International Journal of Scientific and Technical Advancements

ISSN: 2454-1532

Synthesis and Applications of Stannic (IV) Oxoarsenotungstate based Cation Exchanger for Copper (II)

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Abstract**—** A new four component cation-exchanger stannic (IV) oxoarsenotungstate was synthesized at the pH-1. Ion-exchange capacity of the synthesized material for Na^+ was found to be 1.41 meq/g of the dry exchanger as obtained by column method. The exchanger was characterized on the basis of chemical stability, thermal stability, FTIR, X-ray and TGA analysis. Distribution studies on the exchanger were also carried out for several metal ions. Important quantitative separation of metal ions in binary mixtures included, Cu (II)-Pb (II), Cu (II)- Ni (II), Cu (II)-Co (II) and Cu (II)-Zn (II).

Keywords**—** Cation-Exchanger; IEC, pH Titration; Distribution Coefficient; Binary Separation.

I. INTRODUCTION

In ion-exchange reactions a reversible interchange of ions takes place between two compounds, one of which is the ion-exchanger which is insoluble in the medium, in which the exchange is carried out [1]. Ion-exchange materials developed for this purpose can be divided into two classes in terms of the base matrixes, that is, organic ion-exchangers and inorganic ion-exchangers [2]. Inorganic ion-exchangers are prepared due to their selectivity, temperature and nuclear radiation stability, for the the separation of radionuclides from aqueous nuclear wastes [3]. However ion-exchange material have gained popularity for being selective and less expensive as compared to other methods [4]. The literature reveals that several four component ion-exchangers are reported. The example includes tin (IV) tungstovanadophosphate [5], zirconicum (IV) tungstoiodophosphate [6], titanium (IV) tungstovanadophosphate [7].

The present work is concerned with stannic(IV) based four component ion-exchanger. Ion exchange capacity of the synthesized material is determined by two methods namely column method and pH titration method. Further characterization is also reported in this paper that includes determination of chemical stability, thermal stability and distribution studies. Characterization on the basis of instrumental analysis is also done with the help of FTIR, XRD and TGA techniques. This exchanger is found to possess extensive application in analytical and industrial chemistry.

II. EXPERIMENTAL

Chemicals and Reagents: Stannic chloride pentahydrate (CDH), sodium arsenate (S.D fine), sodium tungstate and oxalic acid (qualigens), were employed for the synthesis of the material. All other reagents were used of analytical grade.

Intrumentation: A digital pH meter (Model pH-110) were used for pH measurements. In equilibrium studies Tanco's electric rotary shaker was used for shaking the solutions to maintain equilibrium. Thermal studies were carried out by using Tanco's electric muffle furnace. For drying the samples NSW India a Oven was used. XRD and TGA were obtained from IIT Roorkee, where Philips analytical X-ray B.V. diffractometer, and thermogram was obtained with the help of Perkin elmer (Pyris Diamond) in alumina pan with a current of nitrogen.

Preparation of Ion-Exchanger Material: Different samples of stannic (IV) oxoarsenotungstate were prepared by adding 0.1M aqueous solution of stannic (IV) chloride to a mixture of 0.1M aqueous solution of sodium arsenate, sodium tungstate and oxalic acid solutions in different volume ratios with continuous stirring to obtain a precipitate and maintained the pH-1 by adding dilute HCl as shown in Table I. The resultant precipitate was allowed to stand by keeping it for 24 hours at room temperature and then filleted. The excess acid was removed by washing with demineralized water so as to obtain the material was cracked into small granules. The dried material was converted into the H^+ form by keeping it in molar HNO_3. The mixture was shaken intermittently and then kept for twenty four hours at room temperature. The products thus obtained were washed with demineralized water in several times and finally dried at $40\underline{+}1^{0}$C in an oven.

TABLE I. Synthesis of Stannic (IV) oxoarsenotungstate.

Sr. No.	**Mixing Ratios**				**pH**	**Appearance of Precipitate**	**IEC (meq/g)**
	S	O	A	T			
1	1	1	1	1	1	Off White ppt.	1.25
2	1	2	2	2	1	Off White ppt.	0.62
3	1	2	2	1	1	Off White ppt.	0.55
4	2	1	1	1	1	Off White ppt.	1.41
5	2	2	1	1	1	Off White ppt.	1.10
6	1	1	3	2	1	Off White ppt.	1.07
7	3	1	1	3	1	Off White ppt.	0.80

S = Stannic (IV) Chloride, O = Oxalic Acid, A = Sodium Arsenate, T= Sodium Tungstate

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III. CHARACTERIZATION

Ion-Exchange Capacity (IEC): The IEC of the material was determined by the column process (Table I). 500 mg of the exchanger was packed in a glass column and washed with DMW to remove any excess of acid that remained on the particles [8]. Molar sodium nitrate solution was passed slowly by adjusting the effluent rate at 0.5 ml/min. The effluent was collected and titrated against a standard NaOH solution. The ion- exchange capacity of the exchanger for different alkali and alkaline earth metal cations was also determined as shown in (Table II).

TABLE II. Ion-Exchange Capacity of Stannic (IV) oxoarsenotungstate for Different Metal Cations.

Sr. No.	Cation	Salt Used	Concentration of Salt Used	IEC (meq/g)	Hydrated Ionic Radii (A^0)
1	Li^+	LiCl	0.1 M	0.98	10.0
2	Na^+	NaCl	0.1 M	1.41	7.90
3	K^+	KBr	0.1 M	1.62	5.30
4	Mg^{2+}	$MgCl_2$	0.1 M	1.87	10.80
5	Ca^{2+}	$CaCl_2$	0.1 M	1.54	9.60
6	Ba^{2+}	$BaCl_2$	0.1 M	1.71	8.80

pH Titration: Topp and Pepper's method [9], was employed for pH titration. The pH titration of the exchanger in H^+ form was performed in NaCl-NaOH system at room temperature. Eleven equal portion of 500 mg each of the exchanger were placed in eleven 250 ml conical flasks separately and equimolar solution of alkali metal chloride and their hydroxide in different volume ratios, with the final volume being 50 ml to maintain constant ionic strength. The pH of all the solution was recorded after twenty four hours when equilibrium was attained. At equilibrium, pH was plotted against milli-equivalent of hydroxide ions added as shown in (Fig. 1).

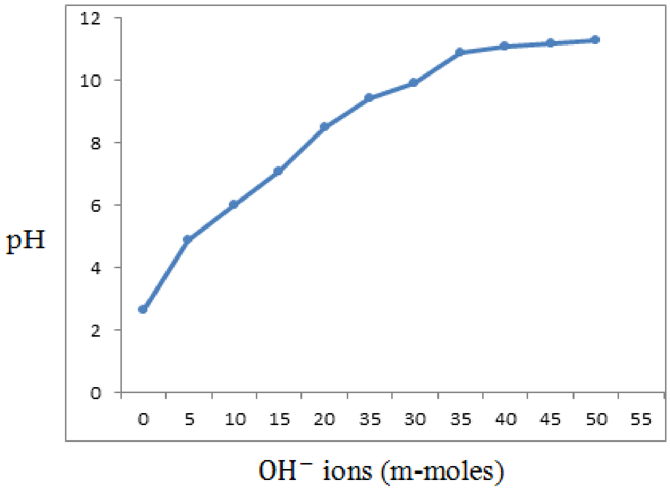

Fig. 3. pH Titration Curve of Stannic (IV) oxoarsenotungstate.

Chemical Stability: For determine the stability of the exchanger against different solvents, twelve equal amount (500 mg each) of the material were kept in 25 ml of different solutions at room temperature for twenty four hours, and then filtered. The residues thus obtained were dried in an electric oven at 40±1^0C, 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 results are summarized in (Table III).

TABLE III. Chemical Stability of Stannic (IV) oxoarsenotungstate.

Sr.No.	Solution	Percentage Weight Loss	Ion-Exchange Capacity
1	1 M HCl	1%	1.20
2	2 M HCl	2%	1.09
3	1 M HNO_3	0%	1.41
4	2 M HNO_3	0%	1.41
5	1 M H_2SO_4	3%	0.91
6	2 M H_2SO_4	6%	0.80
7	1 M CH_3COOH	2%	1.09
8	2 M CH_3COOH	3%	1.98
9	1 M HCOOH	4%	0.89
10	2 M HCOOH	8%	0.58
11	6 M KOH	Completely Dissolve	-----
12	6 M NaOH	Completely Dissolve	-----

Thermal Stability: To examine the effect of drying temperature of the material on the ion-exchange capacity was studied by heating stannic (IV) oxoarsenotungstate from 100 to 800 ^{0}C for 1h in a muffle furnace [10], and their weight losses were observed. The ion-exchange capacity was determined using standard NaOH solution. The colour of the exchanger is also found to be affected with the increase in temperature [11]. The results are given in (Table IV).

TABLE IV. Thermal Stability of Stannic (IV) oxoarsenotungstate.

Sr.No.	Drying Temperature (^{0}C)	Weight of Ion-Exchanger Before Heating (g)	Change in Colour	IEC (meq/g)
1	100 ^{0}C	0.50	Off white	1.21
2	200 ^{0}C	0.50	Off white	0.93
3	300 ^{0}C	0.50	Off white	0.82
4	400 ^{0}C	0.50	Light grey	0.70
5	500 ^{0}C	0.50	Light grey	0.58
6	600 ^{0}C	0.50	Grey	0.32
7	700 ^{0}C	0.50	Black	0.19
8	800 ^{0}C	0.50	Black	--

Distribution Behaviour: Selectivity of the synthesized ion-exchanger for various metal ions, distribution coefficient (kd) values for ten metal ions were determined by batch process [12]. In this process 0.1 M aqueous solutions of metal ions were equilibrated with the equal portions (500 mg each) of the dry exchanger separately. The equilibrium was attained by keeping the solutions overnight. The determination of metal ion concentration in each case was done titrimetrically (Complexometic, Titration) [13], with EDTA solution using suitable indicators. Kd values were calculated of these formula-

$$Kd = \frac{I - F}{F} \times \frac{V}{M}$$

Where I and F is the initial and final metal ion concentration, V is the volume of solution taken and M is the weight of the exchanger. The results are summarized in (table V).

TABLE V. Distribution Coefficient Stannic (IV) oxoarsenotungstate.

Sr.No.	Metal Ions	Form	Kd (mlg^{-1})
1	Ca^{2+}	Carbonate	7.31
2	Mg^{2+}	Acetate	11.18
3	Zn^{2+}	Acetate	10.14
4	Cu^{2+}	Acetate	37.12
5	Mn^{2+}	Acetate	7.82
6	Co^{2+}	Acetate	9.81
7	Ni^{2+}	Ammonium Sulphate	10.25
8	Pb^{2+}	Nitrate	7.89
9	Bi^{3+}	Nitrate	15.17
10	Cd^{2+}	Chloride	18.15

IR Analysis: For IR analysis of stannic(IV) oxoarsenotungstate obtained by Cary Agilent 630 FTIR which was available in Department of Chemistry C.C.S. University, Meerut. The IR obsorption, spectrum was recorded between 800 cm^{-1} and 3800 cm^{-1} as shown in (Fig. 2).

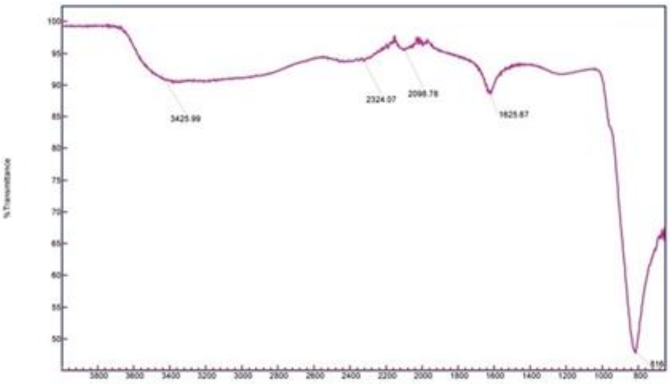

Fig. 2. IR Spectrum of Stannic (IV) oxoarsenotungstate.

X-ray Studies: For X-ray diffraction pattern of the exchanger in the H$^+$ form was obtained with help of Philips analytical X-ray B.V. diffractometer was available in Instrumentation centre, IIT Roorkee in Uttarakhand. The XRD pattern shows a number of peaks of sharp intensities as represented by the zx amorphous nature (Fig. 3).

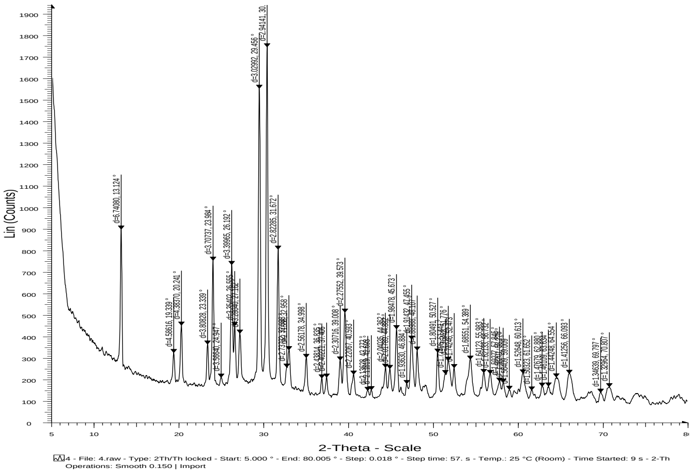

Fig. 3. XRD of Stannic (IV) oxoarsenotungstate.

TGA Curve: Thermo gravimetric analysis (TGA) of the cation-exchanger or in H$^+$ form was carried out at the rate of 10^{0}C/min under nitrogen atmosphere taking alumina as reference shows the loss in weight initially due to loss of water molecules. Further loss in weight is attributed to the loss of different components. The results are shown in (Fig. 4).

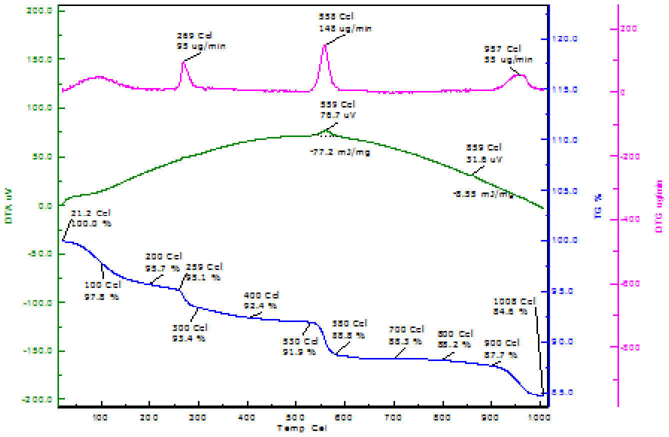

Fig. 4. TGA Curve of Stannic (IV) oxoarsenotungstate.

IV. APPLICATIONS

Binary Separation: Binary separation of those metal ions can be achieved for which the separation factor was greater than three. The result are shown in Table VI and VII. For binary separation of metal ions were achieved on a 0.6 cm diameter glass column using 500 mg of the material in H$^+$ form. The cation-exchanger was loaded after washed thoroughly with demineralized water. A metal ion mixture was poured on the top of the column. The flow rate of eluent was maintained at 5-6 drops/min and recycled at least three times [14]. The effluent was collected in containers, and then determined titrimetrically against EDTA solution.

TABLE VI. Separation Factor of Stannic (IV) oxoarsenotungstate.

Sr. No.	Separation Factor	$\alpha_B^A = \frac{Kd\ value\ of\ A}{Kd\ value\ of\ B}$	Value of Separation Factor
1	α_{Pb}^{Cu}	$\frac{37.12}{7.89}$	4.70
2	α_{Ni}^{Cu}	$\frac{37.12}{10.25}$	3.62
3	α_{Co}^{Cu}	$\frac{37.12}{9.81}$	3.78
4	α_{Zn}^{Cu}	$\frac{37.12}{10.14}$	3.66

Removal of Coloured Transition Metal Ions: In qualitatively determination of coloured metal ions, different definite volumes of the three solutions were loaded on the ion-exchanger packed in three different columns. The flow rate of 10 drops per minute was maintained. The solutions were passed three times through the ion-exchanger. The effluents of the three columns were collected in three different containers. The presence of the metal ions all the containers was

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confirmed by performing qualitative analysis as given in (Table VIII). All the qualitative tests were found to be negative.

TABLE VII. Binary Separation Achieved with the Help of Stannic (IV) oxoarsenotungstate.

Sr. No.	Metal Ion Pair	Amount Loaded (µg)	Amount Found (µg)	% Metal Ion Eluted	% Error	Total Eution Volume	Eluent Used
1	Cu (II) Pb (II)	1207 4641	1171 4430	97.17 95.45	-2.83 -4.55	40 ml 70 ml	0.02 M HNO_3 0.1 M HNO_3+0.1 M NH_4OH
2	Cu (II) Ni (II)	1207 1432	1209 1302	100.16 90.92	+0.16 -9.08	30 ml 50 ml	0.1 M $HClO_4$ 0.1 M CH_3 COOH
3	Cu (II) Co (II)	1207 1245	1012 1320	83.84 106.02	-16.16 +6.02	50 ml 60 ml	0.2 M HNO_3 0.2 M $HClO_4$
4	Cu (II) Zn (II)	1207 1770	1238 1650	102.56 93.22	+2.56 -6.78	30 ml 60 ml	0.1 M HCOOH 0.1 M HNO_3

TABLE VIII. Qualitative Tests for Transition Metal Ions for Stannic (IV) oxoarsenotungstate.

Sr.No.	Metal Ion	Colour of the Salt Solution Before Passing Through Exchanger	Colour of the Salt Solution After Passing Through Exchanger	Detection of Metal Ion in the Effluent
1	Ni (II)	Green	Colorless	Effluent NaOH Solution- No Precipitate Ni (II) Absent
2	Co (II)	Pink	Colorless	Effluent + Sodium Hydroxide Solution-No Precipitate Co (II) Absent
3	Cu (II)	Blue	Colorless	Effluent NaOH Solution- No Precipitate Cu (II) Absent

TABLE IX. Removal of Transition Metal Ions with the Help of Stannic (IV) oxoarsenotungstate.

Sr. No.	Metal Ion	Amount Loaded (µg)	Amount Found (µg)	% of Metal Ion Eluted	% Error	Eluent Used
1	Co (II)	1245	1180	94.77	- 5.23	1.0 M NH_4NO_3
2	Ni (II)	1432	1250	87.29	-12.71	0.1 M $HClO_4$
3	Cu (II)	1207	1207	100	-0.00	0.2 M HNO_3

V. RESULTS AND DISCUSSIONS

Various samples of stannic (IV) oxoarsenotungstate were synthesized in different volume ratios (Table I). Sample four was selected for detailed studies due to its better ion-exchange capacity. IEC for alkali and alkaline earth metal cation are shown in (Table II). It is evident from the table that the affinity sequence for metal ions is $K^+ > Na^+ > Li^+ > Ba^{2+} > Ca^{2+} > Mg^{2+}$. The sequence is in accordance with the hydrated ionic radii of the exchanging cations. Fig. 1, shows the pH titration curve of the stannic (IV) oxoarsenotungstate. The IEC was found to be 1.96meq/g. The pH titration curves revealed that the material behaves as strong cation-exchanger as indicated by a low pH 2.64 of the solution when no of OH^- ions were added to the system. Results showing the extent of dissolution of the material in different solution are given in (Table III). The material was found to be fairly stable in HCl, HNO_3 solutions and less stable in sodium hydroxide solution at high concentration. In organic acid like HCOOH and CH_3 COOH, the exchanger was found to be moderately stable.

Studies of heating effect upto 800 ^{0}C on colour, weight and IEC of exchanger were also observed. The results shows that IEC of the exchanger decreases with increases in temperature (Table IV).

Distribution behaviour of ten metal ions in demineralized water has been studied, and the value obtained for distribution coefficient is given in (Table V). The ion-exchanger shows the selectivity for Cu and Cd for which, the Kd values are 37.12, 18.15 mlg^{-1} respectively. The distribution coefficient for the metal ions follows the sequence Cu > Cd > Bi > Mg > Ni > Zn > Co > Pb > Mn > Ca.

IR spectrum of the synthesized ion-exchanger in H^+ form is shown in (Fig. 2). It shows a strong and broad band in the region 3800 cm^{-1} and 800 cm^{-1}. First band with a maximum peak at 3425.99 cm^{-1} is due to interstitial water molecules and OH groups. Another strong and sharp peaks at 2324.07 cm^{-1} indicates the presence of aqua (H-O-H) bending. It shows a peaks is 1625.67 cm^{-1} and 816 cm^{-1} which indicates the presence of arsenate and tungstate respectively. There last peak shows is due to metal oxide bond.

The X-ray diffraction pattern study of the material in H^+ form, shows some sharp peaks indicating its amorphous nature. The results are shown in (Fig. 3).

The TGA curve of stannic (IV) oxoarsenotungstate was studied (Fig. 4). The weight loss of the ion-exchanger upto 100 ^{0}C (2.2%) is due to removal of water molecules. Shows continuous loss in weight is observed from 200 ^{0}C to 530 ^{0}C and the corresponding weight loss is 35.3%. From 580 ^{0}C to 900 ^{0}C, the loss is very slow i.e. 11.2% at 580 ^{0}C, 11.7% at 700 ^{0}C and 11.8% at 800 ^{0}C, 12.3% at 900 ^{0}C. At 1008 ^{0}C a rapid in decline in weight (15.4%) is noticed. Finally the weight become constant and the residue contains the oxide only.

Selectivity on the basis of high Kd value and separation factors. The separation of the combination of Cu (II) – Pb (II), Cu (II) – Ni (II), Cu (II) –Co (II), Cu (II) – Zn (II) have been achieved on the column of these ion-exchanger. The results are shown in Table VII. The material is slight tailing which leads to their quite, sharp in achieving the separation. In binary separation of Cu–Pb amounts found of copper and lead shows that almost all the copper ions are eluted while 95.45% of lead ion eluted showing the percentage error of -4.45%. In Cu–Ni separation, the difference between loaded amounts and amounts found show that Ni is 90.92% eluted with -9.08% error and copper is eluted to 100.16% with + 0.16% error.

Similarly Cu–Co and Cu–Zn pairs, separation results are satisfactory as copper is removed 90%. These results can be compared with the previously reported binary separation results. Cu–Co and Cu–Zn separations achieved with the help of zirconium tungstate para-chlorophenol shows that it removes only, 92% copper metal ion. Our ion-exchanger is better than, according to the combination of Cu–Co and Cu–Zn. The removal is seen from 83.84% to 102.56% of copper.

The role of exchanger is found to be useful in decontamination of the chemicals. Detection of the metal ions (qualitative analysis) made it possible to decide the determination process. Quantitative determination of metal ions in a sample helped in knowing the amount of metal ion present which in turn was helpful to decide the exchange process. The observation table clearly indicates that ion-exchanger was found to be able the decontaminate 94.77%, 87.29% and 100% of cobalt, nickel and copper respectively.

VI. CONCLUSION

Newly synthesized stannic (IV) oxoarsenotungstate is a promising ion-exchanger, with a high ion-exchange capacity. The material possess selectivity for heavy metals such as Pb, Cd, Cu, Ni that are highly toxic to most of the organism. Therefore from all the results obtained we may conclude that use of their ion-exchanger is easy, effective and economical in the field of separation sciences.

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