



## Efficiency of newly synthesized ion exchangers, zirconium bismuth tungstate and its poly-o-toluidine composite in environmental waste remediation- a comparative study

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### ABSTRACT

In this work, a comparative study of the potential application of two highly efficient ion exchange materials, Zirconium bismuth tungstate (ZBW) and its composite Poly-o-toluidine zirconium bismuth tungstate (POT-ZBW) for the remediation of toxic metal ions and methyl red (MR) dye from aqueous solution has been investigated. The synthesized exchangers were characterized by some physicochemical properties like FTIR, XRD, TGA-DTA and ion exchange properties to validate the structure and ion exchange behavior. Surface morphology can be determined through SEM analysis. The composite exchanger show high  $\text{Na}^+$  ion exchange capacity than its inorganic precipitate. The distribution studies of various metal ions showed that ZBW and POT-ZBW were highly selective for  $\text{Pb}^{2+}$  and  $\text{Th}^{4+}$ . The analytical application has been explored by achieving some binary separation of heavy metal ions such as  $\text{Pb}^{2+}$ - $\text{Hg}^{2+}$ ,  $\text{Th}^{4+}$ - $\text{Al}^{3+}$ ,  $\text{Th}^{4+}$ - $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ - $\text{Mn}^{2+}$  etc. Practical applicability of the material tested in industrial wastewaters indicate that they be used successfully in the separation of toxic heavy metal ions. In order to explore the environmental applicability of the newly synthesized ion exchangers, their adsorption potential towards methyl red dye was studied. The entire studies revealed that the novel exchangers are effective adsorbents for the removal of toxic pollutants from aqueous solution. © 2015 Trade Science Inc. - INDIA

### KEYWORDS

Composite ion exchanger;  
Distribution studies;  
Binary separation;  
Heavy metal ions;  
Dye sorption etc.

### INTRODUCTION

Extensive use of metals, chemicals, natural and artificial materials in manufacturing sector with ineffective treatment of effluent has led to generation of various levels of toxic heavy metals such as Lead, Copper, Zinc, Iron, Nickel, Arsenic, Cobalt, Mer-

cury, Cadmium, Chromium etc., into the environment<sup>[1-5]</sup>. Electroplating, painting, metallurgical, mining, textile, municipal incineration and chemical manufacturing industries all generate toxic heavy metals of various levels<sup>[6,7]</sup>. The discharge of textile effluents to the water bodies has raised much concern because of potential health hazards associated

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with the entry of toxic components into the food chains of humans and animals. Synthetic dyes are extensively used for dyeing and printing in a variety of industries. Methyl Red (MR) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products; however, it may cause eye and skin sensitization<sup>[8]</sup> and pharyngeal or digestive tract irritation if inhaled or swallowed<sup>[9]</sup>. Furthermore, MR is mutagenic under aerobic conditions: it undergoes biotransformation into 2-aminobenzoic acid and N-N'-dimethyl-p-phenylene<sup>[10]</sup>.

Ion exchange 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<sup>[11-13]</sup>. Application of selective inorganic ion exchangers is a known way for recovery of heavy metals as they exhibit high affinities for specific ions<sup>[14-15]</sup>. Zirconium based ion exchangers have received attention because of their excellent ion exchange behavior, stability and some important chemical applications in the field of ion exchange, ion exchange membrane and solid-state electrochemistry<sup>[16]</sup>. Composite materials are also attractive for the purpose of creating high performance that are expected to provide many possibilities, termed as 'organic-inorganic' hybrid ion-exchangers<sup>[17-21]</sup> with better chemical, mechanical, and thermal stabilities, reproducibility and possessing good selectivity for heavy metals indicating its useful environmental applications.

In this manuscript, we describe the synthesis and ion exchange properties of two new inorganic ion exchange materials, Zirconium bismuth tungstate and

its composite exchanger poly-o-toluidine zirconium bismuth tungstate. A comparative study of potentialities of the synthesized materials as sorbents for the removal of toxic metal ions and hazardous organic dyes from waste waters has been the focus of this work.

## EXPERIMENTAL

### Reagents and chemicals

Bismuth nitrate, zirconium oxy chloride, sodium tungstate and o-toluidine were obtained from E.Merck (India). All other chemicals and reagents used were of analytical grade.

### 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

## EXPERIMENTAL

### Reagents and chemicals

Different samples of ZBW were prepared by adding 0.05M sodium tungstate solution to a mixture of 0.05M zirconium oxy chloride solution and 0.05M bismuth nitrate solution in different volume

TABLE 1 : Synthesis and properties of various samples of ZBW

Sample	Volume ratios	pH	Appearance	IEC (meq/g)
	Zr : Bi : W			
ZBW-1	1 1 1	1		0.65
ZBW-2	1 1 2	1		0.79
ZBW-3	1 1 3	1	All	0.92
ZBW-4	1 2 1	1	White	0.66
ZBW-5	2 1 3	1	solids	0.69
ZBW-6	1 2 3	1		0.76

ratios with intermittent shaking of the mixture and keeping the pH at 1.0 as given in TABLE 1. The precipitates were filtered, washed with deionized water and dried. The white coloured precipitate formed was kept for digestion for 24 hours at room temperature.

### Synthesis of poly-o-toluidine

Poly-o-toluidine was prepared by mixing similar volume ratios of 0.4 M ammonium persulfate prepared in 4.0 M HCl into 10% o-toluidine prepared in 2.0 M HCl with continuous stirring by a magnetic stirrer for 2 hours at 0 °C; a green colored gel was obtained. The gel was kept for 24 hours at 0 °C<sup>[22]</sup>.

### Synthesis of POT-ZBW

The synthesis of Poly-o-toluidine zirconium bismuth tungstate composite was carried out by simple stirring process. The ex-situ polymerised gels of poly-o-toluidine were added to the white inorganic precipitate of zirconium bismuth tungstate and mixed thoroughly with constant stirring resulting in the formation of green colored slurry. The green colored slurry was kept for digestion at room temperature for 24 hours. The supernatant liquid was decanted and the gel was filtered. The excess acid was removed by washing with demineralised water (DMW) and the material was dried in an air oven at 30 °C. The dried products were immersed in DMW to obtain small granules. They were converted to H<sup>+</sup> form by treating with 1.0 M HNO<sub>3</sub> for 24 hours with occasional shaking, intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed with DMW and then dried at 30 °C and was kept in desiccator.

## CHARACTERISATION OF THE EXCHANGERS

### Column ion-exchange capacity and thermal effect on ion exchange capacity

The IEC of the material was determined by the column process<sup>[23]</sup>; 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.

In order to determine the effect of heating temperature on ion exchange capacity, 1g sample of the exchanger in H<sup>+</sup> form was heated at different temperatures for one hour 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.

### 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.

### pH titration

Topp and Pepper method<sup>[24]</sup> 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.

### Adsorption (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 Figure 6, 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

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the final volume of EDTA used; 'V' is the volume of the metal ion solution and 'W' is the weight of the exchanger.

### Quantitative separation of metal ions from synthetic binary mixtures

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  $\text{NH}_4\text{NO}_3$  and  $\text{HNO}_3$ ). 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.

### Quantitative separation of metal ions from industrial waste water

Industrial wastewater was collected from textile industry and phosphate fertilizer plant. Samples were first filtered to remove any solid particles and then it was neutralised. The colour producing substances were removed by adsorption using charcoal. The samples were chemically treated for the detection and separation of any heavy element present. The granular ion exchanger having greater selectivity towards heavy metals were packed in a column, 100 ml of the sample was passed through the column. The flow rate was maintained at 0.3-0.5 mL/min. Finally the ions were separated using eluents and determined quantitatively.

### Adsorption of methyl red (MR):

Aqueous solution of methyl red (MR) (20 ml, 40 ppm) were equilibrated with 200mg of exchang-

ers for 24 h. The sample solutions were then filtered and centrifuged to remove the adsorbent prior to analysis. The dye concentration was analyzed by monitoring the absorbance of the dye before and after attainment of equilibrium with the exchangers using UV-Vis Spectrophotometer (UV-1800 Shimadzu, Japan) at a wavelength of 521 nm. The percentage of removal of dyes was calculated using the following formula:

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100$$

Where,  $C_i$  is the initial dye concentration and  $C_e$  is the equilibrium dye concentration in  $\text{mgL}^{-1}$ .

## RESULTS AND DISCUSSION

### Synthesis and characterization of exchangers

Zirconium bismuth tungstate samples of different composition were synthesized and ion exchange capacity was determined (TABLE-1). On increasing the ratio of anionic part (sodium tungstate) in the reaction mixture enhances the ion exchange capacity as the replaceable hydrogen/ ionogenic groups are attached to the  $\text{WO}_4^-$  group whereas an increase in the cationic part did not show any appreciable change in the ion exchange capacity. Among these the sample, ZBW-1, having maximum IEC ( $0.92\text{meqg}^{-1}$ ) was selected and was tried to incorporate in to the polymeric matrix of poly-o-toluidine. Analysis of IEC of composite material reveals that it shows higher IEC ( $1.12\text{meq/g}$ ) than its inorganic counterpart, may be due to more number of freely movable  $\text{H}^+$  ions and  $\text{H}_2\text{O}$  molecules situated in the cavities of the polymeric matrix.

Ion exchange capacity of the material was also affected by heating. On heating at different temperatures for 1 hour, the ion exchange capacity and physical appearance of the dried sample were changed as the temperature increased (TABLE 2). The material ZBW was found thermally stable up to  $600^\circ\text{C}$  as the sample retained 57% of its initial ion exchange capacity without any change in its color and appearance whereas in the case of its poly-o-toluidine composite, only 51% of initial capacity was retained up to  $600^\circ\text{C}$  even though its ion exchange capacity was higher than those of ZBW. Decrease in ion exchange

TABLE 2 : Effect of temperature on IEC

Temperature ( $^{\circ}$ C)	ZBW			POT-ZBW		
	Appearance	IEC (meq/g)	Retention of IEC (%)	Appearance	IEC (meq/g)	Retention of IEC (%)
100	White	0.92	100	Dark green	1.12	100
200	White	0.87	94.56	Dark green	1.08	96.43
300	White	0.80	86.96	Dark green	0.96	85.71
400	White	0.74	80.43	Dark green	0.89	79.46
500	Grey	0.62	67.39	Black	0.71	63.39
600	Dark grey	0.53	57.61	Black	0.57	50.89

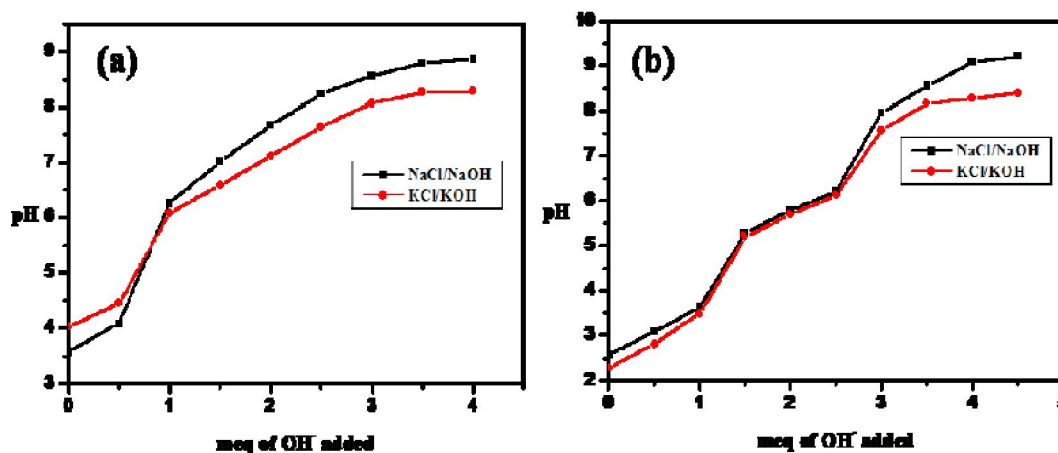


Figure 1: pH titration curves of (a) ZBW and (b) POT-ZBW

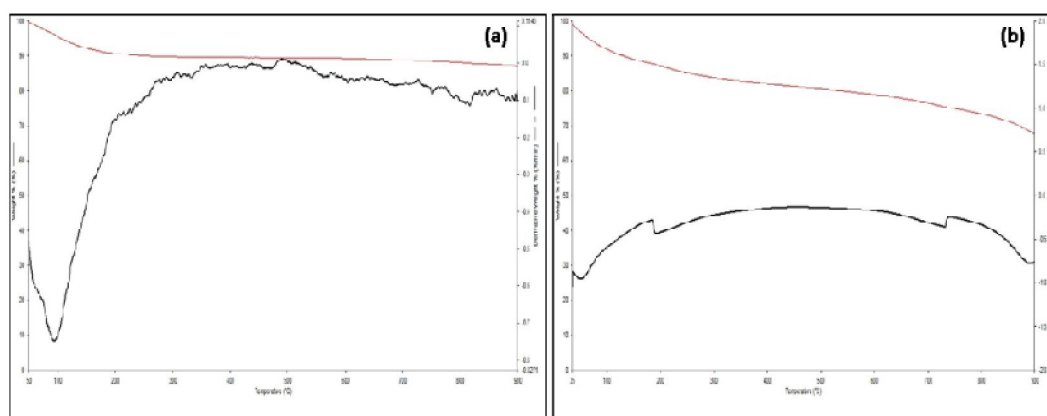


Figure 2: Thermal analysis of (a) ZBW and (b) POT-ZBW

capacity with increasing temperature is attributed to the condensation of structural hydroxyl groups.

The materials were found to be quite stable in different concentrations of mineral acids such as 10 M  $\text{HNO}_3$ , 5.0M  $\text{H}_2\text{SO}_4$  and 12 M  $\text{HCl}$ , 0.05M solutions of bases and organic solvents like ethanol, acetone,  $\text{CCl}_4$ , DMSO, DMF etc.

pH titration curves of ZBW and POT-ZBW were shown in Figure 1(a) and 1(b), reveals that the functionality of the material changed from monofunctional to bifunctional when poly-o-toluidine composite is

formed by the encapsulation of organic part to the matrix of inorganic precipitate which contains only one ionogenic group. The ion exchange capacities obtained from the curves are in agreement with that obtained from the column method.

Thermograms of the synthesized materials were shown in Figure 2(a) and 2(b). thermogram of ZBW shows 8% weight loss due to the evaporation of external water molecules and condensation of structural hydroxyl groups. The endothermic peak at  $100^{\circ}\text{C}$  confirms the evaporation of external water mol-

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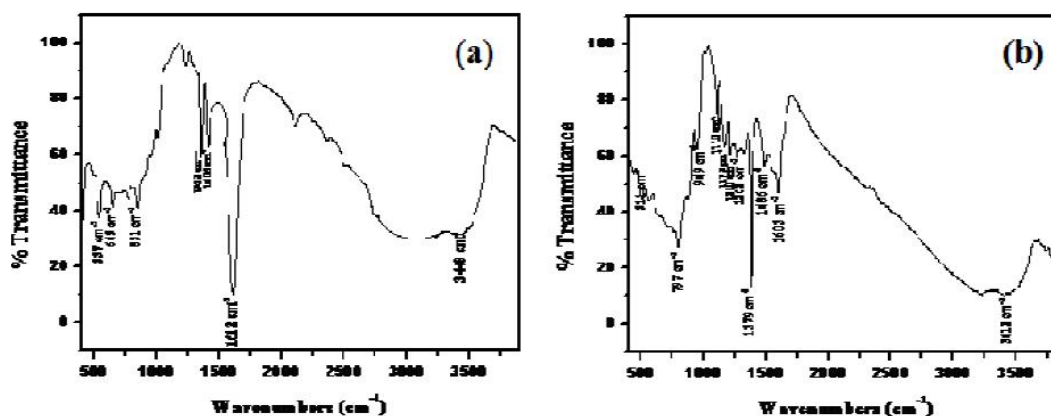


Figure 3 : FTIR Spectra of (a) ZBW and (b) POT-ZBW

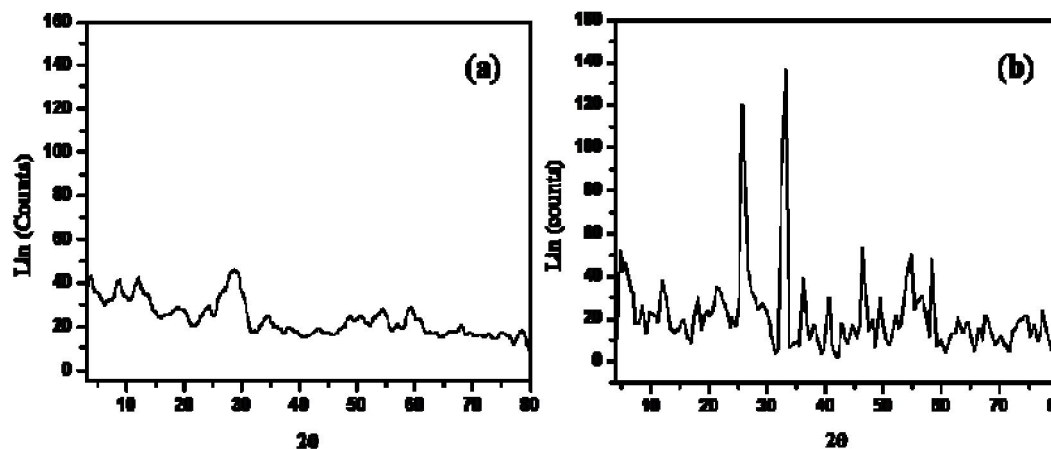


Figure 4 : XRD patterns of (a) ZBW and (b) POT-ZBW

ecules. Above this temperature, the material is almost stable up to 900°C as the sample retained 87% of its initial weight at this temperature. Figure 3 (b) illustrates that weight loss of about 9% up to 100°C, due to the evaporation of external water molecules. The decrease in weight observed up to 338°C may be due to the elimination of interstitial water molecules. The sample retained 68% of its original weight till the temperature reaches 900°C. This clearly reveals that the materials were quite stable at high temperatures and can be used in high temperature applications.

FTIR spectrum of ZBW (Figure 3(a)) shows a broad band in the region 3200–3500 $\text{cm}^{-1}$  and a sharp peak at 1612  $\text{cm}^{-1}$ , justify the presence of -OH stretching and bending modes. The sharp bands at 1406  $\text{cm}^{-1}$  and 1362  $\text{cm}^{-1}$  are attributed to the presence of W-O bond. The bands observed in the region 851–537  $\text{cm}^{-1}$  is due to the symmetric and asymmetric stretching of M-O-H bond<sup>[25]</sup>. The peak values of FTIR spectra (Figure 3(b)) of POT-ZBW in-

dicate that the band centered at 3412  $\text{cm}^{-1}$  shows the characteristics of free N-H stretching vibrations<sup>[26]</sup>. An assembly of bands in the region 1379–1600  $\text{cm}^{-1}$  may be ascribed to the stretching vibration frequency of C-N bonds. The band at 1173  $\text{cm}^{-1}$  indicated the presence of C-H group in semiquinoid ring and the band at 1110  $\text{cm}^{-1}$  is attributed to the presence of C-C methyl substituted semiquinoid and quinoid rings<sup>[27]</sup>. A sharp band at 797  $\text{cm}^{-1}$  shows the presence of para substituted aromatic rings, indicating polymer formation. Other characteristic bands associated with inorganic precipitate are reflected with slight shift in the composite material. The spectra give evidence for the formation of POT-ZBW composite material.

The XRD patterns provide significant informations in relation to the nature and size of the sample. The X-Ray diffraction patterns of inorganic precipitate and its poly-o-toluidine composite were shown in Figure 4(a) and 4(b). XRD pattern of ZBW sample shows an amorphous nature whereas the XRD pat-

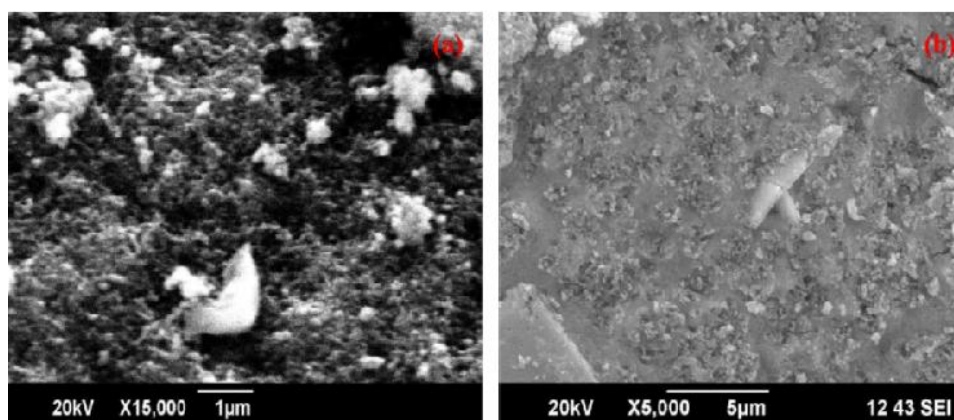


Figure 5 : SEM images of (a) ZBW and (b) POT-ZBW

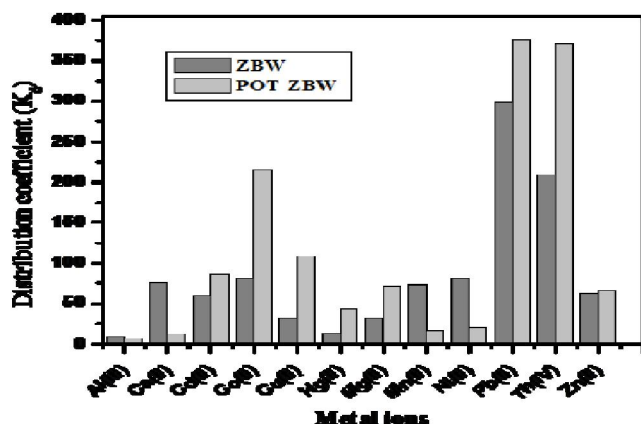


Figure 6 : Distribution studies of various metal ions in DMW on ZBW and POT-ZBW

tern of POT-ZBW shows two sharp intensity peaks at around  $25^\circ$  and  $33^\circ$  and a number of small peaks, signifying the crystalline nature of the composite material. The crystalline size of the material is estimated from the peak width (FWHM) using Scherrer's formula<sup>[28]</sup>;

$$D = \frac{K\lambda}{\beta_{2\theta} \cos \epsilon}$$

Where,  $\lambda$  is the X-Ray wave length,  $K$  is the Scherrer's constant of the order of unity for usual crystals (here  $K = 0.9$ ),  $\beta_{2\theta}$  is full width at half maximum (FWHM) of a diffraction peak and  $\epsilon$  is the diffraction angle. The average crystalline size of the sample was found to be 22.034 nm. Hence XRD studies expose that formation of composite from inorganic precipitate leads to change in crystallinity from amorphous to nanocrystalline.

The scanning electron micrograph (SEM) of ZBW and POT-ZBW were represented in Figure 5 (a) and 5 (b). It is clear from the photographs that after the formation of poly-o-toluidine composite

with inorganic precipitate of ZBW, the morphology of the material has been changed.

Even though SEM images of the samples show granular nature which makes it suitable for column operations. Porous nature increases the surface area.

In order to explore the potentiality of the synthesized exchangers in the separation of metal ions, distribution studies of different metal ions were performed in DMW. It is apparent from the figure that both the exchangers are highly selective for  $Pb^{2+}$  and  $Th^{4+}$ , have been painstaking as the key pollutants in water. The order of selectivity of the studied metal ions was depicted in Figure 6.

### Quantitative separation of metal ions from synthetic binary mixtures

The difference in the  $K_d$  values of metal ions indicated the separation possibilities of certain metal ions of analytical importance and which has been demonstrated by achieving some difficult binary separations (TABLE 3 and 4) such as  $Hg^{2+}$ - $Pb^{2+}$  and  $Al^{3+}$ - $Th^{4+}$  on ZBW and  $Mn^{2+}$ - $Pb^{2+}$  and  $Ni^{2+}$ - $Th^{4+}$  on POT-ZBW. The separation was based on sequential elution of ions through the column using different eluting agents such as  $NH_4NO_3$  and  $HNO_3$ . The sequential elution of ions from the column depends up-on the stability of metal-eluting ligand. The weakly retained metal ions eluted first and the stronger one at the last. The separation was quite sharp and recovery was quantitative and reproducible.

### Quantitative separation of metal ions from industrial wastewater

The specificity of ZBW and POT-ZBW towards

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TABLE 3 : Quantitative separation of metal ions on ZBW

Separations achieved	Separation factor	Eluent	Metal ion (mg)		% Efficiency
			Loaded	Eluted	
Hg <sup>2+</sup>	22.06	0.01M HNO <sub>3</sub>	5.01	4.78	95.41
Pb <sup>2+</sup>		0.4M HNO <sub>3</sub> + 0.4M NH <sub>4</sub> NO <sub>3</sub>	5.15	4.97	96.50
Al <sup>3+</sup>	24.28	0.01M HNO <sub>3</sub>	1.67	1.52	91.02
Th <sup>4+</sup>		0.4M HNO <sub>3</sub> + 0.4M NH <sub>4</sub> NO <sub>3</sub>	5.80	5.62	96.89

TABLE 4 : Quantitative separation of metal ions on POT-ZBW

Separations achieved	Separation factor	Eluent	Metal ion (mg)		% Efficiency
			Loaded	Eluted	
Mn <sup>2+</sup>	18.54	0.01M HNO <sub>3</sub>	1.37	1.32	96.35
Pb <sup>2+</sup>		0.4M HNO <sub>3</sub> + 0.4M NH <sub>4</sub> NO <sub>3</sub>	5.15	5.01	97.28
Ni <sup>2+</sup>	22.79	0.01M HNO <sub>3</sub>	1.46	1.38	94.52
Th <sup>4+</sup>		0.4M HNO <sub>3</sub> + 0.4M NH <sub>4</sub> NO <sub>3</sub>	5.80	5.69	98.10

TABLE 5 : Quantitative separation of metal ions from industrial wastewater effluents

Sample	Metal ions	Conc. of metal ion in water sample loaded (mg)	On ZBW column		On POT-ZBW column	
			Estimated conc. of metal ion eluted (mg)	Removal %	Estimated conc. of metal ion eluted(mg)	Removal %
Paint industry effluents	Pb <sup>2+</sup>	2.87	0.82	71.43	0.59	79.44
Phosphate fertilizer plant	Th <sup>4+</sup>	1.94	0.59	69.59	0.48	75.26

lead and thorium was the promising feature of the materials, as lead and thorium are the key pollutants in the environment. In order to demonstrate the practical utility of the materials, quantitative separations of lead from paint industry effluents and thorium from phosphate fertilizer plant have been achieved on the materials (TABLE 5). Results tabulated showed that the poly-o-toluidine composite is more efficient than the inorganic precipitate in removing these metal ions from industrial wastewater.

### REMOVAL OF METHYL RED (MR) DYE

Another important applicability of the synthesized materials in environmental remediation was achieved by the removal of hazardous organic dye methyl red from aqueous solutions. Both the exchangers have the ability to adsorb methyl red dye on their surfaces and the adsorption experiments are studied with the help of UV-Visible Diffuse Reflectance Spectrophotometer. The absorption spectrum of methyl red before and after attainment of equilibrium with the exchangers was shown in Figure 7. The ef-

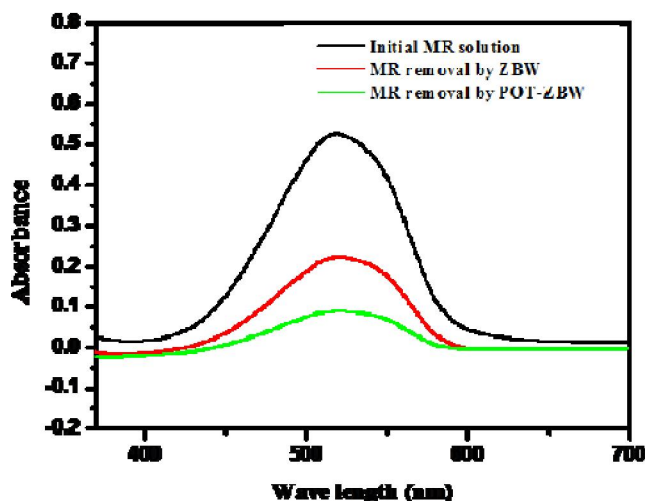


Figure 7 : Absorption spectra of MR on ZBW and POT-ZBW

fectiveness of the exchangers in removing MR from aqueous solution was confirmed by the drastic change in intensity of original peak at absorption maxima.

From figure it is observed that greater than 83% of MR is removed by POT-ZBW within 24 hours under normal conditions. Where as about 58 % of initial MR only is removed by ZBW under the same



conditions. This indicates that the composite poly-o-toluidine was more effective in removing organic dyes from aqueous solution than its inorganic precipitate. However both the exchangers are applicable in wastewater treatment for the removal of organic pollutants.

## CONCLUSION

Two new ion exchangers zirconium bismuth tungstate and its composite poly-o-toluidine zirconium bismuth tungstate were synthesized and were characterized. The poly-o-toluidine composite exhibits good ion exchange properties in comparison with the inorganic precipitate.

The physico-chemical characterizations revealed its nano crystalline nature. Since both the exchangers are selective for lead and thorium, these metal ions were quantitatively separated from synthetic binary mixtures and also from industrial wastewaters. UV-Visible DRS studies on methyl red adsorption enhances the environmental applicability of the synthesized materials towards waste remediation. Over all studies reveal that the composite ion exchanger is the most efficient adsorbent for environmental remediation than its inorganic counter part.

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## REFERENCES

- [1] K.K.Aradhi, M.Satyanarayanan, K.G.Pradip; *J. Hazard. Mater.*, **167**, 366 (2009).
- [2] A.Kaushik, Ankur Kansal, Santosh, Meena, Shivkumari, C.P.Kaushik; *J. Hazard. Mater.*, **164**, 265 (2009).
- [3] E.Moreno-Jimenez, J.M.Penalosa, R.Manzano, R.O.Carbena-Ruiz, R.Gamarra, and E.Esteban; *J.Hazard.Mater.*, **162**, 854 (2009).
- [4] C.Vijayanand,P.Rajaguru, K.Kalaiselvi, K.P.Selvam, M.Palanivel; *J.Hazard Mater.*, **160**, 548 (2008).
- [5] J.Pizarro, P.M.Vergara, J.A.Rodriguez, A.M.Valenzula; *J.Hazard.Mater.*, **181**, 747(2010).
- [6] S.Davydova; *Microchem.J.*, **1**, 133 (2005).
- [7] P.Xia, X.Meng, P.Yin, Z.Cao, X.Wang; *Environ. Pollut.*, **159**, 92 (2011).
- [8] B.B.Hayes, S.Azadi, R.R.Sullivan, B.J.Meade; *J.Allergy Clin.Immunol.*, **113**, S57 (2004).
- [9] Y.Badar, M.G.A El-Wahed, M.A Mahmoud; *J.Hazard.Mater.*, **154**, 245 (2008).
- [10] K.T.Chung, G.E.Fulk, A.W.Andrews; *Applied Environ.Microbiol.*, **42**, 641 (1981).
- [11] C.B.Amphlett; 'Treatment and Disposal of Radioactive Wastes'; Pergamon; Oxford (1961).
- [12] C.Janardanan, S.M.K.Nair; *The Analyst*, **115**, 85 (1990).
- [13] Mu.Naushad; *Ion Exchange Letters*, **2**, 1 (2009).
- [14] A.P.Gupta, G.L.Verma, Saiqa Ikram; *React. Funct.Polym.*, **43**, 33 (2000).
- [15] A.Nilchi, A.Khanchi, M.Ghanadi Maragheh; *Talanta*, **56**, 383 (2002).
- [16] A.S.Weqar, A.K.Shakeel; *Bull.Mater. Sci.*, **30**, 43 (2007).
- [17] Y.Chujo; *Cur.Opin.Solid State Mater.Sci.*, **1**, 806 (1996).
- [18] C.Sanchez, F.Ribot; *New J.Chem.*, **16**, 1007 (1994).
- [19] P.Judeinstein, C.Sanchez; *Chem.*, **6**, 511 (1996).
- [20] J.E.Mark, C.Y.Lee, P.A.Bianconi; Editors, Hybrid organic-inorganic composites, Washington, American Chem.Soc.Symp.Seri, 565 (1995).
- [21] J.C.Douglas, H.Douglas, J.H.Pamela, P.H.Robert, L.Robert, C.H.Robert, J.Zubieta; *Coordination Chem.Rev.*, **737**, 190 (1999).
- [22] Xin-Gui Li, Hung Mei-Rong., Liu Rui, *React.Funct.Polym.*, **63**, 285 (2005).
- [23] O.Samuelson; 'Ion exchangers in analytical chemistry'; Wiley, **45&117** (1952).
- [24] N.E.Topp, K.W.Pepper; *J.Chem.Soc.*, 3299 (1949).
- [25] K.V.Nimisha, Aparna Mohan; *C.Janardanan; Res.J.Rec.Sci.*, **3**, 1 (2014).
- [26] Xin-Guili, M.R.Hung, R.Liu; *React.Funct.Polym.*, **2**, 285 (2005).
- [27] K.M.Zaidan, R.A.Talib, M.A.Rahma, F.H.Khaleel; *Pelagia Research Library, Der.Chemica.Sinica*, **3**, 841 (2012).
- [28] Kiran Kumari, Vazid Ali, Rajesh Gupta; *Chitkara Chemistry Review*, **1**, 53 (2013).