

Synthesis, Ion Exchange Properties and Analytical Applications of a Novel Bimetallic Cation Exchanger

M A Dhanitha¹ and C Janardanan²

Post Graduate and Research Department of Chemistry, Sree Narayana College, Kannur,
Kerala 670007, India

dhanithabiju@gmail.com; jeeje_dianthus@yahoo.com

Abstract

Heavy metal and organic contamination in the environment has been of great concern because of their increased discharge, toxic nature and other adverse effects on the receiving streams. This study investigated the applicability of a novel bimetallic inorganic cation exchanger zirconium tin molybdate (ZrSnMo) in environmental remediation. The material was synthesized by co-precipitation method and characterized by various instrumental techniques. The distribution studies of various metal ions showed that the material was highly selective for Pb^{2+} , Bi^{3+} and Co^{2+} ions. Another analytical application of the new exchanger was explored by studying adsorption of indigo carmine dye from aqueous solution using UV-Visible Diffuse Reflectance spectrophotometer. About 97% of the dye was removed within 2 hours treatment with the exchanger, which indicated that ZrSnMo was an efficient solid adsorbent for the removal of IC from aqueous solution.

Keywords: Bimetallic ion exchanger, heavy metals, distribution studies, adsorption studies etc..

1. Introduction

Extensive studies regarding synthetic inorganic ion exchangers have showed their potential in solving diverse problems of environmental and analytical chemistries. In spite of their advanced stage of development, various aspects and components of ion exchange technologies have been continuously studied to improve the efficiency and economy of their applications. Efforts to develop new ion exchangers for specific applications are

continuing. Although a lot of work has already been done on the synthesis of inorganic ion exchangers, the development of new inorganic ion exchangers with characteristic properties still needed attention and their utility in various fields is yet to be explored.

Several three component ion exchangers based on zirconium(IV) have been well studied, so far. A literature survey shows that mixed materials containing two anions and a cation have been widely investigated¹⁻⁵. However, not much work has been done on mixed materials containing two cations and an anion. Tetravalent bimetallic acid (TBMA) salts, containing two different cations and an anion, are interesting since they exhibit improved properties in comparison to their single salt counter parts.

Waste treatment is one of the major problems faced by chemical, petrochemical, pharmaceutical and textile industries. These industries generate large quantities of organic and inorganic wastes. Textile industry wastewater is heavily charged with unconsumed dyes, surfactants and sometimes traces of metals. These effluents cause a lot of damage to the environment. In most countries researchers are looking for appropriate treatments in order to remove pollutants, impurities and to obtain the decolourization of dyehouse effluents⁶⁻⁸. Various chemical and physical processes are currently used, which work by direct precipitation and separation of pollutants⁹, or elimination by adsorption on activated carbon or similar materials. In this case, the problem is only displaced, and further treatments are indeed necessary in order to separate the purified effluents or to regenerate the adsorbents; therefore, a new and different risk of pollution is

faced¹⁰. This will encouraged us for the development of eco-friendly inorganic ion exchange material and its application in various environmental remediation process.

In this regard our study has been focused on the synthesis of a bimetallic cation exchange material zirconium tin molybdate (ZrSnMo). The ion exchange properties of the material was explored by various techniques and its applications in environmental remediation was achieved by removing toxic heavy metal ions and organic dye from industrial wastewater.

2. Experimental

2.1 Reagents and chemicals

Zirconium oxy chloride, stannic chloride and sodium molybdate were obtained from Loba Chemie (India). All other chemicals and reagents used were of analytical grade.

2.2 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 Avtar 370 and thermogram was run on Perkin Elmer Diamond TG/DTA Analyzer. X-ray diffractometer BrukerAXS 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.

2.3 Synthesis of the exchanger

Different samples of ZrSnMo were prepared by adding 0.05 M sodium molybdate solution to a mixture of 0.05M zirconium oxy chloride solution and 0.05M stannic chloride solution in different volume 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 exchangers were then converted in to the H⁺ 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.

Properties like ion exchange capacity (IEC), chemical resistivity and pH titration studies, distribution studies and effect of temperature on IEC were carried out as reported earlier¹¹.

2.4 Application of ZrSnMo for the Removal of dyes

Batch experiments were performed according to Mahanta et al¹². The initial and final concentrations of indigo carmine solutions were determined by measuring absorbance at 664 nm using UVvisible absorption spectroscopy. Methylene blue solutions (10 mL) of different concentrations (20 ppm to 50 ppm) were mixed with 0.2g of material and kept for 2hrs and their absorbance was measured. The effect of pH (2-12), contact time (10-180), and adsorbent dosage (100-500mg), temperature (30-60⁰C) and initial concentration of IC (10-50ppm) were carried out. The percentage of removal of dyes was calculated using the following formula,

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Where, C_i is the initial dye concentration and C_e is the equilibrium dye concentration in mgL⁻¹.

3. Results and discussions

3.1 Synthesis and characterizations of ZrSnMo

Zirconium tin molybdate samples were obtained as pale yellow solids. The synthesis conditions and properties of the samples were shown in **Table 1**. The sample with highest sodium ion exchange capacity was selected for detailed studies.

The exchanger was found to be stable in lower concentrations of mineral acids such as HNO₃, H₂SO₄ and HCl. It was also found to be stable in 0.1M solutions of bases, 1.0M salt solutions and organic solvents such as ethanol, acetone, carbon tetrachloride etc.

Sample	Volume ratios of 0.05M solutions			pH	Appearance	Na ⁺ ion exchange capacity (meq/g)
	Zr ⁴⁺	Sn ⁴⁺	MoO ₄ ²⁻			
ZrSnMo 1	1	1	1	1	All pale yellow solids	0.98
ZrSnMo 2	1	1	2	1		0.87
ZrSnMo 3	1	1	3	1		1.19
ZrSnMo 4	1	2	3	1		1.04
ZrSnMo 5	1	2	4	1		0.94
ZrSnMo 6	2	1	4	1		0.99

Elemental analysis by EDS measurement (Fig. 1) shows the composition of Zirconium: tin: molybdenum as 1:1.43:1.62

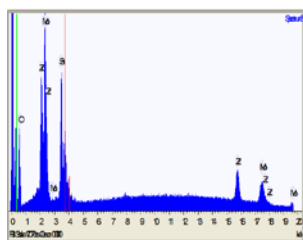


Fig. 1: EDS of ZrSnMo

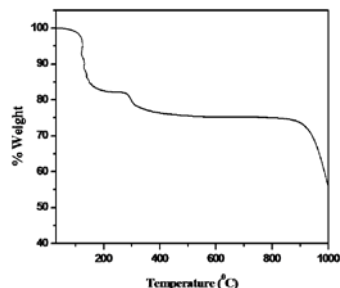


Fig. 2: TGA of ZrSnMo

The thermogram (Fig. 2) of ZrSnMo suffers a first weight loss of approximately 16% up to 163^oC endorsed to the presence of moisture and hydrated water. Then a weight loss of about 3.5% from 280^oC to 314^oC was due to the condensation of structural hydroxyl groups. The material is stable up to 880^oC since only 25% of its initial weight is reduced till the temperature get to 880^oC.

FTIR spectrum of ZrSnMo (Fig. 3) shows a broad band in the region 3445 cm⁻¹, which is ascribed to symmetric and asymmetric –OH stretching. A band at 1623 cm⁻¹ is attributed to H-O-H bending and a band in the region 1374 cm⁻¹ is attributed to the presence of structural hydroxyl protons in the exchanger¹³. Bands at 892 cm⁻¹, 748 cm⁻¹ and 495 cm⁻¹ show the presence of Zr-O, Sn-O and Mo-O bonds in the material. Based on chemical composition,

TGA data and FTIR analysis the tentative formula suggested for the material is [(ZrO₂). (SnO₂). (H₂MoO₄)₂].7H₂O.

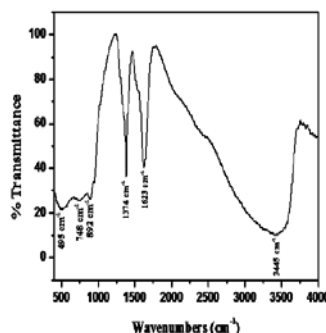


Fig. 3: FTIR

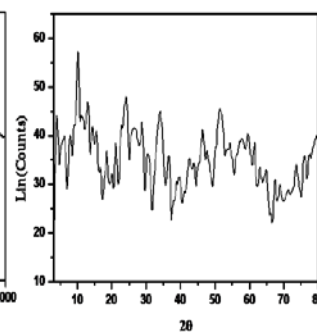


Fig. 4: XRD

The XRD pattern of the material (Fig. 4) shows amorphous nature of the material. Scanning electron microscopic images at different magnification showed the granular nature¹⁴ of the material (Fig. 5).

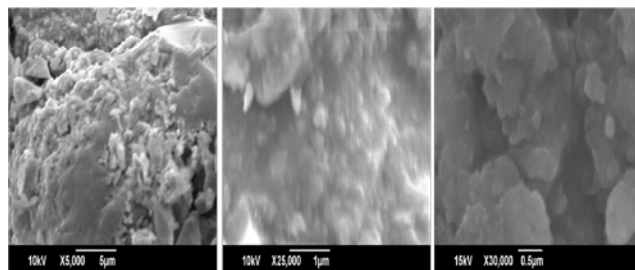


Fig. 5: SEM images of ZrSnMo

The UV-Vis DR spectrum of the material exposed in Fig. 6 indicated that the material absorbs in the UV region with absorption edge, 519 nm, which is in the visible region. Using Kubelka-Munk function^{15,16}, the band gap

energy calculated for the material was found to be 2.43 eV, which is in the range of semiconducting materials (Fig. 7).

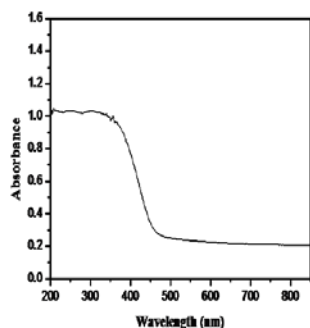


Fig. 6: UV-Vis DRS

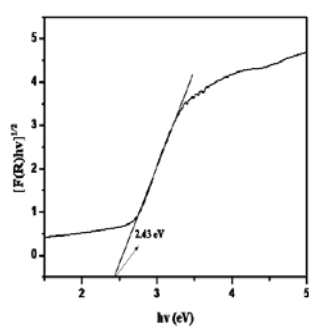


Fig. 7: K-M function Vs hv (eV)

pH titration curves (Fig. 8) drawn for the material in NaCl/NaOH and KCl/KOH systems shows its monofunctional behaviour and the ion exchange capacity obtained from the curve is in conformity with the value obtained from the column method.

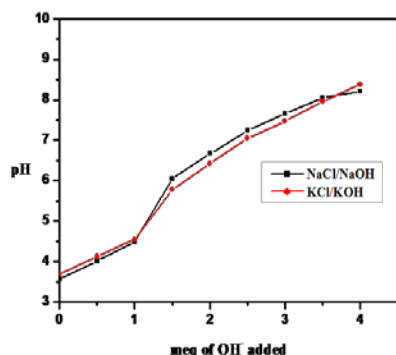


Fig. 8: pH titration curves of ZrSnMo

The separation capability of the material has been assessed by studying distribution coefficients of various metal ions and the results provide the affinity order as $\text{Bi}^{3+} > \text{Pb}^{2+} > \text{Co}^{2+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Cd}^{2+} > \text{Ca}^{2+} > \text{Hg}^{2+}$, shows that the material has very high affinity towards Bi^{3+} , Pb^{2+} and Co^{2+} metal ions. Hence the exchanger can be effectively used for the removal of these metal ions from polluted water. It is also obvious from Table 2.40 that distribution coefficient of metal ions decreases with increase in electrolyte concentrations.

Table 2: Distribution coefficients in water and other electrolytes

Cation	Distribution coefficients (K_d)						
	DM W	HNO ₃ (M)			NH ₄ NO ₃ (M)		
		0.001	0.01	0.1	0.001	0.01	0.1
Al ³⁺	78.57	28.22	10.1	NS	32.43	11.3	NS
Bi ³⁺	324.1	172.5	82.8	25.	185.9	83.1	28.
Ca ²⁺	20.16	4.12	NS	NS	5.23	NS	NS
Cd ²⁺	21.96	4.36	NS	NS	5.67	NS	NS
Co ²⁺	210.5	79.1	33.	18.	82.7	37.	20.
Cu ²⁺	56.4	23.1	9.7	NS	24.2	10.	NS
Hg ²⁺	13.95	1.23	NS	NS	1.34	NS	NS
Mg ²⁺	23.07	9.67	NS	NS	10.0	NS	NS
Mn ²⁺	31.26	11.6	NS	NS	12.3	NS	NS
Ni ²⁺	38.7	14.94	2.09	NS	5.12	2.76	NS
Pb ²⁺	226.4	104.6	57.3	25.	127.4	64.4	26.
Zn ²⁺	24.48	10.45	NS	NS	11.26	NS	NS

NS: No observable sorption

3.2 Analytical applications of ZrSnMo

A. Binary separation of metal ions from synthetic mixtures

Differential selectivity of the metal ions by the exchanger provides possibilities of some analytically complicated binary separations. The significant features of separations carried out are shown in Table 3. Some of the separations are imperative since they engross the separation of toxic heavy metal ions. The results also exemplify that all the separations are quantitative and reproducible.

Separations achieved	Eluent	Metal ion (mg)		% efficiency
		Loaded	Eluted	
Cd ²⁺	0.01M AN	2.86	2.76	96.50
Pb ²⁺	0.5M NA+0.1M AN	4.76	4.65	97.68
Mg ²⁺	0.01M AN	1.42	1.37	96.48
Bi ³⁺	0.5M NA+0.1M AN	5.16	5.08	98.45
Hg ²⁺	0.01M AN	4.86	4.77	98.15
Co ²⁺	0.5M NA+0.1M AN	1.63	1.61	98.77
Zn ²⁺	0.01M AN	1.64	1.62	98.78
Bi ³⁺	0.5M NA+0.1M AN	5.16	5.09	98.64
Ca ²⁺	0.01M AN	1.93	1.89	97.92
Pb ²⁺	0.5M NA+0.1M AN	4.76	4.70	98.74

B. Adsorptive removal of Indigo carmine dye

The exchanger ZrSnMo is also used as an effective adsorbent for the treatment of industrial effluents since it has the ability to adsorb indigo carmine (IC) dye from aqueous solutions. Most of the dyes are toxic and carcinogenic compounds and are stable in the receiving environment and therefore pose a serious threat to the environment. Hence, the removal of organic dyestuff from waste effluents becomes important from the environmental viewpoint.

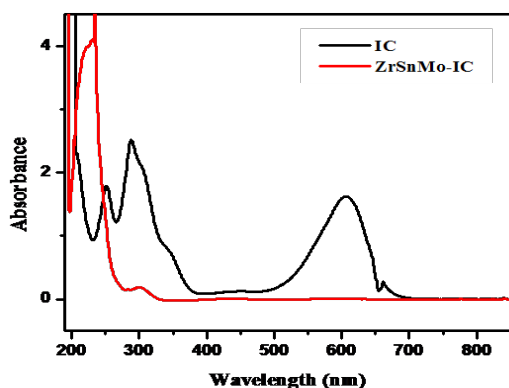


Fig. 9: UV-Vis Spectra of pure IC and IC after treatment with ZrSnMo

Fig. 9 illustrates the absorbance of IC dye solution before and after treatment with the exchanger. It is clear from the spectra that the intensity of the original peaks of IC disappear and no new peaks are observed after its treatment with the adsorbent. About 97% of the dye was removed within 2 hours treatment with the exchanger

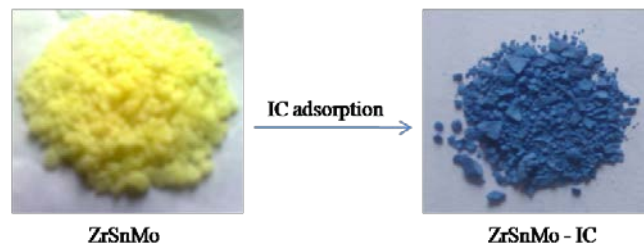


Fig. 10: Images of ZrSnMo before and after adsorption of IC

Fig. 10 shows the images of the exchanger ZrSnMo before and after adsorption of indigo carmine dye. The photographs indicate that the pale yellow colour of ZrSnMo vanishes and it appears as blue after 2 hours of treatment of it with dye solution. This confirms the adsorption of IC molecules on the exchanger surface. The above studies reveal that ZrSnMo can be used as an excellent adsorbent for the removal of organic dye like indigo carmine from industrial effluents.

4. Conclusion

A novel bimetallic cation exchanger ZrSnMo was synthesized and well characterized and is found to be chemically and thermally stable and possess good ion exchange properties. The material is found to be highly selective towards Pb²⁺, Bi³⁺ and Co²⁺ metal ions. The analytical potential of the exchanger has been established by achieving separation of metal ions from synthetic binary mixtures. The environmental utility of the material has been achieved by the removal of one of the toxic organic pollutants like indigo carmine dye from aqueous solution. All these results emphasize the usefulness of the new material in environmental remediation.

ACKNOWLEDGEMENT

Author acknowledges the Council of Scientific and Industrial Research for awarding Junior Research Fellowship and STIC, Cochin, School of Chemical Sciences, M G University, Kottayam for providing technical facilities.

REFERENCE

1. C. Janardanan, B. Preetha, “Ion exchange method for the detection of trace amounts of Mn^{2+} using nano cerium zirconium phosphate cation exchanger”, *Ion Exch. Lett.*, Vol. 3, 2010, pp. 12-18.
2. C. Janardanan, B. Preetha, “Synthesis, Ion Exchange Properties, analytical and catalytic applications of nano sized Cerium Zirconium Phosphate”, *J. Indian Chem. Soc.*, Vol. 8, 2011, pp. 1-6.
3. B. Preetha and C. Janardanan, “UV-Visible Diffuse Reflectance spectroscopic studies on Mn and Cu ion exchange of newly synthesized cerium zirconium antimonate and its application in dye degradation”, *Research Journal of Recent Sciences*, Vol. 1(ISC-2011), 2012, pp. 85-92.
4. G. M. Ibrahim, B. El-Gammal, I. M. El-Naggar, “Synthesis and Characterization of Novel Materials, Tin Potassium Vanadate and Zirconium Potassium Vanadate Inorganic MultiComponent Ion Exchangers”, *Sep. Sci. Technol.*, Vol. 46, No. 4, 2011, pp. 664-678.
5. Parimal Patel, Uma Chudasama, “Synthesis and characterization of a novel hybrid cation exchange material and its application in metal ion separations”, *Ion Exch. Lett.*, Vol. 4, 2011, pp. 7-15.
6. C. Galindo, P. Jacquesa and A. Kalt, “Photodegradation of the aminobenzene acid orange 52 by three advanced oxidation processes: UV/H₂O₂, UV/TiO₂ and VIS/TiO₂ comparative mechanistic and kinetic investigations”, *J Photochem Photobiol A: Chem*, 130, 2000, pp. 35-47.
7. I. Akmeahmet and I. Balcioglu Arslan, “Treatment of textile industry wastewater by enhanced photocatalytic oxidation Reaction”, *J Adv Oxid Technol*, 4, 1999, pp.189-95.
8. T. Porada, R. Gade, D. Fabler and K. Guñther “Quantum yield of TiO₂-photocatalysed degradation of Acid Orange 7”, *J Adv Oxid Technol*, 4, 1999, pp.203-8.
9. J. Wu, M.A Eiteman and S.E Law, “Evaluation of membrane filtration and ozonation processes for treatment of reactive dye wastewater”, *J Environ Eng*, 124, 1998, pp.272-7.
10. M.R Hoffmann, S.T Martin, W. Choi and D. Bahnemann, “Environmental applications of semiconductor photocatalysis”, *Chem Rev*, 95, 1995, pp.69-96.
11. S. Siji, M.A. Dhanitha and C. Janardanan, Efficient Degradation of Dyes in Water by a Novel Inorganic Cation Exchanger Cerium(IV) arsenomolybdate, *Journal of Environmental Nanotechnology*, 2(2), 2013, pp.81-87.
12. D. Mahanta, G. Madras, S. Radhakrishnan, and S. Patil, Adsorption and desorption kinetics of anionic dyes on doped polyaniline, *Journal of Physical Chemistry B*, 113(8), 2009, pp.2293-2299.
13. M.A Dhanitha, K.V Nimisha and C. Janardanan, “Effective removal of hazardous metal ions from waste water using novel titanium(III) tin selenate cation exchanger”, in *International symposium on Integrated Water Resources Management, CWRDM, Kozhikode 2014*, Vol. 1, pp.634-641.
14. Harish K Sharma and Nadeem Sharma, “Synthesis and structural characterization of Tin (IV) Molybdotungstate-A Heteropolyacid Salt”, *Pelagia Research Library, Der Chemica Sinica*, Vol. 4 No. 2, 2013, pp. 182-188.
15. Wei Chao-Hai, Tang Xin-hu and Liang jie-Rong, “Preparation, characterization and photocatalytic activities of boron- and cerium-codoped TiO₂”, *Journal of Environmental Sciences*, Vol. 19, No. 1, 2007, pp. 90-96.



16. G. Krishnaiah, C. Jayachandraiah, K. Siva Kumar, “Ce induced Structural and Optical Properties of Ce Doped ZnO Nanoparticles”, Int. J. ChemTech Research, Vol. 6, No. 6, 2014, pp. 3378.