Synthesis and characterization of zirconium titanium phosphate and its application in separation of metal ions

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ABSTRACT

An advanced inorganic ion exchanger, zirconium titanium phosphate (ZTP) of the class of tetravalent bimetallic acid (TBMA) salt has been synthesized by sol–gel route. ZTP has been characterized for ICP-AES, TGA, FTIR and XRD. Chemical stability of the material in various media-acids, bases and organic solvents has been assessed. Cation exchange capacity (CEC) and effect of calcination ($100–500\,^\circ$C) on CEC has also been studied. Distribution behaviour of metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (d-block), Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+} (heavy) and La^{3+}, Ce^{3+}, Th^{4+}, UO_2^{2+} (f-block) towards ZTP has been studied and distribution coefficient (K_d) determined in aqueous as well as various electrolyte media/concentrations. Based on the differential selectivity, breakthrough capacity (BTC) and elution behaviour of various metal ions towards ZTP, a few binary and ternary metal ion separations have been carried out.

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1. Introduction

Toxic metals have an adverse effect on human health. Water pollution due to wastewater originating from industrial and mining wastewaters is one of the most significant environmental problems. The removal and recovery of toxic/heavy metals is an area of current interest and a challenging task for the environmentalist. Major objectives for the removal of metals from aqueous solutions are toxicity removal which entails an environmental aspect and recovery of valuable metals which involves a technological aspect.

Amongst various processes developed to remove metal ions from wastewater, it is observed that at low concentrations, the removal is more effective by ion exchange. Inorganic ion exchangers have played a prominent role in water processing for the chemical and nuclear industries and also used extensively for the removal and recovery of metal ions. Further, different types of metal pollutants from chemical process industries necessitates finding new ion exchangers, that have good ion exchange capacity, stability towards temperature, ionizing radiation and oxidizing solutions and that are capable of removing toxic substance from aqueous effluents.

Inorganic ion exchangers of the class of tetravalent metal acid (TMA) salts exhibit the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$ where $M(IV) = Zr, Ti, Sn, Ce, Th$, etc. and $X = P, Mo, W, As, Sb$, etc. They possess structural hydroxy protons, the H^+ of the –OH being the

exchangeable sites. A number of cations can be exchanged with H^+ due to which TMA salts possess cation exchange properties. They are obtained in amorphous and crystalline forms. TMA salts have emerged as promising advanced materials owing to their high thermal and chemical stability, resistance towards ionizing radiations as well as its important applications as ion exchangers, in separation science [1–3].

Mixed materials of the class of TMA salts, i.e. compounds containing two different anions and a cation, exhibited improved ion exchange properties and selectivity for particular metal ions, compared to their single salt counterparts. A literature survey shows that mixed materials containing two anions and a cation have been widely investigated [4–7]. However, not much work has been done on mixed materials containing two cations and an anion. They are referred to as tetravalent bimetallic acid (TBMA) salts.

Zirconium phosphate [1] and titanium phosphate [2] of the class of TMA salts are now well-known inorganic ion exchange materials. Although these compounds are not very different as exchangers, slight differences do exist, owing to difference in their ion size parameters. Mixed material, zirconium titanium phosphate (ZTP) of the class of tetravalent bimetallic acid (TBMA) salt has been synthesized, characterized and thermodynamics and kinetics of ion exchange studied and its utility as an ion exchanger established by us [8,9].

In the present endeavor, ZTP has been synthesized and characterized. Distribution behaviour of metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (d-block), Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+} (heavy) and La^{3+}, Ce^{3+}, Th^{4+}, UO_2^{2+} (f-block) towards ZTP has been studied and distribution coefficient (K_d) determined in aqueous as well as various electrolyte

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media/concentrations. Based on the differential selectivity, break-through capacity (BTC) and elution behaviour of various metal ions towards ZTP, a few binary and ternary metal ion separations have been carried out.

2. Experimental

2.1. Synthesis of ZTP

A solution containing 0.1 M $ZrOCl_2 \cdot 8H_2O$ and 0.1 M $TiCl_4$ in 10% (w/v) H_2SO_4 (100 mL) was prepared. To this solution 0.2 M $NaH_2PO_4 \cdot 2H_2O$ (200 mL) was added dropwise (flow rate, 1 mL min^{-1}) with continuous stirring at room temperature. After complete precipitation, the obtained gel was stirred for another 5 h. The precipitates were kept in contact with mother liquor overnight, filtered, washed with double distilled water to remove adhering ions (chloride and sulfate) and dried at room temperature. The material was then broken down to the desired particle size [30–60 mesh (ASTM)] by grinding and sieving. 5 g of material was treated with 50 mL of 1 M HNO_3 for 30 min with occasional shaking. The material was then separated from acid by decantation and treated with double distilled water to remove adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature.

2.2. Physico-chemical and ion exchange characterization

Physical characteristics such as percentage moisture content, bulk density, true density, void volume fraction, concentration of fixed ionogenic groups, volume capacity of the ion exchanger were studied according to literature methods [10,11].

2.2.1. Appearance
The synthesized material was physically observed for colour, shape, size, opacity, transparency, etc.

2.2.2. Percentage moisture content
Percentage moisture content of an exchanger is the ability of the exchanger to hold moisture. For determination of percentage moisture content, ZTP (~1 g) was allowed to stand in distilled water for 24 h. The material was then filtered and dried at room temperature to remove surface moisture and weighed. This material was dried at 110 °C for 4 h and reweighed after cooling in desiccator. The percentage moisture was calculated using the formula, % solid = (weight of dried material/weight of material before drying) × 100 and % moisture content = 100 − % solid.

2.2.3. Apparent/bulk density (D_{col})
The bulk density is the weight of the wet resin per unit volume. The density is specific for each resin and is dependent on the type of exchanger and ionic form. For density measurements, exact weight of exchanger was taken in calibrated glass column. After backwashing, water was drained and exchanger was allowed to settle. Apparent density is determined using the equation, apparent density = weight of ion exchanger/volume of ion exchange bed.

2.2.4. True density (D_{ie})
The true density was determined by taking a definite amount of ZTP in previously weighed specific gravity bottle (W). The bottle was again weighed along with the ion exchanger (W_i). The bottle was now filled with water along with ion exchange material and weighed (W_{is}). The weight of the specific gravity bottle containing water is also noted (W_w). The true density is calculated by using equation, $D_{ie} = (W_i − W)/(W_w − W_{iw}) + (W_i − W)$.

Table 1
Characterization of ZTP.

Properties	Observation
Appearance	White hard granules
Percentage moisture content	4.43%
Apparent density	1.15 g mL^{-1}
True density	2.03 g mL^{-1}
Void volume fraction	0.43
Concentration of fixed ionogenic group	6.52 mmol g^{-1}
Volume capacity of the resin	3.70 meq mL^{-1}
pH titration curve	Weak ion exchanger
Cation exchange capacity (CEC)	3.36 meq g^{-1}
Chemical stability	
Acids (tolerable limits)	36N H_2SO_4, 16N HNO_3, 11.3N HCl
Bases (tolerable limits)	5N NaOH, 5N KOH
Organic solvents	Ethanol, benzene, acetone and acetic acid
ICP-AES	
Elemental analysis	Zr:Ti:P = 1:1:2
FTIR	
Peaks (cm^{-1})	~3400, ~1635, ~1035
Groups assigned	−OH$_{str}$, −OH$_{bend}$, P=O$_{str}$
XRD	
Nature of material	Amorphous
TGA	
Thermal stability	Stable up to 300 °C

2.2.5. Void volume fraction
The void volume fraction was calculated by using the formula, void volume fraction = $1 − D_{col}/D_{ie}$.

2.2.6. Concentration of fixed ionogenic group (C_r)
Concentration of fixed ionogenic group of ZTP was calculated using the equation, $C_r = d_{ie} × (100 − \% \text{ moisture}) × IEC/100$.

2.2.7. Volume capacity of the resin (Q)
Volume capacity of exchanger was evaluated using formula, $Q = (1 − \text{void volume fraction}) × C_r$.

2.2.8. Chemical stability
The chemical stability of ZTP 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 500 mg of ZTP in 50 mL of the particular medium and allowed to stand for 24 h. The change in colour, nature and weight was observed.

2.2.9. 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 of exchanger, weak or strong [10]. For cation exchangers, the acidic sites can be titrated against an alkali hydroxide (used for neutralization) and a salt solution of same alkali metal
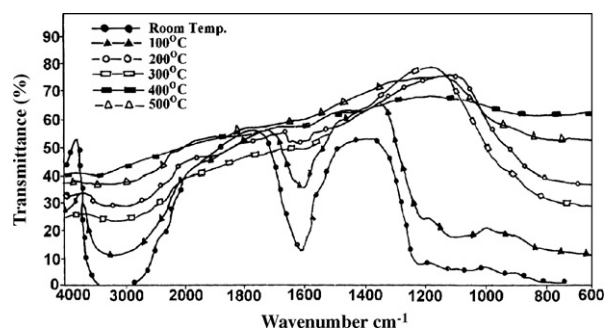
Fig. 1. FTIR spectra of ZTP, as synthesized and calcined at different temperatures.

Table 2
K_d values (in mL g^{-1}) for various metal ions towards ZTP at $30 \pm 1\,^\circ$C.

Metal ion	DMW	0.02 M NH$_4$NO$_3$	0.20 M NH$_4$NO$_3$	0.02 M HNO$_3$	0.20 M HNO$_3$	0.02 M HClO$_4$	0.20 M HClO$_4$	0.02 M CH$_3$COOH	0.20 M CH$_3$COOH
Co^{2+}	1,415	189	8	12	4	19	30	967	220
Ni^{2+}	933	21	83	5	2	5	27	294	610
Cu^{2+}	19,600	251	98	66	81	129	74	19,600	568
Zn^{2+}	187	28	7	12	4	7	2	165	124
Cd^{2+}	244	41	8	7	53	7	90	235	151
Hg^{2+}	2,657	1152	261	172	6	96	14	793	112
Pb^{2+}	19,800	3760	483	625	31	700	36	9,700	4700
Bi^{3+}	54	46	54	40	39	13	93	104	50
La^{3+}	3	15	15	17	5	38	12	52	121
Ce^{3+}	105	28	24	40	23	41	28	58	130
Th^{4+}	161	153	164	210	56	256	86	297	243
UO$_2$$^{2+}$	13	18	168	39	367	32	375	43	208

(used as a supporting electrolyte). In the present case, 500 mg of ZTP 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 is obtained by plotting pH versus volume of NaOH.

2.2.10. Cation exchange capacity (CEC) and effect of calcinations on CEC

The Na$^+$ ion exchange capacity (CEC) of ZTP was determined by the column method [12]. The column was prepared in a burette, provided with glass wool at the bottom. It was filled half way with distilled water, preventing air traps. 0.5 g of the ion exchanger was accurately weighed and transferred through a dry funnel. The water inside the column was kept at a level of about 1 cm above the material. A 250 mL solution of sodium acetate was added into the column and the elution was carried out at a flow rate of 0.5 mL min^{-1}. The eluant was collected in a 500 mL conical flask and then titrated against 0.1 M NaOH solution. The CEC of the exchanger in milliequivalent per gram (meq g^{-1}) is given by, av/w where 'a' is the molarity of the NaOH solution, 'v' is the volume of NaOH required for titration and 'w' is the weight of the exchanger.

The effect of calcination on CEC was studied by calcining several 1 g portions of the material for 2 h in the temperature range 100–500 °C with 100 °C intervals in a muffle furnace, cooling them to room temperature, and determining the CEC by the column method [12] as described above.

2.3. Instrumental characterization

The synthesized material was analyzed for zirconium, titanium and phosphorus content using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Labtam, 8440 Plasmalab). X-ray diffractogram ($2\theta = 5$–80°) was obtained on X-ray diffractometer (Brucker AXS D8) with Cu Kα X-ray source of wavelength 1.5418 Å and nickel filter. FTIR spectra were recorded using KBr wafer on a Perkin-Elmer Paragon 1000 spectrophotometer. Thermal analysis (TGA) was carried out on a Shimadzu DT 30 thermal analyzer at a heating rate of 10 °C min^{-1}.

2.4. Distribution studies

Distribution studies for metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}, La^{3+}, Ce^{3+}, Th^{4+} and UO$_2$$^{2+}$ were carried out by batch method [13]. 100 mg of the exchanger ZTP 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, AAS or UV–vis spectrophotometer [14,15]. Distribution studies have been carried out in aqueous as well as

Table 3
Elution behaviour of metal ions towards ZTP.

Metal ion	E_v/% E	0.05 M NH$_4$NO$_3$	1.0 M NH$_4$NO$_3$	0.05 M HNO$_3$	1.0 M HNO$_3$	0.05 M HClO$_4$	1.0 M HClO$_4$	0.05 M CH$_3$COOH	1.0 M CH$_3$COOH
Co^{2+}	E_v	75	70	40	30	55	50	55	50
	% E	90.2	94.2	98.3	99.1	96.2	97.6	90.1	91.5
Ni^{2+}	E_v	65	55	45	40	60	50	60	55
	% E	85.8	87.6	90.9	98.2	90.2	96.2	88.2	89.9
Cu^{2+}	E_v	75	65	40	35	50	35	60	50
	% E	65.4	70.8	91.2	96.2	85.4	90.2	86.2	86.4
Zn^{2+}	E_v	65	60	45	35	60	45	55	50
	% E	88.4	92.3	98.1	99.3	94.2	96.4	93.3	98.5
Cd^{2+}	E_v	65	60	45	35	60	55	70	60
	% E	87.8	89.9	97.7	99	97	98.1	89.2	93.4
Hg^{2+}	E_v	70	65	45	40	65	55	75	65
	% E	86.5	88.9	96.2	98.8	95.2	96.2	90.2	95.2
Pb^{2+}	E_v	75	65	50	40	65	60	92.3	50
	% E	84.2	86.5	96.5	97.8	92.2	97.5	94.4	96.5
Bi^{2+}	E_v	80	70	50	40	65	55	60	50
	% E	83.2	88.9	97.6	98.2	97	97.9	95.6	97.2
La^{3+}	E_v	75	70	55	50	65	60	65	50
	% E	80.7	88.2	92.2	99.4	90.2	92.9	92.2	93.8
Ce^{3+}	E_v	80	75	50	40	65	55	60	50
	% E	78.9	85.2	94.5	99.2	92.2	94.2	94.5	94.9
Th^{4+}	E_v	80	75	50	40	65	55	75	65
	% E	80.5	86.3	96.2	99.3	93.5	95.6	93.8	96.5
UO$_2$$^{2+}$	E_v	80	70	55	50	75	65	70	60
	% E	81.6	84.2	89.3	99.1	94.1	96.3	90.9	94.8

E_v, mL of eluting agent; % E (percentage elution) = (concentration of metal ion eluted/concentration of metal ion loaded) × 100.

various electrolyte media (NH_4NO_3, HNO_3, $HClO_4$ and CH_3COOH) of varying concentration (0.02 and 0.20 M). 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 metal ions left in the solution after equilibrium; V = volume of the solution; W = weight of the exchanger.

2.5. Breakthrough capacity (BTC), elution and separation studies

For Breakthrough capacity, elution and separation studies, 0.5 g of the ion exchanger, ZTP, was taken in a glass column (30 cm × 1 cm), washed thoroughly with deionized water and flow rate adjusted to 0.5 mL min^{-1}. Metal ion concentration was determined quantitatively by EDTA titration, AAS or UV–vis spectrophotometer [14,15].

For Breakthrough capacity, 5 mL fractions of each individual 0.001 M metal ion solution was passed through the column and effluent collected, till the amount of 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 $(C_0V_{(10\%)})/W$, 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.

For elution studies, column was prepared as above. Metal ion (0.001 M, 5 mL) was loaded onto the column. Metal ion loaded was eluted with reagents like HNO_3, $HClO_4$, CH_3COOH and NH_4NO_3 of 0.5 and 1 M concentration. The amount of metal ion recovered i.e. % E (percentage elution), was calculated as, % $E = (C_e/C_0) \times 100$ where C_e is the concentration of the metal ion in the eluted solution and C_0 is concentration of metal ion loaded onto column.

For binary and ternary separations, column was prepared as above. The mixture of the metal ions (0.001 M, 5 mL of each metal ion) to be separated was loaded on it. The separation was achieved by passing suitable eluant through the column. For a given metal ion pair, the eluant was selected based on the separation factor, calculated using K_d values of respective metal ions in different electrolyte media. The electrolyte media, in which separation factor was highest, was selected as the eluant. The percentage recovery of each metal was calculated using the formula, % recovery = (concentration of metal ion eluted/concentration of metal ion loaded) × 100.

3. Results and discussion

Characterization of ZTP by various physico-chemical and instrumental methods has been presented in Table 1.

The Na$^+$ ion exchange capacity (CEC) of ZTP evaluated at room temperature is 3.36 meq g^{-1}, which is higher compared to their
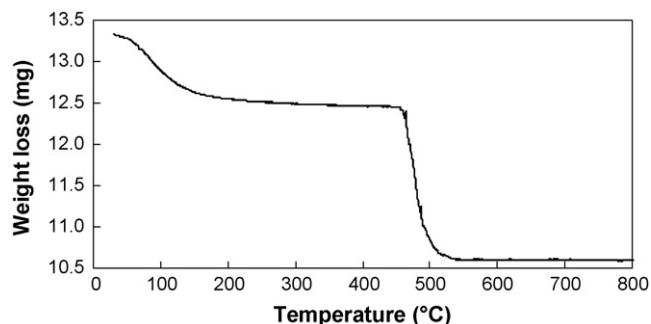
single salt counterparts zirconium phosphate (2.77 meq g^{-1}) and titanium phosphate (3.09 meq g^{-1}) [16]. Since the anion HPO_4^{2-} is common for both ZP and TP, the CEC values should bear a correlation with the acidity of the cations. Acidity of a cation is related to ion size and charge. Ionic radii for Ti^{4+} is 0.745 Å and Zr^{4+} is 0.86 Å. Ti^{4+} with smaller ionic radii and therefore a high charge density exhibits greater CEC. The CEC of ZTP is higher compared with their single salt counterparts. Higher IEC of ZTP may be attributed to some structural changes. Yazawa et al. [17] have observed earlier that, lattice structure in case of TBMA salt (ZTP) is less ordered compared to single salt counterparts ZP and TP, which leads to tilting of phosphate groups, which further affects the CEC.
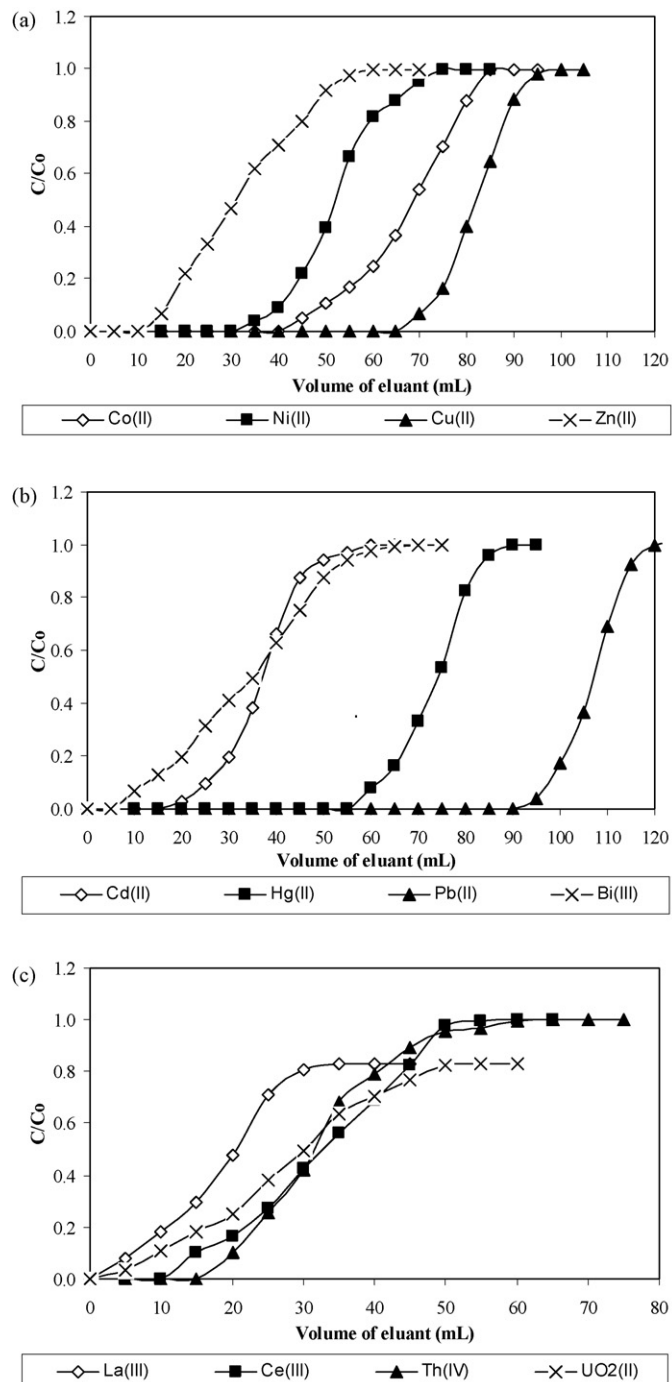

Fig. 2. Thermogram of ZTP.

Fig. 3. Breakthrough curves for: (a) d-block, (b) heavy and (c) f-block metal ions.

A study of the chemical resistivity/stability of ZTP in acid, base and organic solvents (ethanol, benzene, acetone, acetic acid, etc.) media is both useful and important while using the materials for various applications in varied environments. The results presented in Table 1 shows maximum tolerable limits in the particular media. ZTP exhibits good chemical stability in acids and organic solvents but a lower stability in alkaline media.

FTIR spectra of the ZTP (Fig. 1) exhibit broadband in the region $\sim 3400\,cm^{-1}$ which is attributed to asymmetric and symmetric –OH stretches. A sharp medium band at $1620\,cm^{-1}$ is attributed to aquo (H–O–H) bending. A band in the region $\sim 1035\,cm^{-1}$ is attributed to the presence of P=O stretching. A medium intensity band at $1400\,cm^{-1}$ is attributed to the presence of δ(POH) [18]. These bands indicate the presence of structural hydroxyl groups/exchanging sites (H$^+$ of the –OH) in ZTP. Further, from FTIR spectra of the ZTP calcined samples (Fig. 1), it is observed that the intensity of the peaks at ~ 3400 and $\sim 1620\,cm^{-1}$, representative of the –OH group diminishes as the calcination temperature increases. This is also in keeping with CEC values that decrease as calcination temperature increases. The CEC of ZTP on calcination at 100, 200, 300, 400, 500 °C were found to be 3.25, 3.04, 2.67, 2.28, 1.86 meq g^{-1}, respectively. Decrease in CEC with increasing temperature is attributed to the condensation of structural hydroxyl groups.

TGA of ZTP (Fig. 2) indicates two weight loss regions. The first weight loss up to 160 °C is attributed to loss of moisture/hydrated water. The second weight loss in the range 250–500 °C is attributed to condensation of structural hydroxyl groups. These observations are further supported by the fact that CEC decreases on calcination, as discussed above.

Based on the elemental analysis (ICP-AES) and thermal analysis (TGA) data ZTP has been formulated as $Zr_{0.55}Ti_{0.45}(H_2PO_4)_2 \cdot H_2O$, respectively using the Alberti and Torracca formula [19].

It is well known that metals have toxic effects. The main sources of occurrence of transition, heavy and rare earth metal ions in wastewaters is due to electroplating, mining, pharmaceutical, battery, paint and pigments, textile, automotive and aeronautical industries. These metals are known to exhibit toxic effects in humans such as asthma, lung, kidney and tissue damage, liver mal-functions, anemia, nervous disorders and cancer.

The distribution coefficient (K_d) values evaluated for various metal ions towards ZTP have been presented in Table 2. In general, 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 media as well as aqueous medium. This may be attributed to high competition amongst ions for exchange in strong electrolyte media.

Smaller the size of the cation, greater is the tendency to be hydrated and greater the 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, plays a prominent role in determining the selectivity of metal ions [20]. There are several other factors that affect the selectivity with respect to metal ion being exchanged. They are ionic radius, atomic num-

Table 4
Binary separations of metal ions using ZTP.

Separations achieved	$\alpha = K_{d1}/K_{d2}$	Eluant	Metal ion (mg)		Recovery (%)
			Loaded	Eluted	
Cu^{2+}–Co^{2+}	13.85	0.5 M NH$_4$NO$_3$ (Cu^{2+})	32	23.1	72.23
		1.0 M HNO$_3$ (Co^{2+})	29.5	24.5	83.21
Cu^{2+}–Ni^{2+}	21.01	0.5 M NH$_4$NO$_3$ (Cu^{2+})	32	21.8	67.98
		1.0 M CH$_3$COOH (Ni^{2+})	29.5	24.8	83.98
Cu^{2+}–Zn^{2+}	104.81	0.5 M CH$_3$COOH (Cu^{2+})	32	22.1	68.99
		1.0 M HNO$_3$ (Zn^{2+})	32.5	28	86.02
Co^{2+}–Ni^{2+}	1.51	1.0 M NH$_4$NO$_3$ (Co^{2+})	29.5	22.4	75.88
		0.5 M HNO$_3$ (Ni^{2+})	29.5	24.9	84.42
Co^{2+}–Zn^{2+}	7.57	0.5 M HNO$_3$ (Co^{2+})	29.5	23	77.96
		1.0 M HClO$_4$ (Zn^{2+})	32.5	28.6	88.04
Ni^{2+}–Zn^{2+}	4.99	0.5 M HNO$_3$ (Ni^{2+})	29.5	25.9	87.92
		1.0 M HClO$_4$ (Zn^{2+})	32.5	29.9	92.11
Pb^{2+}–Cd^{2+}	80.33	0.5 M HNO$_3$ (Pb^{2+})	103.5	64.2	62.04
		0.5 M HClO$_4$ (Cd^{2+})	56	40.4	72.21
Pb^{2+}–Hg^{2+}	7.38	0.5 M CH$_3$COOH (Pb^{2+})	103.5	66.1	63.88
		1.0 M CH$_3$COOH (Hg^{2+})	100.5	76.7	76.32
Pb^{2+}–Bi^{3+}	362.96	0.5 M HClO$_4$ (Pb^{2+})	103.5	68.4	66.08
		1 M CH$_3$COOH (Bi^{3+})	104.5	77.2	73.89
Cd^{2+}–Hg^{2+}	10.89	0.5 M NH$_4$NO$_3$ (Cd^{2+})	56	43.7	77.95
		1.0 M NH$_4$NO$_3$ (Hg^{2+})	100.5	74.3	73.89
Cd^{2+}–Bi^{3+}	4.52	0.5 M NH$_4$NO$_3$ (Cd^{2+})	56	42.2	75.42
		1.0 M HNO$_3$ (Bi^{3+})	104.5	81.9	78.33
Hg^{2+}–Bi^{3+}	49.2	1.0 M HClO$_4$ (Hg^{2+})	100.5	68.1	67.79
		0.5 M NH$_4$NO$_3$ (Bi^{3+})	104.5	78.4	75.06
Th^{4+}–La^{3+}	53.67	0.5 M CH$_3$COOH (Th^{4+})	116	83.8	72.25
		0.5 M HNO$_3$ (La^{3+})	69.5	61.9	89.11
Th^{4+}–Ce^{3+}	1.53	0.5 M CH$_3$COOH (Th^{4+})	116	85.8	73.96
		1.0 M NH$_4$NO$_3$ (Ce^{3+})	70	54.9	78.41
Th^{4+}–UO$_2$$^{2+}$	12.38	0.5 M HClO$_4$ (Th^{4+})	116	84.9	73.22
		1 M HNO$_3$ (UO$_2$$^{2+}$)	119	102.5	86.12
Ce^{3+}–La^{3+}	35	0.5 M CH$_3$COOH (Ce^{3+})	70	54.1	77.32
		1 M HNO$_3$ (La^{3+})	69.5	61.2	88.04
Ce^{3+}–UO$_2$$^{2+}$	8.08	0.5 M HNO$_3$ (Ce^{3+})	70	54.8	78.29
		0.5 M NH$_4$NO$_3$ (UO$_2$$^{2+}$)	119	101.3	85.15
La^{3+}–UO$_2$$^{2+}$	4.33	0.5 M HNO$_3$ (La^{3+})	69.5	62.8	90.31
		0.5 M CH$_3$COOH (UO$_2$$^{2+}$)	119	102.3	85.99

$\alpha = K_{d1}/K_{d2}$, where K_{d1} and K_{d2} are K_d values of metal 1 and metal 2 in aqueous media. % Recovery = (concentration of metal ion eluted/concentration of metal ion loaded) × 100. Maximum deviation in % recovery = ±3%.

ber, ionic charge and pK_h (K_h = hydrolysis constant) of metal ion. With respect to ion exchanger the factors are structure and complexity of ion exchanger, CEC and acidity. Other factors include, temperature, pH, concentration/nature of electrolyte, etc. in the medium [21]. The overall effect is a result of contribution of the above-mentioned factors. Depending on the predominant factor, the affinity of metal ions towards ZTP varies in each case.

Amongst d-block metal ions, the observed selectivity order is Cu^{2+}(0.74 Å) > Co^{2+}(0.72 Å) > Ni^{2+}(0.72 Å) > Zn^{2+}(0.74 Å), values in parenthesis being ionic radii of respective metal ions. The ionic radii being almost equivalent, this order could be explained based on preference of the cation with low hydrolysis constant (pK_h) in solution [22]. As Cu^{2+} has the lowest pK_h (pK_h = 8.0), the exchange is highest in comparison to Co^{2+} (pK_h = 8.9), Ni^{2+} (pK_h = 9.9) and Zn^{2+} (pK_h = 10.1). Amongst heavy metal ions, the observed selectivity order is Pb^{2+}(1.44 Å) > Hg^{2+}(1.10 Å) > Cd^{2+}(0.97 Å) > Bi^{3+}(0.96 Å), values in parenthesis being ionic radii of respective metal ions. The selectivity order can be explained based on size of ions and hence the nature of hydration. Pb^{2+} having higher ionic radius is less hydrated compared to the other metal ions exhibits higher affinity towards ZTP. Amongst f-block metal ions, the observed selectiv-

ity order is Th^{4+}(0.96 Å) > Ce^{3+}(1.11 Å) > UO_2^{2+}(1.03 Å) > La^{3+}(1.15 Å), values in parenthesis being ionic radii of respective metal ions. Concept of high ionic radius and therefore less hydration is followed by Ce^{3+}, UO_2^{2+} and La^{3+}. The high affinity of Th^{4+} for ZTP is probably due to high ionic potential.

The most promising property of ZTP is its high selectivity for Pb^{2+} (K_d = 19,800 mL g^{-1}) and Cu^{2+} (K_d = 19,600 mL g^{-1}). The high selectivity of Pb^{2+} is also observed in other TMA salts, viz., titanium molybdate (1000), titanium tungstate (1565), niobium arsenate (2980), antimony molybdate (800), antimony tungstate (145), zirconium phosphate (3800), titanium phosphate (2300), polyacrylonitrile thorium phosphate (800), zirconium tungstoiodophosphate (8500), titanium arsenophoshate (9500), antimony molybdotungstate (428), values in parenthesis is K_d in mL g^{-1} [4,5,23–29]. In case of Cu^{2+}, other TMA salts exhibit only moderate or poor selectivity viz. zirconium phosphate (250), titanium phosphate (163), titanium molybdate (12), antimony molybdate (212), antimony tungstate (45), polyacrylonitrile thorium phosphate (80), antimony molybdotungstate (62), zirconium arsenophoshate (804), titanium arsenophoshate (131), zirconium tungstoiodophosphate (7900), values in parenthesis is in mL g^{-1} [4,5,23–29]. An extremely high affinity of Pb^{2+} and Cu^{2+} towards
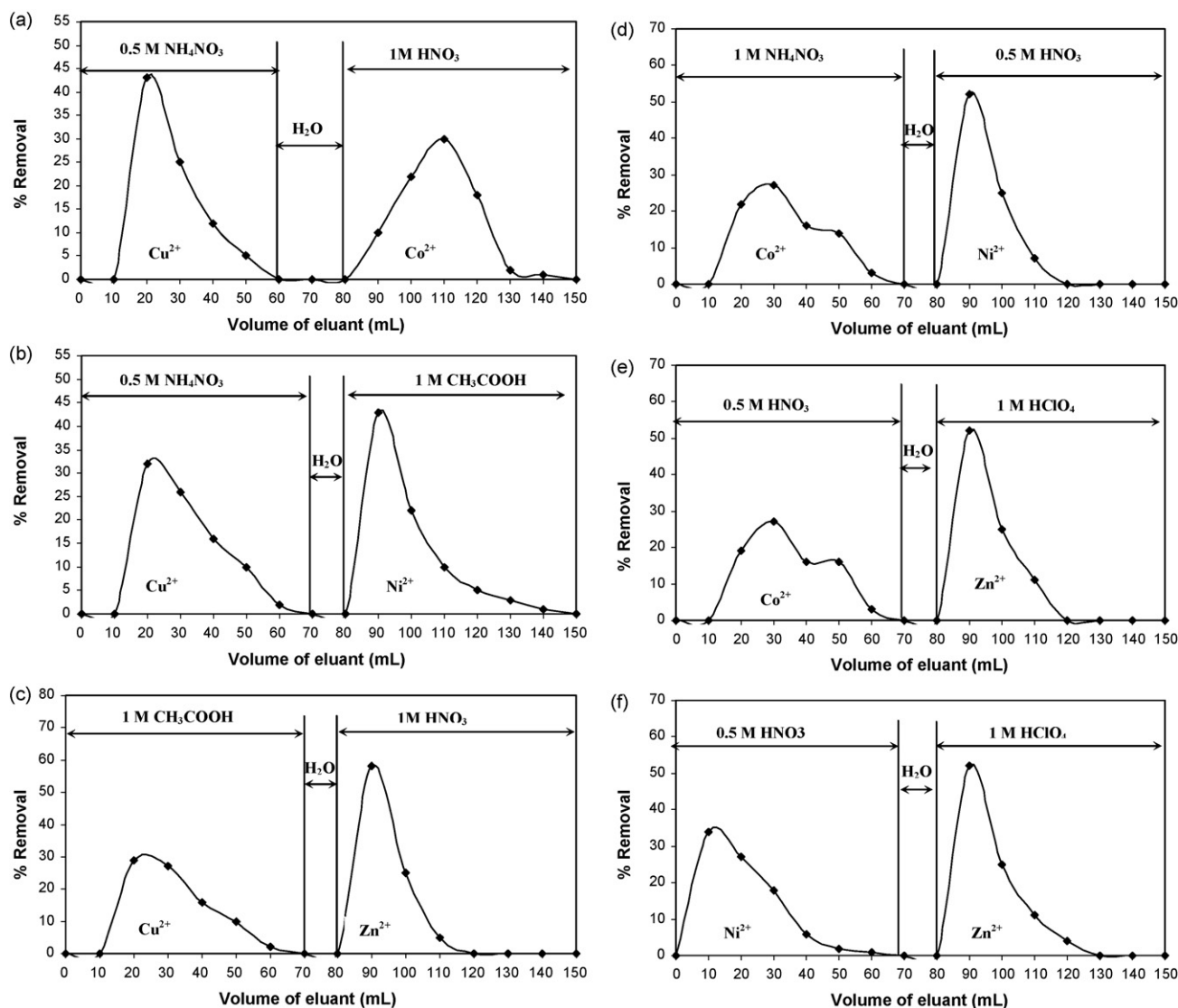

Fig. 4. Binary metal ion separations for d-block elements: (a) Cu^{2+}–Co^{2+}, (b) Cu^{2+}–Ni^{2+}, (c) Cu^{2+}–Zn^{2+}, (d) Co^{2+}–Ni^{2+}, (e) Co^{2+}–Zn^{2+} and (f) Ni^{2+}–Zn^{2+} using ZTP.

ZTP in the present study suggests its possible use for separation from other pollutants.

A breakthrough curve (plot of C_e/C_0 vs. effluent volume) is presented in Fig. 3. BTC is the dynamic capacity or operating capacity of a known amount of ion exchange material towards metal ion in column operation. In simple words, it is the affinity or maximum exchange capacity of the exchanger towards metal ion in operating condition. K_d values also give idea of affinity of metal ion towards ion exchanger. The difference is, K_d is determined by a batch process (static), while BTC is determined by a column process (dynamic). Therefore it is expected that the selectivity order based on K_d values and BTC should be same. The break through capacity is determined by means of breakthrough curves (Fig. 3). The selectivity order based on BTC values is $Pb^{2+} > Cu^{2+} > Hg^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Th^{4+} > Ce^{3+} > Bi^{3+} > UO_2{}^{2+} > La^{3+}$, is similar to that observed based on K_d values, which is expected. However, in dynamic process, exchange of a particular metal ion depends mainly on rate of exchange and contact time as well as flow rate of feed solution through the column, bed depth, selectivity co-efficient, particle size and temperature. The similar order based on K_d values and BTC, reveals good exchange rate/exchange kinetics of metal ions.

Elution behaviour of various metal ions towards ZTP has been presented in Table 3, and it is observed that almost ~80–90% of metal ion is recovered. Higher the concentration of the eluant better is the recovery of metal ion. Acids in general, are better eluants, however, 1 M HNO$_3$ is best eluant for all metal ions. The study shows that, metal ion exchange and elution are easy and possible on ZTP exchanger using above-mentioned electrolytes.

A study on the distribution behaviour of metals ions in aqueous as well as in various electrolyte media gives an idea about the possible binary metal separations as well as the eluants that could be used for separation. Based on K_d values in different electrolyte media, BTC and elution studies as well as trial error method, best suitable eluant is selected for binary and ternary metal ion separations.

K_d values suggest the possibilities for many important binary separations. Based on separation factor α, binary separations for all possible metal ions pairs have been carried out. The details of binary separation studies are presented in Table 4 and plots of percentage metal removal vs. eluate volume are presented in Fig. 4a–f (d-block), Fig. 5a–f (heavy) and Fig. 6a–f (f-block) metal ion separations. Ternary separations for metal ions pairs (each case from d-block, heavy and f-block metal ions), have also been studied. The
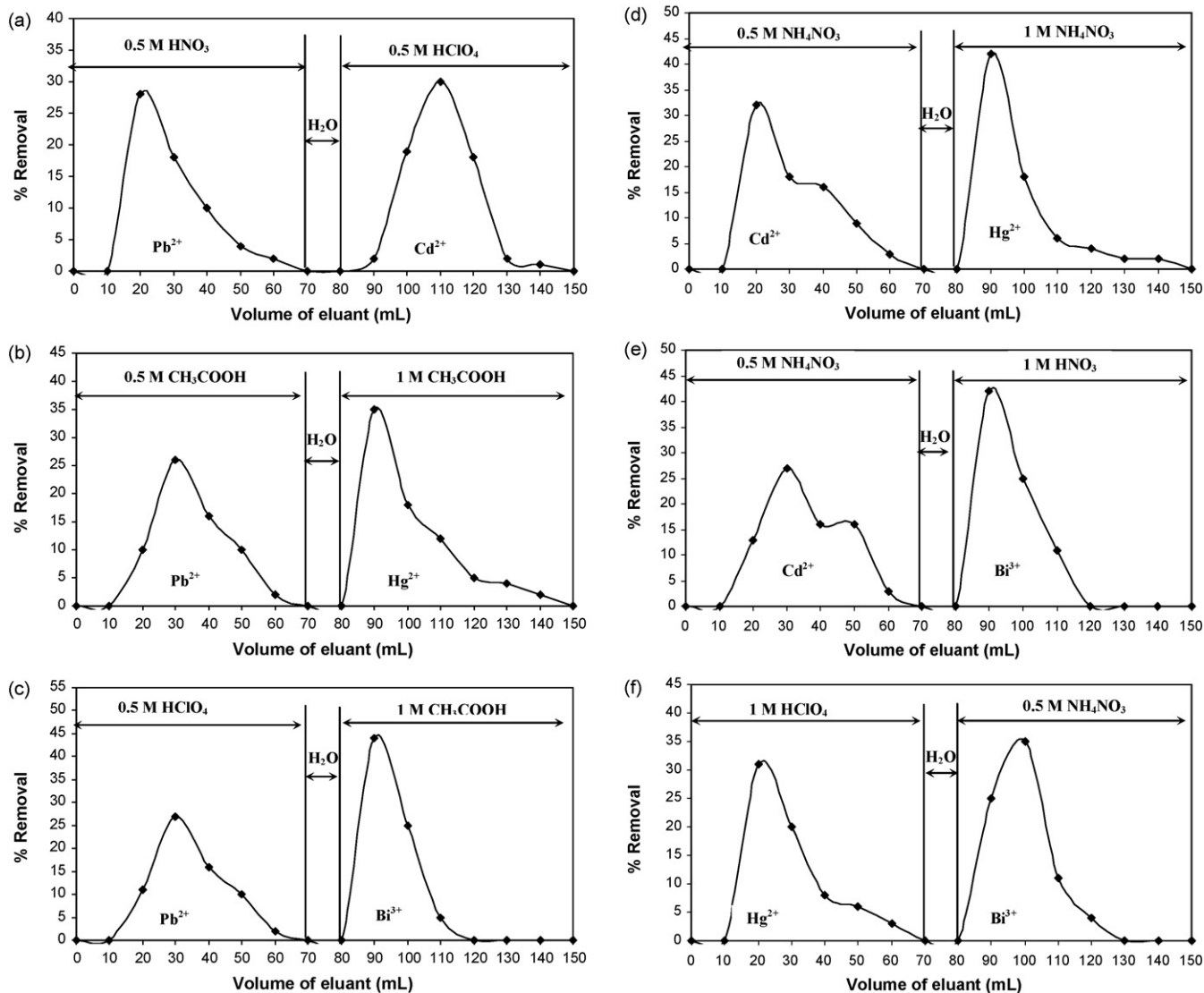

Fig. 5. Binary metal ion separations for heavy metal ions: (a) Pb^{2+}–Cd^{2+}, (b) Pb^{2+}–Hg^{2+}, (c) Pb^{2+}–Bi^{3+}, (d) Cd^{2+}–Hg^{2+}, (e) Cb^{2+}–Bi^{3+} and (f) Hg^{2+}–Bi^{3+} using ZTP.
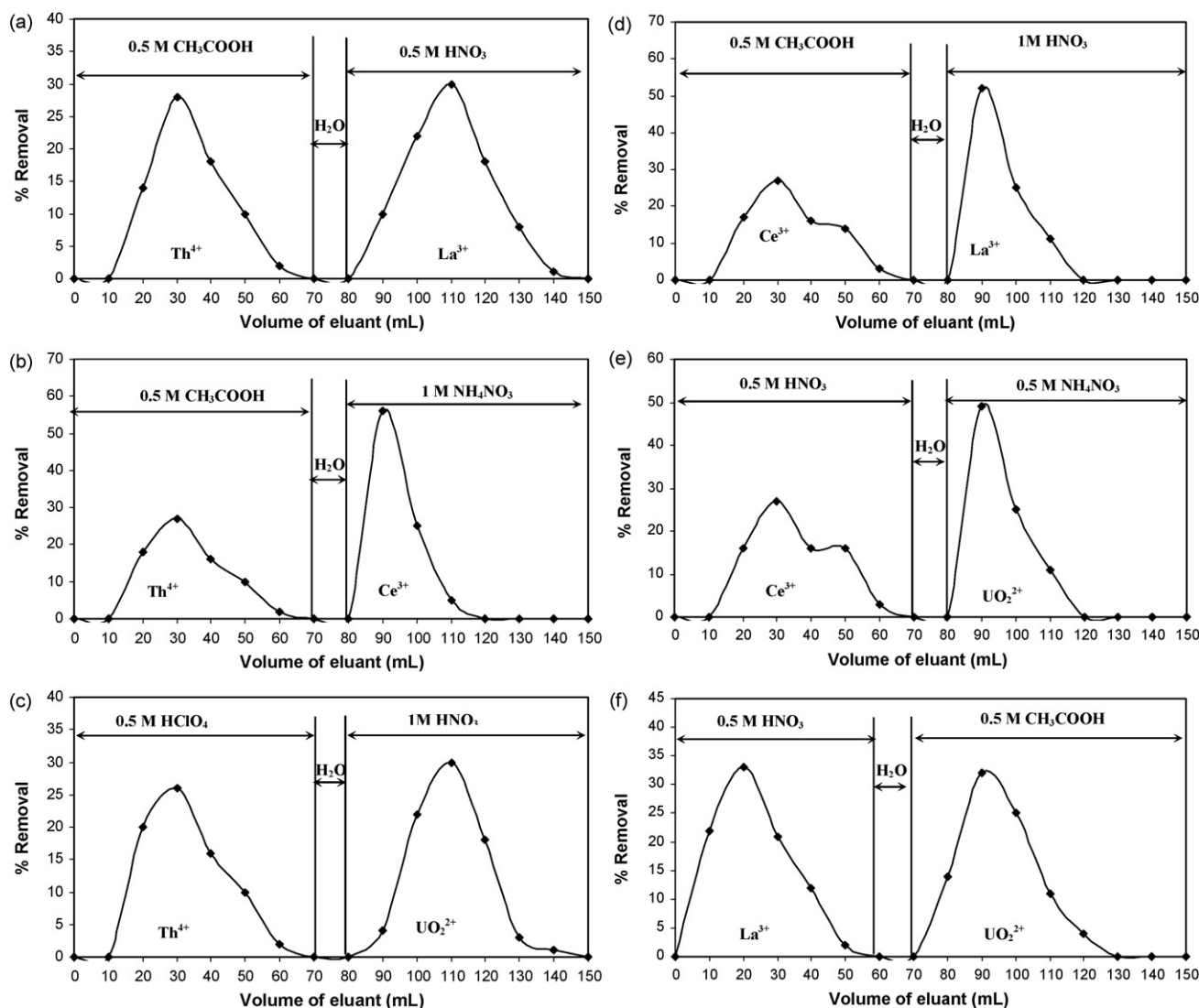
Fig. 6. Binary metal ion separations for f-block elements: (a) Th^{4+}–La^{3+}, (b) Th^{3+}–Ce^{3+}, (c) Th^{4+}–UO_2^{2+}, (d) Ce^{3+}–La^{3+}, (e) Ce^{3+}–UO_2^{2+} and (f) La^{3+}–UO_2^{2+} using ZTP.

details of separation studies are presented in Table 5 and plots of percentage metal removal vs. eluate volume are presented in Fig. 7a–c.

ZTP exhibits 68–92%, 62–78% and 72–90% separation efficiency in binary separations for d-block, heavy and f-block metal ions, respectively. Though separation factor is very less in case of Co^{2+}–Ni^{2+} and Th^{4+}–Ce^{3+} metal ion pairs, the separation is found to be quite efficient. ZTP exhibits 55–66%, 56–64% and 55–58% separation efficiency in ternary separations for d-block, heavy and

f-block meal ions, respectively. The separations are quite sharp and recovery is quantitative and reproducible in all cases. Separation efficiency decreases as we go from single metal ion elution to binary and ternary separations. This may be attributed to loss of metal ions during change over of eluant, difference in metal ion loading, interference of metal ions, pH, simultaneous elution of two or more metal ions with same eluant, experimental error in determination of metal ion in presence of other ions, etc.

Table 5
Ternary separations of metal ions using ZTP.

Separations achieved	Eluant	Metal ion (mg)		Recovery (%)
		Loaded	Eluted	
Zn^{2+}–Ni^{2+}–Cu^{2+}	0.5 M $HClO_4$ (Zn^{2+})	32.5	21.5	66.12
	0.5 M HNO_3 (Ni^{2+})	29.5	18.1	61.29
	1 M HNO_3 (Cu^{2+})	32.0	17.7	55.23
Pb^{2+}–Hg^{2+}–Cd^{2+}	0.5 M NH_4OH (Pb^{2+})	103.5	66.5	64.25
	0.5 M $HClO_4$ (Hg^{2+})	100.5	60.5	60.22
	1 M HNO_3 (Cd^{2+})	56.0	31.5	56.32
La^{3+}–Ce^{3+}–Th^{4+}	0.5 M $HClO_4$ (La^{3+})	69.5	40.6	58.45
	0.5 M NH_4OH (Ce^{3+})	70.0	39.3	56.15
	0.5 M HNO_3 (Th^{4+})	116.0	64.2	55.33

% Recovery = (concentration of metal ion eluted/concentration of metal ion loaded) × 100. Maximum deviation in % recovery = ±3%.
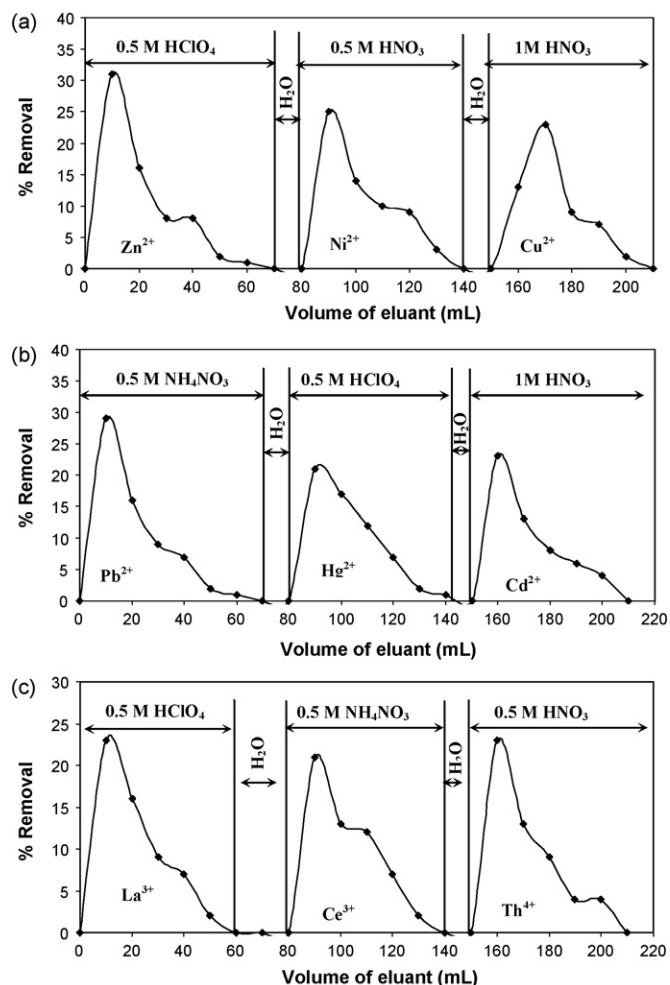
Fig. 7. Ternary metal ion separations for: (a) d-block, (b) heavy and (c) f-block elements using ZTP.

4. Conclusions

ZTP exhibits good CEC compared to single salt counterparts ZP and TP, and is both chemically and thermally stable, which are important characteristics for materials to behave as cation exchangers. Further, it also exhibits preparative reproducibility and high selectivity for Pb^{2+} and Cu^{2+}. Efficient metal separations carried out using ZTP indicate good potential for this material to be used as a cation exchanger.

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