

ADAPTATION OF ANION EXCHANGE PROCESS TO DECONTAMINATE MONAZITE RARE EARTH GROUP FROM ITS URANIUM CONTENT

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Abstract

This paper adapt a process for uranium separation as a radioactive element from the sulfuric liquor, generated after several chemical treatment process for Egyptian black sand monazite mineral, applying ion exchange technique. The influence of several variables such as the resin bed thickness, contact time between phases, concentration of the started solution and its pH were investigated. After the mineral thorium content separation, the results indicated the possibility of separation efficiency of uranium from sulfuric acid media containing a mixture of both uranium and rare earth group by anionic exchange resin. The elution of uranium was carried out with a sodium chloride solution. The behavior of uranyl sulphate anion and trivalent rare earth cations present in the started leach liquor towards anion exchange resin has been studied using Amberlite IRA 402 Cl resin. More than 99% of the rare earth elements passed in the eluate phase of the liquor when the initial concentration of sulfuric acid was between 4 and 6 M. Under these conditions uranyl sulphate anion were readily adsorbed by Amberlite IRA 402 Cl resin and were quantitatively eluted from the column using 2M sodium chloride solution. To fulfill the previous results, pH of starting pregnant solutions was adjusted to 1.75 while the pH of the optimum uranium elution sodium chloride solution was 7 for uranium separation by elution and the most effective flow rate was 1ml/min while the most probable starting solution concentration was 300 ppm and the dimension of fixed bed radius was 1.2 cm and 14 cm height. Under the previous conditions rare earth concentrate was rarely decontaminated with percent recovery and purity (from U) more than 99%. Uranium recovery and purity were more than 99% and 95% respectively.

Keywords: Monazite treatment, Rare earth elements, Uranium separation, Ion exchange resin.

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1. INTRODUCTION

From the 200 best known minerals containing rare earth (RE) elements, only three contain significant amounts bastanite, monazite and xenotime, monazite being the second most important source of rare earths [1]. Monazite is a rare earth phosphate also containing thorium and uranium as associated metals [2-6]. Its structural group consists of arsenate, phosphate and silicate, having the general formula ABO_4 , where A corresponds to RE, Th, U, Ca, Bi, etc. and B corresponds to As^{5+} , P^{5+} or Si^{4+} [7,8]. The Egyptian black sand beach deposits are the chief thorium ore in Egypt due to the presence of monazite [9]. Gupta [10] studied the description of monazite breakdown via acid and alkali digestion and discussed the composition of the concentrates and their effect on solvent extraction and ion exchange processes. The processing of monazite leads to the generation of RE concentrates containing thorium (Th), uranium (U) and phosphate (PO_4^{3-}). Monazite is cracked through one of the two following methods: (i) the basic process with a sodium hydroxide solution where REEs are separated as a group in one hydroxide concentrate in addition to Th and U together in other hydroxide concentrate during

the process. (ii) the acid process with concentrate sulfuric acid (H_2SO_4) where a liquor containing the RE elements, Th and U is generated [1,11-14]. The recovery of mixed rare earths and the removal of thorium and uranium from monazite are accomplished through a variety of methods after chemically attacking the mineral with sulfuric acid or sodium hydroxide [15]. Actually, the outstanding attribute of the acid process is its ability to treat economically all types and grades of monazite, without prior grinding or purification, a condition which is obligatory in case of alkali treatment. A coast comparison between both methods gives a slight advantage to the sulphuric acid process. Mixing of monazite with sulphuric acid is generally performed batch wise in cast iron pots provided with external heating, heavy duty stirrers, covers and a vent system to remove sulphuric acid fumes. A novel method for the separation of uranium from RE elements and thorium has been devised by the authors and in the process; uranium is simultaneously extracted from the sulphuric liquor generated in the monazite process with the use of Oxalic- Nitrate- TBP solvent extraction scheme (liquid-liquid extraction LLE) [16]. A another method for the separation of uranium from RE elements and thorium has been devised by E. Metwally

in which Extraction of U(VI) and Th(IV) from chloride and nitrate solutions with tri-n-dodecylamine impregnated on Amberlite XAD4, was investigated [17]. More recently, the use of solid phase extractants (SPE) have been proved to be more advantageous in view of their total insolubility in aqueous phase, low rate of physical degradation, no disposal of toxic organic solvents as waste and it can be recycled. In SPE, the organic extractants are anchored to an inert. [18]. polymeric support and several methods have been developed for actinide extractions [19–26].

In the present work there has been a great need for separation of uranium as radioactive elements targeted to obtain a pure rare earths cake and improve a high efficient process for uranium recovering, separation and concentration from RE mixture as additive strategic material.

2. EXPERIMENTAL

2.1. Reagents and Solutions

All chemicals used in this study were of analytical grade reagent and were used as received. Amberlite IRA 402 Cl resin (Rohm and Hass) its matrix component is styrene-divinyl benzene (gel type) with a particle size of 0.600 to 0.750 mm and the matrix active group is Tri-methyl ammonium chloride. The resin was washed with distilled water and hydrochloric acid several times in turn, and dried at 50°C. To the dry resin (100 gm in 1L graduated cylinder), acidified water is added and the resin is accurately mixed with water (800 ml), the cylinder is sealed and after 2 h the resin is stirred again to remove all remaining air bubbles to form a homogenous resin suspension. The cylinder is sealed again and after 22 h of the settlement the resin volume is measured for the experiment. Hydrous oxide rare earth concentrate was supplied by Egyptian semi-industrial monazite -RE₂O₃ plant (NMA) [27-29]. All reagents used in the study were of analytical grade and their respective solutions were prepared with distilled water.

2.2. Procedure

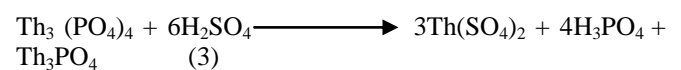
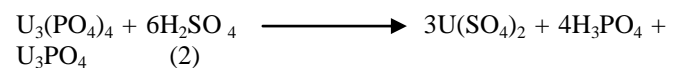
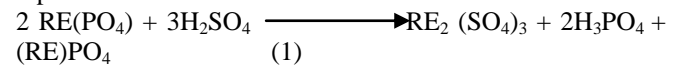
2.2.1. Preparation of Rare Earth-Uranium Starting Sulphate Working Solution

The received hydrous oxide RE concentrate, which formerly prepared via the following summarized steps:-

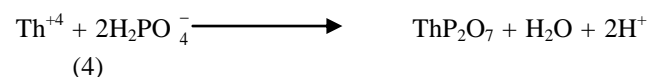
Heating a batch of a concentrated sulphuric acid to a temperature of about 180°C in a closed reactor, then the unground monazite(50%, -125 mesh) sand was added slowly to the concentrated sulphuric acid, in the proportion of one part monazite to 2 parts of the sulphuric acid with continuous stirring. The required time to achieve a complete digestion depends to some extent upon the particle size of the sand, which is left ungrounded at a size range of about 30 to 120 mesh and upon the grade of the received monazite. A total breakdown time of 3-4 hours is necessary. The digestion reaction results in a thick grey paste, which after cooling is cautiously diluted with ice-water for about

twenty times, the weight of the mineral, and the stirring is continued for at least 1 hour. Cooling has to be maintained in order to prevent the temperature from rising above 15°C; the solubility of the rare earth sulphates increase as the temperature is decreased. By this treatment, all rare earths go into solution which is decanted out of the silica, rutile, zircon, and the unreacted monazite that easily settle down in few hours.

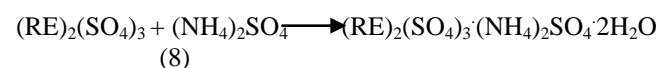
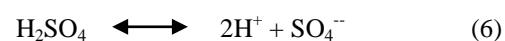
The reactions of the mineral with sulfuric acid might be represented as follows:



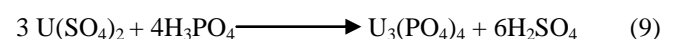
Thorium content was first precipitated quantitatively at pH of 0.9 with ammonia solution (1:1), according to the following equation.



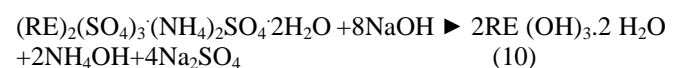
Rare earths are then precipitated as di ammonium sulphate from the filtrate by careful ammonia soln addition to pH 2.6 as in equation (8). By adding barium salts during the sulphuric acid leach, the rare earth concentrate was obtained, free of direct hazardous radioactive materials.



Then finally, major uranium monazite content is precipitated by neutralization with ammonia to a pH of 5.5 - 6 according to the equation.



The obtained rare earth precipitate from steps previous steps is converted into the corresponding mixed hydrous oxides by boiling with sodium hydroxide solution in a stoichiometric ratio for 1 hour. The mixed rare earth hydrous oxides were filtered, washed repeatedly by water until they are only slightly basic.



The obtained precipitate was dissolved in H₂SO₄ amount to obtain thorium free starting working rare earth concentrate

solution. The starting working (loaded) solution was found to contain 6 g/l REEs as a group and 0.3 uranium calculated as their respective oxides in addition to undetectable thorium and phosphorous values.

The capacity of anion exchange resin was directed during its construction and optimizing its sorption condition towards such working solution anionic composition.

2.3 Anion Exchange Resin Column Set-Up

The fixed-bed column was made of cylindrical glass tube of 2.4 cm inner diameter and 30 cm height. The column was packed with adsorbent between two supporting layers of glass wool. The Amberlite IRA 402 Cl was added from the top of the column and allowed to settle by gravity force. A known quantity of the prepared Amberlite IRA 402 Cl was packed in the column to yield the desired height of the adsorbent equivalent to 15, 20, 25 g of Amberlite IRA 402 Cl. The upper portion of the adsorbent was covered with glass beads. The desired volume of RE leachate was taken in a bucket and a peristaltic pump controlled the inlet flow rate. The bottom of the column was connected with rubber tubing with flow adjustable clamp. Thus the outflow rate was controlled by adjusting the clamp. The samples were collected in regular time intervals and analyzed by spectrometer. The schematic diagram of the column study is shown in Fig.1.

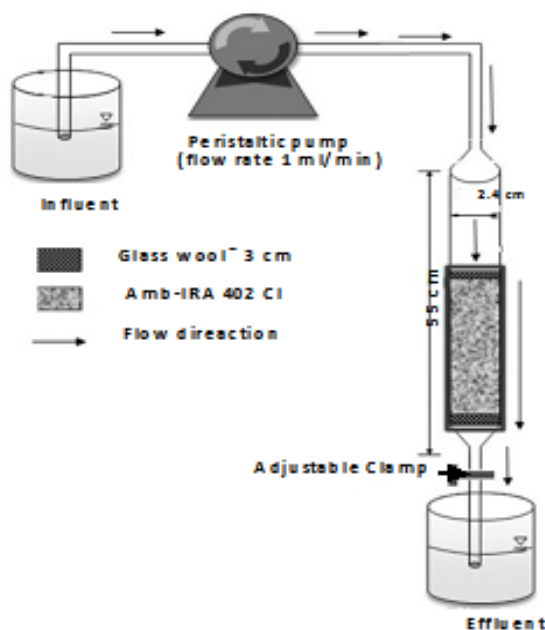


Fig 1 Schematic diagram of lab-scale column study

2.4 Experimental Adsorption Studies

The uranium adsorption with Amberlite IRA 402 Cl was studied with the aim of treating the leachate collected after the mineral monazite (50%) treatment by concentrated sulphuric acid. The uranium concentration in the leachates was observed to a maximum of concentration 800 mg/L and thus this concentration level has been selected for column study.

Fixed-bed column sorption studies of uranium were performed by passing known working solution volume with different PH values between (1-2.5) continuously upon 10.0 g dry Amber lite IRA 402 Cl resin particles in the chloride form with variable flow rate (1ml/min) at ambient temperature (25 °C). Aliquot samples were taken from the column at appropriate time intervals as necessary. Fixed bed sorption studies of uranium were investigated through uranium concentration analysis in the effluent after passing the work solution through the bed and the starting aliquot uranium concentration. The concentrations of uranium were analyzed by spectrophotometric method [30]. All experiments were performed in duplicate and the averaged values were taken. So, Loading of solutions was stopped as soon as metal ion concentration in the effluent equalized to that in the influent which is the saturated point. Lot volumes of 100 mL were collected and analyzed for concentration of metal ion. After the sorbent is saturated with uranium it is eluted with NaCl. The amount of uranyl sulphate adsorbed onto the resin (q , mg g^{-1}) and the uptake percent ($U\%$) were respectively determined using the following relations [32]:

$$q = (C_0 - C_e) \frac{V}{m} \quad (11)$$

$$U\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (12)$$

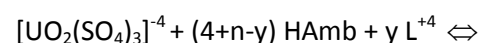
where C_0 and C_e are the initial and equilibrium concentrations of U in the solution (mg/l) respectively, V is the volume of solution (L), m is the weight of the resin (g). The application of Amberlite IRA 402 Cl for removal of uranium from RE leach liquor has been evaluated.

3. RESULTS AND DISCUSSION

The optimum conditions for complete uranium adsorption upon Amberlite IRA-402-Cl is determined after studying the relevant most effective factors to fulfill complete removal of it (minor) from the group of rare earth elements concentrate (major). Particularly resin affinity towards uranium, pH value of the starting loaded working REEs-U solution, Uranium content of the starting working solution, contact time and column bed depth.

3.1. Resin Capacity (Sorption Performance)

The affinity and the capacity (max. loading) of Amber lite IRA-402Cl anion exchange resin towards uranium were tested to follow the following equation.



By contacting acidified uranium containing solutions, with ten gram of the preconditioned resin at ambient temperature, in a batch process.

The uptake percent of uranium from REE-U working solution was increased by time of contact increase till

reaches affixed values of uptake or plateau as shown in figure (2) and demonstrated in table (1) It was clear that most of adsorbed portion of uranium content was carried out after the first thirty five minutes and a steady increase slight obtained after this time. So, one can judge almost that thirty five minutes is the resin breakthrough point (max. loading capacity) for such reaction under such circumstances.

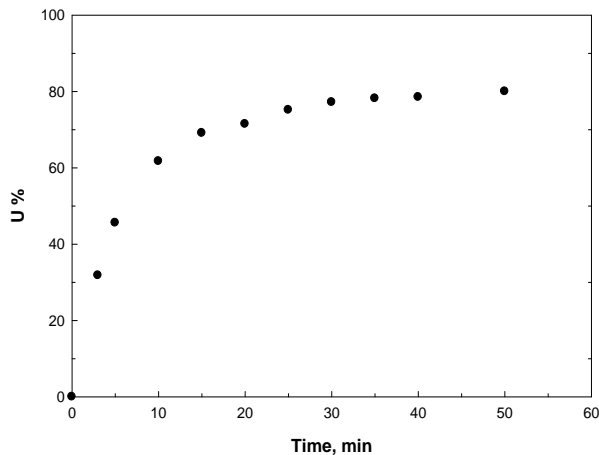


Fig 2 Uptake percent of uranium from solution on Amberlite IRA-402 Cl resin at 25 °C. (Conc. 600 ppm, bedthickness 14 cm, Flow rate 1 ml/min, pH 1.75 at 25 °C)

3.2. Effect of REEs Working Solution Acidity (pH)

The ion exchange of metal ions involves the formation of different mixed species in the resin phase depending on the pH. The pH value of the working system plays an important role on sorption extent because of its influence on the degree of ionization and the surface properties of the applied sorbents. The speciation of uranyl sulphate anions in aqueous solution could be described from the above equation (13).

The variation in the removal extent of U with pH using Amberlite IRA-402Cl was studied by fixed bed experiment as shown in Figure 3. It was found that, The solution pH greatly affects the sorption of uranyl sulphate. As the pH increases the amount adsorbed increases before started to decrease again at pH >1.75. The last observation can be attributed to the hydrolysability of the uranyl sulphate anions, a process which decreases the absorbability of the U ions.

The results of acidity or pH effect were obtained after passing the same volume of rare earth-uranium acidified working solutions with different pH values (1 - 2.5) through a fixed column of resin at ambient temperature. The acidity of the utilized solution portions were adjusted at pH 1.0, 1.5, 1.75, 2, 2.5 before passing through the fixed resin column bed with a flow rate 1 ml/min. It was founded that, The pH has a dramatic effects on the adsorption extent of U on Amberlite IRA-402Cl. The pH influences the degree of ionization of the reactive acidic group of the resin. Since maximum sorption occurs at pH 1.75, this pH was taken as

the optimum value for all sorption studies at the present experimental conditions.

On the other hand after PH ~ 2 value a respective values of REEs were found to captured with uranium may be due to their precipitation or some elemental hydrolyzation on the resin surface competing and or / inhibit uranium adsorption resin capacity resulting in complete uranium adsorption and impure REEs effluents (products).

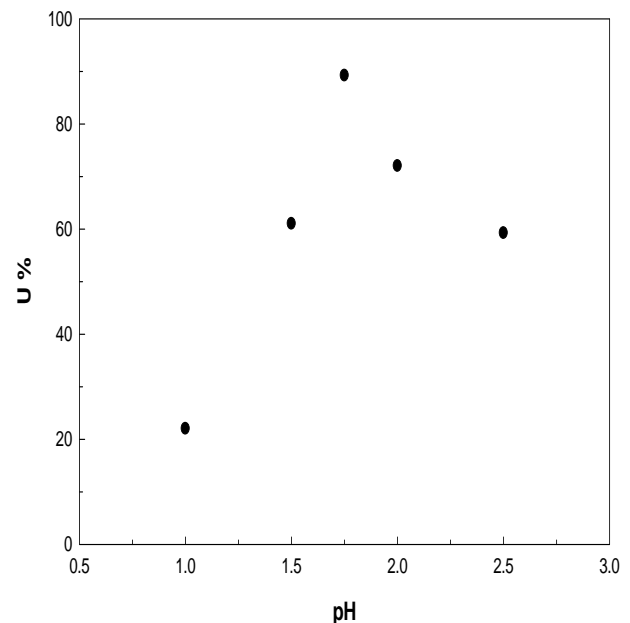


Fig 3 Effect of pH on the adsorption of uranyl sulphate anions on Amb-IRA-402 resin (Conc. 600 ppm, bedthickness 14 cm, Flow rate 1 ml/min at 25 °C)

3.3. Effect of Initial Uranium Content

This effect was studied by passing different volumes of adjusted working solutions containing 300, 500, 600, and 800 ppm uranium (500, 600, 800 ppm concentration were obtained after working mother liquor concentration to such ppm.s) through a fixed column bed with 1ml/min flow rate at pH 1.75. The Results is declared in table (1) and figure (4). However, the break through points for the different concentrations were totally different. The effect of the initial concentration onto the break through curves. It can be seen that a rise in the inlet metal concentration reduces the volumes treated before the packed bed get become saturated. A high metal concentration may saturate the Amberlite IRA-402Cl more quickly, there by decreasing the breakthrough time. These results demonstrate that an increase in the concentration modifies the adsorption rate through the bed and increases the bed adsorption capacity (Table 1). Therefore the diffusion process depends on the inlet concentration [33, 34]. Nevertheless, the saturation of the adsorbent requires much more time. However the breakthrough is reached before all the active sites of the Amberlite IRA-402Cl are occupied by the metallic ions

showed in this study a high affinity for uranium anion under these experimental conditions.

Table 1 Fixed bed column adsorption parameters of the sorption of uranium anion at different initial metal concentrations. (bedthickness 14 cm, Flow rate 1 ml/min, pH 1.75 at ambient temperature)

Initial concentration C_0 (mg l^{-1})	Treated volume V (ml)	Breakthrough point t (min)
300	130	40
500	150	50
600	180	70
800	200	90

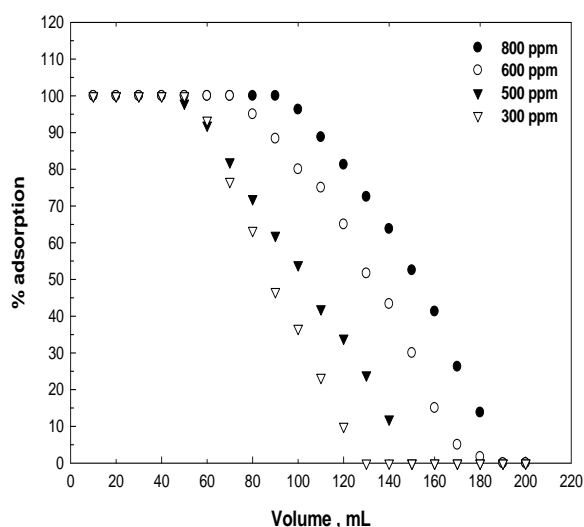


Fig-4 Dependence of uranium anion uptake on the initial concentrations of metal ions. (bedthickness 14 cm, Flow rate 1 ml/min, pH 1.75 at 25 °C)

3.4. Effect of Contact Time

The fact that the section area of the column is uniform implies that the flow rate through the bed, uranyl sulphate anion, is directly proportional to the overall volumetric flow rate through the packed bed. To examine the effect of the flow rate through the bed depth, the initial solute concentration and bed depth were kept constant ($C_0=600 \text{ mg l}^{-1}$, $Z = 14 \text{ cm}$) while the flow rate varied from 0.5 to 2 ml min^{-1} . Results are given in Figure 5 and show that the uptake of metal ions onto the resin decreases when the flow rate through the bed increases. An increase in the flow rate reduces the volume treated efficiently until breakthrough point and therefore decreases the service time of the bed. This is due to the decrease in contact time between the metal ions and the resin at higher flow rates. As the adsorption rate is controlled by intra-particulate diffusion, an early breakthrough occurs leading to a low bed adsorption capacity (Table 2). These results are also in agreement with those referred to the literatures [35, 36]. When the flow rate decreases the contact time in the column is longer, intra-particulate diffusion then becomes effective. Thus the metallic ions have more time to diffuse amidst the particles

of resin bed and a better adsorption capacity is obtained (Table 2). At a higher flow rate, the resin gets saturated early, certainly because of a reduced contact time, a larger amount of ions adsorbed on the resin and a weak distribution of the liquid into the column, which uranium to a lower diffusivity of the solute amidst the particles of the resin[37]. This shows an increase in the uptake of the metallic ions due to the intra-particulate phenomena. Therefore the volume treated, the breakthrough time and the bed adsorption capacity were reduced and a wide volume of solution is purified with an efficient elimination. As can be seen inTable (2), 230 ml of solution were treated at a low flow rate of 0.5 ml min^{-1} while 160 ml were treated at a high flow rate of 3 ml min^{-1} .

Table 2 Fixed bed column adsorption parameters of the sorption of uranium anion at different flow rates. (Conc. 600 ppm, bedthickness 14 cm, pH 1.75 at ambient temperature)

Flow rate (ml min^{-1})	Treated volume V (ml)	Breakthrough point T(min)
0.5	230	200
1.0	200	70
2.0	190	25
3.0	160	10

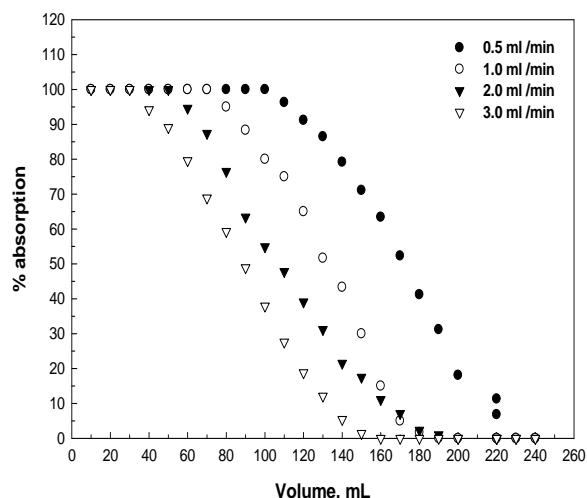


Fig 5 Effect of the flow rate on the sorption of uranium anion ($C_0 = 600 \text{ mg L}^{-1}$). (conc.= 600 ppm, bedthickness 14 cm, pH 1.75 at 25 °C)

3.5. Effect of Bed Depth

The breakthrough curves obtained for uranyl sulphate anions adsorption are illustrated in Figure(6). For different bed depth of Amberlite IRA-402Cl (6, 10, and 14 cm), at a constant flow rate of 1ml min^{-1} . They follow the characteristic "S" shape profile produced in ideal adsorption systems. Results indicate that the breakthrough volume varies with bed depth. This displacement of the front of adsorption with the increase in depth can be explained by mass transfer phenomena that take place in this process. When the bed depth is reduced, axial dispersion phenomena predominate in the mass transfer and reduce the diffusion of

metallic ions. The solute (metallic ions) has not enough time to diffuse into the whole of the adsorbent mass. Consequently an important reduction in the volume of solution treated at the breakthrough point is observed when the bed depth in the column decreases from 14 to 6 cm (Fig.6).

Moreover, an increase in the bed adsorption capacity is noticed at the breakthrough point with the increase in bed depth (Table 3). This increase in the adsorption capacity with that in the bed depth can be due to the increase in the specific surface of the adsorbent which supplies more fixation binding sites. Then it follows that a delayed breakthrough of uranium to an increase in the volume of solution treated.

The increase in adsorption with that in bed depth was due to the increase in adsorbent doses in larger beds which provide greater service area (or adsorption sites). Studies of experimental conditions (i.e. flow rate, bed depth and inlet solute concentration) on the fixation of the metal ions show that the breakthrough time (t_b) depends on depth, flow rate and concentration. The breakthrough time also increased with the height of the bed. Breakthrough time is therefore the determining parameter of the process. The larger it is, the better the intra-particulate phenomena and the bed adsorption capacity are.

Table 3 Adsorption breakthrough data for mini-column scale for the sorption of uranium anion on different bed depth columns. (Conc. 600 ppm, Flow rate 1 ml/min, pH 1.75 at ambient temperature)

Bed depth Z (cm)	Adsorbent mass (g)	Treated volume V (ml)	Breakthrough point T (min)
6	4	180	40
10	6.66	200	70
14	9.33	280	110

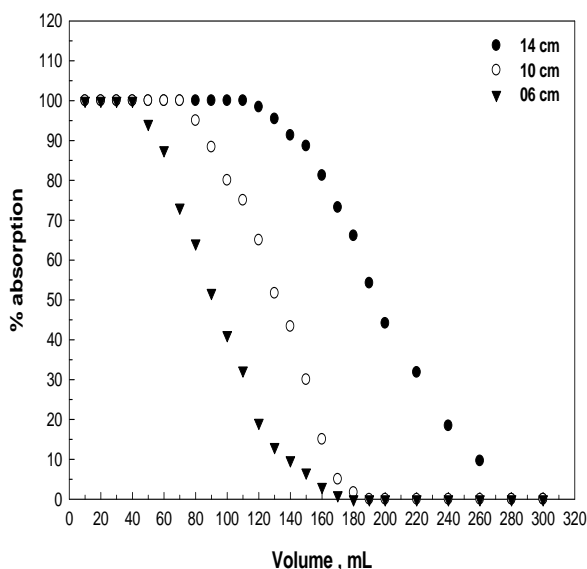


Fig 6 Adsorption breakthrough data for mini-column scale for the sorption of uranium anion on different bed depth columns (conc. 600 ppm, Flow rate 1 ml/min, pH 1.75 at 25 °C)

3.6. Elution Process

Uranium was sorbed on an anion exchange resin bed from sulfate ore leach liquor; the bed was washed with concentrated sodium chloride solution to remove the sulfate, and the uranium was then eluted with water. Elution was carried out with concentrated sodium chloride solutions that offered the advantage of recycling the eluate to the industrial circuit. chloride has an adverse effect on adsorption and, therefore, is an effective eluting agent. The use of diluted industrial effluent as eluant was also assessed. Figure 7. shows the elution curve with laboratory chloride solutions for a retention time of 20 min. Fast reaction is desired for elution process, with the least possible volume of eluate. Observing the plots one can see that chloride elution is best accomplished with concentration of 2 M which provided the sharpest elution curve. It was able to extract 99% of the uranium by using around 80 ml of solution. The average uranium concentration in this eluate was 6000 ppm. The other eluants were not so efficient, presenting a slower elution rate with a long “tailing-off” period required before elution is completed.

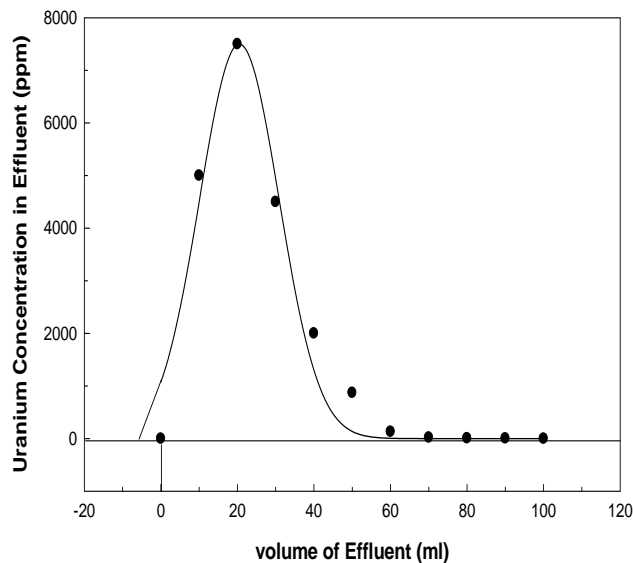


Fig 7 Elution curve of uranium loaded Amb-IRA 402 resin using 2 M sodium chloride at contact time of 10 min

4. PRESENT STATUS , RECOMMENDATIONS, OPTIMUM CONDITIONS, MASS-DIGRAM AND FUTURE PROPOSED COLUMN UNIT CONSTRUCTION

4.1 Present Status

The produced RE concentrate from semi industrial units may contaminated with few hundreds of uranium ppm.s which may retard the after ward individual rare earth

elements separation and commercialization process. As a matter of fact ,there are many attempts to clarify the group of REEs concentrate , one of them was tried through the present work.

4.2 Recommendation and Optimum Conditions

A clear anionic exchange resin REEs decontamination process is recommended for complete uranium separation from REEs cake . The best experimental extraction condition to obtain the aforementioned recovery and purity percents fo uranium of REEs group were indicated in table (4).

Table 4. The experimental extraction condition for uranium and REEs group

Experimental parameter	Condition status
First opening monazite	Conc.H ₂ SO ₄ (W/V) (acid / ore ratio) 1:1.6
Dissolution	ice water 1:20
Precipitation rare earth	NH ₄ OH (1:1)

elements	
Caustification	10% excess of 18% NaOH
Second opening RE ₂ O ₃ :-	Conc.H ₂ SO ₄ (W/V) (acid / ore ratio) 1:3
Adjustable pH	1.75
Resin type	Amberlite IRA 402 Cl form
Flow rate	1 ml/ 1 min
Eluting solution	2 M NaCl
Washing solution	distilled water

4.3 Mass Digram and Proposed Future Column Unit Construction

Partially balanced flow diagram was illustrated in figure (8),From which one can conclude that ,uranium free REEs concentrate can be obtained with 99% recovery ,in addition toall uranium strating content with more than 99% recovery which in turn means more than 99% percent of purity of REEs cake i.e nearly free from uranium representing the main target .

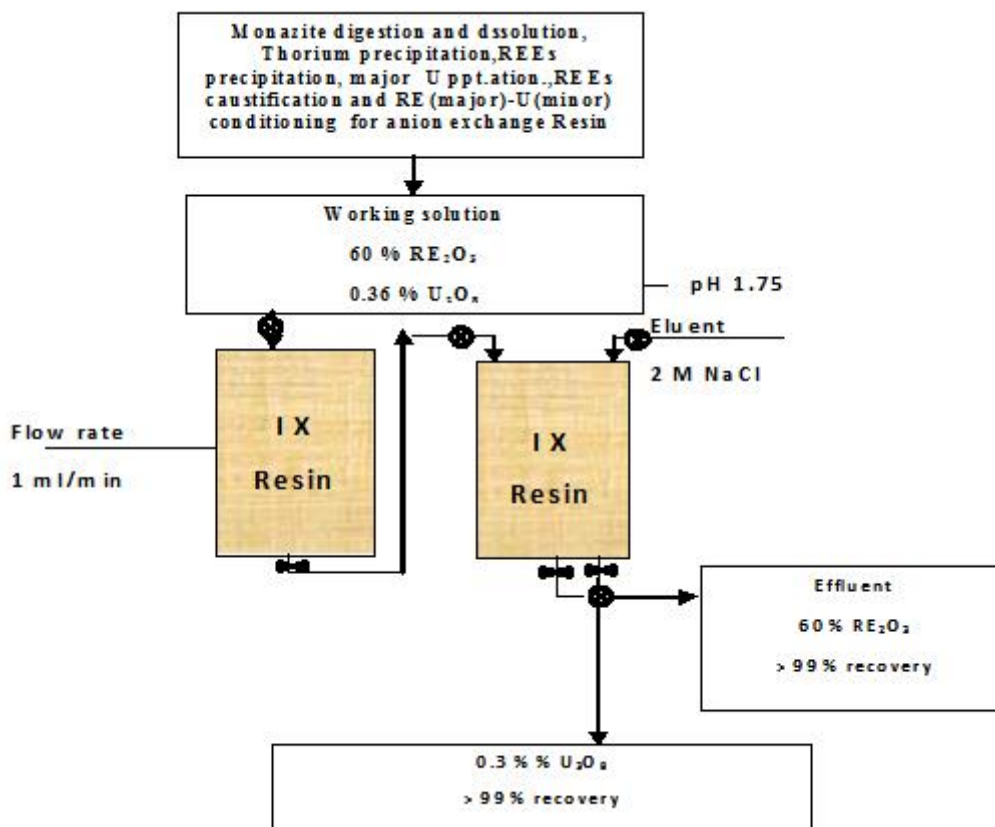


Fig 8 Partially mass-balance , flow digram and REEs decontamination from U unit (uranium removal).

5. CONCLUSIONS

Adsorption of uranium ions through Amberlite IRA-402Cl resin in a packed bed column is an clean economic feasible technique for removing metal ions from a solution. The process allows treatment of a given volume of effluent by

using a minimal mass of adsorbent which concentrates maximal content of metal. The adsorption breakthrough curves obtained at different flow rates indicate that an increase in flow rate decreases the volume treated until the breakthrough point and therefore decreases the service time of the bed. Lower removal capacities were observed,

probably due to the fact that contact times were insufficient for the adsorption equilibrium to develop between the Amber lite IRA-402-Cl resin and the metal ions. The proper ranges of concentration for the sorption of uranium upon Amber lite IRA-402-Cl is 300-500 ppm, flow rate 1ml/min, bed height 16 cm or more.

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