

## Kinetics, thermodynamics and sorption characteristics of an inorganic ion exchanger, titanium phosphate, towards first row transition metal ions

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Amorphous titanium phosphate, an inorganic ion exchanger of the class of tetravalent metal acid salt, has been synthesized by sol-gel method, and characterized for elemental analysis (ICP-AES), spectral analysis (FT-IR), thermal analysis (TGA, DTA, DSC) and X-ray diffraction studies. Chemical resistivity of the material has been assessed in various media, i.e., acids, bases and organic solvents. The  $\text{Na}^+$  ion exchange capacity has been determined and effect of heating on the ion exchange capacity has been studied. The sorption/ion exchange behaviour of the exchanger towards Cu(II), Mn(II), Ni(II) and Zn(II) has been studied at different temperatures (313 K, 323 K and 333 K). Kinetic and thermodynamic parameters have been evaluated and adsorption isotherms have been studied. Based on the above studies the selectivity order is found to be: Mn(II) > Ni(II) > Cu(II) > Zn(II).

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Amongst inorganic ion exchangers, tetravalent metal acid (tma) salts, are widely studied group and have attracted attention due to their excellent thermal stability, chemical resistivity and unique selectivity towards certain metal ions<sup>1</sup>. Tma salts<sup>2,3</sup> are cation exchangers possessing the general formula  $\text{M(IV)}(\text{HXO}_4)_2 \cdot n\text{H}_2\text{O}$ , where  $\text{M(IV)} = \text{Zr, Ti, Sn, Ce, Th}$  etc. and  $\text{X} = \text{P, W, As, Mo, Sb}$ , etc. These materials possess structural hydroxyl groups, the H of the -OH being the exchangeable sites. Tma salts can be obtained as both amorphous and crystalline solids. The ion exchange properties of crystalline modifications have been studied in detail<sup>3-5</sup>. Though crystalline compounds favour a large ion exchange capacity (IEC)<sup>1</sup>, they have not found substantial use as they are produced in powder form which prevents their use in column operations<sup>1,6</sup>. Amorphous materials on the other hand can be obtained in granular form and are very suitable for column operations. However, since they are prepared by precipitation method, it does not

exhibit preparative reproducibility<sup>6</sup>. Materials prepared by sol-gel method, on the other hand, exhibit high homogeneity, high purity, low temperature processing, structural control of materials formed and materials with improved and desired properties<sup>7</sup>.

The present study reports the synthesis of granular amorphous titanium phosphate suitable for column operations, by sol-gel method. Earlier, Parida and co-workers<sup>8</sup> have reported the sorption and ion exchange properties of crystalline  $\alpha$ -titanium phosphate ( $\alpha$ -TiP) towards transition metal ions. Clearfield *et al.* have prepared a modified TiP<sup>9</sup> selective for  $\text{Cs}^{2+}$  and have carried out sorption studies of transition metal ions on  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  substituted forms of amorphous TiP<sup>1</sup>. Recently, Takahashi and co-workers<sup>10</sup> have studied selectivity of alkali metal ions and lithium isotopes towards semi-crystalline TiP. Distribution coefficient,  $K_d$ , for several metal ions have been determined and thermodynamics of exchange on amorphous<sup>11</sup> and crystalline<sup>6</sup> TiP studied by Airoldi *et al.* Literature reveals that no systematic research has been carried out on amorphous TiP to evaluate its sorption and ion exchange characteristics towards transition metal ions.

In the present study, amorphous TiP has been synthesized by sol-gel method. TiP has been characterized and its chemical resistivity assessed in various media along with its ion exchange capacity for  $\text{Na}^+$ . The sorption/ion exchange behaviour of TiP towards Cu(II), Mn(II), Ni(II) and Zn(II) has been studied at different temperatures (313 K, 323 K and 333 K), the kinetic and thermodynamic parameters have been evaluated and adsorption isotherms [Langmuir and Freundlich] have been studied and discussed.

### Experimental

#### Synthesis and characterization of titanium phosphate [TiP]

All chemicals and reagents used were of analytical grade.

To a solution of  $\text{TiCl}_4$  (0.1 M, 50 mL, prepared in 20% HCl),  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  (0.1 M, 50 mL) was added dropwise at 70°C (flow rate 1 mL min<sup>-1</sup>) with continuous stirring. On complete precipitation, the gel obtained was stirred further for 5 h. It was then kept in contact with the mother liquor overnight for ageing. It was then stirred for one hour at 70°C, then filtered

hot and washed with hot conductivity water (80°C) until complete removal of chloride ions, followed by drying at room temperature. The material was sized by sieving through 30-60 mesh ASTM and then acid treated<sup>12</sup>.

The Na<sup>+</sup> IEC of the material was determined by the column method<sup>12</sup>. The effect of heating on IEC was studied by heating 1 g portion of the material for 2 h at temperatures between 100°C-500°C at 100°C intervals in a muffle furnace and determining the Na<sup>+</sup> IEC by the column method<sup>12</sup> at room temperature.

The chemical resistivity of the material in various media-acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl), bases (NaOH and KOH) and organic solvents (ethanol, benzene and acetone) was studied by taking 500 mg of the sample in 50 mL of the particular medium and allowing it to stand for 24 h. The change in nature, weight and colour was observed.

TiP was analyzed for titanium and phosphorus by ICP-AES performed on Perkin-Elmer (model 4300 DV), ICP – AES-Spectrometer. FT-IR spectrum of TiP was obtained using KBr powder on Shimadzu (model 8400S) spectrometer. A differential and thermogravimetric analysis of TiP was performed on a SII Seiko (model TG/DTA – 32) thermal analyzer at a heating rate of 20°C min<sup>-1</sup>. DSC was recorded on a Shimadzu (model DSC – 50), at a heating rate of 10°C min<sup>-1</sup>. XRD was performed on an X-ray diffractometer (model Bruker AXS D8) using Cu - K<sub>α</sub> radiation with a nickel filter. A temperature controlled shaker bath having a temperature variation of ± 0.5°C was used for the equilibrium studies.

#### Sorption studies

Sorption of the metal ions, Cu(II), Mn(II), Ni(II) and Zn(II), using TiP was carried out in the pH range 1-9. To 100 mg of the exchanger, 10 mL of 0.002 M metal ion solution was added and pH adjusted in acidic range using dil. HNO<sub>3</sub> and in alkaline range using dil. NaOH and the mixture was shaken for 30 minutes. The supernatant liquid was used to determine the metal ion concentration by EDTA titrations<sup>13</sup>.

#### Kinetic and thermodynamic studies

TiP particles of definite mesh size (30-60 mesh ASTM) was used to evaluate various kinetic and thermodynamic parameters. The pH of the solution is adjusted to the value at which maximum sorption of respective metal ion takes place. The metal ion solution (10 mL, 0.002M) was shaken with 100 mg of the

exchanger in stoppered conical flasks at the desired temperatures (313 K, 323 K and 333 K) and at different time intervals at increments of 10 min from 10-120 min. The supernatant liquid was removed immediately after each prescribed time interval and the metal ion concentration evaluated by EDTA titrations<sup>13</sup>.

#### Adsorption isotherm studies

The metal ion solution (10 mL) of different concentrations with increments of 0.002M (0.002-0.01M) were equilibrated for a specific period of time with 100 mg of exchanger in stoppered conical flasks at desired temperatures (313 K, 323 K and 333 K). After equilibrium, the supernatant liquid was removed and the metal ion concentration evaluated by EDTA titrations<sup>13</sup>.

#### Results and discussion

TiP was obtained as white granules and elemental analysis by ICP-AES shows the titanium:phosphorous ratio to be 1:1. FTIR spectra of TiP shows broad band in the region ~3400 cm<sup>-1</sup> attributed to symmetric and asymmetric -OH stretching, while the band at ~1614 cm<sup>-1</sup> is attributed to H-O-H bending. A band in the region ~ 975.91 cm<sup>-1</sup> is attributed to P=O stretching. This indicates the presence of structural hydroxyl groups in TiP, the H of the OH being the cation exchange sites. This fact is more evident from the IEC values that have been evaluated. The Na<sup>+</sup> IEC, determined by column method<sup>12</sup> is found to be 3.09 meq. g<sup>-1</sup>. The effect of heating on IEC was studied in the temperature range of 100–500°C at intervals of 100°C and found to be 3.60, 3.40, 1.99, 1.33 and 1.02 meq. g<sup>-1</sup> respectively. The initial increase in the IEC value at 100°C can be attributed to loss of moisture adhered to it, thereby increasing the active exchanger content for same weight of material taken for IEC determination. The decrease in IEC values beyond 300°C is attributed to the condensation of the structural hydroxyl groups. TG-DTA of TiP exhibits two regions of weight loss. The first weight loss within the temperature range ~30 – 154°C is attributed to loss of moisture/hydrated water, while the second weight loss observed in the range ~154 – 493°C is attributed to the condensation of structural hydroxyl groups. DSC curve of TiP exhibits only one endothermic peak at ~135°C which confirms the presence of structural water molecules. However, beyond this temperature no peaks are observed, indicating absence of any phase change in the material upon thermal treatment. Based

on the elemental analysis (ICP-AES) and thermal analysis (TGA) data, TiP has been formulated as  $\text{TiO}(\text{OH})(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$  using the Alberti Torracca formula<sup>14</sup>.

The X-ray of TiP does not exhibit any peak, indicating amorphous nature. TiP is stable in acid medium, maximum tolerable limits being 18 *N*  $\text{H}_2\text{SO}_4$ , 16 *N*  $\text{HNO}_3$  and 11.3 *N*  $\text{HCl}$ . It is also stable in organic solvents like ethanol, benzene and acetone. It is, however, not very stable in basic media, the maximum tolerable limits being 5 *N*  $\text{NaOH}$  and 0.5 *N*  $\text{KOH}$ .

The maximum sorption is observed at *pH* 3 in the case of  $\text{Cu}(\text{II})$  and  $\text{Zn}(\text{II})$ , % uptake being 37.26 and 16.80 respectively. In the case of  $\text{Mn}(\text{II})$  and  $\text{Ni}(\text{II})$ , maximum sorption is observed at *pH* 7, % uptake being 59.96 and 54.83 respectively. Beyond *pH* 5 (for  $\text{Cu}(\text{II})$  and  $\text{Zn}(\text{II})$ ) and *pH* 7 [for  $\text{Mn}(\text{II})$  and  $\text{Ni}(\text{II})$ ] precipitation is observed.

Effect of contact time, and reaction temperature on % uptake of the metal ions under study has been presented in Fig. 1(a-d). It is observed that sorption increases with increase in contact time and reaches a maximum value after which randomness is observed. Increase in % uptake can be attributed to two different sorption processes, namely, a fast ion exchange followed by chemisorption<sup>15</sup>. The % uptake also increases with increase in temperature, which indicates the uptake to be an ion exchange mechanism. However, randomness is observed in the case of  $\text{Zn}(\text{II})$ . Percentage uptake has been calculated using formula,  $[(C_o - C_e)/C_o] \times 100$ , where  $C_o$  = initial concentration of metal ion in  $\text{mg. L}^{-1}$  and  $C_e$  = final concentration of metal ion in  $\text{mg. L}^{-1}$ .

Generally, both Langmuir and Freundlich isotherms are used for explaining the adsorption of metal ions on materials. Freundlich adsorption isotherm is represented by  $\log(X/m) = \log K + (1/n)\log C_e$  where  $X$  is the amount of adsorbate,  $m$  is the amount of adsorbent,  $C_e$  is the equilibrium concentration of the adsorbate in the solution and  $K$  as well as  $1/n$  are Freundlich constants. If the adsorption process follows Freundlich pattern, the plot of  $\log(X/m)$  versus  $\log C_e$  is a straight line. Further, from this plot,  $1/n$  and  $K$  are calculated from the slope and intercept, respectively.

Langmuir adsorption isotherm is represented by,  $C_e/(X/m) = 1/(bV_m) + C_e/(V_m)$ , where  $C_e$ ,  $X$  and

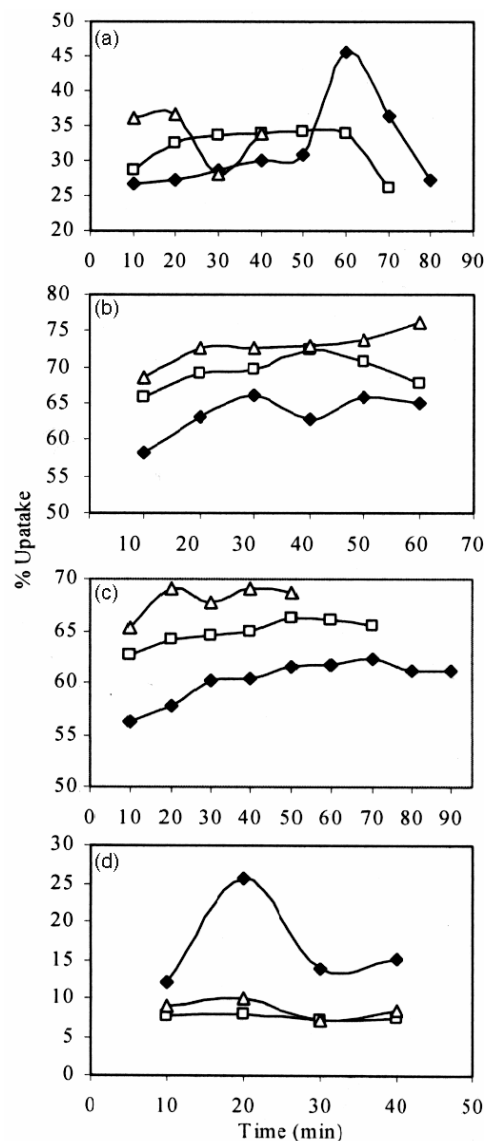


Fig. 1 – The % uptake of metal ion on TiP [a,  $\text{Cu}(\text{II})$  at *pH* 3; b,  $\text{Mn}(\text{II})$  at *pH* 7; c,  $\text{Ni}(\text{II})$  at *pH* 7; d,  $\text{Zn}(\text{II})$  at *pH* 3; —◆— 313 K; —▲— 323 K; —□— 333K].

$m$  have the same meaning as described in Freundlich isotherm;  $b$  is a constant that represents adsorption bond energy and  $V_m$ , a constant that represents maximum adsorption capacity corresponding to a monolayer covering the surface of the adsorbent. If the adsorption process follows the Langmuir pattern, plot of  $C_e/(X/m)$  versus  $C_e$  is linear. Further, from the above plot,  $b$  and  $V_m$  are calculated from the slope and intercept.

Langmuir and Freundlich constants ( $b$ ,  $V_m$ ,  $K$ ,  $1/n$  and coefficient of determination  $R^2$ ) calculated from these isotherms are presented in Table 1. Higher value

Table 1 — Langmuir and Freundlich constants for Cu(II), Mn(II), Ni(II) and Zn(II) towards TiP

Metal ion	Temp. (K)	Langmuir parameters			Freundlich parameters		
		$R^2$	$b$ (dm <sup>3</sup> .mg <sup>-1</sup> )	$V_m$ (mg.g <sup>-1</sup> )	$R^2$	$K$	1/n
Copper(II)	313	0.98	0.0022	18.4843	0.95	2.62	0.8542
	323	0.83	0.0039	15.7729	0.97	4.55	0.4891
	333	0.99	0.0043	15.1976	0.99	5.22	0.4311
Manganese(II)	313	0.99	0.0070	28.6533	0.99	10.93	0.5184
	323	0.96	0.0074	34.4828	0.99	13.87	0.5006
	333	0.96	0.0074	41.1523	0.99	16.40	0.5368
Nickel(II)	313	0.99	0.0088	23.3645	0.96	10.44	0.5738
	323	0.96	0.0584	13.3511	0.64	10.34	0.2930
	333	0.85	0.1071	14.8148	0.67	10.00	0.3190
Zinc(II)	313	0.40	-0.0002	-9.5970	0.99	0.69	0.9899
	323	0.93	0.0012	5.7504	0.99	1.50	0.5118
	333	0.66	0.0004	12.4224	0.98	1.12	0.9451

of  $K$  in the case of Mn(II) and Ni(II) indicates high rate of adsorbate removal. Based on  $R^2$  values, Cu(II), Mn(II) and Zn(II) follow the Freundlich isotherm, while Ni(II) follows the Langmuir isotherm. Variation in  $R^2$  values (Langmuir) in the case of Ni(II) is attributed to the fact that the surface adsorption is not a monolayer with single site. Two or more sites with different affinities may be involved in metal ion sorption<sup>16</sup>. Based on  $V_m$  (maximum adsorption capacity) values, the metal ion selectivity on TiP follows the order, Mn(II) > Ni(II) > Cu(II) > Zn(II) at 313 K. Since sorption has been carried out in aqueous medium, the most important factor responsible for selectivity order is the size of the hydrated ionic radius. Smaller the size of the cation, more heavily it is hydrated and therefore there is more difficulty in exchange. Other factors being temperature,  $pK_h$  ( $K_h$  = hydrolysis constant) and ionic potential, etc. A change in hydration of a metal cation plays a dominant role in determining the selectivity of the exchanger. The overall effect is a result of contribution of the above-mentioned factors. Depending on the predominant factor, the affinity of metal ions towards TiP varies in each case.

Ion exchange of metal ions from the liquid phase on to the solid phase can be considered as a reversible reaction with two phases. Therefore, a simple first order kinetic model is used to establish the rate of reaction<sup>17</sup>.

The first order kinetic equation is,  $Ln[1-U(t)] = -k't$ , where  $U(t)$  is fractional attainment of equilibrium and  $k'$  is the overall rate constant.

Table 2 — Kinetic parameters of the sorption of Cu(II), Mn(II), Ni(II), and Zn(II) towards TiP

Metal ion	Temp. (K)	$k'$ (min <sup>-1</sup> )	$K_c$	$k_1$ (min <sup>-1</sup> )	$k_2$ (min <sup>-1</sup> )
Copper(II)	313	0.0906	0.4451	0.0279	0.0627
	323	0.1105	0.5171	0.0377	0.0728
	333	0.4116	0.5919	0.1530	0.2586
Nickel(II)	313	0.0761	1.6514	0.0474	0.0287
	323	0.0984	1.9554	0.0651	0.0333
	333	0.2906	2.2222	0.2004	0.0901
Manganese(II)	313	0.1544	1.9580	0.1022	0.0522
	323	0.1120	2.6014	0.0808	0.0311
	333	0.0695	3.1800	0.0529	0.0166
Zinc(II)	313	0.0642	0.3433	0.0164	0.0478
	323	0.3296	0.0856	0.0260	0.3036
	333	0.2288	0.1120	0.0230	0.2058

Further,  $k' = k_1(1 + 1/K_c) = k_1 + k_2$  where  $K_c$  is the equilibrium constant and  $k_1$  and  $k_2$  are the first order forward and reverse rate constants, respectively.  $U(t) = C_o - C_t / C_o - C_e$ , where  $C_o$ ,  $C_t$  and  $C_e$  (all in mol L<sup>-1</sup>) are concentrations of metal ions in solution initially, at time  $t$ , and at equilibrium respectively.

From the results presented in Table 2, it is seen that  $K_c$ , equilibrium constant increases as temperature increases for all metal ions except Zn(II), which indicates that the sorption of metal ion on TiP is an ion exchange mechanism.  $k_1$  and  $k_2$  are rate constants related to sorption and desorption respectively. For Mn(II) and Ni(II),  $k_1 > k_2$  indicates favourable sorption of these metal ions at all temperatures, while in the case of Zn(II) and Cu(II), at all temperatures,  $k_2 > k_1$  indicating an unfavourable process. Higher values of  $k_2$  compared to  $k_1$  have also been observed by other

Table 3 — Thermodynamic parameters for the sorption of Cu(II), Mn(II), Ni(II) and Zn(II) towards TiP

Metal Ion	Temp. (K)	$K_c$	$\Delta G^o$ (kJmol <sup>-1</sup> )	$\Delta H^o$ (kJmol <sup>-1</sup> )	$\Delta S^o$ (kJmol <sup>-1</sup> K <sup>-1</sup> )
Copper(II)	313	0.4451	2.11	12.61	0.082
	323	0.5171	1.77	12.04	0.064
	333	0.5919	1.45	-	-
Nickel(II)	313	1.6514	3.22	14.20	0.035
	323	1.9554	-1.35	11.44	0.039
	333	2.2222	-1.86	-	-
Manganese (II)	313	1.9580	-4.67	23.87	0.081
	323	2.6014	-6.57	17.96	0.064
	333	3.1800	-9.45	-	-
Zinc(II)	313	0.3433	2.78	-86.40	-2.77
	323	0.0856	6.60	24.07	0.054
	333	0.1120	6.06	-	-

workers<sup>17</sup>. Further, the distribution coefficient,  $K_d$ , values calculated by us (unpublished work) for the metal ions, Ni(II) (300.04 mL g<sup>-1</sup>), Mn(II) (385.58 mL g<sup>-1</sup>), Cu(II) (162.97 mL g<sup>-1</sup>) and Zn(II) (37.62 mL g<sup>-1</sup>) respectively support the observation made in the present study.

In order to explain the effect of temperature on the adsorption, thermodynamic parameters, standard free energy  $\Delta G^o$ , standard enthalpy  $\Delta H^o$  and standard entropy  $\Delta S^o$  were determined using the following equations:

$$\Delta G^o = -RT \ln K_c,$$

$\Delta H^o = R[T_1T_2/T_1 - T_2] \ln(k_2/k_1)$  and  $\Delta S^o = (\Delta H^o - \Delta G^o)/T$ , where  $R$  is the gas constant,  $K_c$ ,  $k_1$  and  $k_2$  are equilibrium constants at the temperature  $T$ ,  $T_1$  and  $T_2$ , respectively. The values of the equilibrium constants were calculated from,  $k = C_{Be}/C_{Ae}$ , where  $C_{Be}$  and  $C_{Ae}$  are the equilibrium concentrations of metal ions on the sorbent and in solution, respectively<sup>17</sup>.

The results of thermodynamic studies have been presented in Table 3. In the case of Mn(II), the negative  $\Delta G^o$  values confirm feasibility, spontaneous nature of the adsorption process and attainment of more stable energy level after ion exchange. Such results have been also previously reported for trivalent cations<sup>18</sup>. Similarly, in the case of Ni(II), negative  $\Delta G^o$  values are observed, at all temperatures. However, at 40°C, positive value of  $\Delta G^o$  is observed, indicating unfavourable sorption of Ni(II) on TiP. The positive  $\Delta G^o$  values in the case of Cu(II) and Zn(II) reveals lower preference of these metal ions towards TiP and non-spontaneous nature of the process. In general, it has been earlier observed that  $\Delta G^o$  up to -20 kJ. mol<sup>-1</sup>

is consistent with electrostatic interaction between sorption sites and the metal ion<sup>16</sup>.

Positive value of  $\Delta H^o$  shows endothermic nature of Cu(II), Zn(II), Ni(II) and Mn(II) sorption process. Probably, some energy must be supplied to the cation as it leaves the hydration sphere to undergo ion exchange with the ion exchange material TiP<sup>19</sup>. In the case of Zn(II), negative value of  $\Delta H^o$  at lower temperature shows an exothermic nature of the process. It is observed that  $\Delta H^o$  value within the range (8.4-12.6 kJ. mol<sup>-1</sup>) indicate enthalpy change of adsorption for ion exchange<sup>20</sup>. Thus, the sorption process is ion exchange in the case of Cu(II) with  $\Delta H^o$  values 12.60 and 12.03 kJ mol<sup>-1</sup>. For other metal ions, Zn(II), Ni(II) and Mn(II),  $\Delta H^o > 12.6$  kJ mol<sup>-1</sup> indicates presence of another mechanism besides ion exchange<sup>20</sup> for the sorption of metal ions towards TiP.

Entropy reflects the changes in hydration sphere of exchanging cation which occurs during the ion exchange process. In the present study all metal ions exhibit positive  $\Delta S^o$  value which indicates the higher randomness of ion near the adsorbent surface. In the case of Cu(II) and Mn(II), decrease of  $\Delta S^o$  with temperature indicates higher uptake of ions. Negative  $\Delta S^o$  values in the case of Zn(II) has been observed at lower temperatures which indicates the less randomness of ion on adsorbent surface due to ion exchange<sup>19</sup>. A negative entropy change in ion exchange process is possible which has been observed earlier in zeolite systems<sup>21</sup>. The decrease in  $\Delta S^o$  values of the system indicates higher uptake of the ions. A significant negative contribution of  $\Delta S^o$  results from the replacement of cation of high  $S^o$  in the external aqueous phase by one of a lower  $S^o$  in the exchanger phase<sup>22</sup>.

The present study shows that the amorphous inorganic ion exchanger TiP, possesses good chemical resistivity, thermal stability and exhibits a higher IEC value as compared to materials reported earlier<sup>6,10</sup>. The adsorption isotherms reveal preferential uptake of Mn(II) and Ni(II) as compared to that of Cu(II) and Zn(II). Differential selectivity of TiP towards these metal ions can play a significant role in achieving various binary separations.

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