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Synthesis and Characterization of Bismuth (III) Tungustosilicate A New Inorganic Cation Exchanger

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Abstract: *In the present work, synthesis of a new inorganic Cation exchanger is done & the synthesized exchanger is characterized by determining its ion exchange capacity, thermal stability, chemical stability and distribution studies. It has also been characterized by IR, TGA and XRD studies. The state of the exchanger is found to be semicrystalline. The ion exchange capacity of the synthesized ion exchanger has been found 0.80 meq/g. The exchanger has a high stability against temperature and chemicals. Kd Values were also calculated. The inorganic ion exchanger has the maximum Kd value for zinc and minimum for lead ions. As an application part binary separations and removal of toxic metal ions were done.*
Key words: *Bismuth(III) tungustosilicate Inorganic Cation exchanger, ion exchange capacity, Thermal study, chemical study and distribution studies.*

I. Introduction :

Ion exchange is important technique which is extensively used in separation science. Ion exchange includes cation exchange and anion exchange. Ion exchange is a reversible chemical reaction between an insoluble solid and a solution during which ions may be inter-changed.

Ion exchangers comprise two main groups organic and inorganic exchangers. Both groups include synthetic and natural materials. Ion exchangers are either cation exchangers for positively charged cations or anion exchangers for negatively charged anions.

An inorganic three component cation exchanger (Bismuth(III) tungustosiicate) has been sunthesized. The ion exchanger has 0.80 meq/g ion exchange capacity. The ion exchanger can be regenerated, so it can be used more than once. The ion exchange capacity of the material was determined by the column process. The synthesized ion exchanger is characterized by distribution studies, FTIR, XRD & TGA of the exchanger.

II. Experimental:

1. Chemicals & Reagents :

The chemicals used for preparing the exchanger were bismuth nitrate ($Bi(NO_3)_3 5H_2O$), sodium tungustate ($Na_2WO_4.2H_2O$) and sodiummetasilicate ($Na_2SiO_3.5H_2O$). In addition of the above HCl, HNO_3 and pH paper were used to complete the synthesis.

During the characterization of the synthesized ion exchanger a number of chemicals/ reagents such as sodium chloride, sodium hydroxide, sodium salt of EDTA, hexamine, hydroxyl amoniumchloride, triethylamine & erichrome black-T were used. During the entire research work all the chemicals used were of AR grade/ pure for better results. The chemicals used were obtained from Qualigens/CDH Private Ltd. India products.

2. Apparatuses :

Electronic Balance (Samson Model 300 D), Two pen balance, Borosil Glass wares, Magnetic Stirrer with hot plate, Oven (NSW India), Rotary shaker (TANCO), Muffle Furnace (SHIVAKI-T 701 TANCO), Toshniwal research pH meter (model 110) were used. Perkin Elmer (Pyris diamond) in alumina pan with a current of nitrogen for Thermal Gravimetric Analysis (T.G.A.) Thermo nicolet spectrophotometer for Infra Red (I.R.), Phillips analytical X-Ray B.A. Diffractometer for X-Ray were available at IIT, New Delhi from where TGA, FTIR & XRD of the samples were obtained.

3. Synthesis of Matrix :

The ion exchanger was synthesized using different salt solutions of decimolar strength. The solutions were mixed in different ratios at room temperature with continuous stirring with the help of magnetic stirrer. On mixing white precipitates were obtained in all the ten ratios. The pH was set to 1. One of ratios did not give any precipitate. All the precipitates obtained were filtered and washed to make them free from acid. The nine precipitates were obtained. The precipitates were dried in an oven at 40ºC (±5) for 24 hours. The samples appeared to be semicrystalline. The samples were highly insoluble in water. The samples were dried in oven at 40ºC (±5). (Table-1)

4. Granulization :

The dried precipitates were converted into granules by putting them in water. (Table-2)

5. Generation :

The granules so obtained were charged by treating them with 0.1 M HNO_3 solutions for 24 hours. The precipitates got charged and became ready to perform ion exchange.

6. Characterization :

i) Ion exchange capacity (I.E.C.) determination :

The column method was used for the determination of the ion exchange capacity of each sample. 0.5 gm of dry ion exchanger in H^+ form of the nine exchanger samples were loaded into different columns having a glass wool supported for the exchanger bed. Sodium nitrate solution was used to elute the H^+ ions from the exchanger with a flow rate of 0.2 ml min^{-1}. The released H^+ ions were determined titrimetrically using a standard 0.01 molar sodium hydroxide solution. The ion exchange capacity values of the samples are given in Table-3.

ii) Selection of the sample :

Ion exchange capacity of BTS-5 was found to be maximum out of nine samples, therefore this sample was selected for detailed study.

iii) Synthesis in bulk :

BTS-5 was synthesized in large amount by the same method as given earlier in order to study the exchanger is details. This shall be referred as BTS-5B.

iv) Determination of ion exchange capacity (I.E.C.) :

(a) The I.E.C. of the exchanger (BTS-5B) synthesized in bulk was determined by column method. I.E.C. value was found to be close to the earlier value.

(b) pH Titration method :

Ion exchange capacity of the exchanger was also determined by pH titration method. pH titration studies of Bismuth(III) tungustosilicate cation exchanger was done by the added salt method (NaCl, NaOH). Eleven equal portions of the exchanger were placed in eleven different beakers containing equal volumes of the solutions of NaCl & NaOH in ten different ratios (Table-4). The beakers were shaken occasionally and then kept as such for twenty four hours to establish the equilibrium. After twenty four hours pH of all the samples were recorded. A graph was plotted between pH and hydroxyl ion concentration (Fig. 1). This graph was used to calculate the ion exchange capacity of the exchanger.

v) Thermal stability :

For thermal stability determination of seven equal portions (500ml each) of the exchanger (BTS-5B) were heated for 1 hour at different temperatures in the muffle furnace and the ion exchange capacity of all the above was determined as usual by the column process (Table 5).

vi) Chemical stability :

The chemical stability of eleven equal portions of the exchanger was determined in acid & base solutions. HCl, HNO_3, H_2SO_4, NaOH & acetic acid solutions were used. 25 ml of each solution was poured on a 500 mg of the exchanger taken in the eleven different 50 ml beaker with continuous shaking for six hours & then kept them as such for 24 hours at room temperature. Detailed quantitative studies regarding the stability of the exchanger, were made in different solutions as shown in Table-6.

vii) Distribution studies :

Kd values for different metal ions were determined by batch method. 500 mg of bismuth(III) tungustosilicate (BTS-5B) in H^+ form were kept in 25ml of metal ion solution at 25ºC for 6 hours, with intermittent shaking to rech equlibrium. Then the solution was kept as such for twenty four hours. After 24 hours the solution was filtered and metal ion concentration was determine using appropriate indicator has EDTA method. The concentration of the metal ion solution was also determined before treating with the ion exchanger. The difference of metal ion concentration was heated. Different metal ion solution's were treated in the same way as above. The Kd values were calculated by the following equation.

$$kd = \left[\frac{(I-F)}{F}\right]\frac{V}{W}(ml g^{-1})$$

where I & F are the initial and final burett readings, V is volume of solution in ml taken and W is the dry mass of the ion exchanger in gm. Kd values are given in table 7.

X-ray analysis (XRD) :

Powder X-ray diffraction (XRD) pattern was obtained in an aluminum holder for the sample BTS-5B in the original form using a PW 1148/89 based differactometer with Cu Kd radiations. The study was done between 10º to 80º2θ values with the spectrum BTS-5II is given in figure 3.

Fourier transform infrared (FTIR) study :

The Fourier transform infrared spectrum of BTS-5B in original form dried at 40ºC was taken by KBr disc method at room temperature. The observation band in the infrared spectrum of Bismuth(III) tungustosilicate has weak and medium intensities at 449.47 cm^{-1} and 803.36 cm^{-1} which indicates the presence of tungustate and silicate respectively while Bismuth indicated as a weak band at 935.30 cm^{-1} in the spectrum. A strong band at 1620.55 cm^{-1} indicate the presence of water molecules in exchanger. The other broad band and intence band at 2415.00 cm^{-1} shows the presence of O-H group.

Thermogravimetric (TGA) study :

TGA of the synthesized ion exchanger is also obtained here, in which we study the loss of water molecule at different temperature. Thermogravimetric analysis (TGA) data of the inorganic ion exchanger are present in figure 5.

III. Results & discussion :

Various samples of BTS were synthesized under different concentrations (See table 1). The conditions used for the preparation of inorganic ion exchanger have considerable effect on the degree of hydration and the composition of the exchanger. These two factors are responsible for the shape and size of cavities insides the ion exchanger and for other properties of the exchanger. All BTS samples were as white granules and suitable for use in the column operation. The ion exchange capacity of these materials shows that BTS has a good ion exchange capacity.

The chemical stability studies (Table 6) show that BTS samples are highly stable in acids and bases. However, in acidic and basic media with the concentration higher then 0.1 $MolL^{-1}$ respectively the exchanger is completely dissolved. the X-ray diffraction pattern (Fig. 3) shows some intensities, there by suggesting that the various forms of BTS are semicrystalline in nature.

The infrarred spectrum of BTS in H^+ from is shown in (Fig. 4). The asymmetric absorption strong band 3415cm^{-1} is attributed to interstitial water molecules and hydroxyl groups while a sharper peak in the region of 1620cm^{-1} with the characterization for the deformation vibration of fee water molecules.

According to the thermogram of BTS recorded in (Fig. 5) there is loss in weight initially due to loss of water molecules loser loss in weight shows the loss in components.

The ion exchanger properties of the product materials were studied by measuring the distribution coefficients (kd) of 7 elements using batch method in DMW and nitric acid median. The obtained values for kd (given in Table 7).

IV. Conclusion :

Semicrytalline ion exchanger BTS was found to have good ion exchange capacity. High chemical and thermal stabilities.

Acknowledgement:

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Table-1

Synthesis of Ten BTS Samples

Serial Number	Sample Number	Inter-Mixing Ratios			pH Value	Yield (gm)	Colour of ppt.	Colour of ppt after drying
		Bismuth Nitrate Solution	Sodium Tungustate Solution	Sodium Metasilicate Solution				
1	BTS-1	1	1	1	0-1	1.71	White	White
2	BTS -2	2	1	1	0-1	1.95	White	White
3	BTS-3	1	2	1	0-1	0.85	White	White
4	BTS-4	1	1	2	0-1	1.62	White	White

5	BTS-5	2	2	1	0-1	1.27	White	White
6	BTS-6	1	2	2	0-1	0.90	White	White
7	BTS-7	2	1	2	0-1	0.65	White	White
8	BTS-8	3	1	1	0-1	1.15	White	White
9	•BTS-9	1	3	1	0-1	-	-	-
10	BTS-10	1	1	3	0-1	0.86	White	White

Note : • = In sufficient precipitate, 1 = 40ml, 2 = 80ml, 3 = 120 ml
BTS = Bismuth(III) tungustosilicate ppt = Precipitate

Table 2
GRANULIZATION

Serial Number	Sample number	C.O.G.B.G.	C.O.C.G.
1	BTS-1	White	White
2	BTS-2	White	White
3	BTS-3	White	White
4	BTS-4	White	White
5	BTS-5	White	White
6	BTS-6	White	White
7	BTS-7	White	White
8	BTS-8	White	White
9	•BTS-9	-	-
10	BTS-10	White	White

Note : C.O.G.= Colour of granules before generation, •BTS-9= No Granules
C.O.C.G. = Colour of charged granules

Table 3
ION-EXCHANGE CAPACITY

Serial Number	Sample number	C.O.T.E.	I.E.C. (meq/g)
1	BTS-1	White	0.2
2	BTS-2	White	0.4
3	BTS-3	Yellowish	0.2
4	BTS-4	Yellowish	0.3
5	BTS-5	White	0.8
6	BTS-6	White	0.3
7	BTS-7	White	0.2
8	BTS-8	Yellowish	0.3
9	•BTS-9	-	-
10	BTS-10	Yellowish	0.4

Note : C.O.T.E. = Colour of the exchanger, I.EC.=Ion-exchanger capacity
*** = Ion-Exchange Capacity could not be determined because of in sufficient amount of the precipitates.**

Table 4
pH - TITRATION

Serial Number	Sample number	NaOH–NaCl System	
		NaOH solution (ml)	NaCl solution (ml)
1	BTS-5B	0	50
2	BTS-5B	5	45
3	BTS-5B	10	40
4	BTS-5B	15	35
5	BTS-5B	20	30
6	BTS-5B	25	25
7	BTS-5B	30	20

8	BTS-5B	35	15
9	BTS-5B	40	10
10	BTS-5B	45	5
11	BTS-5B	50	0

BTS-5B = Bismuth(III) tungustosilicate (BTS-5) was synthesized in bulk.

Table 5
THERMAL STABILITY

Serial Number	Sample number	IAOIE (mg)	Temp.	FAOIE Temp. (mg)	WLOIE (mg)	Colour	I.E.C. (meq/g)
1	BTS-5B	500	R.T.	500	00	White	0.80
2	BTS-5B	500	100	480	20	White	0.68
3	BTS-5B	500	200	470	30	White	0.46
4	BTS-5B	500	300	460	40	Brownish	0.26
5	BTS-5B	500	400	460	40	White	0.20
6	BTS-5B	500	500	440	60	Yellow	0.14
7	BTS-5B	500	600	440	60	Yellow	0.10

Note :
IAOIE – Initial amount of Ion-exchanger,FAOIE- Final amount of ion-exchanger,
WLOIE – Weight loss of ion-exchanger, I.E.C. – Ion-exchange capacity,
R.T. – Room temperature, Temp.- Temperature

Table 6
CHEMICAL STABILITY

Serial Number	Sample number	IAOIE (mg)	DABS		WLOIE (mg)	FAOIE (mg)	Colour	I.E.C. (meq/g)
			Solution	Concen-tration				
1	BTS-5B	500	HNO_3	1 M	430	70	White	0.4418
2	BTS-5B	500	HNO_3	2 M	360	140	Brownish	0.5
3	BTS-5B	500	HCl	1 M	410	90	Gr. Yellow	0.7073
4	BTS-5B	500	HCl	2 M	340	160	Green	0.5588
5	BTS-5B	500	KOH	1 M	310	190	White	0.5806
6	BTS-5B	500	KOH	2 M	260	240	White	0.5384
7	BTS-5B	500	NaOH	1 M	390	110	Brownish	0.5641
8	BTS-5B	500	NaOH	2 M	290	210	Brownish	0.7241
9	BTS-5B	500	CH_3COOH	2 M	380	120	White	0.5
10	BTS-5B	500	H_2SO_4	1 M	430	70	Brownish	0.6511
11	BTS-5B	500	H_2SO_4	2 M	380	120	Brownish	0.6052

Note :
IAOIE – Initial amount of Ion-exchanger, DABS- Different acid base solution,
WLOIE – Weight loss of ion-exchanger, FAOIE = Final amount of ion-exchanger

Table 7
DISTRIBUTION STUDIES

Serial Number	Sample number	Different Metal	Initial EDTA Reading	Final EDTA Reading	kd Value (mlg^{-1})
1	BTS-5B	Lead	25.4	18.8	94.32
2	BTS-5B	Zinc	26.6	24.2	4.96
3	BTS-5B	Cadmium	23.4	20.8	6.25
4	BTS-5B	Copper	25.2	21.6	8.33
5	BTS-5B	Thorium	26.6	22.5	11.11
6	BTS-5B	Calcium	29	19	26.31
7	BTS-5B	Magnesium	6.1	22.2	8.78

Note : EDTA = Ethylenediaminedetra acetic acid

Fig-1
pH-TITRATION CURVE

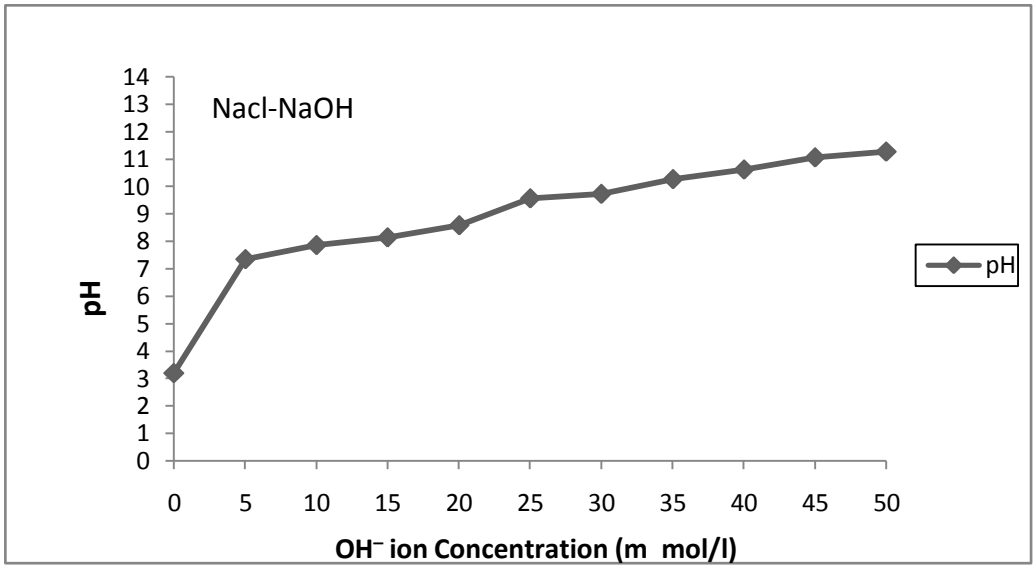
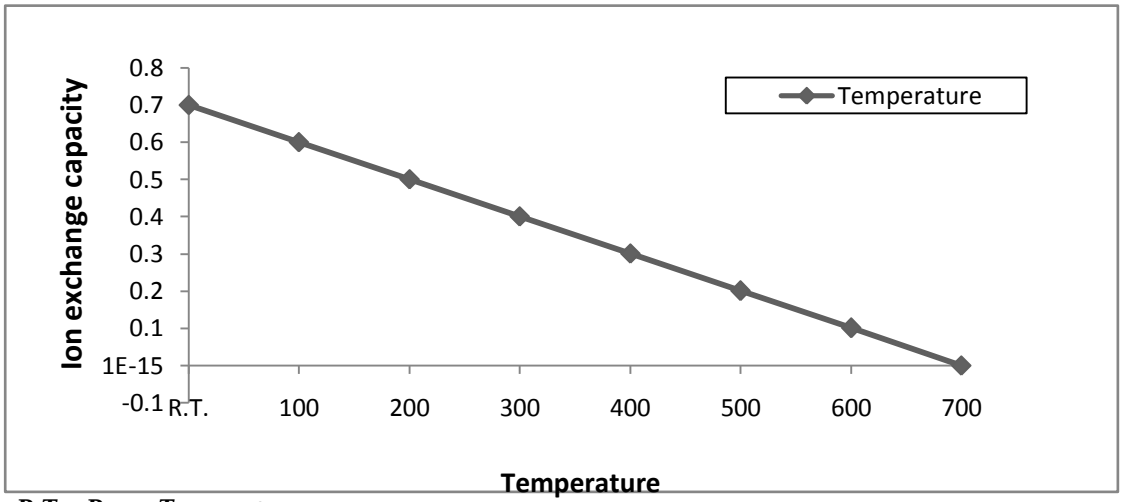


Fig-2
THERMAL STABILITY CURVE



Note : R.T.= Room Temperature

Fig-3
X-RAY ANALYSIS

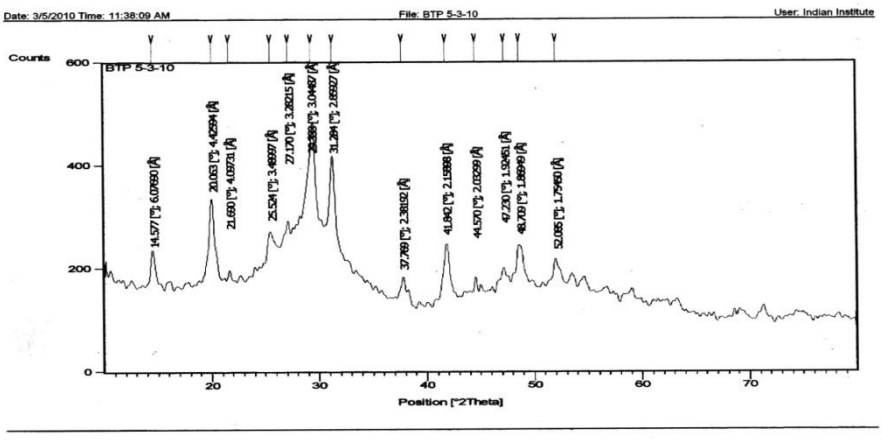


Fig-4
FOURIER TRANSFORM INFRA RED SPECTRUM

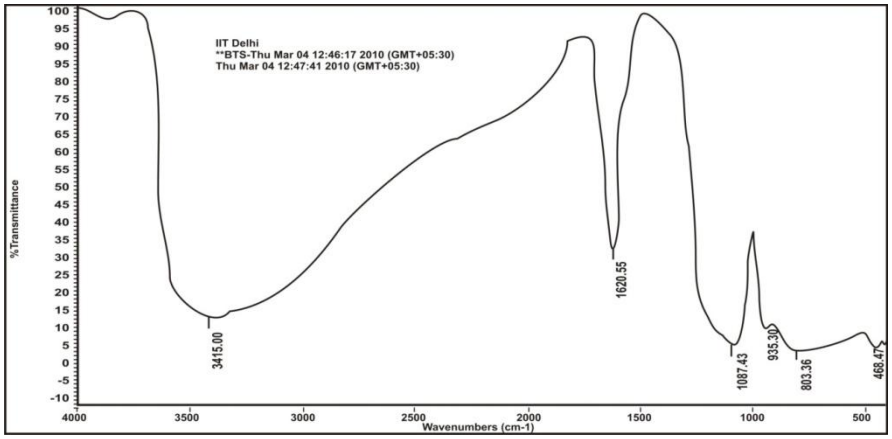
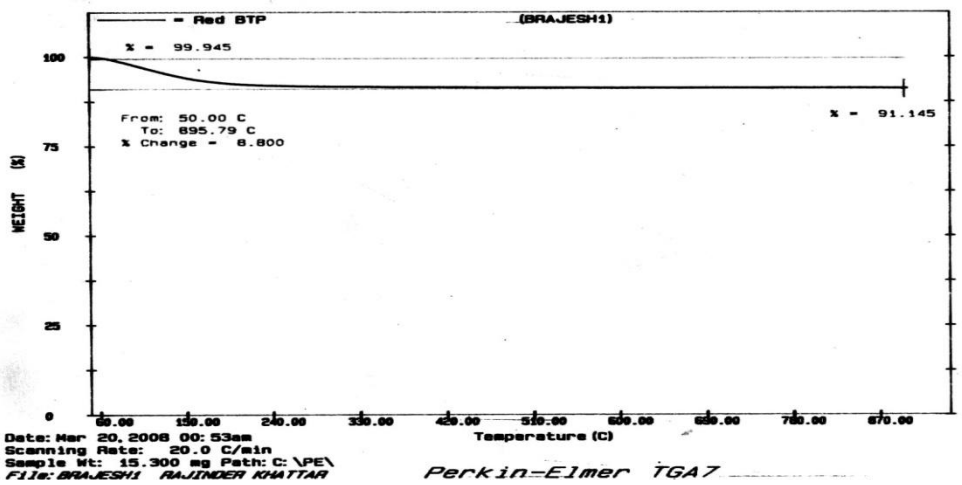


Fig 5
THERMAL GRAMATRIC ANALYSIS CURVE



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