

## Characteristics of uranium recovery from phosphoric acid by an aminophosphonic resin and application to wet process phosphoric acid

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### ARTICLE INFORMATION



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### ABSTRACT

The chelating aminomethylphosphonic resin Amberlite IRC747 is used for uranium recovery from a synthetic phosphoric acid solution. The operating conditions of uranium extraction have been experimentally optimized by the batch technique *viz.*, the phosphoric acid concentration, the contact time, the initial uranium concentration and the temperature. The effect of some interfering ions upon the effective capacity of the resin has also been examined. It has thus been found that the maximum uranium adsorption capacity of the studied chelating resin was found to attain 86.5 mg/g at 5 M phosphoric acid using 0.1 g resin for 120 min contact time with 50 mL acid assaying 200 mg U/L and room temperature. The obtained equilibrium data agreed well with the Langmuir isotherm model and the relevant thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) were evaluated and the uranium adsorption was found to be an endothermic reaction and of spontaneous nature. From the kinetic experiments it was shown that U(VI) adsorption followed the pseudo-second order kinetics model and the intraparticle diffusion model. Also, it has been possible to reveal from the kinetic and isotherm data the chemisorption nature of uranium on the Amberlite IRC747 resin. The adsorbed uranium ions can almost be completely eluted with 0.8 M  $(\text{NH}_4)_2\text{CO}_3$  solution from the loaded resin at room temperature. The studied optimized conditions have successfully been applied for uranium recovery from Abu Zaabal wet process phosphoric acid (WPPA).

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### 1. Introduction

Phosphate rock contains a small amount of uranium depending on its type and origin. Because of the huge reserves and the large quantities that are annually mined, phosphate rock is considered a promising secondary source of uranium. The phosphate reserves in Egypt are assumed to be in the order of 700 million ton that would contain up to 40,000 ton of uranium at an average concentration of 60 ppm [1]. Most of the uranium contained in the phosphate rock is dissolved during its wet decomposition with the mixed acid solution composed of sulfuric acid and the recycled phosphoric acid (assaying 5%  $\text{P}_2\text{O}_5$ ) to produce the wet process phosphoric acid (WPPA) and a calcium sulfate waste as a byproduct. On the other hand, it is known that the tetravalent uranium ions tend to be co-precipitated or captured with calcium sulfate more readily than are the hexavalent uranium ions; a matter which leads to the fact that the major part of uranium passes into solution (about 80-90%) and the rest precipitates in the phosphogypsum [2].

Several techniques have been developed to separate and recover uranium ions from wet process phosphoric acid including chemical precipitation [3], emulsion liquid membrane [4-8], liquid-liquid extraction [9-24] and solid phase extraction. The conventional extraction methods *viz.*,

solvent extraction or precipitation and emulsion liquid membrane are not completely satisfactory because these processes have several disadvantages like finite aqueous solubility of extractants and dilutions. Solid phase extraction has been a basic and powerful method of concentrating desired metal ions. This technique has been proved to be more advantageous in view of their total insolubility in aqueous phase, low rate of physical degradation, high sorption capacity for metal ions, low organic solvent inventory and good flexibility in working conditions. Consequently, several low cost alternatives have been studied for uranium adsorption from crude phosphoric acid including a commercial ceramic sample as a costless non-conventional adsorbent. The adsorption of uranium from Egyptian crude phosphoric acid was achieved after the surface treatment of the activated carbon with nitric acid; a matter which has significantly increased the uranium adsorption capacity from acidic solutions [25]. On the other hand the adsorption of uranium(VI) from both synthetic and Egyptian phosphoric acid onto di-ethyl hexyl phosphoric acid impregnated carbon had been obtained using a batch adsorber [26].

Recently, many works have been reported for uranium extraction using the organic extractant imprinted with an inert polymeric support like polystyrene [27-30]. Also, uranium sorption from phosphoric acid solutions using a series of

polymeric resin beads impregnated with the synergistic combination D<sub>2</sub>EHPA/TOPO at various mole ratios was studied whereas the macroporous polystyrene-divinyl benzene copolymer containing aminophosphonic functional groups (Duolite DES 467) was separately applied [31-33]. These studies have actually received considerable attention due to resins suitability to field conditions and reusability. As a matter of fact, ion-exchange resins with chelating functional groups have been applied for uranium(IV) adsorption e.g. the removal of uranium(VI) from an acetate medium was investigated using Lewatit TP260 (weakly acidic, macroporous type ion exchange resin with chelating aminomethyl phosphonic functional groups) in batch system [34]. On the other hand, experimental measurements have been made on the batch extraction of uranium from phosphoric acid solutions using various chelating ion-exchange resins (RSPO, Diaion-CRP200, Diphonix, Puro-lite S940, Duolite DES467, and Lewatit OC 1060) [35]. Pre-concentration and separation of uranium(VI) from acidic solutions by using a solid phase extractor, Tulsion CH-90 resin which contains imminodiacetic acid functional groups has also been developed [36]. In the meantime, it was possible to recover uranium from pregnant liquor solutions that comprise high levels of chloride ions by passing over the Amberlite IRC747 chelating resin containing amino phosphonic functional groups [37]. The Amberlite™ IRC747 and the Duolite™ C467 resins have actually been used for uranium recovery from phosphoric acid [38]. The resin Puro-lite S940 that contains aminomethylphosphonic acid as functional groups is used as an ion exchange membrane and has been applied to separate uranium from a synthetic phosphoric acid solution [39].

Summing up, a method for uranium recovery from wet process phosphoric acid would be quite beneficial to the phosphoric acid and uranium industries as a result of the inherent safety, capital and operating cost advantages. The present study is mainly concerned with uranium recovery from a synthetic phosphoric acid solution using the Amberlite IRC747 chelating resin, which has aminophosphonic functionalized groups. To realize the objective of this study, the parameters that influence the uranium extraction process are investigated. These include the phosphoric acid concentration, the contact time, the initial uranium concentration, the temperature as well as the effects of the interfering ions. In addition, the equilibrium isotherms, the kinetics models, the diffusion characteristics and the thermodynamics parameters have also been evaluated from the ion exchange measurements. The obtained optimized conditions have then been applied to recover uranium ions from Abu Zaabal wet process phosphoric acid (WPPA).

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Resin characteristics

The working Amberlite IRC747 resin is an amino phosphonic chelating resin of macroporous (macroreticular) structure and in which its polystyrenic matrix is crosslinked with divinyl benzene (DVB). This resin is supplied by Rohm & Haas Company, which is a wholly owned subsidiary of the Dow Chemical Company. Chemically, the aminophosphonic functional groups would form complexes with several metal ions. Besides having excellent regeneration efficiency, the large fixed porosity of the resin bead structure would actually permit an adequately high adsorptive capacity for large molecules. In the meantime, the macroreticular structure of the Amberlite IRC747 resin offers unusually good resistance to organic fouling. The overall properties of this resin are summarized in Table 1. Prior to application, the resin is first activated through its immersion in 1 mol/L H<sub>3</sub>PO<sub>4</sub> for 24 h

followed by washing several times by deionized water to remove all the phosphate component before drying at 45 °C.

**Table 1.** The overall properties of Amberlite IRC747 macroporous aminophosphonic chelating resin.

Characteristic	Value
Matrix	Styrene divinylbenzene copolymer
Functional groups	-CH <sub>2</sub> -NH-CH <sub>2</sub> -PO <sub>3</sub> Na <sub>2</sub>
Physical form	Beige beads
Total exchange capacity	1.75 eq/L (Na <sup>+</sup> form)
Moisture holding capacity	64 to 69% (Na <sup>+</sup> form)
Specific gravity	1.10 to 1.14 (Na <sup>+</sup> form)
Shipping weight	755 g/L
Harmonic mean size	0.520-0.660 mm
Uniformity coefficient	1.8
Fine contents	< 0.300 mm : 2.0% max
Coarse beads	> 1.000 mm : 5.0% max
Maximum reversible swelling	H <sup>+</sup> → Na <sup>+</sup> : 45%
Maximum operating temperature	80 °C
Regeneration	HCl (1 N to 2 N)
Conversion to Na <sup>+</sup> form	NaOH (1 N to 2 N)

#### 2.1.2. Preparation of the working standard solutions

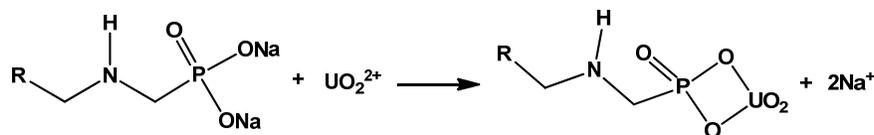
A standard stock solution of 1000 mg/L uranium(VI) has been prepared by dissolving 2.1098 g of uranyl nitrate hexahydrate (Sigma-Aldrich) in 1000 mL distilled water. Also, several standard stock solutions of some interfering ions have been prepared by dissolving suitable weights of their salts in 1000 mL distilled water. Analar grade phosphoric acid (85% H<sub>3</sub>PO<sub>4</sub>, specific gravity 1.68, supplied from Merck, Germany) was used to prepare the required acid stock solutions. The different working synthetic H<sub>3</sub>PO<sub>4</sub> acid solutions were prepared by mixing with proper volumes of the prepared uranium or interfering ions stock solutions.

#### 2.1.3. Preparation of Abu Zaabal WPPA

An adequate volume of an industrial phosphoric acid product as a case study has been kindly supplied from Abu Zaabal Fertilizers and Chemicals Co., Cairo, Egypt. Its chemical composition before dilution was determined by the inductively coupled plasma optical emission spectrophotometer. From this analysis, it was shown that its assay of P<sub>2</sub>O<sub>5</sub>, uranium and total iron, aluminum, sodium, potassium and sulfate ions attain up to 44.0%, 55.0 mg/L, 23.0, 6.0, 2.0, 0.7 and 15 g/L, respectively. Therefore, it was found convenient to dilute it down to 28% P<sub>2</sub>O<sub>5</sub> (5 M H<sub>3</sub>PO<sub>4</sub>) to represent approximately the composition of the WPPA. Prior to uranium adsorption, this acid was subjected to a pretreatment procedure to obtain the clarified green acid by its filtration through a sand filter column (with internal diameter of 1.5 cm; length 15 cm, filled with sand of particle size 64 mesh) for removal of suspended solids and humic matter that might cause physical problems in the extraction system. This was then followed by treatment with activated carbon for the removal of soluble organic matter.

### 2.2. Adsorption procedures

The relevant factors of uranium adsorption from a synthetic phosphoric acid by the Amberlite IRC747 resin have first been studied using the batch technique to determine their optimum values; namely the acid concentration, the contact time, the initial uranium concentration and the temperature. In these experiments, 50 mL of different synthetic acid concentrations and assaying 200 mg/L uranium were mechanically shaken by stirring at 200 rpm with 0.1 g resin samples into 100 mL conical flasks for a definite period of time at different temperatures. Some of these experiments were achieved in triplicates to establish the accuracy of the procedure. The uranium adsorption percent (E%) from the aqueous phase is calculated from the following relation:



R: Polystyrene divinyl benzene

Scheme 1

$$E\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where,  $C_0$  and  $C_e$  are the initial and equilibrium uranium concentrations (mg/L), respectively. The amount of the uranium uptake  $q_e$  (mg/g) by the resin was calculated by the difference between the equilibrium concentration and the initial concentration using the relation:

$$q_e = (C_0 - C_e) \left[ \frac{V}{m} \right] \quad (2)$$

Here,  $V$  is the volume of solution (L) and  $m$  is the dry resin weight (g). In the meantime, the distribution coefficient ( $K_d$ ) was calculated using the equation (3) where  $V$  is the volume of the aqueous phase (mL); viz:

$$K_d = \frac{C_0 - C_e}{C_0} \times \frac{V}{m} \quad (3)$$

For uranium elution procedure, different reagents were studied for different uranium loaded resin samples. Each experiment was performed by shaking 0.1 g of the latter with 5 mL of each individual eluant at different concentration for a contact time of 90 min at room temperature.

### 2.3. Analytical procedures

Uranium was analyzed in the different working aqueous phases by the Unicam UV2-100 UV/Vis Spectrometer using Arsenazo III at 650 nm against proper standard solutions [40]. The results were sometimes confirmed by the titrimetrically determined against ammonium metavanadate [41].

The inductively coupled plasma-optical emission spectrometer ICP-OES (Prodigy high dispersion ICP, TELEDYNE-Leeman Labs, USA) was used to determine the composition of the applied Abu Zaabal concentrated (44%  $P_2O_5$ ) and diluted (28%  $P_2O_5$ ) crude phosphoric acids using proper standards.

Finally, the concentrations of some metal impurities in the yellow cake product that has been precipitated from eluate of the uranium loaded resin by Abu Zaabal WPPA. For this purpose, the atomic absorption spectrophotometer (AAS 6 vario, Analytical Jena GmbH, Germany) was used.

## 3. Results and discussion

### 3.1. Optimization of uranium adsorption by Amberlite IRC747

#### 3.1.1. Effect of phosphoric acid concentration

The effect of phosphoric acid concentration on uranium adsorption by the working resin was systematically investigated over a concentration range between 1 and 9 M. An initial uranium concentration of 200 mg/L (0.84 mmole/L) in 50 mL acid solution, 0.1 g resin for 180 min contact time at room temperature was all the time used. The resin was allowed to equilibrate by agitation on a mechanical shaker at 200 rpm speed. From the obtained results plotted in Figure 1,

it is shown that by increasing the acid concentration from 1 to 5 M, the uranium adsorption efficiency by the resin is decreased from 96 to 86.1%; a matter which indicates that the maximum adsorption occurs at 1 M acid concentration. The uranium adsorption was further diminished as the acid concentration continued to increase from 5 to 9 M. This behavior can be explained as due uranium elution by the increased acid concentration and in turn the increased hydrogen and phosphate concentration, which are capable of eluting the uranium from the chelating resin in addition to its relatively low partial consumption. Taking into account these results, the following experiments were performed upon 5 M acid (which is equivalent to WPPA concentrations).

According to the Dow process for uranium recovery from phosphoric acid [38], the possible adsorption mechanism for the interaction between the aminophosphonic function groups of Amberlite IRC747 resin and  $UO_2^{2+}$  may be illustrated by Scheme 1.

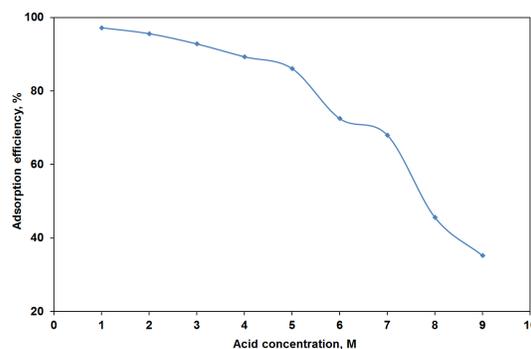


Figure 1. Effect of phosphoric acid concentration upon uranium adsorption efficiency by Amberlite IRC747 resin.

#### 3.1.2. Effect of contact time

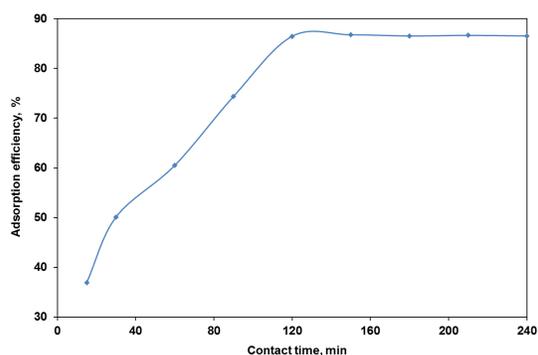
The effect of contact time upon uranium adsorption by 0.1 g Amberlite IRC747 was studied at room temperature between 15 and 240 min using 50 mL of 5 M synthetic phosphoric acid assaying 200 mg/L uranium. From the obtained results shown in Figure 2, it is clearly evident that the time required for the maximum uranium adsorption efficiency of 86.5% i.e. 86.5 mg/g is achieved within 120 min and which remained constant thereafter indicating that the system has attained its equilibrium.

#### 3.1.3. Effect of initial uranium concentration

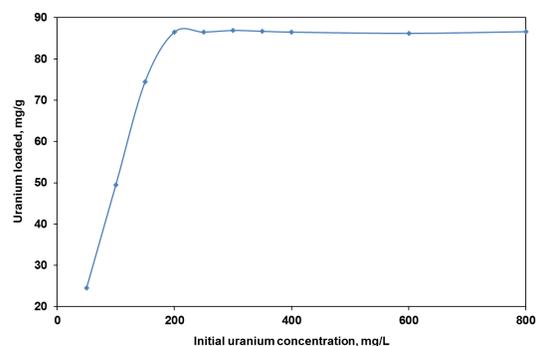
The effect of initial uranium concentration upon its loading capacity by the working resin was investigated by mixing 0.1 g with different 50 mL samples of 5 M acid solution assaying 50 up to 800 mg U/L for 120 min. at room temperature. The results plotted in Figure 3 reveal that by increasing the initial uranium concentration, the amount of uranium loaded ( $q_e$  in mg/g) upon the working aminophosphonic resin has increased to a maximum loading value of 86.5 mg/g when using the acid solution of initial uranium concentration of 200 mg/L.

Increasing the initial uranium concentration thereafter did not affect the obtained capacity. This result confirms that the maximum uranium loading capacity is 86.5 mg/g of dry resin.

The obtained practical uranium loading capacity has then been compared in accordance with the specifications of the working resin where 1 L of the wet resin weighs 755 g dry resin in a manner that 1 g dry resin is equivalent to 1.32 mL wet resin. Assuming that the total exchange capacity of the working resin equals 1.75 equivalent/L in consideration of its Na<sup>+</sup> form and referring to the suggested mechanism by the Dow Chemical Co.; 2009 [38] as well as the divalent cation chelation shown in Scheme 1, the uranium saturation capacity would be 208.3 g U/L resin. However, the obtained practical capacity has however only attains 65.53 g/L. This difference between the total and practical exchange capacities is indeed due to the presence of high concentration of hydrogen ions whose co-loading leads to the replacement of uranyl ions.



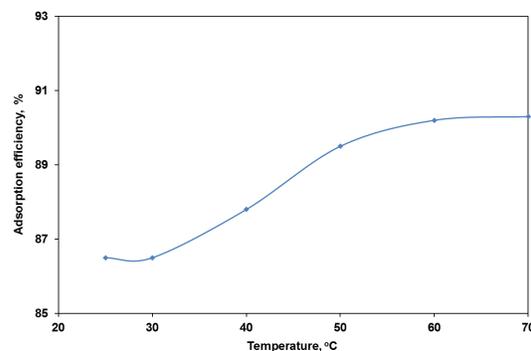
**Figure 2.** Effect of contact time upon uranium adsorption efficiency by Amberlite IRC747 resin.



**Figure 3.** Effect of initial uranium concentration (mg/L) upon its loading capacity by Amberlite IRC747 resin.

### 3.1.4. Effect of temperature

The effect of temperature upon the uranium adsorption efficiency by AmberliteIRC747 from 50 mL of 5 M synthetic phosphoric acid solution assaying 200 mg U/L was studied in the range from 25 to 70 °C while the other parameters were kept constant at 0.1 g resin for a contact time of 120 min. From the obtained results indicate that the uranium adsorption efficiency is only slightly increased to less than 90.3% by increasing the temperature to 70 °C (Figure 4). Accordingly, the efficiency of uranium uptake of 86.5%, equivalent to 86.5 mg uranium per 1 g of resin and which is obtained at room temperature would be considered as the optimum value. In the other words, it can be mentioned that the experimental results indicate that uranium adsorption from 5 M wet process phosphoric acid by Amberlite IRC747 resin can be achieved at any temperature below 70 °C.



**Figure 4.** Effect of temperature upon uranium adsorption efficiency by Amberlite IRC747 resin.

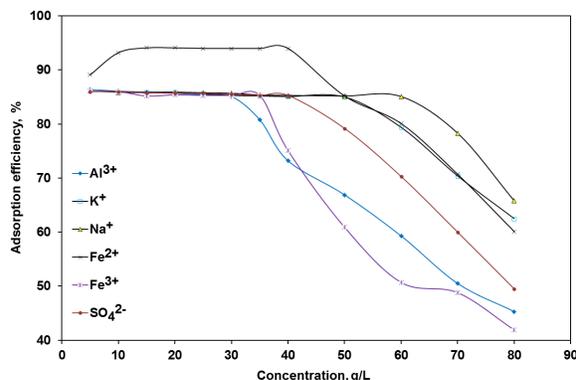
### 3.1.5. Effect of interference from some major ions

The industrial production of wet process phosphoric acid is mainly undertaken by direct mixing the rock phosphate with sulfuric acid and accordingly the resultant acid would contain appreciable amount of several constituents including mainly aluminum, potassium, sodium, ferrous, ferric, sulfate and bisulfate ions after separation of the phosphogypsum. In addition, uranium is present in various forms that might include the neutral ( $\text{UO}_2(\text{SO}_4)_2$ ) and the anionic uranium species ( $\text{UO}_2(\text{SO}_4)_2^{2-}$  and  $\text{UO}_2(\text{SO}_4)_3^{4-}$ ) together with different values of uranium phosphate species. To study the effect of the former components upon uranium extraction efficiency from 5 M synthetic phosphoric acid solutions, a series of experiments were conducted in the individual presence of these ions in a concentration ranging from 5 to 80 g/L. In these experiments, the other factors were kept constant i.e. using 50 mL of 5 M acid assaying 200 mg/L uranium and 0.1 g resin for a contact time of 120 min at room temperature. The obtained results plotted in Figure 5 indicate that  $\text{Al}^{3+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Fe}^{3+}$  did not affect the uranium adsorption efficiency by Amberlite IRC747 resin until their concentration attained 30, 50, 60 and 35 g/L, respectively, and after which the uranium adsorption efficiency has gradually been reduced. On the other hand, while presence of ferrous ions could reduce the hexavalent uranium to its tetravalent state, however, the adsorption of the latter by the studied resin which was found to exceed about 94% and has not been affected until an assay of 40 g/L of  $\text{Fe}^{2+}$ . Similarly, the influence of sulfate anions upon the uranium adsorption is absent below 40 g/L. Due to the high concentration of phosphoric acid (5 M), the interfering metal ions are forming complexes with phosphate ions. However, an excess of the sulfate ions thereafter would lead to uranium elution due the co-presence of bisulfate ions. It is interesting to mention herein that the studied concentration limits of tolerance of these ions are indeed greater than their assay in the Egyptian wet process phosphoric acid produced by Abu Zaabal Fertilizers and Chemicals Co.

## 3.2. Application of the physical parameters

### 3.2.1. Sorption isotherm modeling

The specific relation between the uranium adsorbed amount and its equilibrium concentration in the aqueous phase at the given experimental conditions of using 0.1 g of the aminophosphonic resin versus uranium concentration in 50 mL for 120 min contact time at room temperature was used to quantify the resin adsorption capacity. For this purpose, the two most commonly used isotherms, namely Freundlich and Langmuir have been adopted [42,43].



**Figure 5.** Effect of interfering ions upon uranium adsorption efficiency by Amberlite IRC747 resin.

The Langmuir model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface and that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm model is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{b \cdot q_0} \quad (4)$$

where  $C_e$  is the equilibrium concentration (mg/L) in solution,  $q_e$  the uranium uptake capacity (mg/g) of the resin at equilibrium while  $q_0$  and  $b$  are related to the maximum adsorption capacity (mg/g) and the constant of the adsorption equilibrium (L/mg), respectively. The linear plot of  $C_e/q_e$  versus  $C_e$  in Figure 6 shows that the correlation coefficient for the linear regression fits of the Langmuir plot was found to be 0.999. Also, the  $q_0$  and  $b$  obtained from the Langmuir plot were found to be 92.59 mg/g and 0.324 L/mg, respectively. Therefore, it can be concluded that the working adsorption system obeys Langmuir adsorption model. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter [44] as  $R_L$  which is given by the following equation; namely,

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (5)$$

where  $C_0$  is the initial uranium(VI) concentration (mg/L) and  $b$  is the Langmuir adsorption constant (L/mg). Table 2 tabulates the calculated values of the  $R_L$  for uranium (VI) concentration ranging from 50 to 800 mg/L. The  $R_L$  values observed are found in the range of  $0 < R_L < 1$ , which indicates that the adsorption of uranium(VI) onto Amerlite IRC747 resin is favorable.

**Table 2.** Calculated values of the equilibrium parameter,  $R_L$  of Langmuir equation.

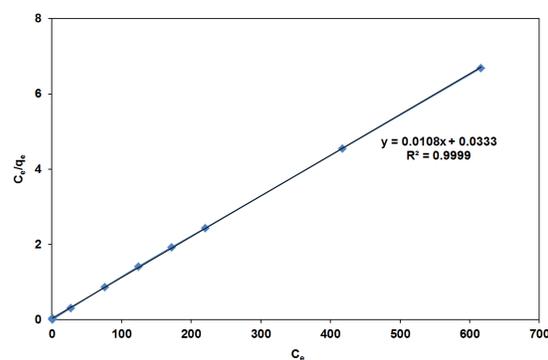
U (VI), mg/L	$R_L$
50	0.060
100	0.030
200	0.015
400	0.008
600	0.005
800	0.004

The Freundlich equation was also applied for the adsorption of uranium onto the working resin. This equation is basically empirical but is often useful as a means of data description. It generally agrees quite well as compared to

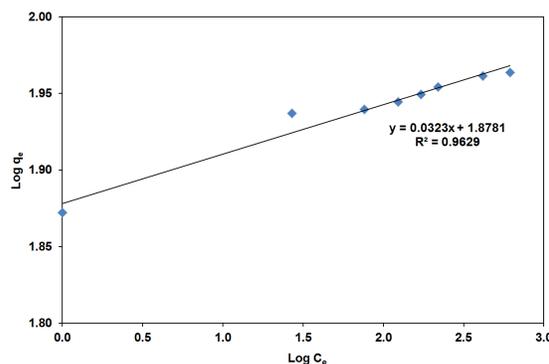
Langmuir equation and with the experimental data over a moderate range of adsorbate concentrations. The Freundlich isotherm is represented by the following equation:

$$\text{Log} q_e = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad (6)$$

where  $C_e$  is the equilibrium concentration (mg/L) and  $q_e$  is the amount of uranium adsorbed per unit mass of resin while  $K_f$  and  $n$  are the Freundlich constants which represent the adsorption capacity (mg/g) and the adsorption intensity respectively. Both  $K_f$  and  $n$  are determined from a linear plot of  $\text{Log} q_e$  against  $\text{Log} C_e$  (Figure 7). From the obtained results, the constants  $K_f$  and  $1/n$  were found to be 75.526 mg/g and 0.323, respectively. The value of  $n$  has also shown a favorable adsorption of uranium(VI) onto Amberlite IRC747 resin due to the  $n$  value is in between 1 and 10. The correlation coefficient for the Freundlich plot was found to be 0.963 indicating that the experimental data are better fitting to Langmuir equation.



**Figure 6.** Langmuir isotherm of U(VI) sorption upon Amberlite IRC747 resin.



**Figure 7.** Freundlich isotherm of U(VI) sorption upon Amberlite IRC747 resin.

### 3.2.2. Sorption kinetics

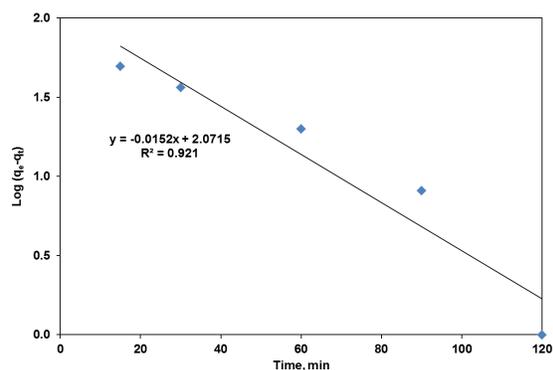
The kinetics of adsorption describes the rate of uranium ions uptake onto the working Amberlite IRC747 resin and this rate control the equilibrium time. The kinetics of adsorbate uptake is required for selecting optimum operating conditions for the batch technique. The kinetic parameter, which is helpful for the prediction of the adsorption rate, gives important information for designing and modeling the processes. The mechanism of U(VI) adsorption upon Amberlite IRC747 resin and the rate constants of the sorption process were determined by using both the pseudo-first order and the pseudo-second order kinetic models [45,46]. The pseudo-first order kinetic model is represented by the following equation:

**Table 3.** Kinetic parameters of uranium sorption upon Amberlite IRC747 resin.

Practical capacity $q_e$ (mg/g)	Pseudo-first order			Pseudo-second order		
	$q_e$ (mg/g)	$K_1$	$r^2$	$q_e$ (mg/g)	$K_2$	$r^2$
86.5	117.89	0.035	0.921	86.95	0.000417	0.993

$$\text{Log}(q_e - q_t) = \text{Log}q_e - \left(\frac{K_1}{2.303}\right)t \quad (7)$$

where  $K_1$  ( $\text{min}^{-1}$ ) is the rate constant of pseudo-first order adsorption,  $q_e$  is the amount of metal adsorbed at equilibrium and  $q_t$  is the amount adsorbed at time ( $t$ ). Plotting  $\text{Log}(q_e - q_t)$  against ( $t$ ) gives a straight line as shown in Figure 8, which would provide the first-order adsorption rate constant ( $K_1$ ) and the  $q_e$  value from its slope and its intercept, respectively, and which have suggested the applicability of the pseudo-first order kinetics model to fit the practical data as given in Table 3. The calculated value of the adsorption capacity ( $q_e$ ) was thus found to attain 117.89 mg/g and which is higher than the practically determined capacity of 86.5 mg/g. Therefore, this data show that the first order kinetic model is not in agreement with experimental data and is therefore is not suitable for the studied system.

**Figure 8.** Pseudo-first order kinetics of uranium sorption upon Amberlite IRC747 resin.

On the other hand, the pseudo-second order kinetic model is represented by the following equation [47]:

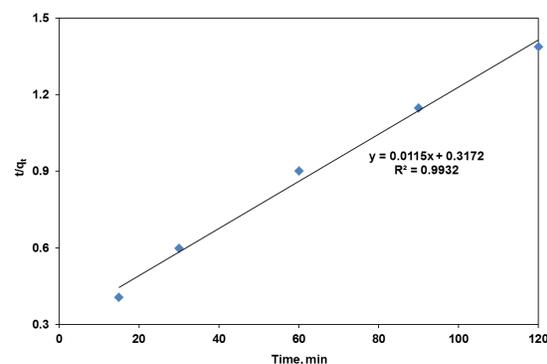
$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \left(\frac{1}{q_e}\right)t \quad (8)$$

where  $K_2$  is the rate constant of the pseudo-second order adsorption ( $\text{g}/\text{mg}\cdot\text{min}$ ). The pseudo-second order model considers the rate-limiting step as the formation chemisorptive bond involving sharing or exchange of electrons between adsorbate and the adsorbent. The straight line of the plot of  $t/q_t$  against  $t$  is thus tested to obtain the rate parameter (Figure 9, Table 3). From the obtained data, it is clear that there is a good agreement between the experimental results and the calculated values. An analysis of the data in Table 3 indicates that the adsorption kinetics of U(VI) can be explained more accurately by the pseudo-second order kinetic model where the value of the correlation coefficient is 0.993 while the calculated value of the adsorption capacity of 86.95 mg/g is quite close to the practically determined capacity of 86.5 mg/g. Therefore, it could be suggested that adsorption behavior of U(VI) onto the chelating Amberlite IRC 747 resin obeys the pseudo-second order kinetic model.

### 3.3. Diffusion characteristics

In order to adequately interpret the obtained data, the adsorption onto ion exchange resins must be considered as a

liquid-solid phase reaction. The rate of ion adsorption at a solid/liquid interface may be controlled via one or more of the following steps [48]: (a) outer-sphere diffusion of the metal ions from the bulk solution to the film surrounding the particle (bulk diffusion); (b) inner-sphere diffusion of the metal ion to the external surface of the adsorbent (external diffusion); (c) intraparticle diffusion (pore diffusion); and (d) interaction between the metal ions and the active sites of adsorbent which can involve several mechanisms including physiochemical adsorption, ion exchange, or complexation. The adsorption rate is indeed affected by the agitation speed for systems controlled by bulk and external diffusion. Increasing the agitation speed increases turbulence in the solution, which in turn reduces the thickness of the external boundary layer and also ignores bulk diffusion [49].

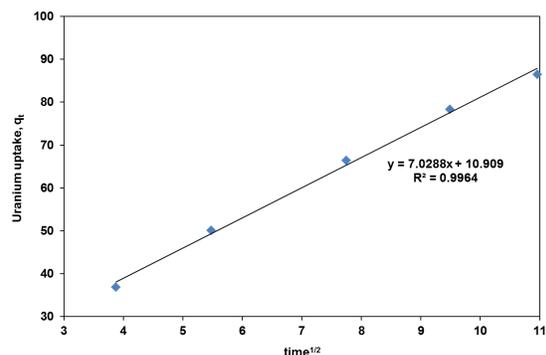
**Figure 9.** Pseudo-second order kinetics of uranium sorption upon Amberlite IRC747 resin.

To investigate the possibility of intraparticle diffusion as the rate controlling step on the adsorption of uranium(VI) from 50 mL of 5 M phosphoric acid solution assaying 200 mg/L initial uranium concentration onto the working chelating Amberlite IRC747 resin as a function of the square root of the contact time ( $t^{1/2}$ ) at room temperature, Weber and Morris [50] equation has been applied. The latter points out that a functional relationship common to the majority of intraparticle diffusion treatment is that the uptake varies almost proportionately with the square root of the contact time by this equation; viz:

$$q_t = K_{id} \cdot t^{1/2} + I \quad (9)$$

where,  $q_t$  is the amount of adsorbed uranium(VI) at time  $t$ ,  $K_{id}$  ( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$ ) is the rate constant of intraparticle diffusion and  $I$  is thickness of the boundary layer. The intraparticle diffusion rate constant was determined from the slope of the linear gradients of the plot  $q_t$  versus  $t^{1/2}$  (Figure 10). From the latter, it was found that the value of the correlation coefficient is 0.9964 while that of the rate constant of intraparticle diffusion is  $7.0388 \text{ mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$  and the thickness of the boundary layer is 10.909. The value of the intercept  $I$  would provide information about the thickness of boundary layer i.e. the larger the intercept, the larger is the boundary layer effect. From the obtained data, it was shown that the obtained straight line and the positive value of  $I$  indicate that the uranium adsorption rate upon the resin is controlled by the intraparticle diffusion and the boundary layer. In other words, the uranium ions are most probably transported from the bulk of the solution into the solid phase by intraparticle diffusion,

which is often the rate limiting step in many sorption processes.



**Figure 10.** Intraparticle diffusion plot of the uranium sorption upon Amberlite IRC747 resin.

### 3.4. Sorption thermodynamics

To study the sorption thermodynamic parameters, series of experiments for uranium adsorption from a synthetic phosphoric acid solution (5 M) and assaying of 200 mg U/L upon the studied resin have been carried out at various temperatures ranging from 298 to 333 K under the previously determined optimum conditions of 50 mL acid solution, 0.1 g resin for 120 min contact time. The thermodynamic parameters including the Gibbs free energy  $\Delta G$  (kJ/mol), the enthalpy  $\Delta H$  (kJ/mol) and the entropy  $\Delta S$  (J/mol.K) were calculated for this system using the following Van't Hoff equations:

$$\Delta G = -2.303.R.T.\text{Log } K_d \quad (10)$$

$$\Delta G = \Delta H - T.\Delta S \quad (11)$$

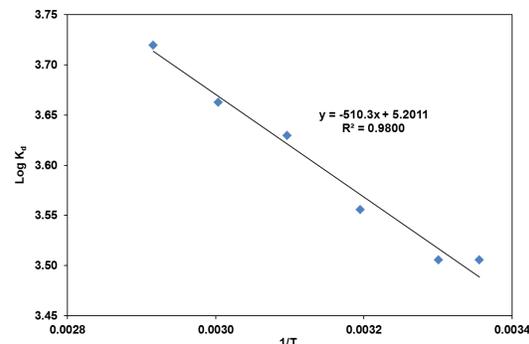
$$\text{Log } K_d = \frac{\Delta S}{2.303.R} - \frac{\Delta H}{2.303.R.T} \quad (12)$$

where  $K_d$  is the distribution coefficient (mL/g),  $R$  is the universal gas constant (8.314 J/mol.K) and  $T$  is temperature (K). Accordingly, the values of both the enthalpy  $\Delta H$  and the entropy  $\Delta S$  were calculated from the slope ( $-\Delta H/R$ ) and intercept ( $\Delta S/R$ ) of the  $\text{Log } K_d$  vs  $1/T$  plot (Figure 11). The obtained values of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for uranium sorption in the study system are reported in Table 4. It has to be mentioned in this regard that the obtained negative value of Gibbs free energy confirms the feasibility and the spontaneous nature of the uranium sorption from the aqueous phase upon the working resin. With increase in temperature,  $\Delta G$  becomes more negative indicating that more efficient adsorption would occur at the studied higher temperature indicating that uranium ions are more readily dehydrated and hence their adsorption would become more favorable. On the other hand, the positive value of  $\Delta H$  reflects the endothermic nature of adsorption while the positive value of entropy  $\Delta S$  suggests an increase in randomness at the solid/liquid interface during the adsorption process as well as it favors the stability of the sorbed complex via covalent interaction type chemisorption. The main source of this entropy gain may be due to the destruction of the hydration shell of uranium ions in the liquid phase to a large extent, a matter which would result in direct interaction of uranium(VI)-functional group complex [51].

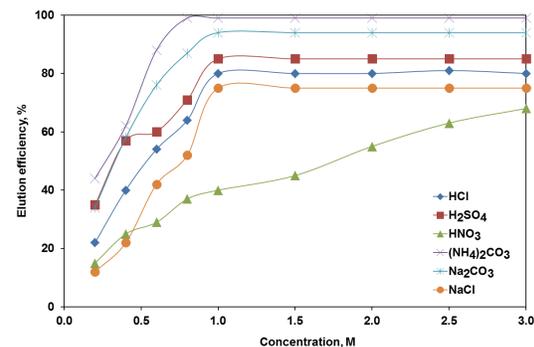
### 3.5. Uranium elution

The uranium(VI) desorption from the loaded Amberlite IRC747 has been carried out using various eluting agents

including HCl,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and NaCl in concentrations ranging from 0.2 to 3.0 M. In these experiments the relevant parameters were kept constant using 0.1 g loaded resin, 5 mL volume of the individual eluant solution for 90 min. contact time at ambient temperature. From the obtained results (Figure 12), it was shown that the elution efficiency of uranium(VI) has increased with increasing the concentration of the eluting agents until maximum values attaining 80, 85, 68, 99, 94 and 75% for 1 M HCl, 1 M  $\text{H}_2\text{SO}_4$ , 3 M  $\text{HNO}_3$ , 0.8 M  $(\text{NH}_4)_2\text{CO}_3$ , 1 M  $\text{Na}_2\text{CO}_3$  and 1 M NaCl, respectively. Therefore, it can be concluded that 0.8 M  $(\text{NH}_4)_2\text{CO}_3$  can be used for the almost quantitative desorption of uranium(VI) from the working chelating resin.



**Figure 11.** Plot of  $\text{Log } K_d$  vs  $1/T$  of the uranium(VI) extraction upon Amberlite IRC747 resin.



**Figure 12.** Effect of concentration of different eluting agents on uranium elution efficiency.

### 3.6. Uranium recovery from Abu Zabaal WPPA

From the above mentioned results, it has been shown that the chelating Amberlite IRC747 resin has a uranium adsorption capacity under the studied optimum conditions of 86.5 mg U/g resin. Prior to applying these conditions upon Abu Zabaal crude phosphoric acid (44%  $\text{P}_2\text{O}_5$  and 55 mg/L uranium), it was diluted down to 28%  $\text{P}_2\text{O}_5$  (5 M  $\text{H}_3\text{PO}_4$ ) and 35 mg/L uranium to simulate the WPPA. The recovery of uranium has then been carried out in a batch technique using 20 g resin in 40 L of the clarified diluted phosphoric acid (WPPA) for 120 min contact time in a mechanical shaker (200 rpm) at room temperature. This was then followed by uranium elution using the chosen eluent solution (100 mL of 0.8 M ammonium carbonate) under fixed conditions of 90 min contact time at room temperature where uranium would be converted to an anionic carbonate complex that has no affinity for the chelating resin. The obtained smaller volume of eluate would thus contain uranium in the form of the ammonium uranyl tricarbonate complex.

**Table 4.** Thermodynamic parameters for U(VI) adsorption from 5 M phosphoric acid upon Amberlite IRC747 resin.

$\Delta H$ (KJ/mol)	$\Delta S$ (J/mol K)	$\Delta G$ (KJ/mol)						
		298 K	303 K	308 K	313 K	318 K	323 K	333 K
9.77	99.59	-19.9	-20.4	-20.9	-21.4	-21.9	-22.4	-22.9

The regenerated resin has then been washed with water, or a slightly acidic solution, to remove any entrained ammonia regeneration solution from the resin prior to its recycle into the uranium extraction stage of the continuous ion exchange system. The eluate was then evaporated to decrease its volume and to decompose excess alkali carbonate and from which uranium was precipitated using a solution of 30% H<sub>2</sub>O<sub>2</sub> after neutralization with sulfuric acid and where at pH = 2.6, the uranium precipitation was completed. The obtained pale yellow uranium peroxide (UO<sub>4</sub>.xH<sub>2</sub>O) was filtered, washed and dried and where the weight of the obtained uranium oxide product attained 2 g and whose uranium assay was found to attain 71.2%. The latter was then subjected to some trace impurities using the flame atomic absorption spectrophotometry. These elements included Fe, Al, K, Na and V and were found to assay 100, 70, 15, 120 and 30 mg/L, respectively.

#### 4. Conclusion

In this study, it has been possible to optimize the uranium adsorption conditions from a synthetic phosphoric acid solution upon the chelating aminophosphonic resin Amberlite IRC747. The optimum adsorption conditions, sorption isotherm models, kinetics characteristics models and thermodynamic parameters are determined to apply for uranium recovery from wet process phosphoric acid. The obtained results have indicated that uranium(VI) adsorption is strongly dependent on the phosphoric acid concentration and where a maximum adsorption capacity of 86.5 mg/g resin was obtained from 5 M phosphoric acid which equivalent to wet process phosphoric acid (28% P<sub>2</sub>O<sub>5</sub>, 5 M H<sub>3</sub>PO<sub>4</sub>). This capacity has been obtained when using 120 min contact time for 0.1 g resin in 50 mL of the synthetic solution assaying 200 mg/L uranium at room temperature.

The obtained capacity was found to fit better with Langmuir isotherm and where the adsorption obeyed the pseudo second order reaction. Concerning the effect of the thermodynamic parameters, the obtained negative  $\Delta G$  value confirms the feasibility and the spontaneous nature of the studied sorption process while the positive  $\Delta H$  value reflects the endothermic nature of adsorption whereas the positive  $\Delta S$  value suggests an increase in randomness at the solid/liquid interface during adsorption besides favoring the stability of the sorbed complex via covalent interaction type chemisorption. It was also indicated that the uranium ions are most probably transported from the bulk of solution into the solid phase by intraparticle diffusion, which is often the rate limiting step in many sorption processes.

On the other hand it was found that the adsorbed uranium was found to be almost completely eluted by 0.8 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solution. The obtained optimum conditions of uranium adsorption and elution have successfully been applied for uranium recovery from the industrial Abu Zaabal crude phosphoric acid. In the meantime, a uranium peroxide product assaying 71.2% uranium has been obtained from the obtained eluate.

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