

ZIRCONIUM SELENITE AND THORIUM TELLURITE CATION EXCHANGERS: SEPARATION OF SOME METAL IONS

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ABSTRACT. Zirconium selenite and thorium tellurite exchangers were synthesized for the first time and their applications were studied. The chemical composition of both exchangers (0.5 molar ratio) showed metal to anion (Zr^{4+} : SeO_3^{2-} or Th^{4+} : TeO_3^{2-}) ratio as 1:2. The IR spectra of both exchangers revealed absorption bands in the region $3500-3000\text{ cm}^{-1}$ due to water and OH groups, and $1700-1600\text{ cm}^{-1}$, which may be due to interstitial water. Other characteristic peaks assignable to the respective exchangers have been noted. The hydrogen ion exchange capacity of zirconium selenite and thorium tellurite (molar ratio 0.5) were found to be 1.2 meq/g and 1.12 meq/g, respectively. Distribution coefficients of some metal ions on both exchangers (molar ratio 0.5) were determined at different pH in the range 2 to 6.5. The distribution coefficients were higher for Pb^{2+} , Co^{2+} and Cu^{2+} than for other metal ions tested. On the basis of distribution coefficients, separations of Pb^{2+} from Cu^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} , Mn^{2+} , and Ni^{2+} , have been achieved. The recovery of almost all metal ions in the effluent collected was quantitative.

INTRODUCTION

Ion-exchange processes were studied systematically in the middle of the last century [1]. The first commercially available ion-exchangers were amorphous aluminosilicate gels [2]. These exchangers were known to be unstable towards acid solutions. This and the variability in their behaviour led chemists to seek alternatives [3]. This search eventually led to the synthesis of the first organic ion-exchange resins [1,4] which dominated the field until the post World War II era. The advent of nuclear technology initiated a search for inorganic ion exchange materials that would remain stable above 150° and in high radiation fields [5,6].

The use of inorganic ion-exchangers have been explored only in the beginning of the last two decades [7-12]. Since then the analytical applications of synthetic inorganic ion-exchangers have attracted great attention [5,6,13,14]. The important features of these materials are: the differential selectivity [13,15], the ease of preparation, the extra stability under ionizing radiations [16-18], and at high temperature. As part of our continuous work in the field [19] we report here the synthesis of zirconium selenite and thorium tellurite ion exchangers and chromatographic separation of some metal ions. Even though Pb^{2+} can be determined in the presence of Zn^{2+} , Cd^{2+} , Co^{2+} , etc. without separation by AAS, it may be necessary to separate and recover quantitatively Pb^{2+} from other metal ions from nuclear and other industrial wastes where this work can be useful.

EXPERIMENTAL

General: A temperature controlled Gallenkamp water bath, 20H and flask shaker were used during shaking. A Beckman Chem-Mate pH meter was used for the pH determination. Zirconium oxychloride, sodium selenite, thorium nitrate, sodium tellurite and all other reagents and chemicals were BDH laboratory grade. Metal ion concentrations were determined by using a Varian Techtron AAS model AA6 (the detection limits range from 0.2 ppm for Co to 2.0 ppm for Cd).

Synthesis: Zirconium selenite was obtained by adding a solution of 0.5 M sodium selenite in 4 M HCl dropwise from a buret into a beaker containing the exact volume of 0.25 M zirconium oxychloride in 4 M HCl at room temperature to give molar ratios (Zr:Se) 0.5, 1.0 and 1.5. The acidity of the mixture was adjusted to about 1 M in HCl. The precipitate was filtered and washed with 2 M HNO₃ followed by distilled water until it was free from chloride ion and dried at 40° for 4 days. The material was ground and sieved through 90-180 mesh, soaked in 2 M HNO₃ overnight, washed with distilled water and dried again at 40°.

This was based on the fact that the ion-exchange capacities of tin(IV)selenite after drying the material at different temperature appears to retain high capacities at temperature between 40 to 100° [20]

Thorium tellurite of molar ratios 0.5, 1.0 and 1.5 were synthesized in a similar manner from a 0.2 M solution of sodium tellurite in 4 M HCl added to a 0.1 M thorium nitrate in 2 M HNO₃.

Hydrogen ion exchange capacity: The hydrogen ion exchange capacities of both the exchangers of compositions 0.5, 1.0 and 1.5 molar ratios were determined by mixing 0.25 g of the exchanger with 1 M NaCl (50 cm³) and kept for 1 day while shaking intermittently (pH of solution was 3.0 ± 0.1). The exchanged protons from the aliquot were titrimetrically determined with a standard solution of 0.1 N NaOH using phenolphthalein indicator.

Composition: For determination of the chemical composition of zirconium selenite, 2 mg of the sample (molar ratio 0.5) was boiled with conc. NaOH (50 cm³) for 2 h to precipitate zirconium and selenium which was redissolved in conc. HCl. The procedures reported were followed to estimate zirconium [21] and selenium [23].

Similarly 2 mg of thorium tellurite (molar ratio 0.5) was boiled with conc. HCl (50 cm³) for 1 h [24]. The solution was cooled and filtered and used for the determination of thorium [25] and tellurium [26]

Distribution coefficient: The values of the distribution coefficients (K_d) of Pb²⁺, Mn²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Zn²⁺ and Co²⁺ were determined [27] by equilibrating 0.1 g exchanger (molar ratio 0.5) with 10 cm³ of solution containing 7x10⁻³ M metal ions at pH 2, 3, 4, 6 and 6.5. The K_d values were calculated from the equation.

$$K_d = \frac{\text{amount of metal ion exchanged}}{\text{amount of metal ion in solution}} \times \frac{\text{volume (cm}^3\text{)}}{\text{exchanger (g)}}$$

For separation studies, 2 g of the exchanger (molar ratio 0.5) in the H^+ form was packed in a 0.69 cm inner diameter glass column up to 3.5 cm in height. A 2 μmol amount of each Ni^{2+} , Mn^{2+} , Zn^{2+} , Fe^{2+} and Pb^{2+} were loaded on top of the column and the elution was carried out after 30 min. with suitable eluting concentration of HNO_3 . The rate of flow was 0.5 cm^3/min and 5 cm^3 fractions of effluent were collected for metal ion determination.

RESULTS AND DISCUSSION

The ratio of $Zr^{4+}:\text{SeO}_3^{2-}$ or $\text{Th}^{4+}:\text{TeO}_3^{2-}$ is largely dependent upon the mixing ratio of the two components, that is, the ratio in the exchanger increases as the mixing ratio increases up to 1.5. The ratio of $Zr^{4+}:\text{SeO}_3^{2-}$ or $\text{Th}^{4+}:\text{TeO}_3^{2-}$ in the exchanger corresponds to the stoichiometric value of $Zn^{4+}:\text{SeO}_3^{2-}$ or $\text{Th}^{4+}:\text{TeO}_3^{2-}$. The hydrogen ion exchange capacity was found to be strikingly dependent upon the ratio of anion to metal. Hence the material with molar ratio 0.5 has a higher capacity of 1.12 meq/g for thorium tellurite (0.88 and 0.30 meq/g for molar ratios 1 and 1.5, respectively) and 1.20 meq/g for zirconium selenite (0.96 and 0.76 meq/g for molar ratios 1 and 1.5, respectively) which indicates that the exchangeable protons originate from the tellurite and selenite, respectively. These results are in agreement with other related works [27-29]. Zirconium selenite and thorium tellurite exchangers are unstable in alkaline solution. Therefore a measure of exchanger capacity as the amount of hydrogen ion exchanged by a neutral salt, such as sodium chloride was performed. The exchange capacity was constant at 2 M concentration of sodium chloride. The material with high capacity (molar ratio 0.5) was tested for its distribution coefficients and separation possibilities.

The ion-exchange properties, and to what extent it takes place, depend on thermodynamic, kinetics and structural factors [30] which are beyond the scope of this work. The products obtained were in the form of amorphous hard white materials. From the chemical analysis the molar composition of zirconium selenite (molar ratio 0.5) shows that zirconium and selenium are present in the ratio of 1.0:2.1. A similar result was also found for thorium tellurite (molar ratio 0.5) where thorium and tellurite are present in the ratio of 1.0:2.2.

The IR spectrum of zirconium selenite in the H^+ form exhibits strong absorption bands in the regions 3500-3000 cm^{-1} (assigned to water and OH groups), 1700-1600 with a maximum at about 1640 cm^{-1} (attributed to interstitial water molecules) [20], 800-650 cm^{-1} (due to ionic SeO_3^{2-}) [31] and 400-500 cm^{-1} (due to Zr-O).

Similarly the IR spectrum of thorium tellurite in the H^+ form revealed absorption bands in the region 3500-3000 cm^{-1} , 1700-1600 (maximum at 1630 cm^{-1}), 800-600 cm^{-1} and 400-350 cm^{-1} . The peak at 800-600 cm^{-1} corresponds to ionic tellurite [32] while the band at 400-350 cm^{-1} may be due to Th-O [31]. These spectra were also compared with the gelatinous precipitates obtained by addition of hydroxyl ions to the solutions of zirconium oxychloride and thorium nitrate. The peaks due to the interstitial water molecules and the ionic species were not revealed.

Distribution coefficients of metal ions on zirconium selenite and thorium tellurite were determined at different pH (Table 1). The change in the K_d values for all the ions in going from pH 2 to 4 is similar to what is reported [20,23,29]. At pH 2 the adsorption of metal ions on zirconium selenite showed the following selectivity order:

$Pb^{2+} > Co^{2+} > Mn^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$, between pH 3 to 6, the order became the same except that Zn^{2+} and Cd^{2+} are interchanged, while at pH 6.5 it changed to $Pb^{2+} > Zn^{2+} > Mn^{2+} > Cu^{2+} > Cd^{2+} > Co^{2+} > Ni^{2+}$. The selectivity series of metal ions on thorium tellurite also showed a dependence on the pH. However, zirconium selenite and thorium tellurite showed higher affinity for Pb^{2+} and Co^{2+} and Pb^{2+} and Cu^{2+} , respectively, at any given pH, and it is therefore possible to separate these metals from other metals that have lower distribution coefficients. Similar affinities for Pb^{2+} have been reported for zirconium antimonate [19], zirconium phosphate [33], titanium antimonate [26], thorium phosphate and cerium phosphate [23].

Table 1. Distribution coefficient of metal ions on the exchanger (molar ratio=0.50), $K_d \times 10^{-4} \text{ cm}^3 \text{ g}^{-1}$

Metal ion	pH = 2		pH = 3		pH = 4		pH = 6		pH = 6.5	
	A	B	A	B	A	B	A	B	A	B
	Cd^{2+}	0.53	0.61	0.02	0.03	0.03	0.04	0.04	0.05	0.53
Mn^{2+}	3.51	1.75	0.05	0.04	0.07	0.06	0.09	0.08	1.75	0.51
Zn^{2+}	0.87	2.59	0.02	0.06	0.02	0.08	0.03	0.10	0.00	0.71
Cu^{2+}	1.87	5.35	0.03	0.08	0.03	0.10	0.04	0.16	1.30	0.93
Ni^{2+}	1.84	1.02	0.03	0.02	0.04	0.03	0.05	0.04	0.24	0.41
Co^{2+}	4.06	1.35	0.09	0.03	0.10	0.05	0.17	0.06	0.35	0.41
Pb^{2+}	16.58	5.68	0.83	0.52	1.14	0.83	1.35	0.94	6.35	1.45

A = Zirconium selenite exchanger; B = Thorium tellurite exchanger

Some inorganic ion exchangers [34] show size preference selectivity for ions having specific radii, but no such correlation was found between K_d values and effective ionic radii in our studies. It is evident that separation of metal ions are achieved on the basis of differences in the K_d values. Hence those metals with higher K_d can be separated from those with lower K_d values. The solubility of the exchangers in 2 M HNO_3 (50 cm^3) has been tested and was found that less than 1% of zirconium and thorium and less than 4% of tellurium and selenium were dissolved after 12 h shaking at 30°. Hence one can assume that the solubilization of the ions during the elution of the ions with HNO_3 at different concentration would be minimal.

Some typical plots of the elution curves of the metal ions are shown in Figure 1. The elution curves for Pb^{2+} are well resolved and Pb^{2+} is separated quantitatively from Mn^{2+} and Co^{2+} and Zn^{2+} and Cu^{2+} (Fig. 1b). Similarly Cd^{2+} from Co^{2+} and Zn^{2+} from Cu^{2+} (Fig. 1a) were separated in good yield. Recoveries were in the range of 95-99% for all metal ions tested.

The tailing observed for some transition metal ions in the separation experiments could be minimized if the columns are pretreated with dilute nitric acid or by the use

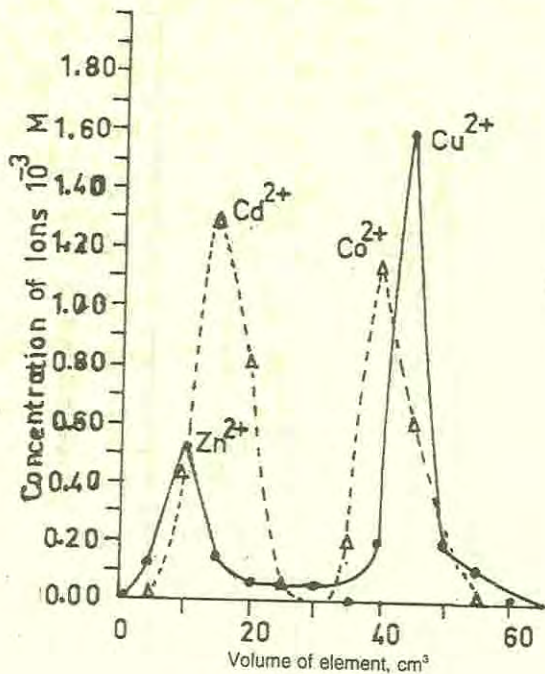


Fig. 1(a)

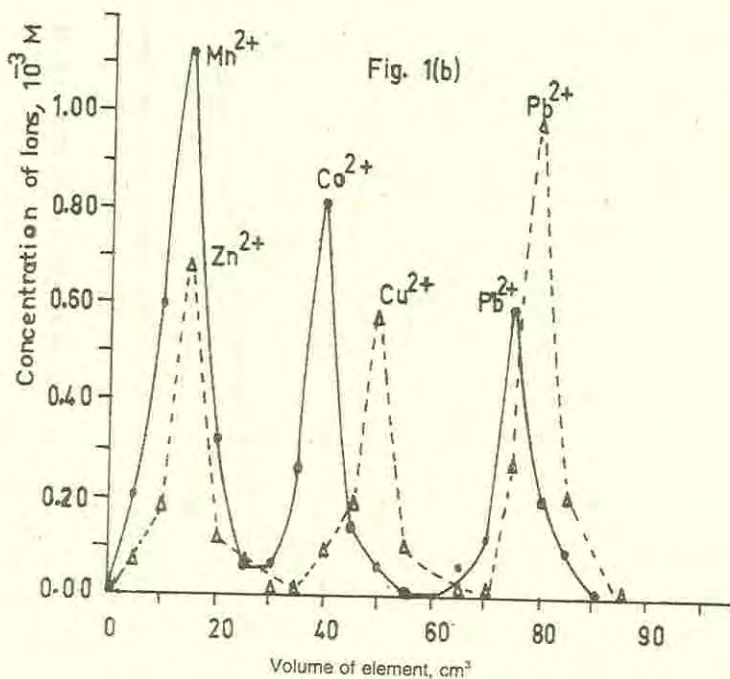


Fig. 1(b)

Fig. 1. Separation of a) Zn^{2+} from Cu^{2+} and Cd^{2+} from Co^{2+} and b) Zn^{2+} and Cu^{2+} and Mn^{2+} and Co^{2+} from Pb^{2+} on zirconium selenite (solid line), and thorium tellurite (dotted line) exchangers.

of 2 M NaNO_3 together with nitric acid as an eluent [19]. The separations achieved on the columns by employing 2 M NaNO_3 and HNO_3 eluent gave a recovery of more than 99% for most of the metal ions studied (Tables 2-4). Relatively low yields in the recovery of some of the metals ions were considered to be due to strong retention of cations by the exchanger particles during the time interval between feeding and elution.

Table 2. Separation of Pb^{2+} from other metal ions on zirconium selenite (A) thorium tellurite (B) columns

	Sample composition	Eluent	Effluent collected (ml)	% Recovery (A)	% Recovery (B)
1	Pb^{2+} and Cd^{2+} (0.41 mg + 0.23 mg)	0.01 M HNO_3	25	100 (Cd^{2+})	98 (Cd^{2+})
		2 M NaNO_3 + 0.15 M HNO_3	40	99 (Pb^{2+})	98 (Pb^{2+})
2	Pb^{2+} and Zn^{2+} (0.41 mg + 0.13 mg)	0.01 M HNO_3	25	94 (Zn^{2+})	99 (Zn^{2+})
		2 M NaNO_3 + 0.15 M HNO_3	40	99 (Pb^{2+})	98 (Pb^{2+})
3	Pb^{2+} and Cu^{2+} (0.41 mg + 0.23 mg)	0.01 M HNO_3	25	94 (Cu^{2+})	97 (Cu^{2+})
		2 M NaNO_3 + 0.15 M HNO_3	40	98 (Pb^{2+})	99 (Pb^{2+})
4	Pb^{2+} and Mn^{2+} (0.41 mg + 0.11 mg)	0.01 M HNO_3	25	100 (Mn^{2+})	100 (Mn^{2+})
		2 M NaNO_3 + 0.15 M HNO_3	40	100 (Pb^{2+})	100 (Pb^{2+})
5	Pb^{2+} and Co^{2+} (0.41 mg + 0.12 mg)	0.01 M HNO_3	25	97 (Co^{2+})	94 (Co^{2+})
		2 M NaNO_3 + 0.15 M HNO_3	40	100 (Pb^{2+})	100 (Pb^{2+})
6	Pb^{2+} and Ni^{2+} (0.41 mg + 0.12 mg)	0.01 M HNO_3	25	100 (Ni^{2+})	99 (Ni^{2+})
		2 M NaNO_3 + 0.15 M HNO_3	40	100 (Pb^{2+})	96 (Pb^{2+})

Table 3. Separation of binary and ternary mixtures on zirconium selenite (A) thorium tellurite (B) columns

	Sample composition	Eluent	Effluent collected (ml)	% Recovery (A)	% Recovery (B)
1	Co^{2+} and Cd^{2+} (0.12 mg + 0.24 mg)	0.2 M HNO_3	30	-	80 (Cd^{2+})
		3 M HNO_3	30	-	94 (Co^{2+})
2	Mn^{2+} and Ni^{2+} (0.11 mg + 0.12 mg)	0.2 M HNO_3	30	94 (Ni^{2+})	91 (Ni^{2+})
		3 M HNO_3	30	98 (Mn^{2+})	99 (Mn^{2+})
3	Cu^{2+} and Zn^{2+} (0.13 mg + 0.13 mg)	0.2 M HNO_3	30	99 (Zn^{2+})	-
		3 M HNO_3	30	97 (Cu^{2+})	-
4	Zn^{2+} , Mn^{2+} and Pb^{2+} (0.13 mg + 0.13 mg + 0.41 mg or 0.12 mg)	0.5 M HNO_3	30	99 (Zn^{2+})	97 (Zn^{2+})
		2 M HNO_3	30	98 (Cu^{2+})	95 (Cu^{2+})
		4 M HNO_3	40	99 (Pb^{2+})	99 (Pb^{2+})

* For A: M = Cu, for B: M = Co

Table 4. Separation of mixture of seven metal ions on zirconium selenite (A) and thorium tellurite (B) columns

	Sample composition	Eluent	Effluent collected (ml)	% Recovery (A)	% Recovery (B)
1	Zn ²⁺ , Cd ²⁺ , Cu ²⁺ , Ni ²⁺ (0.13 mg + 0.23 mg + 0.13 mg + 0.12 mg)	0.04 M HNO ₃	40	87 (Zn ²⁺)	93 (Ni ²⁺)
2	Mn ²⁺ , Co ²⁺ , and Pb ²⁺ (0.11 mg + 0.12 mg + 0.41 mg)	0.1 M HNO ₃	40	97 (Cd ²⁺)	97 (Cd ²⁺)
		0.5 M HNO ₃	40	88 (Cu ²⁺)	93 (Co ²⁺)
		1.0 M HNO ₃	40	94 (Ni ²⁺)	96 (Mn ²⁺)
		2.0 M HNO ₃	40	99 (Mn ²⁺)	91 (Zn ²⁺)
		4.0 M HNO ₃	40	98 (Co ²⁺)	89 (Cu ²⁺)
		5.0 M HNO ₃	40	96 (Pb ²⁺)	96 (Pb ²⁺)

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