PYRIDINE BASED ZIRCONIUM(IV) AND TIN(IV) PHOSPHATES AS NEW AND NOVEL INTERCALATED ION EXCHANGERS
Synthesis, characterization and analytical applications

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Pyridine based zirconium(IV) phosphate (PyZrP) and tin(IV) phosphate (PySnP) have been synthesized as new and novel intercalated ion exchangers. These materials have been characterized using X-ray, IR spectra, TG, DTG and DTA studies in addition to their ion exchange capacity, elution, pH titration, concentration and distribution behaviour. The distribution studies towards several metal ions in different media/concentrations have suggested that PyZrP and PySnP are selective for Hg(II) and Pb(II), respectively. As a consequence some binary separations of metal ions involving Hg(II) and Pb(II) ions have been performed on a column of these materials, demonstrating their analytical and environmental potential.

Introduction

Hybrid ion exchange materials are of recent interest [1] because of their properties intermediate to the organic and inorganic ion exchangers. They have shown good chemical stability in contrast with the organic resins and good thermal stability, well-known characteristics of inorganic ion exchangers. In addition to this, varying the interlayer distances may further enhance the utility of these materials in separation of metal ions. Since zirconium(IV) phosphate type ion exchangers [2] have layered structures, intercalation of polar molecules into the structure can alter the interlayer distances [3–5]. Many of such compounds like alkanols, glycols and amines have been added into the structure of α-ZrP by earlier workers [6].

In our laboratories we are engaged in the synthesis of a number of fibrous [7–12] and non-fibrous [13–17] hybrid ion exchangers, which may show selectivity for different metal ions. They have also been utilized in the separation of metal ions of environmental importance [18–20].

The relationship between the thermolysis and structure of metal compounds, and the study of the influence of metal and ligand nature on the process of thermal decomposition are of a great interest. Therefore, many authors have investigated the metal and ligand nature in many metal compounds of several central atoms, and also studied their thermal, spectral, structural and many other properties [21–48].

The present study is an effort to prepare hybrid ion exchangers intercalated with pyridine, a polar organic molecule. Following pages summarize the synthesis, characterization and analytical applications of pyridine based zirconium(IV) (PyZrP) and tin(IV) (PySnP) phosphates.

Experimental

Materials

Reagents and chemicals

Zirconyl oxychloride ($ZrOCl_2 \cdot 8H_2O$), stannic chloride ($SnCl_4 \cdot 5H_2O$), orthophosphoric acid (H_3PO_4), pyridine and all other reagents and chemicals used in these studies were of AnalaR grade.

Preparation of the reagent solutions

Solutions of zirconyl oxychloride, stannic chloride, orthophosphoric acid and pyridine were prepared in doubly distilled water.

Synthesis of the ion-exchange materials

A number of samples of PyZrP and PySnP were prepared by adding one volume of 0.05 M $ZrOCl_2 \cdot 8H_2O$ (in case of PyZrP) and 0.3 M $SnCl_4 \cdot 5H_2O$ (in case of PySnP) solutions in two volumes of (1:1) mixture of 0.1 M H_3PO_4 (in case of PyZrP) and 0.6 M H_3PO_4 (in

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case of PySnP) and pyridine (varying % age), drop-wise with constant stirring. The resulting slurry obtained was kept for 24 h at room temperature, then filtered and washed with demineralized water (DMW) till the excess acid was removed (pH~6). The materials were finally dried as usual at 45°C. The dried gel was then cracked into small granules by putting in DMW and converted into H^+ form by treating with 1 M HNO_3 for 24 h with occasional shaking and intermittently replacing the supernatant liquid with fresh acid. The materials thus obtained were then washed with DMW to remove the excess acid before drying finally at 45°C and sieved to obtain particle of mesh size 50–70. The ion exchange capacity of PyZrP and PySnP were found to be maximum for sample PyZrP-5 (Table 1) and PySnP-3 (Table 2) respectively. These two samples were selected for further studies.

Instrumental methods

Spectrophotometric determinations were carried out using UV-vis spectrophotometer Elico model SL 171.

- pH measurements were performed using an Elico model LI-10 pH meter.
- X-ray diffraction studies were made on a Philips analytical X-ray B.V. diffractometer type PW-3710.
- IR spectral studies were carried out using a PerkinElmer FTIR spectrophotometer model RX-1.
- TG-DTG-DTA studies were carried out using a PerkinElmer instrument, Pyric Diamond model.
- For atomic absorption studies, a Shimadzu AA-640 model atomic absorption spectrophotometer (AAS) was used.

- Elemental analysis was performed on a Vario ELIII elemental analyzer.

Results and discussion

Composition

100 mg of the samples were dissolved in 3–4 mL of HF acid for PyZrP and in conc. HCl for PySnP. Zr(IV) and Sn(IV) were determined by AAS in PyZrP and PySnP, respectively, while phosphate was determined spectrophotometrically by the phosphovanado molybdate method [51] in both materials. Carbon, hydrogen and nitrogen were determined by the elemental analysis.

On the basis of chemical analysis, the molar compositions of $Zr:P:C_5H_5N$ (PyZrP) and $Sn:P:C_5H_5N$ (PySnP) were found to be 1:2:4 and 1:2:7, respectively, which tentatively suggest the following formulae for PyZrP and PySnP, respectively:

$$[(ZrO_2)(H_3PO_4)_2(C_5H_5N)_4]\cdot nH_2O$$

and

$$[(SnO_2)(H_3PO_4)_2(C_5H_5N)_7]\cdot nH_2O$$
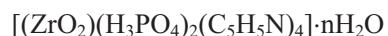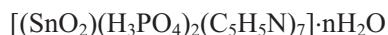
Ion exchange capacity (i.e.c.), elution and concentration behaviour

The most important feature of the materials prepared in these studies is their good ion exchange capacity (i.e.c.) for Na^+ ions [2.0 meq/dry g in PyZrP (Table 1) and 2.10 meq/dry g in PySnP (Table 2)]. It is much higher than the i.e.c. generally shown by the inorganic ion

Table 1 Synthesis of various samples of pyridine based zirconium(IV) phosphate

Sample number	Zr solution/ mMol L^{-1}	H_3PO_4/ mMol L^{-1}	Conc. of pyridine/ %	Na^+ ion-exchange capacity/meq(dry g)$^{-1}$
PyZrP-1	50	100	–	0.3
PyZrP-2	50	100	0.5	0.66
PyZrP-3	50	2000	0.5	0.3
PyZrP-4	50	50	1	0.22
PyZrP-5	50	100	1	2.0
PyZrP-6	50	100	1.5	0.78
PyZrP-7	50	100	2	1.02

Table 2 Synthesis of various samples of pyridine based tin(IV) phosphate

Sample number	Sn solution/ mMol L^{-1}	H_3PO_4/ mMol L^{-1}	Conc. of pyridine/ %	Na^+ ion-exchange capacity/meq(dry g)$^{-1}$
PySnP-1	300	600	–	1.4
PySnP-2	200	600	1	1.32
PySnP-3	300	600	1	2.1
PySnP-4	300	600	0.5	1.17

Table 3 Ion exchange capacity of pyridine based zirconium(IV) and tin(IV) phosphates for various metal solutions

Metal solution	Ion-exchange capacity/meq(dry g^{-1})	
	PyZrP	PySnP
LiNO$_3$	1.60	1.63
NaNO$_3$	2.00	2.10
KNO$_3$	2.41	2.21
Mg(NO$_3$)$_2$	1.63	1.35
Ca(NO$_3$)$_2$	2.85	1.43
Sr(NO$_3$)$_2$	1.93	1.65
BaCl$_2$·2H$_2$O	2.10	1.84

exchangers. The i.e.c. for Na$^+$ and other metal ions were determined by the column process as described earlier [7] for both PyZrP and PySnP. The results are summarized in Table 3. The i.e.c. of alkali metals and alkaline earths (Table 3) on PyZrP and PySnP shows the following trends: Li$^+$<Na$^+$<K$^+$ and Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}. It is in accordance to the decreasing trend in hydrated ionic radii of these metal ions in the same order.

The elution and concentration behaviour were also studied on these materials by a similar method described earlier [7]. Figures 1 and 2 show the elution behaviour of PyZrP and PySnP, respectively. Table 4 summarizes the result of concentration behaviour on both materials. Elution behaviour (Figs 1 and 2) reveals that the exchange is quite fast and almost all the H$^+$ ions are eluted out in the first 120 mL (in PyZrP) and 130 mL (in PySnP) of the effluent from a column of 1.0 g exchanger. The optimum concentration of the eluant was found to be 1 M (Table 4) for a complete removal of H$^+$ ions from the PyZrP and PySnP columns as usual.

pH titrations

pH titrations were performed by the Topp and Pepper's method [49] on both PyZrP and PySnP. Figures 3 and 4 show the results of this study on PyZrP and PySnP, respectively. The pH titration curves of
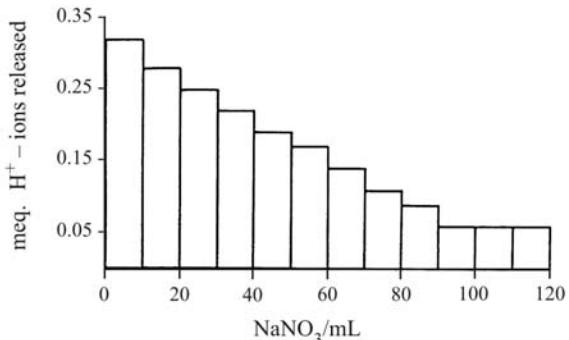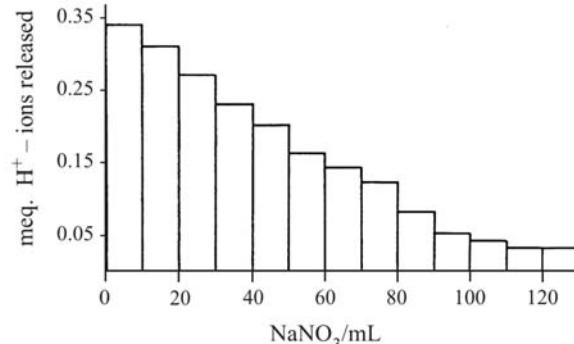
Fig. 2 Histograms showing the elution behaviour of pyridine based tin(IV) phosphate

Table 4 Concentration behaviour of pyridine based zirconium(IV) and tin(IV) phosphates

NaNO$_3$/M	Ion-exchange capacity/meq(dry g^{-1})	
	PyZrP	PySnP
0.2	1.20	1.25
0.4	1.42	1.50
0.6	1.63	1.73
0.8	1.85	1.94
1.0	2.0	2.10
1.2	2.0	2.10

PyZrP (Fig. 3) and PySnP (Fig. 4) were obtained under equilibrium a condition for LiOH/LiCl, NaOH/NaCl and KOH/KCl systems. Both the materials (PyZrP and PySnP) behave as bifunctional acids for Na$^+$ ions showing its theoretical i.e.c. at equilibrium ~3.5 and 3.0 meq g^{-1} for PyZrP and PySnP, respectively. The bifunctional behaviour becomes less prominent in case of H$^+$–K$^+$ exchange. The i.e.c. for this ion is found to be ~3.5 meq g^{-1} in both materials. However, in case of the Li$^+$ both the exchangers appear to be monofunctional acids i.e. the exchange pro-

Fig. 1 Histograms showing the elution behaviour of pyridine based zirconium(IV) phosphate
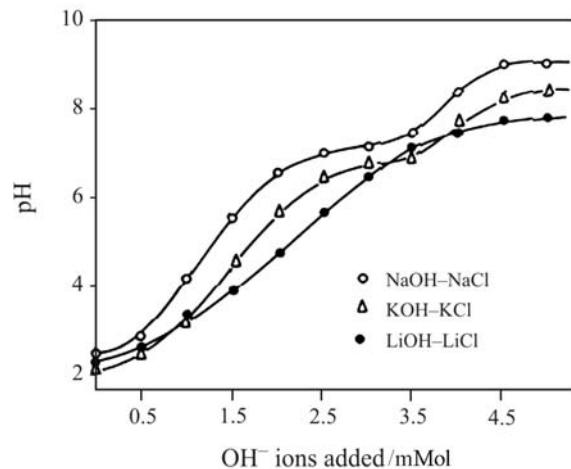
Fig. 3 Equilibrium pH titration curves of pyridine based zirconium(IV) phosphate
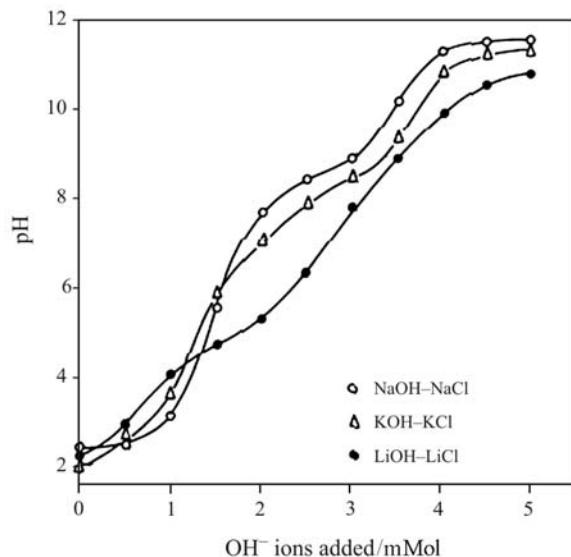
Fig. 4 Equilibrium pH titration curves of pyridine based tin(IV) phosphate

cess is completed in single step. The value of the i.e.c. further decreases in this case (~2.5 meq g^{-1} in both materials). The system contains ionogenic group, the corresponding acid of which i.e. phosphoric acid has three pKa values (pKa$_1$, pKa$_2$ and pKa$_3$) are 2.12, 7.21 and 12.30, respectively. Thus it is evident that the first ionization of this acid is very much faster compared to the other two. Both the materials appear to be strong cation exchangers as indicated by low pH (~2–2.2) of the solutions when no OH$^-$ ions were added to the system.

Distribution studies

200 mg of the exchanger in H$^+$ form were kept in 20 mL of the solvent (doubly distilled water) for 24 h, with intermittent shaking to attain equilibrium. The initial metal ion concentration was so adjusted that it did not exceed 3% of total i.e.c. of the materials. The metal ions in the solutions before and after equilibrium were determined by EDTA titration [50] and the distribution coefficients, K_d, were calculated by the formula:

$$K_d = \frac{I - F}{F} \frac{V}{M} (\text{mL g}^{-1})$$

where *I* and *F* are the initial and final amounts of metal ion in the solution phase, *V* is the volume of the solution, and is *M* the amount (g) of the exchanger. Tables 5 and 6 summarize the result of this study on PyZrP and PySnP, respectively. The distribution studies (Tables 5 and 6) show high selectivity of the materials PyZrP and PySnP for Hg(II) and Pb(II) ions, respectively indicating their importance in environmental studies. It was demonstrated by practically

achieving some binary separations involving Hg(II) in case of PyZrP for example: Hg(II)–Mg(II), Hg(II)–Cd(II) and Hg(II)–Ni(II) as summarized in Table 7 and Pb(II) in case of PySnP for example: Pb(II)–Mg(II), Pb(II)–Cd(II) and Pb(II)–Cu(II) as summarized in Table 8. A binary separation of Pb(II) from Mg(II) in case of PyZrP and Cd(II) from Cu(II) in case of PySnP were also achieved emphasizing the above facts. The results were found to be quite precise and reproducible. Figures 5 and 6 show the separation profiles of PyZrP and PySnP, respectively.

Separations achieved

Several binary separations were tried using column of i.d. ~0.6 cm containing 2 g of the material. The column was washed thoroughly with demineralized water (DMW) and the mixture to be separated was loaded on it, maintaining a flow rate of ~2–3 drops min^{-1} (0.15 mL min^{-1}). The separation was achieved by passing a suitable solvent through the column as eluant and the metal ions in the effluent were determined quantitatively by EDTA titrations. Table 7, Fig. 5 (in case of PyZrP) and Table 8, Fig. 6 (in case of PySnP) give the salient features of the separation.

Thermal stability

1 g samples of the material were heated at various temperatures for 1 h each in a muffle furnace and their i.e.c. was determined by the column process [7] after cooling to room temperature. Table 9 summarizes the result of this study on both materials PyZrP and PySnP. The thermal stability (Table 9) of both materials appears to be less than the non-hybrid materials, due to the organic component present in the system. PySnP appears to be thermally more stable as compared to PyZrP. On heating up to 100°C PySnP and PyZrP show the retention of 82 and 70%, respectively. PySnP and PyZrP show the retention of i.e.c. as 66 and 43%, respectively on heating up to 200°C. Even heating up to 400°C, these materials show an appreciable i.e.c., PySnP retaining about 38% and PyZrP about 23% of the i.e.c. at room temperature. However, on heating up to 600°C both the materials show the sharp decrease in their i.e.c., retaining only the 5% of the total i.e.c.

TG-DTG-DTA studies

TG-DTG-DTA studies were carried out using a PerkinElmer instrument, Pyric Diamond model. Figures 7 and 8 show the TG-DTG-DTA curves of PyZrP and PySnP, respectively.

Table 5 K_d values of metal ions on pyridine based zirconium(IV) phosphate in DMW, hydrochloric acid, nitric acid and perchloric acid media

Metal ions	DMW/mL	HCl			HNO₃			HClO₄		
		0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M
Mg(II)	320	200	110	90.90	200	75	50	250	200	133.33
Ca(II)	500	328.57	275	150	275	233.33	130.76	400	275	233.33
Ba(II)	675	244.44	181.81	158.33	287.5	244.44	210	520	342.85	210
Sr(II)	540	300	255.55	220	300	255.55	220	433.33	357.14	220
Mn(II)	500	200	166.66	140	242.85	200	166.66	242.85	200	166.66
Cd(II)	600	320	200	162.5	250	200	162.5	320	250	250
Pb(II)	633.33	340	340	266.66	450	450	340	450	450	450
Co(II)	1050	666.66	666.66	475	666.66	360	360	566.66	475	360
Cu(II)	1300	600	600	600	600	600	600	600	600	600
Ni(II)	900	566.66	400	300	566.66	400	300	666.66	400	300
Hg(II)	1900	900	900	900	900	900	900	900	900	900
Fe(III)	700	700	700	700	700	700	700	700	700	700
Cr(III)	25	5.26	5.26	2.56	8.10	8.10	8.10	11.11	5.26	2.56

Table 6 K_d values of metal ions on pyridine based tin(IV) phosphate in DMW, hydrochloric acid, nitric acid and perchloric acidd media

Metal ions	DMW/mL	HCl			HNO₃			HClO₄		
		0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M
Mg(II)	320	250	133.33	110	250	162.5	75	200	162.5	133.33
Ca(II)	650	400	328.57	172.72	328.57	275	150	500	328.57	275
Ba(II)	933.33	287.5	210	181.81	342.85	287.5	244.44	675	416.66	244.44
Sr(II)	700	357.14	300	255.55	357.14	300	255.55	433.33	357.14	300
Mn(II)	700	242.85	200	166.66	300	242.85	200	300	242.85	200
Cd(II)	600	320	250	200	250	200	200	250	200	162.5
Pb(II)	1000	633.33	633.33	450	633.33	633.33	450	633.33	633.33	450
Co(II)	1050	666.66	475	475	666.66	475	360	475	360	360
Cu(II)	600	366.66	250	250	366.66	366.66	250	366.66	250	250
Ni(II)	400	300	233.33	233.33	300	233.33	233.33	300	233.33	233.33
Hg(II)	566.66	400	400	400	400	400	400	400	400	400
Fe(III)	700	300	300	166.66	300	300	166.66	300	300	166.66
Cr(III)	21.21	8.10	8.10	5.26	11.11	11.11	8.10	14.28	8.10	5.26

Table 7 Binary separations of metal ions achieved on pyridine based zirconium(IV) phosphate

Sample No.	Separation achieved		Amount loaded/μg		Amount found/μg		Error/%		Eluent used	Vol. of eluent/mL
	M_1	M_2	M_1	M_2	M_1	M_2	M_1	M_2		
1	Mg(II)–Hg(II)		1615.38	2001.66	1653.84	2001.66	2.38	0	Mg: 0.1 M HCl Hg: 1 M HCl+1 M NH$_4$Cl	70 60
2	Cd(II)–Hg(II)		1943.36	2001.66	1897.09	1951.61	−2.38	−2.5	Cd: 1 M HNO$_3$ Hg: 1 M HCl+1 M NH$_4$Cl	50 60
3	Ni(II)–Hg(II)		1744.74	2001.66	1744.74	2001.66	0	0	Ni: 0.1 M HCl Hg: 1 M HCl+1 M NH$_4$Cl	50 60
4	Pb(II)–Mg(II)		2199.19	1615.38	2199.186	1576.92	0	−2.38	Pb: 1 M HCl Mg: 0.1 M HCl	50 60

Table 8 Binary separations of metal ions achieved on pyridine based tin(IV) phosphate

Sample No.	Separation achieved		Amount loaded/µg		Amount found/µg		Error/%		Eluent used	Vol. of eluent/mL
	M_1	M_2	M_1	M_2	M_1	M_2	M_1	M_2		
1	Mg(II)–Pb(II)		1615.38	2199.18	1576.92	2149.20	–2.38	–2.27	Mg: 0.1 M HClO₄ Pb: 1 M HNO₃	60 60
2	Cd(II)–Pb(II)		1943.36	2199.18	1897.09	2149.18	–2.38	0	Cd: 0.1 M HCl Pb: 1 M HNO₃	60 50
3	Cu(II)–Pb(II)		1014.72	2199.18	978.48	2199.18	–3.57	0	Cu: 0.1 M HClO₄ Pb: 1 M HNO₃	50 50
4	Cd(II)–Cu(II)		1943.36	1014.72	1943.36	1050.96	0	3.57	Cd: 0.1 M HCl Cu: 0.1 M HClO₄	60 50
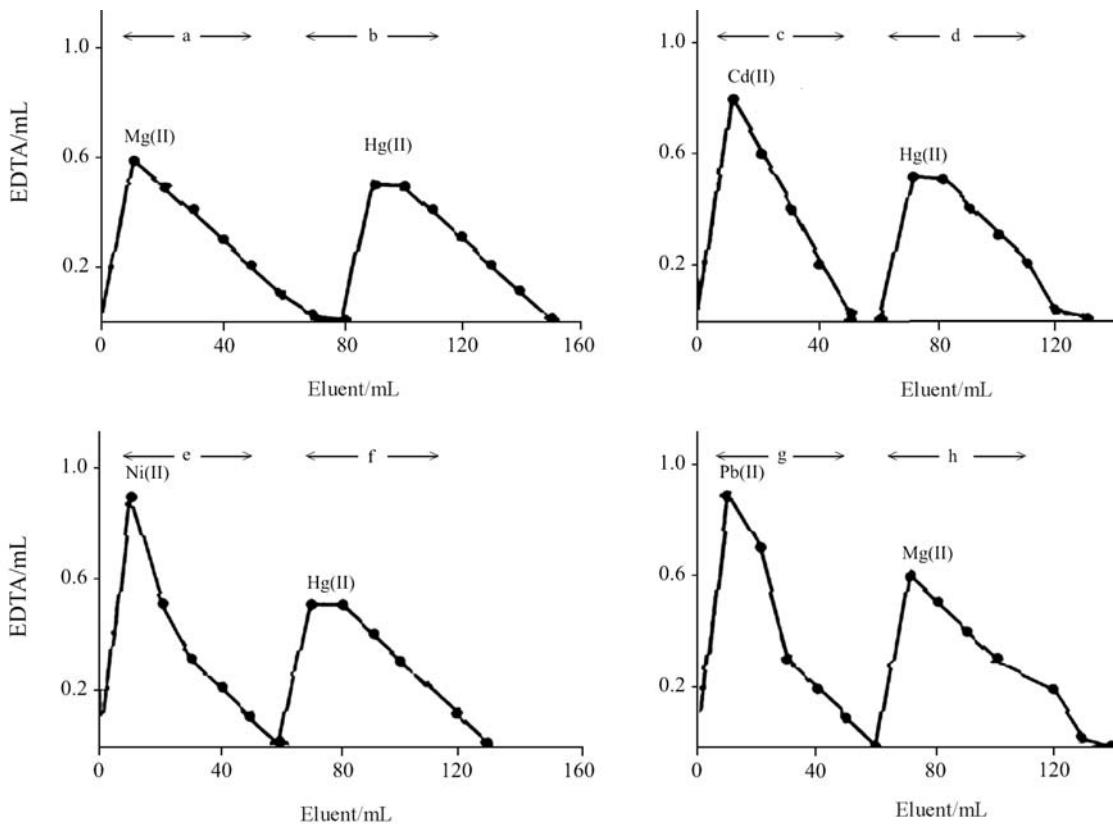
Fig. 5 Separation of Mg(II) from Hg(II); Cd(II) from Hg(II); Ni(II) from Hg(II) and Pb(II) from Mg(II) on pyridine based zirconium(IV) phosphate columns: a, e, h – 0.1 M HCl; b, d, f – 1 M HCl+1 M NH$_4$Cl; g – 1 M HCl; c – 1 M HNO$_3$
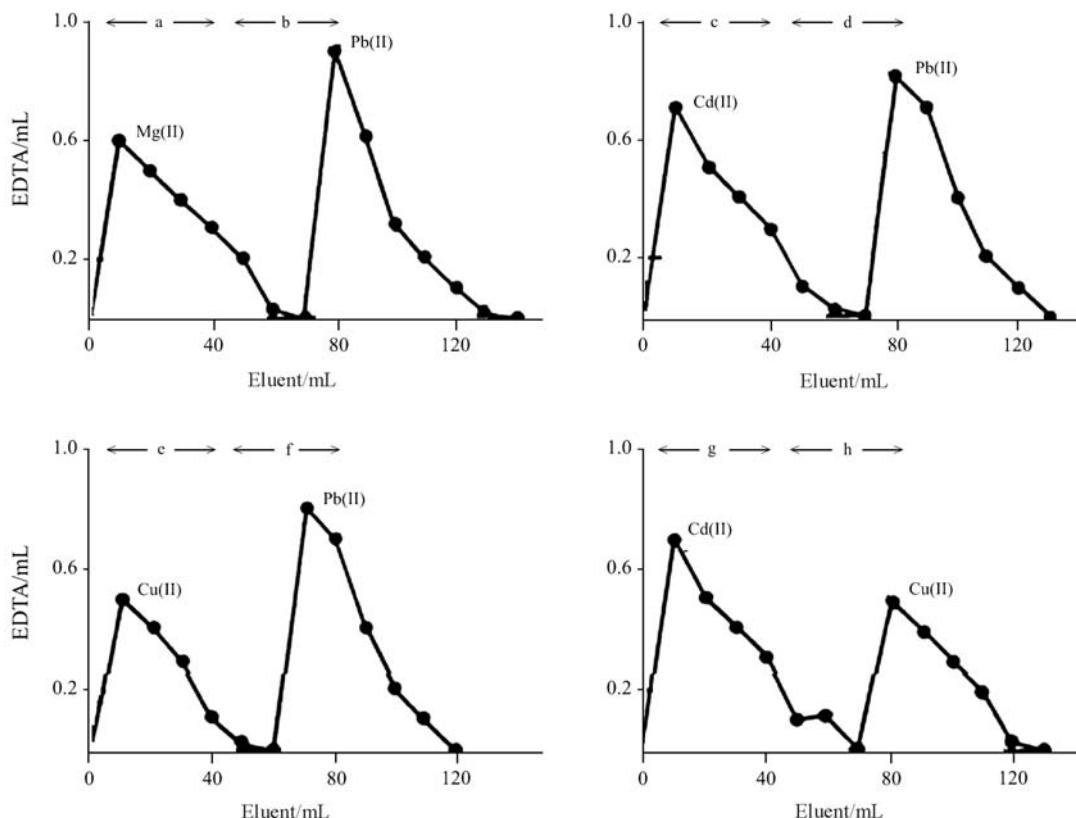
Fig. 6 Separation of Mg(II) from Pb(II); Cd(II) from Pb(II); Cu(II) from Pb(II) and Cd(II) from Cu(II) on pyridine based tin(IV) phosphate columns: a, e, h – 0.1 M HClO$_4$; b, d, f – 1 M HNO$_3$; c, g – 0.1 M HCl

Table 9 Thermal stability of pyridine based zirconium(IV) and tin(IV) phosphates after heating to various temperatures for 1 h

Sample No.	Drying temperature/°C	PyZrP			PySnP		
		Ion-exchange capacity/meq(dry g)$^{-1}$	Change in colour	Retention of i.e.c./%	Ion-exchange capacity/meq(dry g)$^{-1}$	Change in colour	Retention of i.e.c./%
1	45	2.0	White	100	2.1	White	100
2	100	1.4	White	70	1.72	White	81.90
3	200	0.86	Creamish	43	1.38	Dirty white	65.71
4	400	0.46	Dirty white	23	0.8	Dirty white	38.09
5	600	0.1	Greyish	5	0.1	Greyish white	4.76
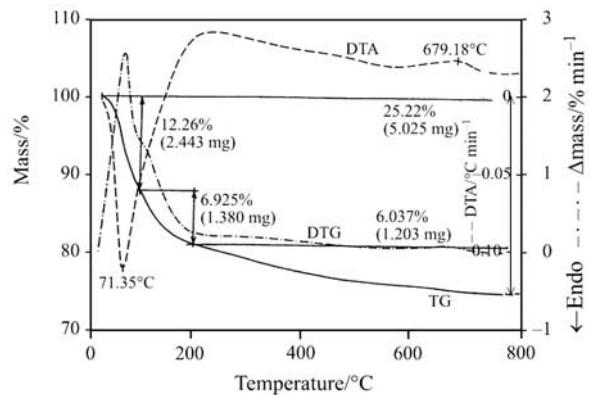
Fig. 7 TG-DTG-DTA curves of pyridine based zirconium(IV) phosphate
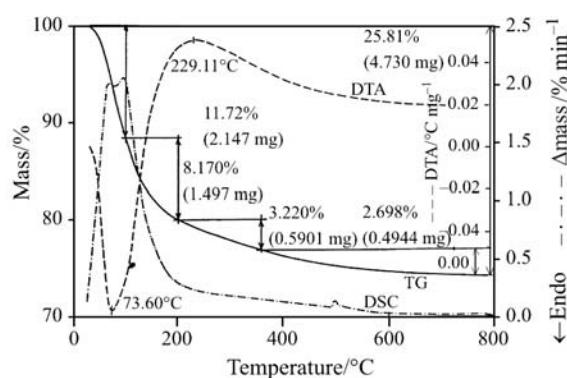
Fig. 8 TG-DTG-DTA curves of pyridine based tin(IV) phosphate

The thermal curves (Figs 7 and 8) show the mass loss of 12.2 and 11.7% on heating up to 100°C for PyZrP and PySnP, respectively, which is due to the removal of the external water molecules 'n' from the materials. The value of 'n' was found to be 5.0 and 6.6 for PyZrP and PySnP, respectively using Alberti's equation [52]. The slow mass loss between 100 and 200°C in case of PyZrP and PySnP, respectively is due to the decomposition of the organic part of the material. At 200°C onwards the smooth horizontal curves indicate the formation of pyrophosphate phase in both materials [53].

IR spectral studies

IR spectral studies were carried out by KBr disc method. Figures 9 and 10 show the IR spectra of PyZrP and PySnP, respectively. The IR spectra of PyZrP (Fig. 9) and PySnP (Fig. 10) confirm the presence of the external water molecules in addition to the OH groups and the metal oxides and metal hydroxides (at the PO_4^{3-} sites) present internally in the materials. The metal oxide and metal hydroxide bands are observed at 728.25 cm^{-1} in PyZrP and at 721.96 cm^{-1} in PySnP. The bands at 515.54 and 1031.36 cm^{-1} in
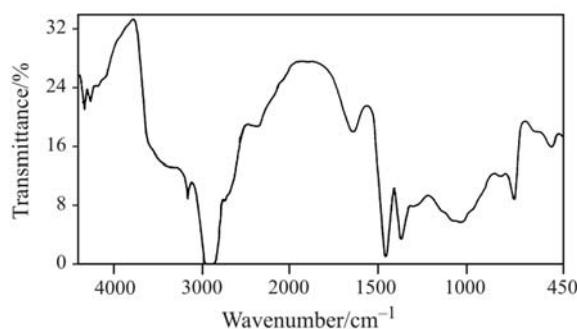

**Fig. 9** Infrared spectrum of pyridine based zirconium(IV) phosphate
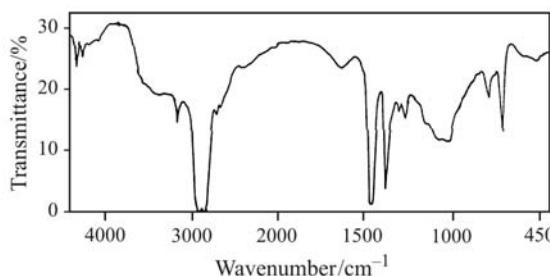
Fig. 10 Infrared spectrum of pyridine based tin (IV) phosphate

PyZrP and 518.69 and 1025.79 cm^{-1} in PySnP indicate the presence of phosphate groups. The absorption bands at 1629.46 and 3190.0 cm^{-1} in PyZrP and 1632.39 and 3200.0 cm^{-1} in PySnP, correspond to the water of crystallization. The bands at 1368.90 cm^{-1} in PyZrP and at 1377.27 cm^{-1} in PySnP are due to the C–N stretching. Absorption bands at 1454.63 cm^{-1} in PyZrP and 1463.24 cm^{-1} in PySnP indicate the presence of C=N stretching [54, 55].

X-ray studies

Figures 11 and 12 show the X-ray diffraction patterns of PyZrP and PySnP, respectively. The X-ray diffractograms (Figs 11 and 12) of the materials ex-
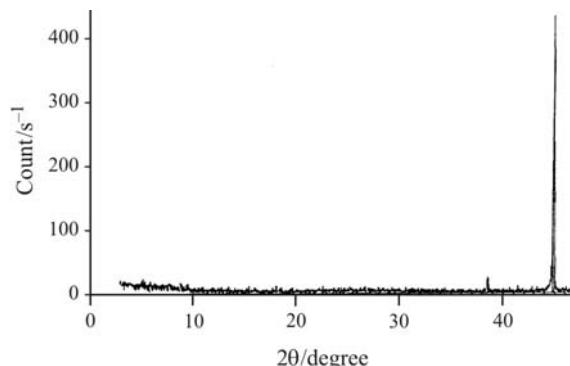

Fig. 11 X-ray diffraction pattern of pyridine based zirconium(IV) phosphate
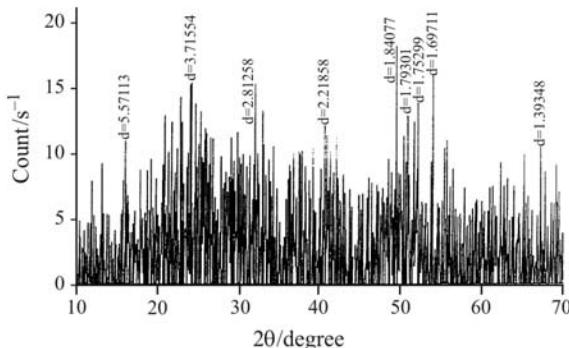
Fig. 12 X-ray diffraction pattern of pyridine based tin(IV) phosphate

hibit some weak peaks, showing their poorly crystalline character, which makes it difficult to evaluate their structures. Due to the lack of information, a detailed mechanism of the ion exchange behaviour cannot be given at this stage correlating the metal ion diameter with cavity sizes of the materials.

Conclusions

Pyridine supported zirconium(IV) phosphate and tin(IV) phosphate are useful ion exchangers with promising ion exchange behaviour, supported by some important separations achieved practically. These two materials may find use in environmental studies because of their selectivity for heavy metal ions. Such explorative studies are in progress in our laboratories.

Acknowledgements

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