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Preparation, Characterization and Analytical Application of Tin(IV) Tungstoselenate-1,10 Phenanthroline

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ABSTRACT

Synthesis of a composite ion exchange material Tin (IV) tungstoselenate-1, 10 phenanthroline has been achieved by mixing different volume ratios of the organic counterpart with the inorganic ion exchanger Tin(IV) tungstoselenate. Final sample, having 0.88mmoles of 1,10 phenanthroline per gram of inorganic ion exchanger, was chosen for characterization, including ion exchange capacity, thermogravimetric analysis, and fourier transform infrared spectroscopy. The ion exchange capacity of Li^+, Na^+, Ca^{2+}, Sr^{2+} metals was determined by using the synthesized material. The adsorption behavior of Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} in various solvent systems have been studied. Based on distribution Coefficient (K_d) values, few analytically necessary separations of metal ions from the synthetic mixture have been achieved on the column of the composite ion exchanger.

Keywords: Composite ion exchanger, Synthesis, Characterization, Tin(IV) tungstoselenate-1,10 phenanthroline, Distribution coefficient.

INTRODUCTION

For decades, inorganic ion exchangers have been known in various fields of sciences due to their radiation and chemical stability, and because of their rigid structures, they possess specific selectivity towards the wide range of metal ions[1]. Numerous materials have been synthesized, the most conventional of which were the salts of tetra and pentavalent metals and hydrous oxides. Even the intercalated compounds have become quite interesting because of their varying interlayer space due to the insertion of organic molecules sandwiched between the layers of the inorganic material[2]. These intercalated compounds have alternating inorganic and organic layers; as a result, their physical and chemical reactivity can be altered. Derivatized organic-inorganic tetravalent metal acid salts have been developed by the intercalation of polar organic moieties such protonated alcohols, acetones, pyridine, or aromatic compounds within the layers of crystalline α-zirconium phosphate[3-6]. They have shown promising features that are important from the analytical point of view.

Several n-alkanols and n-alkylamines have also been intercalated in the γ-zirconium hydrogen phosphate and γ-titanium hydrogen phosphate[7].

Octa decyltrimethyl ammonium ion was intercalated onto zirconium and titanium dihydrogen phosphate[8].

Organic moieties can also get captured into the pores or adsorbed on the surface of the inorganic matrix to form composite or hybrid ion exchangers. Recently the synthesis of organic-inorganic composite exchange materials has been extensive, as these have the added advantage of inorganic and organic analogs regarding their chemical, thermal stability and ion exchange capacity[9]. Composite ion-exchangers have been considered viable in the environmental and analytical chemistry due to their enhanced reproducibility, thermal, chemical, radiational, mechanical stabilities, and selectivity for heavy toxic metals[10]. The literature survey revealed that many inorganic ion exchange materials were used to separate metal ions[11-12]. Inorganic ion exchangers have been extensively used in paper and thin-layer chromatographic separations[13-15]. Pollution due to heavy metals ions is a major environmental problem. Industrial effluent contains a massive amount of these toxic heavy metals, the concentration of heavy metals ions in wastewater is up to the maximum level, which is higher than the safe limit; therefore must be removed before they get mixed into the environment. Among the metals, lead, cadmium, copper, aluminium, cobalt are hazardous for living organisms[16-18].

In this study, an attempt has been made to synthesize an organo-inorganic ion exchanger, Tin (IV) tungstoselenate-1,10 phenanthroline. Studies based on its properties, its practical utility have been explored by the selective separation of heavy metals from binary synthetic samples.

MATERIALS AND METHOD

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

Synthesis of inorganic ion exchanger

The inorganic ion exchanger was prepared by mixing the aq. solutions of 0.05M sodium selenite and sodium tungstate with an aqueous solution of 0.05M of tin (IV) chloride (as reported earlier[19].

The acidic medium was maintained by adding hydrochloric acid to it. The white gelatinous material was obtained, kept in the mother liquor for 12 h for complete digestion at room temperature. The gel was filtered, washed, dried, and converted to hydrogen form by immersing in 1M HNO_3 and was left for 24 h at room temperature with intermittent stirring. After 24 h the supernatant liquid was decanted, and the material was filtered under suction; repeated washing with DMW was done to remove any excess amount of the acid, finally, the obtained product was dried at 40 ± 2°C.

Derivatization of Tin (IV) tungstoselenate with 1,10 phenanthroline

2.5 grams of the synthesized exchanger in H^+ form was reacted with the solution of 1,10 phenanthroline (0.1M) in a temperature-controlled shaker for 6 h at 30 ± 2°C. The pinkish color precipitate was obtained that was filtered, washed, and air-dried. The remaining amount of 1,10 phenanthroline in the filtrate was titrated with standard hydrochloric acid. The amount of 1,10 phenanthroline anchored onto Tin(IV) tungstoselenate was calculated from the difference between the final and initial concentrations of the 1,10 phenanthroline.

Ion exchange capacity

The column was packed with 0.5 g of the derivatized material in hydrogen form. The hydrogen ions were eluted when 0.01M solution of cations was allowed to move through the column of the exchanger. The H^+ ions in the effluent were calculated after titrating against the standard NaOH solution. Ion exchange capacity of univalent and bivalent cations are shown in Table 1.

Table 1: Ion exchange capacity of Tin(IV) tungstoselenate 1, 10 phenanthroline for different metal ions

Metal ions	Salt Used	Ion exchange capacity (meq/g exchanger in H^+ form)
Li^+	LiCl	0.81
Na^+	NaCl	0.98
Ca^{2+}	$Ca(NO_3)_2$	1.6
Sr^{2+}	$Sr(NO_3)_2$	1.4

Characterization

The FT-IR was recorded by pressing the derivatized material into the KBr disc using Perkin Elmer 1730 spectrometer. Scanning electron microscopy was done on the ground sample by LEO 435 VP microscope having an imaging device. The thermal behavior of powdered Tin(IV) tungstoselenate 1,10 phenanthroline was monitored at a heating rate of 10°C per min in a nitrogen atmosphere using a General V4.IC Du Pont 2100 thermo analyzer. A temperature-controlled shaker from 'SICO'was used.

Sorption studies

The distribution coefficient (K_d) of metal ions on the Tin(IV) tungstoselenate with 1,10 phenanthroline was determined by the batch method in many solvent systems, 400 mg of the derivatized material in hydrogen form was equilibrated with the solutions of metal ions (40 mL) in the solvent system for about eight hours with occasional shaking. The remaining amount of the cation in solution was determined by titrating against the standard solution of EDTA. The ion-exchange behavior of Tin(IV) tungstoselenate 1,10 phenanthroline towards Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}, Al^{3+} was studied in different solvents. The Kd values were computed using the formula:

$$K_d = \frac{\text{initial} - \text{final mmoles of metal ions}}{\text{weight of the exchanger}} \times \frac{\text{ml of the solution}}{\text{final mmoles of metal ion}} \, ml/g$$

Analytical applications of Tin (IV) tungstoselenate 1,10 phenanthroline

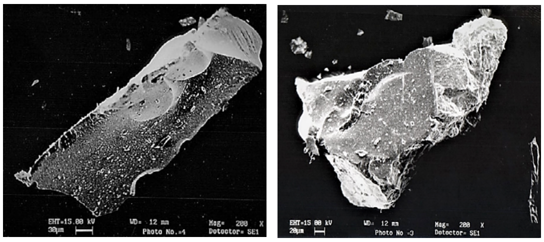
Quantitative binary separation of few essential metal ions was attained using the column packed with 2 g of the synthesized material having nearly 0·6 cm internal diameter. An aliquot of the sample (synthetic mixture of metal ions) was transferred in the column of the composite material, and the chosen volume of the elutant was passed through it, keeping a flow rate of around 3-4 drops per minute. EDTA titrations were performed for the quantitative determination of metal ions present in the effluent. Results are shown in Table 3.

RESULTS AND DISCUSSION

Based on its chemical studies, the tentative formula of Tin(IV) tungstoselenate was given as $[(SnO_2)_7.HSeO_3(HWO_4)_{18}].45H_2O$ which was proposed by Nabi *et al.,*[19]. As mentioned above, the derivatized product of pink color obtained has 0.88 mmoles per gram of 1,10 phenanthroline anchored on the exchanger. As the result of its chemical composition, the mole ratio of Tin (IV) tungstoselenate to 1,10 phenanthroline was assigned as 1.0:5.69. The ion exchange capacity of derivatized material was 1.6 meq per gram, which was quite improved compared with its inorganic counterpart tin (IV) tungstoselenate having 1.4 meq per gram, as Nabi *et al.,*[19].

Scanning electron microscopic photographs of Tin(IV) tungstoselenate and Tin(IV) tungstoselenate 1,10 phenanthroline at 200x and 200x magnifications are presented in Fig. 1a and b. Fig. 1a reveals that Tin(IV) tungstoselenate shows a plate-like morphology, whereas Fig. 1b indicates a relative change in the structure of the derivatized material.

Figure 2 and 3 shows the FTIR spectra of tin tungstoselenate and Tin(IV) tungstoselenate 1,10 phenanthroline respectively. In the FTIR spectrum of Fig. 2 and Fig. 3, a very broad, intense peak is assigned to the surface hydroxyl stretching band between 3500-2000 cm^{-1} [15,20-22]. A prominent peak at 1637 cm^{-1} is due to H-O-H bending[15,20,23,24]. The peaks at 1550 cm^{-1}, 1176 cm^{-1}, and 709 cm^{-1} were assigned to metal-oxygen bonds[22,25-27]. FTIR spectra of Tin(IV) tungstoselenate 1,10 phenanthroline shows a small peak at ~800 cm^{-1}, a peak at ~700 cm^{-1}, and a sharp peak at 475 cm^{-1}, respectively, which indicates the presence of tungstate, selenate groups, and metal-oxygen bonds in the material[22,25-27]. Metal ligand bond can be predicted in the region below 400 cm^{-1} [28]. The change in intensities of different characteristics peaks indicates the incorporation of organic moiety onto the inorganic matrix.



(a) (b)

Fig. 1. SEM images of (a) Tin(IV) tungstoselenate (200x magnification), (b) Tin(IV) tungstoselenate-1,10 phenanthroline (200x magnification)

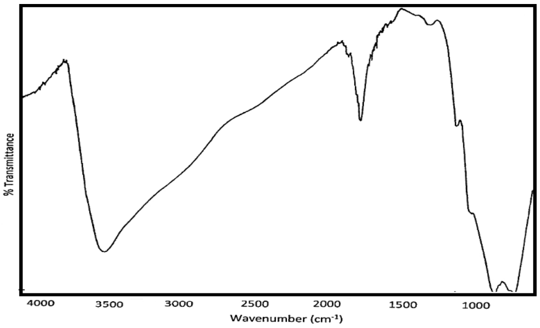


Fig. 2. FTIR spectrum of Tin(IV) tungstoselenate

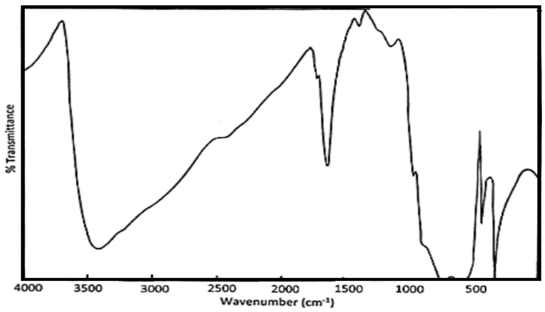


Fig. 3. FTIR spectrum of Tin (IV) tungstoselenate-1,10 phenanthroline

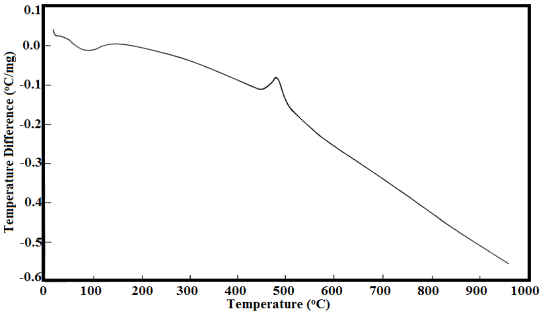


Fig. 5. DTA curve of Tin(IV) tungstoselenate-1,10 phenanthroline

The thermogram of Tin(IV) tungstoselenate to 1,10 phenanthroline Fig. 4 shows definite steps. About 7.5% loss of weight was observed up to 150°C; this loss of weight corresponds to dehydration of the composite material, characterized by an endothermic peak (Fig. 5) in the DTA curve. Then weight loss of 10% till 440°C is due to the evaporation of H_2O molecules formed due to the condensation of hydroxyl groups. Additional, 15% weight loss from 440°C to 520°C was due to the decomposition of 1,10 phenanthroline, with the evolution of gaseous products, confirmed by an exothermic peak at 490°C in the DTA curve. Subsequent weight loss starts from 610°C that continues up to 730°C, probably due to the vaporization of oxides of selenium. After 730°C, the weight becomes approximately constant because of the formation of metal oxides.

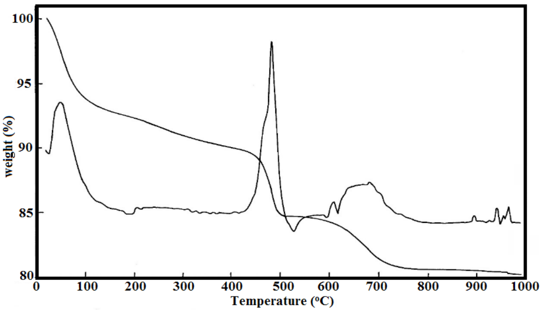


Fig. 4. TGA curve of Tin (IV) tungstoselenate-1,10 phenanthroline

Sorption studies were performed to explore the practical utility of the synthesized material in six different solvent systems. The K_d values are higher for most metal ions studied; data are summarized in Table 2. The composite material shows a high affinity towards Cd^{2+}, Pb^{2+}, Al^{3+} and Co^{2+} in DMW. The distribution coefficients values of Al^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} metal ions increases in general when the ratio of nitric acid increases, whereas the decreasing trend is seen for Cd^{2+} and Pb^{2+} metal ions. Based on the differential selectivity of metal ions in these solvents systems, some binary separations have been achieved from the synthetic mixtures of metal ions quantitatively by using the column of this composite material. Results summarized in Table 3 show that this method can be used for the removal of lead, cadmium, and copper from industrial wastewater.

Table 2: K_d values of metal ions on Tin(IV) tungstoselenate-phenanthroline

Metal	Solvent System*					
ions	1	2	3	4	5	6
Al^{3+}	5455.55	6200	9940	12350	16566.7	24900
Co^{2+}	5455.55	9980	12400	16566	25000	49700
Ni^{2+}	3746.15	3776.92	7071.42	8266.66	9940	16633.3
Cu^{2+}	4900	6175	8233.33	12400	16500	24900
Cd^{2+}	26256	15068	19120	18390	14150	1341
Pb^{2+}	8439	7124	5498	4463	3681	3001

*Solvent System1: DMW, 2: DMSO10% , 3:0.^{1}M HNO_3, 4: 10% DMSO + 0.^{1}M HNO_3 1:1 v/v , 5: 10% DMSO + 0.^{1}M HNO_3 1:2 v/v, 6 : 10% DMSO + 0.^{1}M HNO_3 1:3 v/v

Table 3: Quantitative separation of metal ions on the column of Tin(IV) tungstoselenate-phenanthroline

S. No.	Separation achieved	Amount loaded (mg)	Amount found (mg)	%Recovery	Volume of eluent (mL)	Eluent used
1	Ni^{2+}	2.90	2.81	96.89	80.00	10% DMSO
	Co^{2+}	2.90	2.87	98.96	90.00	DMW
2	Cd^{2+}	5.62	5.41	96.26	60.00	10% DMSO + 0.1M HNO_3 (1:3 v/v)
	Cu^{2+}	2.41	2.35	97.51	80.00	DMW
3	Ni^{2+}	2.90	2.80	96.55	80.00	DMW
	Pb^{2+}	10.36	10.10	97.49	90.00	10% DMSO + 0.1M HNO_3 (1:3 v/v)
4	Cd^{2+}	5.62	5.44	96.79	70.00	10% DMSO + 0.1M HNO_3 (1:3 v/v)
	Al^{3+}	1.34	1.31	97.76	90.00	10% DMSO
5	Pb^{2+}	10.36	10.09	97.39	70.00	10% DMSO + 0.1M HNO_3 (1:3 v/v)
	Cu^{2+}	2.41	2.35	97.51	90.00	DMW

CONCLUSION

A new composite exchange material Tin(IV) tungstoselenate-1,10 phenanthroline has been synthesized that exhibits the characteristic features of an ion exchanger having improved ion exchange capacity. Its practicability can further be applied in the field of ion-exchange chromatography, and its analytical significance can be studied in the selective separation and removal of heavy metals from pharmaceutical and industrial wastewater.

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Conflicts of Interest

There is no conflicts to declare.

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