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Separation of In (III) and Cd (II) Using Zirconium Vanadate As Inorganic Ion Exchanger

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ABSTRACT

In this work, zirconium vanadate as inorganic ion exchanger was chemically synthesized using homogeneous precipitation technique. The obtained zirconium vanadate was mixed with Indium ions to determine its capacity in aqueous solution using batch experiment. Ion exchange capacity of various metal ions was investigated. Effects of pH, initial concentration, weight of the sorbent and contact time on the adsorption of metals were studied. Chromatographic column methods were applied for separation of indium and cadmium. A fixed bed column of zirconium vanadate was successfully used for separation of indium and cadmium. The recovery percentage of both metal ions was about 98.4% using 2M HCl and citrate buffer pH 3.5, respectively.

Keywords, Inorganic exchanger; Zirconium vanadate; Separation of Indium and Cadmium.

INTRODUCTION

Inorganic ion exchangers, due to their resistance to radiation and chemical attack and their compatibility with potential immobilization matrices, find wide applications in industries, including waste treatment, hydrometallurgy, preparation of high purity materials, water purification and several environmental applications. Separation with an inorganic ion exchanger does not involve organic solvents and in that way is cleaner than a conventional liquid–liquid extraction (LLX) process. The advantage of solid phase extractants to be used for practical purposes like ‘water purification’ and ‘decontamination’ lies in the fact that the extractant does not require further treatment after taking up the desired element from its matrix. For an effective application, the inorganic ion exchangers are supposed to contain ions that are exchangeable with others present in a solution in which it is considered to be

insoluble[1].

The use of inorganic ion exchangers, for the separations of metal ions is of wide interest, particularly in the field of radioanalytical chemistry due to the excellent stability of these materials toward thermal and radiation dose. Inorganic ion exchangers have found wide applications during the separation of carrier free daughter nuclides from their respective parents. During the past few years, a wider application of inorganic ion exchangers in nuclear waste treatment has been investigated for fission and activation product elimination [2]. Keeping parity with the modern trends, some authors recently synthesized two new inorganic ion exchangers, viz. zirconium vanadate [3,4]. The zirconium vanadate ion exchanger has already proved and was used a potential adsorber for alkali metals. However, no attention has been paid to zirconium vanadate until now, although it has been used in the separation of other radioisotopes.

In our present work, we have synthesized a granular variety of zirconium vanadate suitable for batch and column operation and we have attempted a separation between Indium(III) from Cadmium(II) using zirconium vanadate inorganic ion exchanger. The exchange capacities of both metal ions as well as the distribution coefficients of different metal ions have been determined. The equilibration time of the exchanger for uptake of a fixed amount of metal ions were also determined. The results suggest that this exchanger may be suitable as a separation for different hazardous metal ions.

MATERIALS AND METHODS

Synthesis of Zirconium Vanadate

An amorphous variety of zirconium vanadate was prepared as follows: 0.1M sodium vanadate solution (100ml) was added dropwise into a solution of 0.1M zirconyl chloride (50ml) in 2M HCl, with constant stirring when a fine yellow precipitate appeared. After the addition was complete, the reaction mixture was diluted to 2l with deionized water and the precipitate was allowed to settle for 24h. The precipitate was washed several times with de-ionized water, filtered and again washed with hot water until chloride free and pH of the final solution was slightly acidic (around pH 4). The washed solid was dried in a reflected bunsen flame and preserved in adesiccator. The compound was then analyzed for its zirconium and vanadium content by fusing a weighed amount of the solid material with caustic soda. The fused mass was poured into hot water and filtered. The residue was dissolved in 2M H2SO4 and analyzed for zirconium by complexometric titration with ethylenediaminetetra acetic acid

(EDTA). The filtrate was analyzed for vanadium by gravimetric method [4-8].

The material was characterized by its elemental analysis, thermal, chemical and radiation stabilities, pH titration and ion exchange capacity (IEC) for different metals; results have been discussed thoroughly in earlier publication [3].

Determination of Ion Exchange Capacity

Ion exchange capacity (IEC) of the exchanger were determined by equilibrating about 0.5g solid with 50ml of 2M solution of different salt solutions and the liberated acid was estimated by inductive coupled plasma (ICP) . The IEC of different ions are tabulated in Table (1).

Table (1): Exchange Capacity of Different Metal Ions

Metal ion	Exchange Capacity (meq/g)	Ref.
In^{3+}	3.6	**Calculated**
Cd^{2+}	1.2	
Na^{+}	4.08	**(4, 5)**
K^{+}	4.32	
Cs^{+}	0.13	
Mg^{2+}	0.88	
Sr^{2+}	0	
Ba^{2+}	0	
Ca^{2+}	0	
Y^{3+}	0.1	

Thermal, Radiation and Chemical Stability

Thermal stability of the zirconium vanadate was studied employing a differential thermogravimetric analysis technique. Radiation stability was checked by determining the IEC of the solid before and after γ-irradiation dose of 2.5Gy/min.Chemical stabilities were determined by 0.1g of the exchanger with 50ml of different solvents for a period of 16h followed by the determination of the percentage of vanadium that has dissolved Table (2).

Table (2): Chemical Stability of Zirconium Vanadate in Different Media

Solvent	Vanadium (%) leached out in the solvent
Water	0
2M HCl	4
4M HCl	9
2M HNO_3	2.2
4M HNO_3	5.3
2M H_2SO_4	4.1
4M H_2SO_4	10.7
0.1M NaOH	6.4
1M NaOH	10.4
Ethanol	0
Benzene	0

Batch experiments:

The sorption behavior of the metal ions of In(III), and Cd(II) towards the prepared zirconium vanadate was studied using the batch technique where, 100mg of zirconium vanadate was equilibrated with 20ml aqueous solution containing the indium(III) and Cadmium(II) ions as a binary component system. The uptake percentage of the studied metal ions on the zirconium vanadate was determined using inductive coupled plasma "Jobin Yvon ICP-AES spectrometry model Ultima2", Made in France. The uptake percentage was determined using the following equation **[9-12].**

$$\text{Uptake \%} = [1\text{-}A/A_o] \text{ X } 100$$

Where A_0, A are the concentration of the metal ion before and after addition the resin, respectively.

The capacity (q) was calculated using the following equation[13]:

$$Capacity(q) = \frac{Uptake\%}{100} X \frac{C_o XV}{M} (mg/g)$$

Where C_0 is the initial concentration of solution in mol/l, V is the volume of the solution in ml, m is the weight of the resin.

Column studies for adsorbing and stripping metals

For continuous separation, a glass column 4.6 diameter x 100 length mm was packed with prepared zirconium vanadate using the slurry-packing

technique. A total of 1.2g of zirconium vanadate was introduced (packing depth 50 mm). The columns were controlled by fraction collector of the flow rate 2 ml per 1 minute. Preliminary experiments were performed using single component solution at a concentration of 100ppm of each metal ions and pH was controlled at the optimum pH for selective separation established in previous batch experiments. Different eluent solutions were used for the recovery of metal ions from the zirconium vanadate column. All the experiments were carried out at ambient room temperature (25±1^{o} C).

RESULTS AND DISCUSSION

Batch ion exchange studies

Effect of pH

Preliminary studies indicated that equilibrium was attained within 4 hours, in a shaker with 220 rpm adjusted at 25±1°C, for the exchange reaction. The distribution coefficients of metal ions in demineralized water are very small so that one can not decide whether or not zirconium Vanadate is selective for any cation.

In order to investigate the selectivity of zirconium vanadate for Indium(III) and Cadmium(II), the distribution coefficients (*K*d) were determined at different pH's for each of Indium(III) and Cadmium(II). The sorption behavior, distribution coefficients (*K*d) for Indium(III) and Cadmium(II) at different pH's on zirconium vanadate is shown in Fig.(1).

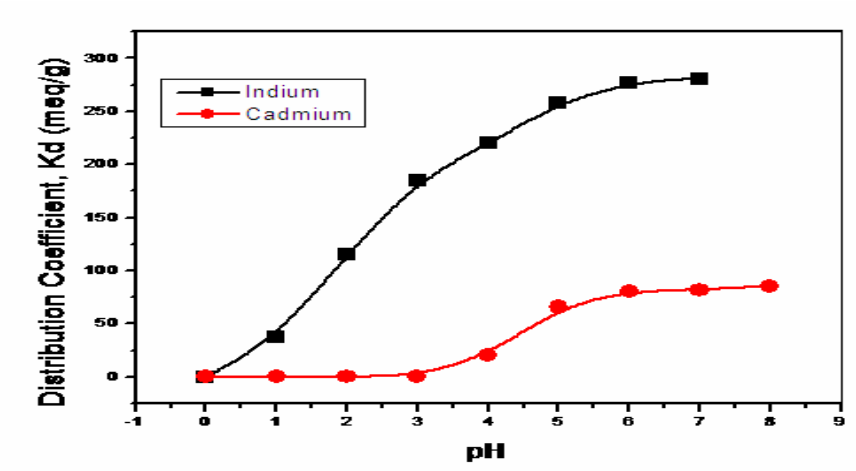

Figure (1): The effect of pH on the distribution coefficient of In(III) from Cd(II) by zirconium Vanadate.

Figure(1): the results show that the distribution coefficient (Kd) of indium(III) and Cadmium(II) increases with increasing pH values. The distribution coefficient values of indium(III) more than cadmium(II) this may be due to the increase of electrostatic interaction of the multivalent cation compared to the divalent cation and to the fact that zirconium vanadate are cation exchangers; their cationic behavior becomes more pronounced by the increase in pH. The extra values of distribution coefficient means that zirconium vanadate more selective for indium(III) than cadmium(II) and to determine the optimum pH value separation of indium (III) and cadmium(II) it must be calculate the separation power.

Separation power

The selectivity coefficient is usually determined using multi-component solutions and calculating the ratio between the distribution coefficients of each metal. To get a separation power coefficient (SP %). This coefficient was calculated using the following equation **[14]**:

$$SP = SE_{M1} - SE_{M2}$$

Where SE_{Mi} (%) is the extraction efficiency at selected pH for metal i.

The values of the distribution coefficients were extrapolated in order to obtain the corresponding values of the separation power. This parameter enables the optimum pH range for metal separation to be predetermined simply and quickly. Using the data of Fig. (1), the separation power was calculated as shown in Fig. (2). From Figure(26), it is clear that pH=4 the optimum pH for separation of Indium(III) from Cadmium(II) using zirconium vanadate.

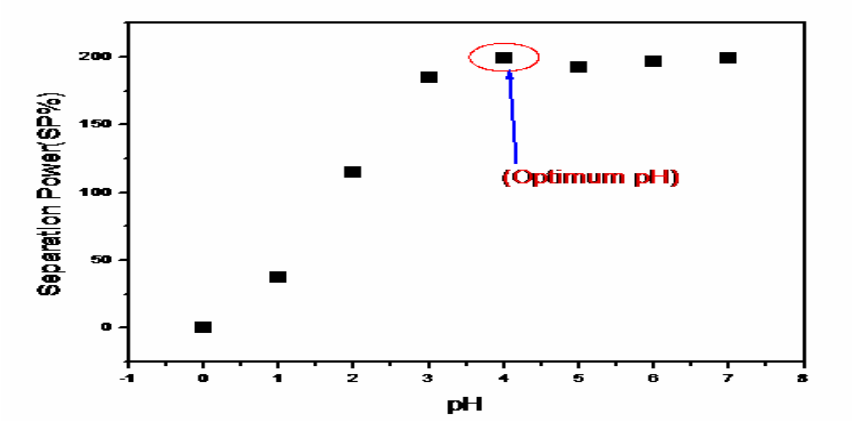

Figure (2): Influence of pH on separation power (SP) for the separation of In(III) from Cd(II) in aqueous solution using zirconium vanadate.

Effect of contact time

The adsorption behavior of In(III) and Cd(II) ions (at concentration 100ppm for each one and pH=4) from aqueous solution was studied with time onto zirconium vanadate. The results are shown in Fig.(3).

The uptake increases with increasing time. The equilibrium time for complete removal of In(III) and Cd(II) onto by zirconium vanadate was found to be 10, 17.5hours respectively. The higher equilibrium time value for Cd(II) relative to In(II) can be attributed the three positive charge on the indium that accelerate the reaction than cadmium. However, the equilibrium time in all studies was set to 12 hours for the sake simplicity as well as to ensure a complete process of adsorption.

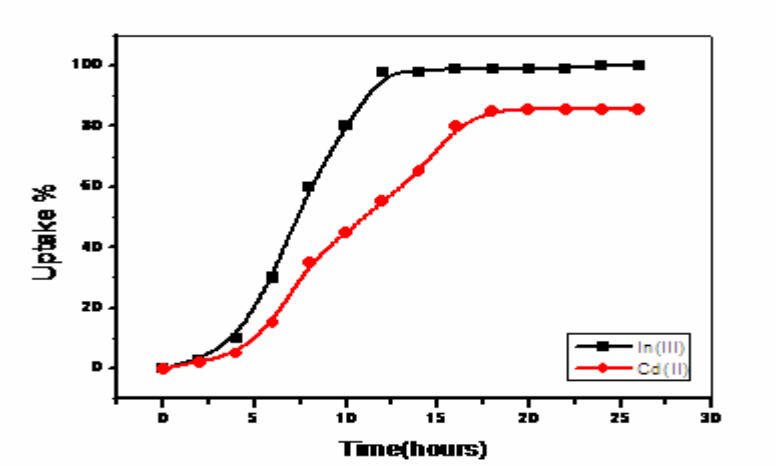

Figure (3): Effect of contact time of zirconium vanadate on In(III) and Cd(II).

3.2. Chromatographic Separation

3.2.1. Effect of flow-rate

The effect of varying flow-rate from 0.25 to 3.5 ml/min. on the separation of In(III) and Cd(II) was investigated in the column procedure. The studies show that these ions can be adsorbed quantitatively by zirconium vanadate at 0.5-1.5 ml/min. However, the increase in flow rate results incomplete sorption due to the insufficient contact period between the resin and the metal solutions

Breakthrough Studies

Zirconium Vanadate-Column for Separation of In(III) and Cd(II)

From batch mode, the optimum conditions for separation of indium(III) and cadmium(II) were obtained which have been used in column mode where the column chromatography is more significant than batch mode for separation of metal ions. Practically, from all given results on zirconium vanadate in batch mode, these elements presented a significant contrast that could facilitate in separation of indium(III) and cadmium(II). Additionally, in the column mode, the effective parameter is the flow rate related to the time. However, for loading step, 100ml has been loaded with flow rate 0.5ml/min. During the loading step , all indium(III) was adsorbed on the zirconium vanadate (inorganic ion exchanger) while cadmium(II) passed through the column. This indicate that separation of indium(III) and cadmium(II) has been occurred (the main task of work) and this means that the zirconium vanadate inorganic ion exchanger has selective for indium(III) ions.

For more details the elution curve for separation of indium(III) and cadmium(II) was given in Fig. (4). As described in the experiment part, for zirconium vanadate inorganic ion exchanger a 100 ml stock solution containing 100ppm of each indium(III) and cadmium(II) at pH 4 was loaded onto a glass column, 22cm long x 1.5cm in diameter, packed with zirconium vanadate with depth of 2cm. At this pH zirconium vanadate showed no specific adsorption of cadmium(II). So cadmium(II) passed through the column with percentage 74% of initial amount. Further step, washing by de-ionized water and showed that trace amount of cadmium(II) passed through the column while indium(III) still remained on the column. A 20ml sample of buffer solution was sufficient for elution of cadmium(II) at a flow rate of 0.5ml/min. then indium(III) retained in the column is eluted with 20ml 2M HCl with the same flow rate Table(3) and Fig.(4).

Table (3): Recovery of indium and cadmium using different eluants

Amount loaded,(ppm)	Element separated	Eluant	Eluant volume(ml)	Amount recovered
100ppm	In(III)	2M HCl	20	98.4%
100ppm	Cd(II)	buffer solution	20	24.98%

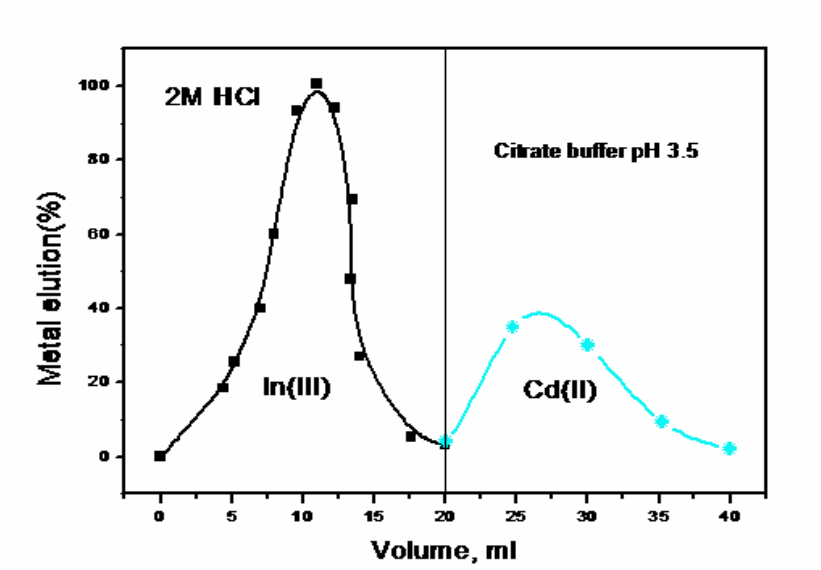

Figure (4):Elution curve of In(III) and Cd(II) onto zirconium vanadate using 2M HCl for indium and citrate buffer pH 3.5 for cadmium

The following flow sheet illustrates the separation and recovery of indium(III) and cadmium(II) using the zirconium vanadate inorganic ion exchanger as shown in Figure(5).

Cyclic properties of the resin

To check the regenerating capacities of the zirconium vanadate, it was subjected to repeated sorption and elution tests of In(III) and Cd(II) at the optimum conditions. It was found that up to five cycles of sorption and elution, there is apparently no change in the sorption capacity of zirconium vanadate.

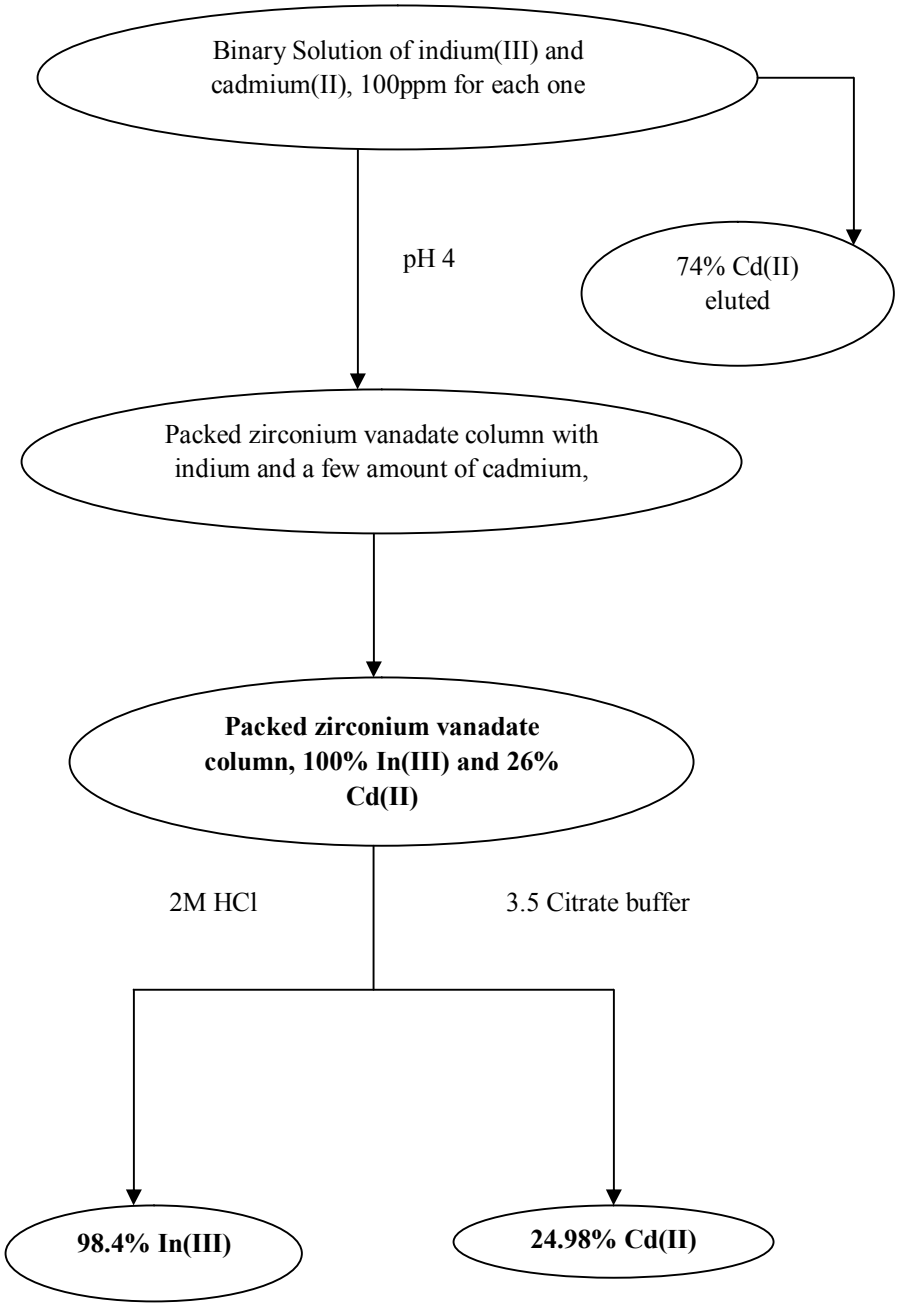

Figure (5): Flow sheet for separation of indium(III) and cadmium(II) onto synthetic inorganic ion exchanger, zirconium vanadate.

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