Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.808796

52 (2014) 481–489
January

Taylor & Francis
Taylor & Francis Group

Separations of lanthanides and actinides using novel hybrid ion exchange materials, M(IV) phosphonates

Parimal R. Patel[a], Uma V. Chudasama[b,*]

[a]*Applied Chemistry Department, S.V. National Institute of Technology, Surat, India*
[b]*Faculty of Technology and Engineering, Applied Chemistry Department, The M.S. University of Baroda, Vadodara, 390 001 Gujarat, India*
Tel. +91 265 2434188x415; Fax: +91 265 2423898; email: uvcres@gmail.com

Received 17 April 2012; Accepted 10 March 2013

ABSTRACT

Zirconium diethylene triamine pentamethylene phosphonate and titanium diethylene triamine pentamethylene phosphonate, novel hybrid cation exchange materials of the class of tetravalent metal acid salts, synthesized by sol-gel method has been characterized by spectroscopy and thermal analysis. Distribution coefficient and breakthrough capacity for La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} (lanthanides) and Th^{4+}, UO_2^{2+} (actinides) have been studied. Based on the differential affinity/selectivity and elution behavior of various metal ions, a few binary and ternary metal ion separations have been carried out.

Keywords: Tetravalent metal acid salts; Hybrid materials; Metal phosphonates; Cation exchangers; Zirconium diethylene triamine pentamethylene phosphonate; Titanium diethylene triamine pentamethylene phosphonate; Metal separations

1. Introduction

Due to unique electronic, optical, and magnetic properties, lanthanides are in increasing demand in high-technology industry. They are thus required in a highly purified form. The separation of lanthanides continues to be a challenging area due to similarity in their ion size and charge, being typically trivalent, and thus their properties are almost identical. Amongst various methods used for lanthanide separations, ion exchange chromatography is the most successful and rapid method [1].

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 tetravalent metal acid (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). 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

---

*Corresponding author.

Presented at the DAE—BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology (SESTEC 2012) Mumbai, India, 27 February–1 March 2012

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. 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 [2]. 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 $-COOH$, $-OH$, and $-SO_3H$, 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 [3–5]. These materials are interesting because of their potential utility as ion exchangers [6].

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 [7,8]. Titania-phosphonate hybrids using claw type aminophosphonic acids have been synthesized and characterized and their utility as adsorbents has been proposed earlier [7]. From our laboratory, Zirconium diethylene triamine pentamethylene phosphonate (ZrDETPMP) and titanium diethylene triamine pentamethylene phosphonate (TiDETPMP) (Fig. 1), novel hybrid metal phosphonates, have been synthesized and characterized, and thermodynamics and kinetics of ion exchange have been studied [9,10]. DETPMP, possessing 10 structural hydroxyl groups, compared to phosphoric acid H_3PO_4 which has three structural hydroxyl groups, is used with the intention of obtaining higher CEC in terms of pendant hydroxyl groups in the resulting metal phosphonate [2,3,11].

In earlier publications, the authors have demonstrated the use of ZrDETPMP [12] and TiDETPMP [13] as ion exchangers for the separations of transition metal and heavy metal ions. In the present endeavour, the possible use of ZrDETPMP and TiDETPMP as ion exchangers for separation of lanthanides and actinides has been explored. Distribution coefficient (K_d) for La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} (lanthanides) and Th^{4+}, UO_2^{2+} (actinides) has been determined in aqueous as well as various electrolyte media/concentrations. Based on the differential affinity/selectivity, breakthrough capacity (BTC), and elution behavior of various metal ions, some binary and ternary metal ion separations have been carried out.

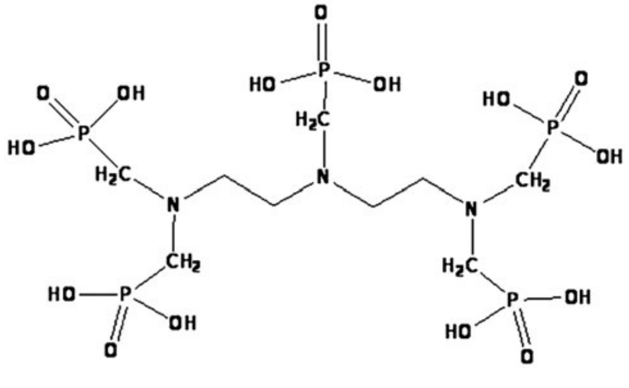

Fig. 1. Structure of DETPMP.

2. Experimental

All chemicals and reagents used are of analytical grade. Double-distilled water was used for all the studies. ZrDETPMP and TiDETPMP synthesized by sol–gel method have been characterized by spectroscopy, thermal analysis, physico–chemical, and ion exchange characteristics as reported earlier [9,10,12,13].

2.1. Distribution studies

Distribution studies for metal ions La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} (lanthanides) and Th^{4+}, UO_2^{2+} (actinides) were carried out by batch method [14]. 0.1 g of the exchanger ZrDETPMP/TiDETPMP 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 spectroscopy [15,16]. 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, $K_d = (I - F)/F \times V/W$ (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; and W = weight of the exchanger.

2.2. BTC, elution studies, and separation studies

For BTC, elution, and separation studies, 0.5 g of the ion exchanger, ZrDETPMP/TiDETPMP, was taken in a glass column (30 × 1 cm), washed thoroughly with deionized water and flow rate was adjusted to 0.5 mL min^{-1}. In all cases, metal ion concentration was determined quantitatively by EDTA titration, AAS, or UV–Vis spectroscopy [15,16]. For BTC, 5 mL fractions of each individual 0.001 M metal ion solution were passed through the column and effluent was 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 solution (0.001 M, 10 mL) was loaded onto the column and eluted with reagents like HNO_3, $HClO_4$, CH_3COOH, and NH_4NO_3 of 0.02 and 0.2 M concentration. The amount of metal ion eluted 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 and mixture of the metal ions (0.001 M, 10 mL of each metal ion) to be separated was loaded on to the column and separation achieved by passing suitable eluent through the column.

3. Results and discussion

3.1. Characterization of ZrDETPMP and TiDETPMP

ZrDETPMP and TiDETPMP have been characterized by spectroscopy, thermal analysis, physico-chemical, and ion exchange characteristics earlier by us [9,10,12,13].

3.2. Distribution studies

Selectivity/affinity of a particular metal ion towards an ion exchanger depends on (1) the ion exchanger, (2) the exchange media, and (3) the exchanging metal ion. Larger ions being less hydrated, less energy is utilized for dehydration of the metal ions to occupy a site on the exchanger, which plays a prominent role in determining the selectivity of metal ions. The overall effect is a result of the contribution of the above-mentioned factors. Depending on the predominant factor, the affinity of metal ions towards the ion exchanger varies in each case [13].

The distribution coefficient (K_d) values evaluated for the metal ions under study towards ZrDETPMP and TiDETPMP have been presented in Tables 1(a) and 1(b). 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 lanthanides, the observed selectivity order is Pr^{3+} (1.13 Å) > Ce^{3+}(1.15 Å) > Nd^{3+}(1.12 Å) > La^{3+}(1.17 Å) > Sm^{3+}(1.10 Å) for ZrDETPMP and La^{3+} (1.17 Å) > Sm^{3+}(1.10 Å) > Ce^{3+}(1.15 Å) > Pr^{3+}(1.13 Å) > Nd^{3+}(1.12 Å) for TiDETPMP, while amongst actinides, the observed selectivity order is Th^{4+} (1.08 Å) > UO_2^{2+} (1.03 Å) for both materials, values in parenthesis being ionic radii of the respective metal ions. The ionic radii being almost equivalent in case of lanthanides, the selectivity order is probably dependant on exchange equilibrium/dissociation of salt [17]. In case of actinides a higher selectivity of Th^{4+} is attributed to high ionic charge.

3.3. Breakthrough capacity

Breakthrough curves (a plot of C_e/C_0 vs. effluent volume) are presented in Figs. 2 and 3. 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.

3.4. Metal elution and separations

An efficient ion exchange separation may be influenced by the amount of metal ion loaded, the eluent used for separation and its flow rate, pH, temperature, nature of ion exchange material, particle size, and length of the column, etc. Factors responsible for observed peak shapes/elution curves are the distribution coefficient (K_d), the 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 elution/recovery and (2) Peak shapes/elution curves of the constituent metal ions, in terms of Langmurian/nonLangmurian, which indicates how well one metal ion is separated in the presence of another metal ion.

When a solution containing a mixture of 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 eluent is eluted first, followed by weakly bound species, and finally

Table 1(a)
K_d values (in mL g^{-1}) and BTC (in mmol g^{-1}) for metal ions towards ZrDETPMP

Metal ion	BTC	DDW	NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH	
			0.02 M	0.20 M	0.02 M	0.20 M	0.02 M	0.20 M	0.02 M	0.20 M
La^{3+}	0.20	94	64	3	83	22	97	140	32	73
Ce^{3+}	0.22	180	367	6	200	220	28	14	55	40
Pr^{3+}	0.23	220	408	976	77	31	78	52	626	380
Nd^{3+}	0.21	170	48	340	116	191	3	271	122	154
Sm^{3+}	0.19	6	20	26	11	72	73	91	41	186
Th^{4+}	0.13	6,723	874	6,244	240	*CS	229	*CS	191	5,786
UO_2^{2+}	0.07	1,840	966	1,655	820	418	1,432	2,200	310	820

*CS = complete sorption, maximum deviation in K_d values = ± 3.

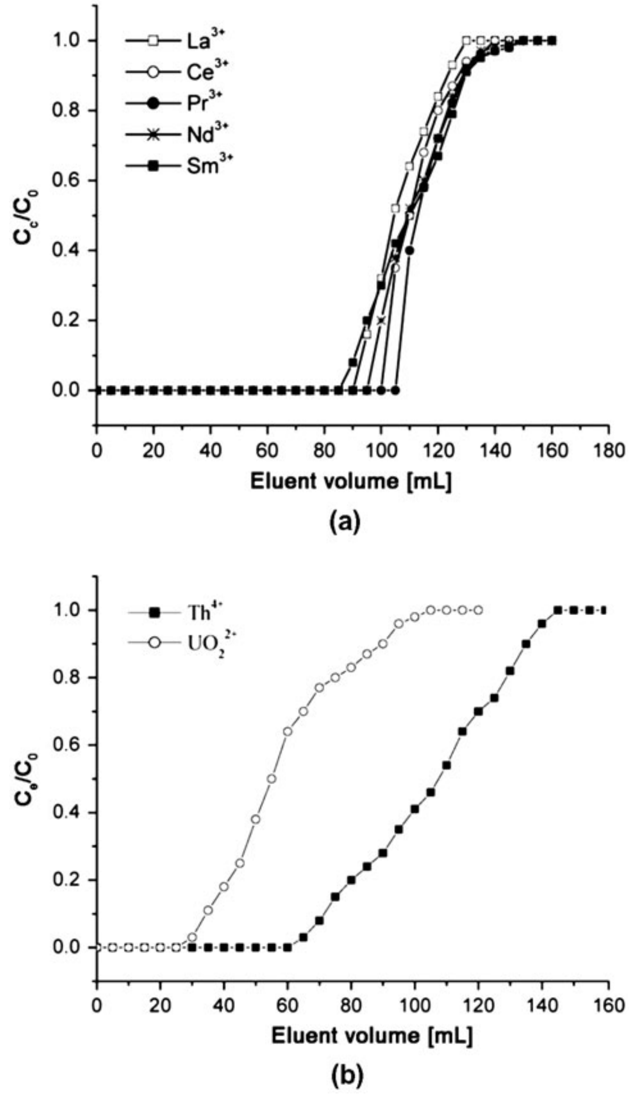

Fig. 2. BTC of (a) lanthanides and (b) actinides using ZrDETPMP.

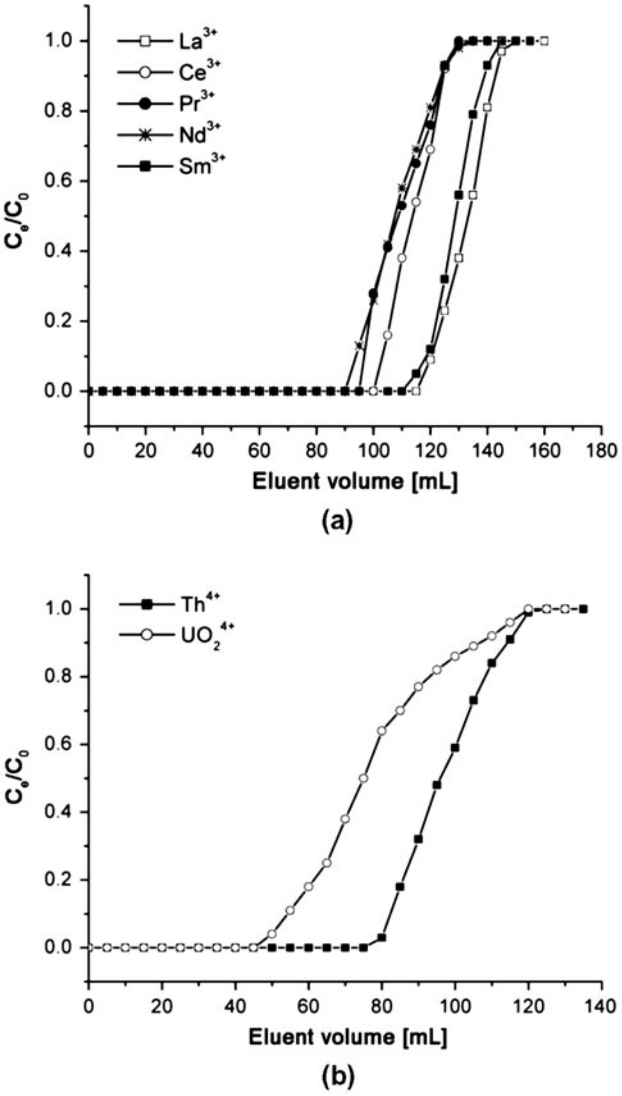

Fig. 3. BTC of (a) lanthanides and (b) actinides using TiDETPMP.

Table 1(b)
K_d values (in mL g^{-1}) and BTC (in mmol g^{-1}) for metal ions towards TiDETPMP

Metal ion	BTC	DDW	NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH	
			0.02 M	0.20 M	0.02 M	0.20 M	0.02 M	0.20 M	0.02 M	0.20 M
La^{3+}	0.25	310	537	394	101	58	190	65	704	771
Ce^{3+}	0.22	147	164	113	65	30	75	40	234	226
Pr^{3+}	0.21	123	197	132	67	19	79	23	255	273
Nd^{3+}	0.20	113	174	162	41	9	69	27	174	180
Sm^{3+}	0.24	203	186	116	79	21	62	30	176	183
Th^{4+}	0.17	1,255	1,255	1,191	481	985	440	1,682	1,255	3,800
UO_2^{2+}	0.11	585	616	1,500	36	556	795	585	264	600

Note: Maximum deviation in K_d values = ± 3.

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 (eluent). 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 noncontrolled flow.

The elution behavior of single metal ions (Tables 2 (a) and 2(b)) using ZrDETPMP and TiDETPMP shows metal ion eluted is in the range ~88–99%. Good elution is observed due to noninterference of elements. Order of maximum percentage metal eluted amongst lanthanides is La^{3+} (98.64) > Sm^{3+} (94.29) > Nd^{3+} (93.10) > Pr^{3+} (91.72) > Ce^{3+} (88.72) for ZrDETPMP and Nd^{3+} (98.8) > Pr^{3+} (98.4) > Ce^{3+} (98.2) > Sm^{3+} (97.2) > La^{3+} (96.4) for TiDETPMP and amongst actinides is UO_2^{2+} (99.10) > Th^{4+} (98.54) for ZrDETPMP and UO_2^{2+} (97.10) > Th^{4+} (96.3) for TiDETPMP. 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 symmetrically bell shaped indicating elution efficiency.

Separation factor, given by K_{d1}/K_{d2}, where K_{d1} and K_{d2} are the distribution coefficients of the two constituents being separated, provide a guideline for

Table 2(a)
Elution behavior of metal ions towards ZrDETPMP

Metal ion	E_v/% E	NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH	
		0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M
La^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	94.70	95.24	92.20	98.64	90.20	96.60	92.20	93.20
Ce^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	86.90	88.72	86.50	88.72	92.20	93.23	90.00	91.73
Pr^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	82.70	91.72	89.20	91.72	89.10	91.03	88.20	90.34
Nd^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	82.90	93.10	91.50	93.10	85.30	87.93	86.50	90.23
Sm^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	89.70	94.29	91.60	94.29	90.20	92.86	90.20	92.86
Th^{4+}	E_v	70	60	70	60	70	60	70	60
	% E	77.50	78.82	77.60	78.82	78.50	80.00	94.80	98.54
UO_2^{2+}	E_v	70	60	70	60	70	60	70	60
	% E	80.60	82.89	81.30	82.89	80.10	87.89	95.90	99.10

Note: E_v = eluent volume, % E = % elution, maximum deviation in % E values = ± 0.5%.

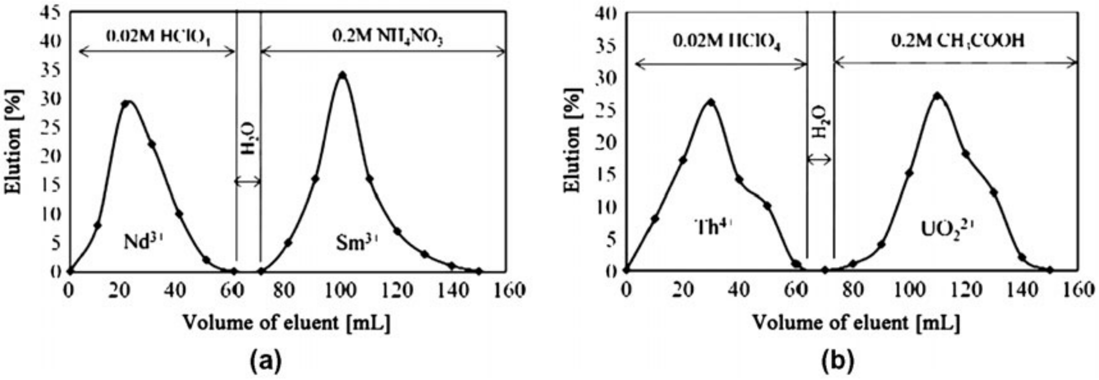

Fig. 4. Binary separation of lanthanides and actinides (a) Nd^{3+}–Sm^{3+} and (b) Th^{4+}–UO_2^{2+} using ZrDETPMP.

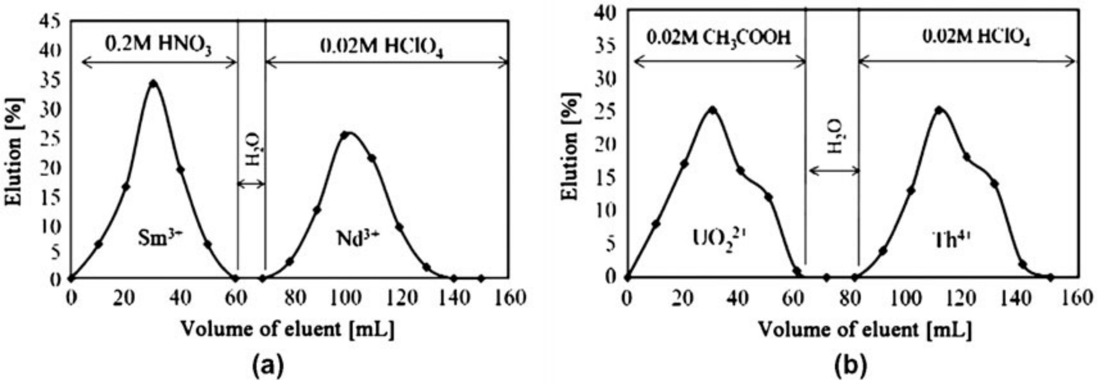

Fig. 5. Binary separation of lanthanides and actinides (a) Sm^{3+}–Nd^{3+} and (b) UO_2^{2+}–Th^{4+} using TiDETPMP.

metal separation. The greater the deviation of 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 favorable to separation. For a given metal ion pair, the electrolyte media in which the separation factor is the highest, is selected as the eluent. Thus, a study on distribution behavior of metal ions in various electrolyte media gives an idea about the eluents that can be used for separation.

In binary separations, separation efficiency is in the range of 74–90% amongst lanthanides and 76–79% amongst actinides (Tables 3(a) and 3(b)). In all cases of binary separation, irrespective of metal ion pair, maximum percentage metal eluted is Sm^{3+} (90.05) $> Pr^{3+}$ (83.17) $> Nd^{3+}$ (80.30) $> Ce^{3+}$ (78.22) $> La^{3+}$ (76.12)

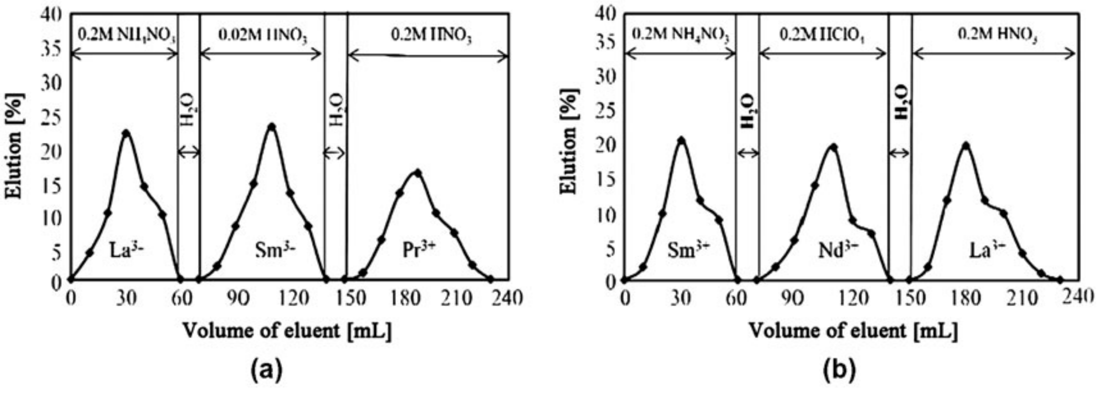

Fig. 6. Ternary separation of (a)La^{3+}–Sm^{3+}–Pr^{3+} using ZrDETPMP (b) Sm^{3+}–Nd^{3+}–La^{3+} using TiDETPMP.

Table 2(b)
Elution behavior of metal ions towards TiDETPMP

Metal ion	E_v/%E	NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH	
		0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M
La^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	80.7	88.2	91.7	96.4	90.5	92.9	90.6	93.8
Ce^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	78.9	85.2	94.5	98.2	92.2	94.2	94.5	94.9
Pr^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	83.4	89.6	92.6	98.4	90.2	94.9	89.3	93.7
Nd^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	81.9	86.2	93.5	98.8	90.1	94.2	88.7	93.9
Sm^{3+}	E_v	70	60	70	60	70	60	70	60
	% E	80.9	87.8	92.7	97.2	89.6	93.2	87.1	92.9
Th^{4+}	E_v	70	60	70	60	70	60	70	60
	% E	80.5	84.3	90.2	96.3	87.5	92.6	86.8	91.5
UO_2^{2+}	E_v	70	60	70	60	70	60	70	60
	% E	81.8	85.2	92.3	97.1	90.1	95.3	85.4	90.8

Note: E_v = eluent volume, %E = % elution, maximum deviation in % E values = ± 0.5%.

for ZrDETPMP and La^{3+} (84.43) > Sm^{3+} (81.13) > Ce^{3+} (79.32) > Pr^{3+} (77.17) > Nd^{3+} (74.24) for TiDETPMP (amongst lanthanides) and UO_2^{2+} (79.24) > Th^{4+} (76.35) for ZrDETPMP and UO_2^{2+} (78.04) > Th^{4+} (75.22) (amongst actinides). This observation is in keeping with separation factor (α) and K_d values of metal ions. The percentage metal eluted decreases with decreasing separation factor and increases with increasing

Table 3(a)
Binary separation of lanthanides and actinides metal ions using ZrDETPMP

Metal ions	Eluent	Metal Loaded	Metal Eluted	Elution (%)
La^{3+}–Ce^{3+}	(a) 0.2 M HNO_3 (La^{3+})	(a) 1.3891	(a) 1.0302	(a) 74.16
	(b) 0.2 M NH_4NO_3 (Ce^{3+})	(b) 1.4012	(b) 0.8725	(b) 62.27
La^{3+}–Pr^{3+}	(a) 0.2 M NH_4NO_3 (La^{3+})	(a) 1.3891	(a) 1.0428	(a) 75.07
	(b) 0.2 M HNO_3 (Pr^{+3})	(b) 1.4091	(b) 1.0758	(b) 76.35
La^{3+}–Nd^{3+}	(a) 0.2 M NH_4NO_3 (La^{3+})	(a) 1.3891	(a) 1.0159	(a) 73.14
	(b) 0.2 M $HClO_4$ (Nd^{3+})	(b) 1.4424	(b) 1.1582	(b) 80.30
La^{3+}–Sm^{3+}	(a) 0.2 M CH_3COOH (La^{3+})	(a) 1.3891	(a) 1.0574	(a) 76.12
	(b) 0.2 M HNO_3 (Sm^{3+})	(b) 1.5036	(b) 1.3436	(b) 89.36
Ce^{3+}–Pr^{3+}	(a) 0.2 M NH_4NO_3 (Ce^{3+})	(a) 1.4012	(a) 1.0960	(a) 78.22
	(b) 0.2 M HNO_3 (Pr^{3+})	(b) 1.4091	(b) 1.1719	(b) 83.17
Ce^{3+}–Nd^{3+}	(a) 0.2 M NH_4NO_3 (Ce^{3+})	(a) 1.4012	(a) 0.9166	(a) 65.42
	(b) 0.2 M $HClO_4$ (Nd^{3+})	(b) 1.4424	(b) 0.8667	(b) 60.09
Ce^{3+}–Sm^{3+}	(a) 0.2 M $HClO_4$ (Ce^{3+})	(a) 1.4012	(a) 1.0956	(a) 78.19
	(b) 0.2 M NH_4NO_3 (Sm^{3+})	(b) 1.5036	(b) 1.3539	(b) 90.05
Nd^{3+}–Pr^{3+}	(a) 0.02 M $HClO_4$ (Nd^{3+})	(a) 1.4424	(a) 0.9829	(a) 68.15
	(b) 0.2 M HNO_3 (Pr^{3+})	(b) 1.4091	(b) 1.0611	(b) 75.31
Sm^{3+}–Pr^{3+}	(a) 0.2 M NH_4NO_3 (Sm^{3+})	(a) 1.5036	(a) 1.3296	(a) 88.43
	(b) 0.2 M HNO_3 (Pr^{3+})	(b) 1.4091	(b) 1.0736	(b) 76.19
Nd^{3+}–Sm^{3+}	(a) 0.02 M $HClO_4$ (Nd^{3+})	(a) 1.4424	(a) 1.0264	(a) 71.16
	(b) 0.2 M NH_4NO_3 (Sm^{3+})	(b) 1.5036	(b) 1.2375	(b) 82.30
Th^{4+}–UO_2^{2+}	(a) 0.02 M $HClO_4$ (Th^{4+})	(a) 2.3204	(a) 1.7716	(a) 76.35
	(b) 0.2 M CH_3COOH (UO_2^{2+})	(b) 2.3803	(b) 1.8862	(b) 79.24

Note: Maximum deviation in % elution = ± 0.5%.

Table 3(b)
Binary separation of lanthanides and actinides metal ions using TiDETPMP

Metal ions	Eluent	Metal loaded	Metal eluted	Elution (%)
Ce^{3+}–La^{3+}	(a) 0.2 M NH_4NO_3 (Ce^{3+}) (b) 0.2 M HNO_3 (La^{3+})	(a) 1.4012 (b) 1.3891	(a) 1.0962 (b) 1.0565	(a) 78.23% (b) 76.06%
Pr^{3+}–La^{3+}	(a) 0.2 M NH_4NO_3 (Pr^{3+}) (b) 0.2 M HNO_3 (La^{3+})	(a) 1.4091 (b) 1.3891	(a) 1.0874 (b) 1.1434	(a) 77.17% (b) 82.31%
Nd^{3+}–La^{3+}	(a) 0.2 M CH_3COOH (Nd^{3+}) (b) 0.2 M HNO_3 (La^{3+})	(a) 1.4424 (b) 1.3891	(a) 1.0708 (b) 1.1726	(a) 74.24% (b) 84.43%
Sm^{3+}–La^{3+}	(a) 0.2 M CH_3COOH (Sm^{3+}) (b) 0.2 M HNO_3 (La^{3+})	(a) 1.5036 (b) 1.3891	(a) 1.1755 (b) 0.9621	(a) 78.18% (b) 69.26%
Pr^{3+}–Ce^{3+}	(a) 0.2 M $HClO_4$ (Pr^{3+}) (b) 0.2 M HNO_3 (Ce^{3+})	(a) 1.4091 (b) 1.4012	(a) 1.0629 (b) 1.1258	(a) 75.43% (b) 78.16%
Nd^{3+}–Ce^{3+}	(a) 0.2 M HNO_3 (Nd^{3+}) (b) 0.02 M $HClO_4$ (Ce^{3+})	(a) 1.4424 (b) 1.4012	(a) 0.9560 (b) 0.9817	(a) 66.28% (b) 70.06%
Sm^{3+}–Ce^{3+}	(a) 0.2 M CH_3COOH (Sm^{3+}) (b) 0.2 M HNO_3 (Ce^{3+})	(a) 1.5036 (b) 1.4012	(a) 1.1444 (b) 1.1114	(a) 76.11% (b) 79.32%
Nd^{3+}–Pr^{3+}	(a) 0.2 M CH_3COOH (Nd^{3+}) (b) 0.2 M HNO_3 (Pr^{3+})	(a) 1.4424 (b) 1.4091	(a) 0.9547 (b) 0.8363	(a) 66.19% (b) 59.35%
Sm^{3+}–Pr^{3+}	(a) 0.2 M CH_3COOH (Sm^{3+}) (b) 0.2 M HNO_3 (Pr^{3+})	(a) 1.5036 (b) 1.4424	(a) 1.0988 (b) 1.0609	(a) 73.08% (b) 75.29%
Sm^{3+}–Nd^{3+}	(a) 0.2 M HNO_3 (Sm^{3+}) (b) 0.02 M $HClO_4$ (Nd^{3+})	(a) 1.5036 (b) 1.4424	(a) 1.2199 (b) 1.0423	(a) 81.13% (b) 72.26%
UO_2^{2+}– Th^{4+}	(a) 0.02 M CH_3COOH (UO_2^{2+}) (b) 0.02 M $HClO_4$ (Th^{4+})	(a) 2.3803 (b) 2.3204	(a) 1.8576 (b) 1.7454	(a) 78.04% (b) 75.22%

Note: Maximum deviation in % elution = ± 0.5%.

separation factor as explained earlier, metal ions with high K_d values are less eluted and vice versa. Efficient separation in terms of percentage metal eluted is observed in case of La^{3+}–Sm^{3+}, Ce^{3+}–Sm^{3+}, Sm^{3+}–Pr^{3+}, Nd^{3+}–Sm^{3+} for ZrDETPMP and Ce^{3+}–La^{3+}, Pr^{3+}–La^{3+}, Nd^{3+}–La^{3+}, Sm^{3+}–Nd^{3+} for TiDETPMP where, α values are high, which is also supported by symmetrical bell-shaped curves (Figs. 4 and 5). In case of metal ion pairs La^{3+}–Ce^{3+}, La^{3+}–Pr^{3+}, La^{3+}–Nd^{3+}, Ce^{3+}–Pr^{3+}, Ce^{3+}–Nd^{3+}, Nd^{3+}–Pr^{3+} for ZrDETPMP and Sm^{3+}–La^{3+}, Pr^{3+}–Ce^{3+}, Nd^{3+}–Ce^{3+}, Sm^{3+}–Ce^{3+}, Nd^{3+}–Pr^{3+}, Sm^{3+}–Pr^{3+} for TiDETPMP (Fig. 6), 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 percentage metal eluted.

In ternary separations for La^{3+}–Sm^{3+}–Pr^{3+}, Ce^{3+}–UO_2^{2+}–Th^{4+} for ZrDETPMP and Sm^{3+}–Nd^{3+}–La^{3+}, Ce^{3+}–UO_2^{2+}–Th^{4+} for TiDETPMP, percentage metal eluted is in the range of 54–68% (Tables 4(a) and 4(b)). In all cases, three distinct peaks are observed (Fig. 6); however, with tailing effects for every metal ion eluted. Percentage metal eluted is also lower as compared to single and binary metal ion separations.

Table 4(a)
Ternary separation of lanthanides and actinides metal ions using ZrDETPMP

Metal ions	Eluent	Metal ion (mg)		Elution (%)
		Loaded	Eluted	
La^{3+}–Sm^{3+}–Pr^{3+}	0.2 M NH_4NO_3 (La^{3+})	1.3891	0.8297	59.73
	0.02 M HNO_3 (Sm^{3+})	1.5036	1.0286	68.41
	0.2 M HNO_3 (Pr^{3+})	1.4091	0.7775	55.18
Ce^{3+}–UO_2^{2+}–Th^{4+}	0.2 M NH_4NO_3 (Ce^{3+})	1.4012	0.9286	66.27
	0.2 M CH_3COOH (UO_2^{2+})	2.3803	1.4622	61.43
	0.2 M HNO_3 (Th^{4+})	2.3204	1.2978	55.93

Note: Maximum deviation in % elution = ± 0.5%.

Table 4(b)
Ternary separation of lanthanides and actinides metal ions using TiDETPMP

Metal ions	Eluent	Metal ion (mg)		Elution (%)
		Loaded	Eluted	
Sm^{3+}–Nd^{3+}–La^{3+}	0.2 M NH_4NO_3 (Sm^{3+})	1.5036	0.8124	54.03
	0.2 M $HClO_4$ (Nd^{3+})	1.4424	0.8403	58.26
	0.2 M HNO_3 (La^{3+})	1.3891	0.8504	61.22
Ce^{3+}–UO_2^{2+}–Th^{4+}	0.2 M $HClO_4$ (Ce^{3+})	1.4012	0.9015	64.34
	0.2 M CH_3COOH (UO_2^{2+})	2.3803	1.4089	59.19
	0.2 M HNO_3 (Th^{4+})	2.3204	1.3103	56.47

Note: Maximum deviation in % elution = ± 0.5%.

Probably the separation process becomes complex, attributed to the loss of metal ions during the change-over 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. Separation of lanthanides and actinides with eluents forming complexes with the ions is in progress for better and efficient separations.

4. Conclusion

The present study reveals the promising use of ZrDETPMP and TiDETPMP as ion exchangers in the separation of some binary and ternary metal ions involving lanthanides and actinides, the salient feature being very high selectivity for Th^{4+} and UO_2^{2+} towards both the materials. In case of single metal ions efficient elutions is in the range of ~88–99%, which is supported by symmetrical bell-shaped curves. In binary separation of metal ion pairs La^{3+}–Sm^{3+}, Ce^{3+}–Sm^{3+}, Sm^{3+}–Pr^{3+}, Nd^{3+}–Sm^{3+} for ZrDETPMP and Ce^{3+}–La^{3+}, Pr^{3+}–La^{3+}, Nd^{3+}–La^{3+}, Sm^{3+}–Nd^{3+} for TiDETPMP, efficient separation in terms of percentage metal eluted (74–90%) is observed which is also supported by symmetrical bell shaped curves. Further, good ternary separations are also observed for La^{3+}–Sm^{3+}–Pr^{3+}, Ce^{3+}–UO_2^{2+}–Th^{4+} using ZrDETPMP and Sm^{3+}–Nd^{3+}–La^{3+}, Ce^{3+}–UO_2^{2+}–Th^{4+} using TiDETPMP.

Acknowledgment

The authors thank the Gujarat Mineral Development Corporation, science and research centre, Gujarat, India for financial support.

References

[1] K.L. Nash, M.P. Jensen, Analytical separation of the lanthanides: Basic chemistry and methods, in: K.A. Gschneidner, Jr., and L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 28, Elsevier Science, Amsterdam, 2000, (Chapter 180), pp. 311–371.

[2] G. Alberti, M. Casciola, U. Costantino, R. Vivani, Layered and pillared metal(IV) phosphates and phosphonates, Adv. Mater. 8 (1996) 291–303.

[3] A. Clearfield, Z.J. Wang, Organically pillared microporous zirconium phosphonates, J. Chem. Soc. Dalton. Trans. (15) (2002) 2937–2947. doi: 10.1039/B202371G

[4] Z. Wang, J.M. Heising, A. Clearfield, Sulfonated microporous organic-inorganic hybrids as strong bronsted acids, J. Am. Chem. Soc. 125 (2003) 10375–10383.

[5] M.M. Gomez-Alcantara, A. Cabeza, M. Martinez-Lara, M.A. G. Aranda, R. Aarau, N. Bhuvanesh, A. Clearfield, Synthesis and characterization of a new bisphosphonic acid and several metal hybrids derivatives, Inorg. Chem. 43 (2004) 5283–5293.

[6] J.G. Mao, Z. Wang, A. Clearfield, Building layered structures from hydrogen bonded molecular units and 1D metal phosphonate chains: Synthesis, characterization and crystal structures of N,N′-dimethyl-N,N′-ethylenediamine-bis(methylenephosphonic acid), its Ni(II) and Pb(II) complexes J. Chem. Soc. Dalton. Trans. (24) (2002) 4541–4546. doi: 10.1039/B206343N

[7] X.J. Zhang, T.Y. Ma, Z.Y. Yuan, Titania–phosphonate hybrid porous materials: Preparation, photocatalytic activity and heavy metal ion adsorption, J. Mater. Chem. 18 (2008) 2003–2010.

[8] R.C. Holz, G.E. Meister, W.D. Horrocks, Spectroscopic characterization of a series of europium(III) amino phosphonate complexes in solution, Inorg. Chem. 29 (1990) 5183–5189.

[9] P. Patel, U. Chudasama, Thermodynamics and kinetics of ion exchange using titanium diethylene triamine pentamethylene phosphonate—A hybrid cation exchanger, J. Sci. Ind. Res. 69 (2010) 756–766.

[10] P. Patel, U. Chudasama, Thermodynamics and kinetics of ion exchange of a hybrid cation exchanger, zirconium diethylene triamine pentamethylene phosphonate, Indian J. Chem. A. 49 (2010) 1318–1324.

[11] A. Clearfield, Metal phosphonate chemistry, in: K.D. Karlin (Ed.), Progress in Inorganic Chemistry, Vol. 47, Wiley, New York, NY, 1998, pp. 371–510.

[12] P. Patel, U. Chudasama, Synthesis and characterization of a novel hybrid cation exchange material and its application in metal ion separations, Ion Exchange Lett. 4 (2011) 7–15.

[13] P. Patel, U. Chudasama, Application of a novel hybrid cation exchange material in metal ion separations, Sep. Sci. Technol. 46 (2011) 1346–1357.

[14] M. Qureshi, K.G. Varshney, A.H. Isaraili, Synthesis, ion-exchange behavior and composition of tin(IV) hexacyanoferrate(II), J. Chromatogr. 59 (1971) 141–150.

[15] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Vogel's Text Book of Quantitative Inorganic Analysis, 5th ed., Longman Group Green, London, 1978.

[16] J.W. Frank, The Analytical Uses of Ethylenediamine Tetra-acetic Acid, D. Van Nostrand Company, New Jersey, 1965.

[17] M.M. Abou-Mesalam, Sorption kinetics of copper, zinc, cadmium and nickel ions on synthesized silico-antimonate ion exchanger, Colloids Surf. A 225 (2003) 85–94.