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Preparation, characterization and ion-exchange properties of a new 'organic–inorganic' composite cation exchanger polyaniline silicotitanate: Its applications for treatment of hazardous metal ions from waste solutions

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ABSTRACT

Polyaniline silicotitanate an 'organic–inorganic' composite material, was prepared via sol–gel mixing of organic polymer polyaniline into the matrices of the inorganic precipitate of silicotitanate. The physico-chemical properties of this hybrid material were determined using atomic absorption spectrophotometry (AAS), CHN elemental analysis, ICP_S, X-ray (XRD and XRF), IR, TGA-DTA and scanning electron microscopy (SEM). The data obtained proposed that the chemical formula of polyaniline silicotitanate may be written as: $[Ti_4O_9H_7Si + (-C_6H_5NH-)]\ 4H_2O$. Ion-exchange capacity (IEC), thermal stability and distribution behavior, etc. were also carried out to understand the cation-exchange behavior of the material. On the basis of distribution studies, the material was found to be highly selective for Cs^+ and the selectivity sequence for sorption of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} ions on polyaniline silicotitanate was found to be; $Cs^+ > Pb^{2+} > Co^{2+} > Cu^{2+} > Cd^{+2}$. Thermodynamic parameters (i.e. ΔG^o, ΔS^o and ΔH^o) have also been calculated for the adsorption of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} ions on polyaniline silicotitanate showing that the overall adsorption process is spontaneous and endothermic.

KEYWORDS

Organic–inorganic hybrid;
Cation-exchanger;
Synthesis;
Characterization;
Distribution studies;
Polyaniline silicotitanate;
Heavy toxic metals;
Thermodynamic parameters.

INTRODUCTION

The removal of pollutants from industrial wastewaters has recently become one of the most important processes because of which its importance is becoming more profound with increasing industrial activities. Cesium is one of these pollutants that its separation from aqueous solution is mostly needed. The amount control of cesium isotopes, particularly ^{137}Cs and ^{135}Cs, in liquid wastes has become an issue of great concern because of their destructive effects on the environment. They are potentially dangerous to human health and also to the environment, because the high solubility of cesium can cause its migration through groundwater to the biosphere. Furthermore, they can be easily incorporated in terrestrial and aquatic organisms because they are chemically similar to potassium[1]. In case of exposure to ingestion route, Cs metal is confidently adsorbed to the body and can be easily distributed throughout the soft tissues of body. Thyroid cancer is one of the terrible consequences of ^{137}Cs adsorption via the contaminated food and water[2].

The materials used as ion exchangers have attained an appreciable status in current research and become a part of a number of laboratories and industrial units. Organic as well as inorganic ion-exchange materials have been frequently used in environmental pollution remediation and exhibited merits and demerits over one another. Organic ion-exchangers (ion-exchange resin) possessed high ion-exchange capacity, chemical stability and better regeneration characteristics, while inorganic ion-exchangers exhibited higher thermal and radiation stability, rigid structure and undergo negligible swelling during use. To develop these advantages and overcome the obstacles of both organic and inorganic ion exchangers, researchers have been motivated to develop organic–inorganic composite cation-exchangers. Composite cation-exchangers possessed striking features as compared to organic as well as inorganic ion-exchange media[3–6]. In view of the above mentioned facts, an organic–inorganic composite cation-exchanger polyaniline silicotitanate was prepared and characterized for ion-exchange properties to explore the utility of the material.

In the proposed study of the incorporation of polyaniline into the matrix of inorganic cation-exchanger silicotitanate overcame the low thermal stability of the inorganic silicotitanate which loses about 64.41% of its ion exchange capacity on heating at 400°C, while polyaniline silicotitanate loses about 40.68% of its ion exchange capacity on heating at the same drying temperature. Furthermore the high selectivity of polyaniline silicotitanate for Cs(I).

In the present paper polyaniline silicotitanate was synthesized in identical conditions. The prepared ion exchanger was characterized using different analytical techniques such as thermal and chemical stabilities, XRD analysis, and IR spectra. In addition to the thermodynamics parameters (ΔG^o, ΔS^o and ΔH^o) for the adsorption of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} on polyaniline silicotitanate, ion exchange capacity and equilibrium distribution coefficients of metal ions on the prepared ion exchanger were determined to explore the separation potential of the studied cations on the matrices.

EXPERIMENTAL

Chemical reagents and instruments

The main reagents used for the synthesis of the material were obtained from BDH (England) and Loba Chemie (India). All other reagents and chemicals were of analytical reagent grade purity and used without further purification. pH measurements were performed using pH meter of the bench, model 601A, USA. An atomic absorption spectrophotometer, ICPs, XRD and (DTA and TG) were made on a Shimadzu, Kyoto, Japan, while XRF was made on a Philips, Holland.

Preparation of polyaniline silicotitanate

Preparation of reagents

0.1 M sodium metasilicate ($Na_2O_3Si.9H_2O$) was prepared in demineralized water (DMW) while 0.1 M of titanium tetrachloride ($TiCl_4$) was prepared in 4 M HCl. Solution of 10% (v/v) aniline ($C_6H_5NH_2$) and potassium persulfate ($K_2S_2O_8$) were prepared in 1 M HCl.

Preparation of polyaniline silicotitanate

Polyaniline gels were prepared by mixing aqua volumes of the solutions of 10% aniline ($C_6H_5NH_2$) and 0.1 M potassium persulfate ($K_2S_2O_8$) with continuous stirring by a magnetic stirrer. Green colored polyaniline gels were obtained by keeping the solutions below 10°C for half an hour. A precipitate of silicotitanate (SiTi) was prepared by dropwise addition of sodium metasilicate ($Na_2O_3Si.9H_2O$) (0.1 M) dissolved in demineralized water (DMW) to titanium tetrachloride ($TiCl_4$) (0.1 M) dissolved in 4M HCl at Si/Ti molar ratio of 1.0 with continuous stirring. The white precipitate was obtained when the pH of the mixture was adjusted to ≈ 2.36 by adding aqueous ammonia (NH_4OH). The gels of polyaniline were added to the white inorganic precipitate of silicotitanate and mixed thoroughly with constant stirring. The resultant green colored gels were kept for 24 h at room temperature (25±2°C) for digestion. The supernatant liquid was decanted and the gel was rewashed with bidistilled water in order to remove fine adherent particles and was filtered using a centrifuge (about 10^4 rpm), and dried at 50±1°C. The dried products were immersed in DMW to obtain small granules and converted to H^+ -form by treating with 1M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washing with DMW, dried at 50°C and sieved to obtain particles of particular size range (0.12 – 0.75 mm). The percentage of yield and physical appearance of beads was selected for further studies. The results are given in TABLE 1, the polymerization reaction is given in Figure 1.

TABLE 1 : Synthesis and properties of polyaniline silicotitanate

Sample	Mixing volume ratio (v/v)						properties	
	$TiCl_4$ in 4M HCl (0.1M)	$Na_2O_3Si.9H_2O$ in DMW (0.1M)	*Precipitating* agent	pH of the Inorganic precipitate	$K_2S_2O_8$ in 1 M HCl (0.1M)	Aniline in 1 M HCl (10%)	Appearance of beads after drying at 50±2°C	XRD
Polyaniline SiTi	1	1	NH_3	2.36	1	1	Green granular	amorphous

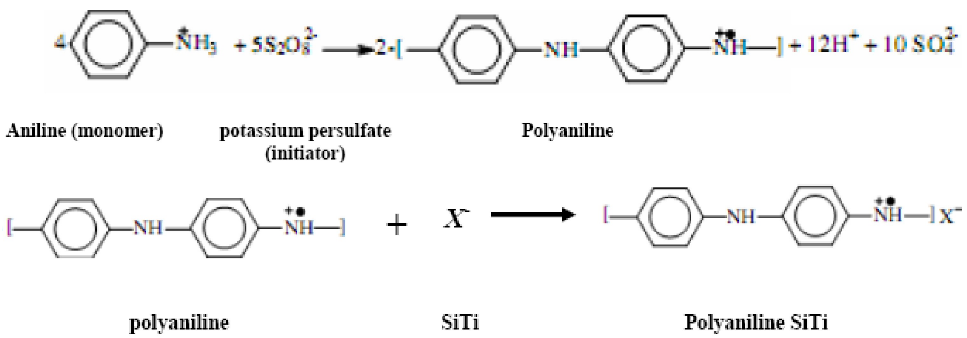


Figure 1 : Schematic representation of polyaniline silicotitanate preparation

Characterization of the prepared polyaniline silicotitanate

Some physical and chemical properties of the prepared polyaniline silicotitanate were investigated by using different techniques such as X-ray diffraction patterns (XRD), X-ray fluorescence spectrometry (XRF), infrared (IR), scanning electron microscopy (SEM) and thermal analysis (TGA and DTA).

pH titration

The pH titration method for the prepared polyaniline silicotitanate was carried out as follow; (0.3 g) of the prepared material was placed in a column fitted with glass wool at its bottom. A glass bottle containing 50 mL of 0.001 M HCl was placed below the column, and for determination of pH, a glass electrode was placed in the solution, then 100 mL of 0.01 M (LiOH, NaOH or KOH) was poured into the column. Titration was carried out by passing the alkali metal hydroxide at a drop rate of about 10 drop/min, and continued to a pH of about ≈10[7]. The results are shown in Figure 7.

Thermal stability

Thermogravimetric analysis of the material in the H^+ form was performed at a heating rate of 10°C min^{-1}. The effect of heating on the ion-exchange capacity of the material was also examined. The material in H^+ form was heated at different temperatures for 4 h in a muffle furnace and the ion-exchange capacity for Cs^+ was evaluated by batch experiment technique process after cooling it at room temperature. The results are summarized in TABLE 3.

Chemical stability

The chemical stability of the prepared polyaniline silicotitanate and silicotitanate (SiTi) was studied in water, acid (HNO_3 and HCl) at different concentrations [0.5,1,2,3,4,5, 6 and 7 M] and base (KOH and NaOH) at different concentrations [0.1 M and 1 M], by mixing 100 mg of each of the prepared samples of polyaniline silicotitanate and silicotitanate (SiTi) and 100 ml of the desired solution with intermittent shaking for about one week at 25±1°C as given in in TABLE 4.

Capacity measurments

The capacity of polyaniline silicotitanate sample was determined by batch experiment technique. 0.1g of the solid material was equilibrated with 10ml of ionic strength about 0.1 (Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and/or Pb^{2+}) chloride solution with V/m ratio equal 100 ml/g for all polyaniline silicotitanate samples. The mixture was shaked in a shaker thermostat at 25 ± 1°C. After overnight standing the solid was separated and the concentration of the metal ions was measured instrumentally (using atomic absorption spectrophotometer and I.C.Ps). The capacity value was calculated by the following formula;

$$\text{Capacity} = \%\ \text{uptake} / 100 \times C_0 \times V/m \times Z\ (\text{meq./g}) \quad (1)$$

where C_o is the initial concentration of the ions in solution, V is the solution volume, m is the sorbent mass and Z is the valence of the exchanged ions.

Distribution studies

The distribution coefficient (K_d) of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} ions on polyaniline silicotitanate were determined by batch equilibration as a function of hydrochloric acid concentration. 0.1g of the prepared ion exchanger was shaken with 10 ml at a V/m ratio of 100 ml/g of 10^{-3}M of the above mentioned metal ions solution.

The mixture was placed overnight (time within an equilibrium was attained) in a shaker thermostat adjusted at 25 ± 1°C. After equilibrium, the solutions were separated by centrifugation and the concentration of metal ions in the exchanger and in the solution was deduced from the concentration relative to the initial concentration in the solution.

The pH values were measured before and after equilibration by using a pH meter of the bench, model 601A, USA., the concentration of the metal ions was measured instrumentally (using atomic absorption spectrophotometer and I.C.Ps). All tests were repeated two or three times and the total experimental error were about ± 3%.

The distribution coefficients (K_d) and separation factor values were evaluated;

$$K_d = \frac{A_o - A_f}{A_f} \times \frac{V}{m} \text{ (ml/g)} \qquad (2)$$

Where A_o and A_f are the concentrations of the ions in solution before and after equilibration, respectively, V is the solution volume (ml) and m is the exchanger mass (g).

Water content

The water content of polyaniline silicotitanate in the H^+, Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} forms were determined by using thermal analysis technique (TG and DTA). The water loss (W / W) data were determined at 850°C and summarized in TABLE 7.

Chemical composition

The material was analyzed for Si(IV) and Ti(IV) by X- ray fluorescence spectrometry. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis. The weight percent composition of the material was: Si, 6.96; Ti, 49.01; C, 16.86; H, 3.10; N, 4.82.

Separation factor

The separation factor may be considered as the relative tendency of two ions to be adsorbed in an exchanger from solutions of equal concentration. It is used as a measure of possibility of chromatographic separa-

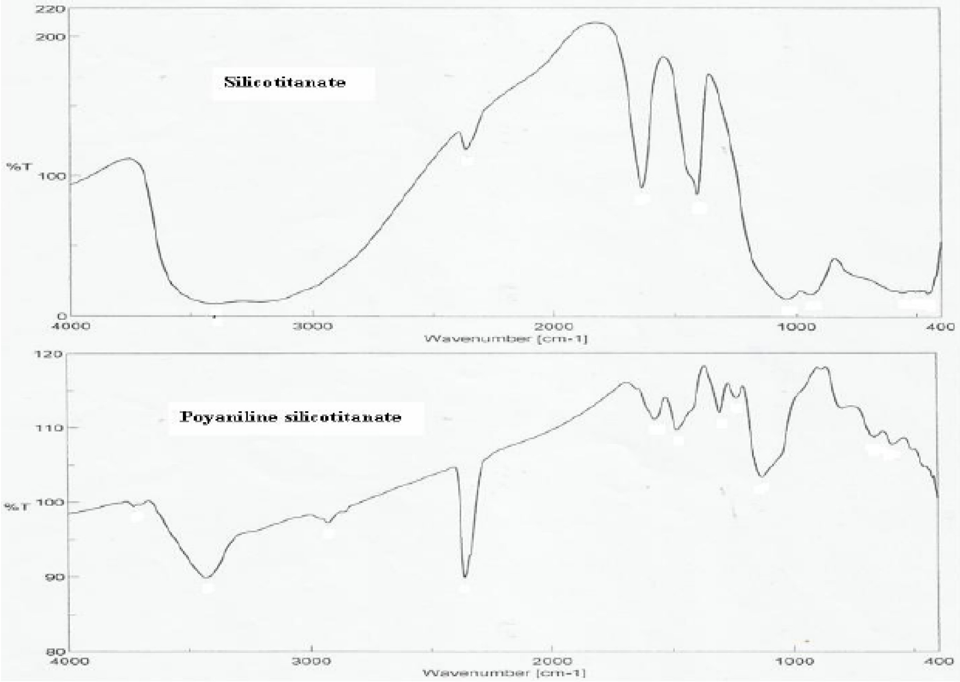


Figure 2 : Infrared spectra of the prepared silicotitanate and polyaniline silicotitanate dried at 50°C

tion and is also expressed as the ratio of the distribution coefficients of the elements to be separated as:

Seperation factor $(\alpha^{A}_{B}) = K_d(A)/K_d(B)$

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

RESULTS AND DISCUSSION

In this study, a new organic-inorganic ion exchanger, polyaniline silicotitanate has been developed which possesses good ion exchange capacity. The infrared spectrum of silicotitanate is recorded in Figure 2 and TABLE 2.

The peak at ≈ 3405cm^{-1} is characteristics to the stretching mode of free water and OH groups adsorbed on silicotitanate[8,9]. The peak at ≈ 1635cm^{-1} represents the bending mode of water molecules[9]. The peak at ≈1406cm^{-1} is due to the deformation vibration of hydroxyl groups (Si and Ti-OH deformation vibration)[10,11]. The two peak at ≈1042 cm^{-1} with a band between 942-1042cm^{-1} and 560cm^{-1} with a band between 456-560cm^{-1} are associated with metal oxygen bonds[12,13]. The infrared spectrum of polyaniline silicotitanate is recorded in Figure 2 TABLE 2. It was found that all the above absorption bands occurred in

TABLE 2 : Assignments of IR bands (cm^{-1}) of polyaniline silicotitanate and silicotitanate

Polyaniline silicotitanate	Silicotitanate (SiTi)	Calculated [14,15]	Vibration [14,15]
Observed band	Observed band		
3429	3405		ע. OH and ע. H_2O [8,9,14,15]
2925		3171	ע$_s$. NH_2
1569	1635		δ H_2O [9]
1477	1406		δ. M–OH [10]
1303			ע.C–N
1233		1208	ω. NH_2
1130		1120	ע$_a$. C–C
660,587	456-560, 942-1042		metal oxygen bonds [12,13]

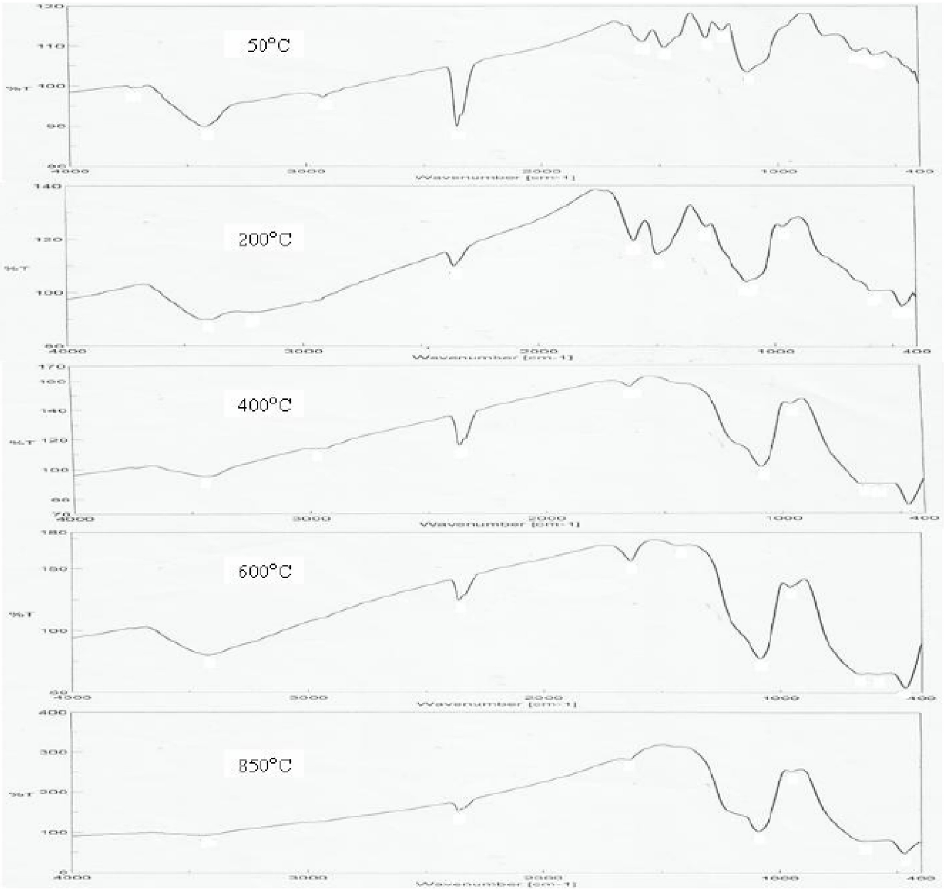


Figure 3 : Infrared spectra of the prepared polyaniline silicotitanate at different drying temperatures

the spectrum of polyaniline silicotitanate, beside four absorption band (≈1130cm^{-1}, ≈1233cm^{-1}, ≈1303cm^{-1} and ≈2925cm^{-1}) occurred in polyaniline silicotitanate spectrum. The peak at ≈1130cm^{-1} is characteristics to the asymmetric stretching vibration of the C–C (ν_a.C–C)[14,15], the peak at ≈1233cm^{-1} is characteristics to (ω. NH$_2$)[14,15], the peak at ≈1303cm^{-1} is characteristics to the stretching vibration of the C–N[11], the peak at ≈2925cm^{-1} may be attributed to symmetric stretching vibration of the NH$_2$ group (ν_s. NH$_2$)[14,15]. In the polyaniline silicotitanate in Figure 2, there is C–N stretching band around 1303cm^{-1} region and C–C stretching band around 1130cm^{-1}. These characteristic stretching frequencies show close resemblance with the inorganic precipitate, i.e. in polyaniline silicotitanate in Figure 2, indicating the binding of inorganic precipitate with organic polymer and formation of 'organic–inorganic' composite 'polyaniline silicotitanate.' This indicates that the polyaniline silicotitanate contains considerable amount of aniline. It is clear that the characteristic H$_2$O bands which appear at ≈ 3429 cm^{-1} and 1569cm^{-1} for all samples were decreased as demonstrated by the decrease in bond intensities of molecular water for all samples which goes parallel to increase in the heating temperature from 50°C to 850±1°C as shown in Figure 3. From 400°C, the peaks characteristic to polyaniline species (ν_s. NH$_2$, ν C–N, ω. NH$_2$ and ν_a. C–C) disappeared, this sequence can be confirmed by data obtained from Thermogravimetric analysis Figure 8.

From Figure 4, it was found that the prepared silicotitanate heated at 50±1°C has amorphous structure and the degree of crystallinity of the prepared silicotitanate slightly improved when doped with the organic part polyaniline. Figure 5 shows that the crystal structure of the prepared polyaniline silicotitanate is slightly improved as the heating temperatures increased from 50°C to 850±1°C, and there is a sharp improvement of crystallinity occurs at 850±1°C as shown in Figure 5.

The scanning electron microphotograph (SEM) of polyaniline silicotitanate and silicotitanate are represented in Figure 6 indicating the binding of the inorganic ion-exchange silicotitanate material with the organic polymer, i.e. polyaniline. It has been revealed that after binding of polyaniline with silicotitanate, the morphology has been changed.

Figure 7 shows the pH-titration curve of polyaniline silicotitanate. In this figure, the *X*-axis represents the number of millimoles of 0.01 M alkali metal hydroxide (LiOH, NaOH or KOH) passed through per gram of the prepared exchanger; and the *Y*-axis shows the pH value of the effluent passed through the column. The pH titration curve for the prepared exchanger under studied show only one inflection point indicating that the prepared polyaniline silicotitanate behaves as monofunctional. This behavior similar to polyacrylamide

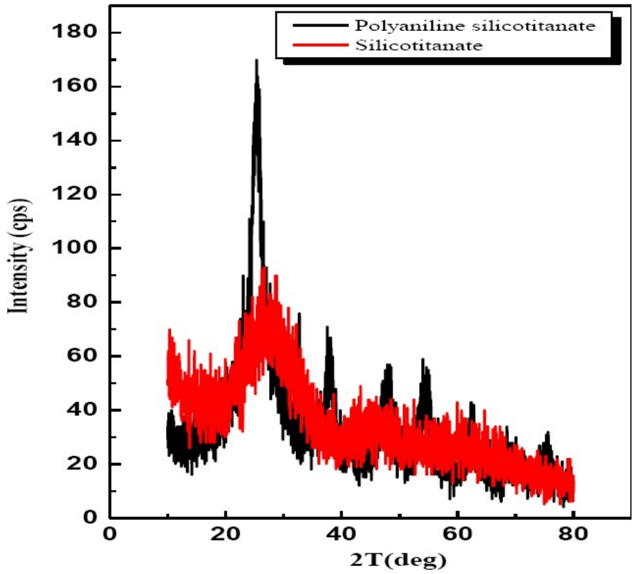


Figure 4 : X-ray diffraction patterns for the polyaniline silicotitanate and silicotitanate dried at 50°C

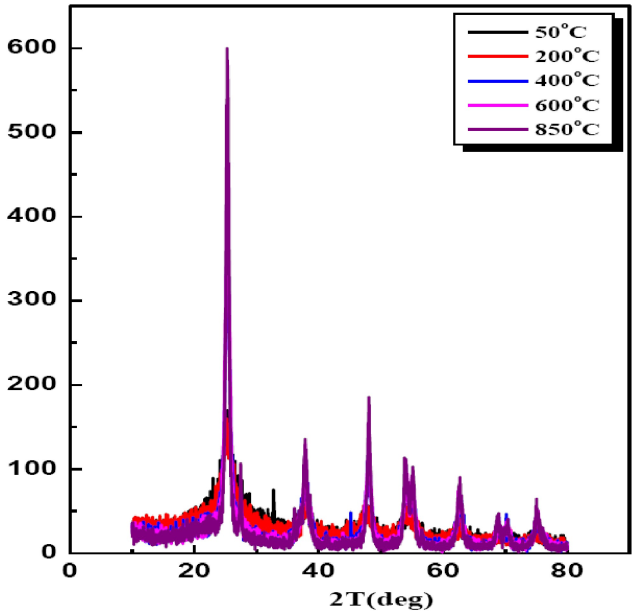


Figure 5 : X-ray diffraction patterns for the prepared polyaniline silicotitanate at different drying temperatures

Sn(IV) molybdophosphate prepared by El-Naggar et al., 2010[16], cerium (IV) molybdate prepared by Nilchi et al., 2006[7], ZrP-001 prepared by Pan et al., 2007[17] and stannic silicomolybdate prepared by Nabi and Khan, 2006[18]. Furthermore, it appears to be a strong cation-exchanger as indicated by a low pH (~3) of the solution when no $OH^{''}$ ions were added to the system and the rate of H^+–Na^+ exchange was faster than those of H^+–Li^+ and H^+–K^+ exchanges. The adsorption behavior for alkali metals on this material was observed to be in the order of Na(I) > Li(I) > K(I) in acidic and basic media.

Thermogravimetric study was also carried out on heating polyaniline silicotitanate (as prepared) up to 800^{O}C at a constant rate (~10^{O}C min^{-1}) in the air atmosphere. The TGA–DTA analysis curve Figure 8 of polyaniline silicotitanate showed weight loss of ~13.44% up to 180^{O}C, may be due to the loss of external water molecule present[19] as confirmed by the endothermic peak of the DTA curve at 95.36^{O}C. A slow weight loss of about 9.24% observed between 250 and 420°C may be due to the loss of constitution water, which forms part of the crystalline network and it is generally presented like hydroxyl groups[20] as confirmed by the endothermic peak of the DTA curve at 350^{O}C. Also, at this temperature, where the compound have been transformed to anew crystalline form; energy has to be released to perform such transformation (show the XRD figure for the prepared polyaniline silicotitanate dried at 200^{O}C). Further weight loss (~11.86%) between 580^{O}C and 630$^{æ\%}$C may be due to complete decomposition of the organic part of the material[16,21,22] as confirmed by the endothermic peak of the DTA curve at 611^{O}C. An exothermic peak appears at ~500^{O}C accompanied with mass change equals (~13.21%), which may be assigned to a phase transformation,[23].

Effect of heating at different temperature for 4 h, indicated that on heating at elevated temperature the mass, physical appearance and ion-exchange capacity of the dried hybrid cation-exchanger was changed as the temperature increased as shown in TABLE 3. It was also observed that the hybrid cation-exchanger possessed higher thermal stability as the sample maintained about 76.72% of the initial mass by heating up to 400^{O}C and maintained about 47.07% of the initial mass by heating up to 800^{O}C. However, in terms of ion-exchange capacity, this hybrid material was found stable up to 400^{O}C and it retained about 59.32% of the initial ion-exchange capacity by heating up to 400^{O}C TABLE 3. polyaniline silicotitanate possess high thermal stability compared with

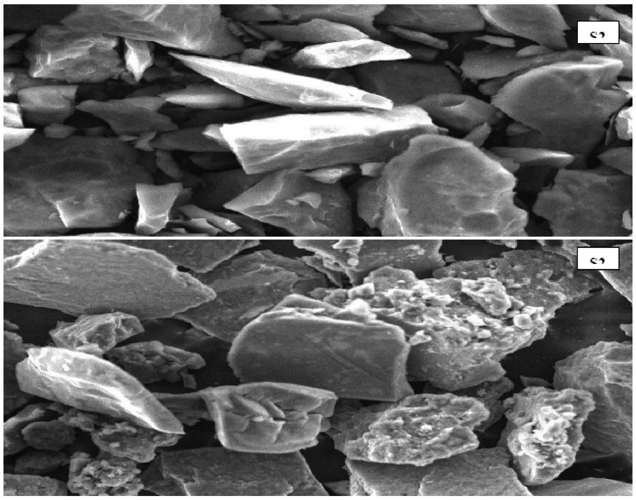


Figure 6 : Scanning electron microphotographs (SEM) of chemically prepared silicotitanate (S-1) and polyaniline silicotitanate (S-2) at the magnification of 7.00k×

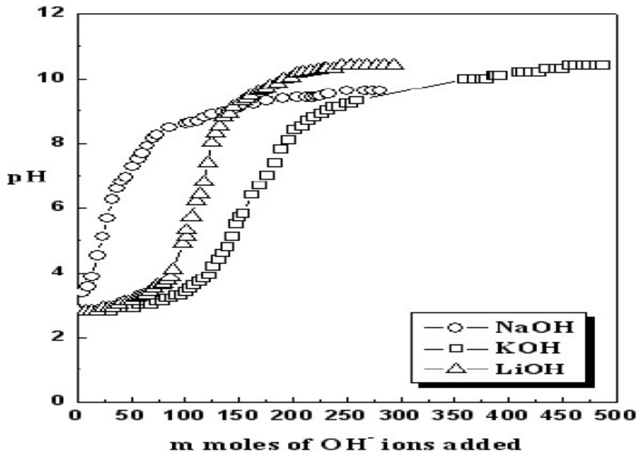


Figure 7 : pH titration curves for polyaniline silicotitanate hybrid cation exchanger with various alkali metal hydroxides

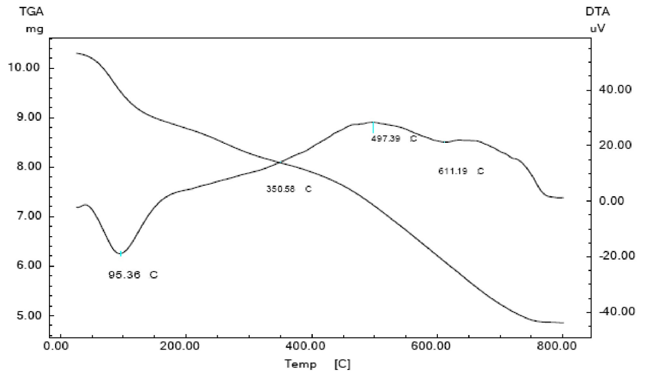


Figure 8 : Thermogravimetric analysis (TGA) curve of polyaniline silicotitanate (as-prepared)

TABLE 3 : Effect of temperature on ion-exchange capacity of polyaniline silicotitanate and silicotitanate on heating time for 4 h

Heating temperature ($^?$C)	polyaniline silicotitanate					silicotitanate			
	Appearance (color)	Weight loss (%)	Cs^+ ion-exchange capacity (m eq g?1)	capacity loss (%)	% Retention of IEC	Weight loss (%)	Cs^+ ion-exchange capacity (m eq g?1)	capacity loss (%)	% Retention of IEC
50^{o}C	dark black	-	5.31	000.00	100.00	-	0.59	000.00	100.00
200^{o}C	dark black	14.76	4.35	18.080	81.921	18.84	0.39	33.90	66.10
400^{o}C	yellowish	23.28	3.15	40.678	59.322	24.01	0.21	64.41	35.60

TABLE 4 : Chemical stability of the prepared polyaniline silicotitanate and silicotitanate samples at different acid and base concentrations

Solubility	Solvents															
	H_2O	HNO_3, M							HCl, M							
		0..5	1	2	3	4	5	6	7	0..5	1	2	3	4	5	6	7
Polyaniline SiTi	BD	0.102	0.120	0.246	0.280	0.320	0.396	0.450	CD	0.160	0.206	0.276	0.326	0.376	0.440	0.566	CD
SiTi	BD	0.150	0.171	0.302	0.332	0.351	0.420	0.481	CD	0.180	0.220	0.306	0.352	0.412	0.480	0.594	CD

BD: Below detection; CD: Complete dissolution

other composite ion exchangers, such as; polyanilin Sn(IV) arsenophosphate prepared by[24], it loses about about 93% of its ion exchange capacity on heating up to 400^{o}C, Acrylonitrile based cerium (IV) phosphate prepared by[25] which loses 93% on heating up to 400^{o}C, Nylon-6,6, Polyaniline Sn(IV) phosphate prepared by[3] which loses 60.71% on heating at the same temperature, poly-*o*-toluidine Th(IV) phosphateand prepared by (Khan et al., 2007) [26] which loses 89.48% on heating up to 400^{o}C, Zr(IV) phosphate prepared by (Inamuddin et al., 2007) [27] which loses 47.22% on heating up to 400^{o}C and Polypyrrole thorium(IV) phosphate prepared by[28] which loses 71.15% on heating up to 400^{o}C. TABLE 3 shows that, the prepared polyaniline silicotitanate possess high thermal stability compared with the inorganic silicotitanate, polyaniline silicotitanate loses about 40.68% of its ion exchange capacity on heating up to 400^{o}C, while, the inorganic silicotitanate loses about 64.41% of its ion exchange capacity on heating at the same drying temperature. Through this study, we can overcome the low thermal stability of the inorganic silicotitanate.

From TABLE 3, It was found that the ion exchange capacityies of polyaniline silicotitanate and silicotitanate for Cs^+ are decreased with increasing the heating temperatures from 50^{o}C to 400^{o}C. This may be due to the loss of free water and chemical bond water which may be act as exchangable active site[29]. This trend agrees with the ion exchange capacities of K^+ ion on stannic vanadate (sample 4)[30] and polyacrylamide Sn(IV) molybdophosphate[16] at different drying temperatures.

From TABLE 4, it was found that the prepared polyaniline silicotitanate and silicotitanate samples are stable in water and acid solutions up to 6M HNO_3 and HCl, while the samples are completely dissolved at 7M acids. Polyaniline silicotitanate and silicotitanate samples are completely dissolved in 0.1M and 1M (NaOH and KOH).

The chemical stability of the prepared polyaniline silicotitanate is higher than silicotitanate, this proves thate the prepared composite overcame the low chemical stability of inorganic silicotitanate. Polyaniline silicotitanate is more stable than polypyrrole Th(IV) phosphate prepared by[21], especially at high acid concentration (4M HCl and 4M HNO_3), polypyrrolel/ polyantimonic acid prepared by[31] especially at DMW

TABLE 5 : Ion-exchange capacity of various exchanging ions on a hybrid cation-exchanger polyaniline silicotitanate

Exchangingions	pH of the Metal solutions	Ionic Radii (Å)	Hydration energy	ion-exchange Capacity (m mol g$^-$1)
Cs^+	5.70	1.67	263	5.310
Pb^{2+}	4.35	1.20	1480	4.440
Co^{2+}	4.19	0.72	2054	3.950
Cu^{+2}	4.30	0.72	2100	3.850
Cd^{2+}	4.60	0.97	1806	3.750

and high acid concentration (4M HCl and 4M HNO_3) and polyaniline Sn(IV) tungstoarsenate prepared by[22] especially at DMW and high acid concentration (4M HCl and 4M HNO_3), while polyaniline Sn(IV) phosphate prepared by[3], polyaniline Sn(IV) arsenophosphate prepared by[24], polyacrylamide Sn(IV) molybdophosphate prepared by[16], acrylamide zirconium (IV) arsenate prepared by[32] and acrylonitrile based cerium (IV) phosphate prepared by[25].

The effect of the size and charge of the exchanging ion on the ion-exchange capacity was also observed for this hybrid material. The ion-exchange capacity of the hybrid cation-exchanger for the studied metal ions increases according to the decrease in the hydrated ionic radii and hydration energy[33-36] as evident from TABLE 5.

TABLE 6 : K_d values and separation factors (α) of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} as a function of pH on polyaniline silicotitanate

pH	K_d, (ml g^{-1})				
	Cs^+	Pb^{2+}	Co^{2+}	Cu^{2+}	Cd^{2+}
1	371.50	13.18 (28.18)	6.92 (53.68) (1.90)	7.41 (50.13) (1.78) (0.93)	16.22 (22.90) (0.81) (0.43) (0.46)
1.5	562.34	28.18 (19.95)	13.18 (42.66) (2.14)	13.18 (42.66) (2.14) (1)	18.62 (30.20) (1.51) (0.71) (0.71)
2	831.76	60.25 (13.80)	25.12 (33.11) (2.40)	23.44 (35.48) (2.57) (1.07)	22.39 (37.15) (2.69) (1.12) (1.05)
3	1862.10	295.12 (6.31)	93.32 (19.95) (3.16)	72.44 (25.70) (4.07) (1.29)	30.20 (61.66) (9.77) (3.09) (2.40)

From TABLE 5, polyaniline silicotitanate composite cation ion exchanger gives higher ion exchange capacity than other compsite and inorganic ion exchangers, e.g. (Pb^{2+} 1.74 $meqg^{-1}$, Cd^{2+} 1.418 $meqg^{-1}$, Cs^+ 1.19 $meqg^{-1}$, Co^{2+} 1.152 $meqg^{-1}$ and Cu^{2+} 1.090 $meqg^{-1}$) on polyacrylamide Sn(IV) molybdophosphate[16], (Cu^{2+} 3.510 $meqg^{-1}$ and Cd^{2+} 2.510 $meqg^{-1}$) on polyacrylamide ferric antimonite[37] and (Cs^+ 1.820 $meqg^{-1}$) on polyaniline titanotungstate[38], (Cs^+ 0.45 $meqg^{-1}$ and Co^{2+} 0.62 $meqg^{-1}$) on iron-silicate[39], (Cs^+ 0.57 $meqg^{-1}$, Cd^{+2} 0.82 $meqg^{-1}$ and Cu^{+2} 0.60 $meqg^{-1}$) on magnesosilicate[40], (Cs^+ 0.77 $meqg^{-1}$, Co^{+2} 1.00 $meqg^{-1}$ and Cu^{+2} 0.88 $meqg^{-1}$) on magnesium alumino-silicate[40], (Co^{2+} 0.073 $meqg^{-1}$) on zirconium molybedate[41], (Co^{2+} 0.23 $meqg^{-1}$) on zirconium silicate[41], (Cs^+ 0.13 $meqg^{-1}$) on ceric vanadate[42], (Cs^+ 0.59 $meqg^{-1}$ and Co^{2+} 0.31 $meqg^{-1}$) on silico titanate[43], (Co^{2+} 0.86 $meqg^{-1}$) on cerium antimonate[44,45] and (Cd^{+2} 0.79 $meqg^{-1}$ and Cu^{+2} 0.44 $meqg^{-1}$) on silico antimonite[46].

Distribution studies

The K_d was calculated by the following formula;

$$K_d = \frac{\textit{Concentration of the cation in exchanger}}{\textit{Concentration of the cation in solution}} \qquad (3)$$

When log K_d values are plotted against log [H^+], a straight line having slope – n should be obtained.

Figure 9 and "Table 6" show that, the pH dependency of K_d values of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+}. On the other hand, the linear relations between log K_d and pH were observed for Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} ions with slopes (0.567, 0.490, 0.141, 0.349 and 0.682), respectively. These slopes did not equal to the valence of the metal ions sorbed, which prove the non ideality of the exchange reaction. These findings can not be explained only in terms of electrostatic interaction between the hydrated cations and the anionic sites in the exchanger. It may therefore be considered that

TABLE 7 : K_d values of various exchanging ions on polyaniline silicotitanate

Exchanging ions	pH of the metal solutions	K_d (ml g^{-1})	Ionic radii (A°)	Hydration energy	Water content %		Metal exchanging as
					M-form	H-form	
Cs^+	3.00	1862.10	1.67	263	54.091	51.01	Hydrated
Pb^{2+}		295.12	1.20	1480	58.115		Hydrated
Co^{2+}		93.32	0.72	2054	54.800		Hydrated
Cu^{2+}		72.44	0.72	2100	52.073		Hydrated
Cd^{2+}		30.2	0.97	1806	52.078		Hydrated

the dependence of K_d for cations cannot be understood by a purely columbic interaction with the anionic sites, but also may be due to the formation of a covalent bond similar to a weakly acidic resin, such as the carboxylic acid and phosphoric acid resin, such interaction would be closely related to the ionic potential of the cations[47]. It was found that, the selectivity order of the investigated cations on polyaniline silicotitanate in the same conditions has the following sequence;

$Cs^+ > Pb^{2+} > Co^{2+} > Cu^{2+} > Cd^{+2}$

This sequence is in accordance with the hydrated ionic radii and hydration energy of the exchanged ions which take the order ($Cs^+ < Pb^{2+} < Co^{2+} < Cd^{2+}$). The ion with smaller hydrated ionic radii and hydration energy is easily exchanged and moves faster than that the ion with greater ionic radii TABLE 7.

The K_d values and separation factors ($\alpha = K_{dA}/K_{dB}$, where A and B are any neighboring pair ions) of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} ions in different pH on polyaniline silicotitanate samples are summarized in TABLE 6, it is clear that the separation factors between Cs^+ and the other metal ions are larger on polyaniline silicotitanate. It is evident from the above studies of the separation factors on polyaniline silicotitanate, some selective separation is feasible for various metal ions.

Such separation of Cs^+-Pb^{2+}, Cs^+-Co^{2+}, Cs^+-Cu^{2+} and Cs^+-Cd^{2+} may be taken on polyaniline silicotitanate at pH 1.00, 1.50, 2.00 and 3.00, and Pb^{2+}-Co^{2+}, Pb^{2+}-Cu^{2+} and Pb^{2+}-Cd^{2+} may be taken on polyaniline silicotitanate at pH 1.5, 2.00 and 3.00, but Co^{2+}-Cd^{2+} and Cu^{2+}-Cd^{2+} may be achieved on polyaniline

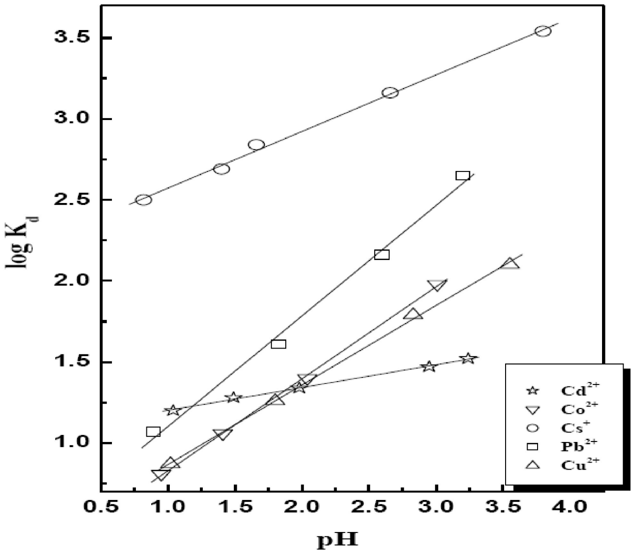


Figure 9 : log Kd of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} ions as a function of pH on polyaniline silicotitanate at 25°C

TABLE 8 : Comparison of Kd, values of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^+ and Pb^{2+} ions for various inorganic ion exchangers in DMW

Inorganic ion exchanger	K_d (ml g^{-1})				
	Cs^+	Pb^{2+}	Co^{2+}	Cu^{2+}	Cd^{2+}
Polyaniline[a] silicotitanate	3467.370	446.680	95.500	125.890	33.110
Zirconium(IV) [48] antimonoarsenate	-	-	-	-	-
Stannic [49] molybdophosphate	>5000	-	-	-	-
Cerium(IV) [44] antimonate	265	-	-	-	-
Silico titanate [50]	-	-	-	2200	1050
Silico[50] antimonate	-	-	-	1100	155
Zirconium [42] vanadate	46.9	-	-	-	-
Ceric vanadate [42]	91.1	-	-	-	-
Silico titanate [43]	38.9	-	12.02	-	-
Cerium [51] phosphate(Li)	-	-	-	1132	-
Cerium [51] phosphate(Na)	-	5000	-	245	-
Zr(IV) [10] tungstomolybdate	-	1628	1217	84	298
Thorium [52] tungstophosphate:	32	110	-	18	-
magneso-silicate[40]	58.95	-	39.43	13.66	24.68
Magnesium [40] alumino-silicate	77.46	-	98.01	34.12	73.31
Iron-silicate [39]	602.56	-		-	-

a: the material under study

TABLE 9 : Comparison of Kd, values of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^{+} and Pb^{2+} for various composite cation ion exchangers in DMW

Composite cation ion exchanger	K_d (ml g^{-1})				
	Cs^{+}	Pb^{2+}	Co^{2+}	Cu^{2+}	Cd^{2+}
Polyaniline[a] silicotitanate	3467.370	446.680	95.500	125.890	33.110
Polyacrylamide [16] Sn(IV) molybdophosphate	3090.290	20892.96	346.7300	957.1900	1096.470
Polyaniline Sn(IV) [3] phosphate	-	2900	-	-	-
Polypyrrole [53] thorium(IV) phosphate	-	900	-	-	-
Polypyrrole Th(IV)[54] phosphate	-	900	180	233	37
Polyaniline Sn(IV) [22] tungstoarsenate	-	203	300	180	2920
poly-*o*-toluidine Th(IV) phosphate [26]	-	425	20	25	25
Nylon-6,6, Zr(IV) phosphate [27]	-	1335	1375	1300	750
Polyanilin Sn(IV) [24] arsenophosphate	-	8700	3700	8100	4600
Polyanilin Sn(IV) [55] phosphate	-		400	771	1169
Poly(methyl methacrylate) Zr(IV) phosphate [4]	-	5500	750	2100	1100
Acrylonitrile based cerium (IV) phosphate [25]	-	100	233.33	100	33.33
Poly-*o*-toluidine [56] Zr(IV) phosphate	-	116	67	200	157
Cellulose acetate-Zr(IV) molybdophosphate[57]	-	410	110	98	166
Tamarind [58] iminodiacetic acid (TIDAA)	-	1.26×10^{4}	-	9.78×10^{3}	7.59×10^{3}
polyaniline [38] titanotungstate	1256.2	-	199.4	163.5	69.9

a: the material under study

silicotitanate at pH 3.00. From these results polyaniline silicotitanate can be used for recovery of hazardous metal ions (radioactive nuclides and heavy metal ions) from waste streams.

TABLES 8 and 9 show the distribution coefficient values of polyaniline silicotitanate for the studied metal ions as compared to the other ion exchange materials.

Figure 10 shows the linear relation between ln K_d and 1/T according to the Van't Hoff relation;

$$Ln\ K_d = \frac{\Delta S^o}{T} - \frac{\Delta H^o}{RT} \qquad (4)$$

Where ΔS^o is the entropy change, ΔH^o is the enthalpy change, R is the gas constant, and T is the absolute temperature.

It was found that the distribution coefficient (K_d) of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^{+} and Pb^{2+} on polyaniline silicotitanate increased with increasing temperature from 298°K to 338°K (i.e. the distribution coefficient decreased with increasing 1/T). This trend can be attributed to acceleration of some originally slow adsorption steps and creation of some new active sites on the adsorbent surfaces[59,60]. From the slopes and intercepts of these straight lines represented in Figure10, the enthalpy change (ΔH^o) and entropy change (ΔS^o) were evaluated and summarized "in Table 10".

The positive values of (ΔH^o) indicate the endothermic nature of the adsorption process, while the positive values of ΔS^o for Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^{+} and Pb^{2+} indicate the increased randomness at solid-solution interface during the adsorption of these cations on polyaniline silicotitanate.

The free energy change of specific adsorption (ΔG^o)

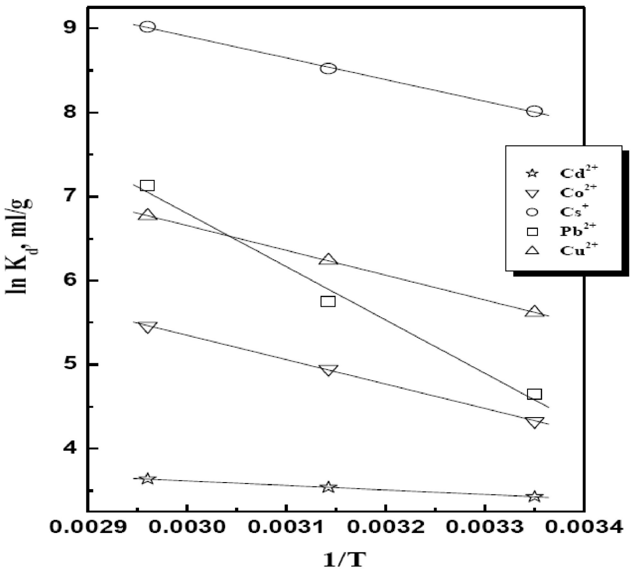


Figure 10 : Van,t Hoff plot of the adsorption of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^{+} and Pb^{2+} ions on polyaniline silicotitanate

TABLE 10 : Thermodynamic parameters for adsorption of Co^{2+}, Cu^{+2}, Cd^{2+}, Cs^{+} and Pb^{2+} ions on polyaniline silicotitanate

Metal ions	Temp., (K)	ΔG^o, ($KJ\ mol^{-1}$)	ΔH^o, ($KJ\ mol^{-1}$)	ΔS^o, ($J\ mol^{-1}\ K^{-1}$)
Cs^+	298	-19.850	20.915	136.81
	318	-22.155		135.44
	338	-25.347		136.87
Pb^{2+}	298	-13.924	23.913	126.97
	318	-16.498		127.07
	338	-19.025		127.03
Cu^{2+}	298	-11.520	50.727	208.88
	318	-15.202		207.32
	338	-20.036		209.36
Co^{2+}	298	-10.728	24.102	116.88
	318	-13.087		116.95
	338	-15.343		116.70
Cd^{2+}	298	-8.498	44.840	43.57
	318	-9.359		43.53
	338	-10.229		43.53

was calculated using the relation;

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \qquad (5)$$

and

$$\Delta G^o = - RT\ ln\ K_d \qquad (6)$$

The negative values of the free energy change (ΔG^o), Table 10, for the investigated metal ions indicate that the adsorption process is spontaneous and indicate the preferable adsorption of these cations on polyaniline silicotitanate as compared to H^+ ion. It was found that the negativity of ΔG^o increases in the order, $Cs^+ > Pb^{2+} > Cu^{2+} > Co^{2+} > Cd^{+2}$ which agrees with the selectivity sequence of the material for these cations.

Composition studies indicate the molar ratio of Si(IV), Ti(IV), C, H and N in the material as 1:4:6:13:1 which tentatively suggests the following formula:

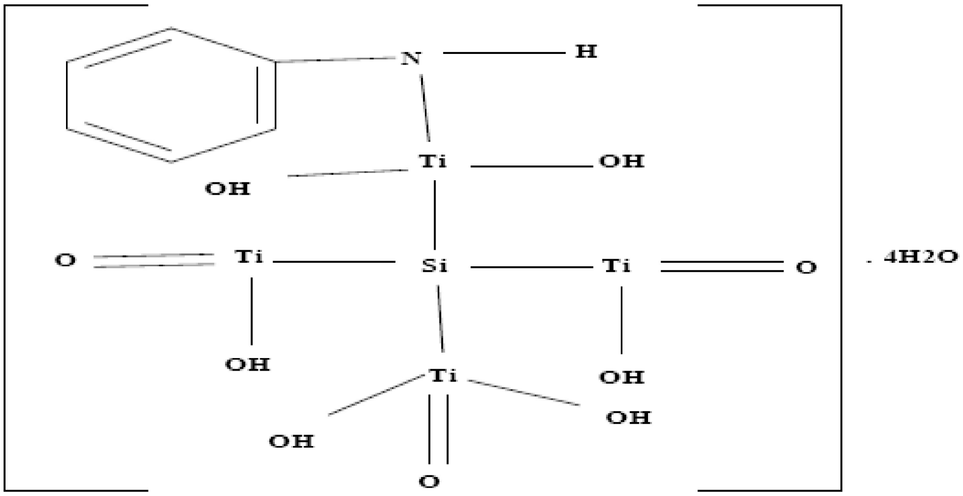
$[Ti_4O_9H_7Si + (–C_6H_5NH–)]\ nH_2O$

Assuming that only the external water molecules are lost at 95.36°C and ~ 13.40% weight loss of mass represented by TGA curve must be due to the loss of nH_2O from the above structure, the value of (n) the external water molecules can be calculated using "Alberti's equation"[61]:

$18n = X (M + 18n) / 100$

Where X is the percent weight loss (~13.40%) of the exchanger by heating up to 95.36°C and (M + 18n) is the molecular weight of the exchanger without water molecules. The calculations give ~ 4 for the external water molecule (n) per molecule of the cation –exchanger. So, a tentative molecular formula for the exchanger can be written as:

$[Ti_4O_9H_7Si + (–C_6H_5NH–)]\ 4H_2O$



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