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Research Article

STUDIES ON A NEWLY SYNTHESIZED TIN(IV) VANADOMOLYBDATE: AN INORGANIC CATION EXCHANGER SELECTIVE FOR NICKEL(II) IONS

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ABSTRACT

Tin based ion exchanger tin (IV) vanadomolybdate has been synthesized as a new inorganic cation exchanger. The material was synthesized by adding 0.1 M stannic chloride solution to a mixture of 0.1 M sodium metavanadate solution and 0.1 M sodium molybdate solution in different volume ratios to get seven samples. Ion exchange capacity of all the seven samples has been ascertained by column method. The maximum ion exchange capacity was found to be 0.76 meq/g of one of the samples. This sample was selected for detailed study. The ion exchange capacity for various alkali and alkaline earth metal ions has also been determined. The exchanger was characterized on the basis of ion exchange capacity, thermal stability, chemical stability, FTIR, TGA and X-ray analysis. Distribution coefficient for various metal ions has also been determined. The exchanger shows the selectivity for Ni^{2+} and Cu^{2+}.

Keywords: *Inorganic Cation Exchanger, Ion Exchange Capacity, pH Titration, Thermal Stability, Chemical Stability, FTIR, TGA And X-ray Analysis*

INTRODUCTION

Ion exchange is the process in which ions are exchanged between a solution and an insoluble solid. Ion exchange serves as one of the most important analytical technique for the separation of charged species from a solution that would ordinarily be very difficult and time consuming. The main principle of the ion exchange method may be said to be the exchange with the help of an ion exchanger, of all exchangeable ions of the same charge by other ions of the same charge (Samuelson, 1954). The earliest systematic studies in which ion exchange properties were described are concerned with base exchange in minerals present in the soil (Amphlett, 1964).

Ion exchange may be natural or synthetic. Most natural ion exchangers like zeolites are crystalline materials with cation exchange properties. First synthetic industrial ion exchanger was reported in 1905. In recent years various zeolites with completely regular crystal structure have been synthesized and these products are exact counterparts of the natural materials. The examples of such kind of material include zeolite 4A (Chand *et al.*, 2013).

Nowadays, synthetic inorganic ion exchangers have drawn the attention since they are less sensitive to higher temperature and to different chemicals and are also selective to certain ions. Further it was shown in literature that three component ion exchanger shows a better IEC than the two component ion exchanger (Nabi and Khan, 2005).

Tin(IV) based ion exchangers have been studied in detail previously various three component ion exchangers based on tin(IV) were reported in the literature. Similarly, some examples of three component ion exchangers reported in literature are stannic(IV) silicomolybdate (Nabi and Khan, 2006), stannic(IV) iodophosphate (Siddiqui *et al.*, 1983), stannic(IV) molybdophosphate (Marageh *et al.*, 1999), stannic(IV) phosphotungstate (Mittal *et al.*, 2007) and stannic(IV) arsenophosphate (Nabi *et al.*, 1981).

The present work is concerned with the synthesis and characterization of a new three component cation exchanger. The IEC of the material was determined by column method and pH titration method. Further characterization of the material was done by thermal studies, FTIR, TGA and XRD studies. Chemical studies of the exchanger were also made in various solutions.

Distribution behavior of the material was also studied for ten different metal ions which reveal its selectivity for Ni^{2+} and Cu^{2+}.

MATERIALS AND METHODS

Reagents and Chemicals

Stannic chloride ($SnCl_4.5H_2O$) was a CDH product while sodium metavanadate ($NaVO_3$) and sodium molybdate ($Na_2MoO_4.2H_2O$) were obtained from E.Merck and Qualigens respectively. All reagents of analytically pure grade were used for the preparation of ion exchanger.

Instrumentation

Thermonicolet IR Spectrophotometer and Philips Analytical X-ray B.V. Diffractometer were used for FTIR and XRD respectively. Exstar TG/DTA 6300 was used for obtaining TGA curve in nitrogen atmosphere. For weighing, Samson S-300D Electronic Balance was used. NSW India's Oven was used for drying the samples.

Thermal studies and equilibrium studies were performed with the help of Tanco's Electric Muffle Furnace and Tanco's Electric Rotary Shaker respectively. A Toshniwal Digital pH Meter (Model pH-110) was used for measuring the pH. All glasswares that are used throughout the experimental work were of Borosil make.

Synthesis

The seven different samples of tin(IV) vanadomolybdate were prepared by adding 0.1 M aqueous solution of stannic chloride to a mixture of 0.1 M aqueous solution of sodium metavanadate and 0.1 M aqueous solution of sodium molybdate with constant stirring under the conditions given in Table 1.

The samples that are prepared under different volume ratios are named as TVM-I, TVM-II, TVM-III, TVM-IV, TVM-V, TVM-VI and TVM-VII.

The required pH of the products was adjusted by adding concentrated HCl. All the products were kept as such at room temperature for twenty four hours and then filtered. The precipitates were washed with demineralized water to ensure complete removal of acid.

Then, the seven samples were dried in an oven at 40±1°C and converted into the H^+ form by treatment with molar nitric acid for twenty four hours.

The products thus obtained were washed with demineralized water several times and finally dried at 40±1°C in an oven (Rawat *et al.*, 2002).

Table 1: Synthesis of Tin(IV) Vanadomolybdate

Sample No.	**Molar Conc. (M)**			**Mixing Ratio**	**pH**	**Appearance of Beads After Drying (40±1°C)**	**Yield (g)**	**IEC (meq/g)**
	Sn^{4+}	**VO_3^-**	**MoO_4^{2-}**					
TVM-I	0.1	0.1	0.1	1:1:1	1	Dark Yellow	0.57	0.50
TVM-II	0.1	0.1	0.1	2:1:1	1	Dark Yellow	1.56	0.46
TVM-III	0.1	0.1	0.1	1:1:2	1	Yellow	0.55	0.76
TVM-IV	0.1	0.1	0.1	1:2:2	1	Light Yellow	1.68	0.38
TVM-V	0.1	0.1	0.1	2:1:2	1	Light Yellow	1.20	0.54
TVM-VI	0.1	0.1	0.1	3:1:1	1	Mustard Yellow	1.98	0.48
TVM-VII	0.1	0.1	0.1	1:1:3	1	Light Yellow	0.75	0.21

TVM - Tin(IV) vanadomolybdate 1=50ml, 2=100ml, 3=150ml

Characterization

Ion Exchange Capacity

The measurement expressed as milliequivalents of exchangeable ion per dry gram of exchanger is commonly referred to as the ion exchange capacity (Kunin, 1958). The IEC of the various samples of tin(IV) vanadomolybdate was determined by column operation. The ion exchanger in the H^+ form was placed in the column with a glass wool support and washed with demineralized water. All the seven samples (ion exchanger) were placed in different columns. Sodium nitrate solution (1 M) was used as the eluent and the effluents were collected separately in every case. The hydrogen ions eluted from the exchanger through column were titrimetrically determined with the help of standard solution of sodium hydroxide. Sample TVM-III was chosen for further studies owing to its high ion exchange capacity.

The IEC of TVM-III was also determined by eluting some alkali and alkaline earth metals as represented by Table 2. 0.1 M solution of LiCl, NaCl, KBr, $MgCl_2$, $CaCl_2$ and $BaCl_2$ were taken as eluent for this purpose. The ion exchange capacity was calculated using the formula:

IEC =av/w

Where, a is the molarity, v is the volume of NaOH used during titration and w is the weight of the exchanger taken.

Table 2: Ion Exchange Capacity for Different Cations (meq/g)

Cation	**Salt Used (Concentration)**	**IEC (meq/g)**	**Hydrated Ionic Radii (A^o)**
Li^+	LiCl (0.1 M)	0.54	10.00
Na^+	NaCl (0.1 M)	0.76	7.90
K^+	KBr (0.1 M)	0.82	5.30
Mg^{2+}	$MgCl_2$ (0.1 M)	0.38	10.80
Ca^{2+}	$CaCl_2$ (0.1 M)	0.50	9.60
Ba^{2+}	$BaCl_2$ (0.1 M)	0.68	8.80

pH Titration

The pH titration of the exchanger was employed for (Topp and Pepper, 1949). The pH titration was carried out using NaCl-NaOH system. To determine the IEC of the exchanger with the help of pH titration method, eleven equal portions (500 mg each) of the exchanger were placed in 250 ml conical flasks separately and equimolar solutions of sodium chloride and sodium hydroxide in different volume ratios were added. The total volume of the solution was kept 50 ml so as to maintain the ionic strength constant. Then, the mixture was kept at room temperature for twenty four hours with intermittent shaking. Figure 1, depicts the pH titration curve of tin(IV) vanadomolybdate.

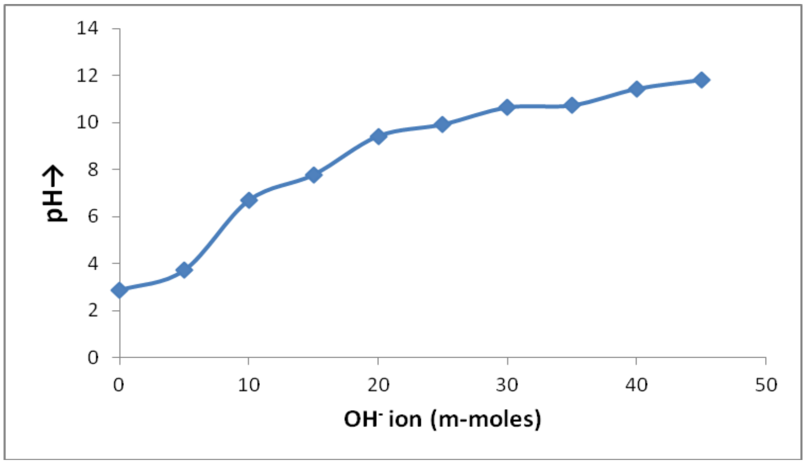

Figure 1: pH Titration Curve of TVM

Thermal Stability

To examine the effect of drying temperature on the ion exchange capacity seven equal portions of 500 mg each, were heated at different temperatures upto 700°C in a muffle furnace for one hour and then cooled to room temperature in a dessicator. First of all the loss in weight of the exchanger was observed in each case and then their ion exchange capacity was determined by employing column method (Chand *et al.*, 2010). The change in color of the exchanger was also noted. The results are given in Table 3.

Table 3: Thermal Stability of TVM Exchanger

Sl. No.	Drying Temperature (°C)	Weight of Ion Exchanger Before Heating (g)	Change in Colour	Percentage Weight Loss	IEC (meq/g)
1	100	0.50	Dark Yellow	8%	0.70
2	200	0.50	Yellowish Brown	14%	0.67
3	300	0.50	Brown	18%	0.63
4	400	0.50	Dark Brown	24%	0.53
5	500	0.50	Dark Brown	30%	0.51
6	600	0.50	Brownish Black	38%	0.42
7	700	0.50	Black	44%	0.36

Chemical Stability

To determine the chemical stability of the exchanger, fifteen equal amounts (500 mg each) of the exchanger were kept separately in 25 ml of different solutions at room temperature for twenty four hours. The different solutions include solutions of mineral acids, organic acids and bases of different concentrations. After keeping the solutions for twenty four hours, these are filtered and finally the residues were dried in an oven at 40±1 °C. Then, the residues were cooled to room temperature and the weight losses of the samples were observed. The ion exchange capacity of the samples was also determined by the usual column technique. The observations are summarized in Table 4.

Table 4: Chemical Stability of TVM

Sl. No.	Solution	Percentage Weight Loss	Ion Exchange Capacity (meq/g)
1	1 M HCl	0%	0.76
2	2 M HCl	2%	0.71
3	1 M HNO_3	0%	0.76
4	2 M HNO_3	2%	0.69
5	3 M HNO_3	4%	0.60
6	1 M H_2SO_4	22%	0.26
7	2 M H_2SO_4	44%	0.18
8	3 M H_2SO_4	64%	0.13
9	4 M H_2SO_4	Completely Dissolved	-
10	1 M HCOOH	6%	0.54
11	2 M HCOOH	12%	0.41
12	1M CH_3COOH	2%	0.73
13	2M CH_3COOH	4%	0.71
14	2 M KOH	Completely Dissolved	-
15	3 M NaOH	Completely Dissolved	-

Distribution Behavior

In order to examine the affinity of tin(IV) vanadomolybdate towards various metal ions, distribution coefficient (K_d) values for ten metal ions were determined by batch process (Teena *et al.,* 2015). In this process ten equal portions 500 mg each of the exchanger were treated separately with 25 ml of 0.1 M aqueous metal salt solutions. The mixtures were then kept for twenty four hours at room temperature and subsequently determination of metal ions was done by titrating the solutions against the standard solution of EDTA, complexometric titration (Vogel, 1968), with the help of appropriate indicators. The K_d values as given in Table 5, were calculated according to the formula-

$$K_d = \frac{I - F}{F} \text{ x } \frac{V}{W}$$

Where, I – Initial volume of the EDTA solution used.
F – Final volume of the EDTA solution used.
V – Volume of the metal ion solution taken.
W – Weight of the exchanger.

Table 5: Distribution Coefficient for Different Metal Ions

Sl. No.	Cation	Form	K_d (ml/g)
1	Ca^{2+}	Carbonate	2.54
2	Mg^{2+}	Acetate	6.11
3	Zn^{2+}	Acetate	5.33
4	Cu^{2+}	Acetate	12.25
5	Mn^{2+}	Acetate	0.40
6	Co^{2+}	Acetate	0.20
7	Ni^{2+}	Ammonium Sulphate	23.67
8	Pb^{2+}	Nitrate	5.09
9	Bi^{3+}	Nitrate	10.73
10	Cd^{2+}	Chloride	6.36

TGA Curve

TGA of tin(IV) vanadomolybdate in H^+ form was obtained at a heating rate of 10°C/min with the help of Exstar TG/DTA 6300 instrument available at Instrumentation Centre, IIT Roorkee (figure 2).

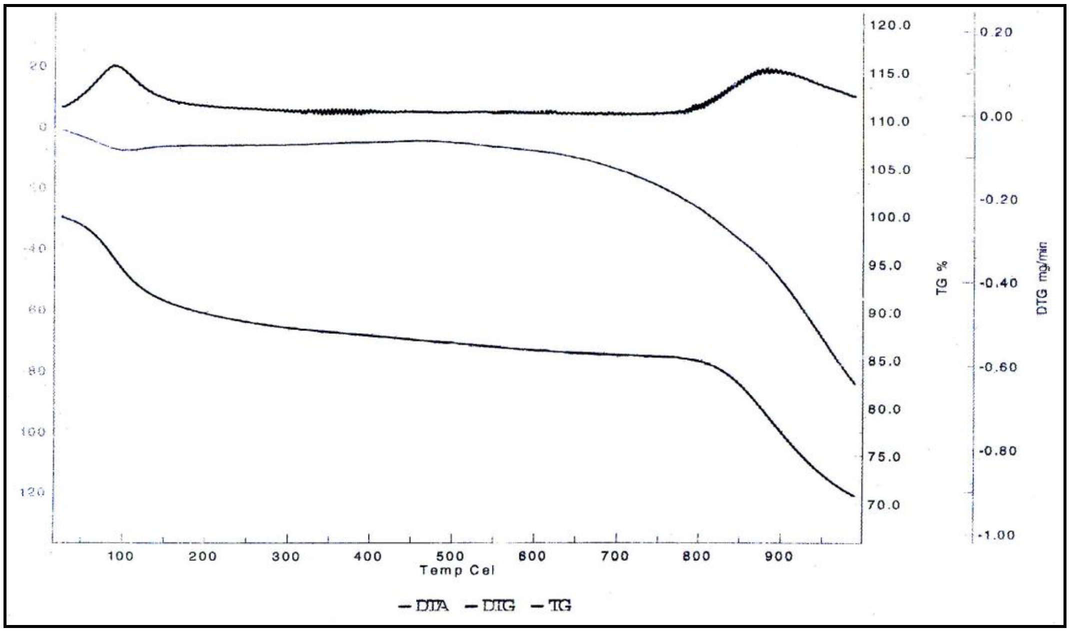

Figure 2: Thermogravimetric Analysis Curve

FTIR Study

FTIR spectrum of tin(IV) vanadomolybdate was obtained by Thermonicolet IR Spectrophotometer available at Instrumentation Centre, IIT Roorkee. KBr disc method was used for obtaining the spectrum. The IR absorption spectrum was recorded over the wavelength range 4000-400 cm^{-1}. The FTIR spectrum of the material was shown in Figure 3.

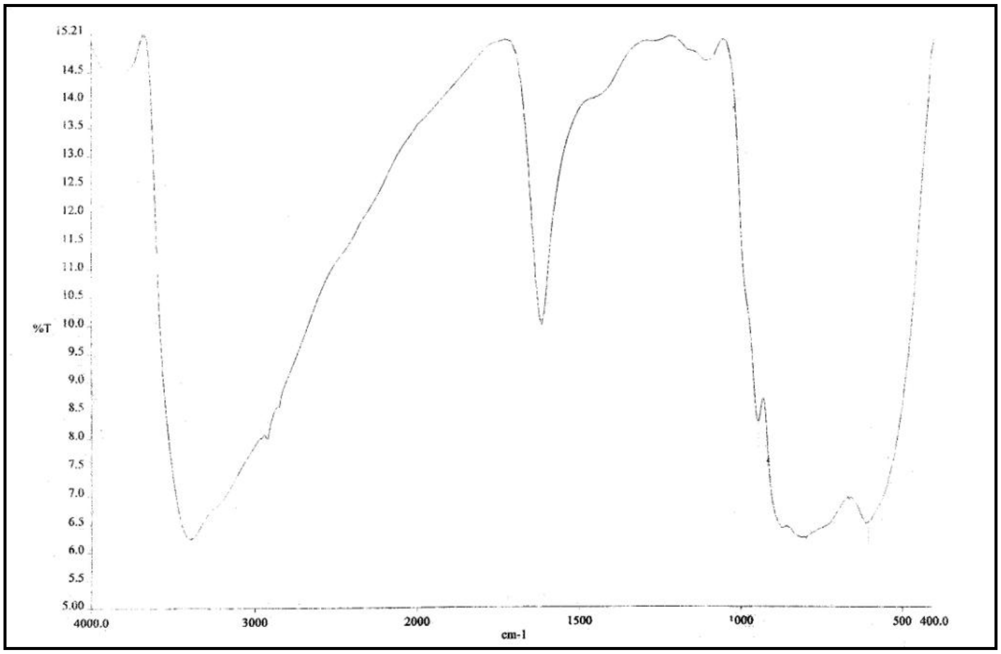

Figure 3: FTIR Spectrum of TVM

XRD

Nature of the particle of tin(IV) vanadomolybdate was ascertained with the help of XRD which was obtained by Philips Analytical X-ray Diffractometer available at Instrumentation Centre, IIT Roorkee. The X-ray diffraction analysis of the material shows a number of peaks of weak intensities which are shown in Figure 4.

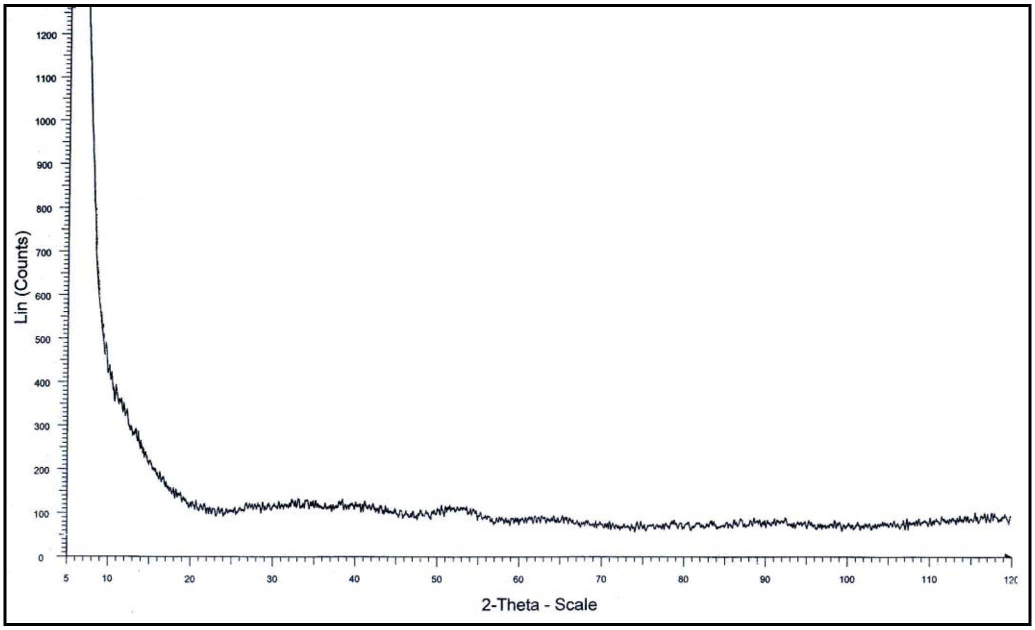

Figure 4: XRD Pattern of TVM

SEM

The scanning electron microscope photographs were obtained for tin(IV) vanadomolybdate by the instrument available at Instumentation Centre, IIT Roorkee. SEM photographs are shown in Figure 5.

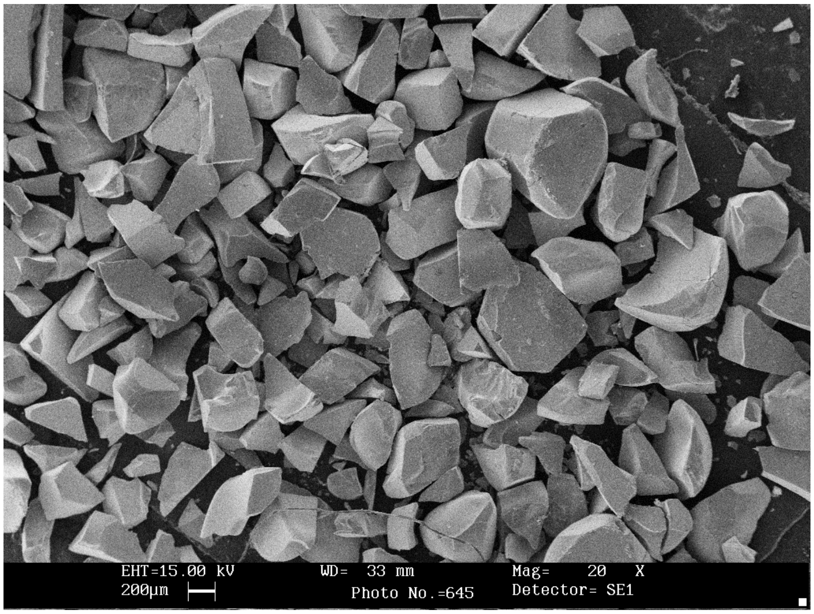

Figure 5: SEM Photograph of TVM

RESULTS AND DISCUSSION

Seven different samples of tin(IV) vanadomolybdate were synthesized in different volume ratios. The results given in Table 1 show that IEC of sample TVM-III is highest (0.76 meq/g), therefore, all studies were made on this sample. The ion exchange capacity of TVM-III was also calculated for different alkali and alkaline earth metal cations (Table 2). The IEC is high for alkali metal ions and the order of IEC is $K^+ > Na^+ > Li^+$. In contrast to the alkali metal ions, the IEC of alkaline earth metals is low and the order is $Ba^{2+} > Ca^{2+} > Mg^{2+}$.

pH titration studies using NaCl-NaOH system were carried out under equilibrium conditions. The IEC of the exchanger by this method was found to be 0.80 meq/g. The pH titration curve (Figure 1) revealed that the material behaves as strong cation exchanger as indicated by a low pH (~2.87) of the solution when no OH^- ions were added to the system.

The effect of heating upto 700°C on color, weight and IEC of exchanger were also observed. It can be inferenced from Table 3 that the IEC of the exchanger decreases with the increase in temperature.

The material was found to be fairly stable in HCl and HNO_3 and less stable in H_2SO_4 at lower concentration. In organic acids like HCOOH and CH_3COOH, the exchanger was found to be moderately stable. The material was found to be completely soluble in 4M H_2SO_4, 2M KOH and 3M NaOH.

The study of the values obtained for distribution coefficient revealed that the material shows high selectivity for Ni(II) and Cu(II) for which the K_d values were 23.67 ml/g and 12.25 ml/g respectively. The distribution coefficient for the metal ions (Table 5) follows the sequence:

$Ni^{2+} > Cu^{2+} > Bi^{3+} > Cd^{2+} > Mg^{2+} > Zn^{2+} > Pb^{2+} > Ca^{2+} > Mn^{2+} > Co^{2+}$

Thermogram for the material was recorded in Figure 2. The weight loss of the ion exchanger upto 100°C (5.6%) is due to removal of external water molecules. At high temperature upto 299°C condensation of exchangeable hydroxyl group takes place, which is a characteristic of synthetic inorganic ion exchangers and the corresponding weight loss is 11.6%. Above 300°C, a gradual loss in weight was observed i.e. 12.4% at 400°C, 13.1% at 500°C, 13.9% at 600°C, 14.4% at 700°C and 15.1% at 800°C. From 800°C to 900°C a rapid decline in weight was observed which may be attributed to the loss of components and finally at 988°C the weight becomes constant.

IR spectrum of the material under study is shown in Figure 3. Here the first band with a maximum peak at 3391 cm^{-1} is due to interstitial water molecule and OH group. The sharp peak at 1616 cm^{-1} indicates the presence of aqua (H-O-H) bending. The spectrum of tin(IV) vanadomolybdate shows a strong and weak band at 945 cm^{-1} and 798 cm^{-1} which indicates the presence of molybdate and vanadate respectively. The peak at 606 cm^{-1} is associated with metal oxygen bond.

The X-ray diffraction pattern of the material (Figure 4) exhibits a large number of weak peaks. Hence tin(IV) vanadomolybdate is amorphous in nature.

The scanning electron microscopy of newly synthesized tin(IV) vanadomolybdate shows a regular uniform morphology, indicating its amorphous nature (Figure 5).

Conclusion

Tin (IV) based ion exchanger prepared under the conditions of concentration and acidity was characterized on the basis of distribution behavior, thermal stability and chemical stability. Further investigation, the synthesized material use in analytical chemistry for the separation of trace metal.

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REFERENCES

Amphlett CB (1964). *Inorganic Ion Exchangers*, (Elsevier Publishing Company, Amsterdam, Netherland).

Chand S, Teena and Manju (2010). Synthesis and Characterization of an Inorganic Ion Exchanger Based on Tin(IV). *International Transactions in Applies Sciences* **2**(1) 181-190.

Chand S, Teena and Manju (2013). Cadium(II) Selective A New Inorganic Cation Exchanger Based on Antimony (III). *International Transactions in Applied Sciences* **2**(1) 181-190.

Kunin R (1958). *Ion Exchange Resins*, (John Wiley & Sons Inc., New York, USA).

Marageh MG, Husain SW and Khanchi AR (1999). Selective Sorption of Radioactive Cerium and Strontium on Stannic Molybdophosphate Ion Exchanger. *Applied Radiations and Isotopes* **50**(3) 459-465.

Mittal SK, Nath R and Banait JS (2007). New Method of Synthesis of Stannic Phosphatetungstate and Its Characterization as Ion Exchanger. *Journal of Chemistry* **1**(1).

Nabi SA and Khan A (2005). Synthesis and Characterization of a New Phase of Stannic Arsenate Ion Exchanger and its Use in TLC Separation of Metal Ions. *Indian Journal of Chemistry* **44**(A) 1383-1387.

Nabi SA and Khan AM (2006). Synthesis, Ion-Exchange Properties and Analytical Application of Stannic Silicomolybdate: Effect of Temperature on Distribution Coefficient of Metal Ions. *Reactive and Function Polymers* **66** 495-508.

Nabi SA, Siddiqui WA and Farooqui WU (1983). A Comparative Study of the Synthesis and Ion Exchange Properties of Iodophosphate of Tin(IV), Zirconium(IV) and Iron (III): Separation of Metal ions on Tin(IV) Iodophosphate. *Bulletin of the Chemical Society of Japan* **55** 495-502.

Rawat JP, Singh P and Rahman N (2002). Synthesis, Characterization and Ion Exchange Properties of a New Inorganic Ion Exchange Material: Zirconium(IV) Iodoxalate. *Indian Journal of Chemistry* **41**(A) 1616-1618.

Samuelson O (1954). *Ion Exchangers in Analytical Chemistry*, (John. Wiley and Sons & Inc., New York, USA).

Siddiqui RA, Nabi SA and Khan R (1981). Synthesis, Ion Exchange Properties and Application of Thermally Stable Stannic Selenophosphate: Comparison with other Tin(IV) Based Ion Exchanger. *Journal of Liquid Chromatography* **4**(7) 241-246.

Teena, Chand S & Sonia (2015). Analytical Application of Some Three Component Cation Exchanger Based on Tin(IV) and Antimony(III). *International Journal of Basic and Applied Chemical Sciences* **5**(2) 29-39.

Topp NE and Pepper KW (1949). Properties of Ion Exchange Resin in Relation to Their Structure, I. Titration Curves. *Journal of Chemical Society* **690** 3299.

Vogel AI (1968). *A Textbook of Quantitative Inorganic Analysis*, (The English Language Book Society and Longmans, London, UK).