Ion exchange behavior of a new thermally-chemically stable inorganic ion exchanger Zr(IV)tungstomolybdate and its application for selective separation of hazardous metal ions

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ABSTRACT
A thermally and chemically stable cation exchanger Zr(IV)tungstomolybdate has been synthesized. The effect of experimental conditions such as order of mixing, volume ratio, pH stirring time, drying temperature was examined. The cation exchanger showed good ion exchange capacity, higher stability, reproducibility and selectivity for heavy metals. On the basis of distribution studies, the exchanger was found to be highly selective for a toxic and environmentally pollutant mercury ion. Its selectivity was demonstrated by achieving some important binary separations, Fe^{3+}-Hg^{2+}, Co^{2+}-Hg^{2+} and Fe^{3+}-Zn^{2+}. The exchanger provided a technological opportunity for quantitative determination and separation of Hg^{2+} ions from waste effluents.
Key Words: Synthesis; inorganic cation exchanger; Zr(IV)tungstomolybdate; selectivity; toxic metal ion.

1. INTRODUCTION

The toxicity of heavy metals is not new but the problem was brought in to focus recently when various lakes and rivers were found dangerously polluted due to industrial and agricultural activities. Mercury is one of the most dangerous metal ions in our environment. Ion exchange method is one of the best methods for selective removal of metal ions. Generally, inorganic ion exchangers are superior to organic exchangers as they are resistant towards high ionizing radiation [1, 2]. They have selectivity towards certain metal ions and can be used at higher temperatures without any decomposition. The importance of the synthetic ion exchangers is due to their growing application for pollution abatement, preconcentration and recovery of ionic species from aqueous solutions. Furthermore, they are useful in portable renal dialysis, kidney dialysis, desalination plants, biochemical and pharmaceutical industrial. Two component ion exchangers have been studied the most but it has been found that three component inorganic ion exchangers show relatively increased ion exchange capacity and selectivity [3-5].

2. EXPERIMENTAL

2.1. Reagents:

All the reagents and chemical used were of Analar grade obtained from Merck or Aldrich.

2.2. Instrumentation:

The pH measurement was made with a Schott CG841 pH-meter and a Sico thermostated shaker was used.

2.3. Synthesis:

A number of Zr(IV)tungstomolybdate samples were prepared by mixing aqueous solution of appropriate reagents in different mixing ratio. The desired pH was adjusted by adding either dilute HCl or ammonia solution to the precipitate. The gelatinous precipitate was kept in the mother liquor for 24 h and then divided into two parts. One part was filtered and washed with demineralized water directly and the second part was refluxed for 6 h first prior to being filtered and washed with demineralized water. The products were dried at 40 ºC in an oven. The dried product were converted to H^+ form by 1M HNO_3 solution and then washed with demineralized

water to remove excess acid, and finally dried at 40 ºC. Hence, a number of samples were prepared, and on the basis of ion exchange capacity and percentage of yield, sample Z1 was selected for detailed studies.

2.4. Ion Exchange Capacity:
1g of the ion exchange material in H^+ form was placed in a glass column with glass wool supported at the bottom. The H^+ form was eluted with 1M solution of different salts. The flow rate was adjusted to 8-10 drops/min. The effluent was collected and titrated against a standard solution of sodium hydroxide using phenolphthalein as an indicator.

2.5. Effect of eluent concentration:
250 mL of $NaNO_3$ solution of different concentration were passed through the columns containing 1g of the exchanger in H^+ form with a flow rate of 0.5 mL min^{-1}. The effluents were titrated against a standard alkali solution of 0.1M NaOH using phenolphthalein as an indicator.

2.6. Elution behavior:
The optimum concentration of $NaNO_3$ solution for complete elution of H^+ ions was passed through 1g of the cation exchanger (H^+ form) with a flow rate of 0.5 mL min^{-1}. The effluent was collected in 109 mL fractions and each fraction was titrated against a standard alkali solution.

2.7. pH titration:
0.5g of the exchanger in H^+ form was placed in each of several 250 mL conical flasks, followed by the addition of equimolar solutions of alkali and alkaline earth metal chlorides and their hydroxides in different volume ratios. The final volume remains 50 mL to maintain the ionic strength constant. The pH of each solution was determined after 24 h and plotted against milliequivalents of OH^- ions added.

2.8. Distribution Coefficient:
0.4g of the exchanger in H^+ form was treated with 40 mL solution of metal ion. The mixture was placed in a thermostated shaker for 6 h at 25 ºC. The amount of metal ions left in the solution after adsorption was then determined by titration against the standard solution of 0.01 M di-sodium salt of EDTA. The K_d values are expressed by

$$K_d = \frac{I - F}{F} \cdot \frac{V}{M} mLg^{-1} \qquad \text{"eq 1"}$$

where I is the initial amount of metal ion in the solution; F is the final amount of metal ion in the solution; V is the volume of the solution (mL) and M the amount of exchanger (g).

2.9. Separation factor:
In order to explore the possibility of metal ion separation, a factor has to be ascertained. It is is expressed as follows:

$$Separation\ Factor\ (\alpha_B^A) = \frac{K_d(A)}{K_d(B)} \qquad \text{"eq 2"}$$

where $K_d(A)$ and $K_d(B)$ are distribution coefficients for the two competing species A and B in the ion exchange system.

2.10. Quantitative separation of metal ions:

1 g the exchanger in H^+ form was packed in a glass column with 0.8 cm internal diameter with glass wool support at the bottom. The column was washed thoroughly with demineralized water and then 2 mL mixture of metal ions was loaded and allowed to pass through the column at a flow rate of 4-5 drops min^{-1}, till the solution level was just above the surface of the material. The column was then washed with demineralized water. Individual metal ions were eluted using the appropriate eluting agents. The flow rate of eluent was maintained at 1 mL min^{-1} throughout the process. The effluent was collected in 10 mL fractions and was titrated against the standard solution of 0.01 M di-sodium salt of EDTA.

3. RESULTS AND DISCUSSION

Cation exchanger Zr(IV) tungstomolybdate was prepared in different conditions as shown in Table 1. The sample Z1 with the highest ion exchange capacity and greater yield was chosen for detailed studies. Ion exchange capacities for mono and bivalent ions were determined for both refluxed and un-refluxed samples (Table 2). The refluxed sample has higher ion exchange capacity for each metal ion. The higher ion exchange capacity for refluxed sample is due to more liberated H^+ ions being attached to the exchanger. Table 3 shows that ion exchange capacity is also affected by temperature. On heating at different temperatures for one hour, the mass, physical appearance and ion exchange capacity of the sample Z1 were changed. A sharp loss in ion exchange capacity after temperature increase could be due to formation of mixed oxides of zirconium, tungsten and molybdenum groups.

In order to achieve complete elution of H^+ ion, the concentration of the eluent plays an important role. Fig. 1 shows that the maximum molar concentration of $NaNO_3$ as eluent was 1 M for maximum release of H^+ ions from 1g of the cation exchanger. The elution behavior shows the ion exchange is relatively fast and maximum H^+ ions are eluted out in the first 100 mL by using 1M $NaNO_3$ for 1g of the exchanger (Fig. 2).

The pH titration of Zr(IV) tungstomolybdate was performed for NaCl-NaOH, $MgCl_2$-$Mg(OH)_2$ and $CaCl_2$-$Ca(OH)_2$ systems. The pH titration curve, Fig. 3, shows one inflection point that indicates the monofunctional behavior of the exchanger.

The chemical stability studies show that the exchanger is quite stable in common mineral acids and other common electrolyte solutions. The distribution coefficients for some metal ions have been determined in some prospective solvents as shown in Table 4. It has been found that solvents have profound effect on the adsorption potential of the resin. It was observed that the K_d values in presence of 0.1M formic acid is higher than those of 0.1M formamide for all metal ions studied. It's worth noting that, the adsorption of Hg^{2+} was much higher than other metal ions. On the basis of K_d values, separation factors were calculated as shown in Table 5. A number of binary separations Fe^{3+}-Hg^{2+}, Co^{2+}-Hg^{2+} and Fe^{3+}-Zn^{2+} have been achieved on the column of Zr(IV)tungstomolybdate (Table 6). The sequential elution of ions through the column depends upon metal-eluting ligand stability, and strongly retained metal ions elute last.

4. CONCLUSION

Zr(IV)tungstomolybdate as a new cation exchange material possessed a high chemical, mechanical stability in comparison to other double salts. The ion exchange material was used for the separation of heavy toxic metal ions from aqueous medium, due to its high selectivity. It may also be used in nuclear thermal power plants for waste effluent treatment, due to its high thermal stability.

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Table 1 Conditions of synthesis of Zr(IV)tungstomolybdate cation exchanger

Sample Code	Mixing volume v/v/v			pH	Conditions	Physical appearance of the beads	IEC for Na^+ ion $Meqg^{-1}$
	0.1M $ZrOCl_2.8H_2O$	0.1M $Na_2MoO_4.2H_2O$	0.1M $Na_2WO_4.2H_2O$				
Z1	1	1	1	1	Refluxed	Yellowish	2.40

Table 2 Ion exchange capacity of various exchanging ions on Zr(IV)tungstomolybdate cation exchanger

Sample	Exchanging ions	Ionic Radii (Å)	Hydrated Radii (Å)	IEC $meqg^{-1}$ of dry exchanger (refluxed)	IEC $meqg^{-1}$ of dry exchanger (Un-refluxed)
1	Li^+	0.68	10.0	1.09	0.97
2	Na^+	0.97	7.90	2.40	2.00
3	Ca^{2+}	1.06	9.60	1.16	1.07
4	Sr^{2+}	1.27	9.40	1.90	1.51
5	Ba^{2+}	1.43	8.80	2.10	1.80

Table 3 Effect of temperature on ion exchange capacity of Zr(IV)tungstomolybdate cation exchanger

Temperature/ºC	Appearance (color)	IEC for Na^+ ion $meqg^{-1}$ exchanger	% Weight loss	% Retention of ion exchange capacity
100	pale yellow	2.40	2.50	100.00
200	pale yellow	2.38	10.00	99.90
300	pale yellow	2.38	10.10	99.90
400	greyish	2.20	13.00	91.66
500	Pale brown	2.14	14.00	89.16
600	Brownish/blue	2.10	15.00	87.50
700	Pale blue	2.09	16.10	87.00
800	whitish/grey	2.00	16.10	83.33
900	white	1.40	17.00	58.33

Table 4 Distribution coefficients of metal ions in various solvent systems

Metal ion	0.1M $HCONH_2$	0.1M HCOOH	0.1M $HCONH_2$ +0.1M HCOOH (!:!)	0.1M $HCONH_2$ +0.1M HCOOH (2:1)	0.1M $HCONH_2$ +0.1M HCOOH (3:!)	0.1M NH_4Cl
Zn^{2+}	110	980	549	440	380	200
Co^{2+}	450	810	592	502	480	778
Fe^{3+}	510	540	518	518	514	1140
Hg^{2+}	6840	7800	7240	7204	7102	5048

Table 5 Separation factors achieved on Zr(IV)tungstomolybdate column using 0.1M $HCONH_2$ eluent

Separation factor	Value
α_{Co}^{Hg}	15.20
α_{Zn}^{Hg}	62.18
α_{Fe}^{Hg}	13.30

Table 6 Qualitative separations of metal ions in binary mixtures on Zr(IV) tungstomolybdate column

Binary Separations	Amount loaded (µg)	Amount found (µg)	%Recovery	% Error	Volume of eluent used (mL)	Eluent used
Zn^{2+}	327	328	100.30	+0.30	45	0.1M $HCONH_2$
Hg^{2+}	1002	998	99.60	-0.40	80	0.1M NH_4Cl
Fe^{3+}	279	2.70	96.77	-0.23	60	0.1M $HCONH_2$
Hg^{2+}	1002	998	99.60	-0.40	80	0.1M NH_4Cl
Co^{2+}	295	298	98.30	-0.70	50	0.1M $HCONH_2$
Hg^{2+}	1002	998	99.60	-0.40	80	0.1M NH_4Cl

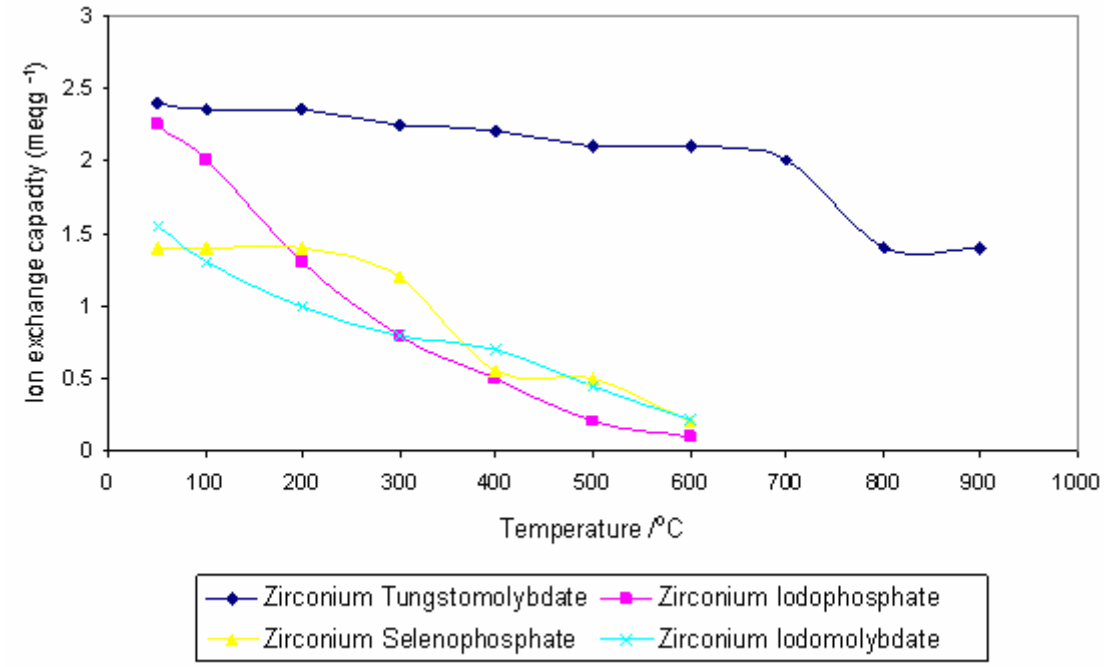

Fig.1 Comparison of the ion exchange capacity of different ion exchange at various temperature

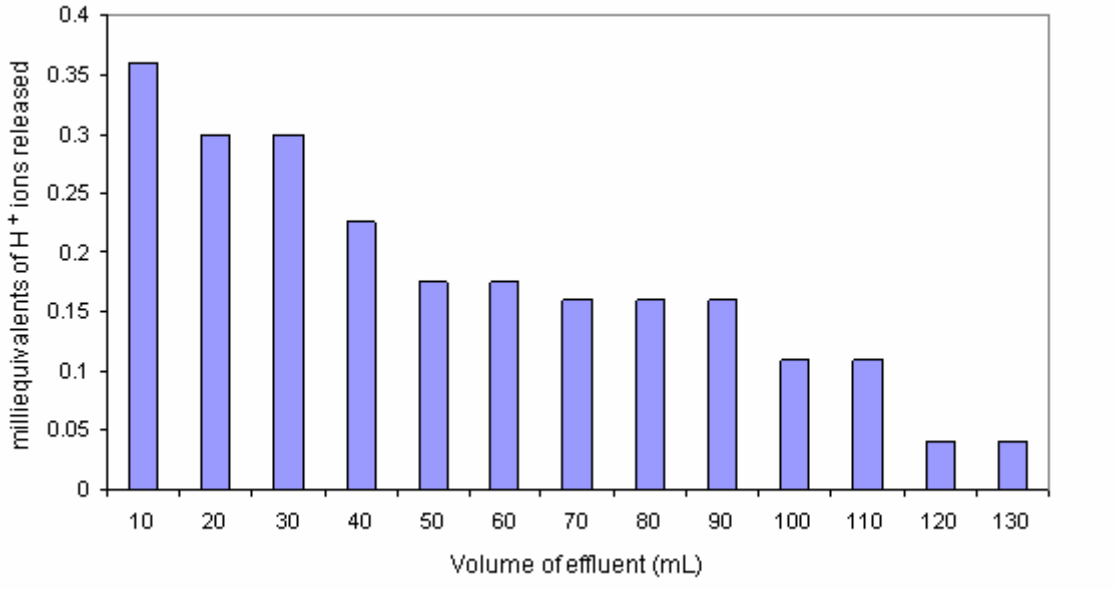

Fig.2 Histogram showing the elution behavior of Zr(IV) Tungstomolybdate cation exchanger

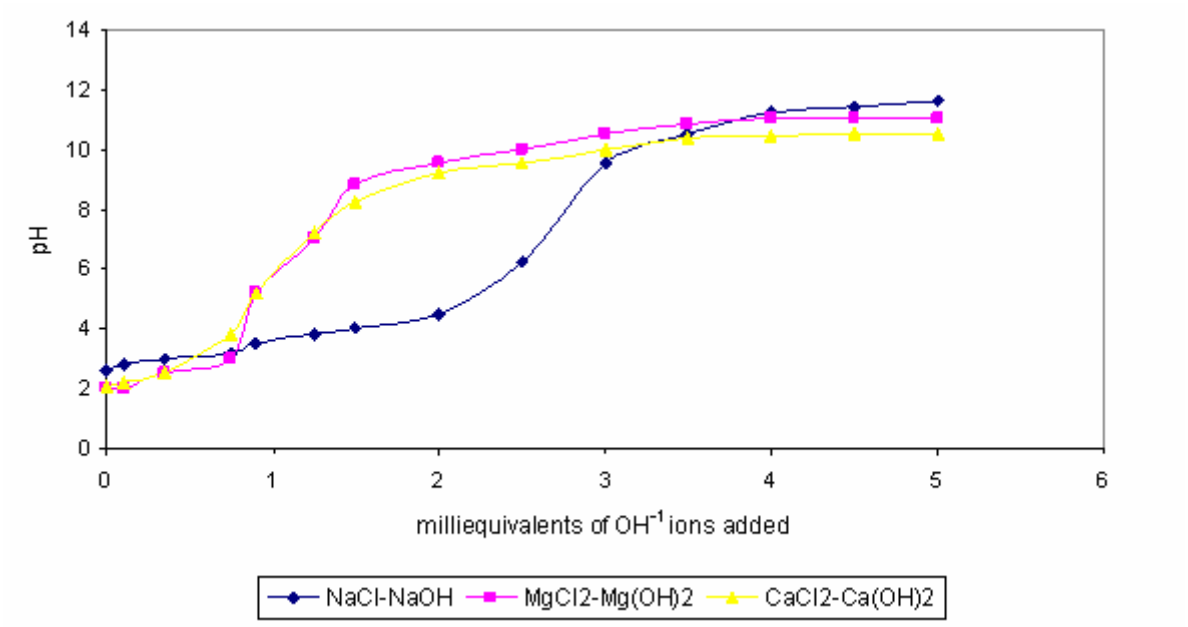

Fig.3 pH titration curves for Zr(IV) Tungestomolybdate cation exchanger with alkali and alkaline metal hydroxides