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Synthesis, Characterization and Analytical Applications of A New Ion Exchange Material Based on Antimony(III)

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Antimony based inorganic cation exchanger [antimony(III) molybdosilicate] has been synthesized. It has been characterized using XRD, I.R., TGA studies in addition to its ion exchange capacity, pH titration, chemical stability, thermal stability and distribution behaviour. The ion exchange capacity of the synthesized ion exchanger in H^+ form is found to be satisfactory. Ion exchange capacity has also been determined for various metal ions such as K^+, Mg^{2+}, *etc.*, pH titration method was also used for the determination of ion exchange capacity. K_d values have also been determined for ten different metal ions. The exchanger is found to be selective for Pb^{2+}. Ion exchanger column was used for binary separation and water softening.

Key Words: Ion exchanger, Ion exchange capacity, Thermal studies, Chemical stability, Distribution behaviour, Selectivity, Binary separation, Water softening.

INTRODUCTION

Inorganic ion exchangers are in general superior to organic exchangers in some aspects as they are resistance towards high ionizing radiations[1,2] and can be used at elevated temperatures without being there any danger of decomposition. Moreover, they often exhibit specificity towards certain metal ions. It is for these reasons that there has been a revolutionary growth in the field of synthetic ion exchangers. Some synthetic inorganic ion exchangers are: iron(III) antimonosilicate[3], zirconium iodooxalate[4], antimony(III) tungstovanadate[5], zirconium(IV) sulphosalicylate[6], titanium molybdophosphate[7], zirconium(IV) tungstomolybdate[8], zirconium(IV) iodotungstate[9], stannic silicomolybdate[10], zeolite $A(SiO_2:Al_2O_3:H_2O:Na_2O)$[11] zirconium(IV) selenomolyb-date[12] and zirconium(IV) antimonotungstate[13]. Introduction of polymeric species into an inorganic ion exchanger may greatly enhance its mechanical strength, making it potentially more useful in industrial and environmental applications. Some novel ion exchange materials based on polymeric species are polystyrene cerium(IV) phosphate[14], acrylamide cerium(IV) phosphate[15] and polyaniline Sn(IV) tungstoarsenate[16]. Both antimony(III) molybdate[17] and antimony(III) silicate[18] are well known inorganic ion exchangers. In this paper we have reported the synthesis, characterization and ion exchange behaviour of a new three component inorganic ion exchanger based on antimony(III).

EXPERIMENTAL

Antimony trichloride, sodium molybdate and sodium metasilicate were Qualigens (India) products. All other reagents and chemicals used were also of analytical grade.

Synthesis: Eight samples or matrices were precipitated by adding a mixture of 0.1 M sodium molybdate and 0.1 M sodium metasilicate solution to 0.1 M antimony trichloride solution with continuous stirring in different volume ratios (Table-1). The desired pH was adjusted by adding dilute HCl. The precipitates were aged in the mother liquors for 24 h at room temperature. The precipitates of different eight samples were filtered. After filtration continuous washing of all the samples was done to remove excess acid, with distilled water. pH of the effluents was checked with the help of pH paper. When the effluent become neutral, then precipitates were assumed to be free from excess acid. Now these eight different samples were kept in an oven (NSW India's) at 40 ± 1 ℃ for drying. After more than 24 h, precipitates become dry and ready for further treatment *i.e.* granulization. The colour of the precipitates were recorded (Table-1). For granulization the materials were cracked when they were immersed in hot water. Generation of granules into the H^+ form was done by treating them with molar HNO_3 solution.

Determination of ion exchange capacity

Column method : 0.50 g (dry mass) of antimony(III) molybdosilicate in H^+ form was packed in glass column having

a glass wool support at the base. 1 M $NaNO_3$ solution was passed through the column (Table-2).

TABLE-1

Sample No.	Mixing volume ratio			pH value	*Appearance of precipitate	I.E.C. (meq/g)
	AC	SM	SMS			
AMS-I	2	1	1	0-1	Dusky green	0.132
AMS-II	2	2	1	0-1	Dusky green	0.220
AMS-III	2	1	2	0-1	Dusky green	0.220
AMS-IV	3	1	1	0-1	Dusky green	0.154
AMS-V	3	1	3	0-1	Dusky green	0.220
AMS-VI	3	3	1	0-1	Dusky green	0.264
AMS-VII	1	3	3	0-1	Dusky green	0.220
AMS-VIII	1	2	2	0-1	Dusky green	0.733

AMS-antimony(III) molybdosilicate; AC-antimony trichloride; SM-sodium molybdate, SMS-sodium metasilicate; *Colour of precipitate after drying them at 40 ± 1 ºC

TABLE – 2
I.E.C. OF ANTIMONY(III) MOLYBDOSILICATE FOR VARIOUS CATIONS

Cations	Salt of cation	Solution concentration	Hydrated radii (A⁰)	IEC (meq/g)
Na^+	$NaNO_3$	0.1M	7.90	0.74
Li^+	LiCl	0.1M	10.0	0.65
Na^+	NaCl	0.1M	7.90	0.72
K^+	KBr	0.1M	5.30	0.75
Mg^{2+}	$MgCl_2$	0.1M	10.80	0.41
Ca^{2+}	$CaCl_2$	0.1M	9.60	0.48
Ba^{2+}	$BaCl_2$	0.1M	8.80	0.51

I.E.C. : Ion exchange capacity

pH titration method: Toshniwal research pH meter' (model pH-110) was used for equilibrium studies. Ion exchange capacity of the exchanger can be determined by this process also. In this method 0.5 g of the exchanger was treated with 50 mL of the NaCl-NaOH solution by Topp and Pepper[19] method (Fig. 1).
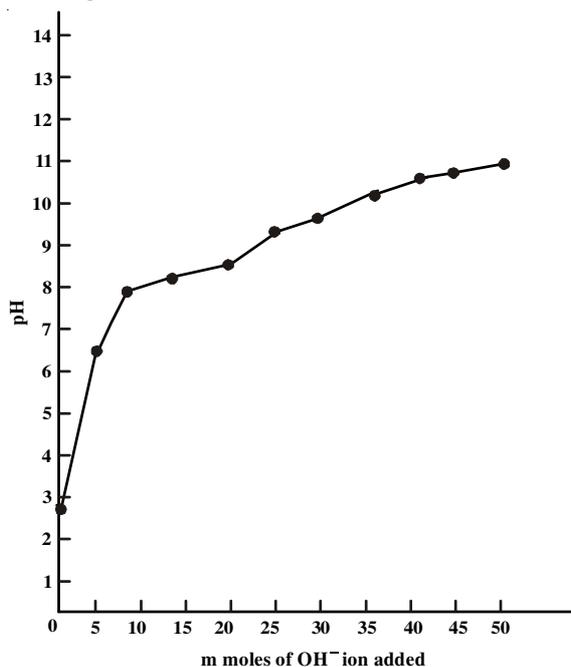
Fig. 1. pH titration

Thermal treatment: Heating effect on weight and ion exchange capacity of the ion exchanger was studied using a Toshniwal's electric muffle furnace in which a temperature upto 900 ºC can be maintained. For thermal stability seven equal parts of 0.50 g each of the exchanger were heated in different crucibles for 1 h at different temperatures from 50 to 700 ºC in a muffle furnace. The cooled crucibles were weighed to find the weight loss. Ion exchange capacity of all the samples was also determined by the usual column method using 1 M $NaNO_3$ (Table-3).

TABLE-3
THERMAL STABILITY

Sample no.	Temp (ºC)	WBH (g)	WAH (g)	LIW (g)	CAH	I.E.C. (meq/g)
AMS	50	0.50	0.50	0.0	Dusky green	0.730
AMS	100	0.50	0.50	0.0	Dusky green	0.730
AMS	200	0.50	0.49	0.01	Light green	0.584
AMS	300	0.50	0.48	0.02	Blackish green	0.280
AMS	400	0.50	0.47	0.03	Blackish green	0.219
AMS	500	0.50	0.45	0.05	Black	0.219
AMS	600	0.50	0.38	0.12	Black	0.120
AMS	700	0.50	0.30	0.20	Black	0.120

WBH–weight before heating, WAH- weight after heating, LIW–loss in weight, CAH– colour after heating, I.E.C.–ion exchange capacity; AMS – antimony(III) molybdosilicate

Chemical stability: To see the effect on ion exchange capacity of the exchanger in different chemical solutions of different concentrations, the study was done. Tanco's electric rotary shaker' was used for shaking the solutions. The extent of dissolution of the material in different mineral acids, organic acids and bases was recorded. The ion exchange capacity of remaining material was determined by usual column method (Table-4).

TABLE-4
CHEMICAL STABILITY

Solution	Weight before treatment (g)	Weight after treatment (g)	I.E.C. (meq/g)
DMW	0.50	0.500	0.73
1M HCl	0.50	0.280	0.10
2M HCl	0.50	0.217	0.06
1M HNO_3	0.50	0.350	0.18
2M HNO_3	0.50	0.304	0.14
1M H_2SO_4	0.50	0.260	0.12
2M H_2SO_4	0.50	0.170	0.08
2M CH_3COOH	0.50	0.260	0.12
2M HCOOH	0.50	0.217	0.10
2M NaOH	0.50	Dissolve completely	-
2M KOH	0.50	Dissolve completely	-

I.E.C.- ion exchange capacity

Distribution studies: Distribution studies were carried out for ten metal ions by batch process[20]. The distribution coefficient (K_d) values were calculated for metal ions using the following equation:

$$K_d = \frac{I - FA}{FW}$$

where, I-burette reading for the metal ion solutions before treatment with ion exchanger; F-burette reading for the metal ion

solutions after treatment with ion exchanger; A-volume of metal ion solution taken; W-weight of the ion exchanger (Table-5).

TABLE-5
K_d VALUES OF METAL IONS ON ANTIMONY(III)
MOLYBDOSILICATE IN DEMINERALIZED WATER

Metal ion	Taken as	K_d (mL/g)
Mg(II)	Acetate	1.134
Zn(II)	Acetate	10.240
Cu(II)	Acetate	5.590
Mn(II)	Acetate	3.262
Co(II)	Acetate	11.519
Ni(II)	Ammonium sulphate	16.519
Pb(II)	Nitrate	21.300
Bi(II)	Nitrate	8.900
Cd(II)	Chloride	7.010
Ca(II)	Carbonate	0.890

XRD: The X-ray diffraction pattern of the exchanger was also obtained from the Instrumentation Centre, IIT Roorkee where Philips Analytical X-ray B.V. diffractometer was available. The diffraction pattern is exhibited in Fig. 2.
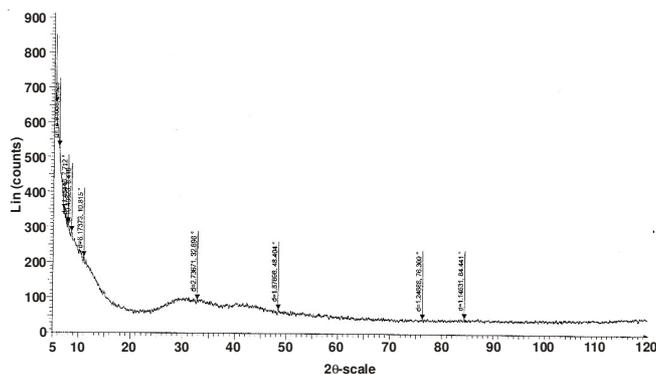
Fig. 2. XRD pattern of the exchanger

FTIR study: FTIR spectrum of the sample was obtained from Instrumentation Centre, IIT Roorkee where thermonicolet IR spectrophotometer was available. KBr disc method was used to get the spectrum. The IR absorption spectrum was recorded between 400 and 4000 cm^{-1} (Fig. 3).
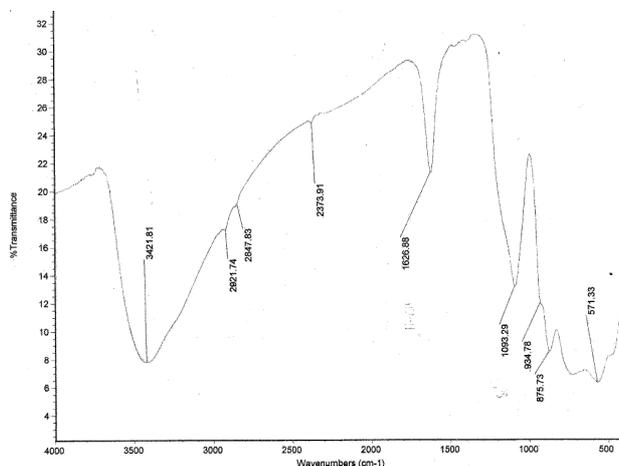
Fig. 3. FTIR spectruym

TGA curve: The TGA curve of antimony(III) molybdo-silicate was studied (Fig. 4). The curve shows the weight loss from 0 to 800 ºC.
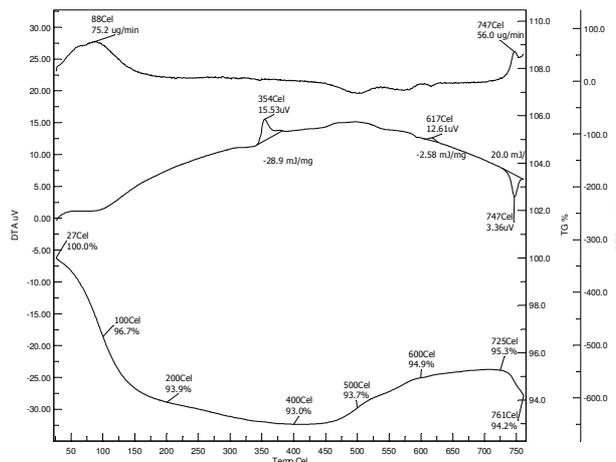
Fig. 4. TGA curve of antimony(III) molybdosilicate

Scanning electron microscopy: Electron micrographs were recorded for antimony(III) molybdosilicate. Results are obtained from Instrumentation Centre, IIT Roorkee. The details are shown in the SEM photographs (Fig. 5).
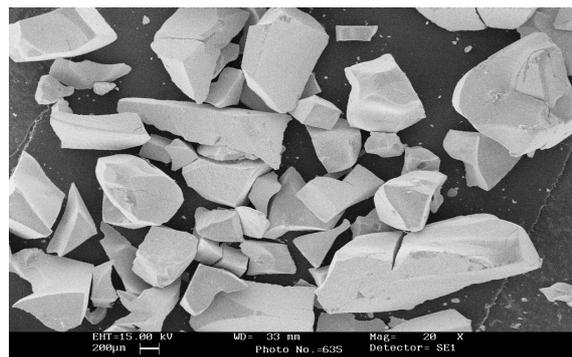
Fig. 5. SEM of antimony(III) molybdosilicate

Binary separation: In the present work binary separations by column method have been done. For separation studies of binary mixture, 0.50 g of the exchanger in H$^+$ from was taken in a glass column (0.6 cm diameter). The column was washed with about 20 mL demineralized water and then a mixture of metal ions was introduced in to the column for exchange. The exchanged metal ions were then eluted with appropriate eluents. The effluents were collected and metal ions contents were determined titrimetrically against EDTA titration (Table-6).

Removal of hardness causing metal ions: For removal studies of hardness causing metal ions, 0.50 g of the exchanger in H$^+$ form was taken in a glass column. The column was washed with some demineralized water and then solution of metal ion was introduced in to the column for exchange. The flow rate of the eluent was maintained at 8-10 drops per min throughout the elution process and recycled three times. The exchanged metal ions were then eluted with appropriate eluent. The flow rate of the effluent was maintained at 1 mL/min throughout the elution process. The effluent was collected and metal ion content was determined titrimetrically against EDTA solution (Table-7).

TABLE-6
SEPARATION OF METAL IONS ACHIEVED ON ANTIMONY(III) MOLYBDOSILICATE COLUMN

Sample	Separation achieved	Metal ions (µg)		Error (%)	Fluent used	Volume of fluent used (mL)
		Loaded	Recovered			
1	Pb	1927	1907.73	-1.0	1 MHNO$_3$	40
	Mg	40	38.80	-3.0	0.1 MHClO$_4$	50
2	Mg	40	39.00	-2.5	0.4 MNH$_4$NO$_3$	70
	Cd	1028	1026.00	-0.20	0.25 MHNO$_3$	50
3	Mg	40	38.50	-3.75	0.4 MNH$_4$NO$_3$	70
	Ni	1600	1596	-0.25	IMHNO$_3$	80

TABLE-7
REMOVAL OF HARDNESS CAUSING METAL IONS ON
ANTIMONY(III) MOLYBDOSILICATE

Sample	Metal ion	Amount loaded (µg)	Amount found (µg)	Error (%)	Fluent used
1	Mg^{2+}	40	39.6	-1.0	0.01 M HClO$_4$
2	Ca^{2+}	24	24.0	-0.0	1.0 M HNO$_3$

RESULTS AND DISCUSSION

Antimony(III) molybdosilicate obtained as a dusky green amorphous powder was found to be stable in water, quite soluble in 2 M HCl, 2 M HNO$_3$, 2 M H$_2$SO$_4$, 2 M CH$_3$COOH, 2 M HCOOH and fairly soluble in 2 M NaOH and 2 M KOH. The maximum capacity for Na$^+$ ion was found to be 0.72 meq/g. For the alkali and alkaline earth metal ions, the sequence shown by the exchanger is as follows: K$^+$ > Na$^+$ > Li$^+$ and Ba^{2+} > Ca^{2+} > Mg^{2+} respectively. The trend in ion exchange capacity confirms that the ion exchange takes place with the hydrated form of the ions.

The pH titration curve (Fig. 1) was obtained under equilibrium conditions for NaOH-NaCl system. It appears to be strong cation exchanger as indicated by a low pH (2.49) of the solution when no OH$^-$ ion were added.

The study of thermal effect on ion exchange capacity of antimony(III) molybdosilicate shows that the ion exchange capacity decreases with increase in temperature, although the sample retains a small exchange capacity 0.12 meq/g even at 700 ºC.

In the FTIR spectrum broad bands in the region of 3600-2800 cm^{-1} and a sharp peak at 1626 cm^{-1} indicate the O-H stretching vibration of interstitial water[21] and 3421 cm^{-1} bending mode respectively. Frequencies in the region of 900-400 cm^{-1} are due to the Mo-O stretching vibration mode[22]. The band at 1080 cm^{-1} and two peaks at 934 and 1093 cm^{-1} are characteristics of silicates. The spectrum had a intense band at 571 cm^{-1} that shows the presence of Sb-O group.

X-ray diffraction pattern of antimony(III) molybdosilicate does not show sharp peak. XRD and SEM revealed the fact that the exchanger in H$^+$ form is amorphous.

The thermogram of the antimony(III) molybdosilicate is shown in Fig. 4. It shows 3.3 % loss of weight at 100 ºC, which may be attributed to the loss of external water molecule from the exchanger. From 100 to 200 ºC, 2.8 % loss may be attributed to the loss of water of crystallization. Beyond 200 ºC the loss may be attributed to the effect on component and loss of coordinated water and hydroxyl groups. It also involves the production of Sb$_2$O$_3$. These losses follow the regular trend of inorganic ion exchanger[23,24].

Distribution behaviour of ten metal ions in demineralized water were studied (Table-5). The study revealed that the material, in demineralized water showed high preference in the following order: Pb^{2+} > Ni^{2+} > Cd^{2+} > Bi^{3+} > Cu^{2+} > Mn^{2+} > Zn^{2+} > Mg^{2+} > CO^{2+} > Ca^{2+}. Antimony(III) molybdosilicate separates magnesium from lead, cadmium and nickel. The percentage error is from 0.25 to 3.75 %, so the ion exchanger separates some metal ions almost 100 % and removed 100 % Ca^{2+} and 99.0 % Mg^{2+} from hard water.

REFERENCES

1. Y. Ioune, *J. Inorg. Nucl. Chem*, **26**, 2241 (1964).
2. C.B. Amphlett, Inorganic Ion Exchangers; Elsevier, Amsterdam (1964).
3. D.K. Singh and N.K. Mishra, *Bull. Soc. Chem. Fr.*, **127**, 204 (1990).
4. P. Singh, J.P. Rawat and N. Rahman, *Indian J. Chem.*, **41A**, 1616 (2002).
5. C. Janardanan and K.K. Arvindakshan, *Indian J. Chem.,* **40A**, 1356 (2001).
6. D.K. Singh and P. Yadav, *Chem. Anal. (Warsaw)*, **46**, 515 (2001).
7. R. Yavari, S.J. Asimadi, Y.D. Huang, A.R. Khanchi, G. Bagheri and J.M. He, *Talanta*, **77**, 1179 (2009).
8. A.S. Nabi, M. Naushad and Inamuddin, *J. Hazard. Mater.*, **142**, 404 (2007).
9. A.S. Nabi, Alimuddin and A. Islam, *J. Hazard. Mater.*, **172**, 202 (2009).
10. A.S. Nabi and M.A. Khan, *React. Funct. Polym.*, **66**, 495 (2006).
11. A.A. Ismail, R.M. Mohamed, I.A. Ibrahim and B. Koopman, *Colloid. Surf. A*, **366**, 80 (2010).
12. A.P. Gupta, G.L. Verma and S. Ikram, *React. Funct. Polym.,* **43**, 33 (2000).
13. P. Sharma and Neetu, *Desalination*, **267**, 277 (2011).
14. K.G. Varshney, N. Tayal and P. Gupta, *Colloid. Surfaces,* **28**, 11 (2003).
15. A.A. Khan and M.M. Alam, *React. Funct. Polym.*, **55**, 277 (2003).
16. A. Agarwal and M. Drabik, *Indian J. Chem.,* **43**, 2586 (2004).
17. K.G. Varshney, N. Tayal, P. Gupta, C. Janardanan and S.N. Madhavankutty, *Analyst*, **115**, 85 (1990).
18. C. Reetha, K.K. Arvindakshan and C. Janardanan, *Indian J. Chem.*, **41**, 1438 (2002).
19. N.E. Topp and K.W. Pepper, *J. Chem. Soc.*, 3299 (1949).
20. M. Qureshi, K.G. Varshney and A.H. Israili, *J. Chromatogr.*, **50**, 141 (1972).
21. A.K. Jain, S. Agarwal and R.P. Singh, *J. Radioanal. Nucl. Chem.*, **54**, 171 (1979).
22. J.S. Gull and S.N. Tandon, *J. Radioanal. Nucl. Chem.*, **36**, 345 (1979).
23. M. Qureshi, J.P. Gupta and V. Sharma, *Anal. Chem.*, 45 (1973).
24. J.P. Rawat and S.Q. Mujtaba, *Can. J. Chem.*, **53**, 286 (1975).