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Application of zirconium phosphonate—a novel hybrid material as an ion exchanger

Brijesh Shah, Uma Chudasama*

Applied Chemistry Department, Faculty of Technology & Engineering, The M. S. University of Baroda, Vadodara, Gujarat 390 001, India
Tel. 0265 2434188 Extn. 212; Fax: ± 91 265 2423898; email: uvcres@gmail.com

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ABSTRACT

In the present endeavour, zirconium amino tris(methylenephosphonic acid) (ZrATMP)—a novel hybrid ion exchange material of the class of tetravalent metal acid (TMA) salts has been synthesized by sol gel method. Physico-chemical and instrumental methods of analysis [Elemental analysis (ICP-AES, CHN analysis), FTIR, TGA, XRD and SEM] have been used to characterize the material. Cation exchange capacity (CEC) has been determined and the distribution behaviour of metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ce^{3+} and Th^{4+} in aqueous and various electrolyte media/concentrations determined and confirmed with breakthrough capacity values.

Keywords: Tetravalent metal acid salt; metal phosphonate; zirconium phosphonate; hybrid ion exchanger; cation exchanger; metal aminophosphonate

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1. Introduction

Recently, interest has been generated in the preparation of some organic based inorganic ion exchangers, where there is a promise of developing new materials, giving rise to new, composite and interesting properties [1–3]. Tetravalent metal acid (TMA) salts are inorganic ion exchangers, in which the protons present in the structural hydroxyl groups can be exchanged for several cations and thus they behave as cation exchangers [4,5]. Anchoring of organic units on the backbone of TMA salts is of particular interest, since they have a rigid inorganic back bone and flexibility of the organic groupings. M(IV) phosphates where M(IV) = Zr or Ti of the class of TMA salts have been studied as ion exchangers for metal separations [6,7]. In the tetrahedral moiety of phosphoric acid, $PO(OH)_3$, if H or OH is replaced by R (where R = alkyl or aryl possessing ionogenic groups such as –COOH, –OH, $–SO_3H$ etc.), phosphonic acid is obtained, which when treated with tetravalent metals such as Zr, Ti, Sn, Th, Ce etc. give rise to novel metal phosphonates [1,8–12].

Aminophosphonic acids possess effectiveness of donor groups in the binding of tetravalent metal ions, and have received considerable attention due to the diverse binding abilities [13,14]. High surface area, porous titanium phosphonate materials for multiphase adsorption of metal ions [15,16] and with large ion exchange capacity [17] have been synthesized using 1-hydoxyethylidene-1,1-diphosphonic acid. A porous titanium phosphonate with large adsorption capacity for heavy metal ions using amino tris(methylenephosphonic acid) has been synthesized by a hydrothermal process [18]. Titania phosphonate porous hybrid materials using claw type amino phosphonic acid ethylenediamine tetrakis(methylenephosphonic acid) [19] and diethylenetriamine pentakis(methylenephosphonic acid) [20] have been synthesized and used for heavy metal ion adsorption. From our laboratory we have

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*Corresponding author.

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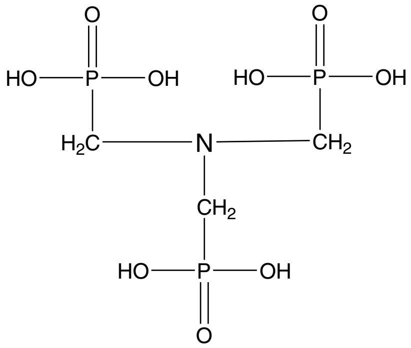

Fig. 1. Structure of ATMP.

reported the synthesis of zirconium [21] and titanium [22] based phosphonates using diethylenetriamine pentakis(methylenephosphonic acid). These materials have been used as cation exchangers for metal ion separations [21,22].

In the present endeavour, ZrATMP (where, ATMP = amino tris(methylenephosphonic acid), a novel hybrid metal phosphonate, has been synthesized by sol-gel route. Further, the possible use of ZrATMP as a cation exchanger has been explored. ATMP (Fig. 1) possessing six structural hydroxyl groups, compared to phosphoric acid (H_3PO_4) which has three structural hydroxyl groups was used with the intention of obtaining higher cation exchange capacity in terms of pendant hydroxyl groups in the resulting metal phosphonate [5]. ZrATMP has been characterized for elemental analysis (ICP-AES,CHN analysis), TGA, FTIR, X-ray diffraction and SEM. Physical and ion exchange characteristics as well as chemical stability of the material in various acids, bases and organic solvent media have also been studied.

The selectivity order of metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ce^{3+} and Th^{4+}) towards ZrATMP has been obtained, based on evaluation of distribution coefficient (K_d), studied in aqueous and various electrolyte media/concentrations. The trend in selectivity order is further confirmed by breakthrough capacity (BTC).

2. Experimental

2.1. Materials and methods

Zirconium oxychloride ($ZrOCl_2.8H_2O$) was procured from Loba Chemicals. 50% (~1.18 M) ATMP (Amino trismethylene phosphonic acid) with density = 1.3 g/cm^3 and molecular weight = 299.04 g (CAS No.6419-19-8) was obtained from Hydrochem India Pvt. Ltd. Appropriate/required concentration of ATMP was prepared from 50% (~1.18 M) ATMP solution for synthesis of ZrATMP. All other chemicals and reagents used were of Analytical grade. Double-distilled water was used for all the studies. For equilibrium time determination studies, an electric temperature controlled shaker bath having a temperature variation ±0.5°C was used.

2.2. Synthesis of ZrATMP

ZrATMP was synthesized by sol-gel method, the main objective being to obtain a material with high ion exchange capacity, varying several parameters to achieve this objective. Several sets of materials were prepared varying conditions in each case using IEC as the indicative tool in all cases. The optimized parameters for synthesis of ZrATMP has been presented in Table 1. We describe herewith the synthesis of ZrATMP at optimized condition. An aqueous solution of ATMP (0.2 M, 50 ml) was added drop wise to a solution of $ZrOCl_2$ (0.1 M, 50 ml) at room temperature(~25°C) with continuous stirring. A gelatinous precipitate was obtained, and solution along with precipitate further stirred for 1 h. The resulting gelatinous precipitate was allowed to stand for 1 h, then filtered, washed with double distilled water till 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 the acid form by taking 5 g of the material and treating it with 50 ml of 1 M HNO_3 for 30 min with occasional shaking. The material was then separated from acid by decantation and washed with double distilled water for removal of adhering acid. This process (acid treatment) was repeated at least five times. After the final washing, the material was dried at room temperature. This material was used for all studies.

2.3. Physical and ion exchange characteristics

Physical characteristics such as appearance, percentage moisture content, apparent density, true density and ion exchange characteristics such as void volume fraction, concentration of fixed ionogenic groups and volume capacity of ZrATMP were studied according to literature methods [23–25] and presented in Table 2.

2.3.1. Cation exchange capacity (CEC) and effect of calcination on CEC

The Na^+ ion exchange capacity (CEC) of ZrATMP was determined by the column method by optimizing volume and concentration of sodium acetate solution [26]. In the first case, a fixed volume (250 ml) of sodium acetate solution of varying concentration (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 *M*) was passed through a glass column [30 cm × 1 cm (internal diameter)] containing 0.5 g of the exchanger, maintaining a flow rate of 0.5 ml·min^{-1}. The effluent (containing H^+ ions eluted out) was titrated against 0.1 M NaOH solution. The optimum concentration of eluant is thus determined. In the second case the

Table 1
Parameters optimized for synthesis of ZrATMP

Parameters	No	Mole ratio Metal: anion (M)	Volume ratio Metal: anion (ml)	Temperature (°C)	Stirring time (h)	Aging time (h)	IEC (meq/g)
Concentration	1	0.1:0.1	50:50	RT	1	1	3.19
	2	0.1:0.2	50:50	RT	1	1	3.61
	3	0.2: 0.1	50:50	RT	1	1	2.68
Volume	4	0.1:0.2	50:100	RT	1	1	2.46
	5	0.1: 0.2	100:50	RT	1	1	2.24
Temperature	6	0.1:0.2	50:50	70	1	1	3.19
Aging time	7	0.1:0.2	50:50	RT	1	15	2.99
	8	0.1:0.2	50:50	RT	1	3	2.84
Stirring time	9	0.1:0.2	50:50	RT	2	1	2.61
	10	0.1:0.2	50:50	RT	3	1	2.94
pH	11	0.1:0.2	50:50	RT	1	1	3.09
Mode of addition	12	0.1:0.2	50:50	RT	1	1	3.12[a]

[a] Change in mode of addition-$ZrOCl_2$ to ATMP.
RT = room temperature (25°C).

Table 2
Physical and ion exchange characteristics

Characteristics	Observation
Appearance	White hard granules
Particle size(range)	250–590 µm
% Moisture content	6.49%
True density	1.78 $g \cdot ml^{-1}$
Apparent density	0.35 $g \cdot ml^{-1}$
Void volume fraction	0.79
Concentration of fixed ionogenic groups	6.30 $mmol \cdot g^{-1}$
Volume capacity of resin	1.26 $meq \cdot mL^{-1}$
Nature of exchanger	Weak cation exchanger
CEC (RT)	3.61 $meq \cdot g^{-1}$
100°C	2.93 $meq \cdot g^{-1}$
200°C	2.11 $meq \cdot g^{-1}$
300°C	2.26 $meq \cdot g^{-1}$
400°C	2.73 $meq \cdot g^{-1}$
500°C	1.76 $meq \cdot g^{-1}$
Chemical stability	Maximum tolerable limits
i. Acids	18 N H_2SO_4, 16.3 N HNO_3, 11.3 N HCl
ii. Bases	0.01 NaOH, 0.01 N KOH
iii. Organic solvents	Ethanol, benzene, acetone, acetic acid
Pore area	59 $m^2 \cdot g^{-1}$ (microporous)
Pore size distribution	1.42 $ml \cdot g^{-1}$

eluant of optimum concentration was used and 10 ml fractions passed through the column keeping a flow rate 0.5 ml min^{-1}. This experiment was conducted to find out the minimum volume necessary for complete elution of the H^+ ions, which reflects the efficiency of the column. Using these optimized parameters, the Na^+ CEC was determined, using the formula aV/W, where a is molarity and V the amount of alkali used during titration, and W is the weight of the exchanger.

The effect of calcination on CEC (Table 2) was studied by calcining several 1 g portions of the material for 2 h in the temperature range 100–500°C at 100°C intervals in a muffle furnace, cooling them to room temperature, and determining the Na^+ CEC by the column method as described above.

2.3.2. pH titration curve

"pH titration curve" or the "potentiometric curve", a plot of pH versus number of milliequivalents of OH^- ions, gives an idea regarding the acidic nature, weak or strong of exchanger [23]. For cation exchangers, the acid sites can be titrated against an alkali hydroxide (used for neutralization) and a salt solution of same alkali metal (used as a supporting electrolyte). In the present case, 0.5 g of ZrATMP was placed in NaCl (0.1 M, 100 ml) solution. This solution mixture was titrated against NaOH (0.1 M) solution. After addition of every 0.5 ml of titrant, sufficient time was provided for establishment of equilibrium, till the pH is constant. A pH titration curve was obtained by plotting pH versus volume of NaOH (Fig. 2).

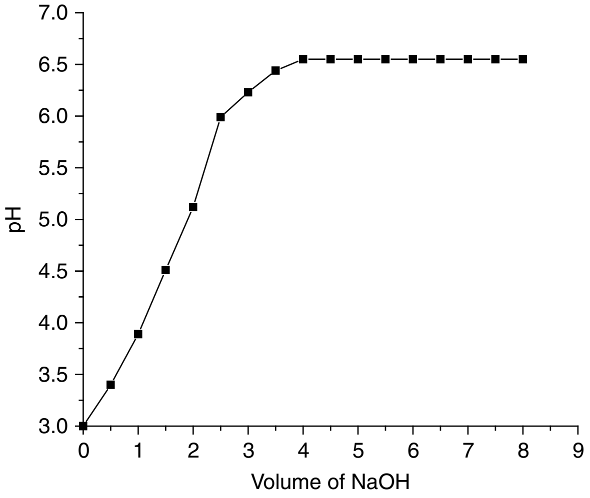

Fig. 2. pH titration curve.

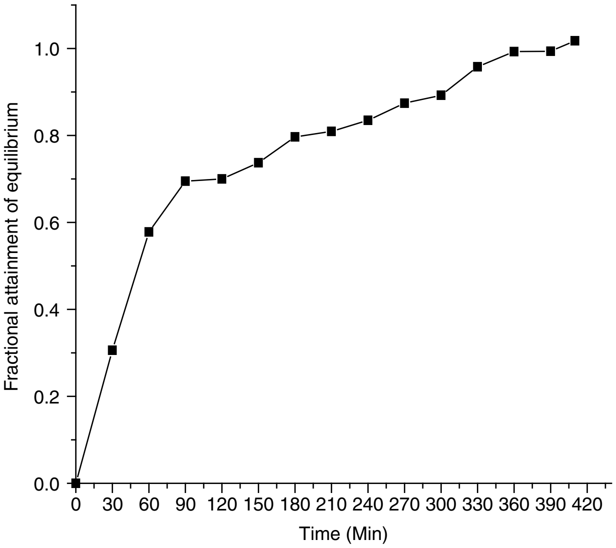

Fig. 3. Fractional attainment of equilibrium $U(\tau)$ vs. time (t).

2.4. Chemical stability

The material synthesized is an ion exchange material. When in use, ion exchangers are subjected to a variety of physical and chemical effects that cause a loss of capacity, physical weakening of the exchange material and partial solubilization. A study of the chemical resistivity/stability of materials in mineral acids, bases and organic solvent media is both useful and important while using the material for various applications in varied environments.

The chemical stability of ZrATMP in various media -acids (HCl, H_2SO_4 and HNO_3), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid) was studied by taking 0.5 g of ZrATMP in 50 ml of the particular medium and allowed to stand for 24 h. The change in colour, nature, weight, solubility, metal washout and particle size etc. was observed. To confirm the solubility of exchanger in a particular medium, supernatant liquid was checked qualitatively for respective elements of exchanger and also by ICP-AES. Maximum tolerable limits evaluated in a particular medium have been presented in Table 2.

2.5. Distribution studies

2.5.1. Equilibrium time determination

20 ml metal ion solution was shaken with 200 mg of exchanger ZrATMP (in $H^{\pm}$ form) in stoppered conical flasks at 30°C for different time intervals (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0, 7.0 h). The supernatant liquid was removed after every prescribed time interval, and the metal ion concentration evaluated by EDTA titration. A plot of the fractional attainment of equilibrium $U(\tau)$ versus time (t) gives an idea about maximum equilibrium time (Fig. 3).

2.5.2. Evaluation of distribution coefficient (K_d)

Distribution coefficient (K_d) is a measure of the fractional uptake of metal ions in solution, competing for H^+ ions, in case of a cation exchange material. Almost, all ion exchange reactions being reversible, at equilibrium, the favoured direction of an exchange reaction is determined by the relative affinity of the ion exchanger for the ions entering into the exchanger matrix. The distribution studies for metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions), Cd^{2+}, Hg^{2+}, Pb^{2+} (heavy metal ions), Ce^{3+} and Th^{4+} (f-block elements) were carried out by batch method. 0.1 g of the exchanger ZrATMP was equilibrated with 20 ml of 0.001 M metal ion solution for 24 h at room temperature. The metal ion concentration before and after sorption was determined by EDTA titration. Distribution coefficient (K_d) was evaluated using the expression, $K_d = [(I - F)/F] \times V/W$ (ml·g^{-1}), where, I = total amount of the metal ion in the solution initially; F = total amount of the metal ion left in the solution after equilibrium; V = volume of the solution; W = weight of the exchanger.

Distribution studies were carried out in both aqueous and various electrolyte media like NH_4NO_3, HNO_3, $HClO_4$ and CH_3COOH of 0.02 M and 0.2 M concentration. Results have been presented in Table 3a.

K_d was also evaluated varying temperatures (30–60°C with 10°C intervals). 20 ml, 0.002 M metal ion solution was equilibrated with 0.2 g of exchanger in stoppered conical flasks at a particular temperature for 6 h (maximum equilibrium time). The supernatant liquid was removed in each case after 6 h and the metal ion concentration evaluated by EDTA titration. From these experiments equilibrium values have also been determined. Results have been presented in Table 3b.

Table 3a
Distribution coefficients (K_d) (ml·g^{-1}) in aqueous and various electrolyte media/concentration and breakthrough capacity (BTC) (mmol·g^{-1})

Metal ion	Ionic radius (A°)	BTC	K_d values in aqueous and various electrolyte media/concentration								
			Aqueous media	NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH	
				0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M
Co^{2+}	0.72	0.24 ± 0.01	600.0 ± 0.02	514.2 ± 0.05	154.8 ± 0.02	371.4 ± 0.05	59.7 ± 0.03	489.6 ± 0.05	59.7 ± 0.03	976.4 ± 0.01	466.6 ± 0.03
Ni^{2+}	0.72	0.40 ± 0.02	1550.0 ± 0.02	850.0 ± 0.03	325.0 ± 0.03	436.3 ± 0.05	14.1 ± 0.01	367.5 ± 0.05	44.1 ± 0.02	2425.0 ± 0.05	1300.0 ± 0.02
Cu^{2+}	0.74	0.64 ± 0.04	CS	3100.0 ± 0.01	1450.0 ± 0.03	1600.0 ± 0.02	104.6 ± 0.01	1384.0 ± 0.02	124.5 ± 0.03	CS	CS
Zn^{2+}	0.74	0.20 ± 0.01	584.6 ± 0.03	4171.4 ± 0.01	1330.0 ± 0.05	1715.5 ± 0.04	177.7 ± 0.02	1840.0 ± 0.03	187.5 ± 0.01	4900.0 ± 0.02	1984.5 ± 0.03
Cd^{2+}	0.97	0.28 ± 0.01	1037.5 ± 0.01	842.1 ± 0.05	592.2 ± 0.05	1450.1 ± 0.02	533.0 ± 0.02	460.2 ± 0.03	438.0 ± 0.04	742.8 ± 0.05	240.0 ± 0.02
Hg^{2+}	1.44	0.09 ± 0.03	56.4 ± 0.05	312.2 ± 0.03	61.8 ± 0.01	69.8 ± 0.03	211.3 ± 0.02	239.5 ± 0.03	312.9 ± 0.05	157.3 ± 0.04	65.0 ± 0.02
Pb^{2+}	1.10	0.37 ± 0.01	1261.5 ± 0.03	1126.6 ± 0.02	486.2 ± 0.01	1242.2 ± 0.04	1101.5 ± 0.04	1330.8 ± 0.03	847.0 ± 0.03	2287.2 ± 0.02	1790.0 ± 0.03
Ce^{3+}	1.10	0.43 ± 0.05	2000.0 ± 0.04	2628.5 ± 0.05	1450.0 ± 0.01	4750.0 ± 0.03	1450.0 ± 0.05	3110.0 ± 0.02	1037.5 ± 0.05	CS	6400.0 ± 0.02
Th^{4+}	0.96	0.10 ± 0.01	114.7 ± 0.02	100.0 ± 0.01	37.0 ± 0.04	440.0 ± 0.03	95.3 ± 0.02	348.5 ± 0.04	86.5 ± 0.02	462.0 ± 0.03	114.7 ± 0.03

CS = complete sorption.

Table 3b
Distribution coefficients (K_d) (ml·g^{-1}) and Equilibrium values (meq. g^{-1}) for metal ions varying temperature

Metal ions	30°C		40°C		50°C		60 °C	
	K_d	EV	K_d	EV	K_d	EV	K_d	EV
Co^{2+}	26.6 ± 0.02	0.39 ± 0.05	40.4 ± 0.03	0.59 ± 0.02	53.5 ± 0.03	0.72 ± 0.03	75.2 ± 0.02	0.91 ± 0.05
Ni^{2+}	42.0 ± 0.05	0.45 ± 0.05	52.2 ± 0.01	0.56 ± 0.03	60.0 ± 0.04	0.86 ± 0.05	98.0 ± 0.03	1.02 ± 0.03
Cu^{2+}	100.4 ± 0.01	0.49 ± 0.04	159.7 ± 0.04	0.76 ± 0.01	199.4 ± 0.03	0.86 ± 0.04	283.7 ± 0.02	0.94 ± 0.01
Zn^{2+}	44.4 ± 0.03	0.42 ± 0.02	62.9 ± 0.03	0.52 ± 0.01	96.7 ± 0.04	0.67 ± 0.05	100.7 ± 0.03	0.74 ± 0.01
Cd^{2+}	31.9 ± 0.03	0.32 ± 0.05	88.7 ± 0.02	0.56 ± 0.05	121.9 ± 0.02	0.76 ± 0.02	142.6 ± 0.02	0.89 ± 0.02
Hg^{2+}	227.7 ± 0.02	0.91 ± 0.05	233.3 ± 0.04	0.99 ± 0.03	245.5 ± 0.03	1.08 ± 0.02	272.2 ± 0.03	1.10 ± 0.03
Pb^{2+}	12.5 ± 0.03	0.77 ± 0.02	19.4 ± 0.02	0.88 ± 0.02	34.8 ± 0.01	0.92 ± 0.03	50.4 ± 0.05	1.04 ± 0.04
Ce^{3+}	31.2 ± 0.04	0.67 ± 0.05	138.0 ± 0.03	0.76 ± 0.03	165.2 ± 0.02	0.89 ± 0.02	208.2 ± 0.02	1.26 ± 0.05
Th^{4+}	63.9 ± 0.02	0.63 ± 0.01	79.3 ± 0.02	0.87 ± 0.02	82.1 ± 0.03	0.96 ± 0.01	91.2 ± 0.01	0.99 ± 0.03

EV = Equilibrium value.

2.5.3. Breakthrough capacity (BTC)

0.5 g of the ion exchanger, Zr-ATMP, was taken in a glass column [30 cm × 1 cm (internal diameter)] and washed thoroughly with deionized water and flow rate adjusted to 0.5 ml·min^{-1}. 5 ml fractions of each individual metal ion (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ce^{3+} and Th^{4+}) of 0.001 M concentration was passed through the column and effluent collected, till the metal ion concentration was same in feed and effluent. A breakthrough curve was obtained by plotting the ratio C_e/C_0 against the effluent volume, where C_0 and C_e are the concentrations of the initial solution and effluent, respectively. BTC is calculated using formula [12], $(C_0V(10\%))/W$, where C_0 is concentration of metal ion in mol·l^{-1}, V (10%) is the volume of metal ion solution passed through column when exit concentration reaches 10% of the initial concentration in ml and W is the weight of the exchanger in g.

2.6. Instrumental methods of characterization

Elemental analysis ICP-AES for Zr-ATMP was performed on Labtam, 8440 Plasmalab, while carbon, hydrogen and nitrogen contents were analyzed on a CHN analyzer (Perkin Elmer-2400). FTIR spectra was obtained using KBr pellet on a Shimadzu (model 8400S). TGA was performed on a thermal analyzer Shimadzu (model TGA-50) at a heating rate of 10°C/min. X-ray diffractogram was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-K$_\alpha$ radiation with nickel filter. SEM of the material was obtained on Jeol JSM-5610-SLV scanning electron microscope.

3. Results and discussion

3.1. Characterization of ZrATMP

Physical and ion exchange characteristics of ZrATMP have been presented in Table 2. ZrATMP is obtained as white hard granules. Pore size indicates material to be microporous in nature. In Zr-ATMP, elemental analysis performed by ICP-AES shows Zr = 18.8% and P = 26.6%. CHN analysis shows C = 8.03%, H = 3.45% and N = 2.96%. Based on ICP-AES and CHN data, ZrATMP has been formulated as $(ZrO)(C_3H_{12}NP_3O_9)_{0.9} \cdot 2H_2O$ based on earlier studies on metal phosphonates [16,20,22].

The Na^+ ion exchange capacity (CEC) in meq.g^{-1} evaluated by column method at room temperature is found to be 3.61 meq·g^{-1} (using 190 ml, 0.5 M of sodium acetate solution). pH titration curve shows that ZrATMP is a weak cation exchanger. It is observed that, the curve exhibits an almost constant pH 6.55 from volume 3.5 to 8.0 ml. At volume 8.5 ml of 0.1N NaOH the material starts dissolving and dissolves completely at 9 ml of 0.1N NaOH. A study on the chemical stability of ZrATMP shows that it is stable in acid and organic solvent media. It is however not so stable in base medium. The maximum tolerable limits are presented in Table 2. Zr-ATMP is the rigid framework. No transmetalation or Zr washout is observed during ion exchange studies, conforming chemical stability of the material.

The FTIR spectrum of ZrATMP (Fig. 4) exhibits broad band in the region ~3413 cm^{-1} which is attributed to symmetric and asymmetric O–H stretching vibrations due to residual water and presence of structural hydroxyl groups, H^+ of the –OH being cation exchange sites. These sites are also referred to as defective P–OH groups [5]. A sharp medium band at ~1,625 cm^{-1} is attributed to aquo H–O–H bending [27]. The broad band at ~1,035 cm^{-1} is attributed to Zr–O–P framework vibrations [18,20]. The band at ~1,438 cm^{-1} is due to overlapped C – H bending of – CH_2 groups, P – C stretching vibrations and presence of tertiary amine [20]. Slade et al. [28] attribute the band at ~1,400 cm^{-1} to be due to $\delta_{P\text{–}OH}$ stretching vibrations referred to as defective P–OH groups responsible for cation exchange capacity.

Using TGA thermogram presented in Fig. 5, the percentage weight loss has been calculated for every 50°C intervals and presented in Table 4. It is observed that percentage weight loss decreases with increase in calcination temperature in general. ~10% weight loss upto 100°C is attributed to loss of moisture and hydrated water, ~3.3% weight loss in temperature range 100–200°C is attributed to the beginning of condensation of structural hydroxyl groups. Between 200°C and 500°C the weight loss is attributed to both collapse of structural hydroxyl groups and decomposition of the organic moiety. The Na^+ CEC of the calcined samples (Table 2) exhibits decrease in the CEC value upto 200°C which is attributed to loss of moisture, hydrated water and condensation of structural hydroxyl groups. Increase in CEC at 300°C and 400°C could be attributed to decomposition of organic moiety leading to the formation of active

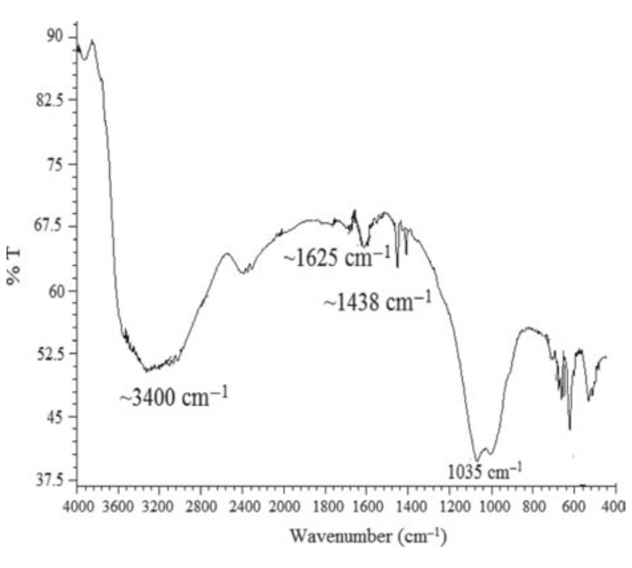

Fig. 4. FTIR of ZrATMP.

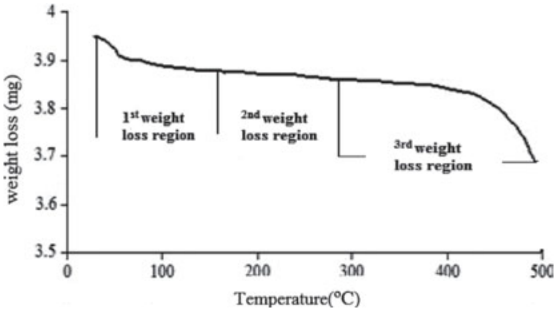

Fig. 5. TGA of ZrATMP.

Table 4
Percentage weight loss of ZrATMP from TGA thermogram

TGA	
Temperature	% Weight loss
50°C	2.12
100°C	7.34
150°C	1.89
200°C	1.52
250°C	1.32
300°C	0.89
350°C	0.78
400°C	0.69
450°C	0.89
500°C	0.92

carbon. Decrease in CEC after 400°C is attributed to the loss of active carbon in the form of CO_2. Similar observations have been made in our earlier reports [21,22].

X-ray diffractogram of ZrATMP does not exhibit any sharp peaks, indicating ZrATMP to be an amorphous material. SEM of ZrATMP (Fig. 6) exhibits irregular particle size which indicates amorphous nature of the material which is also supported by XRD of the material.

3.2. Distribution studies

The distribution coefficient (K_d) values evaluated for the metal ions under study towards ZrATMP have been presented in Table 3a. In general, it is observed that the K_d values are lower in high concentration of electrolyte and vice versa. Further, the K_d values in strong electrolyte media are lower as compared to weak electrolyte and aqueous media. This may be attributed to the high competition amongst ions for exchange in strong electrolyte media.

Selectivity/affinity of a particular metal ion towards an ion exchanger depends on (1) the ion exchanger, (2) the exchange media and (3) the exchanging metal ion. Larger ions being less hydrated, less energy is utilized for dehydration of the metal ions to occupy a site on the exchanger, which plays a prominent role in determining the selectivity of metal ions. The overall effect is a result of the contribution of the above mentioned factors. Depending on the predominant factor, the affinity of metal ions towards the ion exchanger varies in each case [25].

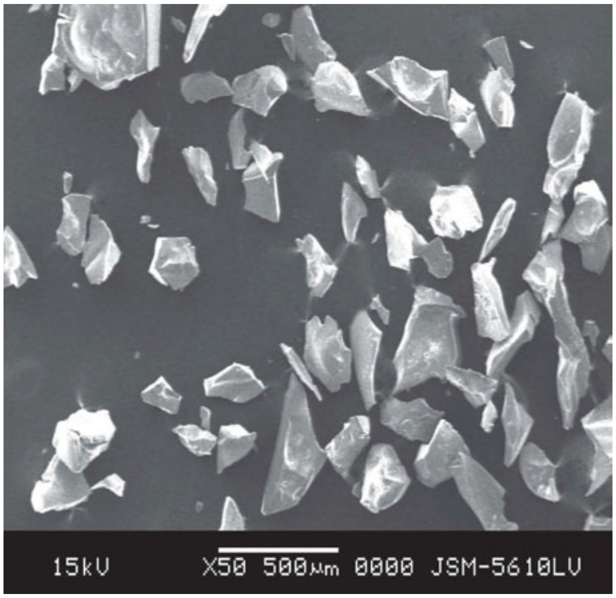

Fig. 6. SEM of ZrATMP.

The observed selectivity order (Table 3a) in aqueous media is Cu^{2+} (0.74 À) > Ni^{2+} (0.72 À) > Co^{2+} (0.72 À) > Zn^{2+} (0.74 À) amongst the transition metal ions, Pb^{2+} (1.44 À) > Cd^{2+} (0.97 À) > Hg^{2+} (1.10 À) amongst the heavy metal ions and Ce^{3+} (1.10 À) > Th^{4+} (0.96 À) amongst the f-block elements, values in parenthesis being ionic radii of respective metal ions. The ionic radii being almost equivalent in case of transition metal ions, the selectivity order is probably dependant on rate of exchange/equilibrium and dissociation of salt, while selectivity order in case of heavy metal ions and f-block elements can be explained on the basis of size of ions and hence hydrated ionic radii. Larger ions being less hydrated, less energy is utilized for dehydration of the metal ions to occupy a site on the exchanger [25].

It is observed that both K_d and equilibrium values increase with increase in temperature (Table 3b). This could be attributed to increase in mobility of the ions with increasing temperature and higher affinity of metal ion towards the exchanger compared to H^+ ions.

3.3. Breakthrough capacity

Breakthrough curves (a plot of C_e/C_0 vs. effluent volume) are presented in Fig. 7. Breakthrough capacity (BTC) is the dynamic capacity or operating capacity of a

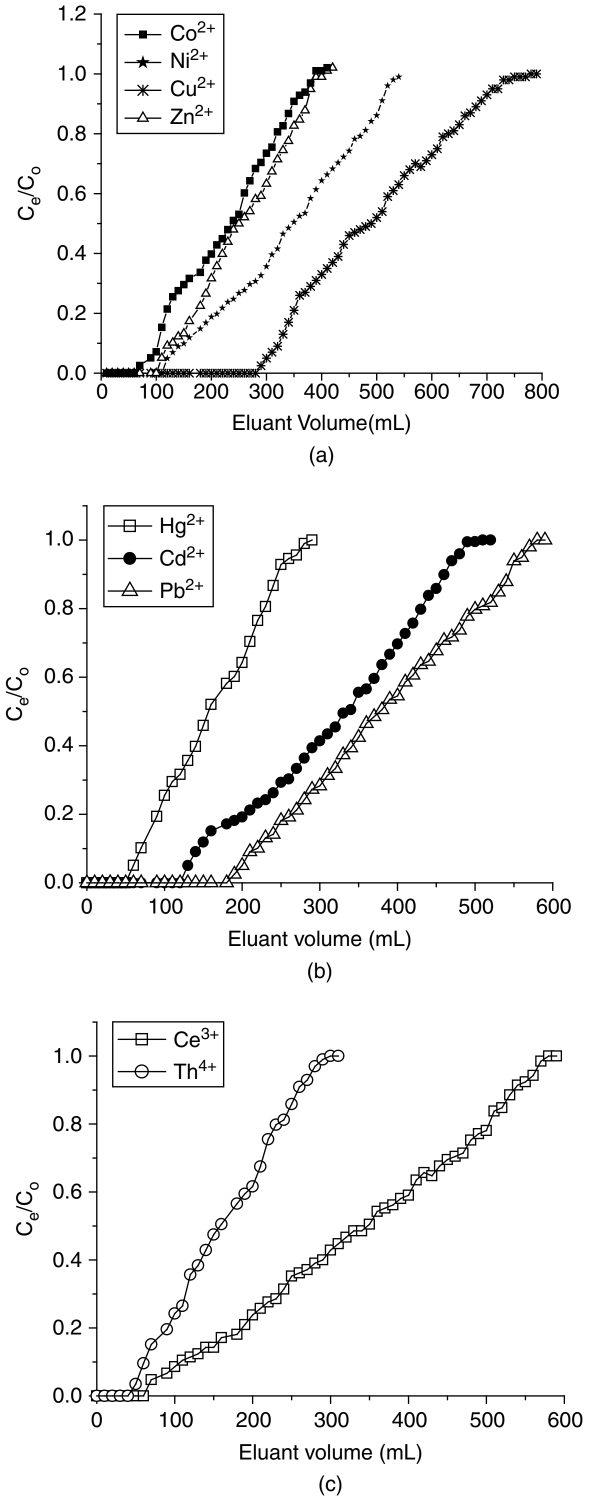

Fig. 7. Breakthrough curves (a) transition metal ions (b) heavy metal ions and (c) f-block elements.

known amount of ion exchange material towards metal ion in column operation. In dynamic process, exchange of a particular metal ion depends mainly on the rate of exchange, contact time, flow rate of feed solution through the column, bed depth, selectivity coefficient, particle size and temperature. K_d values also give an idea of affinity of metal ion towards ion exchanger. However, K_d is determined by a batch process. It is expected that the selectivity order based on K_d and BTC should be same, which is observed (Table 3a) in the present study confirming the order of selectivity.

Table 5
Proposed metal ion pair separations based on separation factor (α)

Metal ion pairs	Separation factor(α)
Cu^{2+}–Zn^{2+}	16.9
Cu^{2+}–Co^{2+}	16.5
Pb^{2+}–Hg^{2+}	22.51
Cd^{2+}–Hg^{2+}	18.51
Ce^{3+}–Th^{4+}	17.54

3.4. Metal separations and separation factor (α)

A study on distribution behaviour of metal ions in various electrolyte media gives an idea about the eluants that can be used for separation [25,29]. Separation factor α, the rate at which two constituents separate on a column, given by, $\alpha = K_{d1}/K_{d2}$, where K_{d1} and K_{d2} are the distribution coefficients of the two constituents being separated, provides a guideline for metal separation. The greater the deviation of α from unity, better is the separation. The efficiency of an ion exchange separation depends on the condition under which α has a useful value, or influencing in a direction favourable to separation. For a given metal ion pair, the electrolyte media in which the separation factor is the highest, is selected as the eluant.

In the present study, the most promising features of ZrATMP is complete sorption observed in case of Cu^{2+} (aqueous medium, 0.02 and 0.2 M CH_3COOH) and Ce^{3+} (0.02 M CH_3COOH). Zn^{2+} exhibit high K_d values in aqueous and 0.02 M CH_3COOH respectively, while Ni^{2+}, Hg^{2+} and Th^{4+} exhibit very low K_d values in 0.2 M HNO_3, aqueous medium and 0.2 M NH_4NO_3 respectively. These features suggest the removal/separations of the various metal ions under study. The separation factor (α) values presented for few metal ion pairs (Table 5) are very high indicating efficient separations which are in progress in our laboratory.

4. Conclusions

ZrATMP, a novel hybrid metal phosphonate, exhibits good CEC, thermal stability and chemical stability which are characteristics of a good ion exchange material. The most promising features of the material is its high selectivity for Cu^{2+} (complete sorption is observed), Ce^{3+} and very low selectivity for Ni^{2+}, Hg^{2+} and Th^{4+} ions. High separation factor (α) values also indicate efficient separations.

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