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Studies on kinetics, thermodynamics and sorption characteristics of an inorganic ion exchanger—Titanium phosphate towards Pb(II), Bi(III) and Th(IV)

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Abstract

Amorphous titanium phosphate (TiP), an inorganic ion exchanger of the class of tetravalent metal acid (tma) salts has been synthesized by sol–gel method. TiP has been characterized for elemental analysis (ICP–AES), spectral analysis (FT–IR), thermal analysis (TGA and DSC) and X-ray diffraction studies. Chemical resistivity of the material has been assessed in various media–acids, bases and organic solvents. The Na^+ ion exchange capacity (IEC) has been determined and the effect of heating on IEC studied. The sorption/ion exchange behaviour of TiP towards Pb(II), Bi(III) and Th(IV) has been studied at different temperatures (313, 323 and 333 K). Kinetic parameters (overall rate constant k', equilibrium constant K_c, forward and reverse reaction rate constant k_1 and k_2, respectively) and thermodynamic parameters (standard free energy ΔG^0, standard enthalpy ΔH^0, and standard entropy ΔS^0) have been evaluated and adsorption (Langmuir and Fruendlich) isotherms have been studied. Based on the above studies, the selectivity order is found to be Pb(II) > Th(IV) > Bi(III) at 333 K.

Keywords: Titanium phosphate, inorganic ion exchanger, tetravalent metal acid salts, kinetics and thermodynamics of ion exchange, adsorption isotherms.

1. Introduction

Industrial and mining wastewaters are important sources of pollution of heavy metals [1]. A number of technologies have been developed over the years for the efficient removal of toxic/heavy metal from wastewater [2]. The most important of these methods include filtration, chemical precipitation, ion exchange, adsorption, electrodeposition and membrane systems. All these approaches have their inherent advantages and limitations. Although filtration and chemical precipitation are low cost and effective in removing large quantities of metal ions quickly, neither is capable of removing at trace levels. Adsorption is also ineffective at very low concentrations. Ion exchange can be used to reduce metal concentrations to the region of parts per million.

Amongst the synthetic inorganic ion exchangers, tetravalent metal acid (tma) salts [3–7] are gaining importance due to their excellent thermal stability and chemical resistivity. They are cation exchangers, possessing the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$, where M(IV) = Zr, Ti, Sn, Ce, Th, etc. and X = P, W, As, Mo, Sb, etc. These materials possess

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structural hydroxyl groups, the H of the –OH being the exchangeable sites. They possess an appreciable ion exchange capacity as well as high selectivity for certain metal ions. Tma salts can be obtained in both amorphous and crystalline forms. Though structures of crystalline materials are well known, they have not been found to be suitable in column operations as they are obtained in powder forms. Amorphous materials on the other hand can be obtained in granular form, very suitable for column operations [8–12]. Tma salts being synthesized by sol–gel routes, materials with varying water content, composition, ion exchange capacity and crystallinity can be obtained by varying parameters such as stoichiometry and concentration of the reagents used, temperature at which they are mixed, rate of addition, mode of mixing, pH, etc. Ion exchange materials with higher selectivities are continuously being investigated [13].

Titanium phosphate with varying degrees of crystallinity has been synthesized, characterized and its ion exchange behaviour studied [14–19]. The removal and recovery of toxic/heavy metals is an area of current interest [20]. In the present endeavour, a new phase of amorphous titanium phosphate (TiP), an inorganic ion exchanger of the class of tma salt, has been synthesized by sol–gel method. It has been characterized for elemental analysis (ICP–AES), spectral analysis (FT–IR), thermal analysis (TGA and DSC) and X-ray diffraction studies. Chemical resistivity of the material has been assessed in various media—acids, bases and organic solvents. The Na^+ ion exchange capacity (IEC) has been determined and the effect of heating on IEC studied. In the absence of detailed knowledge of the structure of the system, thermodynamic and kinetic studies provide information relating to the mechanism and feasibility of ion exchange process occurring on the surface as well as the ability to predict correlation among experimental results. The sorption/ion exchange behaviour of TiP towards Pb (II), Bi (III) and Th (IV) has been studied at different temperatures (313, 323 and 333 K). Kinetic parameters (overall rate constant k', equilibrium constant K_c, forward and reverse reaction rate constant k_1 and k_2, respectively) and thermodynamic parameters (standard free-energy ΔG^0, standard enthalpy ΔH^0, and standard entropy ΔS^0) have been evaluated and adsorption (Langmuir and Fruendlich) isotherms studied.

2. Experimental

All chemicals and reagents used were of analytical grade.

2.1. *Synthesis of TiP*

To a solution of $TiCl_4$ (0.1 M, 50 ml, prepared in 20% HCl), 0.1 M $NaH_2PO_4 \cdot 2H_2O$ (0.1 M, 50 mL) was added dropwise at 70°C (flow rate 1 ml min^{-1}) with continuous stirring. On complete precipitation, the gel obtained was stirred for further 5 h. It was then kept in contact with mother liquor overnight for ageing. It was further stirred for one hour at 70°C and then filtered hot and washed with hot conductivity water till the complete removal of chloride ions, followed by drying at room temperature. The material was then broken down to the desired particle size (30–60 mesh ASTM) by grinding and sieving, and converted to acid form by treating 5 gm of the material and with 50 ml of 1 M HNO_3 for 30 min with occasional shaking. The sample was then separated from acid by decantation and washed with conductivity water for removal of adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature. It was used for all studies. The Na^+ ion exchange capacity of the material was determined by column method [21].

2.2. *Calcination studies*

The effect of heating on ion exchange capacity was studied by heating 1 gm portion of the material for 2 h at temperatures between 100 and 500°C with 100°C intervals in a muffle furnace and determining the Na^+ ion exchange capacity by the column method [21] at room temperature.

2.3. *Chemical resistivity*

The chemical resistivity of the material in various media—acids (H_2SO_4, HNO_3, 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 color, nature and weight was observed.

2.4. *Instrumentation*

TiP has been analyzed for titanium and phosphorus by ICP–AES. FT–IR spectrum of TiP was obtained using KBr powder on Shimadzu (Model 8400S). TGA of TiP was performed on a SII Seiko (Model TG/DTA-32) thermal analyzer at a heating rate of 20°C/min. DSC was recorded on a Shimadzu DSC-50, at a heating rate of 10°C/min. XRD was performed on an X-ray diffractometer (Brucker AXS D8) using CuKα radiation with a nickel filter. A temperature controlled shaker bath having a temperature variation of ± 0.5°C was used for the equilibrium studies.

2.5. *Sorption studies*

2.5.1. *Effect of pH*

Sorption of metal ions Pb(II), Bi(III) and Th(IV) using TiP was carried out in the pH range 1–9. To 100 mg of exchanger, TiP, 10 mL of 0.002 M metal ion solution was added and pH adjusted in acidic range using dilute HNO_3 and in alkaline range using dilute NaOH and the mixture was shaken for 30 min. The supernatant liquid was used to determine the metal ion concentration by EDTA titrations [22].

2.5.2. *Kinetic and thermodynamic studies*

TiP particles of definite mesh size [30–60 mesh (ASTM)] were used to evaluate various kinetic and thermodynamic parameters. pH of the solution was adjusted to the value at which maximum sorption of respective metal ion takes place. Metal ion solution (10 ml of 0.002 M), was shaken with 100 mg of exchanger in stoppered conical flasks at the desired temperatures (313, 323 and 333 K) and at different time intervals with increments of 10 min (10, 20, 30, … 120). The supernatant liquid was removed immediately after each prescribed time interval and the metal concentration evaluated by EDTA titrations [22]. Results obtained from this study are utilized to evaluate kinetic parameters ($U(t)$, k', k_1, k_2 and K_c) and thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) using the equations which are given in the results and discussion section.

2.5.3. *Adsorption isotherm studies*

For adsorption isotherm studies, 10 mL metal ion solution of different concentrations with increment of 0.002M (0.002, 0.004, … 0.01 M) was equilibrated for a specific period of time with 100 mg of exchanger in stoppered conical flasks at desired temperatures (313, 323 and 333 K). The supernatant liquid was removed immediately and the metal concentration evaluated by EDTA titrations [22].

3. Results and discussion

3.1. *Characterization*

TiP was obtained as white granules. Elemental analysis by ICP–AES shows titanium to phosphorous ratio to be 1 : 1. FTIR spectra (Fig. 1) of TiP shows broad band in the region ~ 3400 cm^{-1} attributed to symmetric and asymmetric –OH stretching, while band at ~ 1614 cm^{-1} is attributed to H–O–H bending. A band in the region ~ 975.91 cm^{-1} is attributed to P = O stretching. This indicates the presence of structural hydroxyl protons in TiP. This fact is more evident from the IEC values that have been evaluated. The Na^+ ion exchange capacity, determined by column method [21], is found to be 3.09 meq g^{-1}. The effect of heating on IEC was studied in the temperature range of 100–500°C with 100°C intervals and found to be 3.60, 3.40, 1.99, 1.33 and 1.02 meq g^{-1}, respectively. The initial increase in the IEC value at 100°C could be attributed to loss of moisture adhered to it, thereby increasing the active exchanger content for same weight of material taken for IEC determination. Decrease in IEC beyond 300°C could be attributed to the condensation of structural hydroxyl groups. TGA of TiP (Fig. 2) exhibits two regions of weight loss. The first weight loss within the temperature range 30–154°C is attributed to the 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 (Fig. 3) exhibits an endothermic peak at ~ 135°C which confirms the presence of external water molecules. However, beyond this temperature no peaks are observed indicating the absence

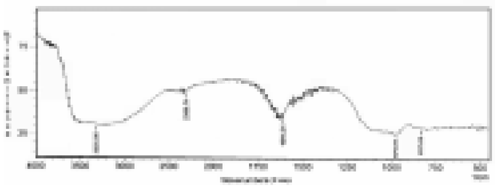

FIG. 1. FTIR of TiP.

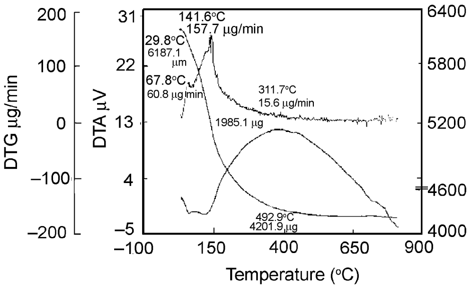

FIG. 2. TG/DTA Curves of TiP.

Table I
% Uptake at various pH

pH	% Uptake of metal ion		
	Pb(II)	Bi(III)	Th(IV)
1	19.55	27.18	15.39
2	37.13	44.11	24.78
3	53.72	53.65	46.29
4	57.11		

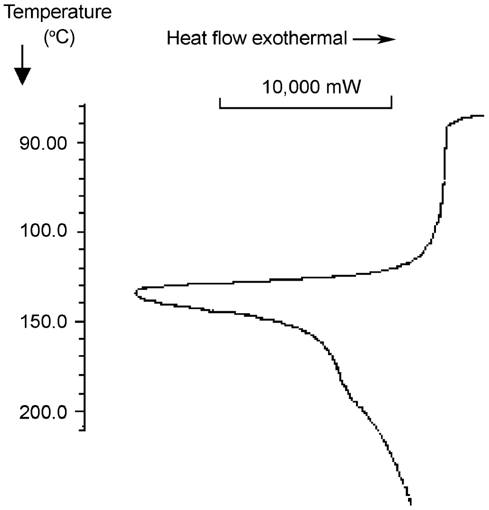

FIG. 3. DSC Curve of TiP.

of any phase change in the material upon thermal treatment. The absence of sharp peak in X-ray diffractogram of TiP indicates amorphous nature of the material. Based on titanium and phosphorus content determined by ICP–AES and thermal analysis (TGA) data, TiP has been formulated as TiO (OH) $(H_2PO_4)\cdot H_2O$ using the Alberti Torracca formula [23].

TiP is found to be stable in acid medium, maximum tolerable limits being (18 N H_2SO_4, 16 N HNO_3, 11.3 N HCl) and also stable in organic solvent media (ethanol, benzene and acetone) but not so stable in base medium, maximum tolerable limits being 5 N NaOH and 0.5 N KOH).

3.2. *Sorption studies*

3.2.1. *Effect of pH*

Effect of pH on sorption of metal ions, is shown in Table I. At pH values less than ~3, very less sorption has been observed for all metal ions. The lack of sorption at low pH could be attributed to the hydrogen ions competing with the metal ions for sorption/ exchange sites.

3.2.2. *Effect of contact time and temperature on the sorption/ion exchange*

Effect of contact time, reaction temperature and % uptake of metal ion is presented in Table II. It is observed that sorption increases gradually with increase in contact time and reaches a maximum value after which randomness is observed. Increase in % uptake could be attributed to two different sorption processes, namely, a fast ion exchange followed by chemisorption [24]. It is observed that uptake of Pb(II), Bi(III) and Th(IV) increases with increase in temperature, which indicates the uptake to be an ion exchange mechanism. Percentage uptake has been calculated using formula, [(Co–Ce)/Co] × 100, where Co is the ini-

Table II
Effect of contact time and temperature on the sorption/ion exchange of Pb(II), Bi(III) Th(IV) towards TiP

Time (min)	Percentage uptake of Pb(II) (K)			Percentage uptake of Bi(III) (K)			Percentage uptake of Th(IV) (K)		
	313	323	333	313	323	333	313	323	333
10	58.82	58.37	64.00	52.12	60.80	75.90	34.25	42.55	48.41
20	61.87	64.32	68.00	66.21	76.77	82.79	43.25	49.46	68.15
30	66.88	68.06	72.40	72.20	78.22	89.31	46.25	57.44	73.88
40	68.63	68.94	74.60	80.88	88.75		51.75	61.97	77.31
50	71.24	71.15	79.00	81.27			56.75	70.48	89.17
60	72.76	71.81	79.60	81.85			56.75	71.80	91.08
70	73.09	74.45	80.80	83.40			58.00	74.20	92.36
80	74.51	77.53	81.00	86.68			62.75	78.72	93.63
90	75.38	80.18	82.60	88.03			59.25	80.59	93.63
100	78.00		83.00				65.62	88.00	96.81
110			83.20				68.37	90.46	
120			84.80				70.50	90.77	
130			85.00				72.75		
140			86.00				74.50		
150			87.60				77.50		
160							78.75		
170							79.25		
180							85.12		

tial concentration of metal ion in mg/l and Ce, the final concentration of metal ion in mg/l. The time taken for attainment of equilibrium is Th(IV) 180 min > Pb(II) 100 min > Bi(III) 90 min. This could be explained on the basis of ionic radii. Ionic radii of Th(IV), Bi(III) and Pb(II) are 0.95, 1.20 and 1.26 Å, respectively [25]. Smaller the size of cation greater is the hydration. Therefore, Th(IV) having higher hydrated ionic radius will require longer time for attaining the exchange equilibrium as compared to Pb(II) and Bi(III) with not much difference in their hydrated ionic radius.

3.2.3. *Adsorption isotherms*

Generally, both Langmuir and Freundlich isotherms are used for explaining the adsorption of metal ions on materials. Freundlich adsorption isotherm is represented by,

$$\log(X/m) = \log K + (1/n)\log \mathrm{Ce}, \tag{1}$$

where X is the amount of adsorbate, m, the amount of adsorbent, Ce, 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, plot of $\log(X/m)$ vs log Ce is a straight line. Further, from the above plot, $1/n$ and K are calculated from the slope and intercept, respectively.

Langmuir adsorption isotherm is represented by,

$$\mathrm{Ce}/(X/m) = 1/(bV_m) + \mathrm{Ce}/V_m, \tag{2}$$

where Ce, X and 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

Table III
Langmuir and Freundlich's parameters of Pb(II), Bi(III) and Th(IV) towards TiP

Metal ion	Temperature (K)	Langmuir parameters			Fruendlich parameters		
		R^2	$b$dm^3 g^{-1}	V_m mg g^{-1}	R^2	K	$1/n$
Lead(II)	313	0.9914	0.0058	64.5161	0.9940	29.85	0.2531
	323	0.9996	0.0095	65.7894	0.9747	41.79	0.1488
	333	0.9953	0.0070	86.2069	1.0000	10.00	1.0000
Bismuth(III)	313	0.9456	-0.0097	37.5940	0.0325	55.71	–0.0512
	323	0.7897	0.0081	55.8659	0.0004	51.40	–0.0041
	333	0.7997	0.0128	64.1026	0.0567	53.70	0.0483
Thorium(IV)	313	0.9835	0.0061	78.1250	0.9928	33.94	0.2788
	323	0.9877	0.0065	82.6446	0.9987	37.58	0.2854
	333	0.9938	0.0129	80.6452	0.9571	48.33	0.2954

adsorption capacity corresponding to a monolayer covering the surface of the adsorbent. If the adsorption process follows the Langmuir pattern, plot of Ce/(X/m) vs Ce is a straight line. 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 III.

Based on R^2 values, Bi(III) and Th(IV) follow the Langmuir pattern, while Pb(II) follows the Freundlich's pattern. Variation in R^2 values 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 [26]. Based on V_m (maximum adsorption capacity) values, the metal ion selectivity towards TiP follows the order, Pb(II) > Th(IV) > Bi(III) at 333 K.

3.2.4. *Kinetic studies*

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 [27].

The first-order kinetic equation is

$$\mathrm{Ln}[1-U(t)] = -k't, \tag{3}$$

where $U(t)$ is fractional attainment of equilibrium and k' is the overall rate constant.

Further,

$$k' = k_1(1 + 1/K_c) = k_1 + k_2, \tag{4}$$

where K_c is the equilibrium constant and k_1 and k_2 are the first-order forward and reverse rate constants, respectively.

$$U(t) = \mathrm{Co–Ct/Co–Ce}, \tag{5}$$

where Co, Ct and Ce (all in mole/L) are concentrations of metal ion in solution initially, at time t, and at equilibrium, respectively.

Table IV
Kinetic parameters for the sorption of Pb(II), Bi(III) and Th(IV) towards Ti P

Metal ion	Temperature (K)	k' (min^{-1})	K_c	k_1 (min^{-1})	k_2 (min^{-1})
Lead(II)	313	0.0377	3.5445	0.0294	0.0083
	323	0.0427	4.0444	0.0347	0.0085
	333	0.0286	7.0645	0.0250	0.0035
Bismuth(III)	313	0.0522	7.3548	0.0460	0.0062
	323	0.0685	7.3064	0.0603	0.0081
	333	0.1308	8.3559	0.1170	0.0140
Thorium(IV)	313	0.0152	6.0175	0.0130	0.0023
	323	0.0532	11.533.	0.0489	0.0042
	333	0.0379	30.400	0.0367	0.0012

From Table IV, it is observed that K_c, equilibrium constant, increases with increase in temperature for all metal ions, which indicates the sorption of metal ions on TiP to be an ion exchange mechanism. k_1 and k_2 are rate constants related to sorption and desorption, respectively. For all metal ions $k_1 > k_2$ indicates favorable sorption of these metal ions at all temperatures. Greater time taken for attainment of equilibrium for Th(IV) as compared to Pb(II) and Bi(III) (Table II) discussed earlier in Section 3.2.2 can also be explained on the basis of k_1, the rate constant for the forward exchange reaction. Higher the values of k_1, faster will be the attainment of equilibrium in lesser time. From Table IV the order of k_1 is Th(IV) < Pb(II) < Bi(III), i.e. the time taken for exchange equilibrium for Th(IV) (180 min) is higher compared to Pb(II) (100 min) and Bi(III) (90 min).

3.2.5. *Thermodynamic parameters*

In order to explain the effect of temperature on the adsorption, thermodynamic parameters, standard free energy change ΔG^0, standard enthalpy change ΔH^0, and standard entropy change, ΔS^0 were determined using the following equations:

$$\Delta G^0 = -RT \ln K_c, \tag{6}$$

$$\Delta H^0 = R[T_1 T_2 / T_1 - T_2] \ln(k_2/k_1) \tag{7}$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T, \tag{8}$$

where R is the gas constant, K_c, k_1 and k_2 are equilibrium constants at the temperatures T, T_1 and T_2, respectively. Numerical values of the equilibrium constants were calculated from:

$$k = C_{\text{Be}}/C_{\text{Ae}}, \tag{9}$$

where C_{Be} and C_{Ae} are the equilibrium concentrations of metal ions on the sorbent and in solution, respectively [27].

From Table V, it is observed that ΔG^0 values are more negative for Th(IV) compared to Bi(III) and Pb(II). Negative ΔG^0 values indicate feasibility and spontaneous nature of the sorption process and attainment of a more stable energy level after ion exchange of metal ions. ΔG^0 depends on several factors such as temperature, heat consumed and released for removal of H^+ and intake of the incoming cation in terms of hydration and dehydration as

Table V
Thermodynamic parameters for the sorption of Pb(II), Bi(III) and Th(IV) towards TiP

Metal ion	Temperature (K)	K_c	ΔG^0 (KJ/mole)	ΔH^0 (KJ/mole)	ΔS^0 (KJ/mole K)
Lead(II)	313	3.5445	–3.292	110.89	0.046
	323	4.0444	–3.752	49.88	0.166
	333	7.0645	–5.412		
Bismuth(III)	313	7.3548	–5.192	5.87	0.035
	323	7.8871	–5.546	5.16	0.033
	333	8.3559	–5.877		
Thorium(IV)	313	6.0175	–4.670	54.68	0.189
	323	11.533	–6.566	86.67	0.289
	333	30.400	–9.453		

well as the size of the hydrated ionic radii of the cation. In the present study, the ion exchanger being used is amorphous in nature. It is therefore expected that all exchange sites may not be energetically equivalent. The incoming cation or the exchanging cation would first occupy the most favourable sites, which require little or no dehydration energy for exchange. As exchange proceeds, the sites become progressively less favourable. This causes greater dehydration at the expense of more energy. The overall ΔG^0 value is a result from the contribution of the above-mentioned factors. Depending on the predominant factor, the ΔG^0 values vary in each case [28]. Further, the observed values of ΔG^0 up to –20 kJ mol^{-1} are consistent with electrostatic interaction between sorption sites and the metal ion. This fact is also observed by other workers [26].

Positive values of ΔH^0 show endothermic nature of the sorption/exchange 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 [29].

The entropy reflects changes in hydration sphere of exchanging cation which occurs during the ion exchange process. In the present study, all metal ions exhibit positive ΔS^0 values which indicates the higher randomness of ion near the adsorbent surface due to ion exchange [29].

4. Conclusion

Amorphous inorganic ion exchanger TiP possesses good ion exchange capacity, chemical resistivity and thermal stability, which are characteristics of a good ion exchange material. Kinetics and thermodynamics of exchange as well as adsorption isotherms for the metal ions studied reveal good sorption for Th(IV) compared to Pb(II) and Bi(III) towards TiP, which further indicates good separation characteristics of the metal ions, concerned in the study.

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