Poll Res. 40 (3) : 1030-1034 (2021)
Copyright © EM International
ISSN 0257–8050

QUANTITATIVE SEPARATION OF METAL IONS FROM CERTAIN MULTI-MINERAL SUPPLEMENTS USING COMPOSITE EXCHANGE MATERIAL: TIN (IV) TUNGSTOSELENATE - 1, 10 PHENANTHROLINE

E. LAIQ[1]*, S. JABIN[2] AND N. SHAHID[3]

** [1]Chemistry Section, Women's College, Department of chemistry, Aligarh Muslim University, Aligarh 202 002, U.P., India*

[2]Department of Chemistry, Faculty of Engineering, Manav Rachna International Institute of Research and Studies, Faridabad, Haryana, India

[3]Department of Chemistry, Arya Mahilla (P.G.) College, Shahjahanpur 242 001, U.P., India

(Received 11 May, 2021; Accepted 29 June, 2021)

ABSTRACT

Composite ion exchangers have several specific features which have led to their various applications in diversified fields of sciences. Progress in the technology of retrieval of materials from industrial, pharmaceutical, nuclear wastes has necessitated the synthesis of highly selective ion exchange materials. An essential feature of composite ion-exchanger is the more excellent selectivity they offer than conventional ion exchangers. Such composites have played a significant character in the field of separation sciences. Composite ion exchange materials were prepared by introducing an organic moiety (1, 10 phenanthroline) in the matrix of the inorganic ion exchanger tin (IV) tungsto-selenate. Sorption studies of some analytically essential metal ions have been performed by column chromatography using suitable solvent systems quickly. The quantitative separation of iron and zinc from some multi-mineral supplements has been reported in this paper. This method is easy, rapid and, extremely selective with good precision and accuracy within the experimental error range (±2%).

KEY WORDS : Quantitative Separation, Composite Material, Metal ions, Column Chromatography.

INTRODUCTION

Organic-inorganic composite ion exchange materials possess several distinguishing features, which have led to their several applications in various fields (Kaushal *et al.*, 2017). Composite ion exchangers are recognized for chemical and mechanical stability as well as for the selectivity of metal ions (Khan *et al.*, 2014). The composite material is prepared with modifications in the inorganic counterpart by organic moieties, due to which the enhancement in its granulometric properties makes them more appropriate for the application in column chromatographic methods. The binding of the organic moiety introduces better mechanical properties in the composite ion exchange materials. Such composites have established their place in analytical and environmental, and material science due to their differential selectivity for metal ions (Vikas *et al.*, 2019). Such compounds have become quite interesting because of their varying interlayer spacing due to the incorporation of organic molecules between the layers of the host material. They have shown promising features that are important from the analytical point of view. These composite ion exchange materials possess better and different characteristics than that of their parent counterpart.

The ion-exchange chromatography is one of the essential adsorption techniques which has been used

for decades (Nabi *et al.*, 2004). The separation is generally based on the formation of ionic bonds between the charged species and an ion-exchange gel/support carrying the opposite charges. The practical utility of composite materials has been explored by the separation of metal ions, ionic compounds, and organic species such as peptides, proteins, nucleic acids, biopolymers, which are charged molecules in different molecular sizes and nature (Levison, 2003 and Bruch *et al.*, 2009 and Nabi *et al.*, 2001 and Figueiredo *et al.*, 2018).

We summarize our studies on the quantitative separations of metal ions from binary synthetic samples and some multi-minerals by using composite material. In the present endeavor, an attempt has been made to study the practical utility of the composite material tin (IV) tungstoselenate – 1, 10 phenanthroline in column chromatography, an effective analytical technique for the quantitative determination and separation of metal ions.

MATERIALS AND METHODS

Sodium selenite and Sodium tungstate dihydrate (BDH, India), Tin (IV) chloride pentahydrate (Baker analyzed, USA), and 1, 10 Phenanthroline (E.Merck, India), and all the other chemicals were of A.R. grade.

Preparation of tin (IV) tungstoselenate

Tin (IV) tungstoselenate was synthesized by gently mixing the mixture of the 0.05M aqueous solution of sodium tungstate and sodium selenite with 0.05M aq. Solution of tin (IV) chloride in a ratio of 1:1:4. The pH was maintained at 0 to 1. The white gelatinous material was kept in the mother liquor for 12 h at 24 ± 2 °C, and then filtered under suction, and dried at 40 ± 2 °C. On immersion in DMW, the product broke up into small particles and was then totally converted to H+ form by treating with an excess of 1 M HNO_3 for 24 h at 24 ± 2°C with occasional shaking. The excess acid was removed by continual washing with demineralized water and then dried at 40 ± 2°C.

Synthesis of tin (IV) tungstoselenate-phenanthroline

Tin (IV) tungstoselenate-phenanthroline was prepared when 2.5 g of tin (IV) tungstoselenate in H^+ form was treated with 10.0 mmoles of an aqueous solution of (0.1 M) 1,10 phenanthroline in a temperature-controlled shaker for six hours at 30 ±1 °C After filtration and washing with demineralized water, the composite was air-dried, and then the filtrate was titrated with standard HCI solution to determine the remaining 1, 10 phenanthroline content. The amount of 1, 10 phenanthroline sorbed onto tin (IV) tungstoselenate was estimated by the difference between initial and final concentrations of 1, 10- phenanthroline.

pH Titration

Topp and Pepper method (Topp *et al*., 1949) was applied for pH titration studies of the composite material. 0.2 g of composite material was equilibrated with a constant amount of each (0.03 mmoles) metal ion in buffer solutions (20.0 ml) of pH values from 3.0 to 5.5 for six- hour at 30 ± 1 °C.

Distribution studies

Ion exchange behavior of the composite material towards several metal ions viz. Mg^{2+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, were studied, and their distribution coefficients (K_d) were determined by the batch method in several solvent systems (Table 1). The K_d values were calculated by using the following expression:

$$K_{d=}\frac{I-F}{F}\times\frac{V}{W}\left(\frac{mg}{L}\right)$$

Where; the initial amount of the metal ion in the solution = I and F= the final amount of the metal ion in the solution, the volume of the metal ion solution taken for study = V (ml), and the weight of the

Table 1. Distribution Coefficient of metal ions in different solvent system for tin (IV) tungstoselenate - phenanthroline

Metal ions	DMW	10% DMSO	0.1M HNO_3	10% DMSO + 0.1M HNO_3 1:1 v/v	10% DMSO + 0.1M HNO_3 1:2 v/v	10% DMSO + 0.1M HNO_3 1:3 v/v
Mg^{2+}	6150	5478	4446	4083	3761	3486
Ca^{2+}	9900	7100	5455.55	4464	3761	3247
Mn^{2+}	16566	7071	9940	12350	12500	16633
Zn^{2+}	8233	5500	4463.63	3762	3485	3247
Fe^{3+}	9900	7200	12450	16633	24900	49900

composite material taken for analysis = W (g). The composite ion exchanger (0.4g) was equilibrated with a 0.0IM solution of the metal ion (40 ml) in a temperature-controlled shaker at 25 ± 2 °C for six hours in the Erlenmeyer flasks to attain equilibrium. Distribution studies of these metal ions were carried out in several solvents, namely DMW, Dimethylsulphoxide (DMSO), Nitric acid (HNO_3), and DMSO-HNO_3 systems.

Quantitative separation of the metal ions in binary synthetic samples

Separations of few transition metal ions of analytical utility were attained on tin tungstoselenate-phenanthroline column. 2.0g of the composite material in H^+ form was packed in a glass column (30 cm x 1.1 cm diameter). The mixture of metal ions that is to be separated was loaded on the column. The separation was achieved by passing an appropriate solvent at a flow rate of 0.5-0.6 ml per min through the column. The effluent was quantitatively determined by titrating it with EDTA. Results are discussed in Table 2.

Quantitative separation of the metal ions from some Multi-mineral supplements

Multi-mineral commercial tablets were selected for the analysis. The preparation of the sample was done by grinding the tablets and treating them with the mixture of HNO_3 and HCl (1:3) on a water bath till the fumes of nitrous oxide were disappeared. The solution was then filtered, and the clear solution obtained was made up to 100 ml with DMW in a volumetric flask. Different portions of the aliquots were used to separate the particular metal ions using the elution techniques. The results are reported in the Table 3.

RESULTS AND DISCUSSION

The tin (IV) tungstoselenate was synthesized by a procedure described earlier (Nabi *et al.*, 1985). In this study the composite material was synthesized by equilibrating 0.1M solution of 1-10 phenanthroline in ethanol: water (1:1) at 30 ±1 °C for six hours with an inorganic ion exchanger (tin (IV) tungstoselenate). A white-colored material changed to a slightly pink color signifying that the composite is formed.

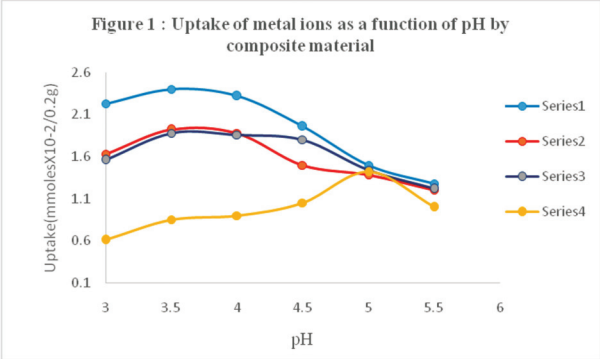
The ion exchange capacity (IEC) of tin (IV) tungstoselenate was 1.4 meq g^{-1}, whereas that of the tin (IV) tungstoselenate –phenanthroline was 1.67meq g^{-1}. A slightly higher value of IEC in this composite material may be due to the binding of the organic part to the inorganic ion exchanger. The uptake of metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+}) on tin tungstoselenate – phenanthroline was studied as a pH function; Figure 1 shows the results, indicating

Table 2. Quantitative separation of metal ions on the column of tin (IV) tungstoselenate - phenanthroline

S. No.	Separation achieved	Amount loaded (mg)	Amount found (mg)	% Recovery	Eluent used
1	Zn^{2+}	2.97	2.85	95.95	10% DMSO + 0.1M HNO_3 (1:3 v/v)
	Fe^{3+}	4.04	3.95	97.77	10% DMSO
2	Mn^{2+}	1.97	1.9	96.44	0.1M HNO_3
	Fe^{3+}	1.04	1.01	97.11	10% DMSO
3	Ca^{2+}	2.36	2.3	97.45	10% DMSO + 0.1M HNO_3 (1:3 v/v)
	Fe^{3+}	4.04	3.98	98.51	10% DMSO
4	Mg^{2+}	2.56	2.5	97.65	10% DMSO + 0.1M HNO_3 (1:3 v/v)
	Fe^{3+}	4.04	3.98	98.51	10% DMSO

Table 3. Separation on Zn^{2+} and Fe^{2+} present in the pharmaceutical sample1 on the column of composite material.

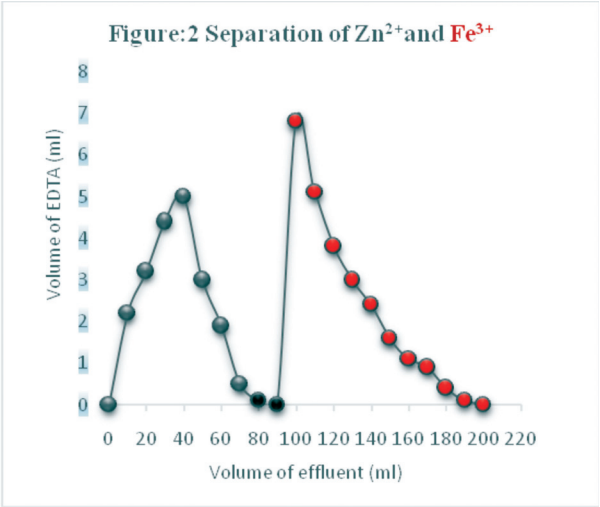
S.No.	Separation achieved	Amount loaded (mg)	Amount found (mg)	Recovery	Effluent used	Volume (ml)
1	Zn^{2+}	1.24	1.19	95.97%	10%DMSO+0.1M HNO_3	90
2		1.84	1.78	96.74%		
3		2.46	2.38	96.75%		
1	Fe^{3+}	1.0	0.98	98.00%	10% DSMO	110
2		1.5	1.47	98.00%		
3		2.0	1.98	99.00%		



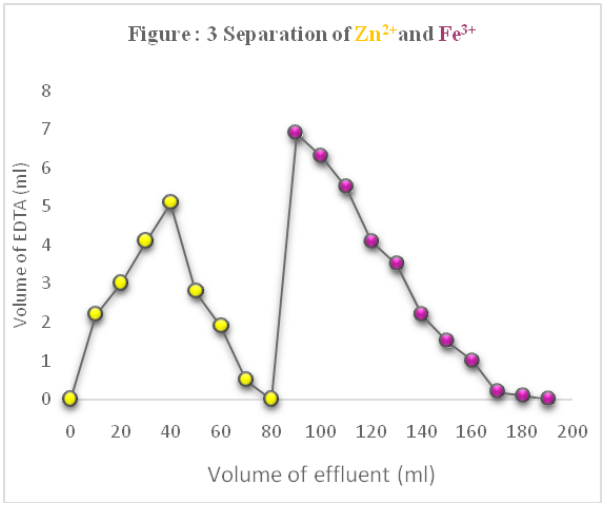
Series1: Cu^{2+}; Series 2: Co^{2+}; Series 3: Ni^{2+}; Series 4: Fe^{3+}

that the maximum uptake of metal ions was within the pH range of 3.5 to 4.5; beyond this pH range, the uptake of metal ions starts reducing.

The distribution coefficients (K_d) of metal ions in the different solvent systems on tin (IV) tungstoselenate-phenanthroline are summarized in Table 1. In order to find the potentiality of the composite material, distribution studies for several metal ions were performed in differentsolvent systems. It is apparent from the table 1 that the K_d values vary with the composition and nature of the contacting solvent. It is also observed from the



sorption studies that the material has maximum selectivity towards some metal ions than other metal ions. Based on differential selectivity towards metal ions, some binary separations of analytical importance have been achieved utilizing appropriate eluting solutions using the column of this material. The weakly retained metal ions emerge out of the column faster than those having high K_d values. The results of the binary separations are given in Table 2. The practical utility of tin (IV) tungstoselenate-phenanthroline in column



chromatography has been validated by performing some analytically significant separations of metal ions in a short span of time.

These separations have also been utilized in the analysis of metal contents in commercially available multi-mineral supplement samples. This paper reports the analysis of Zn^{2+} and Fe^{3+} in some commercially available multi-mineral supplement samples using the column of this material. The accuracy and reproducibility of the method have been checked statistically. The results of the analysis are shown in Table 3-5. The method can be successfully applied to medicinal, pharmaceutical, and environmental sciences to diagnose and

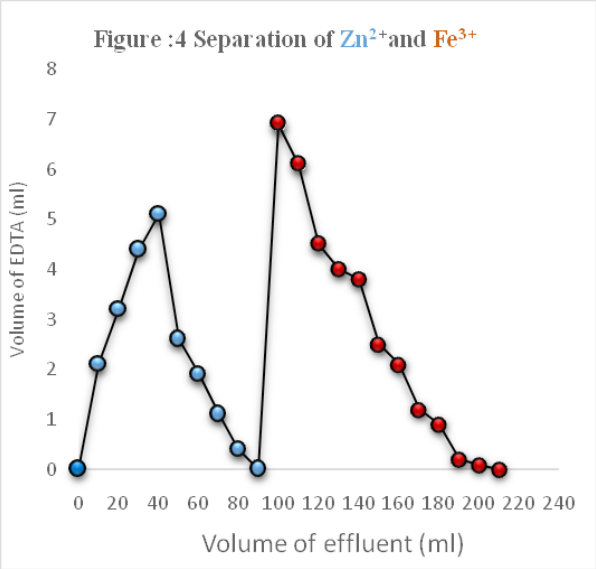
Table 4. Separation on Zn^{2+} and Fe^{3+} present in the pharmaceutical sample 2 on the column of composite material.

S. No.	Separation achieved	Amount loaded (mg)	Amount found (mg)	Recovery	Effluent used	Volume (ml)
1	Zn^{2+}	0.035	0.034	97.14%	10%DMSO+0.1M HNO_3	80
2		0.05	0.048	96.00%		
3		0.07	0.0675	96.43%		
1	Fe^{3+}	1.0	0.98	98.00%	10% DSMO	100
2		1.5	1.46	97.33%		
3		2.0	1.97	98.50%		

Table 5. Separation on Zn^{2+} and Fe^{3+} present in the pharmaceutical sample 3 on the column of composite material.

S.No.	Separation achieved	Amount loaded (mg)	Amount found (mg)	Recovery	Effluent Used	Volume (ml)
1	Zn^{2+}	0.08	0.077	96.25%	10% DMSO+0.1M HNO_3	80
2		0.13	0.126	96.92%		
3		0.17	0.167	98.24%		
1	Fe^{3+}	1.0	0.975	97.50%	10% DSMO	120
2		1.5	1.46	97.33%		
3		2.0	1.96	98.00%		

determine iron and zinc, respectively. The utility of this exchanger can further be explored by using it in column chromatography for the recovery and removal of metal ions from the industrial effluents and contaminated wastewater having pharmaceutical waste. The elution curves for each sample are shown in figures (2-4), indicating the separation of metal ions by using a suitable solvent system.



REFERENCES

Bruch, T., Graalfs, H., Jacob, L. and Frech, C. 2009. Influence of surface modification on protein retention in ion-exchange chromatography Evaluation using different retention models. *Journal of Chromatography A*. 1216 : 919-926 https://doi.org/10.1016/j.chroma.2008.12.008

Figueiredo, B. R., Cardoso, S. P., Portugal, I., Rocha, J. and Silva, C.M. 2018. Inorganic Ion Exchangers for Cesium Removal from Radioactive Wastewater. *Separation and Purification Reviews*. 47(4) : 306-336. https://doi.org/10.1080/15422119.2017.1392974

Kaushal, S., Mittal, S. K. and Singh, P. 2017. Developments in synthesis, characterization and applications of composite ion-exchange materials: A review. *Oriental Journal of Chemistry*. 33 (4) : 1726-1735. https://doi.org/10.13005/ojc/330417

Khan, M. A., Bushra, R., Ahmad, A., Nabi, S. A., Khan, D. A. and Akhtar, A. 2014. Ion exchangers as adsorbents for removing metals from aquatic media. *Archives of Environmental Contamination and Toxicology*. 66 (2) : 259-269. https://doi.org/10.1007/s00244-013-9970-9

Levison, P.R. 2003. Large-scale ion exchange column chromatography of proteins Comparison of different formats. *Journal of Chromatography B*. 790 : 17-33. https://doi.org/10.1016/S1570-0232(03) 00087-4

Nabi, S. A., Laiq, E. and Islam, A. 2004. Selective separation and determination of cephalosporins by TLC on stannic oxide layers. *Acta Chromatographica*. 14 : 92-101.

Nabi, S. A., Laiq, E. and Islam, A. 2001. Selective separation of metal ions on strong acid cation-exchange resin loaded with crystal violet. *Acta Chromatographica*. 11 : 118-120.

Topp, N. E. and Pepper, K. W. 1949. Properties of ion-exchange resins in relation to their structure. Part I. Titration curves. *Journal of the Chemical Society*. 3299-3303. https://doi.org/10.1039/jr9490003299

Vikas, S., Gaurav, G., Kumar, A. and Stadler, F.J. 2019. Preparation and Characterization of Gum Acacia / Ce(IV) MoPO 4 Nanocomposite Ion Exchange for Photocatalytic Degradation of Methyl Violet Dye. *Journal of Inorganic and Organometallic Polymers and Materials*. 29 : 1171-1183. https://doi.org/10.1007/s10904-019-01080-9