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## Separation of Toxic Metal Ions Such as Pb(II), Cu(II) and Hg(II) from Industrial Waste Water Using Newly Synthesised tinzirconium molybdophosphate Cation Exchanger

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### Abstract

A novel four component inorganic cation exchange material tinzirconium molybdophosphate with two cations and two anions has been synthesized. Chemical composition of the compound was determined by ICP-AES method and structural studies were carried out using TGA, XRD, and FT-IR, SEM. Bifunctional behaviour of the material has been indicated by its pH titration curves. The material shows high ion exchange capacity of 1.96 meqg<sup>-1</sup>. The distribution coefficient studies of metal ions on the material were performed in different solvent systems and the material was found to be selective for Pb(II), Cu(II) and Hg(II) ions. On the basis of distribution coefficient value, some analytically important binary separations of metal ion like Pb(II)-Co(II), Pb(II)-Ni(II), Pb(II)-Mg(II), Pb(II)-Hg(II), Cu(II)-Bi(III), Cu(II)-Zn(II), Cu(II)-Mg(II), Hg(II)-Zn(II), Hg(II)-Bi(III), Hg(II)-Mg(II) were achieved on tinzirconium molybdophosphate column. In order to demonstrate the practical utility of the material, quantitative separation of Pb(II), Cu(II) and Hg(II) from textile effluent, paper industry and wood industry have been achieved.

**Keywords :** Binary Separation, Ion Exchanger, Tetravalent Metal Acid Salts

### 1. INTRODUCTION

The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological system. Industrial and mining wastewaters are important sources of pollution of heavy metals Sankaramakrishnan . N et al., (2007), Nghiem L.D. et al., (2006). The metals like lead, copper, mercury, etc when present beyond the certain concentration are not only toxic but also can lead to serious health problems Hutchinson, T.C et al., (1987), Davidson, P.W et al., (2004). Lead and mercury fulfil no essential function in the human body, it can merely do harm after uptake from food, air or water. . Lead in the environment arises from both natural and anthropogenic sources.

Generally, human exposure to lead comes from the following main sources: using leaded gasoline; using lead based paint; having lead pipes in water supply systems; battery industries and exposure to industrial sources from process such as lead mining, smelting, and coal combustion Lin, S.H. et al., (2000). Copper is mainly comes from the textile industries and fertilizers and Mercury arises mainly from chemical industries, battery industries and wood industries Pehlivan, E. et al., (2007), Sajidu S.M.I. et al (2007). So every possible care should be taken to keep them isolated from getting mixed into air, water and soil. A number of technologies have been developed over the years for the efficient removal of toxic/heavy metals from polluted water such as filtration, chemical precipitation, ion exchange, adsorption, electrodeposition and electrophoresis. All these approaches have their inherent advantages and limitations. Although filtration and chemical precipitation are low cost and effective in removing large quantities of metal ions

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quickly, neither is capable of removing at tracelevels. Adsorption is also ineffective at very low concentrations. In the last decade, ion exchangers have been used extensively in the chemical decontamination process for metal ion recovery, regeneration of decontaminants, removal of the formulation chemicals from the coolant and aqueous effluents. Advancement of ion exchange technique is not only due to its selectivity for ionic species but also for the simplicity and low operation cost Sharma S.D., *et al* (1994), Gupta A.P *et a.,l* (1997). Ion exchange can be used to reduce metal concentrations to the region of parts per million. The materials used as ion exchangers have attained an appreciable status in current research and become a part of number of laboratories and industrial units.

New mixed materials of the class of tetravalent metal acid salts (TMA salts), i.e. compounds containing two different cations and a given anion or two different anions are interesting since they show improved ion exchange properties and selectivity for particular metal ions in comparison to their single salt counterparts. A literature survey shows that mixed materials containing two anions and two cations have not been widely investigated. Zirconium and tin phosphates are now very well-known inorganic ion exchange materials of the class of TMA salts Vesely, V. *et al.*, (1972). Although these compounds are not very different as exchangers, slight differences do exist owing to the difference in their ion size meters.

Here in this work we prepared new cation exchanger with tin and zirconium as cations and phosphate and molybdate as anions which showed high selectivity towards toxic metal ions especially towards lead, copper and mercury. The objective of the present work is to explore the separation potential and analytical application of tinzirconium molybdophosphate. Cation exchanger synthesized was successfully used for the quantitative separation of lead, copper and mercury metal ions from wastewater from paint industries, textile industries and wood industries respectively.

## 2. EXPERIMENTAL METHODS

*Reagents:* Zirconium oxy chloride (Loba Chemie, India), Stannic chloride (E.Merck) and Sodium dihydrogen phosphate (E.Merck), Sodium molybdate (E.Merck) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

*Apparatus and instruments:* A glass column was used for column operations. ELICO LI613 pH meter was used for pH measurements. Chemical composition was determined by ICP-AES method using ICP-AE Spectrometer Thermo Electron IRIS Intrepid II. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies. Perkin Elmer Diamond TG/DTA Analysis System for thermal analysis and an electric shaking machine for shaking were also used.

*Synthesis of the exchanger:* zirconium oxy chloride solution (0.05M), stannic chloride solution (0.05M), sodium molybdate (0.05M) and sodium dihydrogen phosphate solution (0.05M) were prepared. Mixture of sodium molybdate and sodium dihydrogen phosphate solution was added to mixtures of zirconium oxy chloride solution and stannic chloride solution with constant stirring in different volume ratios. The resulting gel was kept for 24 hrs at room temperature maintaining the pH at 1. pH was adjusted with 1.0 M NaOH/1.0 M HNO<sub>3</sub>. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H<sup>+</sup> form by treating with 1.0 M HNO<sub>3</sub> for 24 hrs with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60- 100 mesh.

*Ion exchange capacity (IEC):* The ion exchange capacity of the material was determined by column method. 1.0 g of the exchanger in H<sup>+</sup> form was taken in a glass column of 1.1 cm diameter. The H<sup>+</sup> ions were eluted by percolating 100 ml of

1.0 M NaCl solution. The effluent was collected and titrated against standard sodium hydroxide solution. The exchange capacity in meqg<sup>-1</sup>, IEC was calculated using the formula,

$$IEC = \frac{av}{w}$$

Where, *a* is the molarity, *v* is the volume of alkali used during titration and, *w* is the weight of the exchanger taken Vogel, A.I., (1975).

**Chemical resistivity:** The chemical resistivity of the sample was assessed in mineral acids like HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this, 0.5 g of the sample was soaked in 50 ml of different solvents, kept for 24 hrs and changes in colour, nature and weight of the sample were noted.

**Effect of temperature on IEC:** The effect of temperature on ion exchange capacity was studied by heating several 1.0 g samples of the exchanger at different temperatures for three hours in an air oven and Na<sup>+</sup> ion exchange capacity in meqg<sup>-1</sup> was determined by the column method after cooling them to room temperature.

**pH titrations:** Topp and Pepper method was used for pH titrations using NaOH/NaCl, KOH/KCl, systems. 0.5g of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. After equilibrium, the pH of the solutions was measured and plotted against the milli equivalents of OH<sup>-</sup> added.

**Distribution coefficient (K<sub>d</sub>):** Distribution studies were carried out for various metal ions in demineralized water by batch process. In this method, 0.1 g of the exchanger (60-100 mesh) was equilibrated with 20 ml of the metal ion solutions for 24 hrs at room temperature. The metal ion concentrations before and after sorption were determined spectrophotometrically/ complexometric titration against standard EDTA solution. In the

complexometric method, the K<sub>d</sub> values were calculated using the formula,

$$K_d = \frac{(I - F)}{F} \times \frac{V}{W}$$

Where, I is the initial volume of EDTA used, F is the final volume of EDTA used, V is the volume of the metal ion solution (ml) and W is the weight of the exchanger.

**Table 1. Synthesis and properties of various samples of exchanger using 0.05 M solutions each.**

S.No	Sample	Volume ratios	pH	Appearance	Ion Exchange Capacity for Na <sup>+</sup> (meqg <sup>-1</sup> )
1	SnZrMoP	1: 1: 1: 1	1		0.79
2	SnZrMoP	1: 1: 2: 1	1		0.82
3	SnZrMoP	1: 1: 1: 2	1		1.02
4	SnZrMoP	1: 1: 3: 1	1	White Colour	1.42
5	SnZrMoP	1: 1: 1: 3	1		1.96
6	SnZrMoP	1: 1: 2: 2	1		0.83

**Binary separation of metal ions:** Separation of some metal ions of analytical utility was achieved on the column of tinzirconium molybdophosphate (SnZrMoP). The column on which the separations were to be carried out was filled uniformly with the exchanger. First of all distilled water was added to pack the granules so that no air bubbles get stuck. Then the mixture of the metal ion solutions was slowly poured. The process was repeated for maximum sorption. The exchanged metal ions were eluted using suitable eluent.

**Separation of Pb(II), Cu(II) and Hg(II) from industrial effluents using tinzirconium molybdophosphate columns:** Industrial wastewater was collected from textile, paint and wood industries. Samples were first filtered to remove any solid particles and then it was neutralised. The colour producing substances were removed by

adsorption using charcoal. The treated samples were the chemically treated for the detection and separation of any heavy elements presents. 100ml of the sample was passed and repeated 3-4 times using effluent collected at the bottom. This was for the maximum uptake of cation. Care was taken to restrict the flow by 0.5ml/minutes. The eluent used for Pb(II), Cu(II) and Hg(II) were 0.5 M HNO<sub>3</sub>, 0.3 M HNO<sub>3</sub> and 0.2 M HNO<sub>3</sub> respectively. Finally the ions were eluted out using respective eluents and then determined titrimetrically.

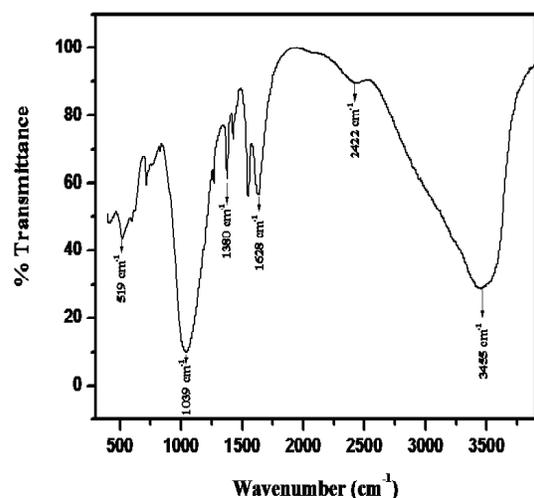


Fig. 1: FT-IR of SnZrMoP

### 3. RESULTS AND DISCUSSION

The exchanger, SnZrMoP5, mixed material of class of tetravalent bimetallic acid salts containing two cations and two anions, obtained as white solid having maximum ion exchange capacity of 1.96 meqg<sup>-1</sup> was selected for detailed study Table 1. It was found to be stable in water, acetic acid, one molar nitric acid and sulphuric acid.

Elemental analysis by ICP-AES revealed tin, zirconium, molybdenum, phosphorous ratio of 1: 1: 0.3: 2. FTIR spectra of SnZrMoP (Fig.1). showed a broadband in the region ~3455 cm<sup>-1</sup> which is attributed to symmetric and asymmetric

-OH stretching, while the band at ~1628 cm<sup>-1</sup> is attributed to H-O-H bending. This indicated the presence of structural hydroxyl protons in SnZrMoP, which is more evident from the obtained IEC values. A band in the region ~1039 cm<sup>-1</sup> is attributed to P=O stretching and a band at ~1380 cm<sup>-1</sup> is attributed to the presence of δ (POH). Bands at ~519 cm<sup>-1</sup> may be due to the presence of Zr-O and Sn-O bonds.

XRD analysis (Fig. 2) showed some prominent peaks together with a number of low

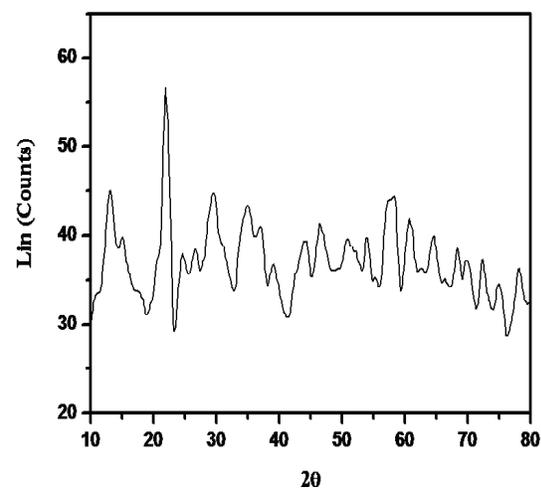


Fig. 2: XRD of SnZrMoP

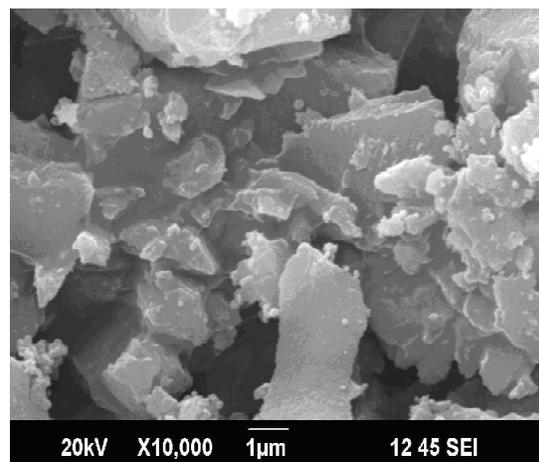


Fig. 3: SEM image of SnZrMoP

intensity peaks which suggest the semicrystalline nature of the exchanger. Scanning electron microscope images at different magnification reaffirms the semi crystalline morphology of the exchanger Fig. 3.

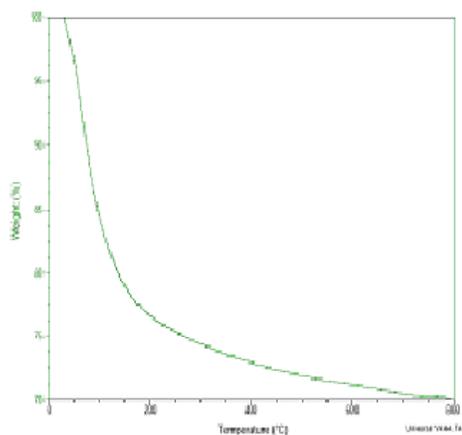


Fig. 4: TGA of SnZrMoP

The thermogram of SnZrMoP composite cation exchanger (Fig. 4) showed that the weight loss (about 10%) of the ion exchanger up to 147°C is due to the removal of free external water

molecules Nilchi A. *et al.*, (2006). Further, a gradual loss of mass (about 5%) up to 350 °C may be due to the condensation of hydroxyl groups. Above 350 °C, the weight loss was very less and it showed 4 % weight loss up to 700 °C indicating

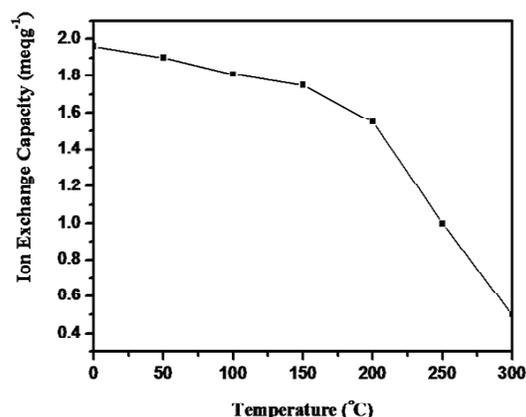


Fig. 5: Effect of temperature on IEC

the removal of structural water. Further there was not much difference in weight up to 800 °C. The effect of the size and charge of the exchanging ion on the ion exchange capacity was also

Table 2.  $K_d$  values of various metal ions in different electrolyte

Metal ion	DMW	0.001 M HNO <sub>3</sub>	0.01 M HNO <sub>3</sub>	0.1 M HNO <sub>3</sub>	0.001 M NH <sub>4</sub> NO <sub>3</sub>	0.01 M NH <sub>4</sub> NO <sub>3</sub>	0.1 M NH <sub>4</sub> NO <sub>3</sub>
Pb(II)	227.00	216.00	194.00	166.09	220.00	201.90	177.00
Zn(II)	7.00	NA	NA	NA	NA	NA	NA
Mn(II)	42.01	30.50	12.00	2.00	29.00	10.00	2.99
Ni(II)	31.00	25.01	8.00	NA	23.00	4.00	NA
Hg(II)	59.12	32.22	20.90	8.80	28.30	18.00	10.99
Ca(II)	38.11	29.00	19.76	9.99	34.34	25.23	12.00
Cd(II)	39.00	28.00	24.00	18.10	33.00	29.24	12.40
Co(II)	26.00	9.00	NA	NA	16.00	2.01	NA
Cu(II)	90.90	73.23	46.00	29.00	80.00	73.00	66.00
Bi(III)	10.90	NA	NA	NA	NA	NA	NA
Mg(II)	1.10	NA	NA	NA	NA	NA	NA

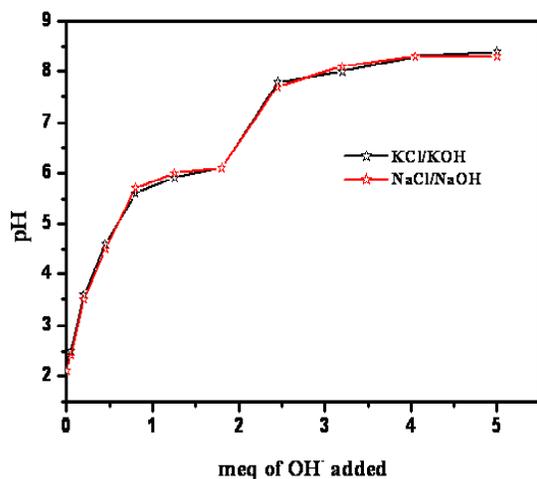


Fig. 6: pH titration curve of SnZrMoP

observed for this material. The affinity for alkali and alkaline earth metals towards the material follows the sequence  $\text{Li(I)} < \text{Na(I)} < \text{K(I)}$  and  $\text{Mg(II)} > \text{Ca(II)} > \text{Ba(II)}$ . Ions with the smaller hydrated radii easily enter the pore of the exchanger,

which results in higher adsorption. Therefore the ion exchange capacity should increase with decreasing hydrated radii. The ion exchange capacity and physical appearance of the exchanger change by heating at different temperature for 3 hrs and retained prominent capacity up to 300 °C shown in Fig. 5.

pH titration curve obtained under equilibrium conditions for each of NaOH/NaCl and KOH/KCl system showed two inflection points which indicate the bifunctional strong cation exchange behaviour Fig. 6. The exchange capacity obtained from the curve is in agreement with that obtained by the column method.

### 3.1 Distribution Studies

In order to explore the potentiality of the new four component cation exchange material in the separation of metal ions, distribution studies

Table 3: Binary separation of metal ions on tin zirconium molybdophosphate

Separation achieved	Eluent	Metal ion (mg)		% Efficiency
		Loaded	Eluted	
Co(II) Pb(II)	0.01 M HNO <sub>3</sub> 0.4 M HNO <sub>3</sub> +0.4 M NH <sub>4</sub> NO <sub>3</sub>	1.92 2.80	1.90 2.75	98.96 98.21
Ni(II) Pb(II)	0.1 M HNO <sub>3</sub> 0.4 M HNO <sub>3</sub> +0.4 M NH <sub>4</sub> NO <sub>3</sub>	3.20 2.80	3.10 2.75	96.88 98.21
Mg(II) Pb(II)	0.001 M HNO <sub>3</sub> 0.4 M HNO <sub>3</sub> +0.4 M NH <sub>4</sub> NO <sub>3</sub>	2.80 2.41	2.72 2.36	97.14 97.93
Hg(II) Pb(II)	0.2 M HNO <sub>3</sub> 0.4 M HNO <sub>3</sub> + 0.4 M NH <sub>4</sub> NO <sub>3</sub>	2.80 2.80	2.77 2.78	98.93 99.29
Bi(III) Cu(II)	0.001 M HNO <sub>3</sub> 0.2 M HNO <sub>3</sub> + 0.2 M NH <sub>4</sub> NO <sub>3</sub>	3.50 2.00	3.40 1.97	97.14 98.50
Zn(II) Cu(II)	0.001 M HNO <sub>3</sub> 0.2 M HNO <sub>3</sub> + 0.2 M NH <sub>4</sub> NO <sub>3</sub>	1.98 2.25	1.98 2.18	100.00 96.89
Mg(II) Cu(II)	0.001 M HNO <sub>3</sub> 0.2 M HNO <sub>3</sub> + 0.2 M NH <sub>4</sub> NO <sub>3</sub>	2.41 2.14	2.38 2.10	98.76 98.13
Zn(II) Hg(II)	0.001 M HNO <sub>3</sub> 0.2 M HNO <sub>3</sub>	1.37 2.35	1.35 2.33	98.54 99.15
Bi(III) Hg(II)	0.001 M HNO <sub>3</sub> 0.2 M HNO <sub>3</sub>	2.62 1.71	2.55 1.68	97.33 98.25
Mg(II) Hg(II)	0.001 M HNO <sub>3</sub> 0.2 M HNO <sub>3</sub>	2.13 2.65	2.11 2.65	99.06 100.00

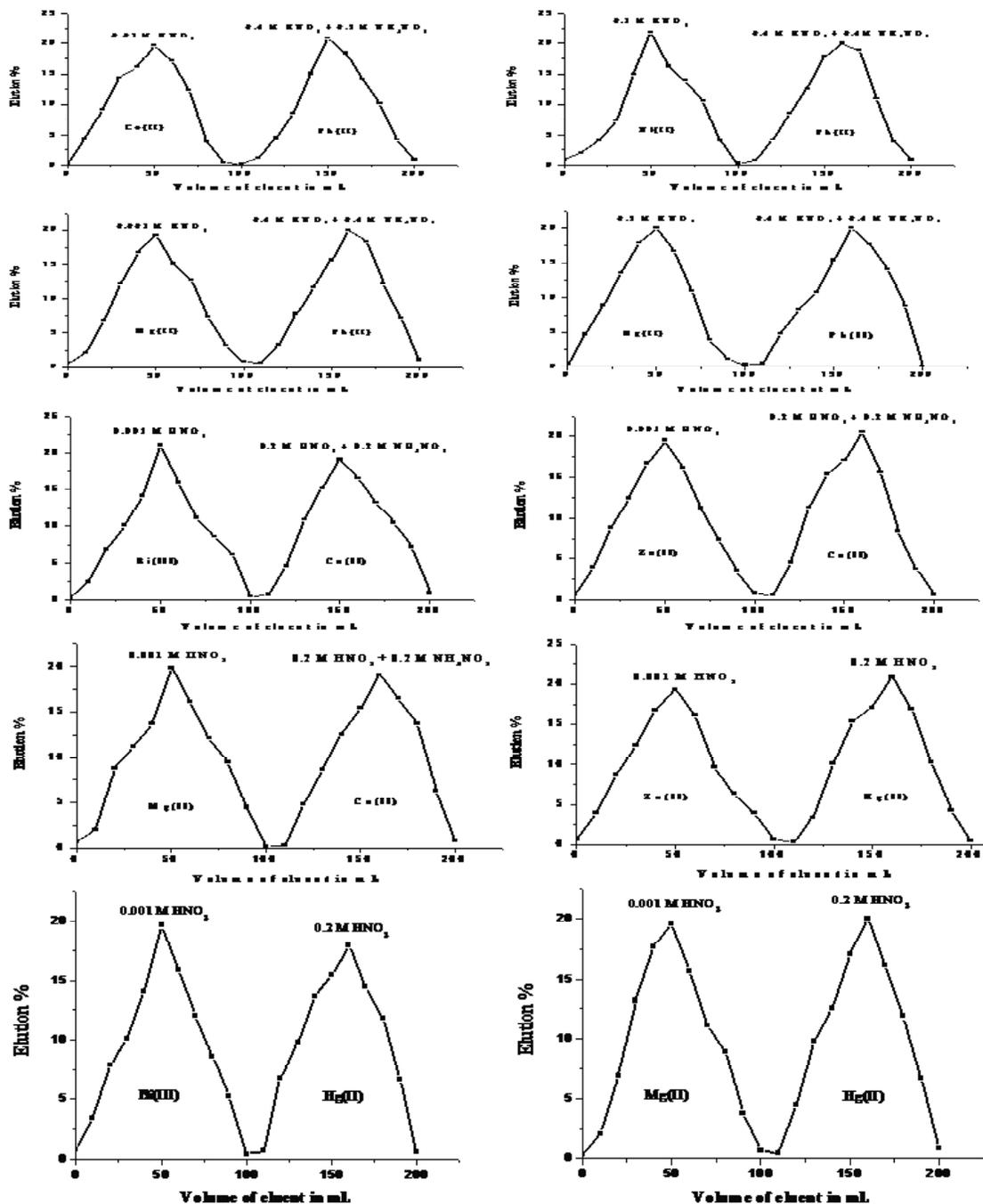


Fig. 7: Elution curves for the separation of metal ions on SnZrMoP

for metal ions were performed in different solvent systems shown in Table 2. The distribution studies of metal ions showed that the exchanger has very high affinity towards Pb(II), Cu(II) and Hg(II) ions in comparison to other metal ions studied. The selectivity was found to be in the order Pb(II) > Cu(II) > Hg(II) > Mn(II) > Cd(II) > Ca(II) > Ni(II) > Co(II) > Bi(III) > Zn(II) > Mg(II). The effect of electrolyte concentrations on distribution coefficients showed that the value decreases with increase in electrolyte concentrations.

The separation capability of the material has been demonstrated by achieving binary separations of some important metal ions viz. Co(II)-Pb(II), Ni(II)-Pb(II), Hg(II)-Pb(II), Mg(II)-Pb(II), Bi(III)-Cu(III), Zn(II)-Cu(II), Mg(II)-Cu(II), Zn(II)-Hg(II), Bi(III)-Hg(II) and Mg(II)-Hg(II). The separation was based on sequential elution of ions through the column depending upon the metal-eluting ligand (eluent) stability. The weakly retained metal ions get eluted first, followed by stronger one. The order of elution and eluents used for the binary separation are also shown in Table 3. and (Fig. 7). The separations are quite sharp and recovery was quantitative and reproducible.

**Table 4. Separation of effluent ions on tinzirconium molybdophosphate**

Samples of waste water	Metal Ion	Eluent used	In mg/100 ml
Textile industries	Cu(II)	0.3M HNO <sub>3</sub>	1.0 - 2.0 mg
Paint industries	Pb(II)	0.5M HNO <sub>3</sub>	0.8 - 1.7 mg
Wood industries	Hg(II)	0.2M HNO <sub>3</sub>	0.7 - 1.2 mg

### 3.1. Applications

*Removal of lead, copper and mercury metal ions from textile, paint and wood industrial effluents*

*respectively using SnZrMoP column:* Samples of effluent collected from textile, paint and wood industries showed that 100 ml of water contains 1.0 - 2.0 mg of Cu(II), 0.8 - 1.7 mg of Pb(II) and 0.7 - 1.2 mg of Hg(II) ions respectively. These can be separated from the waste water so that we can avoid pollution due to these heavy metal ions. Details of analysis are given in the above Table 4.

### 4. CONCLUSION

Semicrystalline Tinzirconium molybdophosphate cation exchanger can be used in column packing for quantitative separation of metal ions. Removal of Pb(II), Cu(II) and Hg(II) ions in effluents from paint industries, textile industries and wood industries respectively have been practically demonstrated using this material. The four component tinzirconium molybdophosphate, heteropolyacid based cation exchanger is a promising and useful material where the effective method is needed for the removal and isolation of toxic metal ions from industrial effluents and other water bodies.

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