Separation of Cyclotron Produced In-111 (III) from Cadmium (II) and Copper (II) Ions Using Ion Exchange Technique in Different Media

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Abstract

The commercial cation exchangers TSKgel BioAssist S, TSKgel CM-2SW and TSKgel CM-STAT have been used for the separation of 111In (III) from Cd (II) and Cu (II) ions. The separation was carried out using low cost cation exchangers based on the differences in the sorption affinity of In, Cu and Cd towards the ion exchanger from 0.01 mol L⁻¹ HCl. The effects of various parameters such as shaking time, HCl concentration and acetate buffer concentration were examined. A comparative study between cation exchangers showed the best one for radiochemical separation yielded more than 98% within 50 min by using column study.

Keywords: Cation exchangers; Radioindium; Separation; Hydrochloric acid; Cadmium; Copper; Column study

Introduction

Indium-111 or 111In is one of the most important radioactive elements which are used in nuclear medicine. It is used for surveying in vivo cell distribution in various contexts such as brain tumors and myocardial damage detections [1].

Several techniques have been identified for separation of In-111 from Cd target using different types of cation exchangers [1]. The sorption behavior of 111In and 113Cd on cation exchangers was investigated at different molarities of HCl; the sorption capacity of Cd on a cation exchanger was higher than on an anion exchanger [3].

A chromatography method using inorganic exchange and organic exchange Doex and Amberlit was described [2]. Sorption of 112Cd and 115In by organic ion exchangers was studied at different molarities of hydrochloric acid the sorption capacity of Cd on a cation exchanger was higher than on an anion exchanger [3].

111In has been amongst the frequently used radionuclides in diagnostic nuclear medicine. Therefore, its production and subsequent separation chemistry have been widely investigated since the late 40s. Indium is a rare element evenly distributed in the earth crust. It has no material of its own character. Therefore, it has to be recovered as by-product from other metallurgical process, most commonly associated with copper, zinc and tin. Indium and its compounds have been found in wastewater discharged from optoelectronic plants and they are suspected to be carcinogenic to humans, therefore, the removal of In (III) ions from aqueous solutions has become a significant subject [4].

The proton or α-particle induced reactions on cadmium or silver targets are the most common production techniques for 111In. Recently, production using various activation routes of heavier ions such as 7Li, 12C, 13B, 14C have been proposed.

A portray for the production routes of 111In and chemical separation methodologies has been reported [4-6]. Also, 111In was produced from an irradiated natural cadmium target using AG 1-X8 anion exchanger under various conditions.

A simple and reliable way of 111In production with the highest radionuclide purity from its grandparent 112Sn and parent 113Sn nuclei, produced by the 115Sn(p,2n)113Sn and 115Sn(p, pn)111Sn reactions, respectively.

Conventional techniques were reported for separation of 111In from Cd target using different types of cation exchangers [7], and synthetic polymeric resin [8]. A chromatographic method using inorganic ion exchanger (zirconium oxide) for radiochemical separation of non-carrier added In-115 from Cd-115 over a column of zirconium oxide was described [9]. Recently, numerous alternative techniques have been examined for the separation of indium from cadmium and copper using silica extracted agricultural wastes. Column separation technique is widely applied to separate 110In from interfering ions based on the evaluation of distribution coefficient Kd.

Modern separation techniques for separation of Ga(II) using poly(acrylamide-acrylic acid disodium EDTA) were studied. The prepared inorganic ion exchangers used separation of radioactive elements such as cesium [10].

In the present work we investigated the possibility of using cation exchangers for separation of radioindium from cadmium and copper, the distribution coefficients of the three elements on different types of cation exchangers were measured in 0.01 M HCl, acetate buffer at pH 4 and EDTA (10⁻³ M) to find the best conditions for separation.

Materials and Methods

Materials

Indium metal (99.9% purity), anhydrous cadmium chloride (CdCl₂), cupric chloride dehydrate (CuCl₂·2H₂O), sodium hydroxide (NaOH), anhydrous sodium acetate (CH₃COONa), Diethylene Tetramine Penta Acetic acid (DTPA), and Ethylene Diamine Tetra Acetic acid (EDTA) were reagent grade chemicals and supplied by Merck (Darmstadt, Germany).

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Results and Discussion

Batch experiments

Effect of shaking time: The first batch experiment included the aqueous phase with reasonable count of radioindium in 0.05 mol L⁻¹ HCl and CMcation exchangers as solid phase extractor using the strong cation exchanger TSKgel BioAssist S and two weak cation exchangers TSKgel CM-2SW and TSKgel CM-STAT.

The samples were shaken for different time intervals of times, a 1 mL aliquot from the aqueous phase was pipetted out and the concentration of In was determined using the gamma counter. The uptake of In during each interval of shaking was determined according to Figure 1. It can be seen that, the uptake of indium increased with shaking time, reaching a plateau within 80 min. corresponding to sorption or uptake of 65, 85 and 92% for TSKgel BioAssist S, TSKgel CM-2SW and TSKgel CM-STAT, respectively.

A similar sorption profile was observed in case of TSKgel CM-2SW and TSKgel CM-STAT exchangers while the TSKgel BioAssist S profile was always at lower sorption (%). This indicates the better accessibility of the first two exchangers than the latter and accordingly, the stability of In is expected to be higher with the first two exchangers than the latter one.

Effect of hydrochloric acid concentration: The influence of acid concentration on the sorption Cd, Cu and In was studied. Maximum sorption of the three elements was achieved at a concentration of 0.05 mol L⁻¹ HCl solution on the cation exchangers as shown in Figures 2-4. It can be observed that, the sorption or uptake of ions decreased sharply with increasing the acid concentration. The high sorption values at concentration 0.05 mol L⁻¹ could be due to capability of metal exchange at low acidity [13], which can be exchanged with 3H⁺, 2H⁺ and 2H⁺ ions of the resin. On other hand, the decrease in the sorption at high concentration of the acid can be attributed to the formation of various species of indium chloride complexes, e.g., InCl₃, InCl₂ and InCl₃, cadmium chloride complexes e.g., CdCl₂, CdCl₄ and tetra chloro copper CuCl₄⁻. Another plausible interpretation could be due to the distribution of the studied metal ions is controlled by the solution pH. At high acidity, the H⁺ ions may compete with metal ions on the adsorption sites of the exchangers by decreasing the extent of adsorption sites of the exchangers by decreasing the extent.

Table 1: Effect of hydrochloric acid concentration on the sorption Cd, Cu and In

<table>
<thead>
<tr>
<th>pH</th>
<th>Vol. of 0.1M Acetic acid</th>
<th>Vol. of 0.1M Sodium acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>982.3 ml</td>
<td>17.7 ml</td>
</tr>
<tr>
<td>4</td>
<td>847.0 ml</td>
<td>153.0 ml</td>
</tr>
<tr>
<td>5</td>
<td>357.0 ml</td>
<td>643.0 ml</td>
</tr>
<tr>
<td>6</td>
<td>52.2 ml</td>
<td>947.8 ml</td>
</tr>
</tbody>
</table>

Preparation of EDTA solutions: Stir 186.1 g disodium ethylenediamine tetraacetate•2H₂O into 800 ml of distilled water.

Add 0.1M HCl solution to adjust the pH to 4.0. The EDTA will slowly go into solution as the pH of the solution nears 4.0.

Dilute the solution to 1 L with distilled water.

Filter the solution through a 0.5 micron filter.

Separation experiments: Separation of radioindium from Cd and copper ions was carried out using different cation exchangers at room temperature. Experiments were carried in five clean and dry penicillin bottles. For this purpose, an amount of 100 mg of the cation exchanger was placed in each bottle and an aliquot equivalent to 1000 µg of Cd or Cu was added. To each bottle, an accurate amount corresponding to a count (3.7 MBq) of In-111 was added. The final mixture was prepared by double distilled water.

After attaining equilibrium time, an aliquot of the aqueous phase was taken and analyzed for radioactivity of In-111 (Aaq.) and compared to an initial solution (Aᵢ). The distribution coefficient (Kᵣ) for indium was calculated according to the following equation [11-14]:

\[ Kᵣ = \frac{Aᵢ – Aaq}{Aaq} \times \frac{V}{m} \]

Where, V is the volume of the aqueous phase in ml and m is the mass of the ion exchanger in g. Cadmium and copper were determined spectrophotometrically in the solution using the method of atomic absorption and their distribution coefficients were determined. In these experiments the concentration of cadmium and copper was found to be 0.91 and 1.5 mol L⁻¹, respectively.
Worth mention, all ion exchangers indicated sharp decrease in the distribution coefficient at approximately the same acid concentration. This might be due to the independence of exchanging mechanism on the chemical structure of the exchanging groups but mainly on the chemical composition of solution.

Effect of acetate buffer concentration: The distribution coefficient of the studied metal ions was determined at various concentrations of acetate buffer at pH 4. The results showed that, the metal ions were sorbed to a great extent at low concentrations of the buffer within the range 0.01-0.1 mol L⁻¹ as depicted in Figures 5-7. The sorption behavior of ¹¹¹In on three cation exchangers was quite different according to the evaluated K_d values. It was found to be 10535, 11245 and 8640 for TSKgel BioAssist S, TSKgel CM-2SW and TSKgel CM-STAT, respectively. Therefore, a 0.01 mol L⁻¹ solution of EDTA can be used as an eluent in case of TSKgel BioAssist S and TSKgel CM-2SW cation exchangers to separate ¹¹¹In from Cd²⁺ and Cu²⁺ in aqueous media consisting of a 0.01 mol L⁻¹ HCl or 0.01 mol L⁻¹ acetate buffer at pH 4. In case of the three ion exchangers, the distribution coefficient decreased gradually by increasing the EDTA concentration. This explains the competitive reaction between the ligand and the ion exchangers towards metal ions. However, EDTA showed a pronounced effect on the decrease of the sorption and becomes adversely affecting when its concentration exceeded 0.01 mol L⁻¹.

Effect of EDTA concentration: The purpose of adding the ligand EDTA to the sample is to investigate the competition between the ion exchanger and the ligand on metal ions. The effect of EDTA concentration on the K_d values of these metal ions is shown in Figures 8-10. It can be observed that, the K_d for Cd and Cu at EDTA concentration of 0.01M mol L⁻¹ are very high with values of 12890 and 9750, and 2040 in case of TSKgel BioAssist S, TSKgel CM-2SW and TSKgel CM-STAT, respectively. Therefore, a 0.01 mol L⁻¹ solution of EDTA can be used as an eluent in case of TSKgel BioAssist S and TSKgel CM-2SW cation exchangers to separate ¹¹¹In from Cd²⁺ and Cu²⁺ in aqueous media consisting of a 0.01 mol L⁻¹ In or 0.01 mol L⁻¹ acetate buffer at pH 4. In case of the three ion exchangers, the distribution coefficient decreased gradually by increasing the EDTA concentration. This explains the competitive reaction between the ligand and the ion exchangers towards metal ions. However, EDTA showed a pronounced effect on the decrease of the sorption and becomes adversely affecting when its concentration exceeded 0.01 mol L⁻¹.

![Figure 2: Effect of HCl concentration on the sorption of metal ions onto TSKgel Bio Assist S cation exchanger.](image2)

![Figure 3: Effect of HCl concentration on the sorption of metal ions onto TSKgel CM-2SW cation exchanger.](image3)

![Figure 4: Effect of HCl concentration on the sorption of metal ions onto TSKgel CM-STAT cation exchanger.](image4)

![Figure 5: Effect of acetate buffer concentration on the sorption of metal ions onto TSKgel Bio Assist S.](image5)
Column experiments

Breakthrough capacity: The loading capacity of two packed columns with TSKgel BioAssist S and TSKgel CM-2SW cation exchangers used for sorption the $^{111}$In$^{3+}$ could be determined from the breakthrough curve.

For this purpose, a glass column with 7 mm diameter and 12 cm length was packed with 0.7 g of dry exchanger. A model solution contains 0.09 mol L$^{-1}$ of inactive indium with a reasonable count of $^{111}$In$^{3+}$ was prepared in 0.01 mol L$^{-1}$ HCl was passed through the column at a flow rate of 1 mL min$^{-1}$.

Figure 11 shows the breakthrough curve of In$^{3+}$ plotted as variation of the concentration of metal in effluent as function of effluent volume. It was observed that in the first 10 mL of effluent, In$^{3+}$ ions are completely retained onto the columns. Gradually, the 50% breakthrough of In$^{3+}$ occurred at 65 mL, and 45 mL in case of TSKgel BioAssist S sorbent and TSKgel CM-2SW, respectively.

Elution studies: Elution of indium ions from the packed column TSKgel BioAssist S sorbent or TSKgel CM-2SW was investigated using 0.01 mol L$^{-1}$ of acetate buffer at pH 4. The obtained results are represented in Figure 12. In case of TSKgel BioAssist S cation
exchanger, indium was eluted in the first 30 mL, while cadmium and copper were eluted after 50 and 80 mL, respectively. Whereas, Indium was completely eluted within 20 mL in case of TSKgel CM-2SW cation exchanger, while, cadmium and copper were eluted after 40 and 70 mL, respectively. Also, the TSKgel BioAssist S exchanger indicated the ability to separate higher sample concentrations than TSKgel CM-2SW which confirm higher capacity for metal ions. Finally, the separation pattern shows adequate elution conditions and quantitative recovery of the separated elements.

Conclusions

Comparison between three cation exchangers for the separation of In\textsuperscript{111} from Cd\textsuperscript{2+} and Cu\textsuperscript{2+} was undertaken. It could be concluded that, the TSKgel BioAssist S is very effective for the separation of In\textsuperscript{111} from Cd\textsuperscript{2+} and Cu\textsuperscript{2+}. Also, it could be successfully used to retain the three metal ions from 0.01 mol L\textsuperscript{-1} HCl. Then, In\textsuperscript{111} was removed in the first 30 mL, followed by Cd and Cu at 50 and 80 mL respectively using 0.01 mol L\textsuperscript{-1} acetate buffer at pH 4.

Competing Interests

The authors declare that they have no competing interests.

Author’s Contributions

The authors consider two members in the isotope production unit in cyclotron project-Egyptian Atomic Energy Authority.

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References