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Chromatographic separation of In(III) from Cd(II) in aqueous solutions using commercial resin (Dowex 50W-X8)

Research Article

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Abstract: This work assesses the potential of an adsorptive material, Dowex 50w-x8, for the separation of indium ions from cadmium ions in aqueous media. The adsorption behavior of Dowex 50 w-x8 for indium and cadmium ions was investigated. The effect of pH, initial concentration of metal ions, the weight of resins, and contact time on the sorption of each of the metal ions were determined. It was found that the adsorption percentage of the indium ions was more than 99% at pH 4.0. The result shows that In (III) was most strongly extracted, while Cd(II) was slightly extracted at this pH value. The recovery of In(III) and Cd(II) ions is around 98% using hydrochloric acid as the best eluent.

Keywords: *Separation of indium and cadmium • Dowex 50w-x8*

1. Introduction

Indium is a crystalline, very soft, ductile, and malleable metal that retains its highly plastic properties at cryogenic temperatures. The addition of indium generally increases the strength, corrosion resistance, and hardness of an alloy system. It is also used in electrical contacts, liquid crystal displays, low-pressure sodium lamps, alkaline dry batteries, and semiconductors [1]. Recently, many applications for indium and its compounds have been found in electronics. In the near future, a significant increase in indium demand is expected because of its use in many new technologies. Indium is used in the field of electronics for semiconductor devices, thermistors and optical devices, electronic soldering (alloys); in the nuclear field it is being used for control rods in reactors; indium is also used to improve some dental alloys [2,3]. Cyclotron-produced ^{111}In is widely used in nuclear medicines for labeling blood cell elements and monoclonal antibodies. ^{111}In was produced by the ^{111}Cd (p, n), ^{111}In and ^{112}Cd (p,2n) ^{111}In nuclear reactions at the MGC-20E Cyclotron [4].

Indium is widely spread in nature, generally in very low concentrations. The direct determination of extremely low concentrations is limited not only by low sensitivity, but also by matrix interference. For this reason, the preliminary separation and preconcentration of trace indium from its matrix is often required. The most widely used techniques for the separation and preconcentration of trace indium include liquid-liquid extraction [5], ion-exchange [3] and solid-liquid separation [6,7].

Recently, solid-phase extraction has gained increasing favor because of its simple procedure, higher preconcentration factor, rapid phase separation and ease of combination with different detection techniques. The main requirements for substances to be used as solid-phase extractants are as follows [8]: ability to extract a large number of elements over a wide pH range, fast and quantitative adsorption and elution, high capacity and ease of accessibility. Numerous substances have been proposed and utilized as solid-phase extractants, such as modified silica [9,10] and alumina [11], magnesia [12], active carbon [13] and cellulose [14]. Separation studies are mainly carried out by ion exchange and solvent extraction techniques. ^{67}Ga can be separated

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from an irradiated target by a pre-conditioned Dowex-50 resin column (H+ form, 10 cm×1cm). In the column, ^{67}Ga is retained while copper and zinc pass through. The column is washed thoroughly with concentrated HCl until the washing is colorless, *i.e.*, free of copper; Gallium is then eluted from the column with 3.5 M HCl. Also, gallium can be separated from ^{68}Zn with 8M HCl from a cation exchange AG 50W-X8 column [15,16].

The aim of this work is to investigate the adsorption behavior of indium ions on the commercial resin Dowex 50w-x8 and the conditions for separation of Indium(III) from Cadmium(II) in an aqueous medium. This method was successfully applied to inactive as well as active indium such as ^{111}In, which was produced in a low energy cyclotron (<20 MeV).

2. Experimental Procedure

2.1. Instrumentations and Materials

An inductively coupled plasma spectrometer, "Jobin Yvon ICP-AES spectrometry model Ultima2", made in France, was used to determine the concentrations of all metal ions. A WTW pH meter Model No. 315i, made in Germany was used to measure the pH of all solutions. A LAB-LINE shaker, Model No. 4626-1CE, made in USA, was used for shaking of all batch experiments (adjusted at 220 rpm).

Dowex 50w-x8 (H^+ form) resin, mesh size 200-400, product serva, was obtained from Feinbiochemica, Heidberg, Germany. The properties of the resin are given in Table 1. Both acidic and salt forms of the resin are stable at temperatures up to 120°C.

2.2. Sample preparation

2.2.1. Preparation of Indium stock solution

Indium stock solution was prepared by dissolving 1 g of pure Indium metal in concentrated HCl. The solution was left for 24h to complete reaction. The remaining amount of HCl was evaporated, and the sample was diluted to 1000mL with double-distilled water. The solution contained 1000µg/mL (1000ppm) of indium. Ten milliliters of the solution was pipetted out and added to 100 mL to give 100µg/mL (100ppm) of indium.

2.2.2. Preparation of Cadmium Stock Solution

Table 1. Characteristic of Dowex 50w-x8

Type	Strong acid cation exchanger
Active group (Function group)	Sulfonic acid ($-SO_3H$)
Matrix	Styrene and divinylbenzene(DVB)
Ionic form as shipped	H^+
Physical form	Spherical beads (orange)
Standard mesh size	200-400
Effective pH range	0-14
Total exchange capacity,(meq ml)	H^+ form, (1.7)
Water retention capacity %	50-58

Cadmium stock solution was prepared by dissolving 1.63 g of pure cadmium chloride in double-distilled water. The solution contained 1000 µg mL^{-1} (1000 ppm) of cadmium. Ten milliliters of the solution was pipetted out and added to 100 mL to yield a solution with a concentration of 100 µg mL^{-1} (100 ppm) of cadmium.

2.3. Batch technique

The ion exchange behavior of the metal ions of In(III) and Cd(II) interacting with the Dowex 50W-X8 resin was studied using a batch technique where 100 mg of Dowex 50w-x8 resin was equilibrated with 20 mL aqueous solution containing the indium(III) and cadmium(II) ions as a single component system. The uptake percentage of the ion studied on the Dowex 50W-X8 was determined using the Jobin Yvon ICP-AES spectrometry model Ultima2 inductively coupled plasma spectrometer. The uptake percentage was determined using the following equation [17]:

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

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

2.4. Column studies for adsorbing and stripping metals

For continuous extraction, a glass column with a diameter of 4.6 mm and a length of 100 mm was packed with Dowex 50w-x8 resin using the slurry-packing technique. A total of 1.0 g of resin was introduced (packing depth 50 mm). The columns were controlled by fraction collection with a flow rate of 2 mL min^{-1}. Preliminary experiments were performed using the single component solution at a concentration of 100 ppm of metal ions, and the pH was controlled at the optimum pH for selective separation established in previous batch experiments. Eluant solutions of HCl, HNO_3 and H_2SO_4 were used for the recovery of metal ions from the resin. All the experiments were carried out at ambient room temperature (25±1°C).

3. Results and Discussion

3.1. Batch Technique

3.1.1. Effect of pH

In this study, knowledge of pH was important because the pH of the solution influences the ion exchange properties of the Dowex 50w-x8 resin. At higher pH, the OH^- on the surface of Dowex 50w-x8 enables cations to bind. A decrease in pH leads to the neutralization of surface charge, and OH^- is displaced from the surface. When the surface of Dowex 50w-x8 carries positive charges, it begins to adsorb anions. Therefore, the effect of the initial pH on the adsorption of In(III) and Cd(II) ions was investigated in the pH range of 1– 6 by using 120 mg of Dowex 50w-x8 at a fixed concentration of In(III) and Cd(II) ions of 100 ppm. The variation of adsorption percentage with the pH of the solution is shown in Fig. 1.

Fig.1 shows the effect of pH on the adsorption of In(III) and Cd(II) by Dowex 50w-x8, which indicates that the adsorption of indium increases with increasing pH from pH 1 to pH 4, but in the case of cadmium the adsorption increases with increasing pH of the solution from pH 1 to pH 6. The uptake percent of indium was found to be more than that of cadmium due to the larger positive charge of the indium ion.

The effect of pH on In(III) adsorption can be explained as follows: the surface charge is neutral at the isoelectric point (IEP), which corresponds to a pH value of 6.8 for Dowex 50w-x8. The surface of the sorbent carries positive charges at pH values lower than the IEP, which enhances the electrostatic force of attraction with $InCl_3$. (In the system studied, the main chemical species of indium in solutions is $InCl_4^-$ [18]). As a result, the process of sorption takes place more easily in a pH range of 2-4, so the adsorption percentage of In(III) is higher. At pH <2, there is a balance reaction:

$H^+ + InCl_4 \rightleftharpoons HInCl_4$. As a result, the main chemical species of In(III) becomes $HInCl_4$ [19-21], so the adsorption percentage of In(III) is lower. Therefore, pH 4 was chosen for adsorption of In(III) in the experiment.

3.1.2. Effect of resin weight

Different amounts (from 10 to 160 mg) of Dowex 50w-x8 resin were used for the adsorption of 100 ppm In(III) and Cd(II) individually from aqueous solution at pH 4.0. A shaking time of 120 minutes was used in all cases. The results are shown in Fig. 2.

The uptake percentage increased with increasing amount of resin and reached its maximum value at 120 mg in the case of In(III), whereas in the case of Cd(II) the optimum weight for complete removal of Cd(II) was 100 mg. For both metal ions, 120 mg is an optimum amount of resin for the sorption process.

3.1.3. Effect of contact time

The adsorption behavior of In(III) and Cd(II) ions from aqueous solution onto Dowex 50w-x8 resin at a concentration of 100ppm for each ion and pH 4 was studied as a function time. The results are shown in Fig. 3.

In both cases, the uptake increases with increasing time. The time for complete removal of In(III) and Cd(II) onto Dowex 50w-x8 was found to be 40 and 90 min, respectively. The higher removal time for Cd(II) relative to In(II) can be attributed to the +3 charge of the indium atom,which accelerates the adsorption compared to cadmium. However, the total exposure time in all subsequent experiments was set to 120 minutes for the sake simplicity, as well as to ensure complete

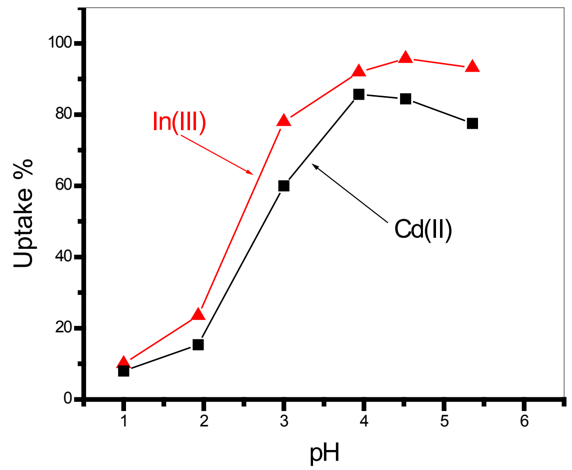

Figure 1. The effect of pH on the adsorption of In(III) and Cd(II) by Dowex 50w-x8.

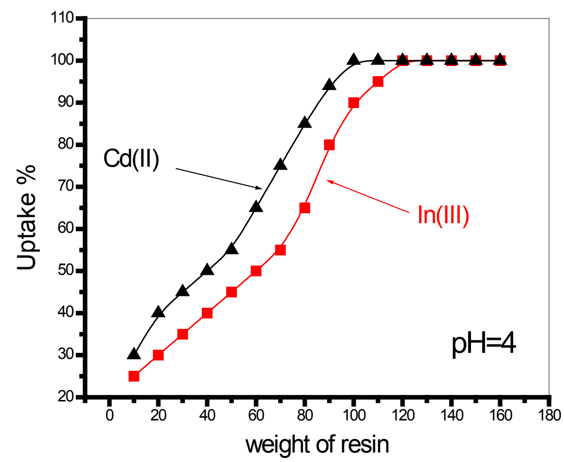

Figure 2. Effect of resin weight of dowex 50w-x8 on In(III) and Cd(II).

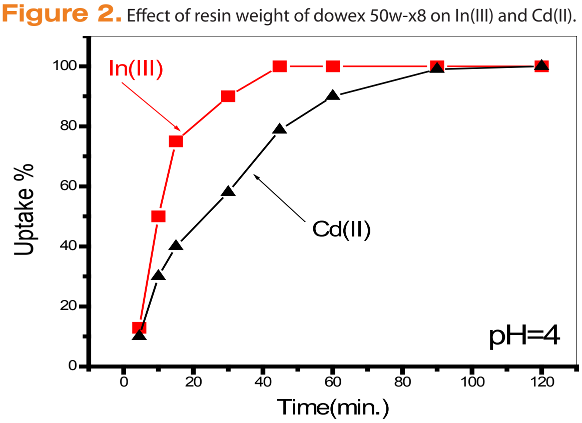

Figure 3. Effect of contact time on the uptake percentage of In(III) and Cd(II) on dowex 50w-x8.

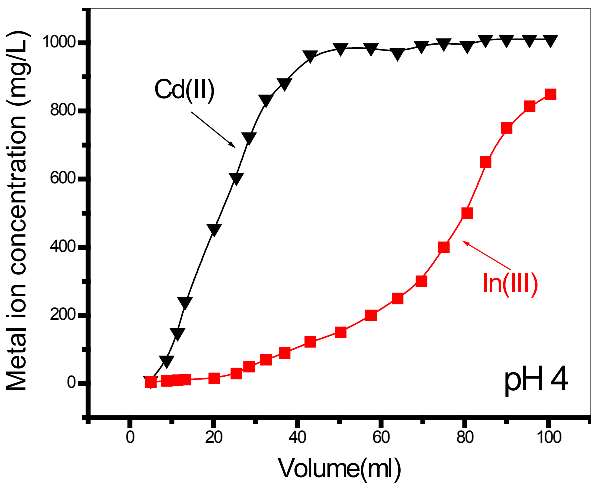

Figure 4. Loading curves of In(III) and Cd(II) onto Dowex 50w-x8.

adsorption.

3.2. Chromatographic Separation

3.2.1. Effect of flow-rate

The effect of varying flow rate from 0.5 to 3 mL min^{-1} on the separation of In(III) and Cd(II) was investigated in the column procedure. The experiments show that these ions can be sorbed by Dowex 50w-x8 at 0.5-3.0 mL min^{-1}. However, an increase in flow rate results in incomplete sorption due to the insufficient contact time between the resin and the metal solutions.

3.2.2. Breakthrough Studies

The breakthrough studies are more significant for chromatographic separation of metal ions than batch studies. The breakthrough curves for In(III) and Cd(II) at a flow rate of 2 mL min^{-1} and a bed depth 50 mm on Dowex 50w-x8 are shown in Fig. 4.

The breakthrough curve shows that In(III) was completely adsorbed onto Dowex 50w-x8 resin at 100 mL. By increasing the volume up to 100 mL, the concentration of In(III) increased due to the disappearance of the active site of Dowex 50w-x8 resin. Cd(II) slightly adsorbed on the resin, especially after 40 mL due to competition between the In(III) and Cd(II) ions. Therefore, it is clear that the Dowex 50w-x8 resin is more selective for In(III) than for Cd(II). Also, it is clear that the affinity of Dowex 50w-x8 resin for In(III) typically increases with increasing charge as well as increasing atomic number of the exchanging cation.

3.2.3. Effect of eluants

A mixture of indium and cadmium (100 ppm each) was passed through the column after adjusting the pH to 4. The elution of indium and cadmium onto Dowex50w-x8 resin in a column by various eluants and different concentrations of mineral acids is shown in Figs. 5, 6

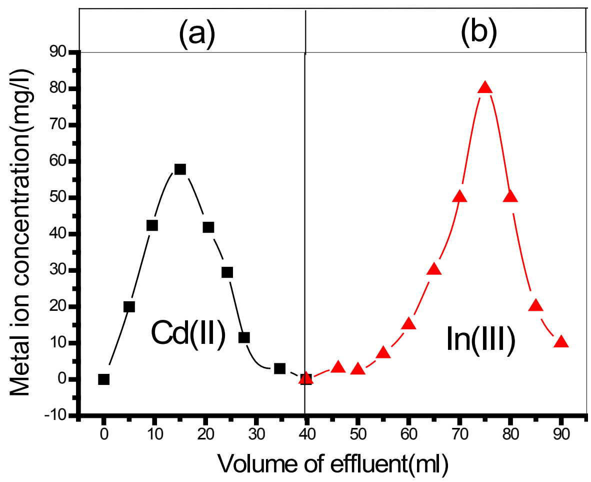

Figure 5. Elution curve of separation of In(III) and Cd(II) from Dowex 50w-x8 using (a) 0.05 M HCl and (b) 1 M HCl.

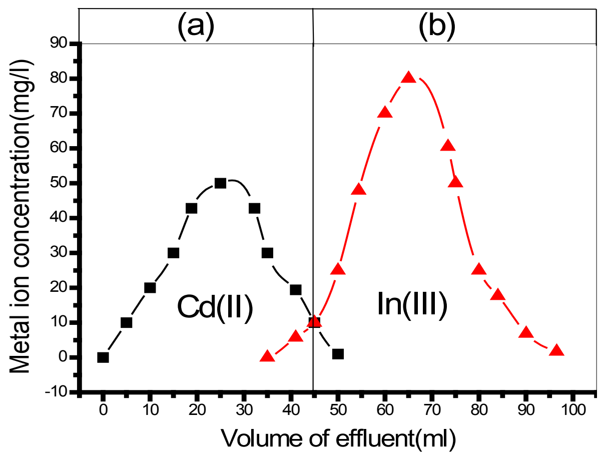

Figure 6. Elution curve of separation of In(III) and Cd(II) from Dowex 50w-x8 using (a) 0.05 M HNO_3 and (b) 1 M HNO_3.

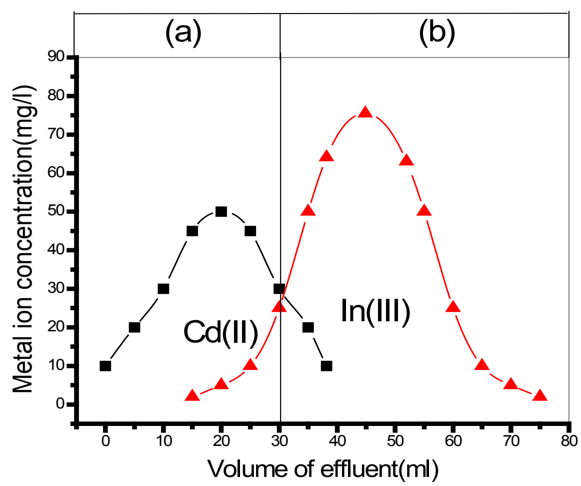

Figure 7. Elution curve of separation of In(III) and Cd(II) from Dowex 50w-x8 using (a) 0.05 M H_2SO_4 and (b) 1 M H_2SO_4

and 7.

Hydrochloric acid was used as the stripping agent, as its stripping ability is greater than that of sulfuric acid and nitric acid. A slightly higher concentration of acid was required for the elution of indium compared to the adsorbed cadmium on the column. This means that indium and cadmium that were adsorbed on the same resin column could be separated in a single step using different concentrations of hydrochloric acid.

In Fig.5, 0.05 M HCl is used for the elution of cadmium, while 1 M HCl is used for the elution of indium. The data show that there is no interference between the two peaks. Indium and cadmium have different extents of extraction at pH 4, as reflected by the different acid concentrations. Thus, the hydrochloric acid was considered the best eluent for separation of indium and cadmium. Such differences can be exploited to devise a technique to extract and separate these ions with Dowex 50w-x8 resin in a two-component mixture.

In Figs. 6 and 7, 0.05 M HNO_3 and H_2SO_4 were used to elute Cd(II), while 1 M HNO_3 and H_2SO_4 were used to elute In(III) from a packed column. The data show that there are interferences between the two peaks. Therefore, the separation would be difficult because the two metal ions are eluted together.

The following flow sheet illustrates the separation of In(III) from Cd(II) in aqueous solution using the commercial resin Dowex 50w-x8 as shown in Fig. 8.

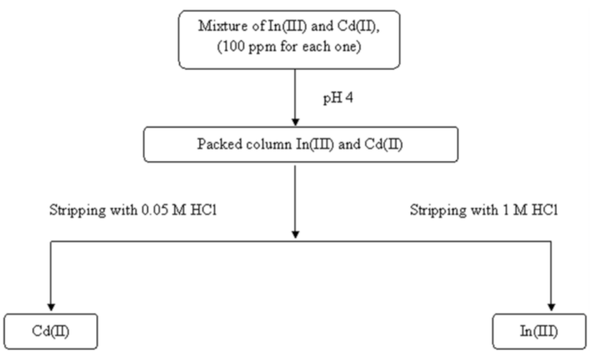

Figure 8. Flow sheet for the separation of In(III) from Cd(II) onto commercial resin, Dowex 50w-x8.

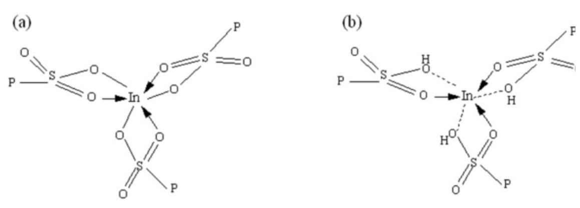

Figure 9. Proposed In(III) adsorption mechanism with Dowex 50w-x8 (a) complexation and ion exchange (b) complexation.

3.2.4. Proposed Adsorption Mechanism for Metal Ions on Dowex 50w-x8 resin

The main complexing sites on the resin consist of sulfonic acid groups ($-SO_3H$). The adsorption mechanism might be partly a result of ion exchange or complexation between the In(III) and sulfonic acid groups. Thus, the metal ion reaction may be represented in two ways, as shown in Fig. 9.

Since the oxygen of the sulfonic acid groups has a pair of electrons that can transfer to a proton or metal ion to form a complex through a coordinated covalent bond, it leads us to propose that the complexes between metal ions In(III) and Dowex 50w-x8 are formed according to the mechanism illustrated in Fig. 9a. In this mechanism, the In(III) ions with empty orbitals function as a Lewis acid capable of accepting electron pairs. In contrast, the sulfonic acid groups that have non-shared electron pairs function as Lewis bases, donating their electrons pairs [22].

This behavior depends on the pH of the solution. That is, if the desorption system is in a neutral or slightly acidic pH, the mechanism shown in Fig. 9a will dominate. However, in an acidic environment, the metal adsorption capacity diminishes as the solution pH decreases. This may be a result of the decrease of the retention efficiency of the absorbent due to the occupation of the active sites of the weak ion exchanger by protons. This proposed mechanism is illustrated in Fig. 9b [22].

3.2.5. Cyclic properties of the resin

To check the regenerating capacities of the commercial Dowex 50w-x8, 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 ten cycles of sorption and elution, there is apparently no change in the sorption capacity of Dowex 50w-x8.

4. Conclusions

The aim of this work was the investigation of the sorption properties and separation capabilities of Dowex 50w-x8 resin for indium and cadmium in aqueous solutions. The results show that Dowex 50w-x8 has a high sorption capacity for In(III) than Cd(II) in the case of a mixture. The ion exchange behavior of both metal ions on Dowex 50w-x8 depends on pH, amount of resin and initial concentration of the solution. At pH 4, resin sorption enabled the separation of both metal ions by passng different suitable concentrations of eluent (HCl) through the column. The resin may be regenerated using 2M hydrochloric acid.

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