Synthesis, characterization and ion exchange properties of zirconium(IV) tungstoiodophosphate, a new cation exchanger

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Abstract. Zirconium(IV) tungstoiodophosphate has been synthesized under a variety of conditions. The most chemically and thermally stable sample is prepared by adding a mixture of aqueous solutions of 0.5 mol L^{-1} sodium tungstate, potassium iodate and 1 mol L^{-1} orthophosphoric acid to aqueous solution of 0.1 mol L^{-1} zirconium(IV) oxychloride. Its ion exchange capacity for Na^+ and K^+ was found to be 2.20 and 2.35 meq g^{-1} dry exchanger, respectively. The material has been characterized on the basis of chemical composition, pH titration, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis. The effect on the exchange capacity of drying the exchanger at different temperatures has been studied. The analytical importance of the material has been established by quantitative separation of Pb^{2+} from other metal ions.

Keywords. Synthesis; characterization; zirconium(IV) tungstoiodophosphate.

1. Introduction

Ion exchangers have played a prominent role in water processing and in the chemical industry. Meeting the stringent coolant purity requirements of the nuclear industry is solely attributable to ion exchangers. In the last decade, ion exchangers have been used extensively in the chemical decontamination process for metal ion recovery, regeneration of decontaminants and removal of the formulation chemicals from the coolant (Velmurugan *et al* 1991). Therefore, there is a continuing need to find new inorganic ion exchangers, which are capable of removing toxic substances from aqueous effluents (Hafez *et al* 2001), as they have good stability toward temperature, ionizing radiation, and oxidizing solutions.

Synthetic inorganic ion exchangers based on tetravalent metals have been objects of considerable study in recent years because of their selectivity and intercalation properties (Qureshi *et al* 1996; Zhaong *et al* 1996; Jaimez *et al* 1997; Sirlei and Claudio 1997; Ferragina *et al* 2001; Clearfield and Wang 2002; Hayshi *et al* 2002). Zirconium-based ion exchangers have received attention because of their excellent ion-exchange behaviour and some important chemical applications in the field of ion exchange, ion-exchange membrane, and solid–state electrochemistry. Heteropolyacid salts based on tin(IV), titanium(IV), zirconium(IV), and thorium(IV) have been reported in the literature as ion-exchange materials. These materials have been found to have better properties than the simple salts of metals. The selectivity may be enhanced by varying the composition of materials.

The present work is concerned with zirconium(IV)-based four-component ion exchangers. The literature reveals that several three-component ion exchangers, i.e. zirconium (IV) iodooxalate (Singh *et al* 2002), zirconium(IV) iodovanadate (Singh *et al* 2003), zirconium(IV) phosphosilicate (Choube and Turel 2003), zirconium(IV) selenomolybdate (Gupta *et al* 2000), zirconium(IV) aluminophosphate (Varshney *et al* 1998), zirconium(IV) arsenovanadate (Qureshi *et al* 1995), zirconium(IV) phosphoborate (Mittal and Singh 1995), zirconium(IV) tungstophosphate (Gupta and Varshney 1997), zirconium(IV) tungstatephenolate (Tandon *et al* 1996), zirconium(IV) iodophosphate (Nabi *et al* 1996), zirconium(IV) selenophosphate (Qureshi and Rehman 1987a) and zirconium(IV) iodomolybdate (Qureshi and Rehman 1987b) have been studied for their synthesis, ion-exchange behaviour and analytical applications. However, the newly synthesized ion-exchanger, zirconium(IV) tungstoiodophosphate has increased ion exchange capacity and higher stability at elevated temperature.

This paper deals with the synthesis, characterization and ion exchange properties of zirconium (IV) tungstoiodophosphate as a new inorganic ion exchanger.

2. Experimental

2.1 *Reagent and chemicals*

Zirconium(IV) oxychloride ($ZrOCl_2 \cdot 8H_2O$), sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) and potassium iodate (KIO_3) were

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Table 1. Conditions of synthesis and few properties of different samples of zirconium(IV) tungstoiodophosphate.

Sample no.	Molar conc. (M)				Mixing	pH	Appearance of beads after drying at 40°C	I.E.C. (meq/g)
	Zr	WO_4^{2-}	IO_3^-	PO_4^{3-}				
ZTIP1	0·1	0·5	0·5	1	1:1:1:1	1	White gelatinous	1·20
ZTIP2	0·1	0·5	0·5	1	1:2:1:1	1	White gelatinous	0·78
ZTIP3*	0·1	0·5	0·5	1	1:1:3:1	1	White gelatinous	2·20
ZTIP4	0·1	0·5	0·5	1	2:1:1:1	1	White gelatinous	1·40
ZTIP5	0·1	0·5	0·5	1	1:1:2:1	1	White gelatinous	1·00

obtained from CDH (India), while orthophosphoric acid (H_3PO_4) was a Qualigens (India) product. All other reagents and chemicals were of analytical grade.

2.2 *Instrumentation*

Systronic digital pH meter, Bausch and Lomb spectronic 20, FTIR model Shimadzu 820 pc, Philips X-ray unit, Duprot 900 and 950 thermal analyser and an electric shaking machine were used for pH measurements, absorbance measurements, IR studies, X-ray diffraction, thermal analysis and shaking, respectively.

2.3 *Synthesis of ion exchange material*

A number of samples were prepared by adding 0·1 M $ZrOCl_2 \cdot 8H_2O$ solution to a mixture of 0·5 M sodium tungstate, potassium iodate and 1 M orthophosphoric acid, in different volume ratios with intermittent shaking of the mixture and maintaining the pH at 1, as given in table 1.

The resultant gel was allowed to stand by keeping it for 24 h at room temperature and then filtered. The excess acid was removed by washing with demineralized water and the material was dried in an electric oven at $50 \pm 5°C$. The dried gel was put into the demineralized water to obtain granules of uniform size suitable for column operation. The dried granules were converted into the H^+ form by keeping them immersed with HNO_3 (1 mol L^{-1}) for 24 h with occasional shaking and intermittently replacing the supernatant liquid with fresh acid. The material thus obtained was then washed with demineralized water to remove the excess acid before drying finally at $50 \pm 5°C$ and sieved to obtain particles of size 50–70 mesh.

2.4 *Ion-exchange capacity (IEC)*

The ion exchange capacity of the material was determined by the column process (table 2). One g of the exchanger (H^+ form) was packed in a glass column and washed with DMW to remove any excess of acid that remained on the particles. 250 ml of 1 M solution of different salts was passed through the column maintaining the flow rate at 1 ml min^{-1}. The effluent was collected and titrated against a standard NaOH solution to determine the total H^+ ions released.

Table 2. Ion exchange capacity (meq g^{-1} dry exchangers) of zirconium(IV) tungstoiodophosphate (ZTIP3).

Sl. no.	Cation	Salt used	I.E.C (meq g^{-1})	pH titration
1.	Li^+	LiCl	1·90	
2.	Na^+	NaCl	2·20	2·28
3.	K^+	KCl	2·35	2·45
4.	Mg^{2+}	$Mg(NO_3)_2$	1·45	
5.	Sr^{2+}	$Sr(NO_3)_2$	1·68	
6.	Ca^{2+}	$Ca(NO_3)_2$	1·85	

2.5 *Chemical composition*

For the determination of chemical composition of the sample, ZTIP3, 0·1 g of exchanger was dissolved in minimum amount of hot concentrated H_2SO_4. The solution was diluted to 100 ml with DMW. The amounts of zirconium and iodate were determined spectrophotometrically using Alizarin Red-S and pyrogallol as colouring reagents, respectively. Tungsten was determined gravimetrically and phosphate was determined titrametrically using the standard method (Reilley *et al* 1959).

2.6 *Thermal stability*

Thermogravimetric analysis of the material in the H^+ form was performed at a heating rate of 10°C min^{-1}. The effect of heating on the ion-exchange capacity of the material was also examined. The material in H^+ form was heated at different temperatures for 1 h in a muffle furnace and the ion-exchange capacity for Na^+ was evaluated by the column process after cooling it at room temperature. The results are summarized in table 3a.

2.7 *pH titration*

pH titration was performed by the batch process using the method of Topp and Pepper (1949). 500 mg portions of the exchanger in the H^+ form were placed in each of the several 250 ml conical flasks followed by equimolar solution of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 ml to maintain the ionic strength constant. The pH of each solution was

Table 3a. Thermal stability of zirconium(IV) tungstoiodophosphate (ZTIP3) after heating to various temperatures for 1 h.

Drying temp (°C)	Na^+ ion exchange capacity (meq dry/g)	Change in colour	% Retention
40	2·20	White	100·00
100	1·82	White	82·73
200	1·60	White	72·73
300	1·35	White	61·37
400	1·00	White	45·46
500	0·90	Gray	40·91
600	0·78	Dark gray	35·46

Table 3b. Effect of drying temperature on ion exchange capacity for various inorganic ion exchangers.

	Ion exchange capacity (meq g^{-1} dry exchanger) at different temperatures						
Inorganic ion exchanger	40°C	100°C	200°C	300°C	400°C	500°C	600°C
Zirconium(IV) tungstoiodophosphate	2·20	1·82	1·60	1·35	1·00	0·90	0·78
Tin(IV) tungstovanadophosphate	1·83	1·80	1·50	1·25	0·97	0·85	–
Zirconium(IV) iodophosphate	1·75	1·60	1·40	1·00	0·92	0·82	0·66
Zirconium(IV) iodomolybdate	1·54	1·30	1·00	0·78	0·66	0·42	0·16

measured and plotted against milliequivalents of OH ions. The capacity corresponding to inflection point was also calculated from the curve.

2.8 *Chemical stability*

500 mg of the sample, ZTIP3, was shaken with 50 ml of the various solutions at 30 ± 2°C for 6 h. The amounts of zirconium, iodate and phosphate released in the solutions were determined spectrophotometrically with alizarin red-s, pyrogallol and molybdophosphoric acid, and tungsten was determined gravimetrically (Reilley *et al* 1959; Davis 1963).

The material is found to be quite stable in lower concentration of mineral acid, such as HCl, H_2SO_4, and HNO_3. However, the sample is quite stable in organic acid like acetic acid. The results are summarized in table 4.

2.9 *Distribution studies*

200 mg portion of the dry exchanger in H^+ form were equilibrated with 20 ml of different metal ion solutions in the required medium and kept for 24 h with intermittent shaking. The initial metal ion concentration (0·01 M) in the solution was so adjusted that it did not exceed 3% of total ion exchange capacity of the material. The determination before and after equilibrium were carried out volumetrically using EDTA as the titrant (Reilley *et al* 1959).

The *Kd* values, as summarized in table 5, were obtained by the formula

$$Kd = (I – F)/F*V/M \text{ (ml/g)},$$

where *I* is the initial metal ion concentration, *F* the final metal ion concentration, *V* the volume of solution and *M* the mass of the exchanger.

2.10 *FTIR spectrum*

FTIR spectrum of sample ZTIP3 was obtained by KBr disc method.

2.11 *Separation of metal ions achieved*

Several binary separations were tried using a column of internal diameter, $\sim 0\cdot6$ cm, containing 2 g of the material. The column was washed thoroughly with demineralized water and the mixture to be separated was loaded on to 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 eluent and the metal ions in the effluent were determined quantitatively by EDTA titrations. Table 6 gives the salient features of the separations.

3. Results and discussion

The results from the study of the ion-exchange capacity of various samples of zirconium (IV) tungstoiodophosphate are presented in table 1. The improvement in the ion-exchange capacity and chemical stability seem to be much higher for sample ZTIP3 and, therefore, this sample

Table 4. Chemical stability of zirconium(IV) tungstoiodophosphate (ZTIP3) in different solvents.

Solution	Zr(IV) released (mg/50 ml)	WO_4^{2-} released (mg/50 ml)	IO_3^- released (mg/50 ml)	PO_4^{3-} released (mg/50 ml)
H_2O	0·00	0·00	0·00	0·00
0·1 M $HClO_4$	0·00	0·28	0·38	0·039
1·0 M $HClO_4$	0·46	0·98	1·38	1·10
0·1 M HNO_3	0·00	0·18	0·22	0·31
0·5 M HNO_3	0·00	0·38	0·28	0·90
1·0 M HNO_3	0·30	0·78	0·98	0·18
0·1M H_2SO_4	0·00	0·34	0·34	0·34
0·5 M H_2SO_4	0·91	0·78	0·94	1·00
1·0 M H_2SO_4	1·41	0·94	1·78	0·19
0·1 M HCl	0·00	0·00	0·18	0·78
0·5 M HCl	0·68	0·42	0·68	1·30
1·0 M HCl	1·55	0·78	1·20	0·31
1 M CH_3COOH	0·00	0·21	0·28	0·39
0·1 M NaOH	0·98	3·10	3·19	3·28
2·0 M NaOH	Completely dissolved			

Table 5. *Kd* values of metal ions on zirconium(IV) tungstoiodophosphate (ZTIP3) in different solvents.

Metal ions	DMW	0·01 M HNO_3	0·1 M HNO_3	1 M HNO_3	0·01 M HCl	0·1 M HCl	1 M HCl	0·01 M $HClO_4$	0·1 M $HClO_4$	1 M $HClO_4$
Al^{3+}	9100	4500	2950	2150	3100	2050	1620	4500	3041	2150
Ba^{2+}	2916	1002	832	650	1540	1150	720	1000	740	610
Ca^{2+}	1700	1100	602	540	1050	640	520	1175	710	510
Cu^{2+}	7900	3600	1440	910	2153	975	821	2633	1171	711
Co^{2+}	3600	1400	940	800	1220	880	840	1402	1260	940
Cd^{2+}	4500	1224	904	740	1350	1071	1000	1460	741	510
Fe^{3+}	5400	2700	2700	2700	5100	2600	2600	2700	1450	830
Hg^{2+}	4100	1900	1504	1066	2133	1850	1500	1850	1530	1230
K^+	1000	445	320	240	521	380	280	410	340	340
Mn^{2+}	2455	840	740	610	785	848	730	750	730	580
Mg^{2+}	1600	1132	900	700	1600	840	741	1040	821	640
Ni^{2+}	2400	1142	918	740	1100	821	710	1300	845	631
Pb^{2+}	8500	8600	7100	1250	7700	200	1150	8600	2840	990
Sr^{2+}	2100	950	612	510	1233	800	636	940	721	667
Zn^{2+}	4100	1050	79	550	1133	820	640	1070	640	422

was selected for detailed studies. The ion-exchange capacities for mono- and bivalent metal ions are shown in table 2.

It is clear from the table that the capacity increases with decreasing hydrated ionic radii for both mono and bivalent metal ions. The capacities for Na^+ and K^+ obtained from pH titration are also presented in table 2 and it was found that the values obtained by pH titration are slightly higher than those obtained by column operation. Further, the pH titration curve showed one inflection point confirming the monofunctional behaviour of the exchanger.

The ion exchange capacity of zirconium(IV) tungstoiodophosphate is also affected by drying temperature. As the drying temperature of the material increases ion-exchange capacity decreases. The results are given in table 3a.

A comparative study of the ion exchange capacity of different zirconium and tin based ion exchangers dried at 600°C gave the sequences: zirconium(IV) tungstoiodophosphate > tin(IV) tungstovanadophosphate (Nabi and Siddiqui 1986) > zirconium(IV) iodophosphate (Nabi *et al* 1996) > zirconium(IV) iodomolybdate (Qureshi and Rehman 1987b). Moreover, zirconium(IV) tungstoiodophosphate also seems to be most thermally stable, because it retains considerable ion exchange capacity even at 600°C.
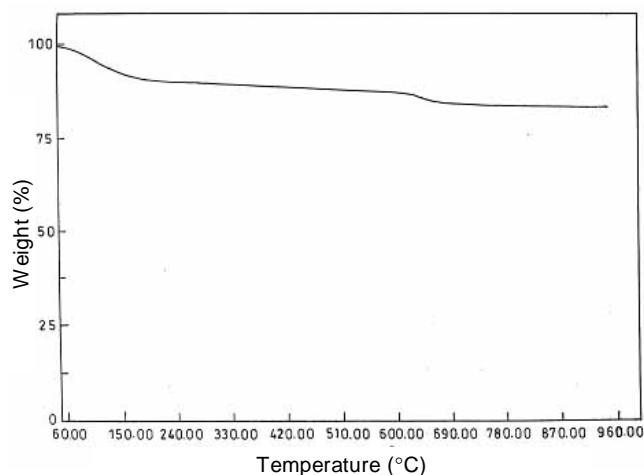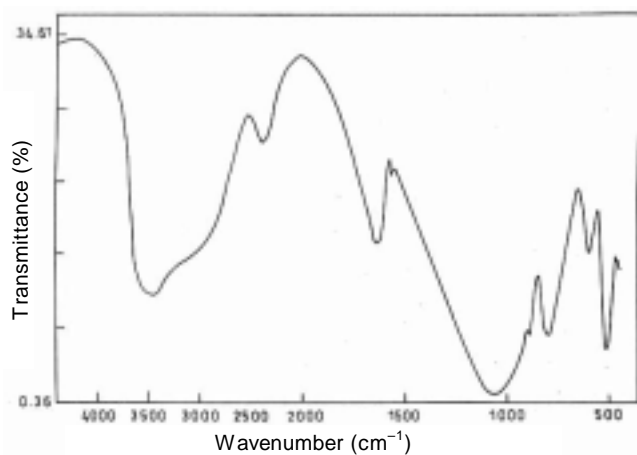
Results showing the extent of dissolution of the material in different solutions are given in table 4. It is apparent from the table that the exchanger is quite stable in water and fairly stable in mineral acids and organic acids of moderate concentration whereas it is less stable in bases.

The titration curves with added salts are shown in figure 1. The curve in the presence of sodium salt was slightly different from that in the presence of potassium salt.

The ion exchange capacities (at pH 7) calculated from these curves is 2·28 and 2·45 meq g^{-1} exchanger, which is close to the values obtained from column technique.

Table 6. Separation of metal ions achieved on zirconium(IV) tungstoiodophosphate (ZTIP3) columns.

Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluent used	Volume of eluent (ml)
Pb(II)	1078	1038	–3·7	1 M HNO$_3$	40
Mg(II)	286	292	+2·1	0·1 M HClO$_4$	50
Pb(II)	1091	1091	0·00	1 M HNO$_3$	30
Cd(II)	586·3	612·0	+4·3	0·1 M HCl	40
Pb(II)	856·4	812·2	–5·2	1 M HNO$_3$	40
Cu(II)	515·0	515·0	0·00	0·1 M HClO$_4$	50
Pb(II)	1020	1020	0·00	0·1 M HNO$_3$	40
Ni(II)	688	704·2	+2·2	0·1 M HClO$_4$	50
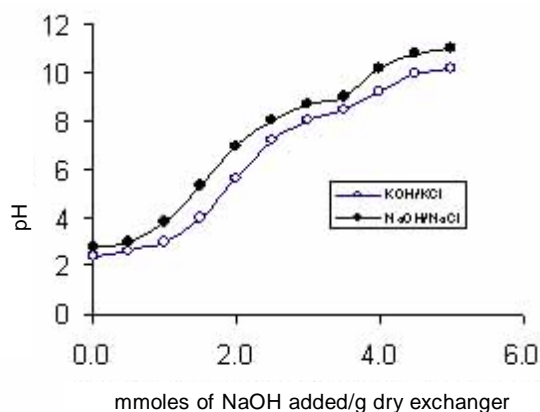
Figure 1. pH titration curve for zirconium(IV) tungstoiodophosphate.

Figure 2. FTIR spectrum of zirconium(IV) tungstoiodophosphate.

The molar ratio of Zr, W, I and P in the ion exchanger material was estimated to be 2 : 1·01 : 1·08 : 2·01, by performing chemical composition studies which can suggest the following formula of the material

$$[(ZrO)_2(WO_3)(IO_3)(H_3PO_4)_2] \cdot nH_2O.$$

Figure 3. Thermogram of zirconium(IV) tungstoiodophosphate.
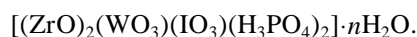
Thermogram of zirconium (IV) tungstoiodophosphate (ZTPI3) is shown in figure 3. Assuming that only the external water molecules are lost at 260°C, the ~ 9·73% weight loss of the mass represented by TGA curve must be due to the loss of nH$_2$O. Thus from the above structure the value of 'n' of the external water molecules can be calculated using Alberti equation (Alberti *et al* 1966)

$$18n = x(M + 18n)/100,$$

where x is the percent weight loss (~ 9·73%) of the exchanger when heated up to 260°C and ($M + 18n$) is the molecular weight of the material. The calculation gives ~ 5 for the external water molecule (n) per molecule of the cation exchanger.

In FTIR (figure 2) studies the broad band in the region 3600–3000 cm^{-1} may be assigned to interstitial water molecule and OH group (Rao 1963). Another strong and sharp peak with a maximum of 1635 cm^{-1} may be due to H–O–H bonding. The spectrum also shows strong band in the region 830–500 cm^{-1} indicating the presence of iodate and metal oxide (Weltner and McLeod 1965; Socrates 1980).

The X-ray diffraction spectrum (figure 4) of cation exchanger zirconium(IV) tungstoiodophosphate shows a
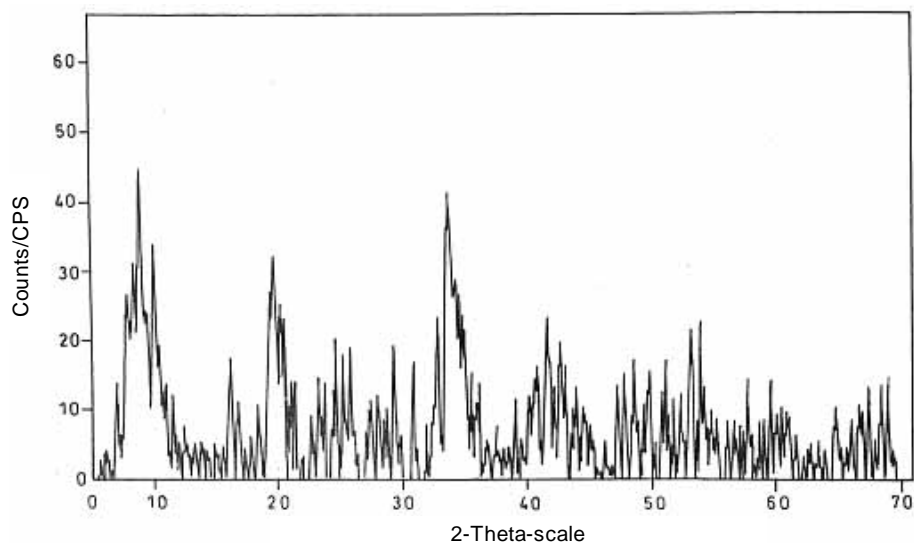
Figure 4. X-ray diffraction pattern of zirconium(IV) tungstoiodophosphate.

number of peaks at different 2θ values. The analysis of these signal peaks supports towards its crystalline nature.

In order to explore the potential of this cation exchange material in the separation of metal ions, distribution studies for 15 metal ions were performed in several solvent systems (table 5). The distribution studies showed that the material was found to possess exceptional high *Kd* values for Pb(II) and hence considered to be highly selective for Pb(II). Pb(II) has been considered as a major polluting material in water. The separation capacity of the material has been demonstrated by achieving some important binary separations such as Pb(II)–Mg(II), Pb(II)–Cd(II), Pb(II)–Cu(II), Pb(II)–Ni(II) etc. Table 6 summarizes the salient features of these separations. The separations are quite sharp and recovery is quantitative and reproducible.

4. Conclusions

The results of this investigation showed that zirconium(IV) tungstoiodophosphate seems to be a promising ion-exchange material with a significant ion-exchange capacity. The ion-exchange capacity (IEC) in meq g^{-1} for different metal ions are: Li^+, 1·90; Na^+, 2·20; K^+, 2·35; Mg^{2+}, 1·45; Ca^{2+}, 1·85; Sr^{2+}, 1·68. The results from investigation of the extent of dissolution of the material in mineral acids and organic acids confirm its better chemical stability. The thermal stability of zirconium(IV) tungstoiodophosphate was compared with that of other zirconium based ion exchangers and it was concluded that it had better resistance to heat and it retains considerable ion exchange capacity even at 600°C. The analytical importance of the material was deduced from *Kd* values for different metal ions in different solvents. The material had high affinity for Pb^{2+} in comparison to other metal ions studied. On the basis of this behaviour, separation of Pb^{2+} from various synthetic water samples has been achieved to prove the analytical applications of the material.

References

Alberti G, Torraca E and Conte A 1966 *J. Inorg. Nucl. Chem.* **28** 607

Choube U N and Turel Z R 2003 *Czech. J. Phys.* **53** 539

Clearfield A and Wang Z 2002 *J. Chem. Soc. Dalton Trans.* **7** 2937

Davis M 1963 *Infrared spectroscopy and molecular structure* (Amsterdam: Elsevier Publishing Co.) p. 145

Ferragina C, Cafarelli P, Di Stefanis A, Di Rocco R and Giannoccaro P 2001 *Mater. Res. Bull.* **36** 1799

Gupta A P and Varshney P K 1997 *React. Funct. Polym.* **32** 67

Gupta A P, Verma G L and Ikram S 2000 *React. Funct. Polym.* **43** 31

Hafez M A, Kenway I M M, Akl M A and Lshein R R 2001 *Talanta* **53** 749

Hayshi H, Onoda Y and Iwasaki T 2002 *Nippon Ion Kokan Gakkaishi* **11** 32

Jaimez E, Robert C T and Slade 1997 *J. Chem. Soc. Dalton Trans.* **8** 1435

Mittal S K and Singh P P 1995 *Indian J. Chem.* **A34** 1009

Nabi S A and Siddiqui W A 1986 *Bull. Chem. Soc. Jpn* **59** 2003

Nabi S A, Usmani S and Rehman N 1996 *Ann. Chim. Fr.* **21** 521

Qureshi S Z and Rehman N 1987a *Bull. Chem. Soc. Fr.* **6** 959

Qureshi S Z and Rehman N 1987b *Bull. Chem. Soc. Jpn* **60** 2627

Qureshi S Z, Khan M A and Rehman N 1995 *Bull. Chem. Soc. Jpn* **68** 1611

Qureshi S Z, Jamhour R M A Q and Rehman N 1996 *Ann. Chim. (Paris)* **21** 609

Rao C N R 1963 *Chemical application of infrared spectroscopy* (New York: Academic Press)

Reilley C N, Schmid R W and Sadek F S 1959 *J. Chem. Edu.* **35** 555

Singh P, Rawat J P and Rehman N 2002 *Indian J. Chem.* **A41** 1616

Singh P, Rawat J P and Rehman N 2003 *Talanta* **59** 443

Sirlei R and Claudio A 1997 *J. Chem. Soc. Dalton Trans.* **14** 2517

Socrates G 1980 *Infrared characteristic group frequencies* (New York: Wiley) p. 145

Tandon S, Pandit B and Chudasama U 1996 *Trans. Met. Chem.* **21** 7

Topp N E and Pepper K W 1949 *J. Chem. Soc.* 3299

Varshney K G, Pandith A H and Gupta U 1998 *Langmuir* **14** 7353

Velmurugan S, Sathyaseelam V S, Narasimhan S V and Mathur P K 1991 *New development in ion exchange*, in *Proceedings of international conference ion exchange ICIE'91, Tokyo*

Weltner W Jr and McLeod D Jr 1965 *J. Phys. Chem.* **69** 3488

Zhaong M, Damodar M, Clearfield A and Peng G 1996 *Chem. Matter.* **8** 1333