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A NEW COST TECHNIQUE FOR SEPARATION OF INDIUM-111 ISOTOPE PRODUCED FROM CADMIUM TARGET IN LOW ENERGY CYCLOTRON .

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ABSTRACT

.A radiochemical procedure for the separation of carrier-free ^{111}In from cadmium target is described. ^{111}In is produced produced by the bombardment of a natural Cd-111 target by proton particles. The separation is carried out by the difference in the sorption of indium, cadmium and copper on an activated carbon samples. Laboratory studies were conducted to evaluate and optimize the various process variables (shaking time, pH and effect of buffer). A quantitative determination of the adsorptive capacity of activated carbons to separated these metals was also determined. The distribution coefficients of the three elements onto different types of adsorbents were evaluated in 0.05M HCl and 1M acetate buffer at pH 4 to find the best conditions for separation of ^{111}In isotope from Cd and Cu.

KEYWORDS:

Activated carbon ; Separation; Radio indium; Cadmium; Copper

NOMENCLATURE::

AC-1: Activated carbon ICI Darco S-51

AC-2: Activated carbon Calgon CAL

AC-3: Activated carbon Westvaco WV-DC

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INTRODUCTION

Indium-111 is a cyclotron produced radionuclide which has very favorable nuclear characteristics ($E = 171.3, 245$ Kev; $t_{1/2} = 2.83$ days) for use in various *in vivo* studies, especially for labeling proteins and peptides.

Nuclear reactions like $^{111}\text{Cd}(p,xn)^{111}\text{In}$, $\text{Cd}(d,xn)^{111}\text{In}$, and $^{109}\text{Ag}(\alpha,2n)^{111}\text{In}$ are used to produce radionuclides for medical use. The yield of radionuclide from the nuclear reaction on silver is much lower than that from the irradiation of cadmium targets with protons (MacDonald *et al.*, 1975 [10]). However, ^{111}In obtained from a silver target is free from long-lived $^{114\text{m}}\text{In}$ ($t_{1/2} = 49.5$ days) which emits high energy γ -radiation, whereas variable amounts of $^{114\text{m}}\text{In}$ are always present in ^{111}In derived from the cadmium route (Dahl and Tilbury, 1972 [3]; MacDonald *et al.*, 1975 [10]; Zaitseva *et al.*, 1990 [15]).

Indium-111 has very favorable physical characteristics for *in vivo* studies. It decays slowly by electron capture to excited states of stable ^{111}Cd which de-excite via the emission of two low-energy photons which are only slightly converted. The photon energies 171 and 245 Kev are optimal for imaging with the Anger camera (Brown, L. C. *et al.* 1972 [1]), (Das, S. K. *et al.* 1996 [5]) has shown that the optimal physical half-life of a radiopharmaceutical to make sufficiently precise measurements, and yet minimize the total radiation exposure of patient, is 0.693 times the time period between administration and observation. The 2.82d half-life of ^{111}In fits this criterion well and is nearly optimum for lengthy 72h studies.

^{110}In ($t_{1/2} = 69$ min, $62\% \beta^+$) is a short-lived positron emitting indium isotope that can be produced in high radioactivity amounts by a low-energy accelerator and from an enriched ^{110}Cd -target. We present a simple, non-destructive and rapid method to separate radioactive indium isotopes from cadmium targets with the special aim to produce ^{110}In . The irradiated target foils were heated up to 306°C , that is close to the melting point of cadmium. At this temperature indium isotopes were diffusing out to the surface of the foils. After the end of the heating a high concentration of indium radioactivity was found at the surface of the target. By dipping the foils into a weak acid more than 60% of the radioactivity was etched off the target with less than 2% loss of the target material (Hans *et al.* 1995 [8]).

Various separation techniques like ion exchange, solvent extraction, and coprecipitation have been employed for the isolation of carrier-free ^{111}In from irradiated cadmium and silver targets (Brown L. C. *et al.*, 1972 [1]; Dahl and Tilbury, 1972 [3]; Thakur and Nunn, 1972 [13]; MacDonald *et al.*, 1975 [10]; Zaitseva *et al.*, 1990 [15]). The separation method followed depends on the type of target used for production of radionuclide. In large scale production, the irradiation is carried out internally and Ag or Cd targets electroplated usually onto a copper support are used.

In the case of ^{111}In production. However, the etched solution might contain, in addition to the target matrix, the supporting material (in varying quantities), which is copper in many situations, and the radiochemical separation procedures should be capable of tackling this situation. Separation of radionuclide from cadmium has been reported previously (Dahl and Tilbury, 1972 [3]; MacDonald *et al.*, 1975 [10]; Zaitseva *et al.*,

1990 [15]). Separation of ^{111}In from an active etched solution containing cadmium, iron and aluminum impurities has also been reported (Brown, L. C. *et al.* 1972 [1]). (Kopecky *et al.* 1976 [9]) used an acid alumina column to separate rain from cadmium and copper and finally employed solvent extraction to remove the aluminum. (Varma *et al.* 1980 [14]) utilized a single step separation method using a silica gel column to separate rain from cadmium and copper. In both these methods, elution of ^{111}In is incomplete and the yield of ^{111}In obtained was about 57% and 70%, respectively. Recently, we have shown (Das M. K. *et al.*, 1997 [4]) that separation of ^{111}In from a pure silver target using Dowex-50 cation exchange resin and concentrated HBr is efficient and simple. However, the presence of a large amount of copper in the solution of the target matrix demanded modification of the separation procedure. We tried to separate ^{111}In from an etched solution which contained cadmium, copper, aluminum and traces of iron. The last two impurities arise from the reagents used for the separation. Since the solvent extraction method is somewhat cumbersome, and in general gives a larger radiation dose, we planned the separation procedure using column ion exchange chromatographic techniques.

We have modified and improved two reported separation procedures, of Zaitseva *et al.* 1990 [15] and Kopecky *et al.* 1976 [9]. The Zaitseva *et al.* (1990) technique for separation of ^{111}In from pure Cd was based on a cation exchange resin and HBr solution (Nelson and Michelson, 1966 [11]). This separation technique as such is not suitable to separate ^{111}In if a large amount of copper is present in the etched solution (Das S. K. *et al.*, 1996 [5]). We have introduced a precipitation technique to separate the bulk of the cadmium and copper from the active radio indium solution and then applied the Dowex-50 ion exchange resin/HBr medium for the separation of radio indium from aluminum and traces of cadmium, copper and iron. In the second method, we have modified the (Kopecky *et al.* 1976 [9]) alumina column separation technique to separate the bulk of cadmium and copper from ^{111}In , and improved the yield of rain. Here also, we replaced their solvent extraction method for removing the aluminum impurity by the Dowex-50 resin and HBr technique.

The extraction of In(III) from HCl, H₂SO₄, and HNO₃ media using a 0.20 mol⁻¹ Cyanex 923 solution in toluene is investigated (Bina Gupta *et al.* 2004 [2]).

In(III) is quantitatively extracted over a fairly wide range of HCl molarity while from H₂SO₄ and HNO₃ media the extraction is quantitative at low acid concentration. The extracted metal ion has been recovered by stripping with 1.0 mol L⁻¹ H₂SO₄. The stoichiometry of the In(III): Cyanex 923 complex is observed to be 1:2. The extraction of In(III) is insignificantly changed in diluents namely toluene, *n*-hexane, kerosene (160–200 °C).

The object of this research was to conduct a study of phenomenon of indium separation of indium isotope from cadmium target in production of indium in cyclotron using low cost technique (activated carbon), the parameters affecting adsorption (i. e. carbon type, solution pH, equilibrium time, carbon dose) were optimized and the possible mechanisms involved were probed and finally elution curve using mini-column technique were studied.

EXPERIMENTAL

2.1. Metal solutions.

Aqueous solutions with variable concentration 10 mg L^{-1} for indium, 100 mg L^{-1} and 10 mg L^{-1} for each copper and nickel ions were prepared. The solution pH was adjusted with reagent grade nitric acid or sodium hydroxide. The solution was then filtered through (Whatman No. 1) filter paper A control sample was taken at this point to determine the exact metal concentration before contact with activated carbon. Exactly 20 ml of the sample solutions were placed into 50 ml glass bottles containing previously weighted samples of activated carbon and the bottles were shaken for specific periods of time, after agitation the samples were filtered through (Whatman No. 1) filter paper and the final metal concentrations were determined using ICP-Jobin Yvon ICP-OES spectrometry model Ultima2.

2. 2. Instrumentation.

The instruments used throughout the work are summarized as follows:

- ICP- Jobin Yvon ICP-OES spectrometry model Ultima2.
- γ -Spectrometer: Multichannel analyzer system EG & G ORTEC model GEM-18190 with a high purity germanium coaxial detector (USA).

2. 3. Activated carbon selection.

Samples of three activated carbon were obtained from Hot Laboratory Centre, Egyptian Atomic Energy Authority will illustrated in Table. (1). The carbons were evaluated for their specific ability to adsorb the individual metals from aqueous solutions. These experiments were conducted at the original pH of the solutions.

2. 4. Optimum pH determination.

Solutions with variable concentration 10 mg l^{-1} for indium, 100 mg l^{-1} and 10 mg l^{-1} for each copper and nickel ions were adjusted to various integral pH values ranging from 2 to 10. The ability of the previously selected activated carbon to adsorb the metals as a function of solution pH was then determined.

2. 5. Minimum contact time determination.

Solutions at the optimum pH containing indium, cadmium, copper or nickel at constant doses of the previously selected carbon were agitated. Various periods of agitation were employed to determine the minimum contact time required for complete or maximum metal adsorption. A second series of tests with all metals in the same solution and with varying doses of the previously selected activated carbon were also conducted to determine the minimum contact time.

2. 6. Breakthrough study.

The loading capacity of the three sorbents for sorption of ^{111}In could be determined by the breakthrough technique. A glass column (5 mm diameter and 10 cm length) contain 0.5 g of dry sorbents was prepared. A solution of 0.009 M of inactive indium with reasonable counts of ^{111}In in 0.05 M HCl was passed through column beds, at a flow rate of 1 ml/min.

2. 7. Elution curve study.

Elution of indium was experimented using 1 M of acetate buffer at pH 4 from a glass column (5 mm diameter and 10 cm length) contain 0.5 g of dry sorbents was prepared.

RESULTS AND DISSCUSION

3. 1. Effect of Shaking Time.

The effect of contact time between the aqueous solution and the solid phase was evaluated using batch experiments. The batch experiment was carried out using reasonable counts of ¹¹¹In in 0.01 M HCl as an aqueous phase and three activated carbon samples as a solid phase. It can be seen that sorption of indium increases with increasing shaking time until it reached equilibrium at 60 min. on shaking with three different sorbents. While in Fig. (2) showed the equilibrium time of cadmium on adsorption with three activated carbon samples was 40 min., wherever, The effect of shaking time on the adsorption of copper found in the irradiated solution, from Fig. (3) the equilibrium time for copper on adsorption at three activated carbon samples was 30 min..

3. 2. Effect of Acid Concentrations.

Maximum sorption of the three elements in different molarities of HCl onto different sorbents are shown in Figs. (4, 5 and 6), we showed that the distribution coefficient of In (III) is the highest one in compared with cadmium and copper on adsorption onto three sorbents but the biggest value for distribution coefficient were shown on sorption onto AC(3).

(Semkow *et. al* [12]) showed that sorption of three metal ions were different onto three sorbents but decreases sharply with increasing the concentration of HCl, due to the formation of InCl_3 , CdCl_2 and CuCl_2 at low acidity.

The decrease in the sorption of three metal ions at high concentration of HCl acid can be attributed to the formation of indium chloride complexes (InCl_4^- , InCl_5^{2-} and InCl_6^{3-}) (Geenwood *et. al* [7]). Cadmium chloride complexes (CdCl_3^- and CdCl_4^{2-}) and copper chloride (CuCl_4^{2-}). These anionic species could not be adsorbed.

3. 3. Effect of buffer acetate concentration at pH 4 on the K_d of In, Cd and Cu.

The distribution coefficient of In^{3+} , Cd^{2+} and Cu^{2+} at various concentrations of acetate buffer at pH 4 on (AC1, AC2 and AC3) were evaluated. The results show that each In^{3+} , Cd^{2+} and Cu^{2+} are sorbed to a great extent from low concentrations of the acetate buffer (10^{-5} to 1 M).

Figs. (7, 8 and 9) showed that the distribution coefficients (K_d) of In^{3+} is greater than Cd^{2+} and Cu^{2+} on adsorption onto three sorbents throughout the whole range of buffer acetate concentration, the sorption behavior of In^{3+} onto different sorbents was quite different, the K_d value were very high in case of sorbent AC3 in compared to the

two different ones. Therefore, 1M of acetate buffer can be satisfactorily used as an eluting agent for the separation of In from Cd and Cu.

3. 4. Breakthrough technique for determination the uptake of In³⁺.

The loading capacity of the sorbent material (AC1, AC2 and AC3) for sorption of the In³⁺ could be determined by the breakthrough technique. Fig. (10) was showed that the breakthrough of In³⁺ as a function of the loaded volume in adsorption onto (AC1, AC2 and AC3). It was observed that in the first 10 ml of the effluent, In³⁺ is completely sorbed onto AC1. Gradually, breakthrough of In³⁺ (50% breakthrough) occurred with 30 ml, 40 ml in case of AC2 and 50 ml in case of AC3 . The saturation uptake is reached after eluting 40 ml in case of AC1, 60 ml in case of AC2 and 100 ml in case of AC3.

3. 5. Elution studies on Indium.

Elution of indium was experimented using 1 M of acetate buffer at pH 4, the obtained results were represented in Figs. (11, 12 and 13). More than 98% of the indium was eluted by 1 M acetate buffer at pH 4 in the first 30 ml of the elute in case of sorbent AC1 and eluted after 20 ml in case of AC2. while indium eluted very fast after 10 ml in case of sorbent AC3. Copper and cadmium are eluted at 50 and 80 ml respectively. But the copper is not completely separated from cadmium.

CONCLUSION

The developing of new adsorption technique for separation of In-111 cyclotron produced isotope using activated carbon is considered as a better replacement of ion exchanging and solvent extraction techniques due to low cost and good efficiency in this application. Activated carbons have been considered a good adsorbent to obtain carrier-free ¹¹¹In of high purity suitable for medical applications, quantitatively from solution containing appreciable amounts of copper and cadmium. The method are equally efficient, quantitative and adaptable for any scale of rain production, also it could be used to retain the three elements from 0.05 M HCl and then indium-111 was completely removed in the first 20 ml, followed by Cd and Cu at 60 and 90 ml respectively, using 1 M acetate buffer at pH 4.

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Table. 1. Properties of three commercially available activated carbons.

Number Designation	AC1	AC2	AC3
Activated carbon	ICI Darco S-51	Calgon CAL	Westvaco WV-DC
Properties			
Surface area (m ² g ⁻¹)	650	1100-1300	1500-1700
Apparent density (g cm ⁻³)	0.24-0.29	0.41	0.24-0.29
Effective Size (mm)	-	0.55-07	0.9-1.0
Iodine	950	1000	850
Maximum moisture	8	2	10
Source	Lignite	Coal	Wood
Size	Powder	12*40	10*25
Mean pore radius (A ⁰)	30	50	23

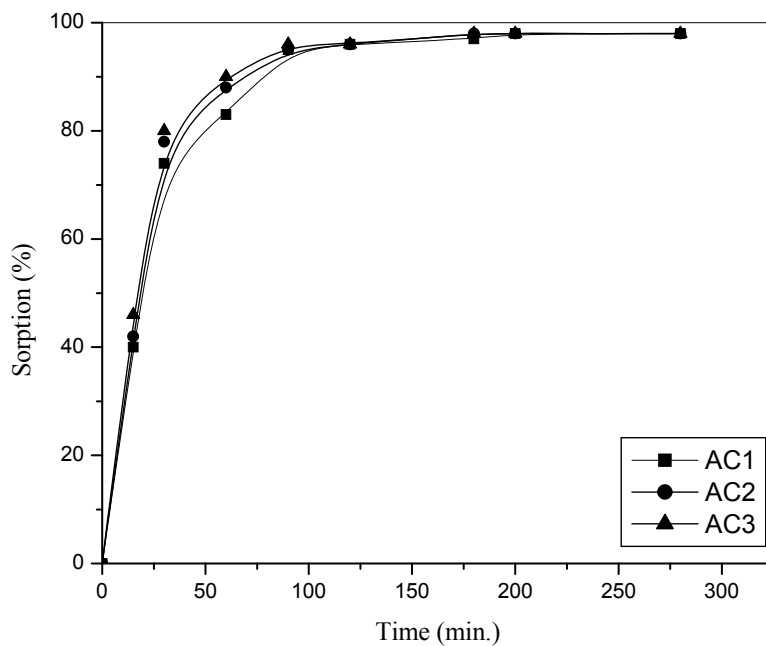


Fig. 1. Sorption of radioindium as a function of time from 0.05 M HCl onto different activated carbon samples

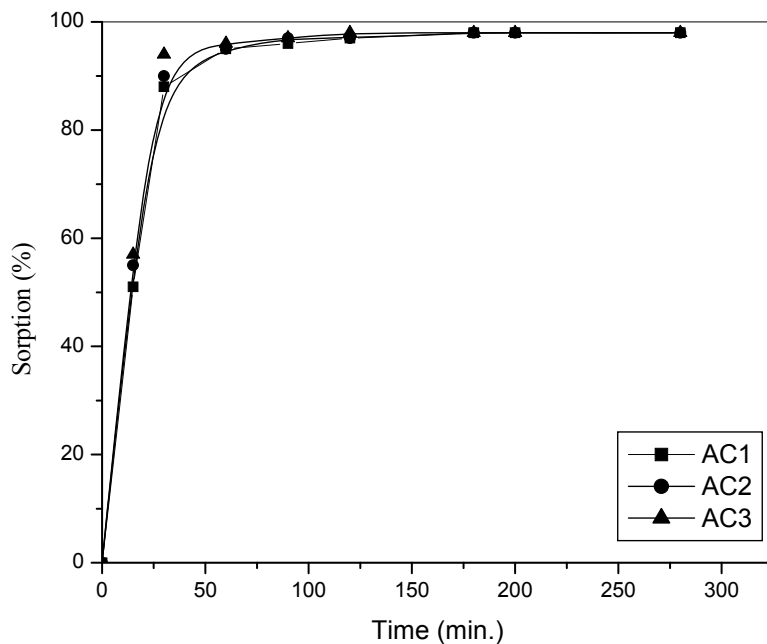


Fig. 2. Sorption of cadmium as a function of time from 0.05 M HCl onto different activated carbon samples

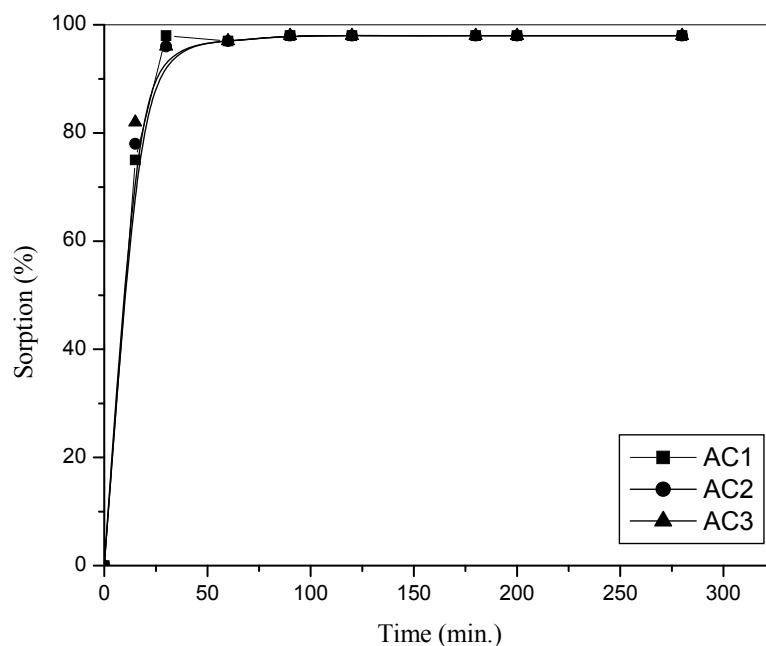


Fig. 3. Sorption of copper as a function of time from 0.05 M HCl onto different activated carbon samples

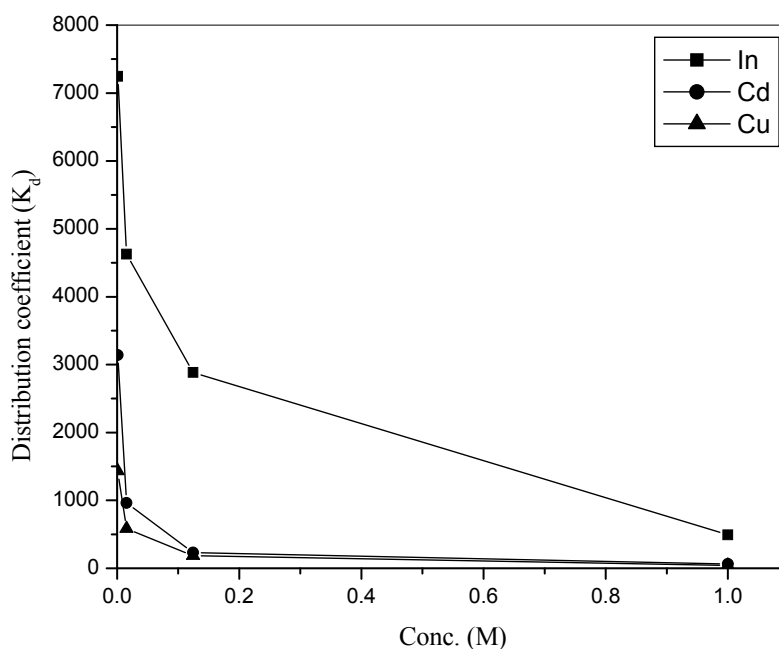


Fig. 4. Effect of HCl concentration on K_d on adsorption of different metal ions onto AC(1)

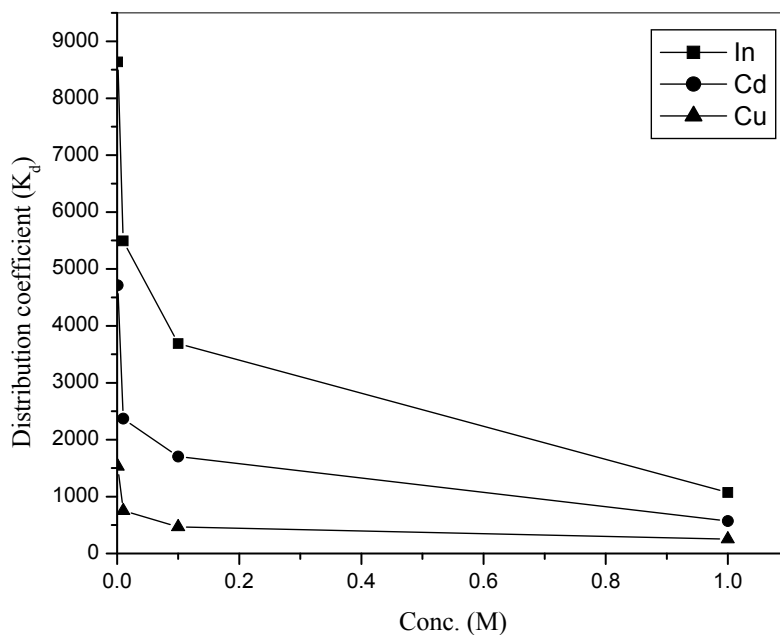


Fig. 5. Effect of HCl concentration on K_d on adsorption of different metal ions onto AC(2)

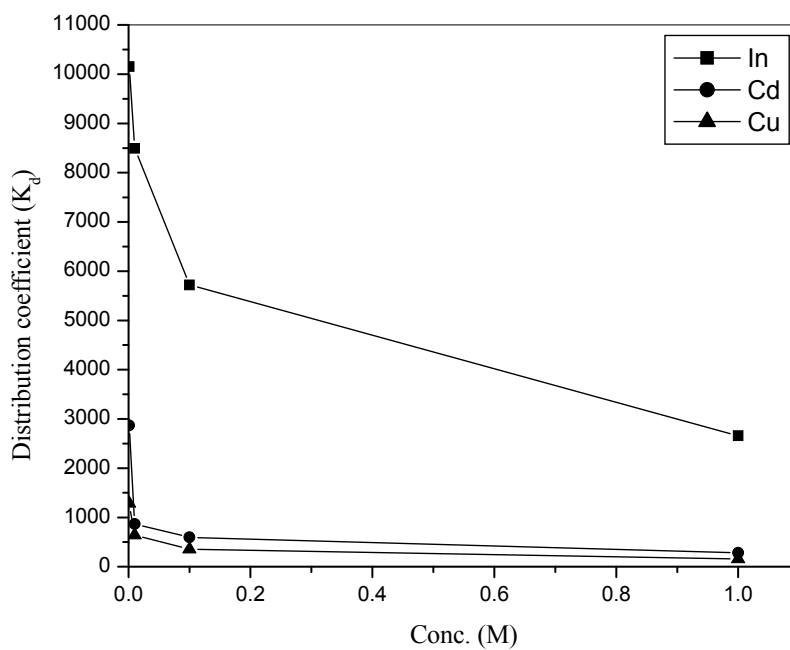


Fig. 6. Effect of HCl concentration on K_d on adsorption of different metal ions onto AC(3)

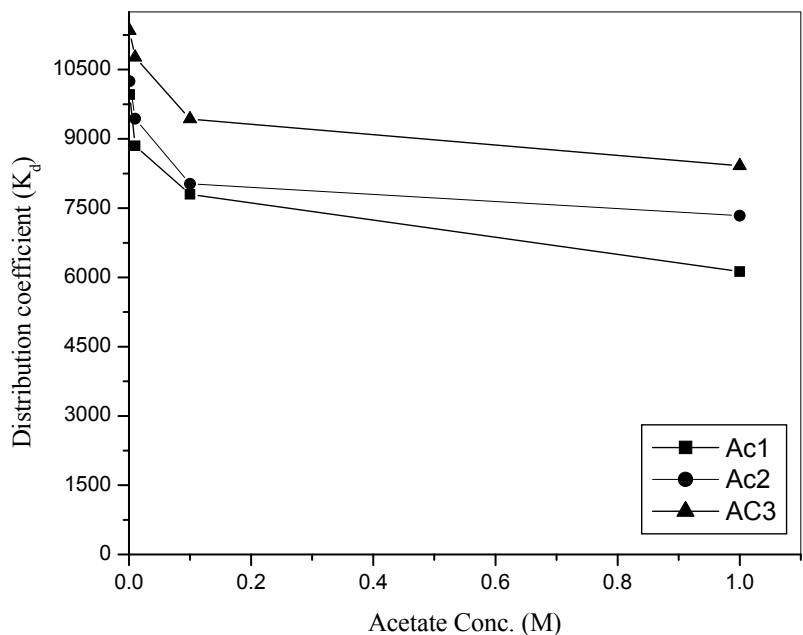


Fig. 7. Effect of buffer acetate concentrations at pH 4 on sorption of radioindium

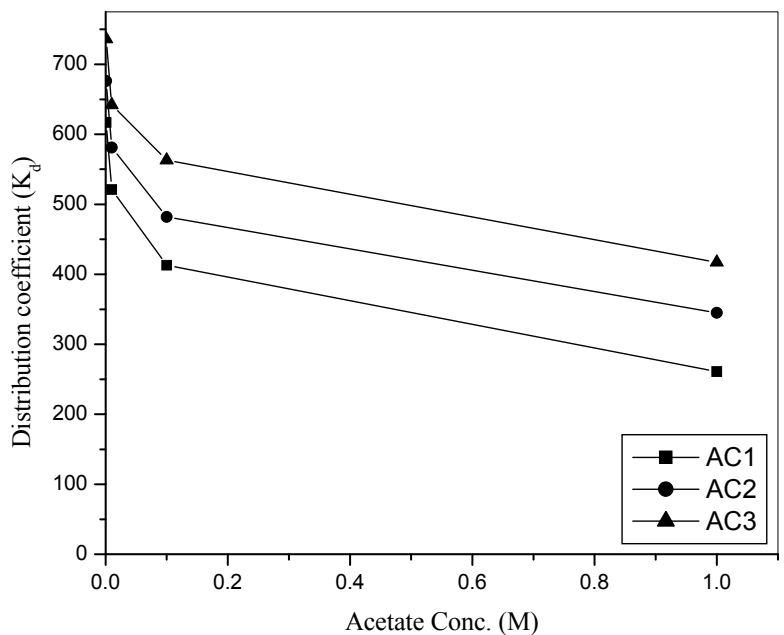


Fig. 8. Effect of buffer acetate concentrations at pH 4 on sorption of cadmium

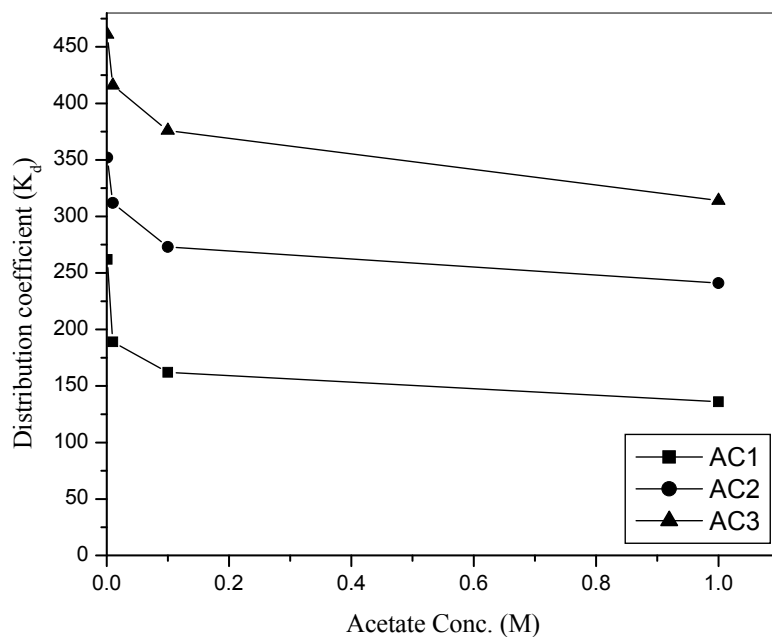


Fig. 9. Effect of buffer acetate concentrations at pH 4 on sorption of copper

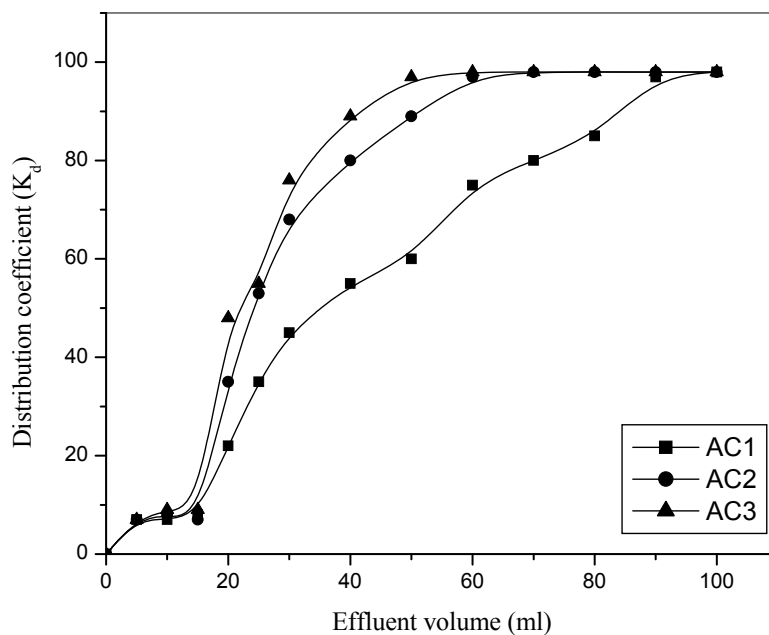


Fig. 10. Breakthrough curve of In^3 from 0.5 g of different sorbents in solution of 0.009M In^3 dissolved in 0.05 HCl at 1 ml/min. flow rate

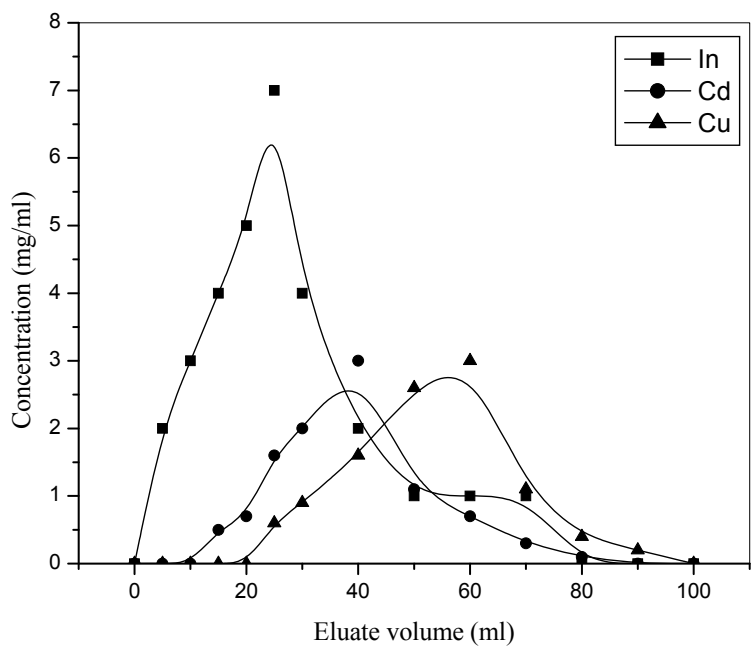


Fig. 11. Elution of radioindium using AC1 adsorbent column and 1M acetate buffer at pH=4 and flow rate of 1 ml/min.

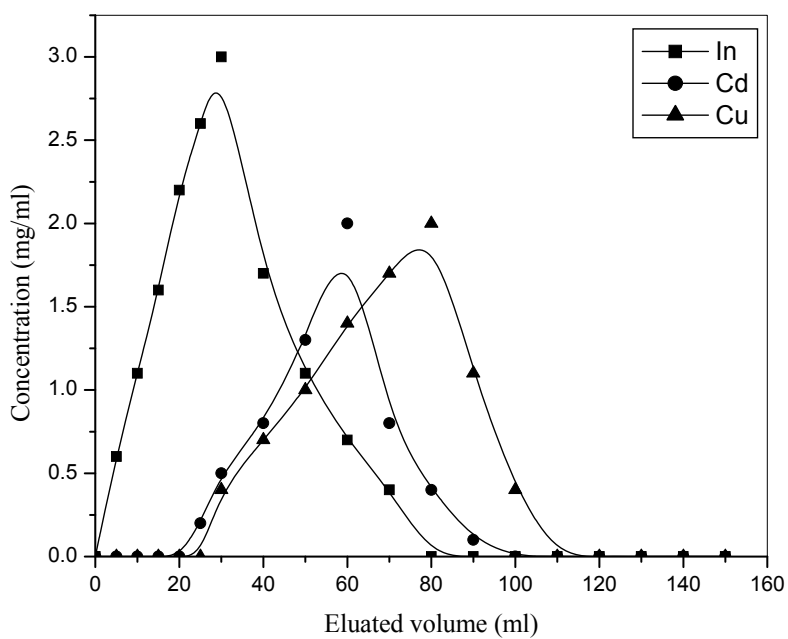


Fig. 12. Elution of radioindium using AC 2 adsorbent column and 1M acetate buffer at pH=4 and flow rate of 1 ml/min.

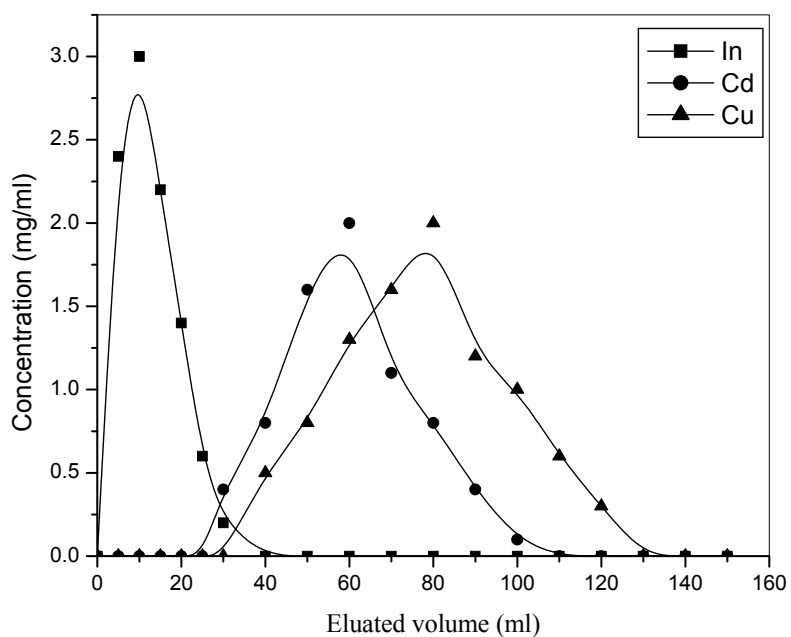


Fig. 13. Elution of radioindium using AC 3 adsorbent column and 1M acetate buffer at pH=4 and flow rate of 1 ml/min.