



Adsorption of selected hazardous metal ions from aqueous solutions using synthetic amorphous silico(IV)titanate as cation exchanger

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ABSTRACT

A silico(IV)titanate (SiTi) ion exchanger has been synthesized and completely characterized using chemical analysis, infrared spectroscopy, thermogravimetric and differential thermal analysis, X-ray diffraction and X-ray fluorescence analysis. Interestingly, this water- and acid-stable compound has shown a high ion exchange capacity for certain divalent metals such as Co(II), Cd(II) and Zn(II). The ion exchange capacity of silico(IV)titanate for the studied cations has the following order; Co > Zn > Cd. The distribution coefficient of the investigated metal ions was evaluated for different nitric acid concentrations. The values of thermodynamics functions for the adsorption of the investigated metal ions were calculated and found to be endothermic. In addition, the sorption isotherms for all cations have proved the applicability of Freundlich isotherm. A practical separation experiment for the investigated metal ions on the SiTi column from aqueous waste solutions was carried out. The values of the breakthrough capacities were found to be 0.96, 0.23 and 0.12 for Zn(II), Cd(II) and Co(II), respectively.

Keywords: Amorphous silico(IV)titanate; Hazardous metal ions; Ion exchanger; Aqueous solutions; Separation

1. Introduction

Inorganic ion exchangers are widely considered as the preferred materials for the removal of hazardous metal ions from surface water and/or aqueous nuclear wastes [1–4]. Studies relating to the utilization and development of new inorganic sorbents and their applications to the treatment of various streams have been carried out over a number of years [2–6]. Different separation techniques were proposed for water treatment or environmental purposes such as; solvent extraction, anionic and cationic exchange or even biosorption [7–11]. Furthermore, Inorganic ion exchangers has high treatment capacity, high removal efficiency, fast kinetics [12–14] and can also be utilized in metal recovery, which are of economical importance [15,16]. In fact, significant attention have been paid to these materials because of their high chemical,

radiation stability and selectivity toward certain metal ions compared with organic resins [17–19]. Therefore, the research in this area has received growing interest current the last few decade and various types of inorganic ion exchangers such as antimonates [20], zirconia [21], phosphate [11], tungstate [22], silicate [5,23], hydrous metal oxides [6,8] and especially titanate [2,24] have been synthesized and investigated. However, the development of new inorganic ion exchangers with characteristic properties is still need attention and their utilities in diverse fields is to be explored.

In the other hand, innovative ion exchanger materials are constantly sought due to diverse of the wastewater media. In a previous works [2,5,10,14,20], we have investigated the synthesis of several inorganic ion exchangers and evaluated their potential use for the removal of heavy metal ions and selected fission from acidic media. The titanosilicates, a new class of inorganic ion exchangers, are widely used and have shown promise in the fine-tuning of ion exchange properties

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[25,26]. In the last decade, many silico(IV)titanate crystalline silicotitanate (CST) was synthesized as a highly crystalline powder. These materials shows excellent selectivity for the uptake of cesium and strontium radioisotopes from complex nuclear waste streams [26–28]. In this context, Chitra et al. [29] reported the synthesis and uses of crystalline silicotitanate inorganic ion exchanger with a sitinakite structure. Chen et al. [30] developed a novel process for CST synthesis using waste cathode ray tube (CRT) panel glass as silicon source. Within this context, we have reported the synthesis of semi-crystalline silico(IV)titanate [10] and its application to the adsorption of certain fission products from nitric acid medium. Although, crystalline silico(IV)titanate have been extensively studied for the removal of selected metal ions relevant for nuclear processing industry, there is no valuable systematic work involving the synthesis and use of amorphous silico(IV)titanate for industrial wastes. Therefore, the ion exchange behaviors of these materials have not understood.

In the present work amorphous silico(IV)titanate was synthesized and characterized using different analytical techniques such as chemical stability, IR spectra, and XRD analyses. It is known that thermal analysis is a very useful technique for characterization of metal and thus is extensively employed for this purpose. The analytical utility of amorphous silico(VI)titanate has been established by determining the adsorption behavior of Co(II), Cd(II) and Zn(II) from aqueous waste solution on this material. One purpose is to explore the usefulness of amorphous silico(IV)titanate for the removal of selected hazardous metal ions from aqueous waste solutions.

2. Experimental

2.1. Chemicals

All reagents used in this study were of analytical grade purity and used without further purification. All salts used were nitrates of at least 99.9% purity and dissolved in deionized water.

2.2. Synthesis and characterization of silico(IV)titanate (SiTi)

Silico(IV)titanate (SiTi) used in this study was synthesized by dropwise addition of 1 M sodium metasilicate (BDH) to 1 M titanium tetrachloride solution (Aldrich) prepared in 4 M HCl with molar ratio Si/Ti equal to 1:1, as described previously [2,10]. The experiment carried out in a shaker thermostat water bath adjusted at $60^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. After an overnight standing, the crude precipitate product filtered, washed with demineralization water to remove excess acid, and finally dried at about 60°C . The dried white solid crushed and sieved to obtain the 2.2–1.0 mm [10]. The total water content of the ion exchanger was determined by calcination of 1.0 g of the prepared SiTi at different heating temperatures (200°C – 800°C) and calculating the percent weight loss. Powder X-ray diffraction patterns of the prepared SiTi carried out using a Shimadzu X-ray diffractometer, XD-D1, with a nickel filter and Cu- K_{α} radiation tube. FTIR spectra were determined with Thermo Scientific Nicolet-6700, with the spectra recorded in the range 400 – $4,000\text{ cm}^{-1}$. Differential

thermal analysis carried out using a Shimadzu DTA thermal analyzer. For the measurement elemental composition of the prepared silicotitanate, the material was analyzed for Si and Ti by X-ray fluorescence.

Chemical stability of the prepared silico(IV)titanate was examined in water, hydrochloric acid and nitric acid (0.1–6 M) by shaking 0.05 g of SiTi in 20 ml of the desired solution for about 4 d at $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. The filtrate was tested and analyzed for silicon and titanium using atomic absorption spectrometry.

2.3. Ion-exchange capacity (IEC)

Repeated batch equilibration of 0.1 M metal nitrate solutions (Co(II), Cd(II) and Zn(II)) with 50 mg of the prepared ion exchanger was carried out for the capacity evaluation. The mixture was shaken in a shaker thermostat at $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. After over-night standing, the solid was separated and the concentrations of the investigated metal ions determined by atomic absorption spectrometry. The capacity value was calculated by the following formula:

$$\text{Capacity} = \frac{\% \text{ uptake}}{100} \times C_o \times \frac{V}{m} \times Z(\text{meq} / \text{g}) \quad (1)$$

where, % Uptake is the percentage of the amount of metal ion in the exchanger to the initial amount of the metal ion solution, C_o is the initial concentration of the ions in solution, V is the solution volume (ml), m is the mass of the exchanger (g) and Z is the valence of the exchanged metal ions.

2.4. Distribution studies

The distribution coefficient (K_d) of Co(II), Cd(II) and Zn(II) on silico(VI)titanate were determined by batch equilibration as a function of nitric acid concentration. 0.1 g of the exchanger was mixed with 5 ml of the investigated metal ions. The exchange system was shaken in a shaker thermostat for 4 h (time to attain equilibrium) at $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. After phase separation by centrifugation, the concentrations of Co(II), Cd(II) and Zn(II) at end of the study period were determined by atomic absorption spectrometry. The initial and final pH of solution was determined. All the adsorption experiments conducted in triplicate and the total experimental error were about $\pm 3\%$. The distribution coefficients (K_d) values were evaluated Eq. (2):

$$K_d = \frac{(I - F)}{F} \times \frac{V}{m} \quad (\text{ml} / \text{g}) \quad (2)$$

where, I and F are the initial and final concentrations of the metal ions in solution (mg L^{-1}), respectively, V is the solution volume (ml) and m is the weight (g) of the exchanger.

2.5. Separation factor

For the preferential uptake of the metal ion, the separation factor (S.F) is determined by the separation of two metal ions, which can be calculated as:

$$S.F = K_d(A) / K_d(B) \quad (3)$$

where, $K_d(A)$ and $K_d(B)$ are the distribution coefficient for the two competing species A and B in the ion-exchange system.

2.6. Adsorption isotherms

The adsorption isotherms was done by the gradual increase in the concentration of sorbate ion in solution and measuring the amount sorbed at each equilibrium concentration. Therefore, the degree of sorption should be a function of the concentration of the sorbate ions only. The adsorption isotherms were investigated for Co(II), Cd(II) and Zn(II) in the concentration range from 5×10^{-4} to 10^{-2} M at pH equal 5 and constant V/m value of 50 ml g^{-1} . The experiment was carried out by mixing 0.05 g of the exchanger with 2.5 ml of the desired metal solutions in a shaker thermostat at $25^\circ\text{C} \pm 1^\circ\text{C}$. Metal ions concentrations changes were recorded with atomic absorption spectrometer. The equilibrium concentration (C) and the amount uptake (W/m) were calculated as follows:

$$W / m = \text{Uptake} \times C_o \times V / m \quad (4)$$

$$C = C_o \{1 - (\% \text{ Uptake} / 100)\} \quad (5)$$

where % Uptake is the percentage of the amount of metal ion in the exchanger after a certain time, t , to the initial amount of the metal ion solution, and C_o is the initial concentration of the metal ion.

2.7. Chromatographic column technique

Silico(IV)titanate was tested with Co(II), Cd(II) and Zn(II) to assess metal sorption performance and its selectivity toward the investigated metal ions. A sample of 0.5 g of SiTi (piratical diameter 0.21 mm) was packed into a glass column of 10 cm length and 0.5 cm internal diameter. A solution containing a mixture of Co(II), Cd(II) and Zn(II) (50 mg/l for each), at pH equal 5, was pumped through the column from the top to bottom with a constant flow rate of 1 ml/min. The effluent from the column was collected every 10 min and analyzed to determine the concentrations of the investigated metal ions. This was continued until the concentration of metal leaving the column was very close to that of the feed.

3. Results and discussion

Preliminary studies of the sorption of Co(II), Cd(II) and Zn(II) on SiTi indicated that equilibrium was attained within 4 h in a shaker thermostat water bath adjusted at $25^\circ\text{C} \pm 1^\circ\text{C}$. This work is attempt to synthesis and uses of a high stable ion exchange ion exchange material with high selectivity for some heavy metals. Silico(IV)titanate ion exchanger have been synthesized with complete characterization for the elucidation of the structure and the chemical formula. The weight losses (water content, %) for the prepared silico(IV) titante at different drying temperatures were found to be

9.82, 12.96, 20.11 and 23.91 at 200°C , 400°C , 600°C , and 800°C , respectively. These weight losses may be correspond to the water content removal of exchanger at these temperatures. On the other hand, the continuous loss in weight is gradually observed up to 800°C . This decrease in weight may be due to the decomposition reaction of material and formation of metal oxide.

To gain an insight into the nature of the structure of the synthesized silico(IV)titanate, the powder X-ray diffraction patterns of the synthesized SiTi was carried out at different heating temperatures (50°C , 400°C and 800°C) as shown in Fig. 1. No line was observed indicating the prepared silico(IV)titanate has amorphous structure. On the other hand, there is no change in structure on increasing the drying temperature up to 800°C .

Infrared spectra of silico(IV)titanate preheated at different temperatures (50°C , 200°C , 400°C , 600°C and 800°C) were analyzed as given in Fig. 2. The IR spectra of all samples were compared. In all the spectra, four main absorption bands at $\sim 3,400$, $\sim 1,630$, $\sim 1,415$, and $\sim 500 \text{ cm}^{-1}$ were detected. Except for at 800°C , the first band at $\sim 3,400 \text{ cm}^{-1}$ can be attributed to the presence of free water and OH groups adsorbed on the ion exchanger. The second observed strong band at $\sim 1,630 \text{ cm}^{-1}$ represents the bending mode of water molecules adsorbed on SiTi. The other two

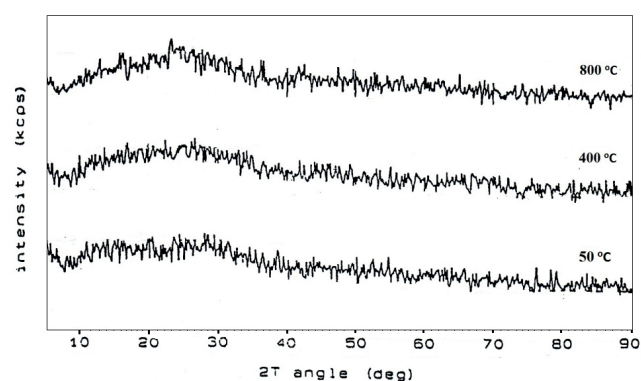


Fig. 1. X-ray diffraction patterns of the prepared silico(IV)titanate at different drying temperatures.

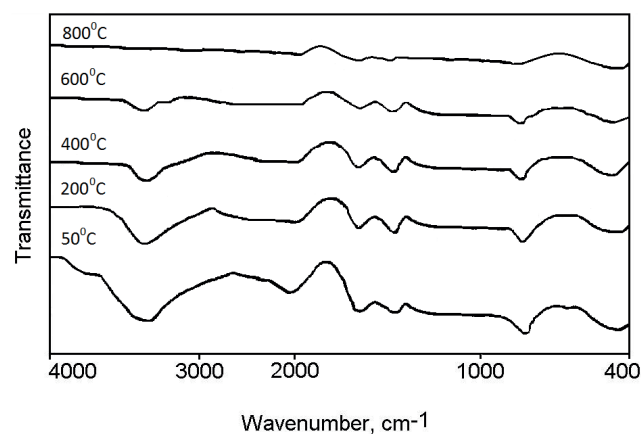


Fig. 2. Infrared spectra of the prepared silico(IV)titanate at different drying temperatures.

adsorption bands at $\sim 1,415$ and ~ 500 cm^{-1} may be attributed to the metal-OH deformation vibration and metal-oxygen bonds in the structure, respectively. On the other hand, the water content of the prepared ion exchanger was found to be gradually decreased with an increase of drying temperatures from 50°C to 600°C . This was verified by the significant decrease in the intensities of molecular water bands at $\sim 3,400$ and $1,630$ cm^{-1} . In addition, these two main characteristic stretching bands of molecular water are absent at 800°C .

Differential thermal analysis (DTA) and thermal gravimetric (TG) for silico(IV)titanate was carried out. It was found that, two characteristic endothermic peaks were observed. The first peak is possible assigned to the dehydration of free absorbed water and the second endothermic peak observed is possible due to crystallization of SiO_2 [31]. Our results are in good agreement with those reported for other inorganic ion exchanger [2,5]. On the other hand, this finding support the fact that the prepared silico(IV)titanate has a good thermal stability, compared with other organic and some of inorganic ion exchangers [25,27]. The prepared material was analyzed for Si(IV) and Ti(IV) by X-ray fluorescence spectrometry. The data obtained indicated that the percent of Si and Ti equal 19 and 61.01, respectively. Composition studies suggested the following tentative formula of silico(IV)titanate: $[(\text{SiO}_2)_4(\text{TiO}_2)_4] n\text{H}_2\text{O}$. The number of water molecules in exchanger was calculated by using the formula [32]:

$$18n = X(M + 18n) / 100 \quad (6)$$

where, X is the percent weight loss of ignition and M is the molecular weight of the exchanger. It was found that, the number of water molecules (n) per mole of the cation exchanger equal ~ 4.63 . So, a tentative molecular formula for the exchanger can be written as; $[(\text{SiO}_2)_4(\text{TiO}_2)_4] 4.63\text{H}_2\text{O}$.

To learn about the stability of prepared ion exchanger against chemical attack, the chemical stability of the prepared silico(IV)titanate was tested in water and at different concentrations of nitric and hydrochloric acids, Table 1. It was found that, the prepared SiTi is very stable in HNO_3 solution up to 5.5 M and physically quite stable up to 5 M HCl. However, it is partially dissolved at 6 M HCl. This behavior was observed

Table 1
Chemical stability of silico(IV)titanate in various solvent systems, at $25^\circ\text{C} \pm 0.5^\circ\text{C}$

Solvent concentration (M)	Solubility (mg L^{-1})				
	H_2O	HNO_3	HCl	NaOH	KOH
0.1	BD	6.3	6.8	0.2	0.23
0.5	BD	11.2	10.3	4.1	4.5
1.0	BD	14.5	15.2	12.5	12.1
2.0	BD	19.8	18.7	–	–
3.0	BD	21.3	24.5	–	–
4.0	BD	22.9	25.4	–	–
5.0	BD	25.9	29.3	–	–
6.0	BD	PD	PD	–	–

BD, Below detection; PD, partially dissolved.

for other inorganic ion exchanger [2,5]. On the other hand, the prepared ion exchanger is high soluble in both NaOH and KOH. It was found that, the solubility increase by increasing the concentration of the base (NaOH or KOH) from 0.1 to 1 M.

3.1. BET surface area analysis

The surface area of the prepared silico(IV)titanate at different drying temperatures (50°C , 200°C , and 400°C) were found to be 155.7, 234.7 and 239.6 m^2/g , respectively. On the other hand, these results indicated that the surface area of silico(IV)titanate increased by increasing the drying temperature from 50°C to 200°C , after which slight increase was obtained at 400°C . This may be due to SiTi losses amount of water, each molecules of water losses by increasing drying temperatures leave space in the ion exchanger, which leads to the increase in surface area. It is also possible that a scratching of crystals occurred during dehydration, which leads to the small increase in surface area. This finding is contrast with that previously reported for semi-crystalline silico(IV) titanate [33].

From the above results, we can conclude that, the prepared material is very stable in water, HNO_3 and HCl and has a good thermal stability. Therefore, this material is suitable for use in industrial chemical waste solutions as well as nuclear technology.

3.2. Equilibrium and distribution coefficient

Fig. 3 shows the K_d -values of Co(II), Cd(II) and Zn(II) on silico(IV)titanate as a function of pH at constant concentration of the investigated metal ions. The cation exchange process between H^+ (solid phase) and M^{n+} in solution can be represented as follows:



In sufficiently diluted solution, where the activity coefficient may be neglected, the selectivity coefficient can be defined by the following equation [34]:

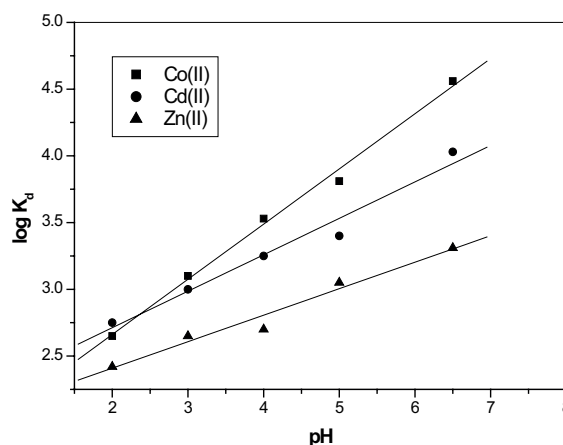


Fig. 3. Distribution coefficient of Co(II), Cd(II) and Zn(II) as a function of pH on SiTi at $25^\circ\text{C} \pm 0.5^\circ\text{C}$.

$$K_H^M = \frac{[\overline{M^{m+}}][H^+]^n}{[H^+]^n [M^{n+}]} \quad (8)$$

where, $[M^{n+}]$ and $[H^+]$ denote to the concentration of M^{n+} and H^+ in the solid phase, respectively, and $[M^{n+}]$ and $[H^+]$ their concentrations in the solution.

The K_d -values can be calculated by the following formula:

$$K_d = \frac{\text{concentration of the cation in exchanger}}{\text{concentration of the cation in solution}} \quad (9)$$

$$K_d = \frac{[\overline{M^{n+}}]}{[M^{n+}]} \quad (10)$$

$$K_d = K_H^M \frac{[H^+]^n}{[H^+]^n} \quad (11)$$

or

$$\log K_d = \log K_H^M \left[\overline{H^+} \right]^n - n \log [H^+] \quad (12)$$

When $[\overline{M^{n+}}] \ll [\overline{H^+}]$ and $[M^{n+}] \ll [H^+]$, the value of K_H^M is considered as constant.

Thus, Eq. (11) can be reduced to:

$$\log K_d = C - n \log [H^+] = C + n\text{pH} \quad (13)$$

Therefore, plot the relation between $\log K_d$ and pH should be given a straight line with a slope equal (n). It was found that, K_d -values of the investigated metal ions increase with increasing pH values in the entire range of acid concentrations as shown in Fig. 3. On the other hand, the linear relations between $\log K_d$ and pH were observed with slopes smaller than the valences of the studied cations were obtained. These results indicated the ion exchange reaction deviated from the ideal process [5,33]. The non-ideality of the exchange reaction may be due to a different mechanism such as physical adsorption, chemical reaction or other effects, which takes place besides the ion exchange process. The obtained K_d -values are relatively high compared with that obtained for other inorganic ion exchanger [20].

On the other hand, the higher water content of SiTi may be act as exchangeable active sites in the exchanger. This finding was confirmed also by the data obtained in IR and DTA. As shown in Fig. 3, the selectivity order of the investigated cations on silico(IV)titanate in the same conditions have the following sequence; $\text{Co} > \text{Cd} > \text{Zn}$.

The batch data obtained suggesting that an effective separation of the investigated metal ions from each other is possible in the most of studied range of nitric acid medium using the synthesized SiTi, as shown in Table 2.

The effect of reaction temperature on the adsorption of Co(II), Cd(II) and Zn(II) at pH = 4.5 on SiTi was carried out at different temperatures (25°C–60°C), as shown in Fig. 4. It was found that the K_d -values of the investigated metal ions increase with increasing temperature. This trend means that the adsorption processes is an endothermic.

To estimate the enthalpy change, ΔH , the following thermodynamic relationship was used:

$$\Delta H = -2.303R \Delta \log K_d / \Delta (1/T) \quad (14)$$

The values of enthalpy change, obtained for the extraction of Co(II), Cd(II) and Zn(II) are 21.8 ± 3.1 , 19.8 ± 2.6 ,

Table 2
Distribution coefficients (K_d) and separation factors for Co(II), Cd(II) and Zn(II) on silico(IV) titanate as a function nitric acid concentrations at $25^\circ\text{C} \pm 0.5^\circ\text{C}$

pH	K_d (ml g ⁻¹)		
	Co	Cd	Zn
2	450	556	265
		(1.23)	(1.69)
			(2.09)
3	1,210	1,003	450
		(1.21)	(2.69)
			(2.23)
4	3,210	1,801	525
		(1.78)	(6.11)
			(3.23)
5	6,380	2,441	1,130
		(2.61)	(5.65)
			(2.16)
6.5	26,509	10,563	2,023
		(2.51)	(13.10)
			(5.22)

Values in the parentheses indicated separation factors values of Co(II), Cd(II) and Zn(II) from each other.

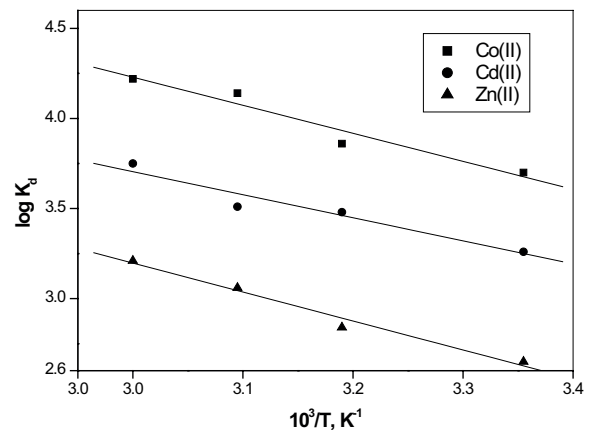


Fig. 4. Adsorption of Co(II), Cd(II) and Zn(II) on silico(IV) titanate at different temperatures, pH = 4.5.

and 24.2 ± 2.8 kJ/ml, respectively. These results are parallel to that reported for other semi-crystalline silico(IV)titanate [33]. El-Naggar et al. [5], studied the adsorption of Cs, Co and Eu on amorphous zirconium silicate as a function of temperature, they found that the adsorption processes is an endothermic.

3.3. Ion exchange capacity

The capacity of silico(IV)titanate heated at different temperatures (up to 800°C) for Co(II), Cd(II) and Zn(II) were determined at different metal ion concentrations and given in Table 3. The capacity of silico(IV)titanate for the investigated metal ions increase with increasing metal ion concentration as shown in Table 3. It was found that the capacity of silico(IV)titanate for the studied cations has the following order; $Co > Zn > Cd$. This sequence is in accordance with the hydrated radii of the exchanged ions. The ions with smaller hydrated radii easily enter the pores of the exchanger, leading to higher adsorption [35,36]. Our results agree with that reported before for other inorganic ion exchangers [2,5]. This supports the finding of El-Naggar et al. [33] for the capacity of semi-crystalline silico(IV)titanate for different concentrations of some hazardous radionuclides. On the other hand, the small radius of dehydrated Co(II) increases the mobility and the packing density of the Co(II) radii compared to the Cd(II), which facilitates the greater adsorption of Co(II) on SiTi. It is very interesting to note the effect of heating on the capacity of silico(IV)titanate. As shown in Table 2, the exchanger has a good ion exchange capacity (IEC) at 50°C. On the other hand, the ion exchange capacities for Co(II), Cd(II) and Zn(II) are decreased with increasing the heating temperatures from 50°C to 600°C. The material loses almost whole of its IEC in the range 600°C–800°C. This trend may be due to the loss of free water, which may act as exchangeable active site for SiTi [5].

Table 3
Ion exchange capacity of silico(IV)titanate with Co(II), Cd(II) and Zn(II) at different drying temperatures

[Metal ions], (M)	Drying Temperature, °C	Capacity, (meq/g)		
		Co(II)	Cd(II)	Zn(II)
5×10^{-2}	50	0.81	0.67	0.78
	200	0.57	0.43	0.47
	400	0.43	0.31	0.35
	600	0.11	0.09	0.09
	800	0.04	–	0.01
5×10^{-3}	50	0.45	0.20	0.31
	200	0.16	0.09	0.095
	400	0.12	0.08	0.08
	600	0.04	0.03	0.04
	800	0.01	–	0.01
5×10^{-4}	50	0.05	0.04	0.03
	200	0.03	0.03	0.02
	400	0.02	0.01	0.01
	600	0.005	0.001	0.003
	800	0.001	–	–

3.4. Sorption isotherm

The adsorption of Co(II), Cd(II) and Zn(II) on silico(IV)titanate over the entire concentration range 5×10^{-2} – 10^{-4} M were fitted by the Freundlich isotherm equation:

$$\text{Log } W / m = K + K' \log C \quad (15)$$

where, W/m is the amount uptake, C is the equilibrium concentration, K and K' are the Freundlich constants, which measure the adsorption intensity and adsorption capacity of the sorbent, respectively.

As shown in Fig. 5, a linear relationship was obtained from the plots of $\log W/m$ for both Co(II), Cd(II) and Zn(II) on silico(IV)titanate against $\log C$. These results indicated that Co(II), Cd(II) and Zn(II) are physically adsorbed on silico(IV)titanate [35,36].

3.5. Application studies

The removal of selected hazardous metal ions with synthetic silico(IV)titanate inorganic ion exchanger from their aqueous waste solutions was investigated by using solid bed columns chromatography. This technique is based on the granular nature of the synthesized ion exchanger and the data obtained from the distribution coefficients of the investigated metal ions on SiTi. In agreement with the batch distribution data, the adsorption of the studied metal ions on SiTi column beds was carried out at pH equal 5. Fig. 6 shows the breakthrough curves for a mixture of Co(II), Cd(II) and Zn(II) on silico(IV)titanate column (particle diameter 0.21 mm).

It was found that, the selectivity order of the investigated cations on silico(IV)titanate in the same conditions have the following sequence; $Zn > Cd > Co$. The breakthrough capacities for Co(II), Cd(II) and Zn(II) on SiTi were calculated from the corresponding breakthrough curve, using the following relation:

$$Q = (V_{50\%} \times C_o) / m \quad (16)$$

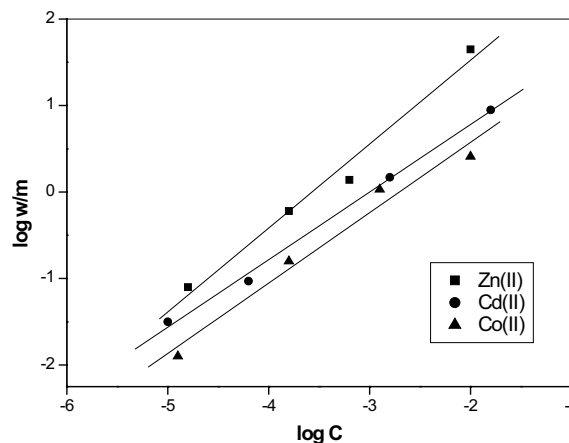


Fig. 5. Freundlich adsorption isotherm for Co(II), Cd(II) and Zn(II) on silico(IV)titanate at 25°C \pm 0.5°C, pH = 4.5.

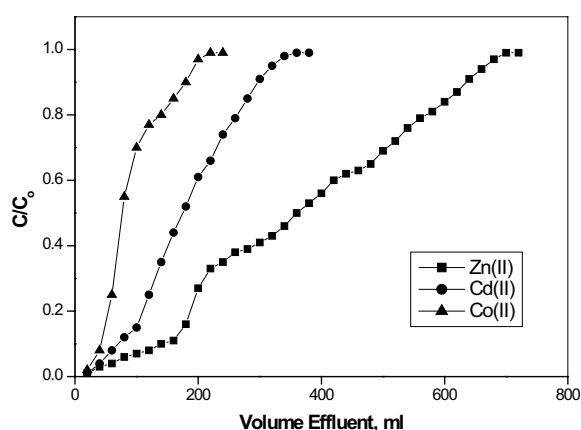


Fig. 6. Breakthrough curves for Co(II), Cd(II) and Zn(II) on silico(IV)titanate column at $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$, $\text{pH} = 5$.

where, Q is the breakthrough capacity, $V_{50\%}$ is the volume at which the metal ion uptake is 50%, C_0 is the initial concentration of the metal ion and m is the weight of the solid.

The values of the breakthrough capacities were found to be 0.96, 0.23 and 0.12 for Zn(II), Cd(II) and Co(II), respectively [35]. This results indicated that the high selectivity of silico(IV) titanate for the adsorption of Zn(II) than Cd(II) or Co(II) from their aqueous waste solution. The elution profile of these metal ions is studied in water and nitric acid solutions (0.05–1 M). At water, no peaks in the elution curves mixture of Co(II), Cd(II) and Zn(II) were observed. At 0.05 M and 0.1 HNO_3 ; sharp peaks for Co(II), Cd(II) and Zn(II) were obtained. At 0.5 M HNO_3 ; sharp peaks for Co(II) were obtained and the peaks of Zn(II) and Cd(II) were disappeared. At 1 M HNO_3 ; all peaks related to the adsorbed metal ions are disappeared. From the presented results, it is clear that the Co(II) can be separated from silico(IV)titanate column by 0.5 M HNO_3 , so we can expect using the column in the regeneration process.

4. Conclusions

- Silico(IV)titanate has been prepared and characterized as a cation ion exchanger. It is amorphous and stable in water and acid solutions up to 5 M HNO_3 or HCl, while completely dissolved at 6 M (HNO_3 or HCl).
- The prepared material shows a good potential for the removal of cobalt, cadmium and zinc from nitric acid solutions.
- The general selectivity sequence of the adsorption of Co(II), Cd(II) and Zn(II) from nitric acid medium on silico(IV)titanate is the following: $\text{Co(II)} > \text{Cd(II)} > \text{Zn(II)}$.
- The capacities of silico(IV)titanate for Co(II), Cd(II) and Zn(II) increases with increasing the metal ions concentration.
- Co(II), Cd(II) and Zn(II) are physically adsorbed on silico(IV)titanate and fitted to the Freundlich isotherm.
- The high chemical stability and granular nature of prepared silico(IV)titanate allowing to be utilized to separate Co(II), Cd(II) and Zn(II) from others in their synthetic mixtures.

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