

## Synthesis and Characterization of Bismuth Based Novel Inorganic Ion Exchange Materials and Their Analytical Applications.

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**Abstract :** Two new inorganic ion exchange materials Bismuth(III) antimonotungstate(BiSbW) and Bi(III) iodotungstate(BiIW), salts of heteropoly acids were compared to evaluate their performance as ion exchangers and to explore their efficacy as dye adsorbents. Amorphous BiSbW and BiIW have been synthesized by co-precipitation methods by varying the mixing ratio of the reagents. The most stable samples of BiIW and BiSbW have been characterized for spectral analysis (FTIR), elemental analysis (SEM-EDS), thermal analysis (TGA and DTA) and X- ray diffraction studies. Their ion exchange capacities for Na<sup>+</sup> ions were found to be 0.85 meqg<sup>-1</sup>(BiSbW) and 2.25 meqg<sup>-1</sup>(BiIW). The effect on the exchange capacity of drying the exchanger at different temperatures has been studied. The distribution coefficient values shows that these two samples are very selective for Pb<sup>2+</sup> ions. Hence their analytical importance has been established by quantitative separation of Pb<sup>2+</sup> from other metal ions and quantitative removal of Pb<sup>2+</sup> ions from textile industry. The adsorption results also reflected the vital influence of the new materials in controlling the hazardous organic pollutants by adsorption of various dyes from waste water.

**Keywords:** cation exchangers, distribution coefficient, dye adsorbents, heteropoly acids, ion exchange capacity etc

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### I. INTRODUCTION

The contamination of water wealth due to the unsystematic dumping of heavy metals and hazardous organic pollutants has been causing international anxiety for the last few decades. Diverse management techniques for wastewater loaded with heavy metals have been developed in recent years both to reduce the amount of wastewater created and to improve the quality of the treated effluents. Nowadays ion exchangers have received prominent position in water processing and in the chemical engineering. Ion exchangers as a separation process is comparatively too simple and energy -efficient compared to other established waste treatment techniques. Inorganic ion exchangers appeared as potential advanced materials to this challenging task exceptionally well, as they have effective properties such as good ion exchange characteristics, thermal stability and chemical resistivity [1-3]. Application of selective inorganic ion exchangers is a known way for recovery of heavy metals as they exhibit high affinities for specific ions [4-5].

The present work is concerned with Bismuth based three-component ion exchangers. By a review of the literature it is obvious that little research works have been done in the field of bismuth based materials as ion exchangers. Bismuth tungstate[6], bismuth nitrate[7], bismuth tellurate[8], bismuth silicate[9], bismuth(III) iodophosphate[10], bismuth(III) tungstosilicate[11] and bismuth(III) tungstomolybdate[12] etc have been studied for their synthesis, ion-exchange behaviour and analytical applications. In this manuscript, we describe the synthesis and ion exchange properties of two new inorganic ion exchange materials, Bismuth(III) antimonotungstate and Bismuth(III) iodotungstate. As per the literature no attempt has been reported on bismuth(III) antimonotungstate and bismuth(III) iodotungstate as ion exchangers. It was found that these exchanger exhibits an extremely high affinity for lead ion in the presence of an excess of other competitive species and, hence, could be regarded as promising materials for the detection of trace amount of lead ion in contaminated water and for the removal and recovery of the same from waste water. Moreover their efficacy intended for adsorption of different dyes from dye effluents was also examined and studied using UV-Vis Visible Diffuse Reflectance spectrometer.

### II. EXPERIMENTAL

#### 1. Reagents and chemicals

Bismuth nitrate, sodium tungstate, potassium pyroantimonate and potassium iodate were obtained from E.Merck (India). All other chemicals and reagents used were of analytical grade.

## 2. Instrumentation

pH measurements were performed using an ELICO LI613 pH meter. Spectrophotometry was done on a UV- Visible Spectrophotometer model JASCO V660 with diffuse reflectance accessory (integrated sphere). IR studies were made using an FTIR spectrometer model Thermo Nicolet Avtar370 and thermogram was run on Perkin Elmer Diamond TG/DTA Analyzer. X-ray diffractometer Bruker AXS D8 Advance for X-ray diffraction studies and an electric temperature controlled shaker was used for shaking. Chemical composition was determined using EDS. A glass column was used for column operations

## 3. Synthesis of the exchanger

Different samples of BiSbW and BiIW were prepared by adding 0.1M Bismuth nitrate solution to a mixture of 0.05M sodium tungstate solution and 0.05M potassium pyroantimonate solution and to a mixture of 0.05M sodium tungstate solution and 0.05M potassium iodate solution respectively in different volume ratios with intermittent shaking of the mixture and keeping the pH at 1.0 as given in table 1 and 2. The precipitates were filtered, washed with deionized water and dried. The exchangers were then converted in to the H<sup>+</sup> form by treating with 1M nitric acid for 24 hrs with occasional shaking and intermittent changing of acid. Then the samples were washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60-100 mesh.

### 3.1. Ion exchange capacity

The IEC of the material was determined by the column process [13]; 1.0 g of the exchanger (H<sup>+</sup> form) was packed in a glass column of 1.1cm diameter. The H<sup>+</sup> ions were eluted by adding 100ml of 1M sodium chloride solution. The effluent was collected and titrated against standard sodium hydroxide solution. The exchange capacity in meq/g was calculated using the formula:

$$IEC = \frac{av}{w}$$

Where 'a' is the molarity, 'v' is the volume of alkali used during titration and 'w' is the weight of the exchanger taken.

### 3.2. pH titration

Topp and Pepper method [14] was used for pH titration using NaOH/NaCl, KOH/KCl systems. 0.5g of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. After equilibrium the pH of each solution was measured and plotted against milliequivalents of OH<sup>-</sup> ions.

### 3.3. Chemical stability

The chemical stability of the exchanger was assessed in mineral acid like HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this 500mg of the exchanger was kept separately in 50ml of different solvents at room temperature for 24 hours. The change in colour and weight were noted.

### 3.4. Effect of temperature

The effect of temperature on ion exchange capacity was studied by heating several 1g sample of the exchanger at different temperatures for three hours in an air oven and Na<sup>+</sup> ion exchange capacity in meq g<sup>-1</sup> was determined by the column method after cooling them to room temperature.

### 3.5. Distribution studies (K<sub>d</sub>)

Distribution studies were carried out for various metal ions in demineralised water by batch process. In this process 100mg of the dry exchanger in H<sup>+</sup> form were equilibrated with 20ml of different metal ion solutions and kept for 24 hours at room temperature. The determination before and after equilibrium were carried out volumetrically using EDTA as the titrant. The K<sub>d</sub> values as depicted in Fig.7, were obtained by the formula:

$$K_d = \frac{I-F}{F} \times \frac{v}{w}$$

Where 'I' is the initial volume of EDTA used, 'F' is the final volume of EDTA used; 'V' is the volume of the metal ion solution and 'W' is the weight of the exchanger.

### 3.6. Binary separations

Separations of some metal ions of analytical utility were achieved on the column of the exchangers by knowing the effect of electrolyte concentration on distribution coefficients. This was studied by equilibrating known amount of exchanger with metal ion solution in electrolytes of varying concentrations (0.1 M, 0.01 M,

0.001 M  $\text{NH}_4\text{NO}_3$  (AN) and  $\text{HNO}_3$  (NA)). The column (30cm x 0.69cm internal diameter) on which the separations were to be carried out was filled uniformly with the exchanger (5g). First of all distilled water was added to pack the granules so that no air bubbles get stuck. Then the mixture of the metal ion solutions of concentration about 0.005 M (10 ml) was slowly added. The process was repeated for maximum sorption. The exchanged metal ions were eluted using suitable eluent. The rate of flow in all separations was 0.2 ml per minute. The concentration of metal ion in the solution was determined by collecting known volume of effluent at regular intervals. Binary separations were carried out on the column.

### 3.5. Recovery of lead from textile wastewater

Samples of waste water were collected from various textile industries. The waste water samples were filtered first to remove suspended particle and then neutralised. The solution was decolourised using charcoal. The samples thus obtained were used to separate and recover the heavy metal present in it. The ion exchange materials having greater selectivity towards lead metal ions were packed in a column, 100 ml of the sample was passed through the column and repeated 3-4 times using effluent collected at the bottom. This was for the maximum uptake of cations. The flow rate was maintained at 0.2ml per minute. Varying concentrations of  $\text{NH}_4\text{NO}_3$  and  $\text{HNO}_3$  as eluents were used to elute the metal ions completely from the cation exchanger column and then determined titrimetrically with standard EDTA solution.

### 3.6. Adsorption of dyes:

Aqueous solution of methyl orange (MO) and methylene blue (MB) (20 ml, 20ppm) were equilibrated separately with 300mg of exchanger for 24 h. The sample solutions were then filtered and centrifuged to remove the adsorbent prior to analysis. Absorbance was recorded before and after equilibration with a UV-Visible Diffuse Reflectance spectrometer at the absorption maximum of each dye (MO (463nm) and MB (665nm)).

## III. Results And Discussion

### 1. BiSbW and BiIW as inorganic cation exchange materials.

BiSbW and BiIW appear to be potential ion exchangers having good ion exchange capacity (IEC). Table 1&2 describes the preparation and properties of the materials. For BiSbW, sample BiSbW-6 and for BiIW, sample BiIW-4 were chosen for detailed studies due to their higher IEC and chemical stability.

The energy dispersive spectrometry (EDS) was used to identify the elements exist in the prepared sample by taking a selective portion of SEM image in the form of peaks of spectrum. The composition of the BiSbW and BiIW was found as Bi: Sb: W; 1:1.4:1.01 and Bi: I: W; 1.8: 1.4: 1

The pH titration curve (Fig. 1) shows that the ion exchange materials release  $\text{H}^+$  ions easily on addition of NaCl and KCl solution to the system in neutral medium, which is indicated by a pH value  $\sim 3.5$  of the solution. As the volume of NaOH added to the system is increased, more  $\text{OH}^-$  ions are consumed suggesting in the increase of the rate of ion exchange in basic medium due to the removal of  $\text{H}^+$  ions from the external solution. Further, the titration curve showed a bifunctional behavior of the exchangers. The IEC calculated from the titration curve is in close agreement to those obtained by the column method.

The effect of heating on IEC of BiSbW has been compared with that of similarly treated BiIW. It is apparent from Fig. 2 that even though the BiIW has the highest IEC, the retention of IEC was higher for BiSbW as the samples were dried at 50 °C and this trend follows up to 300 °C. This indicates the thermal stability of BiSbW as contrast to BiIW.

The materials were found to be stable in 1.0M HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and in 0.1M solutions of KOH and NaOH. The materials were also reasonably stable in organic solvents like methanol, ethanol, acetone, carbon tetrachloride, diethyl ether etc.

The TGA of BiSbW (Fig. 3a) indicates the presence of hydrated water which is lost up to 95°C. A gradual weight loss observed up to 370°C is due to the condensation of exchangeable hydroxyl groups which is the usual behavior of inorganic ion exchangers [15, 16]. After that no sharp change in weight indicates the stability of the compound. The total weight loss up to 900°C is only 13%.

The thermogram of BiIW (Fig. 3b) reveals some remarkable information. The external water molecules are lost up to 180 °C as indicated by the first weight loss of 7.74%. Further, a gradual loss of weight of Ion exchanger was attributed to the condensation of  $\text{IO}_3^-$  group in to  $\text{I}_2\text{O}_5$  [17, 18]. The decrease in IEC on increasing temperature is due to the conversion of  $\text{IO}_3^-$  into  $\text{I}_2\text{O}_5$ . Beyond 500 °C, the weight becomes constant owing to the formation of metal oxide.

To assist the advance characterization of the materials, their FTIR studies (Fig. 4) were performed at room temperature. The strong and broad band in the region 3600-3000  $\text{cm}^{-1}$  present in two materials may be assigned to interstitial water molecule and OH group [19, 20]. A weak band in the region 2360  $\text{cm}^{-1}$  common to both spectrums was due to deformation vibration of the coordinated water molecule. Another strong and sharp peak with maximum at 1619  $\text{cm}^{-1}$  may be due to H-O-H bending and band at 1383  $\text{cm}^{-1}$  was due to deformation

vibrations of metal hydroxyl groups and interstitial water. The spectrum also shows strong band in the region  $715\text{ cm}^{-1}$  indicating the presence of tungstate and other bands in the region  $800\text{-}420\text{ cm}^{-1}$  was attributed to metal oxygen vibrations [21-23].

X-ray diffraction pattern of BiSbW and BiIW in  $\text{H}^+$  form reveals the fact that the exchangers are amorphous (Fig. 5).

SEM images of BiSbW and BiIW (Fig. 6) reveal that the particles having an irregular shape and there is no sign of crystalline structure and these observations strongly support the amorphous nature of the materials.

Distribution studies of metal ions (Fig. 7) were carried out individually with the samples. Sorption of ions was found to be varied in different samples of exchanger. The distribution studies showed that the materials were found to possess exceptional high  $K_d$  values for  $\text{Pb}^{2+}$  and hence considered to be highly selective for  $\text{Pb}^{2+}$ . Pb(II) has been considered as a major polluting material in water. The separation capacity of these materials has been demonstrated by achieving some important binary separations such as Pb(II)-Hg(II) and Pb(II)- Ni(II) effectively.

In order to select suitable eluents for each metal ion, distribution studies were carried out in different electrolytes. Varying molar concentrations of ammonium nitrate (AN) and nitric acid (NA) were used for this study. No significant sorption for Hg(II) and Ni(II) ions was noted in these electrolytes. Sorption of Pb(II) ions was found to be varied in different electrolyte solutions (Fig. 8). Table 3&4 summarizes the salient features of these separations. The separations are rather sharp and recovery is quantitative and reproducible.

Distribution coefficient ( $K_d$ ) values were used as a measure of the selectivity of the materials for lead metal ions. The selectivity determines how competently the element of concern is separated from other elements. In order to reveal the practical usefulness of the material, quantitative separations of Pb(II) from textile industry effluents have been achieved using BiIW and BiSbW (table 5).

## 2. BiSbW and BiIW as efficient dye adsorbents

Again the analytical applications of the materials were studied by controlling the hazardous organic pollutants in waste water by adsorption of Methylene blue and methyl orange on these ion exchange surfaces. UV-Visible absorption spectrum of methyl orange and methylene blue before and after equilibration with the sorbents are shown in Fig. 9. The drastic change in the intensity of each peak at absorption maxima reveals the effectiveness of the adsorbents for removing these dyes from aqueous solution. Greater than 95% of Methylene blue and 80% of Methyl orange dyes were removed within 24 hours under stationary conditions. Since BiIW and BiSbW hold structural hydroxyl group, the dyes could be bond to the sorbents with hydrogen bonds or weak Van der Waal's forces. The high adsorption for methylene blue could be due to the positive charge on the hetero atom. Even small changes in the dye structure can significantly influence its adsorption capacity. In the spectrum of MO, the absorption maxima was shifted to higher wavelength region due to the change in pH of dye solution by the addition of weak acidic cation exchanger. The efficiency of BiIW and BiSbW towards removal of methyl orange and methylene blue from aqueous solution indicates their promising use in waste water containing dyes. Table 6 illustrates the experimental and calculated data for the removal of MB and MO from synthetic wastewater.

## IV. FIGURES AND TABLES

Table-1 Conditions of synthesis and properties of different samples of Bismuth(III) antimonotungstate

sample	Molar conc.(M)			Volume mixing ratio	pH	Appearance	I.E.C(meq/g)
	Bi	Sb	W				
BiSbW1	0.05	0.05	0.05	1:1:1	1	All forms white solids	0.57
BiSbW2	0.05	0.05	0.05	1:2:1	1		0.55
BiSbW3	0.05	0.05	0.05	1:1:2	1		0.77
BiSbW4	0.05	0.05	0.05	1:1:3	1		0.70
BiSbW5	0.05	0.05	0.05	1:3:1	1		0.82
BiSbW6	0.05	0.05	0.05	1:2:3	1		0.85

Table-2 Conditions of synthesis and properties of different samples of Bismuth(III) iodotungstate

sample	Molar conc.(M)			Volume mixing ratio	pH	Appearance	I.E.C(meq/g)
	Bi	I	W				
BiIW1	0.05	0.05	0.05	1:1:1	1	All forms white solids	1.75
BiIW2	0.05	0.05	0.05	1:2:1	1		1.01
BiIW3	0.05	0.05	0.05	1:1:2	1		0.85
BiIW4	0.05	0.05	0.05	1:1:3	1		2.25
BiIW5	0.05	0.05	0.05	1:3:1	1		0.98
BiIW6	0.05	0.05	0.05	1:2:3	1		1.25

Table-3 Binary separation of metal ions on Bismuth iodotungstate

Separations achieved	Separation factor	Eluent	Metal ion(mg)		% efficiency
			Loaded	Eluted	
Hg(II)	26.32	0.01M AN	5.01	4.87	97.21
Pb(II)		1M NA+0.1M AN	4.04	3.91	96.78
Ni(II)	75.91	0.01M AN	1.39	1.34	96.40
Pb(II)		1M NA+0.1M AN	4.04	3.98	98.51

Table-4 Binary separation of metal ions on Bismuth antimonotungstate

Separations achieved	Separation factor	Eluent	Metal ion(mg)		% efficiency
			Loaded	Eluted	
Hg(II)	141.89	0.01M AN	5.01	4.42	88.23
Pb(II)		1M NA+0.1M AN	4.04	3.65	90.34
Ni(II)	11.25	0.01M AN	1.39	1.24	87.05
Pb(II)		1M NA+0.1M AN	4.04	3.53	87.62

Table-5 Removal of Pb(II) from textile industry effluents

Metal Ion	BiIW Column			BiSbW Column	
	Initial Conc.(mg)	Final Conc.(mg)	% Removal	Final Conc.(mg)	% Removal
Pb(II)	2.56	0.61	76.17	0.76	70.31

Table-6 Efficiency of synthesized materials as dye adsorbents

Dye solution	pH(initial)	% of removal on BiIW	% of removal on BiSbI
MB	6.0	98.76	95.60
MO	7.0	88.82	82.02

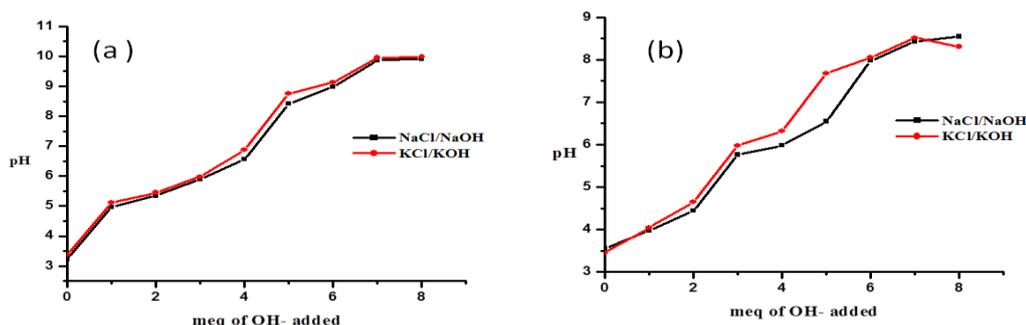


Figure-1. pH titration curves of (a) : BiSbW and (b): BiIW

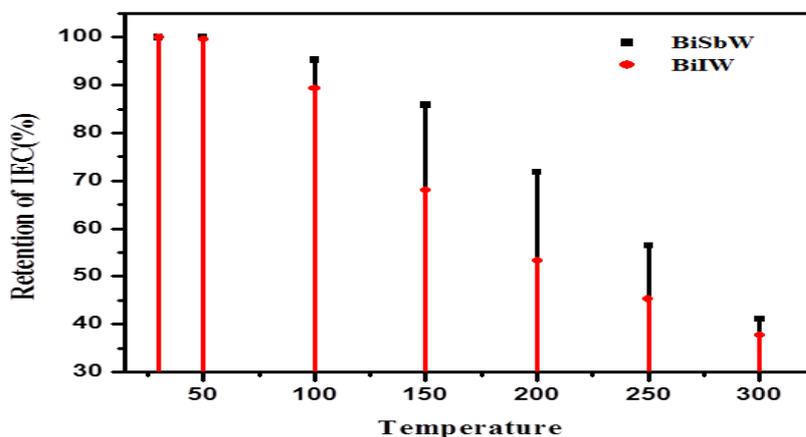


Figure-2. Effect of temperature on IEC

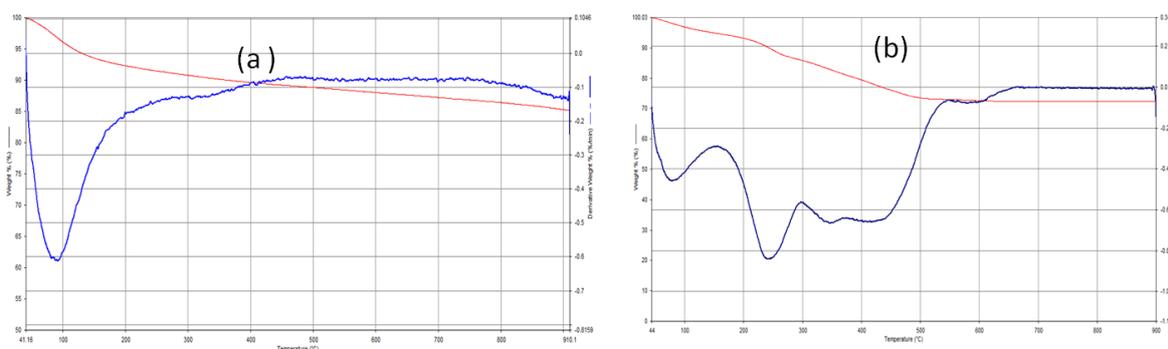


Figure-3. TG/DT analysis of the samples (a): BiSbW (b): BiIW

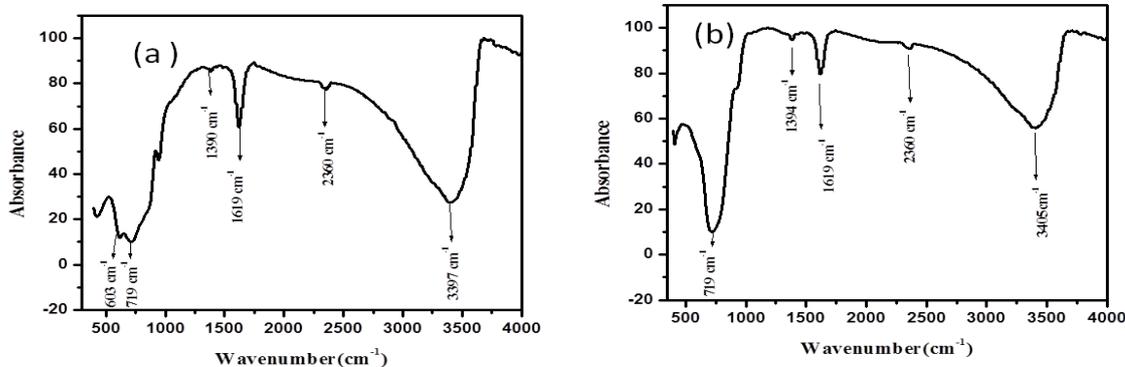


Figure-4. FTIR spectrum of (a) BiSbW and (b) BiIW

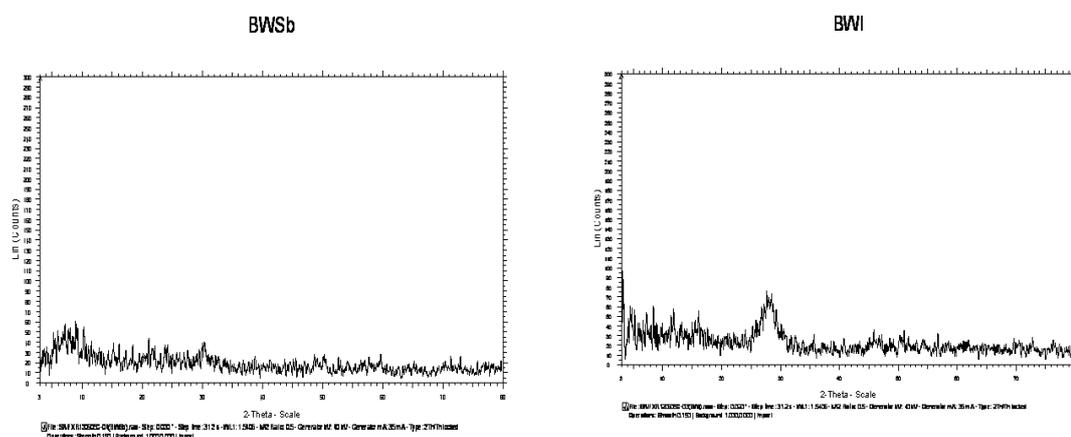
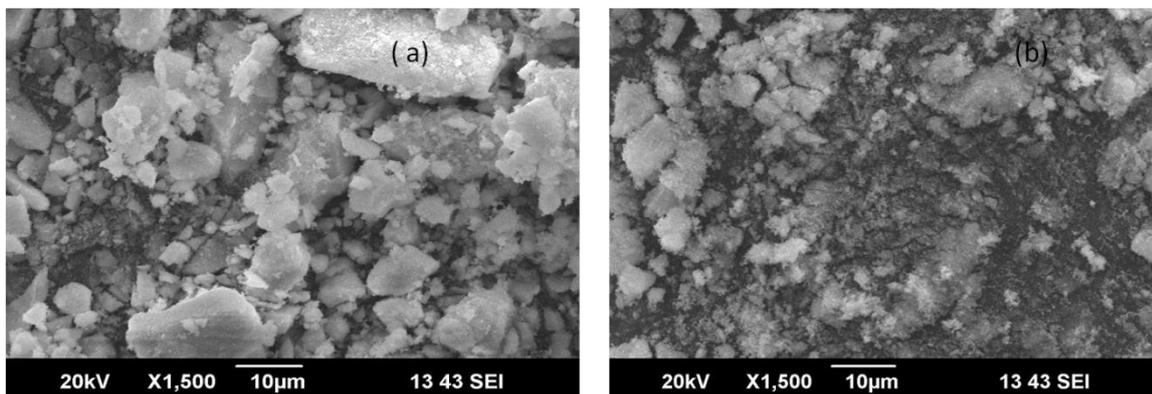
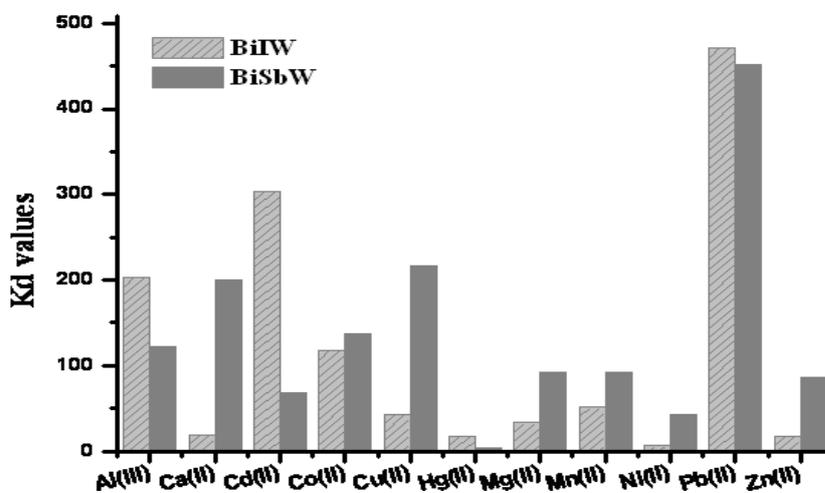


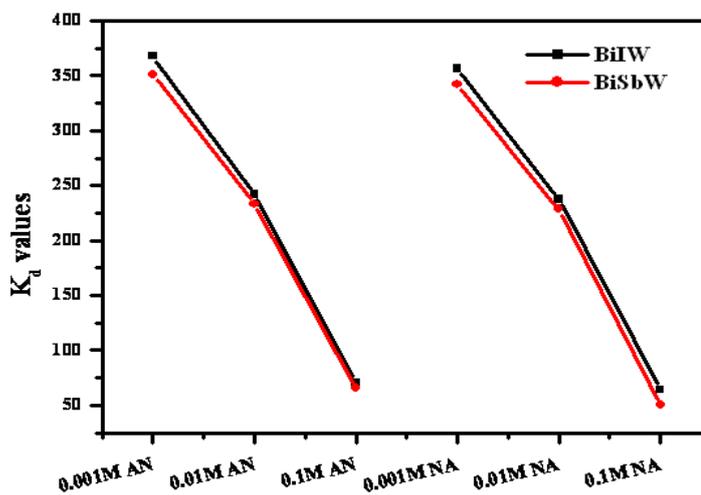
Figure-5. X- ray analysis



**Figure-6.** SEM images of (a): BiSbW and (b): BiIW



**Figure-7.** Distribution studies



**Figure-8.** K<sub>d</sub> values of Pb<sup>2+</sup> ions in different electrolyte concentration (AN: Ammonium nitrate, NA: Nitric acid)

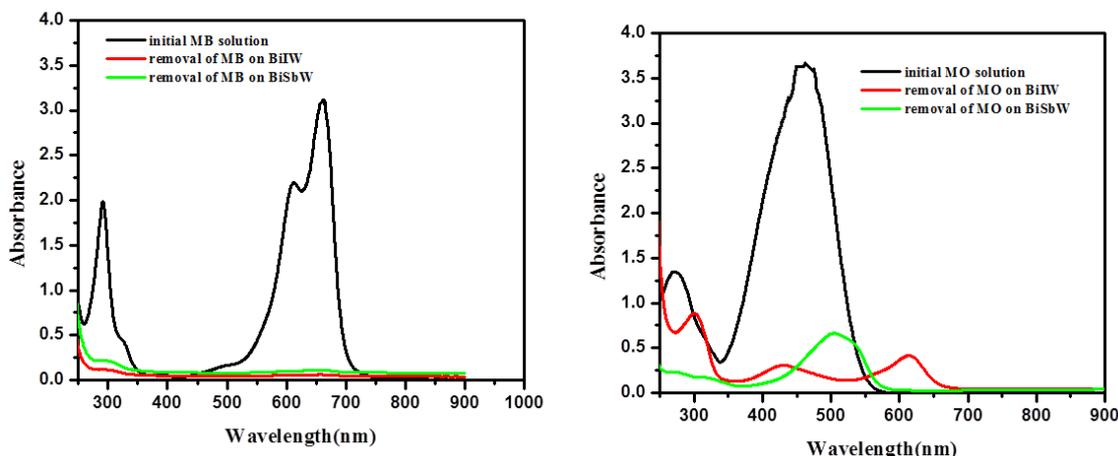


Figure-9. UV-Vis DR spectrum of dye adsorption studies.

## V. Conclusion

BiSbW and BiIW exhibit good ion exchange characteristics, thermal stability and chemical resistivity. The promising feature of these materials is their selectivity for Pb(II) ions, most toxic metal ions present in environment. Their analytical importance has been established by separating lead ions from Pb(II)-Hg(II) and Pb(II)-Ni(II) binary metal ion solutions. Moreover these materials can be used as successful adsorbents for the removal of harmful organic dyes such as MB and MO from aqueous solution.

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