



Synthesis, Characterization and Analytical Applications of Antimony(III) molybdoarsenate as a Cation Exchanger and Selective for Pb(II) and Cu(II) Ions

TEENA^{1*}, VANDANA SHARMA², KOSHAL K.T.³ and VIRENDRA KUMAR

¹Department of Chemistry, Chaudhary Charan Singh University, (U.P 250004), Meerut, India.

²Department of Environmental Sciences, Deen Dayal Upadhyaya College, University of Delhi (110078), India.

³Department of Chemistry, Meerut College, Meerut, (U.P 250004), India.

⁴Department of Chemistry, University of Allahabad, Allahabad, (U.P 211002), India.

*Corresponding author E-mail: teenaparakash15@gmail.com

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ABSTRACT

These three component inorganic ion-exchanger was synthesized under different condition. The most thermal and chemical properties of this material is prepared by intermixing solutions of sodium molybdate (0.1 M), sodium arsenate (0.1 M) and antimony(III) chloride (0.1 M) solution in different volume ratios at pH-1. The Ion-exchange capacity of all the samples was determined by column process. The selected sample was synthesized in bulk for detailed studies. Its ion-exchange capacity of synthesized material for Na⁺ has been found to be 2.30 meq/g. Characterization of the prepared material was done by different parameters like FTIR, TGA curve, X-ray diffraction, and other studies include pH titration, K_d values, thermal & chemical stabilities. The synthesized ion-exchanger has been demonstrated by achieved binary and water softening separations for different analytical practical uses.

Keywords: Cation-exchanger, pH titration, Distribution studies, Thermal and chemical stabilities, Binary separation, Hardness of water.

INTRODUCTION

Ion-exchange may be defined as reversible interchange of ions takes place between two phases is solid and liquid¹. Ion-exchange technology is most important versatile technology in the field of separation science. These techniques can be applied to both macro as well as micro analysis for the

routine separation. Thus separation is a important part of chemical analysis². Mostly synthetic ion-exchangers were inorganic materials. These were the synthetic zealites or permutites which were developed by Grans, and other workers for use in water softening process³. In recent years, various zeolites with completely regular crystal structure have been synthesized like zeolite A⁴.

Inorganic cation-exchanger have drawn the attention to their selectivity, temperature, thermal and chemical stabilities⁵. Synthesized a two component ion-exchanger antimony(III) silicate of the class of multivalent metal acid salt and its ion-exchange behaviour towards alkali and alkaline earth metal ions was determined by the column technique⁶. Similarly a large number of three component ion-exchangers like antimony(III) iodostannate⁷, titanium(IV) tungstoarsenate⁸, stannic(IV) molybdophosphate⁹ and zirconium(IV) selenomolybdate¹⁰, cerium(IV) iodotungstate¹¹, iron(III) tungstomolybdate¹²

In the present work is concerned with the new synthesized and characterized three component ion-exchanger. The ion-exchange capacity was determined by using column and pH titration method. Further characterization of the exchanger was done by chemical and thermal stabilities, FTIR, X-ray, and Kd values. The newly synthesized ion-exchanger

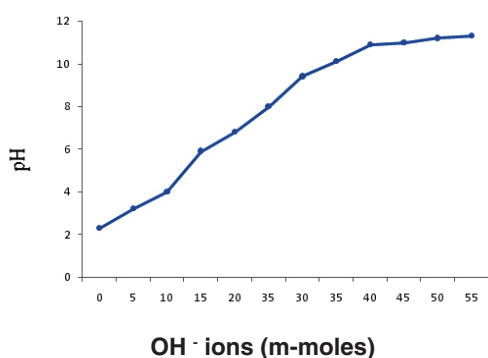


Fig. 1: pH titration curve of antimony(III) molybdoarsenate

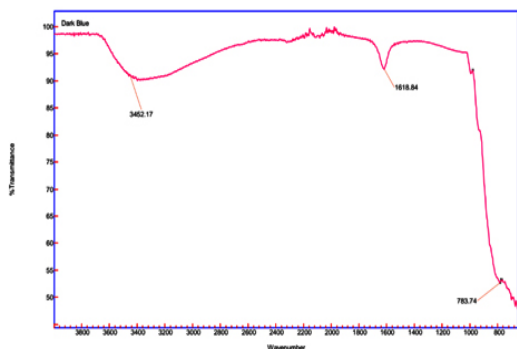


Fig. 2: IR spectrum of antimony(III) molybdoarsenate

is found to be possess extensive application in analytical and industrial chemistry. The important applications achieved with the help of antimony(III) molybdoarsenate are binary separation.

EXPERIMENTAL

Materials and Instrumentation

All chemicals and reagents were used for prepared material. A Digital Toshniwal pH Meter was used for pH measurement. Thermal and equilibrium studies were performed with the help of Tanco's Electric Rotary Shaker respectively. Samson S-300 D Electronic Balance was used for weighing. Philips Analytical X-ray B.V. Diffractometer and Cary Agilent 630 (ATR module) IR Spectrophotometer were used for XRD and FTIR respectively. All glass wares of borosil make are used throughout experiment research work.

Preparation of Ion-Exchanger Material

Three component ion-exchanger was prepared by mixing 0.1 M antimony(III) chloride aqueous solution gradually to adding an aqueous solution of sodium molybdate (0.1 M) and sodium arsenate(0.1 M) in different volume ratios to get various samples. The pH of resulting precipitates was maintained at 1.0 with the help of dil hydrochloric acid and allowed to stand for twenty four hours at room temperature. The precipitates was filtered, and washed with demineralized water. The material was dried at $40 \pm 1^\circ\text{C}$ in an oven. The dried material was broken into small granules by placing in demineralized water. The granules were converted into hydrogen form by keeping with M HNO₃ solution for twenty four hours at room temperature. The material was then washed with demineralized water to remove the excess acid and finally material dried at $40 \pm 1^\circ\text{C}$ in an electric oven. Prepared material are known as an exchanger. The results are shown in Table 1.

CHARACTERIZATION

Ion-Exchange Capacity

IEC of the different samples was determined by column, taken 0.50 g of the material in H⁺ form in a each column having glass wool support and washed them, with demineralized water. A molar solution of sodium nitrate was passed through the each column maintaining the flow rate at 8-10

drops/min. The effluents were carefully collected in 250 ml conical flask separately in each case. The H⁺ ions eluted from the material through column were titrimetrically determined with the help of standard NaOH solution.

The ion-exchange capacity of the material was also determined by monovalent and bivalent, alkali and alkaline earth metals as represented by Table 2.

pH Titration

pH titration was performed by the batch method using the method of, Topp and Pepper¹³. In this method the pH titration of the exchanger in H⁺ form was performed in NaCl-NaOH system. Eleven equal amount of 0.50 g of the exchanger in each were placed in eleven 250 ml conical flasks separately by the addition of equimolar solutions of NaCl and NaOH in different volume ratios, the final volume of the solution was kept 50 ml so as to maintain the

ionic strength constant. Then the intermittent shaking of the mixture was kept at room temperature. The pH titration curve of the exchanger is shown in Figure 1.

Thermal Stability

To determine the thermal stability of the exchanger was evaluated by heating it at different temperatures upto 700°C in a muffle furnace for one hour, and then cooled to room temperature in a desiccators. The loss of weight and change in colour of the ion-exchanger was observed in each case and ion-exchange capacity was determined by column method. The results are given in Table 3.

Chemical Analysis

To examine the chemical stability of the exchanger was assessed in different mineral acids such as H₂SO₄, HNO₃ and HCl bases such as KOH and NaOH, organic acids such as CH₃COOH, HCOOH, 0.50 g of the exchanger was taken in 50

Table 1: Synthesis of antimony(III) molybdoarsenate

Sl.No.	Molar Conc. (M)			Mixing Ratios	pH	Appearance of Precipitate	IEC (meq/g)
	Sb ³⁺	MoO ₄ ²⁻	AsO ₃ ²⁻				
1	0.1	0.1	0.1	1:1:1	1	Mid cream ppt.	0.48
2	0.1	0.1	0.1	1:2:2	1	Mid cream ppt.	0.98
3	0.1	0.1	0.1	1:2:1	1	Sky blue ppt.	1.69
4	0.1	0.1	0.1	2:1:1	1	Sky blue ppt.	1.89
5	0.1	0.1	0.1	2:2:1	1	Sky blue ppt.	1.99
6	0.1	0.1	0.1	1:1:3	1	Dark blue ppt.	1.12
7	0.1	0.1	0.1	1:3:1	1	Light blue ppt.	0.79
8	0.1	0.1	0.1	3:1:1	1	Light yellow ppt.	1.02
9	0.1	0.1	0.1	2:1:3	1	Dark blue ppt.	2.30
10	0.1	0.1	0.1	3:2:1	1	Light yellow ppt.	1.12

Table 2: Ion-exchange capacity of antimony(III) molybdoarsenate for different metal cations

Sl. No.	Cation	Salt Used	Concentration of Salt Used	I.E.C. (meq/g)	Hydrated Ionic Radii (A ⁰)
1	Li ⁺	LiCl	0.1 M	2.10	10.0
2	Na ⁺	NaCl	0.1 M	2.30	7.9
3	K ⁺	KBr	0.1 M	2.47	5.3
4	Mg ²⁺	MgCl ₂	0.1 M	1.76	10.80
5	Ca ²⁺	CaCl ₂	0.1 M	1.89	9.60
6	Ba ²⁺	BaCl ₂	0.1 M	2.05	8.80

ml of several molar solutions and kept for twenty four hours at room temperature and then filtered and finally dried at $40 \pm 1^\circ\text{C}$ in an oven. Now the dry material loss of weight of all samples was observed and ion-exchange capacities were determined by column method as represented in Table 4.

Distribution Studies

Distribution coefficient for several metal ions in demineralized water was carried out by the batch process¹⁴. In this process, 0.50 g portion of the exchanger in H^+ form was equilibrated with 25 ml of 0.1 M solutions of different metal ions. The mixture was shaken for three hours with the help of rotary shaker and then to attain complete equilibrium. The determination of metal ions present in the solution was titrated against the standard solution of EDTA. K_d values were calculated using the formula

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

Where I is the initial volume of EDTA solution, F is the final volume of EDTA solution after equilibrated, V is the volume of the metal ion solution (ml) and W is the weight of the ion-exchanger in gram¹⁵. The results are summarized in Table 5.

FTIR and X-ray Diffraction

IR studies of the material were recorded between 3800 cm^{-1} and 800 cm^{-1} . The spectrum shows a broad bands in the 3452.17 cm^{-1} region, characteristics of the O-H stretching and bending mode. Finally the spectrum also shows strong and weak bands at 1618.84 cm^{-1} and 783.74 cm^{-1} , respectively which indicates the presence of arsenate

and molybdate. The band at 783.74 cm^{-1} shows the presence of metal oxide bond. The spectrum are shown in Figure 2. The X-ray diffraction pattern of the exchanger are given in Figure 3. Data shows an amorphous nature with weak peaks.

TGA Curve

The thermogram of antimony(III) molybdoarsenate in H^+ form was get it done at Instrumentation centre, IIT Roorkee at a rate of $10^\circ\text{C}/\text{min}$. in nitrogen atmosphere from room temperature. The results are shown in Figure 4.

Separations Achieved

The values of separation factor for different metal ions pairs obtained antimony(III) molybdoarsenate were greater than three and their values are given in Table 6.

Binary Separation of Metal Ions

The separation factors are the guiding measure for the separation. Binary separation of metal ions were achieved are given in Table 7. For binary separations, 0.50 g of the exchanger in H^+ form was packed in glass column. The column was washed with demineralized water and then metal ion mixture was poured in column separately. The absorbed metal ions were eluted with appropriate eluents one by one. The flow rate of the effluent was maintained at $1 \text{ ml}/\text{min}$ through the elution process¹⁶. The effluents were collected separately conical flask and metal ion concentration were determined (Complexometric Titration) against disodium EDTA salt solution using suitable indicators.

Table 3: Thermal stability of antimony(III) molybdoarsenate

Sl.No.	Drying Temperature ($^\circ\text{C}$)	Weight of Ion-Exchanger Before Heating (g)	Change in Colour	IEC (meq/g)
1	100°C	0.50	Dark blue	1.90
2	200°C	0.50	Dark blue	1.20
3	300°C	0.50	Light grey	0.81
4	400°C	0.50	Dark grey	0.41
5	500°C	0.50	Dusky black	0.22
6	600°C	0.50	Black	0.10
7	700°C	0.50	Black	—

Water Softening

Hardness causing Ca^{2+} and Mg^{2+} were also removed with help of the synthesized ion-exchanger. Column method was used for the removal of ions. The hardness of the water samples was determined by complexometric titration method in which, Erichrome Black-T was used as an indicator. Hardness causing Ca^{2+} and Mg^{2+} loaded in the column were eluted using 0.01 M HClO_4 and 1.0 M HNO_3 as eluents respectively. The results are summarised in Table 8.

Table 4: Chemical stability of antimony(III) molybdoarsenate

Sl.No.	Solution	Percentage Weight Loss	Ion-Exchange Capacity
1	1M HCl	2	1.50
2	2M HCl	4	1.01
3	1M HNO_3	0	2.30
4	2M HNO_3	0	2.28
5	1M H_2SO_4	6	1.00
6	2M H_2SO_4	12	0.55
7	1M CH_3COOH	6	1.10
8	2M CH_3COOH	12	0.72
9	1M HCOOH	8	0.51
10	2M HCOOH	16	0.26
11	2M KOH	Completely Dissolve	—
12	2M NaOH	Completely Dissolve	—

Table 5: Distribution coefficient studies of antimony(III) molybdoarsenate

Sl.No.	Metal Ions	Form	Kd (mlg^{-1})
1	Mg(II)	Acetate	9.98
2	Ca(II)	Carbonate	10.24
3	Mn(II)	Acetate	7.90
4	Zn(II)	Acetate	7.79
5	Co(II)	Acetate	7.12
6	Cu(II)	Acetate	12.42
7	Cd(II)	Chloride	7.89
8	Ni(II)	sulphate	32.14
9	Pb(II)	Nitrate	11.20
10	Bi(III)	Nitrate	7.03

RESULTS AND DISCUSSIONS

Different samples of the material in various volume ratios have been synthesized (shown in Table 1). One of the sample was selected for detailed studies. The high ion-exchange capacities for mono and divalent metal ions are shown in Table 2. It is evident that the affinity sequence for monovalent metal ions is $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ and for divalent ions is $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. The effect of charge and size of the ion on the ion-exchange capacities show that exchanging ion takes place in the hydrated form. The metal ions with smaller hydrated radii easily enter the pores of exchanger, resulting in higher adsorption¹⁷. The pH titration curve was carried out under equilibrium stage for NaCl-NaOH system. The curve was plotted between pH values and OH^- ions concentration. The results are shown in Figure 1.

The heating effect on the weight and ion-exchange capacity at various temperatures upto 700°C was carried out. Data shows that the ion-exchange capacity decrease with increase in temperature (Table 3). Antimony(III) molybdoarsenate are less stable in lower concentration of HCl, H_2SO_4 and CH_3COOH , HCOOH. The ion-exchanger was completely dissolve in 2 M KOH and 2 M NaOH solution (Table 4).

IR spectrum was performed at room temperature used by KBr disc method. The results are shown in Figure 2.

X-ray diffraction pattern of antimony(III) molybdoarsenate is amorphous nature, which indicate weak peaks with sharp intensities (Figure 3). Thermogram of prepared material recorded in Figure 4. The water molecule are lost upto 100°C (4.6%) as indicated by the first peak of the curve. Further loss in weight is observed from 400°C to 500°C and the corresponding weight loss in 24.6%. From 500°C to 900°C , the loss is very slow. i.e. 13.7% at 600°C , 13.6% at 700°C , 17.5% at 800°C & 27.5% at 900°C . At 1008°C a rapid decline in weight (51.5%) is noticed.

Distribution behaviour indicate that the exchanger is selective for Ni(II), Cu(II), Pb(II), Ca(II), in compare to another metal ions. Solvent are used in binary separation and water softening

0.1 M HNO₃, 0.1 M HNO₃, 0.1 M H₃PO₄, 1 M HClO₄, 0.1 M HNO₃+0.1 M NH₄NO₃ it can be used for the quantitative analysis trace metal ion in environmental purpose. The results are shown in Table 7. Binary separation of Ni-Cd, amounts found of nickel and cadmium shows that almost all the nickel metal are eluted while 100% of cadmium ions are eluted

showing the percentage error of 0.06%. Similarly Ni-Pb, Ni-Mn and Ni-Mg pairs separation results are satisfactory as nickel is removed 95-100%. These results can be compared with the previously reported binary separation results. Ni-Mg separation achieved with the help of stannic(IV) antimonate¹⁸ and tin(IV) tungstate¹⁹. The recovery ranged from 98-100% with

Table 6: Separation factor of antimony(III) molybdoarsenate

Sl. No.	Separation Factor	$\alpha_B^A = \frac{Kd \text{ value of } A}{Kd \text{ value of } B}$	Value of Separation Factor
1	α_{Ca}^{Ni}	32.14/7.89	4.073
2	α_{Pb}^{Ni}	32.14/11.20	2.869
3	α_{Mn}^{Ni}	32.14/7.90	4.068
4	α_{Mg}^{Ni}	32.14/9.98	3.220

Table 7: Binary separation achieved with the help of antimony(III) molybdoarsenate

Sl. No.	Metal Ion Pair	Amount Loaded (µg)	Amount Found (µg)	% Metal Ion Eluted	% Error	Total Elution Volume	Eluent Used
1	Ni(II)	9390	9180	97.76	-2.24	40 ml	0.001 M HNO ₃
	Cd(II)	1624	1625	100.06	0.06	50 ml	0.1 M HNO ₃ +0.5 M NH ₄ OH
2	Ni(II)	9390	9390	95.95	-5.15	50 ml	0.1 M HClO ₄
	Pb(II)	2239	1920	85.75	-5.25	40 ml	0.1 M HNO ₃
3	Ni(II)	9390	8990	95.74	-5.26	50 ml	1 M NH ₄ Cl+0.1 M HCl
	Mn(II)	1337	1223	91.47	-9.53	30 ml	0.1 M HCl
4	Ni(II)	9390	9460	100.75	0.75	80 ml	1.0 M HNO ₃
	Mg(II)	4861	4770	98.12	-2.88	70 ml	0.4 M NH ₄ NO ₃

Table 8: Removal of Ca²⁺ and Mg²⁺ with the help of antimony(III) molybdoarsenate

Sl.No.	Metal Ion Pair	Amount Loaded (µg)	Amount Found (µg)	% Metal Ion Eluted	% Error	Total Elution Volume	Eluent Used
1	Mg ²⁺	4861	4800	98.74	-2.26	50 ml	1.0 M HNO ₃
2	Ca ²⁺	5743	5741	99.96	-1.04	50 ml	0.01 M HClO ₄

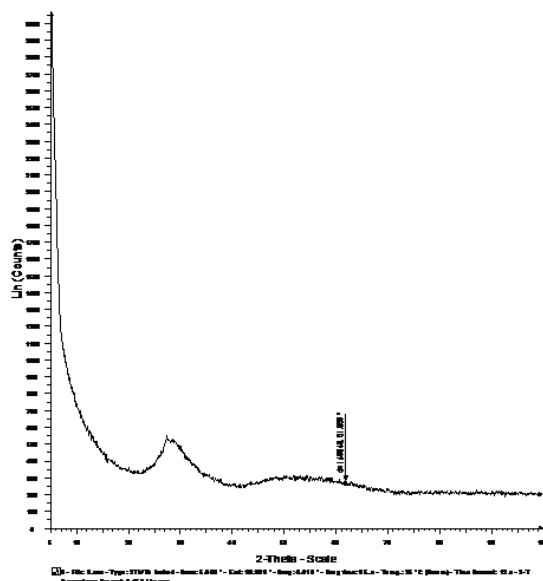


Fig. 3: XRD of antimony(III) molybdoarsenate

variation of 2% for repetitive determinations.

Water softening results obtained for antimony(III) molybdoarsenate revealed that the Ca^{2+} and Mg^{2+} can be removed to a great extent i.e. 99% and 98.74% respectively with the help of these exchanger. The results are shown in Table 8.

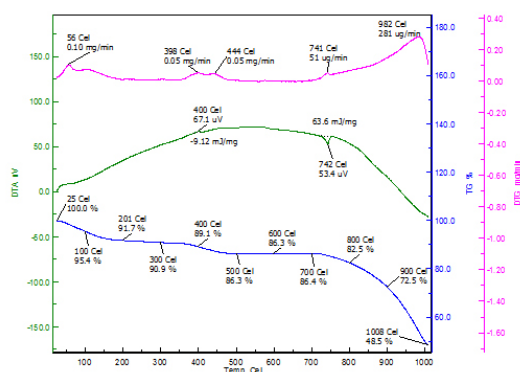


Fig. 4: TGA curve of antimony(III) molybdoarsenate

CONCLUSION

Newly, synthesized cation-exchanger are now the established material in analytical chemistry useful in separation technique. Antimony(III) molybdoarsenate is good ion-exchange capacity and is stable up to a fairly high temperature, and fairly stable in different acidic, basic and organic media. these ion-exchanger possesses selectivity for trace metals such as, Pb, Cd, Ni, Co, Cu. Synthetic ion-exchanger are also employed for the binary separation of heavy metals present in aqueous solution.

REFERENCES

1. Subhash Chand, Seema, Teena and Manju, *International Transactions in Applied Sciences*, **2010**, 2 (1), 181-190
2. Bhawna A., Shah, Ajay V., Shah and Pathik M., Shah, *Iranian Polymer Journal*, **2000**, 15 (10), 809-819.
3. Virendra Kumar, Shuka I.C., Yadav O.P., *J. Indian Chem. Soci.*, **2015**, 91, 825-829.
4. Ismail A. A., Mohamed R.M., Ibrahim I.A., Kini G., and Koopman B., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2010**, 366(1-3), 80-87.
5. Syed Ashfaq Nabi, Amjad M.T., Khan, *Indian Journal of Chemistry*, **2005**, 44(A), 1383-1387.
6. Reetha C, Aravindakshan and Janardanan C, *Indian Journal of Chemical*, **2002**, 41(A), 1438-1440.
7. Subhash Chand, Teena, Manju, *International Transactions in Applied Sciences*, **2013**, 5 (4), 467-478.
8. Varshney K.G., Agarwal K, Agarwal S, Saxena V, Khan A.R., *Colloids and Surface*, **1988**, 29, 175.
9. Qureshi M., Shakeel N A., Rizvi S N A. , Gupta A P., *Journal of Indian Chemical Society*, **1987**, 64, 15.
10. Gupta A P, Verma G L., Saiqa Ikram, *Reactive and Functional Polymers*, **2000**, 43, 33-41.
11. Dhara S., Sarkar S., Basu S., Chattopadhyay P., **2009**, 67 (4), 530-534.
12. Geetha, Janardhan C., *Indian Journal of Chemical Technology*, **2006**, 13, 185-188.
13. Topp N E. and Pepper KW., *Journal Chemical*

- society*,**1949**,3299.
14. Qureshi M, Varshney K G., and Israeli A H J., *Chromatography*,**1972**, 50,141.
15. Virendra Kumar, Shukla I.C., *Asian Journal of Chemistry*,**2017**, 29, 559-564.
16. Teena, Subhash Chand and Sonia, *International Journal of Basic and Applied Chemical Sciences* **2015**, 5 (2), 29-39.
17. Nabi S A, Usmaris and Rahman N., *Ann. Chim. Fr.***1996**, 21,521.
18. Aditya K. Mishra, *Journal of Chemical Technology*,**2000**, 132-136.
19. Alpana H. Parikh, Uma V. Chudasama, *Indian Journal of Chemistry*,**2003**,42, 559-563.