Studies of organic-inorganicnano composite ion-exchanger: Poly (o-toluidine)/Zirconium(IV)tungstoiodophosphate

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Abstract : Nano composite material is growing very rapidly. This is because of using building blocks with the dimension in the nano size range makes it possible to design and create new materials. Nano composites are a special class of materials originating from suitable combination of two or more nano particles in some suitable technique, Organic polymeric part of the composite provide mechanical and chemical stability where as inorganic part support the ion – exchange behaviour, thermal stability and also increase the electrical conductivity. Thus, the synthesis of polymeric/inorganic composites has received a great deal of attention because it provided new materials with special mechanical, chemical, electrochemical and optical as well as magnetic properties. Few such excellent ion – exchange materials have been developed and successfully being used in chromatographic techniques. It was therefore considered to synthesize such hybrid ion–exchangers with a good ion–exchange capacity, high stability, reproducibility and selectivity for heavy metal ions, indicating that they are useful in environmental applications. An organic-inorganic nano composite ion-exchanger, poly(o-toluidine)/Zr(IV) tungstoiodo phosphate was prepared by sol-gel mixing of poly(o-toluidine) into the matrices of inorganic precipitate of Zr(IV)tungstoiodophosphate. The ion-exchange capacity ,effect of eluent concentration, elution behaviour, pH and effect of time on ion exchange capacity were also carried out by using standard procedures.

1. Introduction

Nano composite material is growing very rapidly. This is because of using building blocks with the dimension in the nano size range makes it possible to design and create new materials. Nano composites are a special class of materials originating from suitable combination of two or more nano particles in some suitable technique. One of the best ways is the formation of conducting composites. "Conducting Composites" means incorporation of the Conducting polymer into a suitable matrix. The matrix may beinsulating or conducting. Conducting composites are having attractive properties The conducting polymer based nano composites have shown great potential in gas sensing[1].One of the composites contains a conducting polymer (Polypyrrole,

Polyanilineetc) and metal oxides [2-3]. Nano composite contains polymer and inorganic ion – exchange material prepared by sol – gel method has shown conducting behaviour and excellent ion – exchange properties with electrochemical application.[4-5]

Organic polymeric part of the composite provide mechanical and chemical stability where as inorganic part support the ion – exchange behaviour, thermal stability and also increase the electrical conductivity. Such a modified composite materials can be applied as electrochemically switchable ion – exchanger [6-7] for water treatment, especially water softening. This ion – exchanger can be regenerated without chemical additives or water electrolysis. The synthesis of hybrid ion-exchangers with controlled functionality and hydrophobicity could open new avenues for organometallic chemistry, catalysis, organic host-guest chemistry, analytical chemistry[8-10] ,hydrometallurgy, antibiotic purification and separation of radioactive isotopes, and find large scale application in water treatment and pollution control .Thus, organic-inorganic hybrid materials are expected to provide many possibilities as new composite materials that exhibit very different properties from their original components (organic polymer and inorganic materials), especially in the case of molecular level hybrids. Thus, the synthesis of polymeric/inorganic composites has received a great deal of attention because it provided new materials with special mechanical, chemical, electrochemical and optical as well as magnetic properties[11-14].

Few such excellent ion – exchange materials have been developed and successfully being used in chromatographic techniques[15-17]. It was therefore considered to synthesize such hybrid ion–exchangers with a good ion–exchange capacity, high stability, reproducibility and selectivity for heavy metal ions, indicating that they are useful in environmental applications.

In the present work, the ion-exchange studies of a new and novel organic-inorganic nano composite ion-exchanger by incorporation of organic polymer ie;poly(o-toluidine) and inorganic ion-exchanger ie; Zirconium (IV) tungstoiodophosphate was analysed.

2.Experimental

Preparation of poly(o-toluidine) Zr(IV)tungstoiodophosphate

The composite ion exchanger was prepared by the sol-gel mixing of poly(o-toluidine), an organic conducting polymer, into the inorganic precipitate of Zirconium(IV)TIP. In this process, when the gels of poly(o-toluidine) were added to the white inorganic precipitate of zirconium (IV) tunstoiodophosphate with a constant stirring for 7 hrs. The resultant mixture were turned slowly into a greenish black colored slurries. The resultant greenish black-colored slurries were kept for 24 hrs at room temperature. Now the poly(o-toluidine) based composite gels were filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of KPS. The product was dried in an air oven.

3.Ion exchange properties of poly(o-toluidine)/Zr(IV)tungstoiodo phosphate

3.1) Ion-exchange capacity

The ion exchange capacity, which is generally taken as a measure of hydrogen ion liberated by neutral salt to flow through the composite ion-exchanger was determined by standard column process. 1g of dry cation exchanger in the H^+ form was taken into a glass column. 1M alkali and alkaline earth metal nitrates / chlorides as eluents were used to elute the H^+ ions completely from the cation exchange column maintaining a very slow flow rate (0.5ml min^{-1}). The effluent was titrated against a standard NaOH solution for the total ions liberated in the solution using phenolphthalein indicator. Ion exchange column used for ion exchange studies of organic – inorganic hybrid cation – exchange material is given in the following Table1.

Table.1 IEC of various exchanging on poly(o-toluidine)Zr(IV)TIPnanocomposite ion – exchanger using KPS oxidant.

| Exchanging ions	P^H of the metal solution	Ionic radii (A^0)	Hydrated ionic radii (A^0)	Ion exchange capacity(meq/g)
Li^+	3.3	0.68	3.4	2.72
Na^+	4.9	0.97	2.76	2.92
K^+	6.5	1.33	2.32	3.08

The ion exchange capacity of the hybrid ion exchanger for alkali metal ions increases according to decrease the hydrated ionic radii $K^+ > Na^+ > Li^+$.

3.2)Effect of eluent concentration

The magnitude of elution depends on the concentration of eluent. To find out the optimum concentration of eluent for complete elution of H^+ions, a fixed volume (250ml) of LiCl, NaCl, KCl solutions of varying concentration (0.2-1.8M) were passed through a column containing 1g of the exchanger in H^+ form with a flow rate of 0.5ml/ min. The effluent was titrated against a standard alkali solution of 0.1M NaOH for the H^+ ions eluted out using phenolphthalein as an indicator.

Table- 2 : Effect of concentration of Eluent on IEC of ion exchanger.

Concentration of eluent (M)	Ion exchange Capacity of cation exchanger(m.eq/g)		
	Li+ ion	Na^+ion	K^+ion
0.2	1.52	1.8	2.04
0.4	1.64	1.92	2.2
0.6	1.84	2.08	2.32
0.8	2.04	2.28	2.4
1.0	2.36	2.48	2.56
1.2	2.72	2.92	3.08
1.4	2.72	2.92	3.08
1.6	2.72	2.92	3.08
1.8	2.72	2.92	3.08
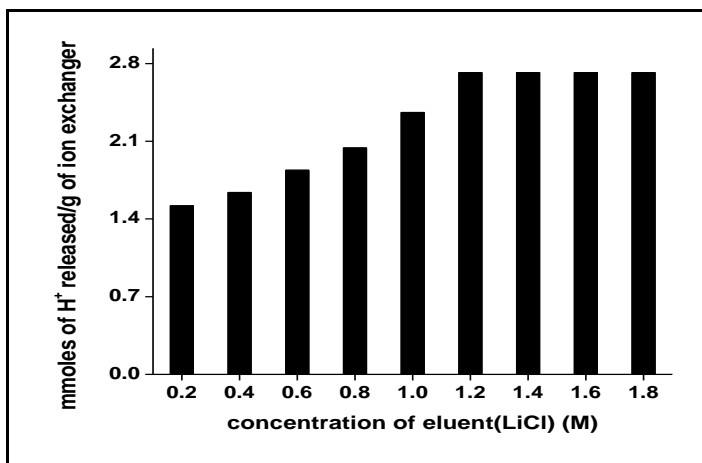
Fig 1:Concentration plot ofpoly(o-toluidine)/Zr(IV)TIP nanocomposite byvarying the concentration of LiCl solution
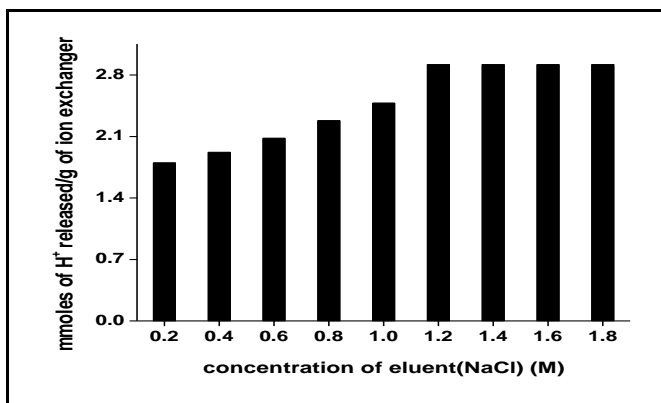
Fig 2: Concentration plot of Poly(o-toluidine)/Zr(IV)TIP nano composite by varying the concentration of NaCl solution
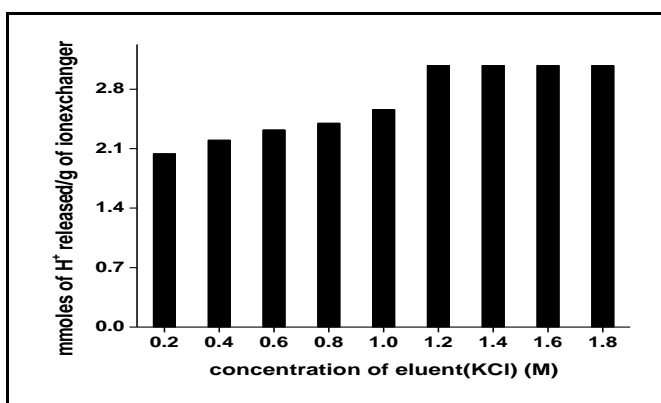

Fig 3: Concentration plot of Poly (o-toluidine)/Zr (IV)TIP nanocomposite by varying the concentration of KCl solution

Theminimum molar concentration of LiCl (resp. NaCl and Kcl) as eluent for poly (o-toluidine) Zr(IV) tungstoiodophosphate cation exchanger asfound 1.2M for maximum release of H$^+$ ions from 1g of the cation exchanger is evidence from fig 1(resp. fig 2 and fig 3).
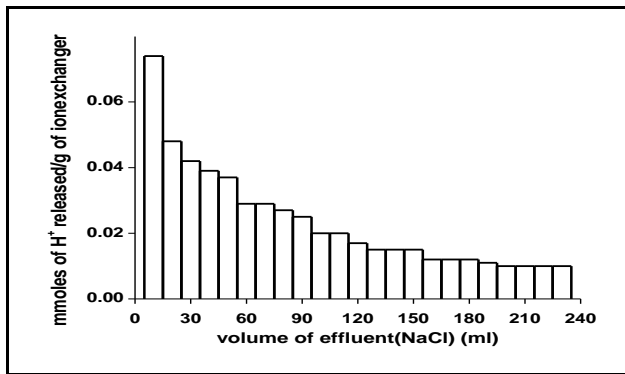
3.3) Elution behaviour

Since, with the optimum concentration for complete elution was observed for Poly(o-toluidine) Zr(IV)tungstoiodophosphate nano composite ion exchanger a column containing 1g of exchanger in H$^+$ form was eluted with LiCl, NaCl, KCl, solutions of 1.2M concentration in different 10ml fractions with minimum flow rate if 0.5ml min^{-1} and each fractions of 10ml effluent was titrated against a standard alkali solution for the H$^+$ ions eluted out. This experiment was conducted to find out minimum volume necessary for complete elution of H$^+$ ions which determines the exchange efficiency of the column as in Fig:4
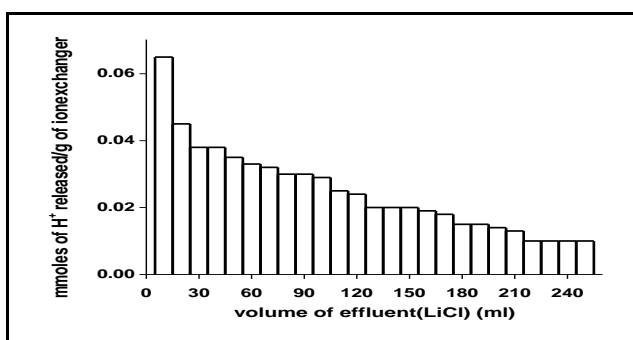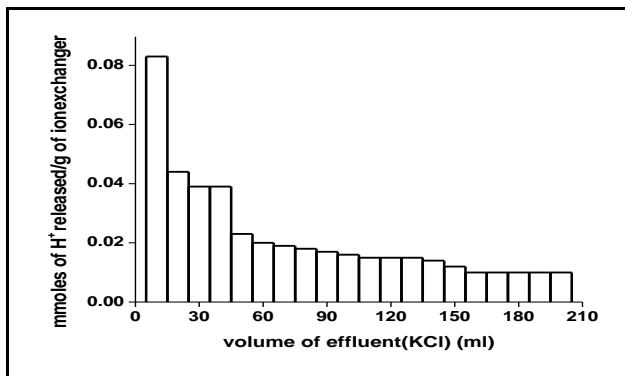

Fig 4: Elution behaviour of Poly(o-toluidine)/Zr(IV)tungstoiodo phosphate ion exchange material using LiCl as eluent

The elution behaviour indicated that the exchange is quite fast because only 250ml of LiCl solution is enough to release the total H^+ ions from 1g of ion exchange material.

Fig 5: Elution behaviour of Poly(o-toluidine)/Zr(IV)TIP ion exchange material using NaCl as eluent.

The elution behaviour indicated that the exchange is also fast because only 230ml of NaCl solution is sufficient to release the total H^+ ions from 1g of cation exchange material.


Fig 6: Elution behaviour of Poly(o-toluidine)/Zr(IV)TIP ion exchange material using KCl as eluent

The elution behaviour indicated that the exchange is also fast because only 210ml of KCl solution is sufficient to release the total H^+ ions from 1g of cation exchange material.

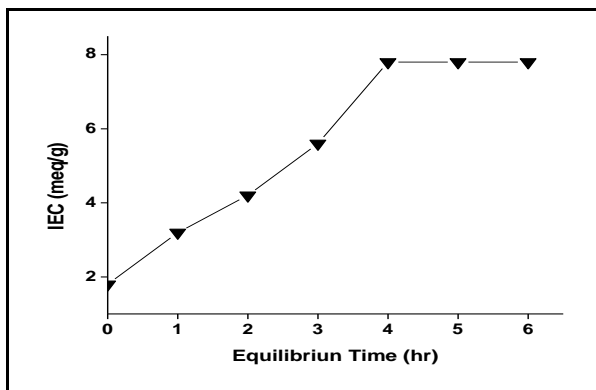**3.4) Effect of time on IEC**

The optimum shaking time of ion-exchanger with LiCl solution for complete elution of H^+ ions were determined 0.25g of ion exchanger was shaken with 25ml of LiCl and the amount of liberated H^+ ions were titrated against the standard NaOH solution after every half an hour interval.
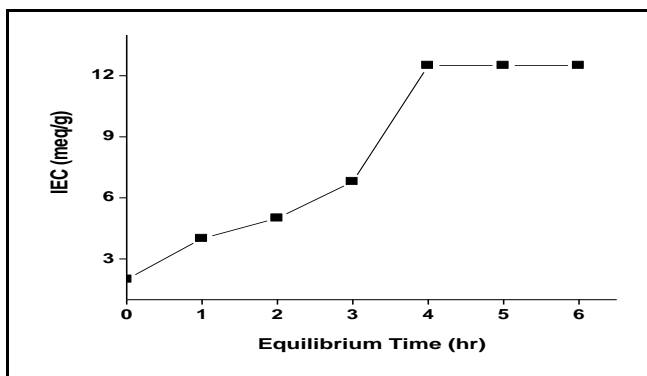
Fig 7:Effect of equilibrium time on IECof poly(o-toluidine)/Zr(IV)TIP

The　effect of equilibration time on exchange capacity of Poly(o-toluidine) Zr(IV) tungstoiodophosphate cation exchanger shows a constant ion exchange capacity only after 4 hrs equilibration.The optimum shaking time of ion exchange with NaCl solution for complete elution of H^+ ion was determined. 0.25g of ion exchanger was shaken with 25ml of NaCl and the amount of liberated H^+ ions were titrated against the standard NaOH solution after every half an hour interval.
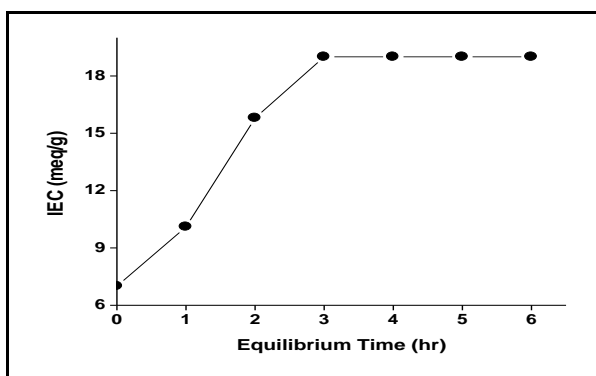

Fig 8: Effect of equilibrium time on IECof poly(o-toluidine)/Zr(IV)TIP

The effect of equilibration time on exchange capacity of Poly(o-toluidine) Zr(IV) tungstoiodophosphate ion exchanger shows a constant ion exchange capacity only after 4 hrs equilibration.The optimum shaking time of ion exchange with KCl solution for complete elution of H^+ ion wasdetermined. 0.25g of ion exchanger was shaken with 25ml of KCl and the amount of liberated H^+ ions were titrated against the standard NaOH solution after every half an hour interval.


Fig 9: Effect of equilibrium time on IECof poly(o-toluidine)/Zr(IV)TIP

The effect of equilibration time on exchange capacity of Poly(o-toluidine) Zr(IV) tungstoiodophosphate cation exchanger shows a constant ion exchange capacity only after 3 hrs equilibration.

3.5) P^H Titration.

200mg portions of the cation – exchanger in the H^+ form were placed in each of the several 250ml conical flasks followed by the addition of alkali metal chlorides (LiCl, NaCl, KCl) and their hydroxides in different volume ratio, the final volume was kept 50ml to maintain the ionic strength constant. The pH of the solution was recorded every 24hr until equilibrium was attained which needed 5 days and pH at equilibrium was plotted against the milli equivalents of OH^- ions added.
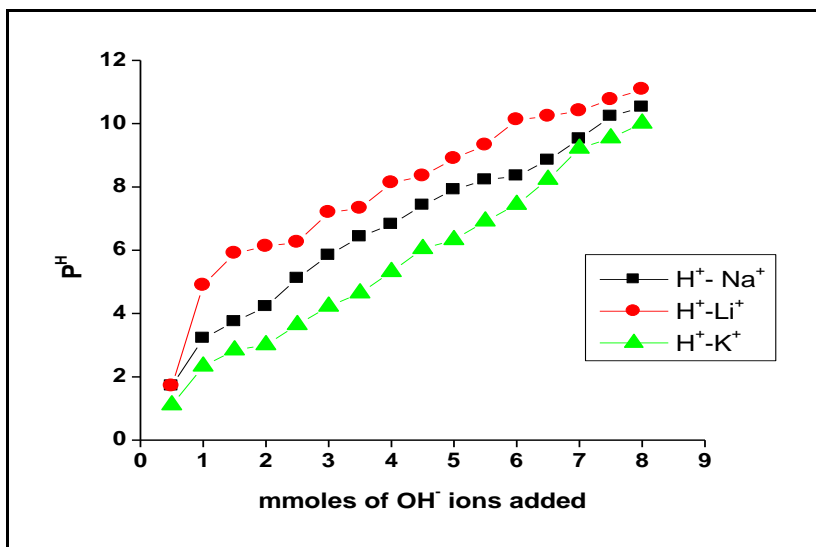
Fig 10: P^H titration curves forpoly(o-toluidine)/Zr(1V)TIP nanocomposite ion exchanger with various alkali metal hydroxides.

The pH titration curves for Poly(o-toluidine Zr(IV)tungstoiodo phosphate was obtained under equilibrium conditions with LiOH / LiCl, NaOH / NaCl, and KOH / KCl system indicating bifunctional behaviour of the material as shown in fig.10. The rate of H^+ - K^+ exchange was faster than those of H^+ - Na^+ and H^+ - Li^+ exchanger.

3.6) Selectivity (sorption) studies

The distribution behaviour of metal ions plays an important role in the determination of selectivity of the material. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution co-efficient of the counter ions.

The distribution coefficient (Kd values) of various metal ions an poly(o-toluidine Zr(IV) tungstoiodophosphate was determined by batch method in various solvent system. Various 200mg of the composite cation exchanger in the H^+ form were taken in flasks with 20ml of different metal nitrate solutions $Pb(NO_3)_2$, $Cu(NO_3)_2$, $CO(NO_3)_2$ in the required medium and kept for 24 hour with continuous shaking. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.25M solution of EDTA. The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase. In other word, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^+ ions from a solution by an ion-exchange material and hence mathematically can be calculated using formula given as,

$$K_d \ (ml \ g\text{-}1) \ = \ \frac{m \ moles \ of \ metal \ ions \ / \ g \ of ion \ exchanger}{m. \ mole \ of \ metal \ ions \ / \ ml \ of \ solution}$$

$$K_d \quad = \quad \frac{(I\text{-}F)}{F} \quad \frac{V}{M} \quad ml \ g^{-1}$$

where

I	-	initial amount of metal ion in the aqueous phase (mol dm^{-3})
F	-	Final amount of metal ion in aqueous phase (mol dm^{-3})
V	-	Volume of the metal ion (ml)
M	-	amountof cation exchanger(g)

Table- 3 K_d values of some metal ions on poly(o-toluidine) Zr(IV) tungsto iodophosphate column in different solvent systems.
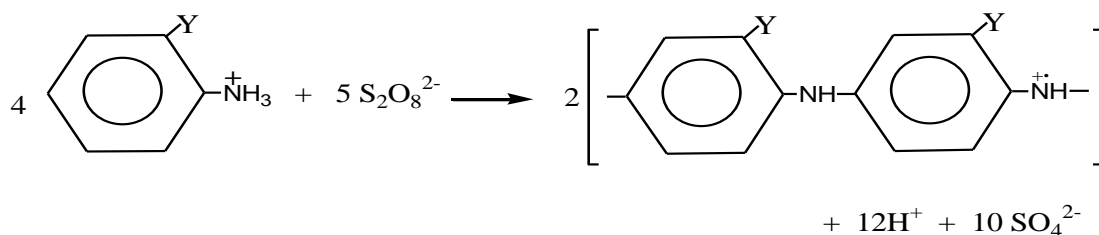
Solvents	Pb^{2+}	Cu^{2+}	Co^{2+}
DMW	334	100	30
10% ethanol	244	112	34
10% acetone	367	150	18
1M H_2SO_4	89	64	42

In order to find out the potentiality of this composite material in the separation of metal ions, distribution studies for three metal ions were performed in four solvent systems. The distribution studies showed that K_d values varied with the nature and composition of contacting solvents. It was also observed from the sorption studies (K_d values) showed that the composite has a maximum selectivity towards Pb^{2+} because lead was highly adsorbed in all solvents, while remaining metal ions were poorly adsorbed. Pb^{2+} is a major pollutant in the environment that can be removed easily by thepoly(o-toluidine)Zr(IV)tungstoiodophosphate.
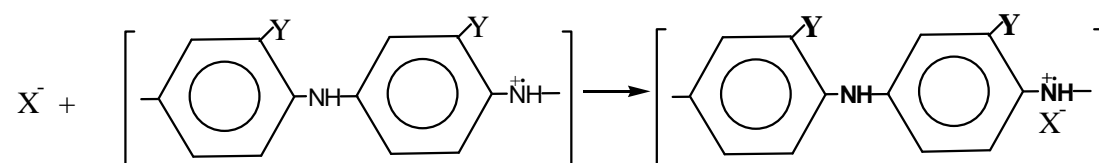
4. Results and Discussion

In the present study, new and novel organic – inorganic electrically conducting nano composite ion exchanger was chemically prepared by sol- gel mixing of organic conducting Polymers like Poly (o- toluidine) into the matrix of inorganic ion – exchangers (ie) Zirconium (IV) tungstoiodophosphate.

The mechanism for the formation of conducting Polymeric – inorganic nanocomposite ion – exchanger.Poly (o- toluidine) gel was prepared by oxidation coupling using $K_2S_2O_8$ in acidic medium.

$$4 \; \text{(aryl-)}\overset{+}{N}H_3 + 5\,S_2O_8^{2-} \longrightarrow 2\left[\text{(aryl)-NH-(aryl)-}\overset{+}{N}H- \right]$$

$$+ \; 12H^+ + 10\,SO_4^{2-}$$

The binding of Poly (o- toluidine) into the matrix of Zr (IV) tungstoiodo phosphate is possible due to ionic interaction between the radical cation of Poly (o- toluidine) and anionic group Zr(IV) tungstoido phosphate.

$$X^- + \left[\text{(aryl)-NH-(aryl)-}\overset{+}{N}H- \right] \longrightarrow \left[\text{(aryl)-NH-(aryl)-}\overset{+}{N}H- \; X^- \right]$$

Zr TIP   Conducting polymer   Conducting polymeric- inorganic
                                                                       ion-exchnager

Where, Y   = $CH_3 \rightarrow$ o – Toluidine

The organic – inorganic nano composite ion – exchanger of Poly- o – toluidine Zirconium (IV) tungstoiodophosphate having good ion – exchange capacity compared to that of the individual ion – exchanger like Zirconium (IV) tungstoiodo phosphate which has the IEC 2.2 m eq /g. The ion – exchange capacity of the nano composite ion exchanger in $meqg^{-1}$ for different metal ions are Li^+, 2.72; Na^+ 2.92; K^+, 3.08.

The IEC of the hybrid ion exchanger for alkali ion increased according to the decrease in the hydrated ionic radii. The rate of elution is governed by the concentration of eluent. The minimum molar concentration of LiCl, NaCl, KCl as eluent for Poly(o-toluidine)/Zr(IV) tungstoiodophosphate was found 1.2 M for maximum

release of H^+ ions from 1g of cation exchanger. The elution behaviour of LiCl, NaCl, kCl indicates that the exchange is quite fast as at the beginning all the exchangeable H^+ ions are eluted out in 250 ml, 230ml, 200ml of the effluent respectively.The P^H titration curve shows slow increase when LiOH, NaOH, KOH were added to the nanocomposite ion exchanger. The P^H curves for POT/ Zr(IV) tungstoiodo phosphate were obtained under equilibrium conditions with NaOH/ NaCl, KOH/ KCl and LiOH/ LiCl systems indicated the rate of H^+- K^+ exchange was faster than those of H^+- Na^+ and H^+- Li^+ exchangers.The effect of equilibration time on exchange capacity of POT/ Zr(IV) tungstoiodo phosphate using LiCl, NaCl, KCl eluent shows a constant capacity only after 4, 4 and 3 hours equilibration respectively.The distribution studies for three metal ions were performed in four solvent system. The K_d values shows the maximum selectivity towards Pb^{2+}, because Pb^{2+} has highly adsorbed in all solvents while remaining metal ion were poorly adsorbed.

5. Conclusion

Conducting organic–inorganic nanocomposite ion–exchange materials were synthesised by sol- gel mixing of organic conducting polymers into the inorganic phosphate.From ion – exchange studies, it is quite clear that the effect of eluent concentration of LiCl, NaCl, KCl was found to be 1.2M. and elution time on exchange capacity of these composite cation exchanger show a constant capacity only after 4, 4 and 3 hours equilibration.The effect of size and charge of exchanging ions on the IEC of nano composite cation exchanger following the order $K^+ > Na^+ > Li^+$.This sequence is in accordance with decrease in size of hydrated ionic radii of the exchanging ions.The analytical importance of the material was deduced from K_d values for different metal ions in different solvents. The material had high affinity for Pb^{2+} ion which is a major polluting metal in the environment.From XRD studies and SEM images, the materials can be considered as nanocomposite materials with semicrystalline structure.

Acknowledgement

6. References

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