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Synthesis and Characterization of Zirconium Titanium Hydroxy Ethylidene Diphosphonate and Its Application in Separation of Metal Ions

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Abstract: A novel hybrid ion exchanger, zirconium titanium hydroxy ethylidene diphosphonate (ZTHEDP), of the class of tetravalent bimetallic acid (TBMA) salt has been synthesized by the sol gel route. ZTHEDP has been characterized for ICP-AES, TGA, FTIR, and XRD. Chemical resistivity of ZTHEDP in various media—acids, bases, and organic solvents have been assessed. Ion exchange capacity (IEC) and the effect of calcination (100°C to 500°C) on IEC has also been studied. The distribution behavior 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 ZTHEDP has been studied and the distribution coefficient (K_d) evaluated in aqueous as well as various electrolyte media/concentrations. Based on differential selectivity, the breakthrough capacity (BTC) and elution behavior of various metal ions towards ZTHEDP, a few binary and ternary metal ion separations have been carried out.

Keywords: Cation exchanger, hybrid material, metal separation, tetravalent bimetallic acid salt, zirconium titanium hydroxy ethylidene diphosphonate

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INTRODUCTION

Toxic metals have an adverse effect on human activities. Water pollution due to wastewater originating from industrial and mining wastewaters is one of the most significant environmental problems (1). The removal and recovery of toxic/heavy metals is an area of current interest and a challenging task for the environmentalist (2). 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 (3).

Amongst various processes developed to remove metal ions from waste water, it is observed that at low concentrations, the removal is more effective by ion exchange (4,5). 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 (IEC), stability towards temperature, ionizing radiation, and oxidizing solutions and that are capable of removing toxic substances from aqueous effluents (6).

Tetravalent metal acid (TMA) salts, possess the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$, where $M(IV) = Zr$, Ti, Sn, Th, Ce etc., and $X = P$, W, Mo, As, Sb, etc. They possess structural hydroxyl 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. 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 (7–9).

Mixed materials of the class of TMA salts, i.e., compounds containing two different anions and a cation (4,10–12), exhibited improved ion-exchange properties and selectivity for particular metal ions, compared to their single salt counterparts. Mixed material containing two different cations and an anion referred to as tetravalent bimetallic acid (TBMA) salt, zirconium titanium phosphate (ZTP), synthesized by us exhibited improved IEC compared to their single salt counterparts, zirconium phosphate and titanium phosphate (13). The thermodynamics and kinetics of ion exchange (14,15), the distribution behavior of metal ions and binary and ternary metal ion separations have been studied, using ZTP and its utility as an ion exchanger established by us (16).

Mixed inorgano-organic hybrids have been attracting significant attention as a new class of materials, since the combination/cooperative interaction between the inorganic and organic component have the potential to provide improved/tunable properties (17–19). Hybrid

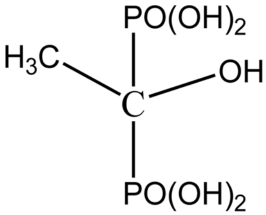


Figure 1. Structure of hydroxy ethylidene diphosphonic acid (HEDP).

materials with a rigid inorganic backbone and flexible organic groupings, possessing functionalities that bear protons (–OH, –COOH, –SO_3H) are synthesized with an aim to modify the number of structural/exchangeable protons that reflects on the IEC values.

Zirconium phosphate and titanium phosphate of the class of TMA salts have shown a number of advantages as an ideal host lattice for the development of new/hybrid materials (20,21). In the tetrahedral moiety of phosphoric acid, $PO(OH)_3$, if H or OH is replaced by R (where R = alkyl/aryl possessing ionogenic groups such as –OH, –COOH, –SO_3H), phosphonic acids are obtained, which when treated with tetravalent metals such as Zr, Ti, Sn, Th, Ce, etc., give rise to novel metal phosphonates. Sol-gel processing is a promising route to synthesis of metal phosphonates using a "Chimie Douce," low temperature approach. Using the sol-gel route, it is possible to introduce a large variety of organic moieties bearing ionogenic groups into an inorganic matrix.

In the present endeavor, a novel hybrid ion exchanger, zirconium titanium hydroxy ethylidene diphosphonate (ZTHEDP) of the class of TBMA salt has been synthesized and characterized. The structure of hydroxy ethylidene diphosphonic acid (HEDP) is presented in Fig. 1. The distribution behavior 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 ZTHEDP has been studied and the distribution coefficient (K_d) evaluated in aqueous as well as various electrolyte media/concentrations. Based on differential selectivity, the breakthrough capacity (BTC) and elution behavior of various metal ions towards ZTHEDP, a few binary and ternary metal ion separations have been carried out.

EXPERIMENTAL

Synthesis of ZTHEDP

A solution containing 0.1 M $TiCl_4$ and 0.1 M $ZrOCl_2 \cdot 8H_2O$ in 10% w/v H_2SO_4 (100 mL) was prepared, to which 200 mL, 0.1 M HEDP solution was added dropwise (flow rate, $1\,\mathrm{mL}\cdot\mathrm{min}^{-1}$) with continuous stirring. After complete precipitation, the gel obtained was stirred for further 3 h, filtered, washed with conductivity water for the removal of adhering ions (chloride and sulphate), and dried at room temperature. The material was then broken down to the desired particle size [30–60 mesh (ASTM)] by grinding and sieving. Five grams of this material was taken and treated with 50 mL, 1 M HNO_3 for 30 minutes with occasional shaking. The sample was then separated from the acid by decantation and treated with conductivity water for the removal of the adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature. This material was used for further studies.

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, and the volume capacity of the ion exchanger were studied according to literature methods (22,23).

Appearance

The synthesized material was physically observed for color, shape, size, opacity, transparency, luster etc.

Percentage Moisture Content

The percentage moisture content of an exchanger is the ability of the exchanger to hold moisture. For the determination of the percentage moisture content, ZTHEDP (~1 g) was allowed to stand in distilled water for 24 h. The material was then filtered and dried at room temperature to remove the surface moisture and weighed. This material was dried at 110°C for 4 h and reweighed after cooling in a 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.

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, the exact weight of the exchanger was taken in a calibrated glass column. After backwashing, the water was drained and the exchanger was allowed to settle. The apparent density is determined using the equation, apparent density = weight of ion exchanger/volume of ion exchange bed.

True Density (D_{ie})

The true density was determined by taking a definite amount of ZTHEDP in a 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 using the equation, $D_{ie} = (W_i - W)/(W_w - W_{iw}) + (W_i - W)$.

Void Volume Fraction

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

Concentration of Fixed Ionogenic Group (C_r)

The concentration of fixed ionogenic group for ZTHEDP was calculated using the equation, $C_r = d_{ie} \times (100 - \%\ moisture) \times IEC/100$.

Volume Capacity of the Resin (Q)

The volume capacity of the exchanger was evaluated using the formula, $Q = (1 - void\ volume\ fraction) \times C_r$.

Chemical Stability

The chemical resistivity of the materials in various media-acids (HCl, H_2SO_4, HNO_3), bases (NaOH and KOH), and organic solvents (ethanol, benzene, acetone, and acetic acid) was studied by taking 500 mg of ZTHEDP in 50 mL of the particular medium and allowed to stand for 24 h. The change in color, nature, and weight was observed.

pH Titration Curve

Acid sites in a material can be titrated against an alkali hydroxide (used for neutralization) and a salt solution of same alkali metal (used as a supporting electrolyte). 500 mg of the material was placed in NaCl (0.1 M, 100 mL) solution. This solution mixture was titrated against the NaOH (0.1 M) solution. After the addition of every 0.5 mL of titrant, sufficient time was provided for the establishment of the equilibrium, till the pH is constant. A pH titration curve is obtained by plotting the pH versus the volume of NaOH.

Ion Exchange Capacity (IEC)

The Na^+ ion exchange capacity (IEC) for materials were determined by the column method (24). 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 IEC of the exchanger in milli equivalent per gram ($meq \cdot g^{-1}$) 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 IEC 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 IEC by the column method (24) as described above.

Distribution Studies

The 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 (25). 100 mg of the exchanger ZTHEDP 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-Visible Spectrophotometer (26,27). Distribution studies have been carried out in aqueous as well as various electrolyte media (NH_4NO_3, HNO_3, $HClO_4$, and CH_3COOH) of varying concentration (0.02 and 0.20 M). The distribution coefficient (K_d) is 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. Each K_d determination was repeated three times and in all cases the deviation from the mean was not greater than ±0.05 mL · g^{-1}.

Breakthrough Capacity (BTC), Elution Studies, and Separation Studies

For the breakthrough capacity, elution, and separation studies, 0.5 g of the ion exchanger, ZTHEDP, was taken in a glass column (30 × 1 cm), washed thoroughly with deionized water, and the flow rate adjusted to 0.5 mL · min^{-1}. 5 mL fractions of each individual 0.001 M metal ion solution was passed through the column and the effluent collected, till the amount of metal ion concentration was the same in the feed and the effluent. The metal ion concentration was determined quantitatively by EDTA titration, AAS, or UV-Visible Spectrophotometer (26,27).

A breakthrough curve was obtained by plotting the ratio C_e/C_o against the effluent volume, where C_o and C_e are the concentrations of the initial solution and effluent respectively. BTC is calculated using the formula $(C_o V_{(10\%)})/W$, where C_o is the concentration of the metal ion (mol L^{-1}), $V_{(10\%)}$ is the volume of the metal ion solution passed through the column when the exit concentration reaches 10% of the initial concentration in mL, and W is the weight of the exchanger in g.

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

For binary or ternary separations, the 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, maintaining a flow rate of 0.5 mL · min^{-1}. The separation was achieved by passing suitable eluants through the column. For a given metal ion pair, the eluant was selected based on the separation factor, calculated using the K_d values of the respective metal ions in different electrolyte media. The electrolyte media, in which the separation factor was the 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.

RESULTS AND DISCUSSION

Characterization of ZTHEDP by various physico-chemical and instrumental methods have been presented in Table 1. A plot of *pH* versus the number of milliequivalents of OH^- ions, is termed as the "*pH* titration curve" or the "potentiometric curve," which gives an idea regarding the acidic nature of the material, weak or strong (22). The *pH* titration curve for ZTHEDP is presented in Fig. 2 which shows that ZTHEDP is a weak cation exchanger.

The Na^+ ion exchange capacity (IEC) of ZTHEDP evaluated at room temperature is found to be $2.26\,meq \cdot g^{-1}$ (24). The IEC (at room temperature) of the calcined samples of ZTHEDP at 100, 200, 300, 400, 500°C were found to be 1.52, 0.16, 0.08, 0.21, 0.22 $meq \cdot g^{-1}$ respectively. The IEC values decrease upto 300°C which could be attributed to the loss of adhered moisture and condensation of structural hydroxyl groups. Further, IEC increases slightly for the samples calcined at 400°C and 500°C. This may be due the fact that, at this temperature, the organic moiety decomposes, leading to the formation of active carbon that may contribute to IEC. This is evidenced by the change in color of the calcined samples to black.

Table 1. Characterization of ZTHEDP

Properties	Observation
Appearance	Light yellow hard granules
Percentage moisture content	$12.54 \pm 0.01\%$
Apparent density	$0.83 \pm 0.01\,g \cdot mL^{-1}$
True density	$1.92 \pm 0.01\,g \cdot mL^{-1}$
Void volume fraction	0.57 ± 0.01
Concentration of fixed ionogenic group	$3.80 \pm 0.01\,mmol \cdot g^{-1}$
Volume capacity of the resin	$1.65 \pm 0.01\,meq \cdot mL^{-1}$
pH titration curve	Weak ion exchanger
Ion exchange capacity (IEC)	$2.26 \pm 0.03\,meq \cdot g^{-1}$
Chemical stability-Acids (maximum tolerable limits)	36 N H_2SO_4, 16 N HNO_3, 11.3 N HCl
Chemical stability-Bases (maximum tolerable limits)	0.25 N NaOH, 0.25 N KOH
Chemical stability-Organic solvents	Ethanol, benzene, acetone, and acetic acid
ICP-AES	
Elemental analysis	Zr:Ti:P = 1:1:3.5
XRD	
Nature of material	Amorphous

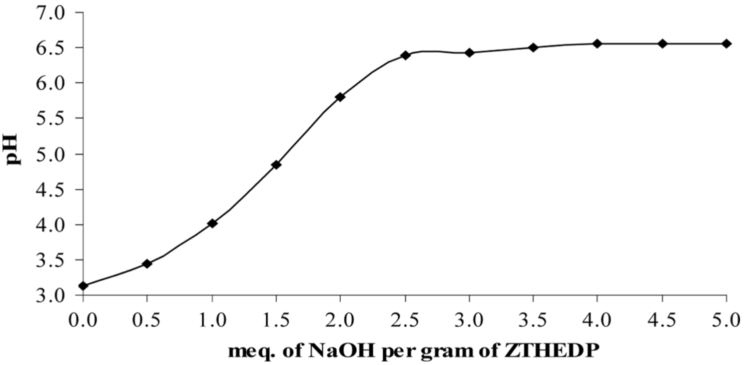


Figure 2. pH titration curve of ZTHEDP.

A study of the chemical resistivity/stability of ZTHEDP 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. No leaching, change in color, nature, and weight was observed, indicating good chemical stability of ZTHEDP in acids and organic solvents media. However, in the base media, above the maximum tolerable limit, the material was completely soluble. This study also gives an idea about the medium, in which separation could be carried out.

The FTIR spectra of ZTHEDP (Fig. 3) exhibits broad bands in the region ~3400 cm^{-1} which is attributed to asymmetric and symmetric –OH stretches. A sharp medium band at ~1620 cm^{-1} is attributed to aquo

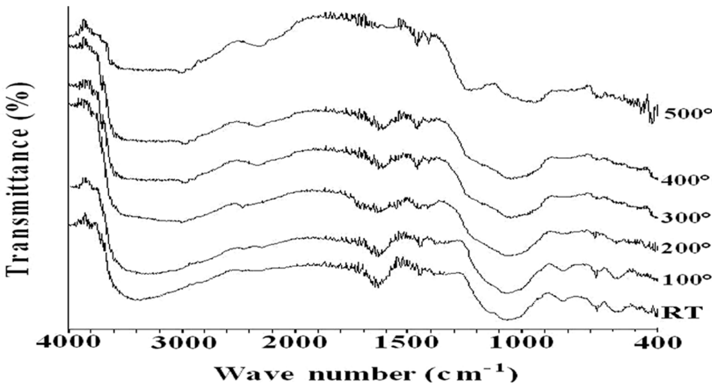


Figure 3. FTIR spectra of ZTHEDP as synthesized (at room temperature) and calcined from 100 to 500°C.

(H–O–H) bending. A band in the region ~1050 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) (28). These bands indicate the presence of structural hydroxyl groups/exchanging sites (H^+ of the –OH) in ZTHEDP. A combination of bands at ~1450 cm^{-1} and ~1375 cm^{-1} is attributed to $\delta_{as}CH_3$ and δ_sCH_3, respectively. Further, from FTIR spectra of calcined samples (Fig. 3), it is observed that the intensity of the peaks at ~3400 cm^{-1} and ~1620 cm^{-1}, representative of the –OH group diminishes as the calcination temperature increases. This is also in keeping with IEC values that decrease as the calcination temperature increases.

Thermal behavior of several TMA salts have been investigated and generally examined for loss of moisture ~80°C, loss of external water molecules, in the range ~100–180°C and in the range ~180°C–400°C and above, for condensation of the structural hydroxyl groups (the H^+ of the –OH being exchange sites for cation exchanger, herein). The Thermogram (Fig. 4) of ZTHEDP, exhibits two regions of weight loss. First weight loss, ~12% within the temperature range 30–120°C, is attributed to the loss of moisture/hydrated water. The second weight loss upto ~23.85% within the temperature range 120–600°C is attributed to condensation of the structural hydroxyl groups as well as the decomposition and the dissociation of organic moieties.

Based on the elemental analysis (ICP-AES) and thermal analysis (TGA) data ZTHEDP has been formulated as $Zr_{0.41}Ti_{0.59}(C_2H_8P_2O_7)_{1.7} \cdot 3H_2O$ respectively using the Alberti and Torracca formula (29).

It is well known that metals have toxic effects. The main sources of occurrence of transition, heavy and rare earth metal ions in waste waters 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

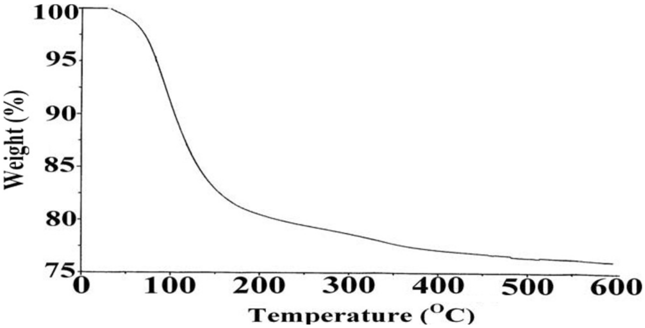


Figure 4. Thermogram of ZTHEDP.

and tissue damage, liver mal-functions, anemia, nervous disorders, and cancer.

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.

With respect to the ion exchanger, the factors responsible are particle size, the presence of functional groups that indicate the nature of the exchanger weak or strong, the ion exchange capacity, the degree of cross linking, and the structure and complexity of the ion exchanger. With respect to exchange media, the factors responsible are concentration, pH, and the nature of the electrolyte, weak or strong, as well as the temperature (30). With respect to metal ion the factors are ionic radius, atomic number, pK_h (K_h = hydrolysis constant), and the ionic charge on the metal ion. Higher valent ions have more affinity for the exchanger. Over and above these three factors the exchange process itself, i.e., the rate of exchange and equilibrium also play an important role in determining the selectivity. On immersing the exchanger in solution, an equilibrium is established between the exchanger and the electrolyte solution, the rate of exchange depending on the size of the exchanging ion and the grain/particle size of the exchanger. The smaller the size of the cation, the greater is the tendency to be hydrated and the 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, which plays a prominent role in determining the selectivity of metal ions (31). 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.

The distribution coefficient (K_d) values evaluated for various metal ions towards ZTHEDP has been presented in Table 2. 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.

The observed selectivity order amongst d-block metal ions is Ni^{2+} (0.72 Å) > Co^{2+} (0.72 Å) > Zn^{2+} (0.74 Å) > Cu^{2+} (0.74 Å); amongst heavy metal ions, Pb^{2+} (1.44 Å) > Cd^{2+} (0.97 Å) > Hg^{2+} (1.10 Å) > Bi^{3+} (0.96 Å) and amongst f-block metal ions, Ce^{3+} (1.11 Å) > La^{3+} (1.15 Å) > Th^{4+} (0.96 Å) > UO_2^{2+} (1.03 Å), values in parenthesis being ionic radii of

Table 2. K_d values (in $\mathrm{mL \cdot g^{-1}}$) for various metal ions towards ZTHEDP at $30 \pm 1°\mathrm{C}$

Metal ion	DMW	0.02 M NH_4NO_3	0.20 M NH_4NO_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_3COOH	0.20 M CH_3COOH
Co^{2+}	2020	263	64	142	85	329	76	2020	1508
Ni^{2+}	2044	239	27	1147	40	234	77	1354	762
Cu^{2+}	1354	577	87	239	548	1063	249	1820	1483
Zn^{2+}	1810	383	53	194	39	150	34	1056	2480
Cd^{2+}	1800	425	52	185	27	128	30	2657	1800
Hg^{2+}	111	19	17	49	52	16	1	2486	24
Pb^{2+}	19800	2657	445	1800	145	1281	1800	6467	6467
Bi^{3+}	53	51	39	42	32	54	45	40	51
La^{3+}	67	233	80	97	24	69	49	198	463
Ce^{3+}	158	99	77	112	41	88	94	152	322
Th^{4+}	58	62	58	62	35	32	91	105	96
UO_2^{2+}	23	29	63	19	161	34	134	31	185

respective metal ions. According to the Bonner series (32), the expected selectivity order for d-block metal ions is $Ni^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+}$; amongst heavy metal ions $Pb^{2+} > Hg^{2+} > Cd^{2+} > Bi^{3+}$ and amongst f-block metal ions $Ce^{3+} > La^{3+} > Th^{4+} > UO_2^{2+}$. The observed selectivity order for most of the metal ions studied can be on the basis of the size of ions and hence the nature of hydration as explained above. Discrepancy in case of Cu^{2+} and Cd^{2+} could be attributed to complexing the ability/stability constant of metal ion with the functional groups (HEDP in the present case) of the exchanger. Pb^{2+} having the highest ionic radii amongst all the metal ions studied, exhibits high selectivity. Th^{4+} with higher valence shows lower affinity due to larger hydrated ionic radii while UO_2^{2+} shows low affinity due to lower valance.

The most promising property of ZTHEDP is its high selectivity for Pb^{2+} as well as all the transition metal ions (Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+}). Further, the K_d values are exceptionally high in the present case compared to earlier work carried out using TMA salts (4,10,33–39).

A plot of C_e/C_o vs. effluent volume is presented in Fig. 5. Breakthrough capacity (BTC) (determined by breakthrough curve, refer to section titled "BTC, separation and Elution studies"), is the dynamic capacity or the operating capacity of a known amount of ion exchange material towards the metal ions in a column in operating condition. K_d values also give an idea of affinity of the metal ion towards the ion exchanger. Therefore, it is expected that the selectivity order based on the K_d values and BTC should be the same. The selectivity order based on the BTC values amongst d-block metal ions is $Cu^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+}$, amongst heavy metal ions $Pb^{2+} > Cd^{2+} > Hg^{2+} > Bi^{3+}$, and amongst f-block metal ions $Ce^{3+} > Th^{4+} > UO_2^{2+} > La^{3+}$. The discrepancy observed compared to the selectivity order based on the K_d values, could be explained to be due to the fact that K_d is determined by a batch process (static), where less amount of exchange material (0.1 g) and sufficient equilibrium time (24 h) is provided to ensure complete exchange, while BTC is determined by a column process (dynamic), where the complete exchange of a particular metal ion depends mainly on the rate of exchange and contact time as well as the flow rate of the feed solution through the column, the bed depth, the selectivity co-efficient, the particle size, the temperature, etc.

Elution behavior of various metal ions towards ZTHEDP has been presented in Table 3, and it is observed that the metal ion recovery is in the range 77–99%. The higher the concentration of the eluant the better is the recovery of the metal ion. Acids in general, are better eluants; however, 1 M HNO_3 is the best eluant for all metal ions. The study shows that, metal ion exchange and elution are easy and possible on the ZTHEDP exchanger using the above-mentioned electrolytes.

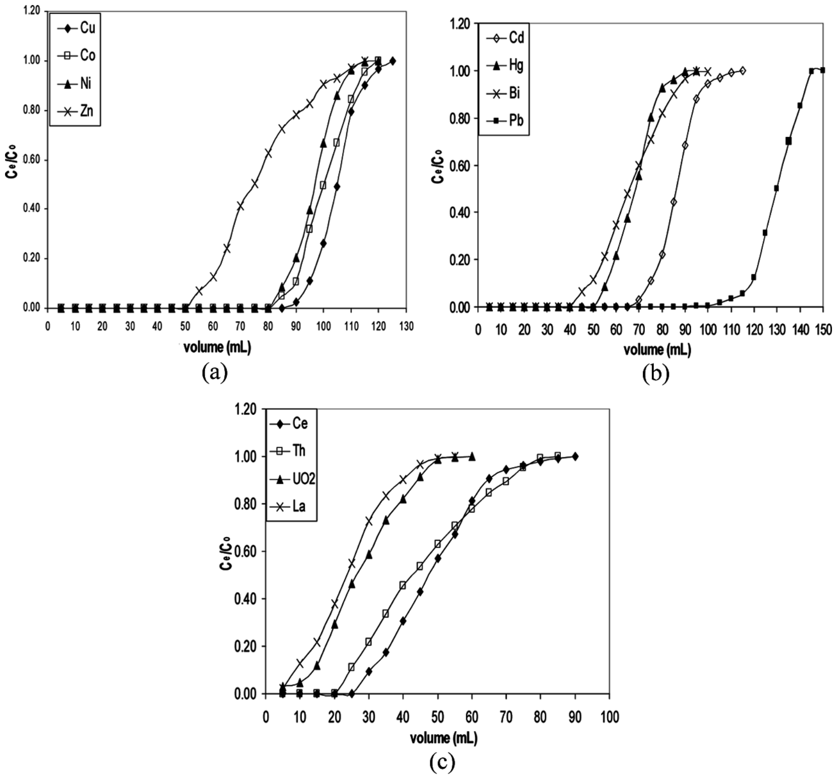


Figure 5. Breakthrough curves for (a) d-block (b) heavy and (c) f-block metal ions.

A study on the distribution behavior 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. The separation factor α, the rate at which two constituents separate on a column, is given by, $\alpha = K_{d1}/K_{d2}$, where K_{d1} and K_{d2} are the distribution coefficients of the two constituents being separated, also provide a guideline for metal separation. The efficiency of an ion exchange separation depends on the condition under which α has a useful value, or influencing in a direction favorable to separation. Since, α is the ratio of the K_d values of the constituent counter ions, the K_d values are determined under the expected solution conditions on the selected ion exchange material. For a given metal ion pair, the eluant was selected based on the separation factor calculated, using K_d values of the respective metal ions in different electrolyte media. The electrolyte media, in which the separation factor was the highest, was selected as the eluant. The greater the deviation of α from unity, the better is the separation.

Table 3. Elution behaviour of metal ions towards ZTHEDP

Metal ion	E_v/%E	0.05 M NH_4NO_3	1.0 M NH_4NO_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_3COOH	1.0 M CH_3COOH
Co^{2+}	E_v	65	60	40	30	55	50	55	50
	%E	85.4	88.1	97.3	99.2	90.2	94.2	92.2	94.1
Ni^{2+}	E_v	75	65	50	40	65	50	70	50
	%E	90.8	93.6	97.9	98.9	90.2	95.2	95.2	97.4
Cu^{2+}	E_v	45	40	45	40	50	45	60	55
	%E	92.4	94.8	97.2	98.1	89.4	90.2	97.2	98.4
Zn^{2+}	E_v	65	60	45	40	60	50	55	50
	%E	88.2	92.2	97.3	99.4	95.2	96.5	92.3	97.2
Cd^{2+}	E_v	55	60	45	40	60	50	70	60
	%E	76.9	82.6	95.2	98.7	90.6	94.8	92.1	95.6
Hg^{2+}	E_v	80	75	45	40	65	55	75	65
	%E	78.4	80.6	96.6	99	95.1	98.1	93.5	96.8
Pb^{2+}	E_v	70	60	50	40	65	50	60	55
	%E	79.2	82.6	97.8	97.9	93.6	96.8	92.8	95.1
Bi^{2+}	E_v	80	70	55	40	65	55	60	50
	%E	80.2	84.1	98.1	99.1	94.8	96.7	94.6	97.9
La^{3+}	E_v	75	70	55	50	65	60	55	50
	%E	87.9	90.3	96.9	98.9	92.5	94.2	92.6	94.6
Ce^{3+}	E_v	80	75	50	40	65	55	60	50
	%E	90.2	92.2	95.5	98.6	93.8	96.3	90.6	93.7
Th^{4+}	E_v	80	75	45	40	65	55	75	65
	%E	89.6	91.8	97.2	99.1	94.9	96.8	89.9	94.8
UO_2^{2+}	E_v	80	70	55	50	75	65	70	60
	%E	88.4	92.8	98.1	99.3	95.1	98	90.9	93.9

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

Table 4. Binary separations of metal ions using ZTHEDP

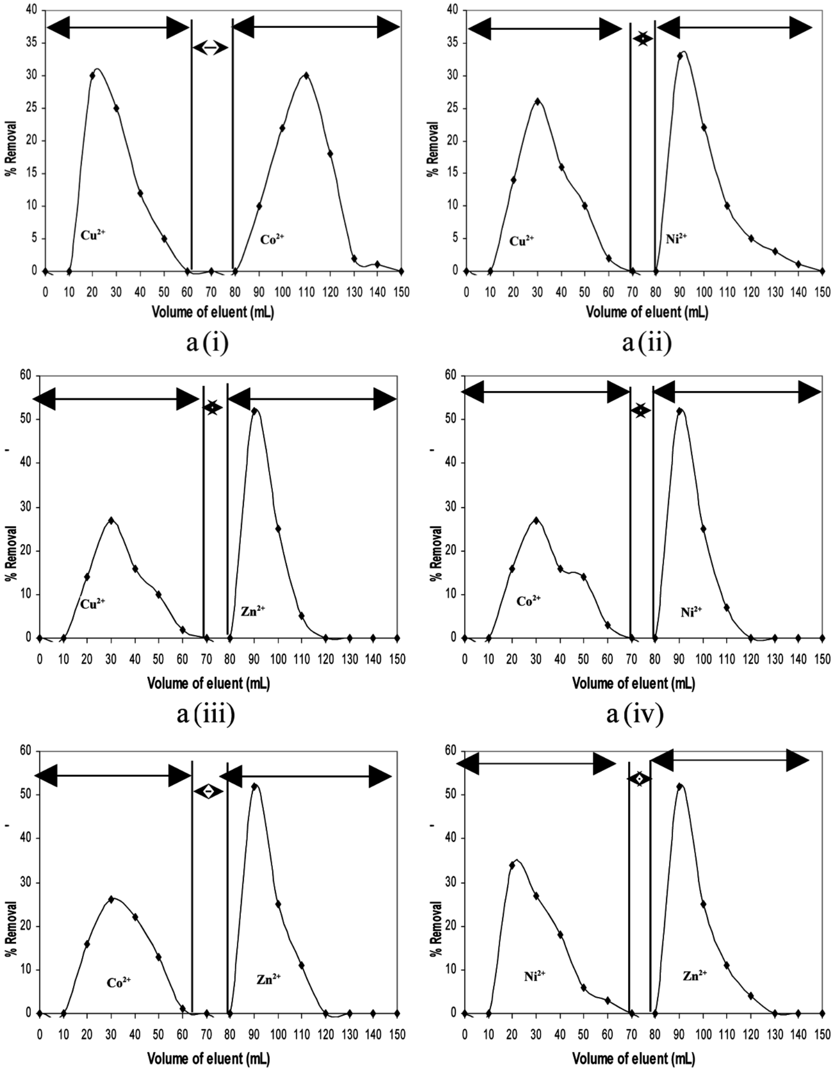
Separations achieved	$\alpha = K_{d1}/K_{d2}$	Eluant	Metal ion (mg)		Recovery (%)
			Loaded	Eluted	
$Cu^{2+} - Co^{2+}$	1.49	0.5 M CH_3COOH (Cu^{2+})	32.0	23.1	72.21
		1.0 M HNO_3 (Co^{2+})	29.5	24.5	83.02
$Cu^{2+} - Ni^{2+}$	1.51	0.5 M HNO_3 (Cu^{2+})	32.0	21.8	67.99
		1.0 M HNO_3 (Ni^{2+})	29.5	24.8	83.98
$Cu^{2+} - Zn^{2+}$	1.34	0.5 M CH_3COOH (Cu^{2+})	32.0	22.2	69.23
		0.5 M HNO_3 (Zn^{2+})	32.5	28.0	86.03
$Co^{2+} - Ni^{2+}$	1.1	0.5 M HNO_3 (Co^{2+})	29.5	22.5	76.43
		1.0 M NH_4NO_3 (Ni^{2+})	29.5	24.9	84.32
$Co^{2+} - Zn^{2+}$	1.12	0.5 M NH_4NO_3 (Co^{2+})	29.5	23.1	78.22
		0.5 M HNO_3 (Zn^{2+})	32.5	28.6	87.89
$Ni^{2+} - Zn^{2+}$	1.13	0.5 M NH_4NO_3 (Ni^{2+})	29.5	26.0	88.04
		0.5 M HNO_3 (Zn^{2+})	32.5	29.9	92.11
Pb^{2+} - Cd^{2+}	11.00	1.0 M CH_3COOH (Pb^{2+})	103.5	65.3	63.11
		1.0 M $HClO_4$ (Cd^{2+})	56.0	42.7	76.23
$Pb^{2+} - Hg^{2+}$	178.38	0.5 M CH_3COOH (Pb^{2+})	103.5	62.5	60.34
		1.0 M $HClO_4$ (Hg^{2+})	100.5	77.7	77.31
Pb^{2+} - Bi^{3+}	373.58	0.5 M CH_3COOH (Pb^{2+})	103.5	66.7	64.42
		1 M CH_3COOH (Bi^{3+})	104.5	81.8	78.31
$Cd^{2+} - Hg^{2+}$	16.22	0.5 M HNO_3 (Cd^{2+})	56.0	42.1	75.26
		0.5 M CH_3COOH (Hg^{2+})	100.5	73.6	73.28
$Cd^{2+} - Bi^{3+}$	33.96	0.5 M $HClO_4$ (Cd^{2+})	56.0	41.4	73.99
		0.5 M CH_3COOH (Bi^{3+})	104.5	81.8	78.26
$Hg^{2+} - Bi^{3+}$	2.09	0.5 M $HClO_4$ (Hg^{2+})	100.5	76.7	76.36
		0.5 M CH_3COOH (Bi^{3+})	104.5	80.8	77.28
$Th^{4+} - La^{3+}$	1.16	0.5 M CH_3COOH (Th^{4+})	116.0	88.5	76.33
		0.5 M $HClO_4$ (La^{3+})	69.5	48.1	69.21
$Th^{4+} - Ce^{3+}$	2.72	0.5 M CH_3COOH (Th^{4+})	116.0	87.2	75.16
		1.0 M $HClO_4$ (Ce^{3+})	70.0	47.1	67.22
$Th^{4+} - UO_2^{2+}$	2.52	0.5 M HNO_3 (Th^{4+})	116.0	89.6	77.22
		1 M HNO_3 (UO_2^{2+})	119.0	95.6	80.36
$Ce^{3+} - La^{3+}$	2.36	0.5 M NH_4OH (Ce^{3+})	70.0	47.8	68.27
		1.0 M $HClO_4$ (La^{3+})	69.5	50.2	72.19
$Ce^{3+} - UO_2^{2+}$	6.87	0.5 M HNO_3 (Ce^{3+})	70.0	48.6	69.44
		1 M HNO_3 (UO_2^{2+})	119.0	96.3	80.96
$La^{3+} - UO_2^{2+}$	2.91	0.5 M HNO_3 (La^{3+})	69.5	49.5	71.25
		0.5 M NH_4NO_3 (UO_2^{2+})	119.0	97.7	82.11

$\alpha = K_{d1}/K_{d2}$, 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%.

K_d values suggest the possibilities for many important binary separations. Based on the separation factor α (K_d in aqueous media), binary separations for all possible metal ion pairs have been carried out. The details of binary separation studies are presented in Table 4 and the plots



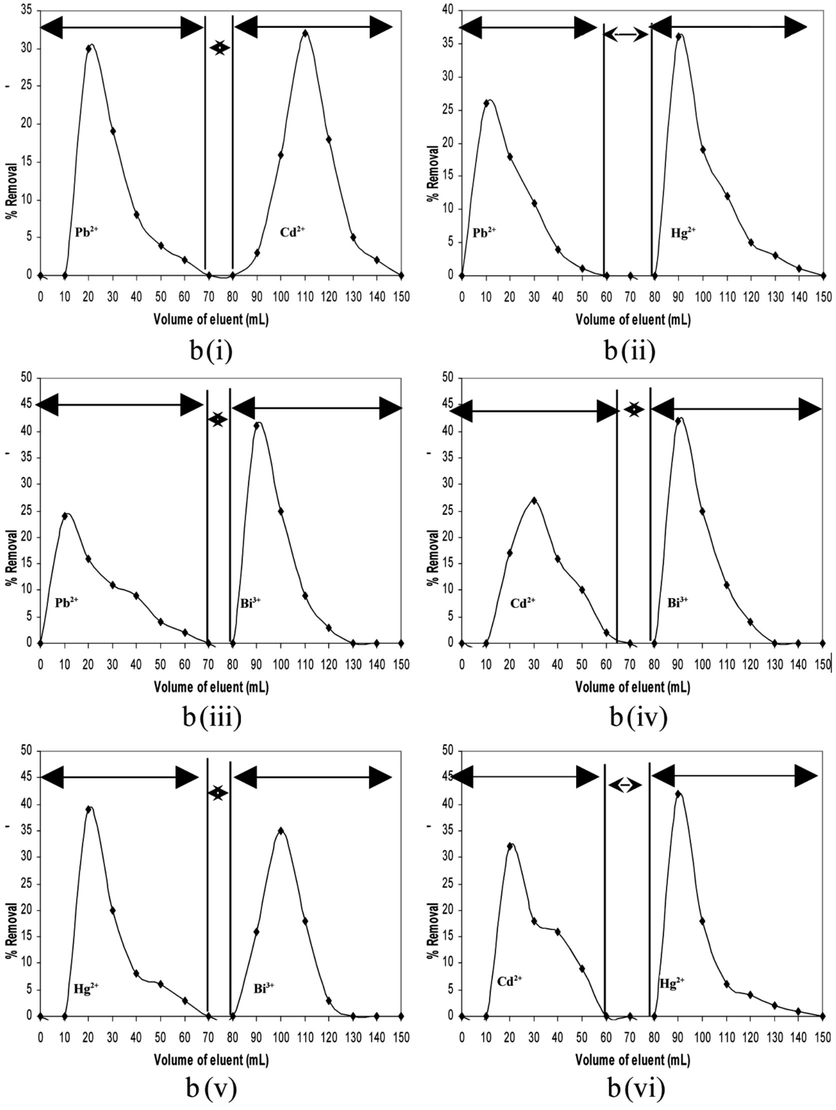
a(i) a(ii)

a(iii) a(iv)

a(v) a(vi)

Figure 6. Binary metal ion separation of (a) d-block (b) heavy and (c) f-block metal ion pair using ZTHEDP.

of the percentage metal removal vs. the eluate volume are presented in Fig. 6. For ternary separation, each case from d-block, heavy, and f-block metal ions have been studied. The details of the studies are presented in Table 5 and the plots of percentage metal removal vs. the eluate volume are presented in Fig. 7.



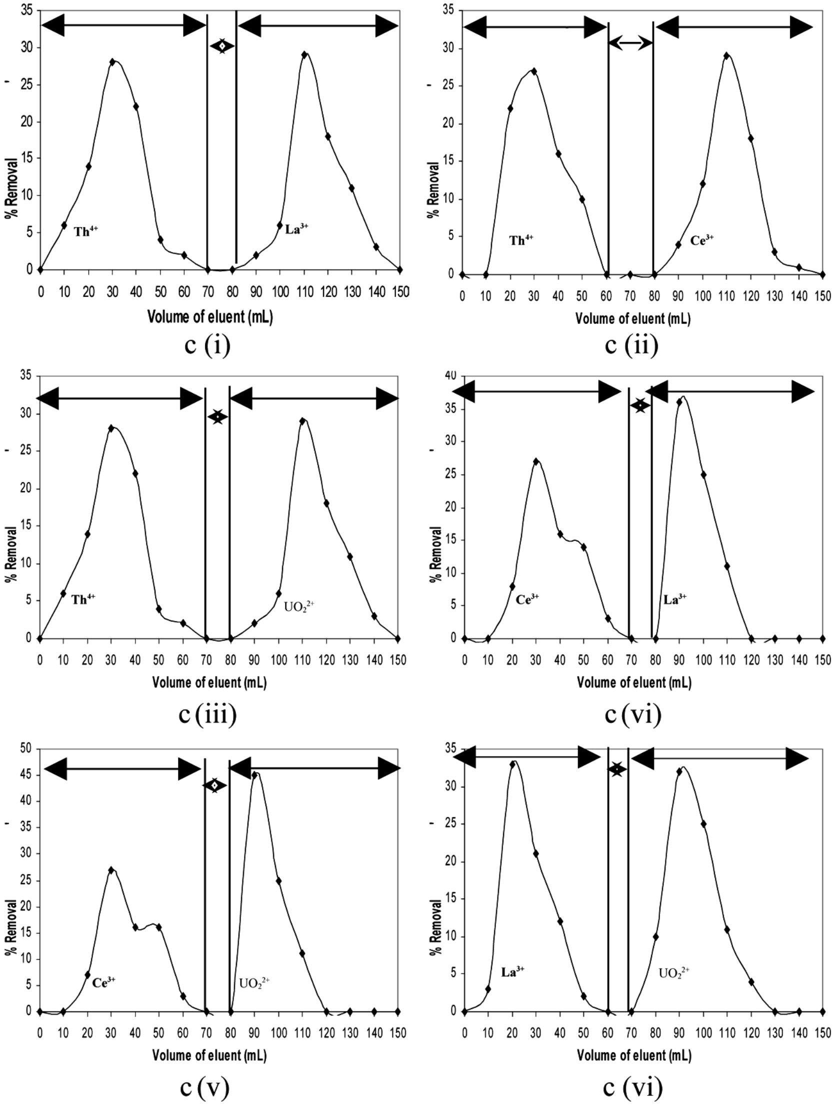
b(i) b(ii)

b(iii) b(iv)

b(v) b(vi)

Figure 6. Continued.

An efficient ion exchange separation may be influenced by the load of the metal ion, the eluant used for separation, flow rate of electrolyte, *p*H, the temperature, the nature of ion exchange material, the particle size, and the length of the column, Other factors responsible for observed peak shapes/elution curves are the distribution coefficient (K_d), the



c (i) c (ii)

c (iii) c (vi)

c (v) c (vi)

Figure 6. Continued.

Table 5. Ternary separations of metal ions using ZTHEDP

		Metal ion (mg)		
Separations achieved	Eluant	Loaded	Eluted	Recovery (%)
$Cu^{2+} - Zn^{2+} - Ni^{2+}$	0.5 M NH_4NO_3 (Cu^{2+})	32.0	21.9	68.45
	0.5 M $HClO_4$ (Zn^{2+})	32.5	21.2	65.33
	0.5 M HNO_3 (Ni^{2+})	29.5	18.4	62.26
$Hg^{2+} - Cd^{2+} - Pb^{2+}$	0.5 M $HClO_4$ (Hg^{2+})	100.5	67.6	67.22
	0.5 M HNO_3 (Cd^{2+})	56.0	35.3	63.12
	1.0 M HNO_3 (Pb^{2+})	103.5	60.2	58.19
$La^{3+} - Th^{3+} - Ce^{4+}$	0.5 M HNO_3 (La^{3+})	69.5	38.3	55.12
	0.5 M $HClO_4$ (Th^{4+})	116.0	61.9	53.36
	1.0 M HNO_3 (Ce^{3+})	70.0	35.9	51.29

%recovery = (concentration of metal ion eluted/concentration of metal ion loaded) × 100.

Maximum deviation in %Recovery = ±3%.

retardation factor (R), the retention volume (V_r), the column capacity, and the temperature.

In binary and ternary separations, the separation efficiency is indicated by

1. percentage recovery and
2. peak shapes/elution curves of the constituent metal ions, in terms of Langmurian/non-Langmurian which indicates how well one metal ion is separated in the presence of another metal ion.

When a solution containing metal ions is passed through a column containing an exchanger, based on differential affinity, the various species get strongly or weakly bound on the exchanger. During the elution process, pure electrolyte is eluted first, followed by weakly bound species, and finally the strongly bound species. The separation efficiency depends on differential migration of metal ion in a mobile/stationary phase. Deviations are observed referred to as "zone spreading," caused by diffusion of metal ion in a stationary phase (eddy diffusion), the concentration gradient in the stationary/mobile phase (longitudinal diffusion), and mass transfer of metal ion in the stationary phase (exchanger), and the mobile phase (electrolyte).

Generally, for single ion elution, symmetrical bell shaped curves are observed.

Further tailing effects are attributed to

1. high K_d values (due to which the metal ion is retained for long time on stationary phase) and
2. irregular or non controlled flow.

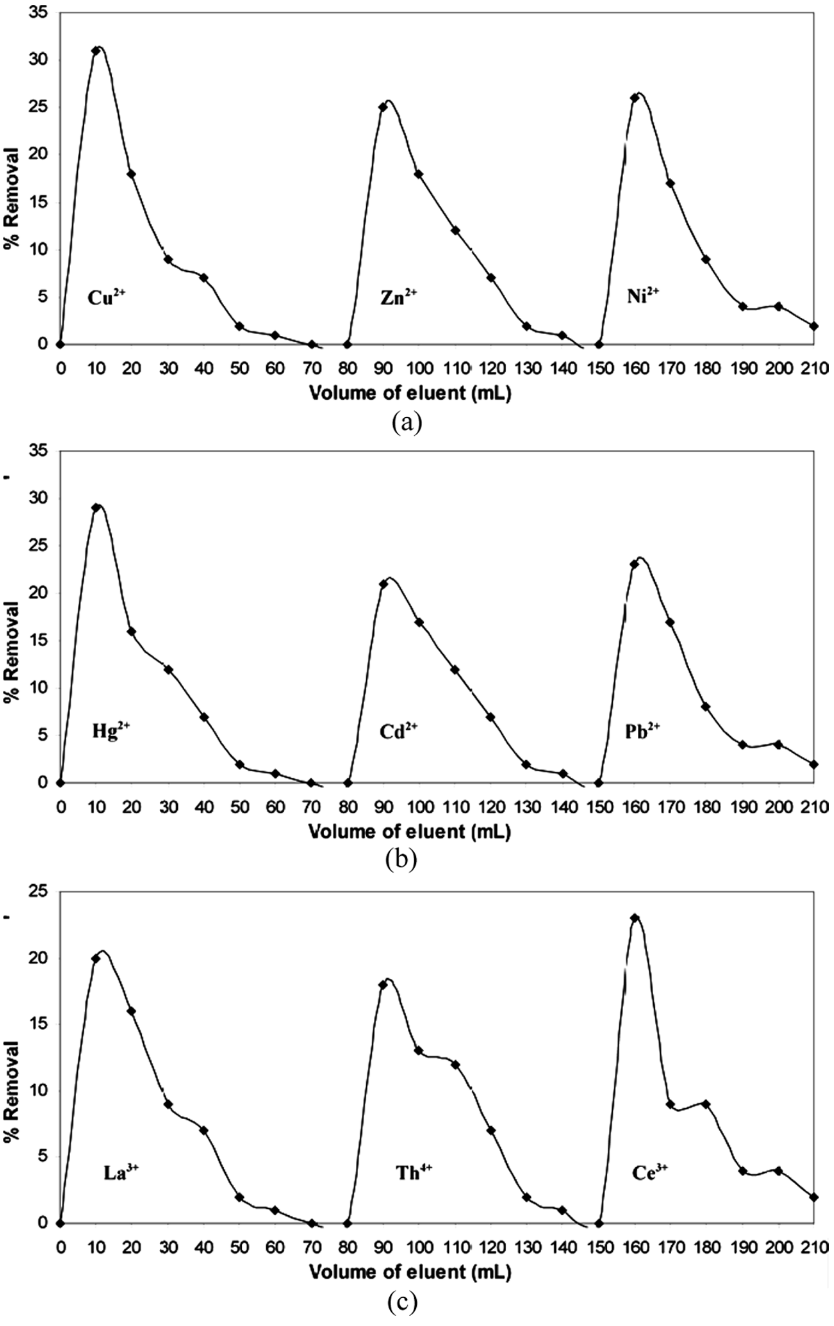


Figure 7. Ternary metal ion separation using ZTHEDP.

From Fig. 6, it is observed that in binary metal ion separations, in all cases, two distinct elution curves are observed (Langmurian type), indicating good separations.

In binary separations for d-block ions, the separation efficiency is in the range 68–92%. Though the separation factor is less in case of transition metal ion pairs, the separation is found to be quite efficient. In most cases, Zn^{2+} exhibits efficient separation in terms of metal recovery (86–92%); however, tailing is observed. Further, for the metal ion pair $Ni^{2+} - Zn^{2+}$, good metal recovery (86–92%) is observed.

In binary separations for heavy metal ions, the separation efficiency is in the range 60–78%. Amongst metal ion pairs, $Pb^{2+} - Cd^{2+}$ and $Cd^{2+} - Bi^{3+}$ exhibit good efficiency in terms of peak shape. For heavy metal ions, irrespective of metal ion pairs, Cd^{2+} (74–76%), Hg^{2+} (73–77%), and Bi^{3+} (77–78%) recoveries are obtained. Poor metal ion recovery (60–64%) in case of Pb^{2+} is probably due to high K_d value. This is also supported by the tailing observed in the elution curves. This observation is also in keeping with the selectivity order based on K_d values, $Pb^{2+} > Cd^{2+} > Hg^{2+} > Bi^{3+}$. Higher K_d values indicate less recovery.

In binary separations for f-block metal ions, the separation efficiency is in the range 67–82%. Good separations are observed for all the metal ion pairs, particularly, $Th^{4+} - La^{3+}$ and $La^{3+} - UO_2^{2+}$ in terms of peak shapes as well as metal ion recovery. Ce^{3+} elution curves show tailing effect, attributed to high K_d value amongst the f-block metal ion studied. UO_2^{2+} having a low K_d value, exhibits good metal recovery and a symmetrical peak shape in all cases.

In ternary separations, for d-block ($Cu^{2+} - Zn^{2+} - Ni^{2+}$), heavy ($Hg^{2+} - Cd^{2+} - Pb^{2+}$) and f-block ($La^{3+} - Th^{4+} - Ce^{3+}$) metal ion separations are in the range 62–68%, 58–67%, and 51–55% respectively. In all cases, three distinct peaks are observed; however, with tailing effects for every metal ion eluted. Probably the separation process becomes complex, attributed to the loss of metal ions during the changeover of the eluant, interference of metal ions, pH, simultaneous elution of two or more metal ions with the same eluant, and lastly, experimental errors involved in the determination of metal ions in the presence of other ions, etc. Overall, good separations are observed (particularly in binary system) and recovery is quantitative and reproducible in all cases.

CONCLUSIONS

ZTHEDP exhibits preparative reproducibility, good IEC, and is both chemically and thermally stable, which are important characteristics for materials to behave as cation exchangers. Further, it exhibits high selectivity for Pb^{2+} as well as transition metal ions (Ni^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}). Efficient metal separations carried out using ZTHEDP indicate good potential for this material to be used as a cation exchanger.

REFERENCES

1. Quek, S.Y.; Wase, D.; Forster, C.F. (1998) The use of sago waste for the adsorption of lead and copper. *Water SA*, *24*: 251.
2. Deans, J.R.; Dixon, B.G. (1992) Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers. *Water Res.*, *26*: 469.
3. Trivedi, R.K. (2000) *Advances in Waste Water Treatment Technologies*; Global Science Publications: Aligarh, India.
4. Siddiqui, W.A.; Khan, S.A. (2007) Synthesis, characterization and ion exchange properties of zirconium(IV) tungstoiodophosphate, a new cation exchanger. *Mater. Sci.*, *30*: 43.
5. Velmurugan, S.; Sathyaseelam, V.S.; Narasimhan, S.V.; Mathur, P.K. (1991) New Development in Ion Exchange, Proc. of Int. Conf. Ion Exch. (ICIE'91), Tokyo.
6. Hafez, M.A.; Kenway, I.M.M.; Akl, M.A.; Lshein, R.R. (2001) Preconcentration and separation of total mercury in environmental samples using chemically modified chloromethylated polystyrene-PAN (ion-exchanger) and its determination by cold vapour atomic absorption spectrometry. *Talanta*, *53*: 749.
7. Varshney, K.G.; Khan, M.A. (1991) *Inorganic Ion Exchangers in Chemical Analysis*, Qureshi, M., Varshney, G.; eds); CRC Press: Boca Raton, Florida.
8. Clearfield, A.. (1982) *Inorganic Ion Exchange Materials*; CRC Press: Boca Raton, Florida, USA.
9. Amphlett, C.B. (1961) *Treatment and Disposal of Radioactive Wastes*; Pergamon: Oxford.
10. Varshney, K.G.; Premadas, A. (1981) Synthesis, composition, and ion-exchange behavior of thermally stable Zr(IV) and Ti(IV) arsenophosphates: Separation of metal ions. *Sep. Sci. Technol.*, *16*: 793.
11. Choube, U.N.; Turel, Z.R. (2003) Radiochemical separation and adsorption of some metal ions with inorganic ion exchanger [Eu(III)]. *Czech. J. Phys.*, *53*: 539.
12. Sing, P.; Rawat J.P.; Rehman, N. (2003) Synthesis and characterization of zirconium(IV) iodovanadate and its use as electron exchanger. *Talanta*, *59*: 443.
13. Jayswal, A.; Patel, H.; Maheria, K.; Thakkar, R.; Chudasama, U. (2006) *Proc. 15th Nat. Symposium on Thermal Analysis*, University of Rajasthan, Jaipur, RamaRao, G.A.; Parida, S.C.; Ravindran, P.V.; Bharadwaj, S.R.; Venugopal, V., eds, 15: 407.
14. Thakkar, R.P.; Chudasama, U.V. (2007) Synthesis, Characterization and thermodynamics of exchange using zirconium titanium phosphate cation exchanger. *Collect. Czech. Chem. Commun.*, *72*: 1306.
15. Amin, J.; Thakkar, R.; Chudasama, U. (2006) A study on equilibrium and kinetics of ion exchange of alkaline earth metals using an inorganic cation exchanger–zirconium titanium phosphate. *J. Chem. Sci.*, *118*: 185.

16. Thakkar, R.; Chudasama, U. (2009) Synthesis and Characterization of zirconium titanium phosphate and its application in separation of metal ions. *J. Hazar. Mat.*, in press.
17. Corriu, R.J.P.; Leclercq, D. (1996) Recent developments of molecular chemistry for sol-gel processes. *Angew. Chem. Int. Ed. Engl.*, *35*: 1420.
18. Sanchez, C.; Soler-Illia, G.J.; de, A.A.; Ribot, F.; Lalot, T.; Mayer, C.R.; Cabuil, V. (2001) Designed hybrid organic–inorganic nanocomposites from functional nanobuilding blocks. *Chem. Mater.*, *13*: 3061.
19. Alexandre, M.; Dubois, P. (2000) Polymer layered silicate nanocomposites: preparation, properties anduses of a new class of materials. *Mater. Sci. Eng., R28*: 1.
20. Varshney, K.G.; Pandit, H.A. (2002) Thermodynamics of the Na(I)-H(I), K(I)-H(I) and Ca(II)-H(I) exchanges on zirconium(IV) aluminophosphate cation exchanger. *Colloids Surf. A*, *201*: 1.
21. Zhilei, Y.; Yasuhiro, S.; Jihong, Y.; Sixiu S.; Osamu, T.; Ruren, X. (2004) Microemulsion-based synthesis of titanium phosphate nanotubes via amine extraction system. *J. Am. Chem. Soc.*, *126*: 8882.
22. Helfferich, F. (1962) *Ion Exchange*; McGraw Hill: New York.
23. Kunnin, R. (1958) *Ion Exchange Resin*; Wiley: London, UK.
24. Maheria, K.; Chudasama, U. (2007) Studies on sorption and elution behavior of dyes using titanium phosphonate. *J. Sci. Ind. Res.*, *66*: 1047.
25. Qureshi, M.; Varshney, K.G.; Isaraili, A.H. (1971) Synthesis, ion-exchange behaviour and composition of tin(IV) hexacyanoferrate(II). *J. Chromatogr. A*, *59*: 141.
26. Jeffery, G.H.; Bassett, J.; Mendham, J.; Denney, R.C. (1978) *Vogel's Text Book of Quantitative Inorganic Analysis*; 5th ed., Longman Group Green: London, UK.
27. Frank, J.W. (1965) *The Analytical Uses of Ethylenediamine Tetraacetic Acid*; D. Van Nostrand Company, Inc: New Jersey.
28. Slade, R.C.T.; Knowels, J.A.; Jones, Roziere, D.J. (1997) The isomorphous acid salts α-$Zr(HPO_4)_2 \cdot H_2O$, α-$Ti(HPO_4)_2 \cdot H_2O$ and α-$Zr(HAsO_4)_2 \cdot H_2O$ Comparative thermochemistry and vibrational spectroscopy. *J. Solid State Ionics*, *96*: 9.
29. Alberti, G.; Torracca, E. (1968) Crystalline insoluble acid salts of polyvalent metals and polybasic acids – VI: Preparation and ion-exchange properties of crystalline titanium arsenate. *J. Inorg. Nucl. Chem.*, *30*: 3075.
30. Sasaki, T.; Komatsu, Y.; Fujiki, T. (1983) Ion-Exchange Properties of hydrous titanium dioxide with a fibrous form obtained from potassium dititanate. *Solv. Extr. Ion Exch.*, *1*: 775.
31. Abou-Mesalam, M.M. (2003) Sorption kinetics of copper, zinc, cadmium and nickel ions on synthesized silico-antimonate ion exchanger. *Colloids Surf. A*, *225*: 85.
32. Khopkar, S.M. (2008) *Basic Concepts of Analytical Chemistry*; New Age International Publishers: New Delhi, India.
33. Qureshi, M.; Rathore, H.S. (1969) Synthesis and ion-exchange properties of titanium molybdates. *J. Chem. Soc. (A)*, *25*: 2515.

34. Pandit, B.; Chudasama, U. (1998) Synthesis and characterization of a new phase of titanium tungstate. *Ind. J. Chem.*, *37*: 931.
35. Qureshi, M.; Rawat, J.P.; Gupta, A.P. (1976) Synthesis and ion-exchange properties of niobium arsenate. *J. Chromatogr.*, *118*: 167.
36. Janardanan, C.; Nair, S.M.K. (1992) The efficacy of antimony(III) molybdotungstate as an exchanger for the separation of lead. *Indian J. Chem.*, *31A*: 136.
37. Jayswal, A.; Chudasama, U. (2007) Synthesis and characterization of a new phase of zirconium phosphate for the separation of metal ions. *J. Iran. Chem. Soc.*, *4*: 510.
38. Maheria, K.; Chudasama, U. (2007) Synthesis and characterization of a new phase of titanium phosphate and its application in separation of metal ions. *Indian J. Chem. Technol.*, *14*: 423.
39. Varshney, K.G.; Tayal, N.; Khan, A.A.; Niwas, R. (2001) Synthesis, characterization and analytical applications of lead(II) selective polyacrylonitrile thorium(IV) phosphate: A novel fibrous ion exchanger. *Colloids Surf. A*, *181*: 123.