

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 ¹¹¹Cd 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.

A chromatography method using inorganic exchange and organic exchange Doex and Amberlit was described [2]. Sorption of ¹¹¹Cd and ^{115m}In 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, ¹¹B, ¹²C have been proposed.

A portrayal 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 ¹¹¹Sb and parent ¹¹¹Sn nuclei, produced by the ¹¹²Sn(p,2n)¹¹¹Sb and ¹¹²Sn(p, pn)¹¹¹Sn reactions, respectively.

Conventional techniques were reported for separation of In-111 from Cd target using different types of cation exchangers [7], and synthetic polymeric resins [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 ¹¹¹In from interfering ions based on the evaluation of distribution coefficient K_d .

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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TSKgel BioAssist S strong cation exchanger, TSKgel CM-2SW (strong or weak exchangers) and TSKgel CM-STAT cation exchanger chromatography, with a mesh size within 50-100 μm was received from Merck. The In-111 radioisotope was obtained by irradiation of cadmium-111 target ^{111}Cd (p, n) ^{111}In in 20 Mev cyclotron at Inshas city (Cairo, Egypt).

Methods

Preparation of standard solutions: A standard solution contains 1000 $\mu\text{g mL}^{-1}$ of indium was obtained by dissolving an accurately weighed amount of 1 g of pure indium metal in concentrated HCl (36% v/v). The mixture was left for 24 h till complete dissolution, the remaining acid was evaporated then the solution was diluted to 1000 ml by double distilled water.

Stock solutions containing 1000 mg L^{-1} from cadmium and copper were prepared by dissolution of 1.631 g of CdCl_2 or 2.73 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 1000 mL measuring flask using double distilled water.

Preparation of buffer solutions: Make up the following solutions

- (1) 0.1M acetic acid
- (2) 0.1M sodium acetate (tri-hydrate) (13.6 g/l)

Mix in the following proportions to get the required pH

pH	Vol. of 0.1M Acetic acid	Vol. of 0.1M Sodium acetate
3	982.3 ml	17.7 ml
4	847.0 ml	153.0 ml
5	357.0 ml	643.0 ml
6	52.2 ml	947.8 ml

Preparation of EDTA solutions: Stir 186.1 g disodium ethylenediamine tetraacetate $\cdot 2\text{H}_2\text{O}$ into 800 ml of distilled water.

Stir the solution vigorously using a magnetic stirrer.

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 in 10 mL HCl at different concentrations (0.05, 0.1, 0.5, 1 and 2 mol L^{-1}). 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 (A_i). The distribution coefficient (K_d) for indium was calculated according to the following equation [11-14]:

$$K_d = \left[\frac{A_i - A_{aq}}{A_{aq}} \right] \times \frac{V}{m}$$

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.

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 ^{111}In was determined using the gamma counter. The uptake of ^{111}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 ^{111}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 of the sorption Cd, Cu and ^{111}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., InCl_4^- , InCl_5^{2-} and InCl_6^{3-} , cadmium chloride complexes e.g., CdCl_3^- , CdCl_4^{2-} and tetra chloro copperate CuCl_4^{2-} . 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

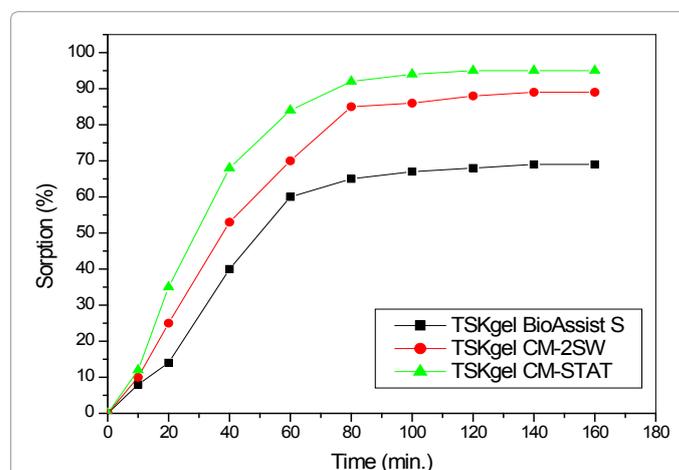
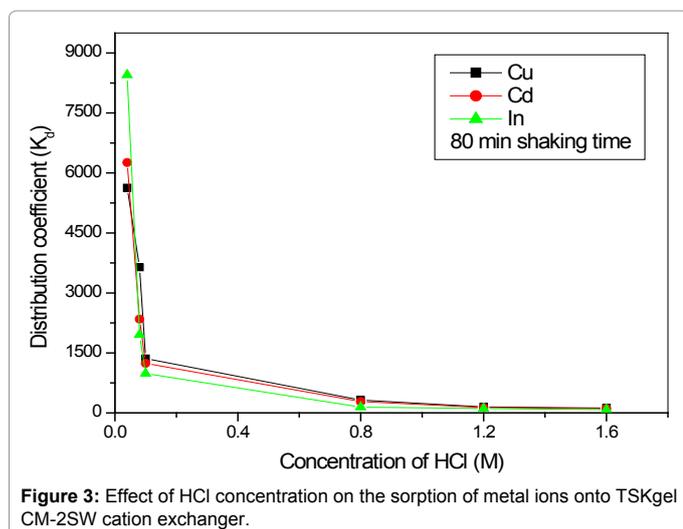
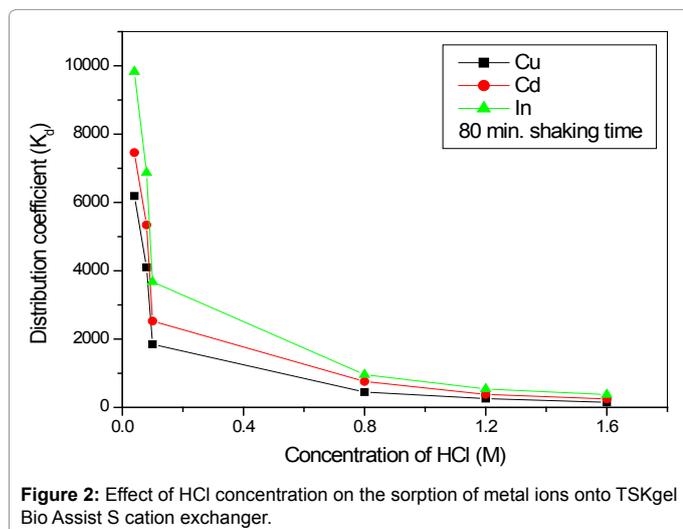


Figure 1: Effect of shaking time on uptake of three metal ions onto different cation exchangers.

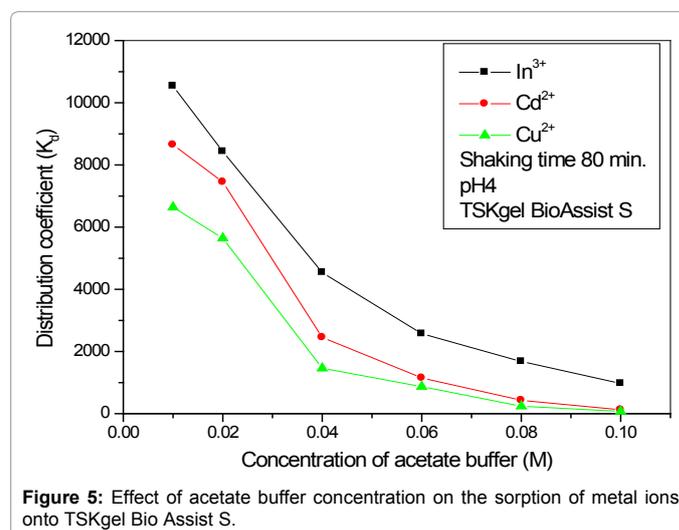
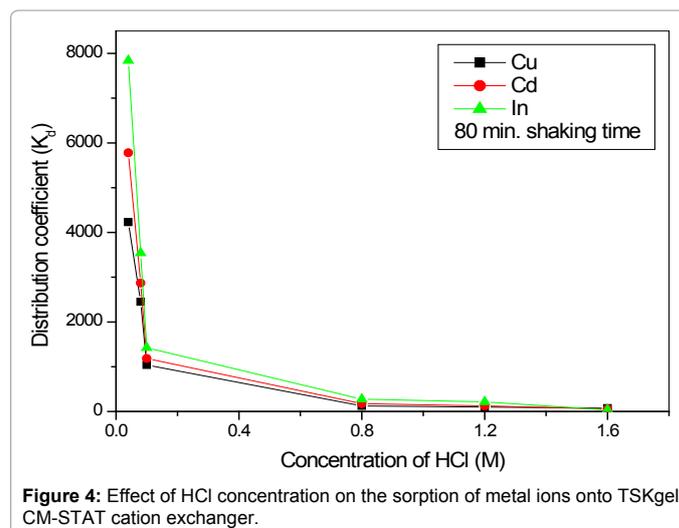


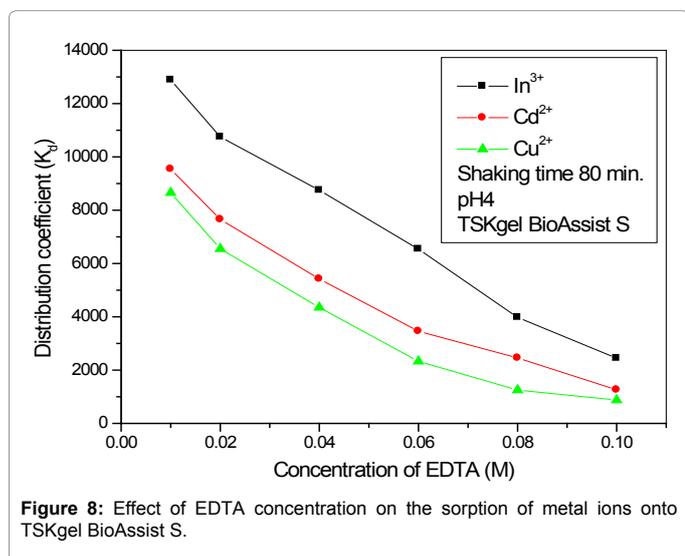
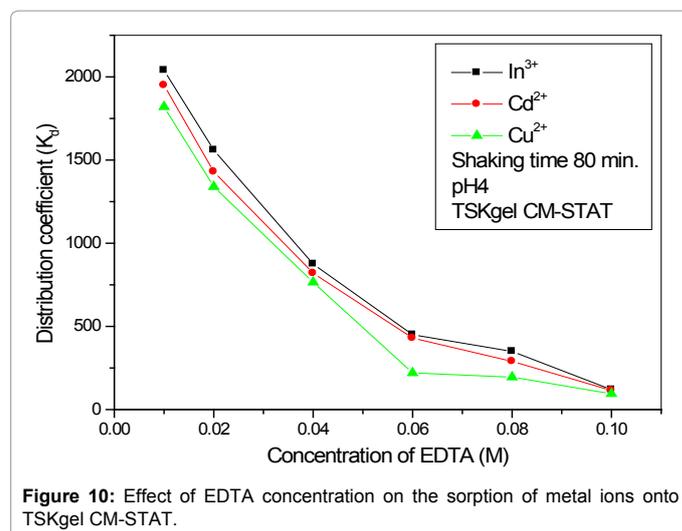
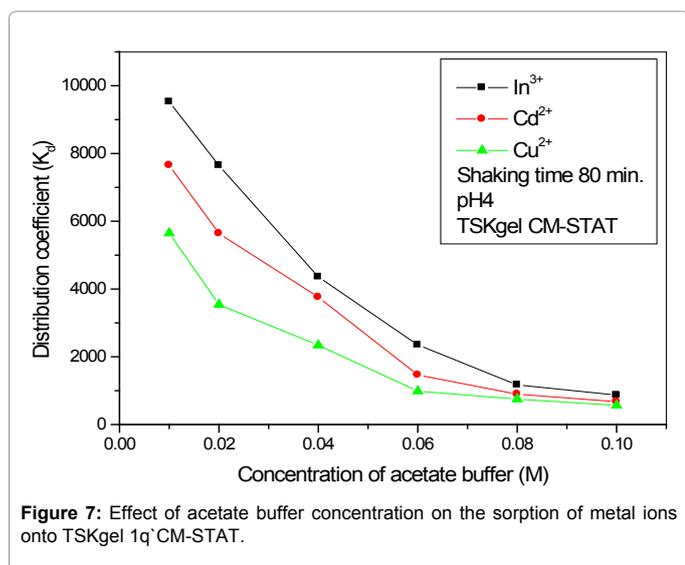
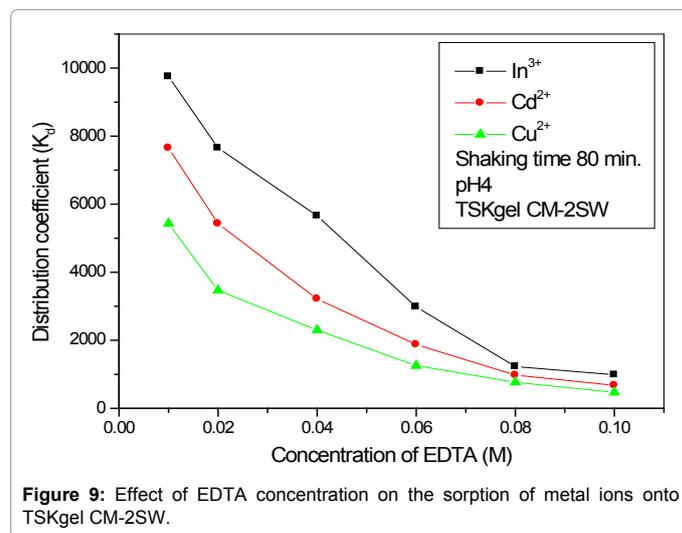
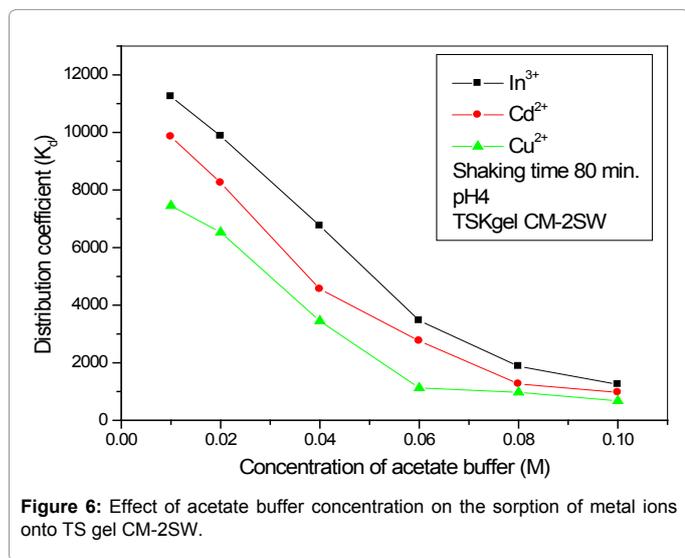
ionization of the exchangeable ions. Worth mention, all ion exchangers indicated sharp decrease in the distribution coefficient at approximately the same acid concentration. This might be due to the independence of exchanging mechanism on the chemical structure of the exchanging groups but mainly on 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 concentration of acetate buffer was considered satisfactorily and used as an eluting agent for separation of In from Cd and Cu. Generally, the sorption of all metal ions decreased abruptly with raising the buffer concentration which can be due to the increase in ionic strength of the medium. Copper sorption was the most strongly decreased with adding the buffer where the possibility of formation of copper-acetate complex is expected. Moreover, the charge of the buffering ion should be identical to the

ion exchange group because if buffering ions of opposite charge are utilized they may participate in the ion exchange process and cause disturbances to sorption. Thus, use of negatively charged acetate ions as a buffer is suitable for optimizing the sorption conditions.

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 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.





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 $^{111}\text{In}^{3+}$ 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 In^{111} 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 a 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

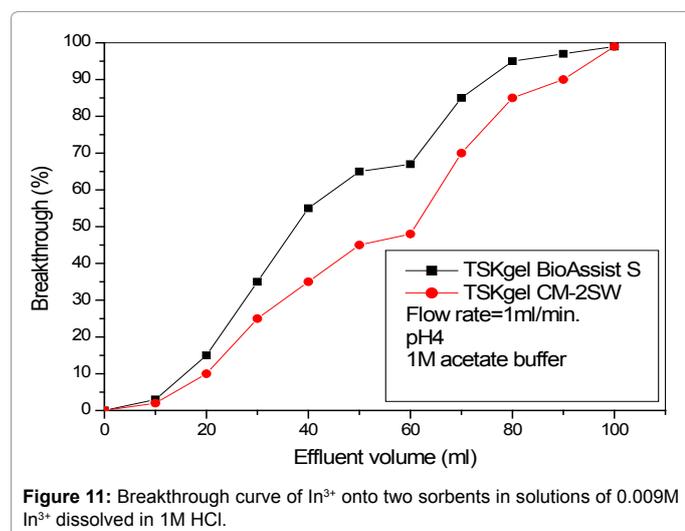


Figure 11: Breakthrough curve of In³⁺ onto two sorbents in solutions of 0.009M In³⁺ dissolved in 1M HCl.

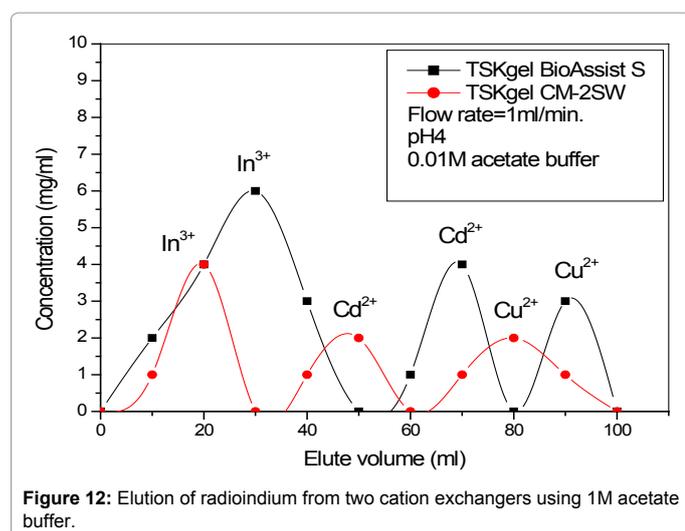


Figure 12: Elution of radioindium from two cation exchangers using 1M acetate buffer.

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 In¹¹¹ from Cd²⁺ and Cu²⁺ was undertaken. It could be concluded that, the TSKgel BioAssist S is very effective for the separation of In¹¹¹ from Cd²⁺ and Cu²⁺. Also, it could be successfully used to retain the three metal ions from 0.01 mol L⁻¹ HCl. Then, In¹¹¹ was removed in the first 30 mL, followed by Cd and Cu at 50 and 80 mL respectively using 0.01 mol L⁻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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