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4. Application of Synthesized Ion Exchanger Tin (IV) Vanadomolybdate

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Abstract:

The distribution coefficient of Tin (IV) vanadomolybdateion exchanger for various metal ions revealed that the exchanger is selective for Ni2+ and Cu2+ ions, by the help of KD values. Binary separation of some important metal ion pairs was achieved. The ion exchanger may also be employed in the removal of transition metal ions from their aqueous solution. The effective separation of Ca2+and Mg2+ ions from hard water and the removal of colour metal ions were also achieved.

Keywords:

Distribution coefficient, Binary separation, Water softening, Removal of transition metal ions.

4.1 Introduction:

Ion exchange[1,2] is the process in which ions are exchanged between a solution and an insoluble solid. Ion exchange serves as one of the most important analytical technique for the separation of charged species from a solution that would ordinarily be very difficult and time consuming. Ion exchange process may be done with the help of an ion exchanger, interchange of ions of the same charge by other ions[3]. The earliest systematic studies of ion exchange were described with base exchange in minerals present in the soil[4].Ion exchanger may be natural or synthetic. Most natural ion exchangers like zeolites are crystalline materials having cation exchange properties. First synthetic industrial ion exchanger was reported in 1905[5]. In recent years' various zeolites with completely regular crystal structure have been synthesized and these products are exact counterparts of the natural materials. The examples of such kind of material include zeolite 4A[6] and zeolite A[7]. Now a day's synthetic inorganic ion exchangers have drawn the attention since they are less sensitive to higher temperature and to different chemicals and are also selective to certain ions. Further it was shown that three component ion exchangers show a better IEC than the two component ion exchangers. Tin (IV) based ion exchangers have been studied in detail previously by Varshney et al[8]. Various two component ion exchangers based on tin (IV) were reported in the literature[9-14]. Similarly, some examples of three component ion exchangers reported are stannic (IV)silicomolybdate[15], stannic(IV)arsenosilicate[16], stannic(IV)iodophosphate[17], stannic(IV)molybdophosphate[18], stannic(IV)phosphotungstate[19] and stannic(IV)arsenophosphate[20]. Trace element can be removed from water by a range of physicochemical method such as membrane filtration, precipitation and ion exchange[21].

The present work is concerned with the application of Tin (IV) vanadomolybdate ion exchanger the synthesized ion exchanger finds several applications in analytical chemistry. Ion exchanger process is applied in several cases for separation of Ions that interfere in many analytical procedures may be removed. Some important application of ion exchanger is binary separation of metal ions, water softening and removal of colour metal ions.

4.2 Requirements:

A. Glasswares: Burette converted into column, Funnel, Glasss wool, Burette stand, Chemical balance, Oven, Mangnetic stirrer, Pipette, Beaker, Glass rod, Test tube with Test tube stand. All glass ware that is used throughout the experimental work was Borosil mark.

B. Reagents and Chemicals: Sodium hydroxide, Lead nitrate, Bismuth nitrate and EDTA were Qualigens product. All the acid that is Perchloric acid Hydrochloric acid, Nitric acid were also Qualigens product. Chemicals such as Zinc acetate, Cobalt acetate, Copper acetate, Nickel acetate, Ammonium chloride were also used in the experimental work.

4.3 Experimental:

A. Distribution Behavior:

In order to examine the affinity of tin (IV) vanadomolybdate towards various metal ions, distribution coefficient (k_d) values for ten metal ions were determined by batch process[22-28]. In this process ten equal portions 0.50g each of the exchanger were treated separately with 25ml of 0.1M aqueous metal salt solutions. The mixtures were then kept for twenty-four hours at room temperature and subsequently determination of metal ions was done by titrating the solutions against the standard solution of EDTA (Complexometric Titration)[23] with the help of appropriate indicators. The k_d values as given in Table 4.1 were calculated according to the formula-

$$K_d = \frac{I - F}{F} \times \frac{V}{W}$$

Where, I – Initial volume of the EDTA solution used

F – Final volume of the EDTA solution used

V – Volume of the metal ion solution taken

W – Weight of the exchanger

Table 4.1: Distribution Coefficient for Different Metal Ions with TVM

Sr. No.	Metal ions	Form	K_d(ml/g)
1	Ca^{2+}	Carbonate	2.54
2	Mg^{2+}	Acetate	6.11
3	Zn^{2+}	Acetate	5.33
4	Cu^{2+}	Acetate	12.25
5	Mn^{2+}	Acetate	0.40
6	Co^{2+}	Acetate	0.20
7	Ni^{2+}	Ammonium sulphate	23.67
8	Pb^{2+}	Nitrate	5.09
9	Bi^{3+}	Nitrate	10.73
10	Cd^{2+}	Chloride	6.36

4.4 Separations Achieved:

The values of separation factor for different metal ion pairs obtained for the exchanger were greater than three and the values are obtained by using following formula.

$$\alpha_B^A = \frac{K_d\, Value\, of\ A}{K_d\, Value\, of\ B}$$

Where

α_B^A is separation factor

A. Binary Separation:

The ion exchanger Tin (IV) vanadomolybdatewas also employed for binary separations of Ni-Pb, Zn-Co, Ni-Co, Ni-Mn, Ni-Mg, Cu-Co Combination as indicated by the value of separation factors for these metalions pairs. In binary separations. 0.50g of the exchanger in H^+ form was packed in glass columns. The column was washed with demineralized water and then metal ion mixtures were poured in column separately. The absorbed metal ions were eluted with appropriate eluents one by one. The flow rate of the effluent was maintained at 1ml/min through the elution process. The effluents were collected separately in different conical flasks and metal ions concentration were determined (Complexometric Titration) against disodium EDTA salt solution using suitable indicators[24-28]. The results are summarized in Table 4.2.

Table 4.2: Binary Separation Achieved with The Help of Tin(IV)Vanadomolybdate

Sr. No.	Metal ion pairs	Amount loaded(μg)	Amount found(μg)	% of Metal ion eluted	% Error	Total elution volume	Eluent used
1	Ni^{2+}	8217	8158	99.21	- 0.79	50ml	0.1M $HClO_4$
	Pb^{2+}	2279	2279	100	0.00	40ml	0.1M HNO_3
2	Zn^{2+}	1831	1766	96.45	- 3.55	40ml	0.2M $HClO_4$
	Co^{2+}	707.16	650.23	91.94	- 8.05	60ml	1.0M NH_4NO_3
3	Ni^{2+}	8217	8334	101.42	+1.42	40ml	0.001M HNO_3
	Co^{2+}	707.16	707.16	100	0.00	60ml	0.1M HNO_3 +0.5M NH_4OH
4	Ni^{2+}	8217	8275	100.71	+ 0.71	50ml	1.0M NH_4Cl + 0.1MHCl
	Mn^{2+}	1540	1428	92.72	- 7.27	30ml	

Sr. No.	Metal ion pairs	Amount loaded(µg)	Amount found(µg)	% of Metal ion eluted	% Error	Total elution volume	Eluent used
							0.1M HCl
5	Ni^{2+}	8217	8099	98.56	- 1.44	80ml	1.0M HNO_3
	Mg^{2+}	1944	1871	96.24	- 3.76	70ml	0.4M NH_4NO_3
6	Cu^{2+}	2923	2796	95.65	- 4.35	50ml	0.2M HNO_3
	Co^{2+}	707.16	707	99.84	- 0.27	60ml	0.2M $HClO_4$

B. Water Softening:

Hardness causing $Ca^{2+}$and Mg^{2+}were also removed with help of Tin (IV) vanadomolybdate. Column operation was used for the removal of metal ions. The hardness of the water sample was determined by complex metric titration method, in which Eriochrome Black-T was used as an indicator. In water softening, definite volume of hard water sample was passed at rate of 10 drops per minutes through the column maintained the bed of ion exchanger in column. This process is repeated for three times. Hardness causing calcium and magnesium loaded in the column were eluents using 1M HNO_3 and 0.01M $HClO_4$ as eluents respectively. The elution rate was maintained at 5 drops per minute. The eluted Ca^{2+} and Mg^{2+} amount was determined by quantitatively with appropriate indicators. The results are shown in Table 4.3.

Table 4.3. Removal of Ca^{2+} and Mg^{2+} With the Help of TVM

Sr. No.	Metal ions	Amount loaded(µg)	Amount found (µg)	% of Metal ion eluted	% Error	Total elution volume	Eluent used
1	Ca^{2+}	240.5	218	90.65	-9.35	50ml	1.0M HNO_3
2	Mg^{2+}	1775	1750	98.59	-1.41	50ml	0.01M $HClO_4$

C. Removel of Transition Metal Ions:

Application of the exchanger in removing the metal ions from different water samples was done using by Column method. The determination of Co^{2+}, $Ni^{2+}$and $Cu^{2+}$was done ascertain the amount of these ions in their aqueous solutions. The method of determination was done on the basis of two types. In qualitative determination, different definite volumes of the three solutions were loaded on the ion exchanger packed in three different columns.

The flow rate of ten drops per minutes was maintained the solution were passed three times through the exchanger. The effluents of the three columns were collected in three different containers. The presence of the metal ions in all the containers was confirmed by performing qualitative analysis as given in Table 4.4. All the qualitative test was found to be negative.

Table 4.4: Qualitative Tests for Transition Metal Ions for TVM

Sr. No	Metal ion	Colour of the salt solution before passing through exchanger	Colour of the salt solution after passing through exchanger	Detection of metal ion in the effluent
1	Ni(II)	Green	Colorless	a) Effluent NaOH Solution- No Precipitate Ni(II) absent b) Effluent Ammonia- No Precipitate Ni(II) absent
2	Co(II)	Pink	Colorless	Effluent + Sodium hydroxide Solution-No Precipitate Co(II) absent
3	Cu(II)	Blue	Colorless	a) Effluent NaOH Solution- No Precipitate Cu(II) absent b) Effluent Ammonia- No Precipitate Cu(II) absent

For quantitative determination of metal ions, suitable eluents were passed through all the columns containing loaded exchanger.

After elution process the amount of metal ions was determined by complex metric titration using suitable indicators. The results are shown in Table 4.5.

Table 4.5. Removal of Transition Metal Ions with The Help of TVM

Sr. No.	Metal ion	Amount loaded (µg)	Amount found (µg)	% of Metal ion eluted	% Error
1	Co^{2+}	707.16	665.45	94.10	-5.89
2	Ni^{2+}	8217	8092	98.48	-1.52

Sr. No.	Metal ion	Amount loaded (µg)	Amount found (µg)	% of Metal ion eluted	% Error
3	Cu^{2+}	2923	2798	95.72	-4.27

4.5 Result and Discussion:

The study of the values obtained for distribution coefficient revealed that the material shows high selectivity for Ni^{2+} and Cu^{2+} for which the k_d values were 23.67ml/g and 12.25ml/g respectively. The distribution coefficient for the metal ions (Table 1) follows the sequence-

$Ni^{2+} > Cu^{2+} > Bi^{3+} > Cd^{2+} > Mg^{2+} > Zn^{2+} > Pb^{2+} > Ca^{2+} > Mn^{2+} > Co^{2+}$

In binary Separation of different combinations were quite successful through ion exchanger. The exchanger removed different metal ions to different extent such as 650.23µg Co^{2+} was removed out of 707.16µg Co^{2+} while 8334µg Ni^{2+} was removed out of 8217µg Ni^{2+}. The removal is seen from 91.94% to 101.42%. In Ni –Pb separation, the difference between loaded amount and amount found show that lead is 100% eluted with 0% error and nickel is eluted to 99.21% with -0.79% error. The recovery ranges of nickel is present in all combination from 95-100% and the results are summarized in Table 2.

The synthesized ion exchanger Tin(IV)vanadomolybdate can removed Ca^{2+} and Mg^{2+} from hard water and it may helpful in water softening. The results for these ion exchanger implies that Mg^{2+} can be removed from hard water up to 98.59% and removed of Ca^{2+} is 90.65% and the results are shown in Table 3.

The role of the ion exchanger is found to be useful in decontamination of the chemicals. Detection of the metal ions are (qualitative analysis) made it possible decide the determination process. The results are shown in Table 4. Quantitative determination of metal ions in a sample helped in knowing the amount of metal ion present which in turn was helpful to decide the exchange process. The observation table clearly indicates that Tin (IV) vanadomolybdate was found to be able to decontaminate cobalt 94.10%, Nickel 98.48% and 95.72% Copper respectively. The results are shown in Table 5.

4.6 Conclusion:

In the present work the analytical applications are performed for Tin (IV) vanadomolybdate. The ion exchanger possesses selectivity for trace metals such as, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}. The ion exchanger is also employed for the binary separation of heavy metals present in aqueous media and also used as in water softening.

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