, J. Colloid Interface Sci., 270 (2004) 436-445.

[7] I. M. El-Naggar, E.A. Moray, Y.F. El-Aryan and M. G. Abd-El-Wahab, Sorption mechanism for Cs^+, Co^{2+} and Eu^{3+} on amorphous zirconium silicate as cation exchanger, Solid StateIon., 178 (2007) 741-747.

[8] G. M. Ibrahim, B. El-Gammal, I. M. El-Naggar, Selectivity modification of some alkali metal ions on silicon antimonate as cation exchanger, Curr. Topics Colloid Interface Sci., 6 (2003) 159.

[9] A. Nilchi, B. Maalek, A. Khanchi, M. G. Maragheh and A. Bagheri, Cerium(IV) molybdate cation exchanger: synthesis, properties and ion separation capabilities, Radiat. Phys. Chem. 75 (2006) 301-308.

[10] M. M. Abou-Mesalm, Applications of inorganic ion exchangers, II. Adsorption of some heavy metal ions from their aqueous waste solution using synthetic iron (III)titanate, Adsorption 10 (2004) 87-92.

[11] G. M. Ibrahim, Preparation and characterization of Titanium Vanadate and its application in the removal of some radionuclides, Arab J. Nucl. Sci. Appl., 39(3) (2006) 61-70.

[12] I. M. El-Naggar, G.M. Ibrahim, E. A. El-Kady and E. A. Hegazy, Sorption mechanism of Cs^+, Co^{2+} and Eu^{3+} ions onto EGIB sorbent, Desalination, 237 (2009) 147-154.

[13] W.J. Boo, L.Y. Sun, J. Liu, A. Clearfield, H.-J. Sue, M.J. Mullins and H. Pham, Compos. Sci. Technol., 67(2) February 2007, 262-269.

[14] J. Celestian, J.B. Parise, J. Narayan, J.D. Kubicki and A. Clearfield, Geochimica et Cosmochimica Acta, 70(18 Supplement 1) August–September 2006, A91.

[15] Aurelio Cabeza, María del Mar Gómez-Alcántara, Pascual Olivera-Pastor, Isabel Sobrados, Jesú Sanz, Bo Xiao, Russell E. Morris, Abraham Clearfield and Miguel A.G. Aranda, J. Micropor. Mesopor. Mater., 114(1–3) 1 September 2008, 322-336.

[16] Jun-Ling Song, Jiang-Gao Mao, Yan-Qiong Sun, Hui-Yi Zeng, Reinhard K. Kremer and Abraham Clearfield, J. Solid State Chem., 177(3) March 2004, 633-641.

[17] Luyi Sun, J.Y. O'Reilly, Deyuan Kong, J.Y. Su, W.J. Boo, H.-J. Sue and A. Clearfield J. Colloid Interface Sci., 333(2) 15 May 2009, 503-509.

[18] A.R. Oki, Q. Xu, B. Shpeizer, A. Clearfield, X. Qiu, S. Kirumakki and Shane Tichy, Catal. Comm., 8(6) June 2007, 950-956.

[19] T. Möller, A. Clearfield and R. Harjula, Preparation of hydrous mixed metal oxides of Sb, Nb, Si, Ti and W with a pyrochlore structure and exchange of radioactive cesium and strontium ions into the materials, J. Micropor. Mesopor. Mater., 54(2002)187-199.

[20] M. Qureshi, J. P. Gupta, Synthesis of a poorly crystalline titanium tungstate: separation of Hf^{4+} from Zr^{4+} and of La^{3+} from Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}, J. Chromatogr., 62 (1971) 439.

[21] M. Qureshi, J. P. Gupta and V. Sharma, Comparison of the ion-exchange behaviour of zirconium, thorium, vanadium, uranium, stannic and titanium tungstates, Talanta, 21 (1974) 102-106.

[22] R. Yavari, S. J. Ahmadi, Y. D. Huang, A. R. Khanchi, G. Bagheri and J. M. He, Synthesis, characterization and analytical application of a new inorganic cation exchanger-titanium (IV)molbdophosphate, Talanta, 77 (2009) 1179-1184.

[23] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A, 5th ed., John Wiley & Sons, Inc., 1997.

[24] C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963.

[25] Hiroki Tamura, J. Colloid Interface Sci., 279 (2004) 1-22.

[26] J. Febrianto, A. N. Kosasih, J. Sunarso, Y. Ju, N. Indraswati, and S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies, J. Hazard. Mater., 162 (2009) 616-645.

[27] A. Delle Site, Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review, J. Phys. Chem. Ref. Data, 30 (2001) 187-439.

[28] I. M. El-Naggar, E. S. Zakaria, and H. F. Aly, Thermodynamics of the H/Na and H/Cs exchange on tin(IV) antimonite in methanolic solution, J. React. Function. Polym., 28 (1996) 215.

[29] Z. Smaczynski and R. Dybczynski, J. Radioanal. Nucl. Chem., 254 (2) (2002) 335-341.

[30] D.R. Turner, M. Whitfield and A.G. Dickson, The equilibrium speciation of dissolved components in freshwater and seawater at 25 °C and 1 atm. pressure, Geochimica et Cosmochimica Acta, 45 (1981) 855-881.