ION EXCHANGE LETTERS

Synthesis and characterization of a novel hybrid cation exchange material and its application in metal ion separations

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ABSTRACT

A novel hybrid cation exchange material of the class of tetravalent metal acid (TMA) salt, zirconium diethylene triamine pentamethylene phosphonate (ZrDETPMP) has been synthesized by sol gel method. The material has been analyzed by spectroscopy and thermal methods. Physico-chemical and ion exchange characteristics have also been studied. Distribution coefficient (K_d) has been determined in aqueous as well as various electrolyte media/concentrations for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+} (heavy metal ions) using ZrDETPMP. Based on the differential affinity/selectivity, breakthrough capacity (BTC) and elution behaviour of various metal ions towards ZrDETPMP, a few binary and ternary metal ions separations have been carried out.

Keywords: Tetravalent metal acid salt; hybrid material; metal phosphonate; cation exchanger; zirconium diethylene triamine pentamethylene phosphonate; metal separation.

INTRODUCTION

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[1,2]. 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[3].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 substances from aqueous effluents[4].

Inorganic ion exchangers of the class of tetravalent metal acid (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[5-7]. TMA salts are cation exchangers that 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 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.

In the search for new ion exchange materials, inorgano-organic hybrids are making a huge impact. A major advantage of inorgano-organic hybrid materials is the rigid inorganic backbone and the flexibility of the organic groupings that give a wide range of properties. Anchoring of organic units on the backbone of TMA salts is of particular interest, since the resulting material has the added advantage of both its counterparts in terms of thermal and chemical stability and cation exchange capacity (CEC). M(IV) Phosphates (where M(IV) = Zr, Ti, Sn, Ce and Th) have been widely used as cation exchangers and have shown a number of advantages as an

ideal host lattice[8]. 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 –COOH, –OH, –SO_3H etc.), phosphonic acids are obtained, which when treated with tetravalent metals such as Zr, Ti, Sn, Th, Ce, etc. give rise to novel metal phosphonates[9-11].

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[12,13]. Claw type phosphonic acid such as diethylene triamine pentamethylene phosphonic acid (DETPMP), Figure 1, possessing ten structural hydroxyl groups, permits versatile control of the surface modification in terms of CEC, having the tendency to offer good affinity as well as selectivity for metal ions. Titania-phosphonate hybrids using claw type aminophosphonic acids have been synthesized and characterized and their utility as adsorbents has been proposed earlier[12]. Novel hybrid metal phosphonates - zirconium hydroxy ethylidene diphosphonate (ZrHEDP)[14], titanium hydroxy ethylidene diphosphonate (TiHEDP)[15] and zirconium titanium hydroxy ethylidene diphosphonate (ZTHEDP)[16,17] have been synthesized and ion exchange characteristics of these materials have been reported earlier by us. In another publication, zirconium diethylene triamine pentamethylene phosphonate (ZrDETPMP) has been synthesized, characterized[18] and thermodynamics and kinetics of ion exchange[19] studied.
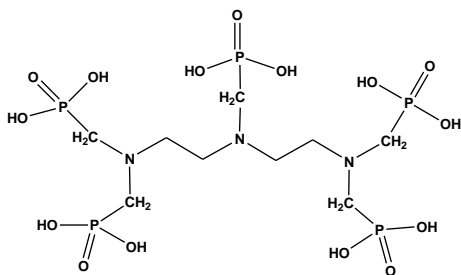

Figure 1 *Structure of DETPMP*

In the present endeavour, the possible use of ZrDETPMP as an ion exchanger for separation of metal ions has been explored. Distribution coefficient (K_d) for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+} (heavy metal ions) towards ZrDETPMP, has been 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 ZrDETPMP, a few binary and ternary metal ion separations have been carried out.

EXPERIMENTAL

All chemicals and reagents used are of analytical grade. Double distilled water was used for all the studies. ZrDETPMP has been synthesized by sol-gel method, as reported earlier[18,19].

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, volume capacity, pH titration curve, CEC) and chemical stability of ZrDETPMP were studied according to literature methods[16,20,21].

ZrDETPMP has been analyzed for zirconium and phosphorus content using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Labtam, 8440 Plasmalab) while carbon, hydrogen and nitrogen content was analyzed on CHN analyzer (Thermo finnigan, Flash EA 1112 series). Composition of ZrDETPMP has been formulated based on earlier studies[22]. FTIR spectra was obtained using KBr wafer on a Shimadzu (Model 8400S). TGA was performed on a Shimadzu, DT-30 thermal analyzer at a heating rate of 10°C per minute. DSC of the material was performed on a Shimadzu, DSC-50 analyzer. X-ray diffractogram ($2\theta = 10 – 90°$) was obtained on an X-ray diffractometer (Brucker AXS D8) with Cu-Kα radition (X-ray source of wavelength 1.5418 Å). SEM of the material was obtained on Jeol JSM-5610-SLV scanning electron microscope.

Distribution Studies

Distribution studies for metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Bi^{3+} were carried out by batch method[23]. 0.1 g of the exchanger ZrDETPMP 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[24,25]. 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). Distribution coefficient (K_d) was evaluated using the expression,

$$K_d = \frac{(I-F)}{F} \times \frac{V}{W} \text{ (mL} \cdot \text{g}^{-1})$$
……………….....(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.

BTC, Elution Studies and Separation Studies
For BTC, elution and separation studies, 0.5 g of the ion exchanger, ZrDETPMP, was taken in a glass column (length = 30 cm, inner diameter = 1 cm, bed height = 1.3 cm), and washed thoroughly with double distilled water and flow rate adjusted to 0.5 mL·min^{-1}. In all cases, metal ion concentration was determined quantitatively by EDTA titration, AAS or UV-Vis spectrophotometer[24,25]. For BTC, 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 (Figure 2) 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,

$$BTC = \frac{C_0 V_{(10\%)}}{W}$$
………………………..(2)

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 (single metal), column was prepared as above. Metal ion (0.001 M, 10 mL) was loaded onto the column. Metal ion loaded was eluted with reagents like HNO$_3$, HClO$_4$, CH$_3$COOH and NH$_4$NO$_3$ of 0.02 and 0.2 M concentration. The % metal eluted is expressed as,

$$\% \text{ Metal eluted} = \frac{\text{Amount of metal ion eluted}}{\text{Amount of metal ion loaded}} \times 100$$
………………...………………………...(3)

For binary and ternary separations, column was prepared as above. The mixture of the metal ions (0.001 M, 10 mL of each metal ion) to be separated was loaded on it. The separation was achieved by passing suitable eluant through the column. The percentage metal eluted was calculated using equation (3).
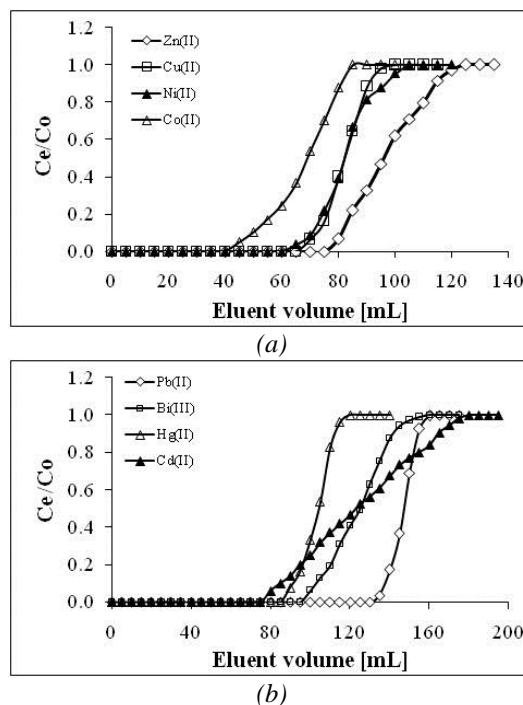
RESULTS AND DISCUSSION
Physico-chemical, ion exchange characteristics and instrumental methods of characterization for ZrDETPMP have been studied earlier[18,19] and presented in Table 1.

The distribution coefficient (K_d) values evaluated for various metal ions towards ZrDETPMP 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. Amongst transition metal ions, the observed selectivity order is Zn^{2+} (0.74 Å) > Cu^{2+}(0.72 Å) > Ni^{2+}(0.72 Å) > Co^{2+}(0.74 Å) and amongst heavy metal ions, the observed selectivity order is Pb^{2+} (1.44 Å) > Bi^{3+}(0.96 Å) > Hg^{2+}(1.10 Å) > Cd^{2+}(0.97 Å), values in parenthesis being ionic radii of the 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 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[16]. Discrepancy observed in case of Bi^{3+}, could be attributed to higher ionic charge.

Breakthrough curve (a plot of C$_e$/C$_0$ vs. effluent volume) is presented in Figure 2. Breakthrough capacity (BTC) is the dynamic capacity or operating capacity of a 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 in the present study confirming the order of selectivity. The BTC values have been presented in Table 2.

Table 1 *Physico-chemical, Ion Exchange and instrumental methods of characterization for ZrDETPMP*

Appearance			White opaque granules
% moisture content			8.54
Particle size [mm]			0.25 – 0.59
Apparent density [g.mL^{-1}]			0.35
True density [g.mL^{-1}]			1.40
Void volume fraction			0.76
Concentration of fixed ionogenic group [mmol·g^{-1}]			3.01
Volume capacity [meq.mL^{-1}]			0.73
pH titration curve			Weak cation exchanger
CEC [meq.g^{-1}]			2.34
Chemical stability (Maximum tolerable limit)	Acids	H_2SO_4	18 N
		HNO_3	16 N
		HCl	11.3 N
	Bases	NaOH	0.5 N
		KOH	0.5 N
	Organic solvents	Ethanol, acetone, benzene, acetic acid	Stable
Elemental analysis			
ICP-AES	Zr : P ratio		1 : 1.65
CHN Analysis [%]			C= 7.6, H=4.0, N=3.9
Molecular formula of ZrDETPMP			$(ZrO)_3C_9H_{23}N_3P_5O_{15}\cdot nH_2O$
FTIR (Band [cm^{-1}] and Group assigned)		~ 3400	-OH$_{str}$
		~1638	-OH$_{bend}$
		~1050	P=O$_{str}$
TGA and DSC	25-120°C	~ 7 % Wt. loss	Due to moisture and hydrated water
	Endotherm at	~105 °C	
	200-700 °C	~ 42 % Wt. loss	Due to condensation of structural hydroxyl groups and decomposition of organic moiety
	Exotherm at	~304 °C	
XRD	Absent of sharp peak		Amorphous
SEM	Irregular particle size		Amorphous

(a)

(b)

Figure 2 *Breakthrough curve of (a) transition metal ions and (b) heavy metal ions*

In binary and ternary separations, the separation efficiency is indicated by (1) Percentage elution/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. Generally, for single metal ion elution, symmetrical bell shaped curves are observed. 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.

The elution behaviour of single metal ions (Table 3) using ZrDETPMP shows metal ion eluted is in the range ~90 to 99 %. Good elution is observed due to non interference of elements. Using 0.2M HNO_3, order of % metal eluted amongst transition metal ions is Co^{2+} (98.2 %) > Ni^{2+} (97.3 %) > Cu^{2+} (95.4 %) > Zn^{2+} (95.3) and amongst heavy metal ions is Cd^{2+} (98 %) > Bi^{3+} (97.6 %) > Hg^{2+} (94.8 %) > Pb^{2+} (93.8). This observation is in keeping with selectivity order of metal ions, which shows that metal ions with high selectivity (high K_d values) are less eluted and vice-versa. Higher concentration of eluent and acids in general, are better eluents. 0.2 M HNO_3 is the best eluent for most metal ions. Further, all elution curves are symmetrical bell

Table 2 *K_d values [in mL·g^{-1}] and BTC [in mmol·g^{-1}] values of metal ions using ZrDETPMP*

Metal ion	BTC	DDW	NH$_4$NO$_3$		HNO$_3$		HClO$_4$		CH$_3$COOH	
			0.02 M	0.20 M	0.02 M	0.20 M	0.02 M	0.20 M	0.02 M	0.20 M
Co^{2+}	0.11	38	189	30	208	*NS	147	*NS	1053	29
Ni^{2+}	0.15	90	149	NS	317	*NS	182	61	21	*NS
Cu^{2+}	0.16	332	195	423	121	173	113	597	242	512
Zn^{2+}	0.18	350	169	236	163	48	106	5	201	168
Cd^{2+}	0.17	579	524	379	94	74	109	74	866	765
Hg^{2+}	0.19	2962	1347	1223	3358	1155	5492	1094	3358	986
Pb^{2+}	0.28	4143	4538	1333	274	22	399	70	4143	1972
Bi^{3+}	0.21	3089	3089	2678	3637	780	1994	721	1992	1239

* *NS = no sorption, DDW= Double distilled water*

Table 3 *Percentage elution of metal ions in different electrolyte media*

Metal ion	0.02 M NH$_4$NO$_3$	0.2 M NH$_4$NO$_3$	0.02 M HNO$_3$	0.2 M HNO$_3$	0.02 M HClO$_4$	0.2 M HClO$_4$	0.02 M CH$_3$COOH	0.2 M CH$_3$COOH
Co^{2+}	92.2	96.4	96.3	98.2	95.2	96.6	90.1	91.5
Ni^{2+}	85.8	87.6	90.9	97.3	90.2	96.2	88.2	89.9
Cu^{2+}	65.4	70.8	90.2	95.4	90.4	92.4	86.2	86.4
Zn^{2+}	88.4	92.3	93.1	95.3	92.2	94.4	91.3	92.5
Cd^{2+}	87.8	89.9	97.7	98.0	96.0	97.1	89.2	93.4
Hg^{2+}	86.5	88.9	91.2	94.8	92.2	93.2	90.2	92.2
Pb^{2+}	84.2	86.5	92.5	93.8	90.2	92.2	90.4	91.5
Bi^{3+}	83.2	88.9	91.6	97.6	93.2	95.6	95.6	96.2

Eluent volume = 70 mL and 60 mL for 0.02 M and 0.2 M electrolytes respectively

shaped indicating elution efficiency.

A study on distribution behaviour of metal ions in various electrolyte media gives an idea about the eluents that can be used for separation. Separation factor α, the rate at which two constituents separate on a column, given by,

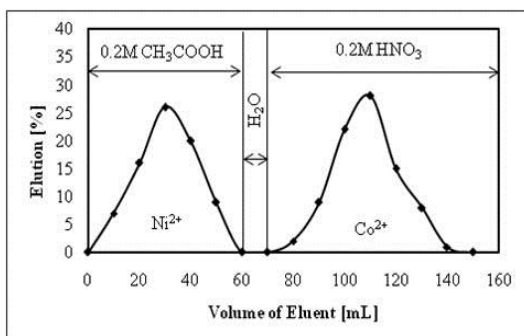$$\alpha = \frac{K_{d1}}{K_{d2}}$$ ……………………………………(5)

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 eluent.
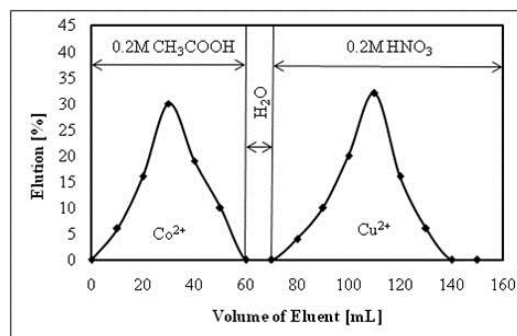
In binary separations, separation efficiency is in the range 72-92 % amongst transition metal ions and 75-91 % amongst heavy metal ions (Table 4 and Table 5). In all cases of binary separation, irrespective of metal ion pair, maximum % metal eluted is Zn^{2+} (92 %), Cu^{2+} (88 %), Co^{2+} (85 %), Ni^{2+} (80 %) (amongst transition metal ions) and Cd^{2+} (90 %), Hg^{2+} (88 %), Bi^{3+} (84 %), Pb^{2+} (79 %) (amongst heavy metal ions). This observation is in keeping with separation factor (α) and K_d values of metal ions. % metal eluted decreases with decreasing separation factor and increases with increasing separation factor and as explained earlier metal ions with high K_d values are less eluted and vice-versa.

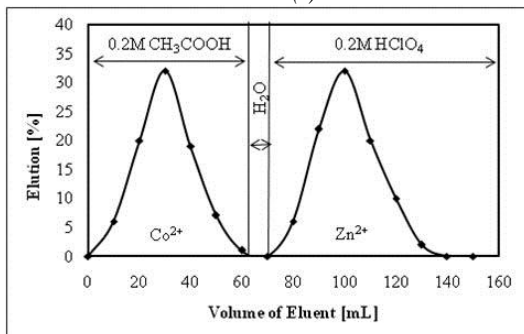**Table 4** *Binary separations of transition metal ions*

Separation achieved	Separation Factor = K_{d1}/K_{d2}	Eluent	Volume [mL]	Metal ion loaded [mg]	Metal ion eluted [mg]	Elution [%]
Ni^{2+}-Co^{2+}	2.37	a) 0.2 M CH$_3$COOH (Ni^{2+})	a) 60	a) 0.5893	a) 0.4604	a) 78.12
		b) 0.2 M HNO$_3$ (Co^{2+})	b) 80	b) 0.5869	b) 0.5004	b) 85.27
Co^{2+}-Cu^{2+}	8.74	a) 0.2 M CH$_3$COOH (Co^{2+})	a) 60	a) 0.5869	a) 0.4757	a) 81.05
		b) 0.2 M HNO$_3$ (Cu^{2+})	b) 80	b) 0.6354	b) 0.5619	b) 88.43
Co^{2+}-Zn^{2+}	9.21	a) 0.2 M CH$_3$COOH (Co^{2+})	a) 60	a) 0.5869	a) 0.4999	a) 85.18
		b) 0.2 M HClO$_4$ (Zn^{2+})	b) 80	b) 0.6539	b) 0.6023	b) 92.11
Ni^{2+}-Cu^{2+}	3.69	a) 0.2 M CH$_3$COOH (Ni^{2+})	a) 60	a) 0.5893	a) 0.4677	a) 79.37
		b) 0.2 M HNO$_3$ (Cu^{2+})	b) 80	b) 0.6354	b) 0.5618	b) 88.41
Zn^{2+}-Ni^{2+}	3.89	a) 0.2 M HClO$_4$ (Zn^{2+})	a) 60	a) 0.6539	a) 0.5773	a) 88.28
		b) 0.2 M CH$_3$COOH (Ni^{2+})	b) 80	b) 0.5893	b) 0.4723	b) 80.14
Zn^{2+}-Cu^{2+}	1.05	a) 0.2 M HClO$_4$ (Zn^{2+})	a) 60	a) 0.6539	a) 0.4728	a) 72.31
		b) 0.2 M HNO$_3$ (Cu^{2+})	b) 80	b) 0.6354	b) 0.5097	b) 80.22
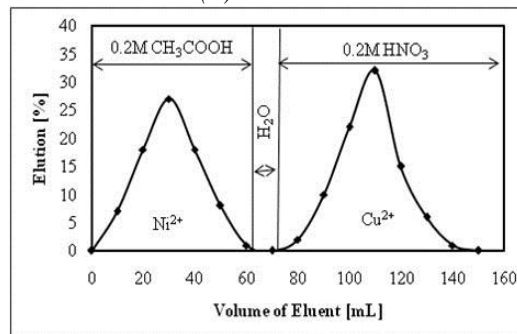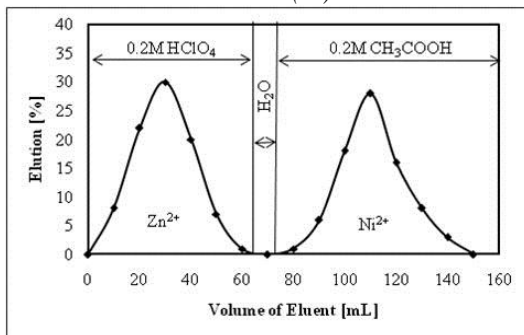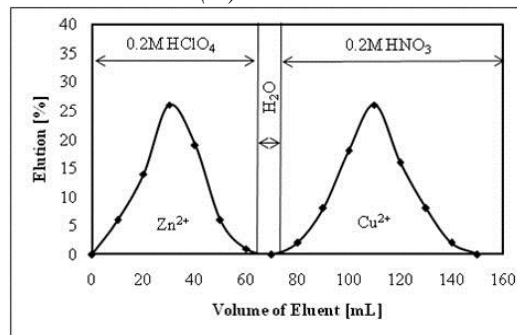
**Figure 3** *Binary separations of transition metal ions (i) Ni^{2+}-Co^{2+}, (ii) Co^{2+}-Cu^{2+}, (iii) Co^{2+}-Zn^{2+}, (iv) Ni^{2+}-Cu^{2+}, (v) Zn^{2+}-Ni^{2+} and (vi) Zn^{2+}-Cu^{2+}*

Table 5 *Binary separations of heavy metal ions*

| Separation achieved	Separation Factor = K_{d1}/K_{d2}	Eluent	Volume [mL]	Metal ion loaded [mg]	Metal ion eluted [mg]	Elution [%]
Cd^{2+}-Hg^{2+}	5.12	a) 0. 2 M $HClO_4$ (Cd^{2+})	a) 60	a) 1.1241	a) 0.9342	a) 83.11
		b) 0.2 M CH_3COOH (Hg^{2+})	b) 80	b) 2.0059	b) 1.7656	b) 88.02
Cd^{2+}-Pb^{2+}	7.16	a) 0.2 M NH_4NO_3 (Cd^{2+})	a) 60	a) 1.1241	a) 0.9922	a) 88.27
		b) 0.2 M HNO_3 (Pb^{2+})	b) 80	b) 2.0720	b) 1.6385	b) 79.08
Cd^{2+}-Bi^{3+}	5.34	a) 0.2 M HNO_3 (Cd^{2+})	a) 60	a) 1.1241	a) 1.0261	a) 91.28
		b) 0.2 M $HClO_4$ (Bi^{3+})	b) 80	b) 2.0898	b) 1.7851	b) 85.42
Pb^{2+}-Hg^{2+}	1.40	a) 0.2 M HNO_3 (Pb^{2+})	a) 60	a) 2.0720	a) 1.5403	a) 74.34
		b) 0.2 M CH_3COOH (Hg^{2+})	b) 80	b) 2.0059	b) 1.7485	b) 87.17
Bi^{3+}-Hg^{2+}	1.04	a) 0.02 M $HClO_4$ (Bi^{3+})	a) 60	a) 2.0898	a) 1.7164	a) 82.13
		b) 0.2 M CH_3COOH (Hg^{2+})	b) 80	b) 2.0059	b) 1.5100	b) 75.28
Pb^{2+}-Bi^{3+}	1.34	a) 0.2 M HNO_3 (Pb^{2+})	a) 60	a) 2.0720	a) 1.5993	a) 77.19
		b) 0.2 M $HClO_4$ (Bi^{3+})	b) 80	b) 2.0898	b) 1.7623	b) 84.33
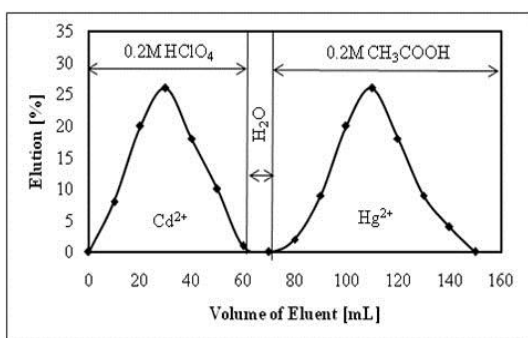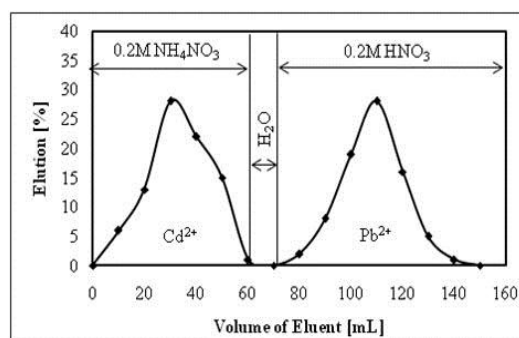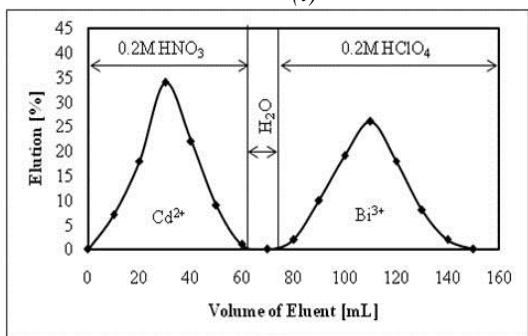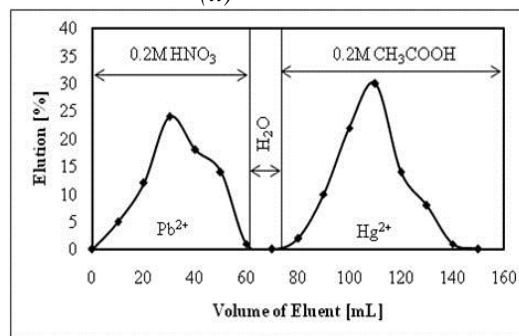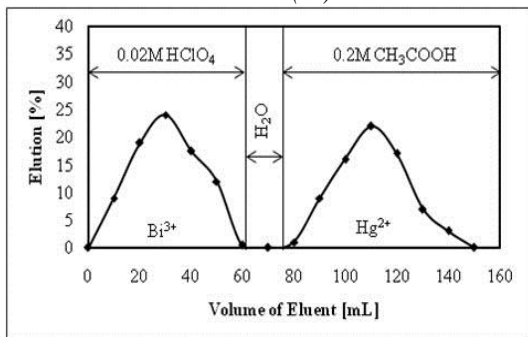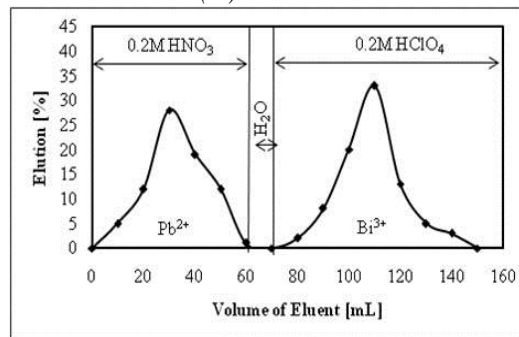
Figure 4 *Binary separations of heavy metal ions (i) Cd^{2+}-Hg^{2+}, (ii) Cd^{2+}-Pb^{2+}, (iii) Cd^{2+}-Bi^{3+}, (iv) Pb^{2+}-Hg^{2+}, (v) Bi^{3+}-Hg^{2+} and (vi) Pb^{2+}-Bi^{3+}*

Table 6 *Ternary separations of metal ions*

Separations achieved	Eluent	Volume [mL]	Metal ion [mg]		Elution [%]
			Loaded	Eluted	
Co^{2+} - Ni^{2+} - Cu^{2+}	a) 0.2 M HClO$_4$ (Co^{2+})	a) 60	a) 0.5900	a) 0.4262	a) 72.23
	b) 0.2 M CH$_3$COOH (Ni^{2+})	b) 80	b) 0.5900	b) 0.4015	b) 68.05
	c) 0.2 M HNO$_3$ (Cu^{2+})	c) 80	c) 0.6400	c) 0.3622	c) 56.59
Ni^{2+} - Co^{2+} - Zn^{2+}	a) 0.2 M CH$_3$COOH (Ni^{2+})	a) 60	a) 0.5900	a) 0.3826	a) 64.85
	b) 0.2 M HNO$_3$ (Co^{2+})	b) 80	b) 0.5900	b) 0.4503	b) 76.33
	c) 0.2 M HClO$_4$ (Zn^{2+})	c) 80	c) 0.6500	c) 0.3886	c) 59.79
Cd^{2+} - Pb^{2+} - Hg^{2+}	a) 0.2 M NH$_4$NO$_3$ (Cd^{2+})	a) 60	a) 1.1200	a) 0.7899	a) 70.53
	b) 0.2 M HNO$_3$ (Pb^{2+})	b) 80	b) 2.0700	b) 1.2822	b) 61.94
	c) 0.2 M CH$_3$COOH (Hg^{2+})	c) 80	c) 2.0100	c) 1.3336	c) 66.35
Cd^{2+} - Pb^{2+} - Bi^{3+}	a) 0.2 M NH$_4$NO$_3$ (Cd^{2+})	a) 60	a) 1.1200	a) 0.7637	a) 68.19
	b) 0.2 M HNO$_3$ (Pb^{2+})	b) 80	b) 2.0700	b) 1.1907	b) 57.52
	c) 0.2 M HClO$_4$ (Bi^{3+})	c) 80	c) 2.0900	c) 1.2552	c) 60.06

(i)

(ii)

(iii)

(iv)
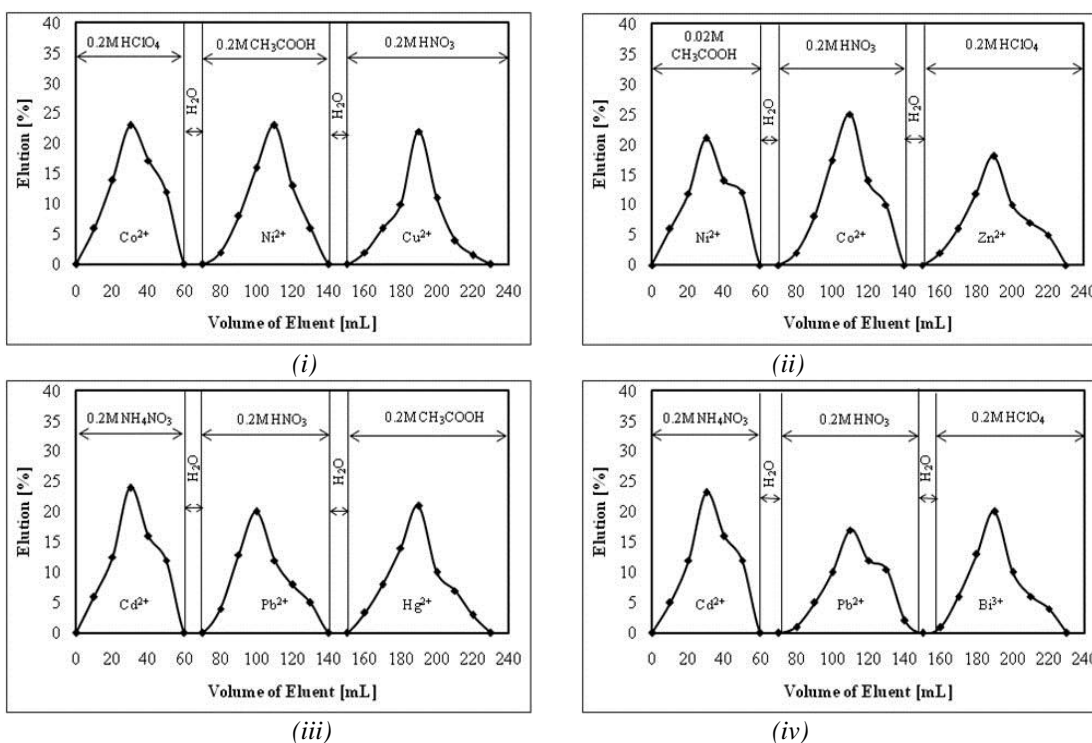
Figure 5 *Ternary separations of metal ions (i) Co^{2+}-Ni^{2+}-Cu^{2+} (ii) Ni^{2+}-Co^{2+}-Zn^{2+} (iii) Cd^{2+}-Pb^{2+}-Hg^{2+} and (iv) Cd^{2+}-Pb^{2+}-Bi^{3+}*

Efficient separation in terms of % metal eluted is observed in case of Co^{2+}-Cu^{2+}, Co^{2+}-Zn^{2+}, Cd^{2+}-Pb^{2+}, Cd^{2+}-Bi^{3+} and Cd^{2+}-Hg^{2+} where, α values are high, which is also supported by symmetrical bell shaped curves (Figure 3 and Figure 4). In case of metal ion pairs Zn^{2+}-Cu^{2+}, Ni^{2+}-Co^{2+}, Ni^{2+}-Cu^{2+}, Zn^{2+}-Ni^{2+}, Pb^{2+}-Hg^{2+}, Pb^{2+}-Bi^{3+} and Bi^{3+}-Hg^{2+}, two distinct peaks are observed, however with tailing effects. This may be attributed to very low α values. However, separation is quite efficient in terms of % metal eluted. In binary separations, the metal eluted first is generally less recovered/ eluted compared

to second metal eluted. There is however, not much difference in % metal eluted when order of metal elution is reversed.

In ternary separations for Co^{2+}-Ni^{2+}-Cu^{2+}, Ni^{2+}-Co^{2+}-Zn^{2+} (transition metal ions) and Cd^{2+}-Pb^{2+}-Hg^{2+}, Cd^{2+}-Pb^{2+}-Bi^{3+} (heavy metal ions) % metal eluted is in the range 56-72%, 59-76%, 61-70% and 60-68% respectively (Table 6). In all cases, three distinct peaks are observed (Figure 5); however, with tailing effects for every metal ion eluted. % metal eluted is also lower as compared to single and binary metal ion separations.

Probably the separation process becomes complex, attributed to the loss of metal ions during the changeover of the eluent, interference of metal ions, pH, simultaneous elution of two or more metal ions with the same eluent, and lastly, experimental errors involved in the determination of metal ions in the presence of other ions, etc.

CONCLUSIONS
ZrDETPMP exhibits CEC comparable to commercially available resins[26], is chemically stable in acidic and organic solvent media and exhibits high selectivity for Zn^{2+}, Hg^{2+}, Pb^{2+} and Bi^{3+}. Efficient binary metal separations carried out using ZrDETPMP indicate good potential for this material to be used as a cation exchanger.

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