

Full Length Research Paper

Kinetic studies of some hazardous metal ions in the particles of titanium potassium vanadate as a cation exchanger

M. M. El-Shorbagy, A. Bendary and A. M. Ali

Nuclear Fuel Technology Department, Hot Laboratory Center, Atomic Energy Authority, Egypt.

Accepted 16 July, 2012

Titanium potassium vanadate (TiKV) as an inorganic ion exchange material was synthesized from titanium tetrachloride, potassium chloride and sodium monovanadate with molar ratio Ti: K: V = 1: 1: 1. The kinetic behaviour of Cs⁺, Co²⁺ and Cd²⁺ have been studied under different conditions of concentration, particle size, reaction temperatures and drying temperatures. The experimental conditions were set to favour particle diffusion control. The values of diffusion coefficient (D_i), activation energy (E_a), entropy of activation (ΔS^\ddagger), enthalpy change (ΔH^\ddagger) and free energy change (ΔG^\ddagger) were calculated and their significance was discussed. The data obtained have been compared with those reported for other inorganic ion exchangers.

Key words: Diffusion, ion exchange, titanium potassium vanadate, thermodynamic parameters.

INTRODUCTION

The presence of heavy metal ions from the transition series, including Cu, Fe, Ni, Pb, etc. in the environment is of major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end products (Gupta et al., 2001). Heavy metals contamination exists in aqueous waste stream from many industries such as metal plating, mining, tanneries, and painting, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray intensively used. The removal of heavy metal in an effective manner from water and wastewater is, thus, ecologically very important. During the last 2 decades much attention has been paid to the development of inorganic ion exchange materials with high selectivity's and higher resistance to temperatures and radiation than those of commercial resins.

A study of kinetics of ion exchange enables us to understand the viability of an exchange material in separation technology. Earlier, the old Bt criterion was

used for such a study (Reichenberg, 1953), which is best for an isotope-exchange process (Herman and Clearfield, 1976) in which ions have similar effective diffusion coefficients.

The study of the kinetics on titanium potassium vanadate is important since it provides information on the reactions accompanying the ion exchange as well as on the internal physical structure of the exchanger and the extent of hydration of the exchanging ions (Shady et al., 2006). The present work reports the kinetics and thermodynamics of exchange of Cs⁺, Co²⁺ and Cd²⁺ ions on synthesized titanium potassium vanadate ion exchanger. Experimental and theoretical aspects are done to show that the rate determining step is diffusion through the particles of titanium potassium vanadate (TiKV). The diffusion coefficients (D_i), activation energies (E_a), enthalpy change (ΔH^\ddagger), entropies and free energies of activation (ΔS^\ddagger and ΔG^\ddagger) have been calculated for Cs⁺, Co²⁺ and Cd²⁺ ions in aqueous solution.

EXPERIMENTALS

Chemical reagents and instruments

The main reagents used for the synthesis of the material were

*Corresponding author. E-mail: m_elshorbagy61@yahoo.com.

obtained from BDH (England) and Loba Chemie (India). All reagents and chemicals were of analytical reagent grade purity and used without further purification. All measurements were performed using an atomic absorption spectrophotometer model AA-6701F – Shimadzu, Kyoto "Japan".

Preparation of titanium potassium vanadate (TiKV)

0.5 M titanium tetrachloride was dissolved in 4 M hydrochloric acid then was added to a mixture of [0.5 M sodium monovanadate and 0.5 M potassium chloride] with a volume ratio Ti:K:V= 1:1:1 with constant stirring at room temperature. After the addition was completed, ammonia was added until a precipitation was occurred and then the reaction mixture was allowed to settle for 24 h. The precipitate was filtered, washed several times with deionized water. The precipitate was dried at 50°C in an electric oven, grained and sieved for different mesh sizes and stored at room temperature.

Kinetic studies

Kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Cs^+ , Co^{2+} and Cd^{2+} on TiKV. The particle diffusion-controlled phenomenon is favored by a high metal ion concentration, a relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture. The particle size of the solid was evaluated by an optical microscope. The particles are assumed to be spherical and a mean equivalent was calculated.

The kinetic measurements were carried out at different concentrations of metal ions (10^{-2} , 5×10^{-3} and 10^{-3} M) and different particle diameters (0.375, 0.185, 0.115 ± 0.02 mm) of TiKV with V/m equals 100 ml g^{-1} . This was performed using an aqueous solution contains the metal cations. All kinetic experiments were done in a shaker thermostat adjusted at the desired temperatures (25, 45 and $65 \pm 1^\circ\text{C}$). After each interval time, the shaker was stopped and the solution was separated immediately from the solid and the extent of sorption was determined, as follows:

$$\text{Sorption (\%)} = [(A_i - A_f) / A_i] \times 100$$

where A_i and A_f are the initial and final concentration of the metal ions in solution.

Analysis

The metal ions (Cs^+ , Co^{2+} and Cd^{2+}) investigated in this work were analyzed by atomic absorption. All tests were repeated two or three times and the experimental error was about $\pm 3\%$, the results agreed that, the reproducibility of measurements was more than 98%.

RESULTS AND DISCUSSION

The rate controlling step in ion exchange is usually either liquid film diffusion or particle diffusion (Rudolf and Clearfield, 1989). The equations developed by Boyd et al. (1947) and improved by Reichenberg (1953) were used for evaluating the kinetics parameters, then the following

equations were used:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 Bt} \quad (1)$$

and

$$B = \frac{\pi^2 D_i}{r^2} \quad (2)$$

where F is the fractional attainment at equilibrium, n is an integer number, B is a mathematical function, D_i is the diffusion coefficient of the ions (cm^2/s) and r is the radius of the particles (cm).

When the fraction attainment of equilibrium F is less than 0.4, the previous equation (Equation 1) can be approximated to a simpler form as follows:

$$F = \frac{6}{r} \left(\frac{D_i t}{\pi} \right)^{\frac{1}{2}} \quad (3)$$

which holds to a fairly good approximation. Therefore, a plot of F against the square root of the contact time must be give a straight line passing through the origin in which F is less than 0.4.

The study of the effect of concentration on the rate of exchange of Cd^{2+} ion on TiKV at $25 \pm 1^\circ\text{C}$ and 0.185 ± 0.02 mm mesh size showed at concentrations 5×10^{-3} , 10^{-3} and 5×10^{-2} M. From the data presented in Figure 1, at the concentrations studied, the rate of exchange is independent of the metal ion concentration. So, this is the evident that the concentrations condition set in this paper are particle diffusion mechanism for all metal ions studied and the film diffusion can be excluded at this concentration condition 5×10^{-3} M (generally used in this work). Similar findings were previously reported (El-Naggar et al., 2007a, b; Varshney et al., 2003; Abou-Mesalam and El-Naggar, 2003).

The effects of particle size of TiKV on the rate of exchange of Cs^+ , Co^{2+} and Cd^{2+} at $25 \pm 1^\circ\text{C}$ are represented in Figure 2 in terms of Bt vs. t plots. It was found that straight lines passing through the origin in all cases are obtained, and the rate of exchange of Cs^+ , Co^{2+} and Cd^{2+} . Our results agree with that reported before (El-Naggar and Aly, 1992; Amphlett et al., 1964) for other ion exchangers.

Table 1 show the averages values of diffusion (D_i) for the investigated metal ions at different particle diameters which are calculated from the relations of Bt vs. t plot (Figure 2). It was found that the effective diffusion coefficient values (D_i) are slightly increased with

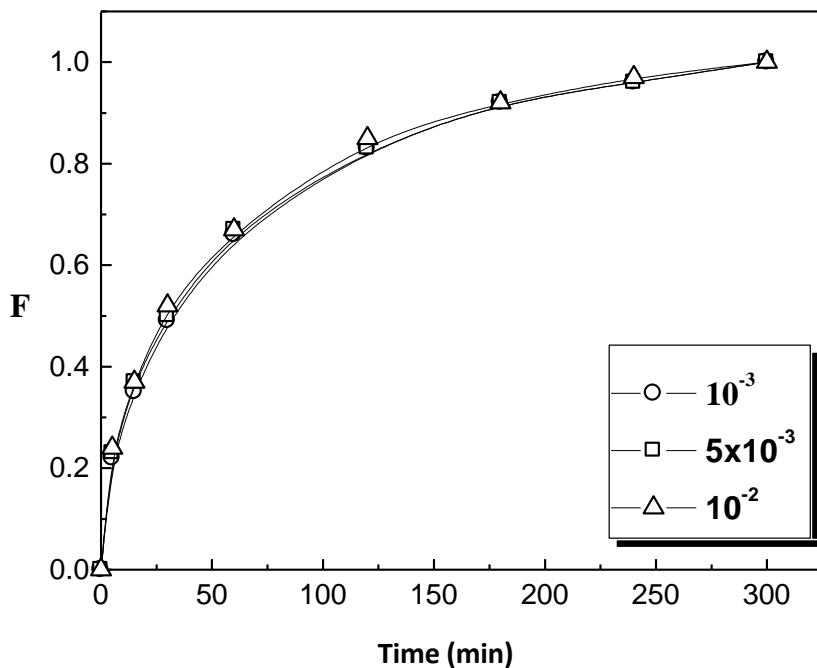


Figure 1. Plots of F against time for the exchange of different concentrations of Cd^{2+} on TiKV at $25 \pm 1^\circ\text{C}$.

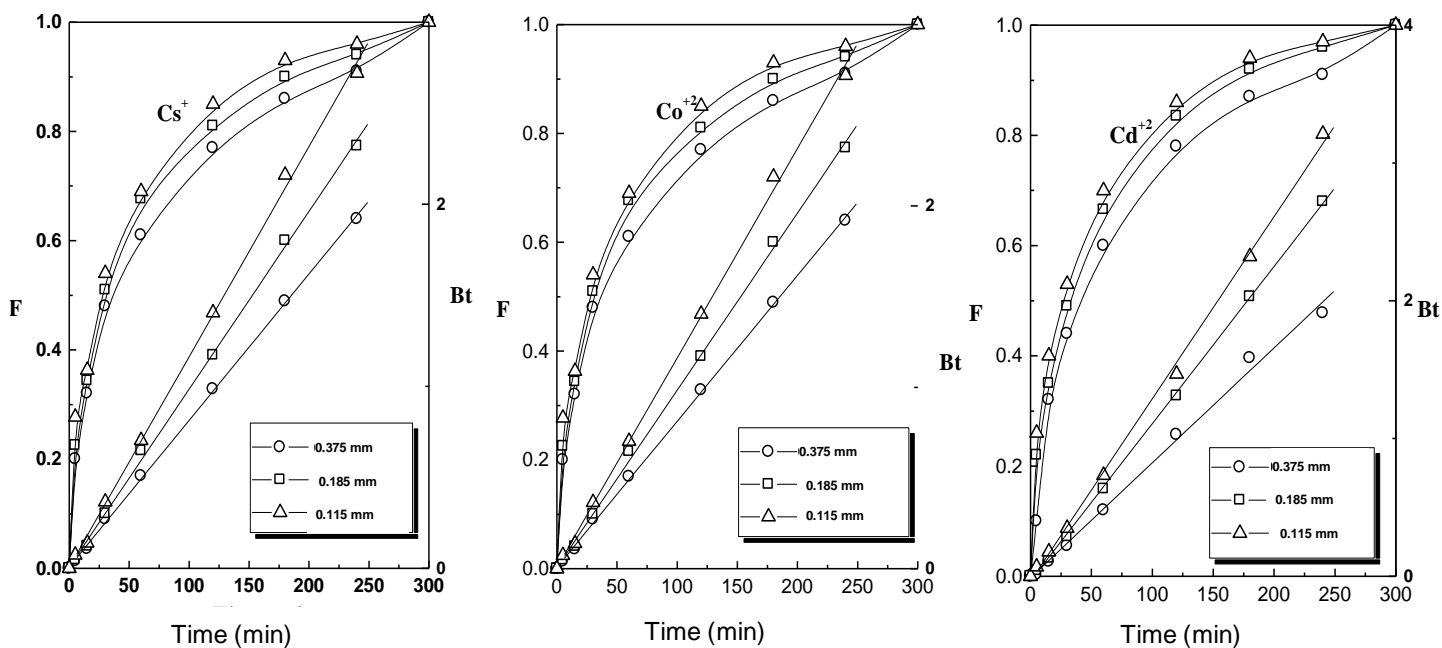


Figure 2. Plots of F and Bt against time for the exchange of Cs^+ , Co^{2+} and Cd^{2+} ions on different particle diameters of TiKV at $25 \pm 1^\circ\text{C}$.

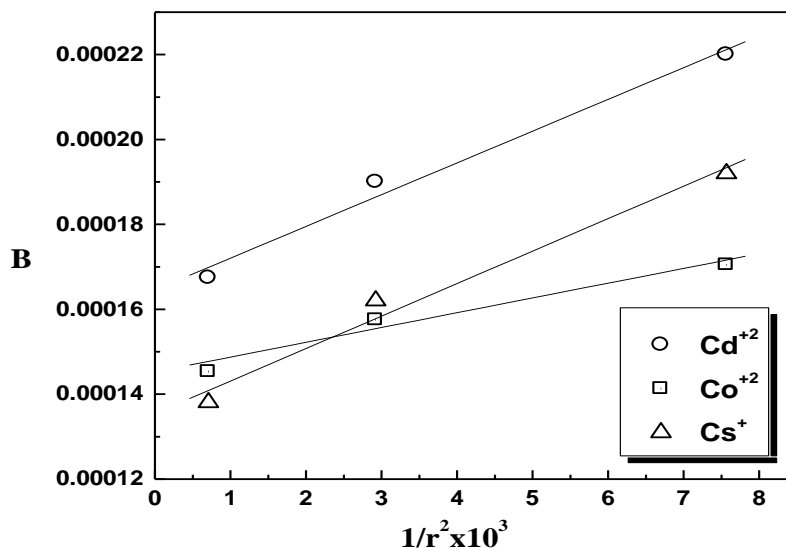
increasing the particle diameters of the prepared ion exchanger. This difference was also observed by others (El-Naggar and El-Absy, 1992; El-Naggar et al., 2010) who assumed that large particles are formed from agglomerated small particle units and, therefore, a

quicker diffusion took place through the channels between these units (El-Naggar et al., 2010).

The rate of exchange of Cs^+ , Co^{2+} and Cd^{2+} ions on TiKV increases with decreasing the particle diameter which agrees with the fundamental conditions of particle

Table 1. Values of the diffusion coefficient of Cs⁺, Co²⁺ and Cd²⁺ ions on different particle diameters of TiKV at 25 ± 1°C.

Particle diameters (±0.02 mm)	D _i (cm ² s ⁻¹)		
	Cs ⁺	Co ²⁺	Cd ²⁺
0.115	2.58 × 10 ⁻⁹	2.26 × 10 ⁻⁹	2.956 × 10 ⁻⁹
0.185	5.65 × 10 ⁻⁹	5.51 × 10 ⁻⁹	6.6 × 10 ⁻⁹
0.375	0.191 × 10 ⁻⁹	0.202 × 10 ⁻⁹	0.198 × 10 ⁻⁹

**Figure 3.** Plots of B against 1/r² for the exchange of Cs⁺, Co²⁺ and Cd²⁺ on TiKV at 25 ± 1°C.

diffusion, which support the particle diffusion mechanism. This trend was reported for others ion exchangers (El-Naggar et al., 2010, 1999).

The highly values obtained for D_i may be attributed to the large particles formed from agglomerated of smaller compact unites. Therefore, a quicker diffusion took place through the channels between these unites (El-Naggar et al., 2010, 1999). Furthermore, the diffusion coefficients of the metal ions studied are independent of the metal ion concentration in solution and dependent on the particle size of exchangers. This indicates that under these conditions, the rate determining step is mainly diffusion through the particle and the film diffusion is nearly neglected and hence the mechanism of diffusion of these ions in our matrix is considered to be unchanged by the composition of the matrix (Misak and El-Naggar, 1989).

Plots of B versus 1/r² are straight lines indicating that the rate of exchange is inversely proportional to the square of the radius of particles as shown in Figure 3. This again verifies that diffusion through the exchanger particle is the rate-determining step.

The effect of varying reaction temperatures (25, 45 and 65 ± 1°C) on the rate of exchange of Cs⁺, Co²⁺ and Cd²⁺

ions was investigated on TiKV as a relation between F and Bt against contact time (Figure 4). It was found that the relation between Bt vs. t gives straight lines passing through the origin in all cases. Furthermore, it is seen from these figures that the rate of exchange reaction of Cs⁺, Co²⁺ and Cd²⁺ on TiKV increases with increasing the reaction temperature from 25 to 65 ± 1°C.

This trend maybe due to increasing the mobility of ions with increasing the reaction temperature from 25 to 65 ± 1°C. Similar findings were obtained for the exchange of Rb²⁺ and Cs⁺ on zirconium antimonate (Misak and El-Naggar, 1989) also for the exchange of Pb²⁺, Cd²⁺ and Zn²⁺ ions on antimonite acid (Barrer et al., 1963).

The values of diffusion coefficient (D_i) were calculated for Cs⁺, Co²⁺ and Cd²⁺ on TiKV and given in Table 3. From this table it is clear that the values of diffusion coefficient of the investigated metal ions increase in the order: Cd²⁺ > Cs⁺ > Co²⁺. This trend could attributed to the ionic radii of the exchanged ions which take the order (Cd < Cs). This ion with smaller ionic radius is easily exchanged and moves faster than that the ion with greater ionic radii, the lower D_i value of Cd²⁺ may be due to the higher hydration energy of Cd²⁺ ion as seen in

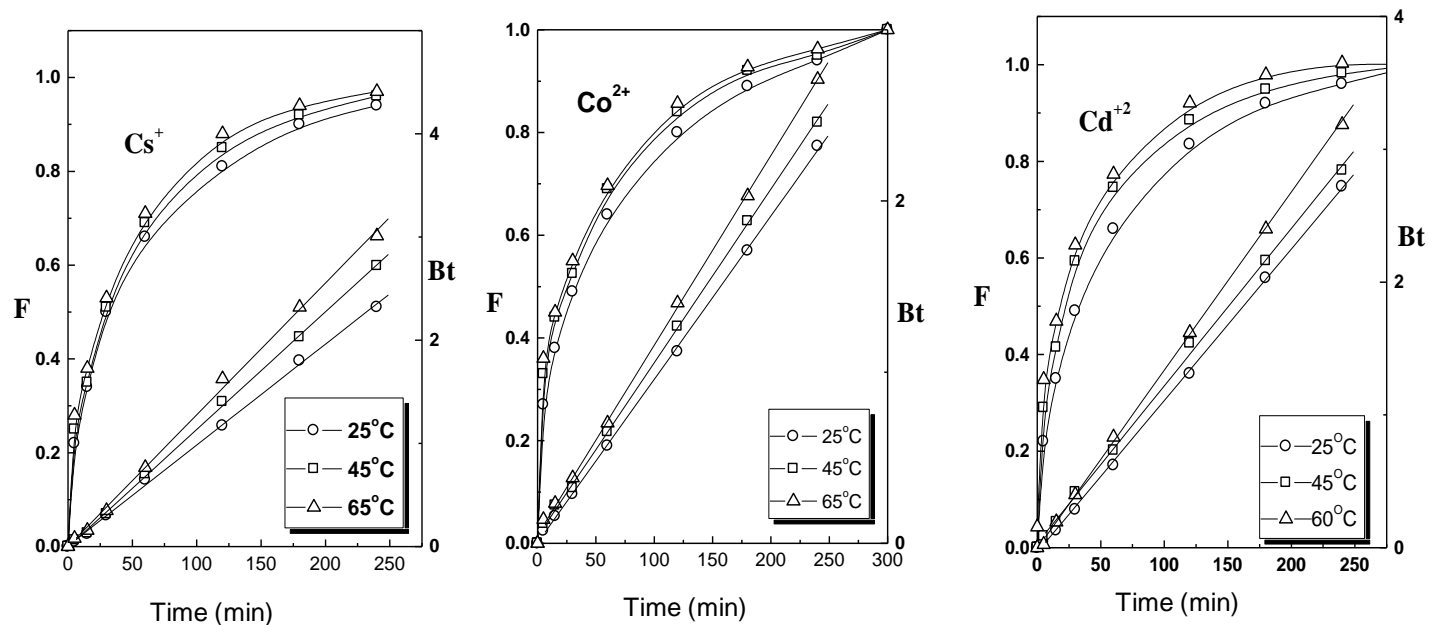


Figure 4. Plots of F and Bt against time for the exchange of Cs^+ , Co^{2+} and Cd^{2+} on TiKV at different reaction temperatures.

Table 2. Ionic radii and hydration energy of exchange systems.

Exchange system	Ionic radii	Hydration energy
$\text{Cd}^{2+}/\text{H}^+$	0.97	1806
$\text{Cs}^{2+}/\text{H}^+$	1.67	263
$\text{Co}^{2+}/\text{H}^+$	0.72	2034

Table 3. Thermodynamic parameters of Cs^+ , Co^{2+} and $\text{Cd}^{2+}/\text{H}^+$ systems on TiKV at different reaction temperatures.

Exchange system	Drying temperature	Particle diameter (mm)	Reaction temperature (K)	D_i ($\text{cm}^2\text{s}^{-1} \times 10^9$)	D_o ($\text{cm}^2\text{s}^{-1} \times 10^8$)	E_a (kJmol^{-1})	ΔS^* (kJmol^{-1})	ΔH^* (kJmol^{-1})	ΔG^* (kJmol^{-1})
Cs^+/H^+			298	5.65	7.25		-110.35	90.37	123.26
			318	6.59	7.19	6.319	-110.98	87.22	122.52
			338	7.38	7.02		-111.69	84.32	122.08
$\text{Co}^{2+}/\text{H}^+$	50°C	0.185 ± 0.02	298	5.51	2.01		-120.99	87.26	123.32
			318	5.85	1.95	3.167	-121.84	84.73	123.48
			338	6.40	1.99		-122.15	81.94	123.23
$\text{Cd}^{2+}/\text{H}^+$			298	6.60	2.82		-118.22	86.75	121.98
			318	6.85	2.69	3.599	-119.14	84.25	122.14
			338	7.76	2.79		-119.36	81.34	121.69

Table 2.

The effect of drying temperature of TiKV (50, 200 and 400 ± 1°C) on the rate of exchange of the investigated metal ions was studied as a relation between F and Bt against time as shown in Figure 5. From these figures, it

is found that the rate of exchange decreases by increasing the drying temperature from 50 to 400 ± 1°C. It is clear that an appreciable decrease of D_i of Cs^+ , Co^{2+} and Cd^{2+} with an increase in the drying temperature TiKV from 50 to 400 ± 1°C as shown in Table 4.

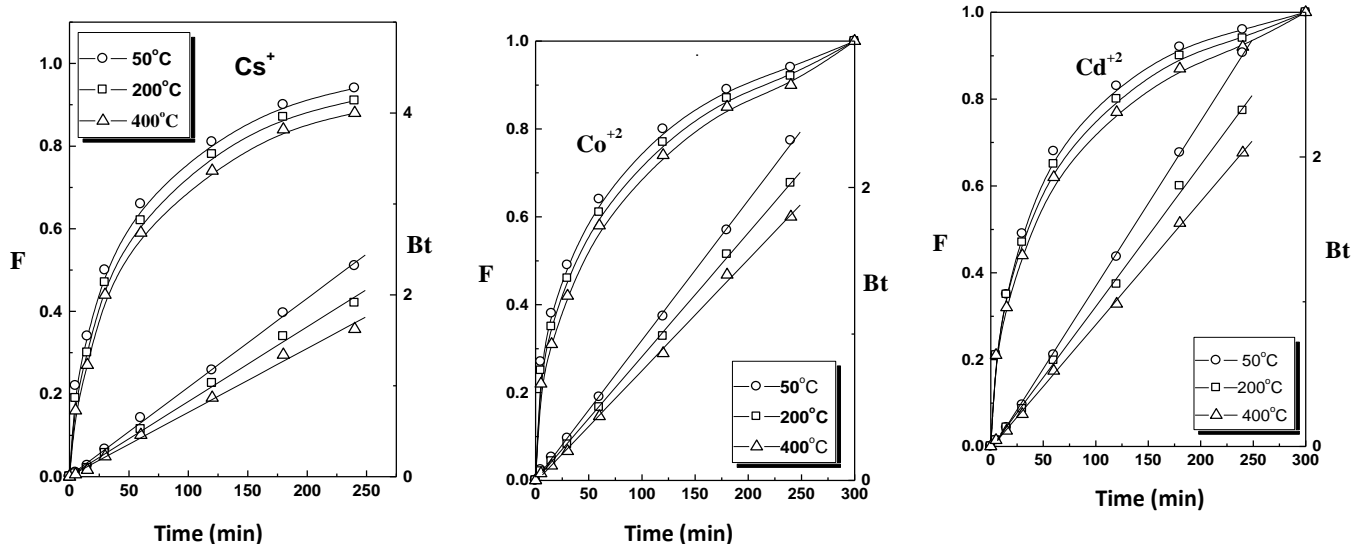


Figure 5. Plots of F and Bt against time for the exchange of Cs⁺, Co²⁺ and Cd²⁺ on TiKV at different drying temperature.

Table 4. Values of diffusion coefficient of Cs⁺, Co²⁺ and Cd²⁺ on TiKV at different drying temperature and at particle diameter 0.185 ± 0.02 mm.

Exchange system	Drying temperature	D _i (cm ² s ⁻¹ × 10 ⁹)
Cs ⁺ /H ⁺	50	5.65
	200	4.74
	400	4.06
Co ²⁺ /H ⁺	50	5.51
	200	4.88
	400	4.39
Cd ²⁺ /H ⁺	50	6.60
	200	5.66
	400	4.93

The lowering in the D_i values for Cs⁺, Co²⁺ and Cd²⁺ ions with increasing the drying temperature of the TiKV from 50 to 400 ± 1°C may be attributed to the lower pore sizes and porosity for the dried exchanger (Boyed and Saldavo, 1953). The lower porosity means less free water inside the exchanger particles which hinders the diffusion of ions (El-Naggar et al., 1999).

When log D_i is plotted against 1/T for the exchange of Cs⁺, Co²⁺ and Cd²⁺ ions on TiKV, straight lines were obtained (Figure 6). From the slope of these lined and applying Arrhenius equation (Equation 4), the energy of activation (E_a) and the diffusion coefficient (D_i) were calculated.

$$D_i = D_o \exp(-E_a/RT) \tag{4}$$

where D_o is the self-diffusion coefficient, E_a is the activation energy, R is the gas constant and T is the

absolute temperature (t + 273K).

The activation energies (E_a) of Cs⁺, Co²⁺ and Cd²⁺ ions are calculated and tabulated in Table 3. Table 3 shows that Co²⁺ has a lower activation energy which reflect the ease with which Co²⁺ ion can pass through the particles of TiKV compared to other cations (Cs⁺ and Cd²⁺). The relatively small activation energies values, (E_a) obtained (Table 3) for Cs⁺, Co²⁺ and Cd²⁺ on TiKV, indicated that the rate of exchange is particle diffusion (El-Naggar et al., 1999).

Calculation of D_o from Equation (4) and substitution in Equation (5), the entropy of activation (ΔS*) can be calculated by using Barrer and Fender (1961) equation:

$$D_o = (2.71 d^2KT/h) \exp(\Delta S^*/R) \tag{5}$$

where d is the ionic jump distance assumed equal to 0.5 mm, K is the Boltzman constant, h is the plank constant

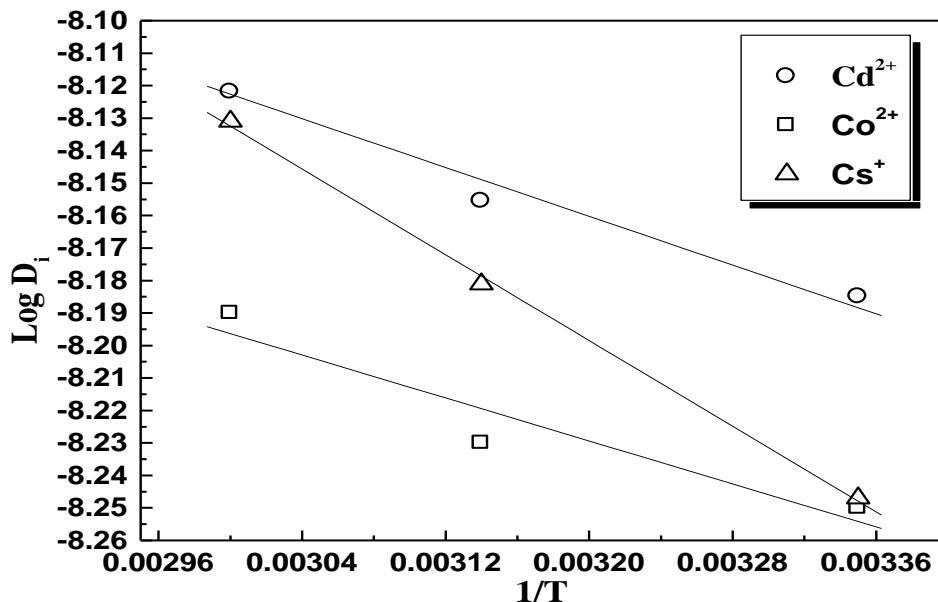


Figure 6. Arrhenius plots for exchange of Cs⁺, Co²⁺ and Cd²⁺ on TiKV at different reaction temperature.

and T is the absolute temperature (K).

The negative ΔS^* values obtained for all systems studied are given in Table 2, the entropy change normally depends on the extent of hydration and the exchangeable and exchanging ions. The negative values obtained for the entropy of activation, suggest that no significant structural change occurs in TiKV, also, the lower values of ΔS^* for Cs⁺, Co²⁺ and Cd²⁺ on TiKV support the higher stability and hence the less steric difference of the system. These results are parallel to those reported for other ion exchangers.

The activation energy was found to decrease with the decrease in the entropy of the activation of the system (Table 3). The same trend was observed for other ion exchange materials (El-Naggar et al. (2007a, b). The relationship between E_a and ΔS^* values for the exchange of Cs⁺, Co²⁺ and Cd²⁺ on titanium potassium vanadate (TiKV) at $25 \pm 1^\circ\text{C}$ gave a linear relationship (Figure 7). This result indicate that the $E_a - \Delta S^*$ compensation mechanism holds for the ion exchange system on the TiKV. Therefore, the physico-chemical origin of the $E_a - \Delta S^*$ compensation is probably related to an intrinsic property of hydration. Thus, from the previous results and the negative values of ΔS^* reported in Table 2, it is anticipated that the Cs⁺, Co²⁺ and Cd²⁺ ions exchange with H⁺ into the exchanger is in the non hydrated form (El-Naggar et al., 2007b).

The free energy of activation (ΔG^*) has been calculated from the equation proposed by Barrer and Fender (1961).

$$D_i = (KTd^2/h) \exp^{(\Delta G^*/R)} \quad (6)$$

and the values of enthalpy (ΔH^*) can be calculated from

the following relation:

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (7)$$

The values of D_i , D_o , E_a , ΔS^* , ΔG^* and ΔH^* for the exchange of Cs⁺, Co²⁺ and Cd²⁺ ions on titanium potassium vanadate ion exchanger have been calculated and tabulated in Table 3. Also, the negative values of ΔS^* suggests that upon exchange of these cations, no significant structural change occur in titanium potassium vanadate ion exchanger.

Additionally, the positive values of free energy (ΔG^*) and enthalpy change (ΔH^*) reported in Table 3 for the exchange of Cs⁺, Co²⁺ and Cd²⁺ ions on the particles of TiKV suggest that these reactions require energy to covert reactants into products and the overall exchange process is non-spontaneous and have endothermic nature.

Conclusion

1. The exchange kinetics of Cs⁺, Co²⁺ and Cd²⁺ on the prepared Titanium Potassium Vanadate (TiKV) were studied as a function of concentration, particle radius, drying temperature of TiKV and reaction temperatures.
2. The rate of exchange is independent on the metal ion concentration and this is a evident that the conditions set in this work to are, particle diffusion mechanism for all investigated metal ions.
3. The rate of exchange increases with decreasing the particle size and drying temperature of the exchange materials. However, the rate increases with increasing

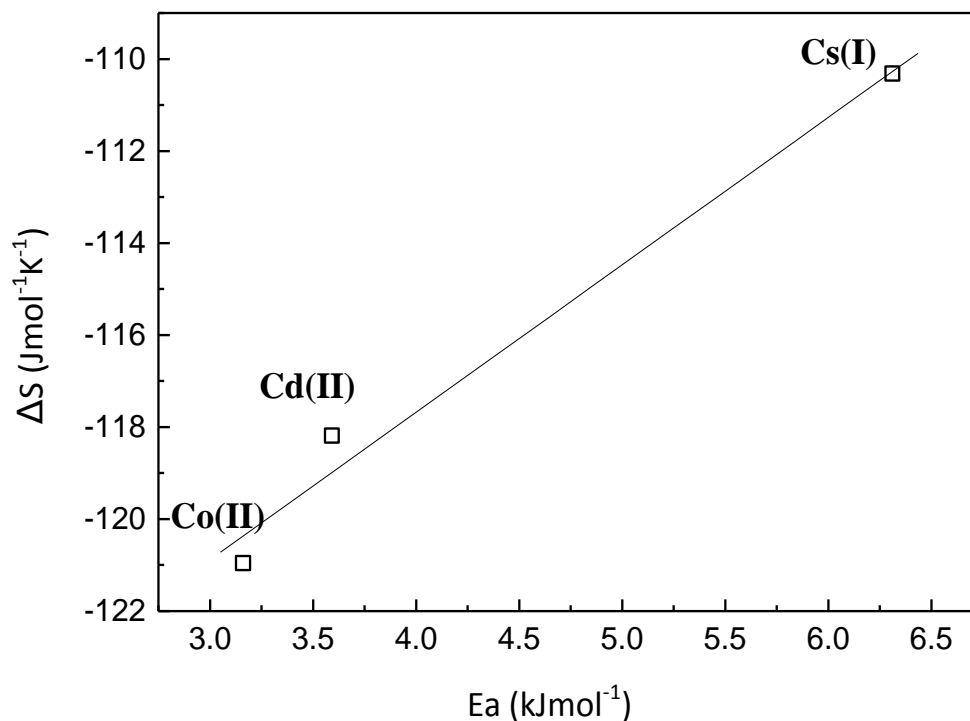


Figure 7. The correlation between ΔS^* and E_a for Cs^+ , Co^{2+} and Cd^{2+} on TiKV at $25 \pm 1^\circ\text{C}$.

the reaction temperature.

4. The diffusion coefficient values (D_i) of Cs^+ , Co^{2+} and Cd^{2+} ions on TiKV at 25°C decrease with increasing the drying temperatures from 50 to 400°C .

5. Negative values of entropy of activation (ΔS^*) were obtained and this anticipate that the investigated metal ions are exchanged with H^+ of TiKV in the non hydrated form.

6. The positive values of free energy (ΔG^*) and enthalpy change (ΔH^*) were obtained and suggest that these reactions require energy to covert reactants into products and the overall exchange process is non-spontaneous and have endothermic nature.

REFERENCES

- Abou-Mesalam MM, El-Naggar IM (2003). Diffusion mechanism of Cs^+ , Zn^{2+} and Eu^{3+} ions in the particles of zirconium titanate ion exchanger using radioactive tracers. *J. Colloid Surf. A* 215(1-3):205-211.
- Amphlett CB, Eaton P, McDonald LA, Miller AG (1964). Synthetic inorganic ion-exchange materials - IV: Equilibrium studies with monovalent cations and zirconium phosphate. *J. Inorg. Nucl. Chem.* 26(2):297-304.
- Barrer RM, Bartholomew RF, Rees LVC (1963). Ion exchange in porous crystals, Part II. The relationship between self- and exchange - diffusion. *J. Phys. Chem. Solids* 24(3):309-314.
- Barrer RM, Fender BEF (1961). The diffusion and sorption of water in zeolites Intrinsic and self-diffusion. *J. Phys. Chem. Solids* 21(1-2):12-24.
- Boyd GE, Adamson AW, Myers LS (1947). The exchange adsorption of ions from aqueous solutions by organic zeolite kinetics. *J. Am. Chem. Soc.* 69(11):2849-2859.
- Boyed GB, Saldavo BA (1953). Self-diffusion of Cations in and through Sulfonated Polystyrene Cation-exchange Polymers1. *J. Am. Chem. Soc.* 75:6091-6099.
- El-Naggar IM, Aly HF (1992). Kinetics of cesium, scandium and europium exchange on crystalline antimonite acid. *J. Solvent Extr. Ion Exch.* 10(1):145-158.
- El-Naggar IM, El-Absy MA (1992). A radiochemical study of the kinetics of ion exchange on hydrous titanium dioxide. *J. Radioanal. Nucl. Chem. Articles* 157(2):313-320.
- El-Naggar IM, Mowafy EA, Abdel-Galil EA (2007a). Diffusion mechanism of certain fission products in the particles of silico(IV)titanate. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 307(1-3):77-82.
- El-Naggar IM, Mowafy EA, El-Aryan YF, Abd El-Wahed MG (2007b). Sorption mechanism for Cs^+ , Co^{2+} and Eu^{3+} on amorphous zirconium silicate as cation exchanger. *Solid State Ionics* 178(11-12):741-747.
- El-Naggar IM, Mowafy EA, El-Kenany WM (2010). Kinetics and adsorption isotherm of some heavy metal ions from aqueous waste solutions by crystalline antimonite acid. *Arab. J. Nucl. Sci. Appl.* 43(2):97-106.
- El-Naggar IM, Zakaria ES, Shady SA, Aly HF (1999). Diffusion mechanism and ion exchange equilibria of some heavy metal ions on cerium(IV) antimonite as cation exchange. *J. Solid State Ionics* 122(1-4):65-70.
- Gupta KV, Gupta M, Sharma (2001). Process development for the removal of lead and chromium from aqueous solutions using red mudan aluminium industry waste. *Water Res.* 35(5):1125-1134.
- Herman RG, Clearfield A (1976). Crystalline cerium (IV) phosphates: The ion exchange characteristics with alkali metal ions. *J. Inorg. Nucl. Chem.* 38(4):853-858.
- Misak NZ, El-Naggar IM (1989). A study of the self-diffusion of sodium and cesium ions in hydrous ceria as a function of ion exchange capacity. *React. Polym.* 10(1):67-72.
- Reichenberg D (1953). Properties of Ion-Exchange Resins in Relation to their Structure. *Kinetics of Exchange.* *J. Am. Chem. Soc.* 75(3):589-597.
- Rudolf PR, Clearfield A (1989). X-ray powder structure and Rietveld

- refinement of the monosodium exchanged monohydrate of .alpha.-zirconium phosphate, $Zr(NaPO_4)(HPO_4) \cdot H_2O$. *Inorg. Chem.* 28(9):1706-1710.
- Shady SA, Abou-Mesalam MM, El-Shorbagy MM (2006). Diffusion mechanism of europium, uranium and thorium in the particles of zirconium molybdate as a cation exchanger. *Arab J. Nucl. Sci. Appl.* 39(1):72-80.
- Varshney KG, Tayal N, Gupta U (2003). Kinetics of ion exchange of alkaline earth metal ions on acrylamide cerium(IV) phosphate: A fibrous ion exchanger. *Colloids and Surfaces B: Biointerfaces* 28(1):11-16.