In Air Synthesis of Psyllium Based Organo-Inorganic Hybrid Ion Exchanger, its Characterization and Studies

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Abstract: **In this research paper in air synthesis of Psyllium and zirconium(IV)tungstoiodophosphate based organo-inorganic hybrid ion exchanger has been reported. Synthesised hybrid ion exchanger has been characterized by FT-IR, SEM, EDS and TGA/DTA/DTG and chemical composition. Ion exchange capacity and thermal studies of the synthesised ion exchanger were investigated using the potassium chloride solution. Further pH titration studies have also been done with KCl/KOH and NaCl/NaOH solutions. Distribution studies shows that synthesized ion exchange has high selectivity for Pb^{2+}.**

Keywords: **Characterization, Ion Exchanger, Synthesis, Zirconium(IV)tungstoiodophosphate**.

I. INTRODUCTION

Ion exchange is basically an adsorption phenomenon where exchange of particular ions between electrolyte solution and complex or between two electrolytes takes place. So ion exchangers are the materials which have loosely held ions which can be easily replaced by the ions of solution which is passed through them. Many synthetic inorganic ion exchangers which are based on tetravalent metals have been studied in recent years because of their selectivity and intercalation properties[1-4] Ion exchangers have been used for recovery of metal ion, in the process of chemical decontamination , regeneration of decontaminants and removal of the formulation chemicals from the coolant [5]. Three component ion exchanger [Bismuth(III)iodophosphate] has been synthesized by mixing different ratio of 0.1M bismuth nitrate, 0.1M potassium iodate, 0.1M orthophosphoric acid at pH between 0-1. The material shows ion exchange capacity for Na^+ ion of 0.5meq/g. The material has been characterized using I.R., X-ray, TGA studies. pH titration, chemical stability, thermal stability and distribution behaviour were also studied. Ion exchange capacity has also been determined for various metal ions such as K^+, Mg^{2+} etc. Kd values and elution pattern shows that the cation exchanger is selective for Pb^{2+} [6]. Nano-powder zirconiumvanadate was chemically . synthesized using homogeneous precipitation technique SEM, XRD, TGA-DSC and FT-IR were used to study the granulometry, morphology, composition and structure of that exchanger .To understand the cation exchange behaviour of the materials Ion exchange capacity (IEC) and thermal stability studies were also carried out. Organic- inorganic hybrid materials enable the integration of useful organic and inorganic characteristics within a molecular-scale composite. So the effect of the binding polymer mixture of polyvinyl alcohol and alginate on the physicochemical properties of prepared zirconium vanadate ion exchanger was studied. [7]. A number of organic–inorganic composite samples of polyaniline Sn(IV) tungstoarsenate have been synthesized. Composite materials formed by the combination of inorganic ion exchangers of multivalent metal acid salts and organic conducting polymers (polyaniline, polypyrrole, polythiophene, etc.), providing a new class of 'organic–inorganic' hybrid ion exchangers with better mechanical and granulometric properties. They have good ion-exchange capacity, higher stability, reproducibility and selectivity for heavy metals. This material was characterized by using atomic absorption spectrometry, elemental analysis, Fourier transform infrared spectroscopy, simultaneous thermogravimetry– differential thermogravimetry, X-ray and scanning electron microscopy studies. Ion-exchange capacity, pH-titrations, elution and distribution behavior were also carried out to characterize the material [8]. Tetravalent metal acid (TMA) salt zirconium tungstate (ZW) has been synthesized, followed by its derivatization using *para*-chlorophenol (*p*CP) [9] .Zirconium (IV) tungstoiodophosphate was synthesized under a variety of conditions. The most chemically and thermally stable sample was prepared by adding a mixture of aqueous solutions of sodium tungstate, potassium iodate and orthophosphoric acid to aqueous solution of zirconium(IV) oxychloride. Its ion exchange capacity for Na^+ and K^+ was found. The material was characterized on the basis of chemical composition, pH titration, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis. The effect on the exchange capacity of drying the exchanger at different temperatures has been studied. The analytical importance of the material has been established by quantitative separation of Pb^{2+} from other metal ions [10]. Other zirconium(IV) based ion exchanger like Zirconium(IV)tungstate as an inorganic ion exchanger has been used for selective removal of Cesium from aqueous solution [11] The literature review shows that many three component ion exchangers i.e zirconium(IV)sulphosalicylophosphate[12] zirconium(IV) iodovanadate[13], zirconiumtitaniumphosphate[14], zirconium(IV)iodooxalate[15],zirconium(IV)selenomolybdate[16] , zirconium(IV)aluminophosphate[17] etc.have been synthesised and characterized. Their analytical applications also have been studied. In the present work we report in air synthesis, characterization and studies of Psyllium and zirconium(IV) tungstoiodophosphate based organo-inorganic hybrid ion exchanger.

II. EXPERIMENTAL SECTION

A. Materials

Psyllium Plantago husk (Sidhpur Sat isabgol Factory Gujarat), Acrylamide(Merck Schuchardt) were used as backbone and monomer respectively. Potassium persulphate(KPS) and Hexamethylenetetramine(HMTA) procured from SD- Fine chemicals were used as initiator and crosslinker respectively. Zirconium(IV) oxychloride ($ZrOCl_2.8H_2O$), sodium tungstate ($Na_2WO_4.2H_2O$) and potassium iodate (KIO_3) were obtained from CDH (India), while orthophosphoric acid (H_3PO_4) was a Qualigens (India) product.

B. Instrumental Analysis

FTIR Spectra of samples were taken in PERKIN ELMER RXI Spectrophotometer using KBr pellets. SEM of the samples was taken on JEOL STEROSCAN 150 MICROSCOPE. In order to have the conducting impact, gold plating was done on the samples. Then the samples were placed on carbon plate and the scanning was synchronized with microscopic beam so as to maintain the small size over a large distance relative to the specimen. A remarkable three dimensional appearance with high resolution was obtained in case of crosslinked graft copolymerized superabsorbent /organic-inorganic hybrid ion-exchanger. TGA/DTA/DTG studies of the synthesized samples were done on TG/DTA 6300, SII EXSTAR 6000 in air at a heating rate of 10°C/min.

C. Synthesis of Organo-Inorganic Hybrid Ion Exchanger of Psyllium

The samples were prepared by adding 0.1 M $ZrOCl_2.8H_2O$ solution to a mixture of 0.5 M sodium tungstate, 0.5M potassium iodate and 1 M orthophosphoric acid, in different volume ratios with intermittent shaking of the mixture. Known volume (20ml) of the resulting solution (mixture) was taken in a reaction beaker. Then a known amount of KPS (0.00924mol l^{-1}) which is an initiator, Psyllium husk (1g) which acts a backbone, Hexamethylenetetramine (HMTA) (0.04279mol l^{-1}) which acts as a crosslinker was added and mixed thoroughly to attain the homogeneity. Then to the reaction mixture acrylamide (0.2812mol l^{-1}), which is a primary monomer was added. Resulting mixture was kept in hot air oven at temperature at 65°C for about 180 minutes. Resulting ion exchangers after cooling to room temperature were washed with acetone and dried. After that the dried ion exchanger was put into demineralized water. The resulting material was dried in the oven at 40ºC until it got dried. After that the dried material was kept in the 1M HNO_3 to convert the ion exchanger into the H^+ form for about 24 hours . The material thus obtained was washed with distilled water to remove excess acid and then dried at 40^o C. The resulting organo-inorganic hybrid ion exchanger Psy-cl-poly(AAm)ZTIP-IA (where Psy- Psyllium, cl-crosslinker HMTA, AAm-Acrylamide and ZTIP-Zirconium(IV)tungstoiodophosphate, IA- In Air) was then crushed to get the particle of mesh size around 50-60.

D. Ion-Exchange Capacity (IEC)

The ion exchange capacity of the material was determined by the column process. 0.5g of the ion exchanger (H^+ form) was packed in a glass column and washed with demineralised water maintaining the flow rate of 20 drops per minute to remove any excess of acid that remained on the particles until it becomes acid free. It was confirmed with the pH paper. After that 0.1 M solution of KCl was passed through the column maintaining the flow rate at 20 drops per minute until the neutralization of effluent occurs. The effluent wascollected and titrated against a standard 0.1N NaOH solution to determine the total H^+ ions released.. The following formula is used to find out ion exchange capacity (IEC).

IEC = (NxV) / W meq/gm

Where N= Normality of NaOH used

V= Volume of NaOH used in mL.

W= Weight of ion exchanger in gms

E. Thermal Stability of Organo-Inorganic Hybrid Ion Exchanger

Thermogravimetric analysis of the material in the H^+ form was performed at a heating rate of 10°C min^{-1}. The effect of heating on the ion-exchange capacity of the material was also examined. The material in H^+ form was heated at different temperatures for 1 h in a hot air oven and the ion-exchange capacity for K^+ was evaluated by the column process after cooling it at room temperature. and the results of Psy-cl-poly(AAm)ZTIP-IA are summarized in TABLE I.

F. pH Titrations of Organo-Inorganic Hybrid Ion Exchanger

pH titration was performed by the batch process using the method of Topp and Pepper [18]. 500 mg portions of the exchanger in the H^+ form were placed in each of the several 250 ml conical flasks followed by equimolar solution of alkali metal chlorides (KCl/NaCl) and their hydroxides (KOH/ NaOH) in different volume ratios, the final volume being 50 ml to maintain the ionic strength constant. The pH of each solution was measured and plotted against milliequivalents of OH^- ions. pH titration curves for the Psy-cl-poly(AAm)ZTIP-IA is shown in Fig.7(a, b).

G. Chemical Stability of Organo-Inorganic Hybrid Ion Exchanger

This study was done to see the effect on ion exchange capacity of the exchanger in different chemical solutions of different concentrations [6].The extent of dissolution of the material in different organic acids was recorded. 0.50g of material was equilibrated with 25ml of the solution of interest for twenty four hours at room temperature. The remaining amount of material was filtered and washed by demineralized water. After removal of excess acid, it was dried in oven at $(40\pm10)^oC$. The ion exchange capacity of remaining material was determined by usual column method TABLE II.

H. Distribution Studies of Organo-Inorganic Hybrid Ion Exchanger

For distribution studies, 0.2g portion of the dry exchanger in with intermittent shaking. The metal ion concentration was 0.01M in the solution. The determination before and after equilibrium were carried out volumetrically usig EDTA as titrant [6]. The *Kd* values were obtained by using the formula

$$Kd = (I-F) / F*(V/M)\ (mL/g)$$

where I is the initial metal ion concentration, F is the final metal ion concentration, V is the volume of solution and M is the mass of the exchanger. The results are summarized in TABLE III.

I. Chemical Composition of Organo-Inorganic Hybrid Ion Exchanger

To determine the chemical composition of the samples, 0.1 g of exchanger was dissolved in minimum amount of hot concentrated H_2SO_4. The solution was diluted to 100 ml with DMW. The amounts of iodate and zirconium were determined spectrophotometrically using pyrogallol and Alizarin Red-S as colouring reagents, respectively. Phosphate was determined titrametrically and tungsten was determined gravimetrically using the standard method [19].

III.RESULTS AND DISCUSSIONS

A. Mechanism

Hydroxyl groups present in the arabinoxylan, which is composed of xylopyranose straight chain with arabinofuranose branches at 2 or 3 positions and is mucilage forming fraction of psyllium, are the active sites for the graft copolymerization of monomer onto it. Persulphate dissociates to give SO_4^-* which further react with water to generate OH*. Then SO_4^-* attacks the psyllium simultaneously, which results in the creation of free radical site on the backbone.

On the other hand, *OH also attacks psyllium resulting in the creation of free radical. Free radicals on monomer moiety are generated through the attacks of OH*. The activated monomer molecules react with the backbone polymer resulting in the formation of graft copolymers and the reaction propagates further. However, the termination of the reaction takes place either by reaction between *OH and backbone free radical or the reaction between two activated chains.

Hexamethylenetetramine has multi-functionality, so it undergoes cross-linking with psyllium and a monomer chain which gives rise to a three dimensional network. The reaction between zirconiumoxychloride, orthophosphoric acid, sodium tungstate, potassium iodate gives rise to ZTIP network as shown in Fig.2 (a)

These two networks then gives rise to three dimensional network. So the proposed structure of Psy-cl-poly(AAm)-ZTIP-IA is shown in Fig. 2 (b).

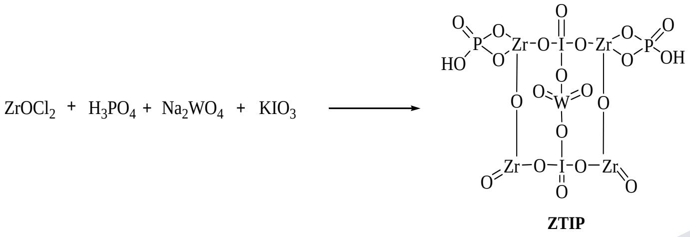


Fig.2 (a) ZTIP network

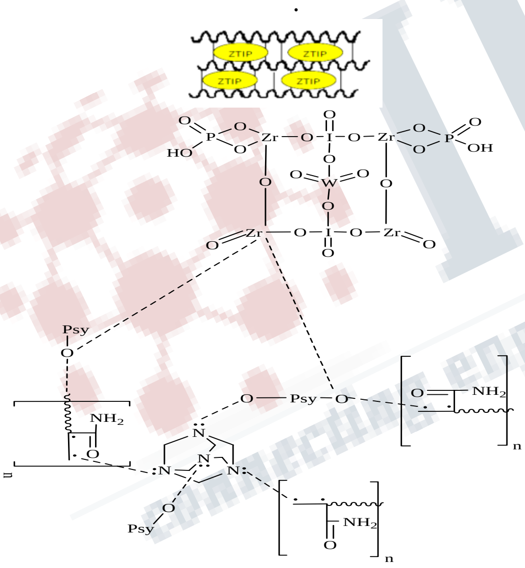


Fig.2 (b).Psy-cl-poly(AAm)ZTIP-IA

where Psy- Psyllium, cl-crosslinker HMTA, AAm-Acrylamide and ZTIP- Zirconium(IV)tungstoiodophosphate, IA- In Air

B. Characterization

1. FTIR spectroscopy

The IR spectrum of Psyllium showed broad peaks at 3416 cm^{-1} (O-H stretching of carbohydrates), 2924 cm^{-1} (CH_2 asymmetric stretching),1378.8 cm^{-1} (CH, CH_2 and OH in-plane bending in carbohydrates), 1020 cm^{-1} (C–O stretching region as complex bands, resulting from C–O and C–O–C stretching vibrations), 897 cm^{-1} and 669 cm^{-1} (pyranose rings). Whereas in case of IR spectra of Psy-cl-poly(AAm)ZTIP-IA besides the peaks for psyllium, the peak at 1643cm^{-1} is due C=O stretching of amide 1st band, peak at 1043cm^{-1} is due to C-N stretching of amines and peak at 1384cm^{-1} shows the stretching of P=O of phosphate group. The spectrum also shows strong band in the region 818–523 cm^{-1} indicating the presence of iodate, tungstate and metal oxides. Fig.3(a) and (3b) represents IR spectrums.

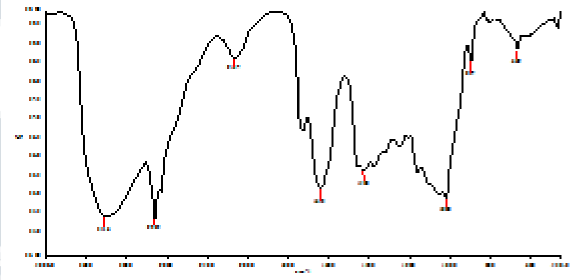


Fig. 3(a) IR spectra of Psyllium

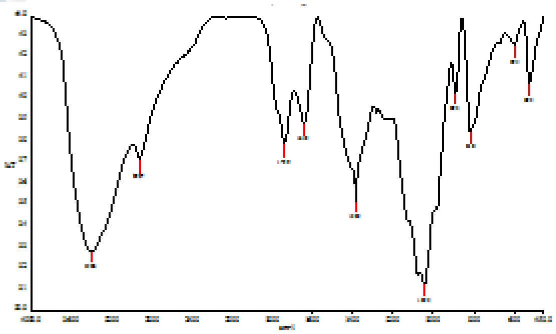
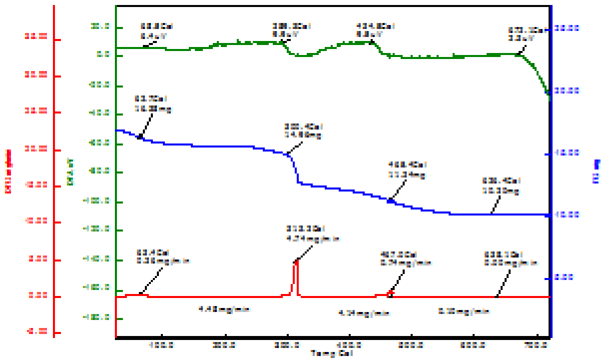
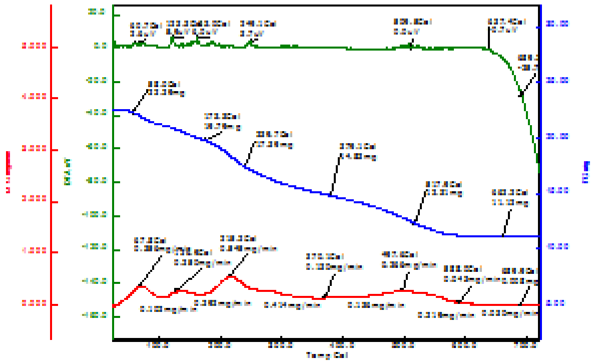


Fig 3(b) IR spectra of Psy-cl-poly(AAm)ZTIP-IA

2. TGA/DTA/DTG

TGA/DTA/DTG of Psyllium and Psy-cl-(AAm)ZTIP-IA were studied as a function of weight loss versus temperature. Psyllium exhibited initial decomposition temperature (IDT) at 62.7^{0}C and final decomposition temperature (FDT) at 626.4^{0}C. Two exothermic peaks at 289.3^{o} C (9.9µV) and at 434.5^{o}C (9.5 µV) were obtained in case of DTA of Psyllium. DTG of Psyllium showed decompositions at 313.2 ^{o}C and 467.0 ^{o}C and 4.74mg/min and 0.74mg/min weight loss, respectively. In case of Psy-cl-(AAm)ZTIP- IA IDT was observed at 58.0^{o}C which is lower than psyllium and FDT was observed at 662.2^{o}C which is higher than that for psyllium. It shows that rate of decomposition of crosslinked organo-inorganic hybrid ion exchanger with respect to temperature is higher than that of psyllium. Hence grafting and crosslinking of psyllium with AAm-HMTA on ZTIP decreases the stability towards the thermal decomposition.





In DTA curve in case of Psy-cl-(AAm)ZTIP- IA, the exothermic peaks were observed at 123^{o}C(5.9µV) and 249.1^{o}C (3.7µV). In DTG curve, the weight loss rate 0.356mg/min at 67.8^{o}C and 0.266mg/min at 497.6^{o}C was observed for Psy-cl-(AAm)ZTIP-IA. Fig..4(a) and 4(b) shows TGA/DTA/DTG curve.

3. Scanning Electron Microscopy SEM

In order to have the conducting impact, the samples were gold plated and the scanning was synchronized with microscopic beam so as to maintain the small size over a large distance relative to the specimen. A remarkable three dimensional appearance with high resolution was obtained in case of crosslinked product. SEM images clearly exhibited the differences in the surface morphology of Psyllium and Psy-cl-poly(AAm)ZTIP-IA. Smaller granules were observed in case of organo-inorganic hybrid ion exchanger as shown by Fig. 5 (a) and 5(b)

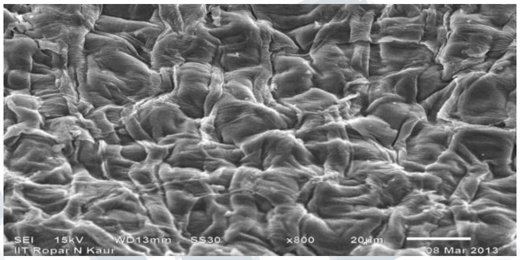


Fig. 5(a) SEM Image of Psyllium

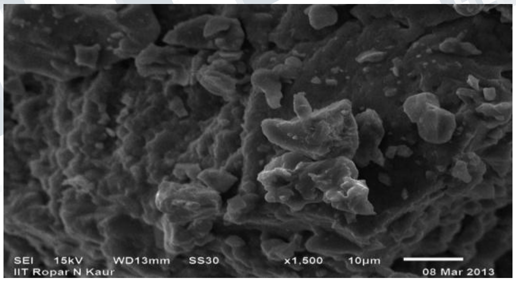


Fig. 5(b) SEM image of Psy-cl-poly(AAm)ZTIP-IA

4. EDS Analysis

In order to have the conducting impact, the samples were gold plated and the scanning was synchronized with microscopic beam so as to maintain the small size over a large distance relative to the specimen. A remarkable three dimensional appearance with high resolution was obtained in case of crosslinked product. In the organo-inorganic hybrid ion exchanger Psy-cl-poly(AAm)ZTIP-IA Tungston(W) and Zirconium(Zr) are present. The other metal ions are also present in hybrid organo-inorganic ion exchanger but it is not detected by the instrument because its composition is very low. EDS results are shown in Fig.6.

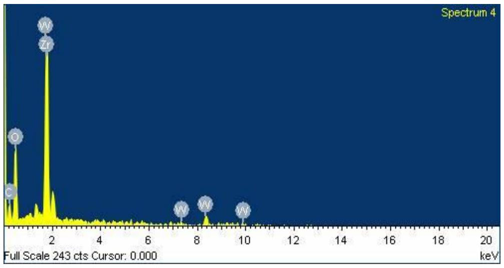


Fig. 6 EDS Spectra of Psy-cl-poly(AAm)ZTIP-IA

C. Ion Exchange Capacities of Organo-Inorganic Hybrid Ion Exchanger

The ion-exchange capacity of organo-inorganic hybrid ion exchangers, which are prepared in air was found to be 0.12meq/g for K^+ ion**.**

D. Effect of Heating On Ion Exchange Capacity/Thermal Stability of Organo-Inorganic Hybrid Ion Exchanger

The effect of heating on the ion-exchange capacity of the material was also examined. The material in H^+ form was heated at different temperatures for 1 h in a hot air oven and the ion-exchange capacity for K^+ was evaluated by the column process after cooling it at room temperature. The results of Psy-cl-poly(AAm)ZTIP-IA are summarized in TABLE I. With the increase in the temperature , the decrease in the ion exchange capacity of the organo-inorganic hybrid ion exchanger is due to the fact that at high temperature physical degradation at both molecular and macroscopic levels takes place.

TABLE I
THE THERMAL STABILITY OF Psy-cl-Poly(Aam)ZTIP-IA AFTER HEATING TO VARIOUS TEMPERATURES FOR 1 H.

S.No.	Drying Temperature (°C)	Change in colour	K^+ IEC (meqg^{-1}dry exchanger)
1.	40	Light yellow	0.12
2.	100	Yellow	0.1
3.	150	Brown	0.08
4.	200	Black	0.04
5.	250	Black	0.02

E. pH Titrations Studies of Organo-Inorganic Hybrid Ion Exchanger

It was noted from the pH titration curve that pH of solution is continuously increasing with the increase in the number of moles of the KCl+KOH/NaCl+NaOH added for Psy-cl-poly(AAm)ZTIP-IA organo-inorganic hybrid ion exchanger. This can be explained on the fact that at the lower pH the organo-inorganic hybrid ion exchanger deswell. As the volume of KOH or NaOH added to the system is increased, more OH^- ions are consumed which suggest that there is an increase of the rate of ion exchange in basic medium due to the removal of H^+ ions from the solution. So more number of hydroxyl ions (OH^-) are available leading to the increase in the pH. The graph is shown in Fig. 7(a) and 7(b).

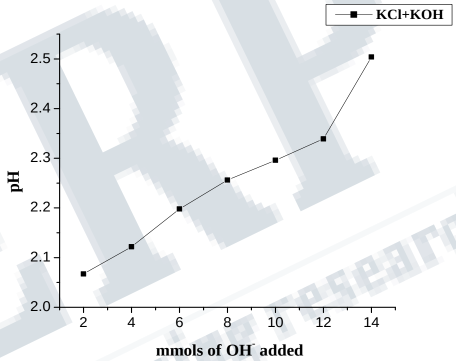


Fig. 7(a) pH Titration Curve for Psy-cl-poly(AAm)ZTIP-IA for KCl+KOH

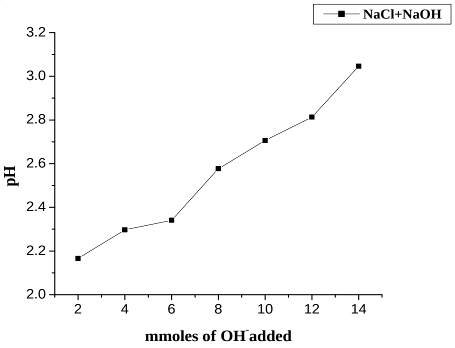


Fig. 7(b). pH Titration Curve for Psy-cl-poly(AAm)ZTIP-IA for NaCl+NaOH

F. Chemical Stablity of Organo-Inorganic Hybrid Ion Exchanger

These studies showed that the weight of organo-inorganic hybrid ion exchangers Psy-cl-poly(AAm)ZTIP-IA decreases when it is placed in different acid solutions for 24 hours and the ion-exchange capacity of dried material for K^+ was evaluated by the column process. The results of Psy-cl-poly(AAm)ZTIP- IA are summarized in TABLE II

G. Distribution Studies of Organo-Inorganic Hybrid Ion Exchanger

These studies showed organo-inorganic hybrid ion exchanger Psy-cl-poly(AAm)ZTIP-IA possess high K*d* values for Pb^{2+} and hence it is highly selective for Pb^{2+}. The results of Psy-cl-poly(AAm)ZTIP-IA are summarized in TABLE III.

TABLE II

THE CHEMICAL STABILITY of Psy-cl-poly(AAm)ZTIP-IA IN DIFFERENT ACID SOLUTIONS.

S.No.	Solution	Weight before treatment(g)	Weight after treatment (g)	K^+ IEC (meqg^{-1})
1.	1M HCl	0.5	0.14	0.142
2	2M HCl	0.5	0.19	0.157
3.	1M HNO_3	0.5	0.16	0.125
4.	2M HNO_3	0.5	0.13	0.231

TABLE III

THE Kd VALUES OF METAL IONS (in mL/g) of Psy-cl-poly(AAm) ZTIP-IA IN DIFFERENT SOLVENTS

S.No	**Metal ion**	**DW**	**0.01 M HCl**	**0.1M HCl**	**0.01M $HClO_4$**	**0.1 M $HClO_4$**
1.	Ca^{2+}	70	27.77	88.33	72.85	100
2.	Mg^{2+}	68.49	66.66	85.71	48.75	154
3.	Pb^{2+}	150	404.76	65.90	190	63.63

***DW-Demineralised Water**

H. Chemical Composition of Organo-Inorganic Hybrid Ion Exchanger

The molar ratio of Zr, W, I and P in the ion exchanger material was estimated to be 2:1:1:1, by performing chemical composition studies which can suggest the following formula of the material $[(ZrO)_2(WO_3)(IO_3)(H_3PO_4)].nH_2O$.

IV CONCLUSION

The results of this investigation showed that organo-inorganic hybrid ion exchangers Psy-cl-poly(AAm)ZTIP-IA seems to be a promising ion-exchange materials with a significant ion-exchange capacity. The thermal stability studies of shows that the organo-inorganic hybrid ion exchangers Psy-cl-poly(AAm)ZTIP-IA is thermally stable even at 250°C.The evidence behind their thermal stability is that even at high temperature they still exhibit some ion exchange capacity. The results of chemical stability shows that Psy-cl-poly(AAm)ZTIP-IA is chemically less stable in different acid solutions. The distribution studies shows that the organo-inorganic hybrid ion exchangers possess high K*d* values for Pb^{2+} and hence they are highly selective for Pb^{2+}.

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REFERENCES

[1] Clearfield A and Wang Z "Organically pillared microporous zirconium phosphonates" *J. Chem. Soc. Dalton Trans. Vol.*7, p.2937,2002

[2] Sirlei R and Claudio A "Crystalline α-titanium(IV) hydrogenphosphateand its sodium- and n-butylammonium-intercalated forms: ion exchange and thermochemistry" *J. Chem. Soc. Dalton Trans. Issue* 14, 1997,p.2517

[3] Ferragina C, Cafarelli P, Di Stefanis A, Di Rocco R and Giannoccaro P "Synthesis and chemical-physical characterization of palladium and rhodium new materials derived from octadecyltrimethylammonium cationic surfactant intercalated into zirconium and titanium dihydrogen phosphate" *Mater. Res. Bull.* vol. 36 issue 10, p. 1799-1812 ,2001

[4] K. Moosavi, S. Setayeshi, M.G. Maragheh, S. Javadahmadi, M.RInorganic Ion Exchanger Zirconium Phosphate. *Journal of Applied Sciences",vol. 9,*p.*2180-2184*,2009

[5] Velmurugan S, Sathyaseelam V S, Narasimhan S V and Mathur P K "New development in ion exchange", in *Proceedings* of international conference ion exchange ICIE'91, Tokyo. 1991

[6] Subash Chand, Seema, Arti, Chandra Vijay Chahal, "Synthesis, Characterization and Ion Exchange Properties of A New Ion Exchange Material: Bismuth (III) Iodophosphate"*Recent Research in Science and Technology*, vol.3 No.(6) ,p.01-08, 2011

[7] M.M. Abd El-Latif and M.F. El-Kady, Developing & Characterization of a New Zirconium Vanadate Ion Exchanger and Its Novel Organic – Inorganic Hybrid *Journal of Applied Sciences Research*, vol.4(1):p1-13, 2008

[8] A. A. Khan and M. M. Alam, "Synthesis, Characterization and Analytical Applications of a New and Novel 'Organic–Inorganic' Composite Material as a Cation Exchanger and Cd(II) Ion-Selective Membrane Electrode: Polyaniline Sn(IV) Tungstoarsenate," *Reactive & Functional Polymers*, Vol. 55, No. 3, p. 277-290,2003

[9] Beena Pandit and Uma Chudasama, "Synthesis, characterization and application of an inorgano organic material: p-chlorophenol anchored onto zirconium tungstate" *Bull. Mater. Sci*., Vol. 24, No. 3, June, p. 265–271,2001. © Indian Academy of Sciences.

[10] W. A. Siddiqui, S. A. Khan, "Synthesis, characterization and ion exchange properties of zirconium(IV) tungstoiodo- phosphate, a new cation exchanger ". *Bull. Mater. Sci*, 30(1), p.43–49.,2007

[11] M.F. Attallah, E.H. Borai, Risto Harjula, Airi Paajanen, Mikko Karesoja and Risto Koivula, "Selective Removal of Cesium Using Zirconium(IV) Tungstate as an Inorganic Ion Exchanger from Aqueous Solution "*Journal of Materials Science and Engineering* B vol.1 issue 6B, p.736-746, 2011

[12] D.K.Singh and Shalini Singh,"Synthesis, characterization and analytical applications of zirconium(IV) sulphosalicylophosphate" *Indian Journal of Chemical Technology* Vol. 11, January 2004, p. 23-28

[13] Singh P, Rawat J P and Rehman N " Synthesis and characterization of zirconium(IV) iodovanadate and its use as electron exchanger", *Talanta* vol.59, p.443-452,2003

[14] Thakkar R.and Chudasama Uma "Synthesis and characterization of zirconium titanium phosphate and its application in separation of metal ions" *Journal of Hazardous Materials*, Vol. 172, Issue 1, p. 129–137,2009

[15] Singh P, Rawat J P and Rehman N , "Synthesis, characterization and Ion Exchange Properties of a New Inorganic Ion Exchange Materials: Zirconium(IV)iodooxalate," *Indian J. Chem.* A vol.41 p.1616, 2002

[16] Gupta A P, Verma G L and Ikram S "Studies on a new heteropolyacid-based inorganic ion exchanger; zirconium(IV) selenomolybdate" *React. Funct. Polym.* vol.43, p.33-41,2000

[17] Varshney K G, Pandith A H and Gupta U "Synthesis and characterization of zirconium aluminophosphate. A new cation exchanger", *Langmuir*, vol. *14*, *1998*, p.*7353*-7358.

[18] Topp N. E. and Pepper K. W. "Properties of ion-exchange resins in relation to their structure. Part I. Titration curves," *Journal of the Chemical Society*, p. 3299–3303, 1949.

[19] Reilley C N, Schmid R W and Sadek F S "Chelon approach to analysis (I) survey of theory and application," *Journal of Chemical Education*, vol. 36, , p. 555, 1959.