Synthesis & Characterization of Bismuth(III) tungstomolybdate as a new cation exchanger, and its analytical applications

Arti and Seema
Department of Chemistry, Meerut College, Meerut -250002, (U.P.) India.

| ARTICLE INFO	ABSTRACT
Article history: Received: 25 October 2012; Received in revised form: 20 November 2012; Accepted: 4 December 2012; **Keywords** Inorganic ion exchanger, Ion exchange capacity, Thermal studies, Chemical stability, Binary separation.	A new heteropolyacid-based cation exchanger [Bismuth(III) tungstomolybdate (BTM)] has been synthesized and characterized using chemical stability, pH titration, distribution studies, thermal stability, FTIR, X-Ray analysis and TGA curve analysis. It exhibits 1.05 meq/g ion exchange capacity for sodium ions. The chemical stability of the material has been tested in acidic, neutral and basic media. Its distribution behaviour for nine metal ions has been studied. Ion exchanger column was used for binary separation and hardness causing metal ions removal.

Introduction

Base exchange, or in modern terminology cation exchange has since the middle of the 19th century been the subject of a great amount of scientific investigation. Ion exchange is with very few exception, a reversible process. The metallic ions are exchanged stoichiometrically with H^+ in exchanger phase and can be determined indirectly by the application of exchange reactions:

$$nRH^+ + M^{n+} \leftrightarrow MR_n + nH^+$$
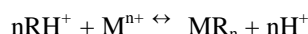
where R represents the structural unit of the ion exchanger, and H^+ and M^{n+} are the cations taking part in the ion exchange . A similar method can be adopted for the replacement of anions by hydroxyl ions stoichiometrically. Now a days, ion-exchange materials have been the essential constituents for a number of processes pertaining to analysis, preconcentration and recovery of a number of ionic species from aqueous as well as from non-aqueous systems. A good number of heteropoly acid salts have been reported in literature as ion exchange material. These materials exhibits improved properties over the simple salts of the metals. One of the salient features is that the selectivity may be enhanced by varying the composition of the ion exchange materials. A large number of such materials were prepared by mixing phosphoric, arsenic, molybdic, antimonic and vanadic acids with tin, titanium, thorium, zirconium, cerium, iron, antimony, niobium, bismuth, tantalum etc. Some of them are stannic molybdophosphate[1], zirconium phosphomolybdate[2], iron(III) tungstophosphate[3], antimony(III) tungstovanadate[4], zirconium arsenovanadate[5], stannic antimonate[6], stannic arsenate[7], cerium molybdate[8], titanium(IV) tungstophosphate[9], stannic phosphotungstate[10], titanium molybdophosphate[11] and zirconium tungstomolybdate[12], zeolite A (SiO_2: Al_2O_3: H_2O: Na_2O)[13] , tin(IV) tungstosilicate[14] , stannic(IV) iodosilicate[15], bismuth(III) iodosilicate[16], zirconium antimonotungstate[17] and antimony(III) molybdosilicate[18]. Bismuth based exchangers have not been studied very much. Bismuth tungstate[19], bismuth nitrate[20], bismuth tellurate[21] and bismuth silicate[22] have been reported to show ion exchange properties. In the continuation of the work on heteropolyacid based ion exchanger, we have synthesized a new heteropolyacid salt, i.e. bismuth(III) tungstomolybdate. As per the literature no work has been reported on bismuth(III) tungstomolybdate as an ion exchanger. This paper presents the synthesis, characterization and analytical applications of bismuth(III) tungstomolybdate.

Experimental

Materials and methods

Bismuth nitrate, Sodium tungstate and Sodium molybdate were Qualigens (India) products. All other reagents and chemicals were also of analytical grade.

pH measurements were performed using a 'Toshniwal Research pH Meter' (Model pH-110) for equilibrium studies.

'Tanco's Electric Rotary Shaker' was used for shaking the solutions for different studies.

Thermal studies were carried out by using 'Tanco's Electric Muffle Furnace'. For drying samples, 'NSW India's Oven' was used. 'Samson S-300D Electric Balance' was used for weighing.

All glasswares used in this work were of 'Borosil' make.

The X-Ray diffraction pattern of the exchanger in H^+ was obtained from Instrumentation Centre, IIT Roorkee where 'Philips Analytical X-Ray B.V. Diffractometer' was used. XRD was obtained between 0 to 120°.

FTIR was also obtained from Instrumentation Centre, IIT Roorkee where 'Thermonicolet IR Spectrophotometer' were used. Infrared spectrum analysis of bismuth (III) tungstomolybdate was done by the KBr disc method. The IR absorption spectrum was recorded between $400 cm^{-1}$ and $4000 cm^{-1}$.

TGA was obtained with the help of 'Perkin Elmer (Pyris Diamond)' in alumina pan at IIT Roorkee (U.K.). Thermogravemetric analysis was done in between $0°$ to $800°$ cel.

Tele: +91-8755510388
E-mail addresses: singh.arti28@gmail.com

Synthesis of Bismuth(III) tungstomolybdate

A number of samples of bismuth(III)-tunstomolybdate were synthesized by mixing solution of 0.1M bismuth nitrate, 0.1M sodium tungstate and 0.1M sodium molybdate in different mixing ratios. The details of samples are given in table 1. Nitric acid was added to the precipitates to obtain the desired pH value. The resulting precipitates were allowed to stand for twenty four hours in the mother liquor.

Similar type of synthesis is found on the literature survey such as an amorphous sample of inorganic cation-exchanger zirconium tungstomolyb-date was prepared by mixing varying ratios of 0.1M aqueous solution of sodium tungstate and 0.1M aqueous solution of sodium molybdate into 0.1M aqueous solution of zirconium oxychloride at pH 1.

The precipitates of different eleven samples were filtered. After filtration continuous washing of all samples was done to remove excess acid, with distilled water. pH of the effluents were checked with the help of pH paper. When it becomes neutral, then precipitates were assumed to be free from excess acid. Now these eleven different samples were kept in an oven at 40 ± 1^0C for drying. After about more than 24 hours precipitates become dry and ready for further treatment i.e. granulization. The colour of the precipitates was recorded (Table-1).

For granulization the materials were cracked when they were immersed in to hot water. Granules of eleven samples were, therefore, obtained.

Generation of granules was done by treating them with M HNO_3 solution. For this, granules of eleven samples were kept separately in said acid solutions taken in eleven different conical flasks and 15 minutes continuous shaking was done with the help of Electric Rotary Shaker. The same process was repeated several times with fresh acid solution each time. After settlement of granules, decant the acid and kept the granules in fresh acid solution and leave them as such for twenty four hours at room temperature. After twenty four hours, decant the acid and filter them. Granules are finally washed with distilled water to remove excess acid and dried them in an oven at 40 ± 1^0C.

Determination of Ion exchange capacity (column method)[23]

0.50g (dry mass) of bismuth(III) tungstomolybdate in H^+ form was packed in glass column having a glass wool support at the base. M $NaNO_3$ solution was passed through the column slowly by adjusting the effluent rate at 9-10 drops per minute. The effluent was carefully collected in a 250 ml conical flask. The complete replacement of H^+ from the ion exchanger by Na^+ was checked by comparing the pH of the influent (M $NaNO_3$) and the effluent with the help of pH paper. The collected effluent was titrated against a standard NaOH solution. Then I.E.C. was calculated using a suitable formula (Table-2).

Sample (BTM-IV) was selected for detailed study on account of its highest ion exchange capacity. The sample was synthesized in bulk to fulfill the purpose.

Bulk synthesis was done by mixing 0.1M sodium tungstate, 0.1M sodium molybdate solution and 0.1M bismuth nitrate solution with continuous stirring in 1:2:2 ratio respectively. The pH was adjusted to 0-1 by adding dil HCl. The precipitate was aged in the mother liquor for twenty four hours at room temperature and filtered. The matrix so obtained was washed to remove the excess acid with distilled water and then it was kept in oven at 40 ± 1^0C for drying. After drying the matrix was converted in to granules as described earlier. After generation excess acid was removed by washing with distilled water and

acid free granules were dried at 40 ± 1^0C in an oven. Now these granules are ready for detailed study.

The ion exchange capacity was determined once again by column method using M $NaNO_3$ solution. The ion exchange capacity was found to be 1.10 meq/g which is nearly equal to the previous value. Similarly the I.E.C. of the synthesized material (BTM-IV B) was also determined by the column process for different alkali and alkaline earth metals. Six equal parts of 0.50g each of the exchanger were packed in six different columns and passed some distilled water through the column to wash and settle the granules to make a bed. Six different metal ion solutions of 0.1 molar concentration were prepared. Each column was treated with a particular salt solution to occur the ion exchange. The flow rate was maintained as one milliliter per minute. The effluents were collected and titrated against a standard sodium hydroxide solution separately to determine the hydrogen ion concentration. The ion exchange capacity was calculated using a suitable formula (Table-3).

pH titration method :

This is the another method of determining ion exchange capacity of the exchanger. In this method 0.50g of exchanger was treated with 50ml of the NaCl-NaOH solution. Eleven different samples of NaCl-NaOH solutions were prepared by varying NaCl and NaOH ratios. Eleven equal parts of 0.50g each of the exchanger were treated with eleven different samples of NaCl-NaOH solution separately. Six hours continuous shaking was done with the help of Electric Rotary Shaker and then kept them as such for twenty four hours to maintain the equilibrium. After twenty four hours pH of different samples were measured with the help of pH meter. Please refer table 4 & figure 1.
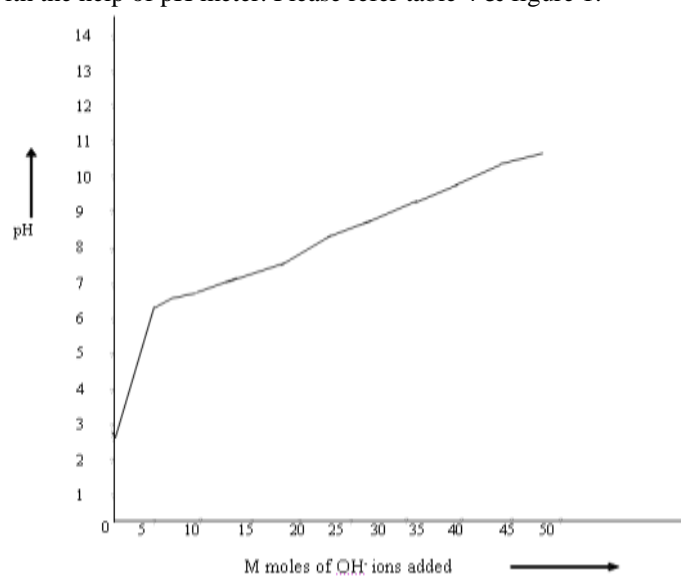

Figure 1

Chemical Stability

To determine the extent of dissolution of the material in different chemical solutions of different mineral acids, organic acids and bases a 0.50g of material was equilibrated with 25ml of the solution of interest by six hours continuous shaking with the help of Electric Rotary Shaker and then left the mixture as such for twenty four hours at room temperature. If there is remaining material in solution then decant them and washed by DMW for the removal of excess acids and bases. After drying at 40 ± 1^0C the ion exchange capacity was determined by column method. This method was used to find the stability of the exchanger towards eleven different solutions therefore eleven

different parts of the exchanger were taken to treat with the said solutions separately (Table-5).

Thermal Stability

Heating effect on weight and ion exchange capacity of the ion exchanger was studied using a muffle furnace in which a temperature upto 900^0C can be maintained. Eight equal parts of 0.50g each of the material were heated at various temprature for one hour in a muffle furnace and their ion-exchange capacity were determined by the column process after cooling them to room temprature. The results are summarised in table-6.

Distribution Studies

The distribution cofficient values for nine metal ions in DMW were determined by batch process. 0.50g of bismuth(III) tungstomolybdate in H^+ form was equilibrated with 25 cm^3 metal salt solutions. This mixture was then shaken for six hours at room temprature with the help of Electric Rotary Shaker. Then solutions were kept as such for twenty four hours at room temperature. The amount of metal ions left in the solution was determined by titrating against the standard solution of EDTA . The blank titration were also carried out using metal ion solutions, EDTA solution and suitable indicators. The distribution coefficient (K_d) values were calculated for metal ions using the following equation.

$$K_d = \frac{I-F}{F} \cdot \frac{A}{W}$$

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

Binary separation

In the present work binary separations by column method have been done. For separation studies of binary mixture, 0.50g of the exchanger in H^+ from was taken in a glass column (0.6 cm diameter). The column was washed with about 20ml DMW and then a mixture of metal ions was introduced in to the column for exchange. The flow rate of the eluent was maintained at 8-10 drops/minute throughout the elution processes and recycled three times. The column was washed with demineralized water to rinse the sides of the column. The exchanged metal ions were then eluted with appropriate eluents. The flow rate of the effluent was maintained at 1ml/minute throughout the elution process. The effluents were collected and metal ions contents were determined titrimetrically against EDTA titration.

Removal of hardness causing metal ions

For removal studies of hardness causing metal ions, 0.50g of the exchanger in H^+ form was taken in a glass column. The column was washed with some DMW 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 1ml per minute throughout the elution process. The effluent was collected and metal ion content was determined titrimetrically against EDTA solution.

Results and discussion :

Bismuth(III) tungstomolybdate was obtained in the form of white amorphous solid. Various ratios of synthesis and ion exchange capacity of BTM samples are shown in table 1 and 2. The sample BTM-IV synthesised at pH 0-1 showed maximum

ion exchange capacity of 1.05 meq/g dry exchanger for sodium ion. Ion exchange capacity of our ion exchanger is found much better than a reported ion exchanger bismuth tungstate.[19] The ion exchange capacity of bismuth tungstate[19] was reported 0.50 meq/g.

The ion exchange capacity for different alkali and alkaline metals was determined by column method. The ion exchanger shows higher capacity for alkali metals than for alkaline earth metals. In both the cases, the capacity increases with the decrease in hydrated radii of ions. This sequence was compared with a reported ion exchanger bismuth tungstate.[19] The ion exchange capacity of bismuth tungstate[19] for alkali and alkaline earth metals varies from 0.30-0.50 meq/g. In the present work the ion exchange capacity of bismuth(III) tungstomolybdate for alkali and alkaline earth metals varies from 0.58-1.30 meq/g. This shows a better range of ion exchange capacity.

The pH titration curve obtained under equilibrium for NaOH-NaCl system. The pH titration curve revealed that the material behaves as strong cation exchanger as indicated by a low pH (2.56) of the solution when no OH^- ions were added to the system.

A study of the ion exchange capacity on heating at various temperatures indicates that the material does not lose its ion exchange capacity up to 100^0C and retain 21% of it even on heating up to 700^0C. The ion exchange capacity for Na^+ was 1.05, 1.05, 0.98, 0.95 in meq/g for the products dried at 50^0C, 100^0C, 200^0C, 300^0C respectively. These values were compared with a reported ion exchanger. The reported ion exchanger bismuth tungstate[19] which was dried at different tempratures in a muffle furnace for 2 hours, shows the ion exchange capacity for Na^+ was 0.52, 0.42, 0.35, 0.30 in meq/g respectively for the products dried at 40^0C, 100^0C, 200^0C, 300^0C respectively. This indicates that with increasing temperature of treatment a slow decrease in ion exchange capacity. We can conclude that the thermal stability of our ion exchanger is much better than the reported ion exchanger.

The material was found to be fairly stable in DMW and lower concentration of mineral acids and organic acids, although it dissolves completely in 2M NaOH.

In the FTIR spectrum of BTM, the peak between 3600-2800 cm^{-1} may be assigned to OH stretching vibration. The presence of external water molecules is indicated by the bands at 1618.30cm^{-1} The peaks at 869.57 cm^{-1} and 759.18 cm^{-1} might be due to W-O and Mo-O stretching vibration mode respectively. The spectrum has intensity band at 556.06cm^{-1} that shows the presence of Bi–O group.
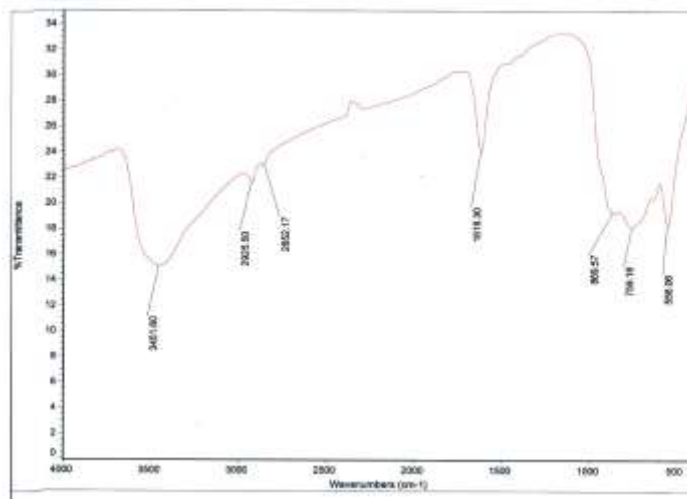
Table- 1

Sl. No.	Sample No.	Molar Concentration of Solution			Mixing Volume Ratio			pH Value	*Appearance of Precipitate
		BN	ST	SM	BN	ST	SM		
1	BTM-I	0.1	0	0.1	1	1	1	0-1	White powder
2	BTM-II	0.1	0.1	0.1	2	1	1	0-1	White powder
3	BTM-III	0.1	0.1	0.1	1	2	1	0-1	Creamy white powder
4	BTM-IV	0.1	0.1	0.1	1	1	2	0-1	White powder
5	BTM-V	0.1	0.1	0.1	2	2	1	0-1	Creamy white powder
6	BTM-VI	0.1	0.1	0.1	2	1	2	0-1	White powder
7	BTM-VII	0.1	0.1	0.1	1	2	2	0-1	White powder
8	BTM-VIII	0.1	0.1	0.1	3	1	1	0-1	White powder
9	BTM-IX	0.1	0.1	0.1	1	3	1	0-1	Creamy white powder
10	BTM-X	0.1	0.1	0.1	1	1	3	0-1	White power
11	BTM-XI	0.1	0.1	0.1	3	3	1	0-1	White powder

BTM - Bismuth(III) tungstomolybdate ,BN- Bismuth nitrate ,ST - Sodium tungstate , SM - Sodium molybdate
* The Colour of ppt. is after drying them at 40 ± 1^0C

Table -2

S. No.	Sample No.	COBBG	COBAG	I.E.C. (meq/g)
1	BTM-I	White powder	Cremy white powder	0.769
2	BTM-II	White powder	White powder	0.936
3	BTM-III	Creamy white powder	Light yellow powder	0.488
4	BTM-IV	White powder	White powder	1.050
5	BTM-V	Creamy white powder	Yellow crystalline	0.000
6	BTM-VI	White powder	Dissolve	-
7	BTM-VII	White powder	White powder	0.707
8	BTM-VIII	White powder	White powder	0.811
9	BTM-IX	Creamy white powder	Dissolve	-
10	BTM-X	White power	White power	0.900
11	BTM-XI	White powder	Creamy white powder	0.624

BTM - Bismuth(III) tungstomolybdate, COBBG - Colour of beads before generation, COBAG- Colour of beads after generation , I.E.C.- Ion exchange capacity

Table- 3
I.E.C. of Bismuth(III) tungstomolybdate for various cations

Cations	Salt of Cation	Solution Concentration	Hydrated Radii (A^0)	I.E.C. (meq/g)
Na^+	$NaNO_3$	0.1M	7.90	1.080
Li^+	LiCl	0.1M	10.0	0.950
Na^+	NaCl	0.1M	7.90	1.100
K^+	KBr	0.1M	5.30	1.300
Mg^{2+}	$MgCl_2$	0.1M	10.80	0.580
Ca^{2+}	$CaCl_2$	0.1M	9.60	0.600
Ba^{2+}	$BaCl_2$	0.1M	8.80	0.612

I.E.C. - Ion exchange capacity

Table- 4

SL. No.	Sample No.	NaCl-NaOH SYSTEM		pH Value
		NaCl solution (ml)	NaOH solution (ml)	
1.	BTM-IV B	50	0	2.56
2.	BTM-IV B	45	5	5.82
3.	BTM-IV B	40	10	6.81
4.	BTM-IV B	35	15	7.24
5.	BTM-IV B	30	20	7.64
6.	BTM-IV B	25	25	8.76
7.	BTM-IV B	20	30	9.80
8.	BTM-IV B	15	35	10.67
9.	BTM-IV B	10	40	10.96
10.	BTM-IV B	5	45	11.14
11.	BTM-IV B	0	50	11.42

BTM-IV Bismuth(III) tungstomolybdate sample no. (IV B)

Table- 5
Chemical Stability

Solution	Wt Before Treatment (g)	Wt After Treatment (g)	I.E.C. (meq/g)
DMW	0.50	0.50	1.050
1M HCl	0.50	0.18	0.690
2M HCl	0.50	0.09	0.230
1M HNO$_3$	0.50	0.38	0.738
2M HNO$_3$	0.50	0.3	0.691
1M H$_2$SO$_4$	0.50	0.42	0.611
2M H$_2$SO$_4$	0.50	0.35	0.693
2M CH$_3$COOH	0.50	0.47	0.823
2M HCOOH	0.50	0.48	0.708
2M NaOH	0.50	Dissolve completely	-
2M KOH	0.50	0.07	0.148

Table- 6
Thermal Stability

Sl. No.	Sample No.	Temp (^{0}C)	WBH (g)	WAH (g)	LIW (g)	CAH	I.E.C. (meq/g)
1	BTM-IV B	50	0.50	0.50	0.00	White	1.05
2	BTM-IV B	100	0.50	0.50	0.00	White	1.05
3	BTM-IV B	200	0.50	0.42	0.08	Light green	0.98
4	BTM-IV B	300	0.50	0.40	0.10	Blackish green	0.95
5	BTM-IV B	400	0.50	0.38	0.12	Black	0.78
6	BTM-IV B	500	0.50	0.35	0.15	Black	0.69
7	BTM-IV B	600	0.50	0.20	0.30	Churned	0.48
8	BTM-IV B	700	0.50	0.20	0.30	Churned	0.22

BTM- Bismuth(III) tungstomolybdate, WBH- Weight before heating, WAH- Weight after heating, LIW- Loss in weight, CAH – Colour after heating, I.E.C. – Ion exchange capacity

Table- 7
K$_d$ values of metal ions on BTM in DMW

| Metal Ion	Taken As	K$_d$ (ml/g)
Mg(II)	Acetate	32.180
Zn(II)	Acetate	29.780
Cu(II)	Acetate	76.380
Mn(II)	Acetate	6.097
Co(II)	Acetate	27.400
Ni(II)	Sulphate	3.012
Pb(II)	Nitrate	170.270
Cd(II)	Chloride	2.242
Ca(II)	Carbonate	8.420

BTM - Bismuth(III) tungstomolybdate

Table- 8
Separation of metal ions achieved on Bismuth(III) tungstomolybdate   Column

| Sample	Sepration achived	Metal ions in µg		% Error	Eluent used	Volume of Eluent used (ml)
		Loaded	Recovered			
1	Pb	3916.00	3857.26	-1.50	1MHNO$_3$	40
	Mg	109.00	97.00	-11.00	0.1MHClO$_4$	50
2	Pb	3916.00	3845.50	-1.80	0.05MHNO$_3$ + 0.5MNH$_4$NO$_3$ 0.5MHNO$_3$ + 0.5MNH$_4$NO$_3$	40
	Zn	316.00	290.72	- 8.00		30
3	Zn	316.00	311.50	-1.40	0.01M HClO$_4$	40
	Cd	33.70	33.00	-2.08	1MHNO$_3$	50
4	Co	285.00	278.84	-2.17	0.5MHNO$_3$	60
	Ni	35.00	34.50	-1.50	0.05MHNO$_3$	40
5	Mg	109.00	106.45	-2.34	0.4M NH$_4$NO$_3$	70
	Cd	33.70	33.50	-0.60	0.25M HNO$_3$	50

Table- 9
Removal of hardness causing metal ions on Bismuth(III) tungstomolybdate column

Sample	Metal ion	Amount loaded (µg)	Amount found (µg)	Error %	Eluent used
1	Mg^{2+}	109.00	108.00	-0.92	0.01M HClO$_4$
2	Ca^{2+}	24.00	23.90	-0.42	1.0M HNO$_3$
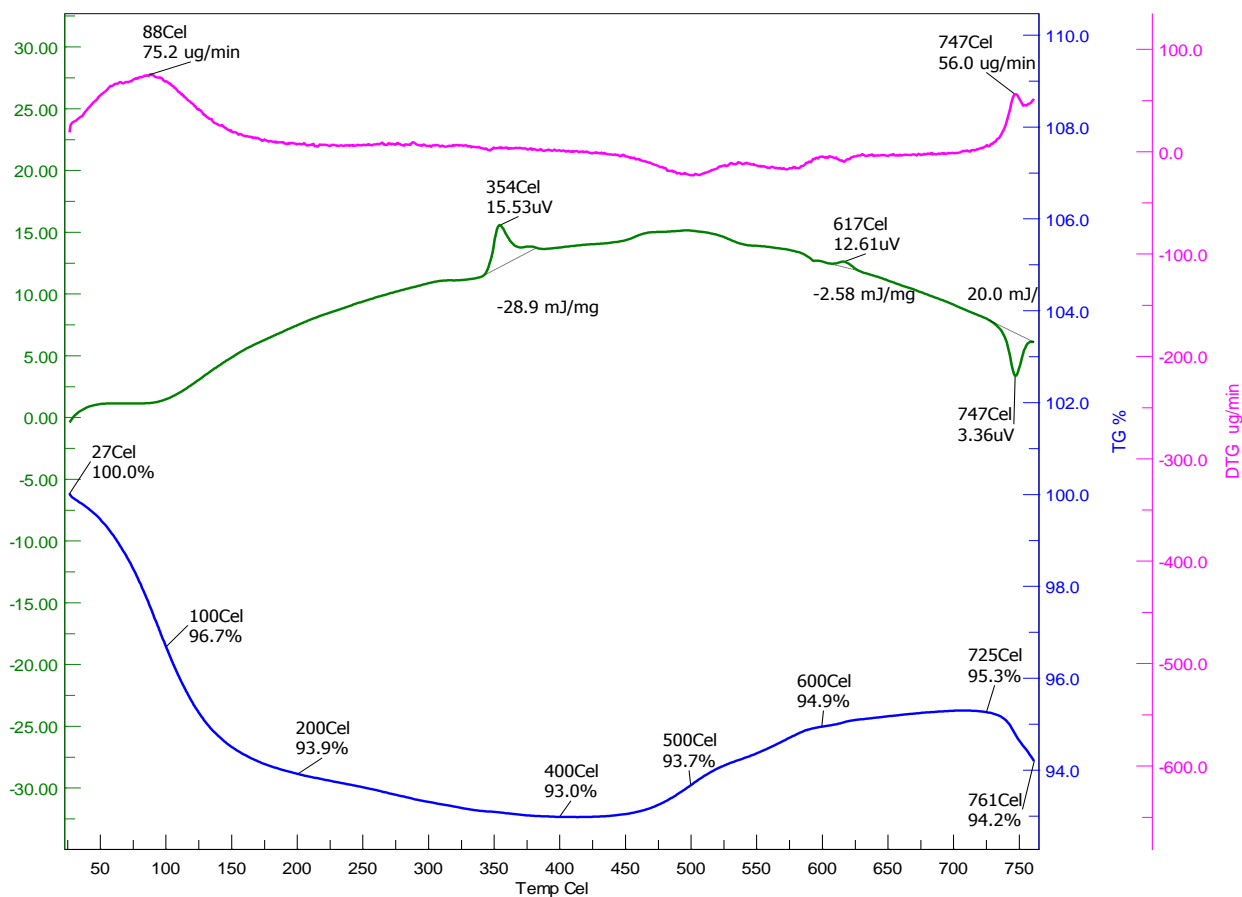
The thermogram of BTM may be interpreted as follows: the ion exchange material experience a sharp loss in weight (3.4%) upto 100^0C, which can be attributed to loss of external water molecules. Further the weight loss in the region 100^0C -600^0C may be due to condensation of other component of ion exchanger. A constant weight after 600^0C seems due to the formation of stable oxide.

The X-Ray analysis shows that there is no sharp peaks, so it revealed that the material is amorphous in nature.
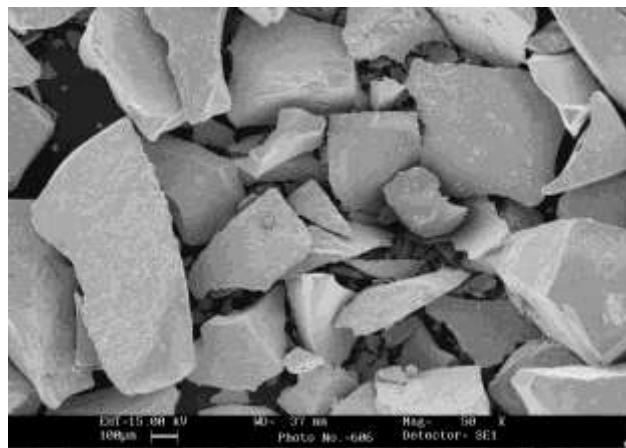

Distribution studies of the studied metal ions revealed that bismuth(III) tungstomolybdate shows high affinity for Pb(II). Similarly literature shows that a reported ion exchanger bismuth tungstate19 has a very high selectivity towards Pb^{2+} ions over other ions. The uptake of Pb^{2+} is so strong that it may be separated from a large number of elements.

In binary separations the bismuth(III) tungstomolybdate separate lead from magnesium and zinc, zinc from cadmium, cobalt from nickel and magnesium from cadmium. The removal of metal ions was from 89% to almost 100%. Ion exchanger was also applied for water softening. It removed 95.6% Ca^{2+} and 99.0% Mg^{2+} from hard water.

Conclusion:

It can be concluded that Bismuth(III) tungstomolybdate is a promising ion exchanger with good ion exchange capacity among known ion exchanger of bismuth. It has good thermal and chemical resistivity. As, it is selective for lead , so it can remove lead from different liquid toxic effluents. Organo –
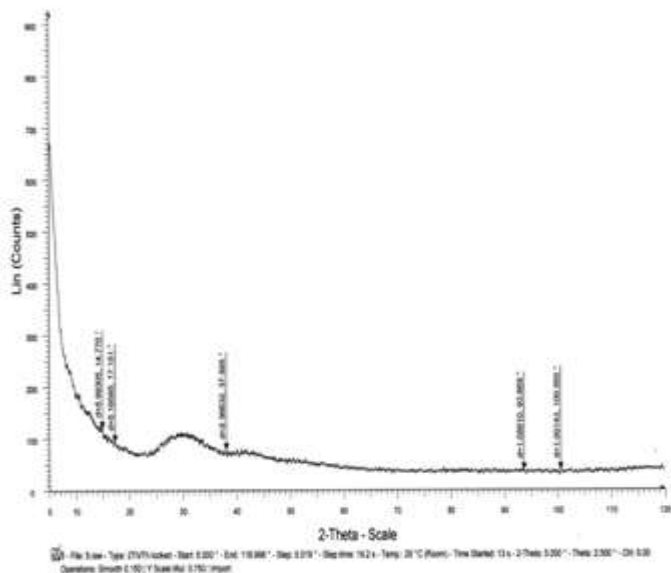
SEM images of ion exchanger sample BTM- IV showed that the material is amorphous in nature.

inorganic ion exchanger based on it can also be prepared for further research.

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