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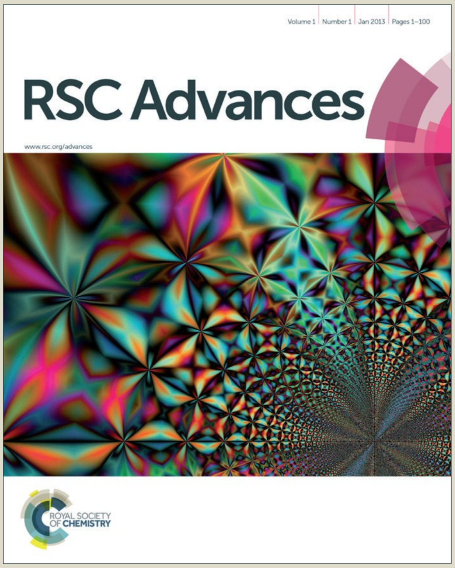

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RECOVERY OF URANIUM, HAFNIUM AND ZIRCONIUM FROM PETROLEUM ASH LEACH LIQUOR

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Abstract

We investigated the optimum adsorption conditions of uranium, hafnium and zirconium elements from petroleum fly ash leach liquor using Dowex 1x8 as a strong basic anion exchange. Uranium was precipitated from acidic solution by adding either NaOH or H_2O_2 solutions at different pH. The remaining concentrate containing hafnium and zirconium was firstly precipitated by using NaOH solution followed by dissolution in HCl solution and individually separated from each other by solvent extraction technique using Alamine 336 extractant. On the other hand, the loaded zirconium was stripped with HCl while hafnium scrubbed by using H_2SO_4 acid.

Keywords: Uranium, Hafnium, Zirconium recovery; Petroleum ash; Dowex 1x8 resin.

Introduction

Coal and petroleum combustion by-products production in *USA* and *EU* is estimated in around 115 million tons per year. A large portion of this production is accounted for the fly ash. Fly ash is rich with inorganic compounds that have great economical value, such as uranium, zirconium and hafnium compounds [1]. Uranium is one of the most used nuclear fuel materials. Hafnium and zirconium compounds have attracted great deal of attentions lately due to their numerous applications [2]. Oxides, carbides and nitrides are well known as structural ceramics due to the high thermal and chemical stability [3]. Elemental zirconium is transparence to thermal neutrons, making it ideal candidate as a structural material in nuclear reactors [4]. Hf has been found to be a good neutrons absorbent, leading to its use as a moderator in control rods in nuclear reactors[5]. Zirconium and hafnium alloys have high corrosion and creep resistance, and therefore they are widely used in extreme environment. Radioisotopes of hafnium have found varied application in biomedical fields that it has been utilized for in vivo and in vitro studies with hafnium-binding to animal proteins [6].

Separation of uranium from ore or from fly ash is a challenge. Also, separation of zirconium and hafnium is also not a trivial task since they are always associated in nature. For nuclear application, the two elements must be separated. [7] In nuclear reactors, zirconium metal should contain less than 100 ppm hafnium. [8] Many methods have been used to separate the two elements to prepare what is known as the nuclear grad compounds. These methods include: fractional crystallization, fractional precipitation, ion exchange, solvent extraction, molten salt distillation and selective reduction. Amongst them, only solvent extraction and molten salt distillation can be used satisfactory in industrial scale. [9] The present work demonstrates an echo-friendly and affordable hydrometallurgical technique to recover hafnium, zirconium, and uranium from petroleum leach liquor. The paper presents detailed separation studies of these elements by utilizing the petroleum ash of an Egyptian Electricity Power Station called El Kriymat as a case study.

Experimental Work

All chemicals used in this study were of analytical reagent grade and used as received. The petroleum ash sample was obtained from the boilers of El Kriymat Electric Power Planets .Before studying the recovery of Hf and Zr from petroleum fly ash leach liquor, [10] a leaching step using sulfate solution was firstly conducted.

The adsorption efficiency of the concerned elements at different pH values was determined in a basket system by equilibration techniques. Sets of leach liquor solutions (20 ml) were set up into bottles. The pH values of such solutions were adjusted in the range of 0.01 - 2 with 5% NaOH solution then 0.5 g of resin samples were individually added into each bottle and shacked for 2 min at room temperature. The precipitation occurs at pH above 2 , since no meaning to complete the adsorption study beyond pH 2.

The analysis of hafnium, zirconium, uranium, vanadium, nickel and iron in both dissolved petroleum ash sample in acid solution as well as in sample leach liquors, or else in the solutions after loading on ion exchange resin, or in the elution and precipitating ones were performed by Inductively Coupled Plasma (Prism *ICP*) High Dispersion (Teledyne Leeman Labs. USA).

Results and Discussion

The analysis of the dissolved elements in the obtained leach liquor solution is presented in table (1), it should be noted that the sulphate content in the leach liquor reached about 3 %, which seem to be high considering the pH of the solution was 0.01.

Table (1): Analysis of petroleum ash sample leach liquor solution

Elements	Conc. (ppm)	Elements	Conc. (ppm)
Hf	171.8	**V**	12010
Zr	558.3	**Ni**	8700
U	62.9	**Fe**	7600
Pb	10.75	**Zn**	2443.2
Cr	391.7	**Cu**	113
Co	140.9	**SO_4^{-2}**	30 g/l

1. Adsorption by Basket System

Conventionally, there are two types of systems to perform U, Hf, Zr, V and Fe adsorption by strong ion exchange resins namely the basket (batch) and column systems. In the first system the concerned elements are extracted from the petroleum ash leach liquor solutions by mixing a certain volume of the leach liquor with certain weight of the ion exchange resin. While in the second system, the leach liquor solution was passed down words through a certain volume of the ion exchange wet settled resin backed in a column which has certain dimensions.

1.1. Effect of Leach Liquor pH on Adsorption Efficiency

From the obtained adsorption data (Fig. 1) one can notice that uranium adsorption efficiency increased with the increase of the pH values while the best results were conducted at pHs from 1.5 to 2. In fact, uranium is existed in the sulphate solutions uranyl ion UO_2^{2+}, as an uncharged complex $UO_2(SO_4)$, as well as the anionic complexes $[UO_2(SO_4)_2]^{2-}$ and $[UO_2(SO_4)_3]^{4-}$ depending on the amount of $(SO_4)^{2-}$ ion in solution can also be adsorbed.

Hydrogen ion concentration plays an important role in uranium adsorption on anion exchange resin that at pH values below 1.5 there are no sufficient SO_4^{2-} ions to furnish the uranium sulfate complexes since HSO_4^- ions are predominant. Moreover, the uranium adsorption from sulfate solution is a function of SO_4^{2-} concentration due to the influence of uranium anion to be formed under equilibrium conditions. Actually, the amount of uranium adsorbed increases when the ratio of $(SO_4)^{2-}/[U]$ is less than 2. Above this ratio, excess SO_4^{2-} competes with the uranium sulfate complex for resin sites, resulting in decreasing uranium adsorption [11].

On the other hand, the data revealed that the adsorption of hafnium and zirconium gives the highest efficiency at pH values between 1 to 1.5. This is in agreement with published data [9]**.** The hafnium and zirconium existe in the sulfate media as $[ZrOSO_4]^{2-}$ and $[HfOSO_4]^{2-}$ [12]**.** Accordingly, the adsorption of hafnium and zirconium ions are inhibited at higher acidity values; this can be attributed to the presence of H^+ ions competing with the hafnium and zirconium ions at the adsorption sites. Interestingly, nickel was not adsorbed on the resin sites while iron and vanadium are adsorbed in values less than 20%, which is much lower than the uranium, hafnium and zirconium contents. Therefore, all the following experiments were performed at pH value about 1.5 in the original feed leach liquor solutions.

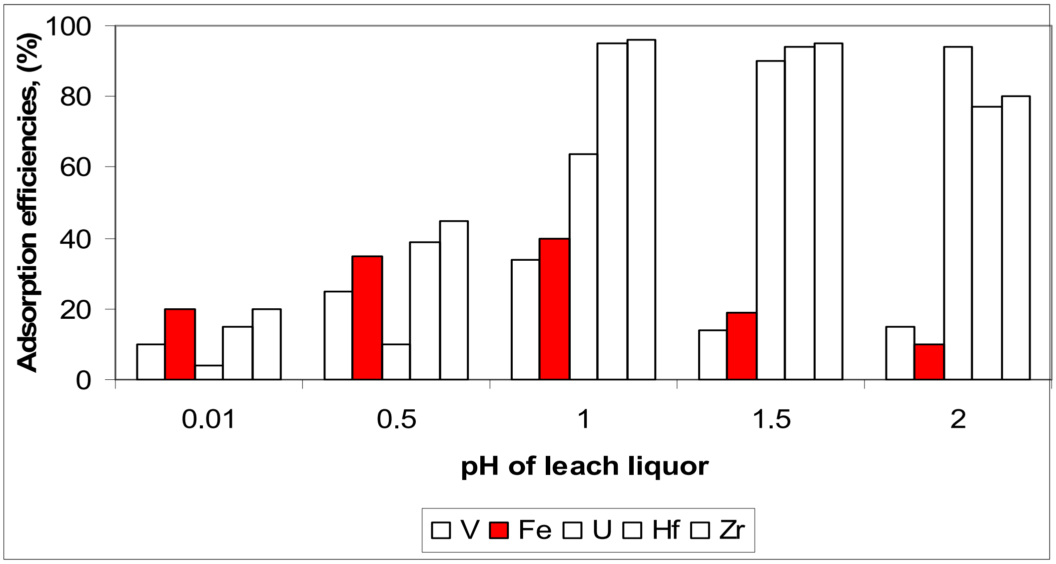


Fig. (1): Effect of pH on adsorption efficiency of the hafnium, zirconium, uranium, vanadium and iron elements onto anion Dowex resin at 1/40 resin/leach liquor ratio with 2 min. stirring time

1.2. Adsorption Kinetics

The study of kinetic models were performed by shaking 50 ml of each leach liquors feed containing about 109, 245 and 929 ppm of uranium, hafnium and zirconium respectively, with 2.0 g of Dowex 1x8 resin for different time at room temperature. The total concentration of hafnium, zirconium, and uranium in the filtered liquor were determined by using *ICP-OES*. The adsorption capacities of uranium, hafnium and zirconium were calculated according to the following equation:

$$Q_e = (C_o - C_e).\frac{V}{m}$$

Where C_o is the initial total metal concentration of hafnium, zirconium and uranium in solution, (g/L); C_e is the equilibrium concentration of hafnium, zirconium or uranium in solution, (g/L); V is the total volume of solution, (ml); and m is the mass of Dowex 1x8 anion exchange resin, (g).

From the obtained results (Fig. 2), it is clear that, the adsorption rate of uranium onto the investigated resin is fast and reached equilibrium in about 7.5 min. While the adsorption rate of both hafnium and zirconium are also fast and the equilibrium time for them is about 15 min in this context, Hf and U adsorption efficiencies were increased by increasing the contact time while Zr adsorption efficiency was decreased by increasing the contact time. The equilibrium adsorption capacity of uranium, hafnium and zirconium reached 2.31, 4.2 and 3.77 mg/g, respectively. Also from the obtained result, it is clear also that, zirconium was firstly adsorbed on the resin, and then the adsorbed zirconium was displaced by uranium and hafnium. This means that the adsorption ability for hafnium onto the resin is stronger than the adsorption ability of zirconium and furthermore, the concentration of zirconium in the effluent solution increases with the increasing the adsorption time.

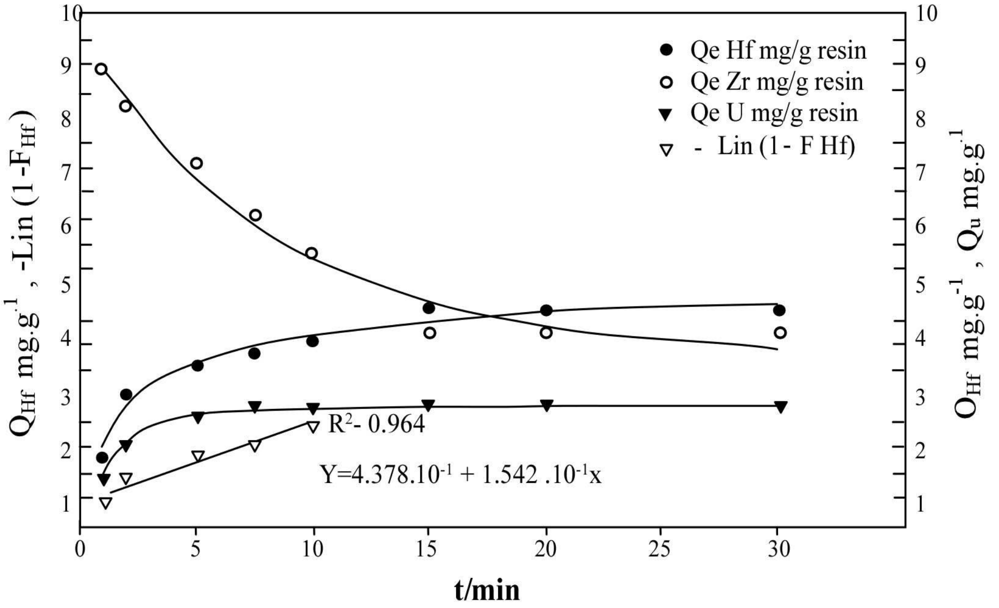


Fig. (2): Adsorption rate curves of hafnium, zirconium and uranium onto anion Dowex resin

In other words, the concentration of zirconium which is much higher than that of uranium and hafnium is adsorbed onto the resin prior to uranium and hafnium even before they can be contacted with the Dowex resin through diffusion. The predominating step zirconium adsorption process may be intraparticle diffusion while it is a film diffusion for uranium and hafnium. To determine which one (film diffusion or intraparticle diffusion) is the predominating step of the adsorption process and also to find the rate parameters, adsorption kinetic data were further processed. According to Boyed method [13], the adsorption rate constant K could be calculated by

$$-\ln(1-F) = K.t$$

Where F ($F = Q_t/Q_\infty$) is the fractional attainment of the equilibrium, Q_t and Q_∞ are the adsorption amounts at certain time while reaching adsorption equilibrium respectively while K is the adsorption rate constant. The obtained results (Fig. 3) show straight line by plotting –ln(1-F) against t where the adsorption rate constant was calculated as 1.542 x 10^{-1} s^{-1}, this was actually calculated from the slope of the straight line. The correlation coefficient ($R^2 = 0.9578$) was obtained via linear fitting. According to Boyd from the linear relationship of –ln(1-F) vs t, it can be deduced that the film diffusion is the predominating step of the adsorption process for either uranium and hafnium. On the other hand, the kinetics study performed that the employment of the Lagergren pseudo-first order and HO pseudo-second order kinetic models [14].

Pseudo-first order model can be obtained from the following equation:

$$\log (Q_e \quad Q_t) = \log Q_e \quad \frac{K1}{2.303}$$

While the Pseudo-second order model can be obtained from the following equation:

$$\frac{t}{Q_t} = \frac{1}{K2\,Q_e^2} + \frac{t}{Q_e}$$

Where Q_t and Q_e are the adsorption amounts at certain equilibrium time respectively, mg/g; K_1 is the pseudo-first order rate constant, min^{-1}; and K_2 is the rate constant of pseudo-second order equation, g/(mg.min). Also, the obtained data revealed that the uranium, hafnium and zirconium extraction are not fitted with the pseudo-first order kinetic model but agree with the HO pseudo-second order kinetic model. By plotting t/Q_t vs t gives a straight line as shown in Figure (3). The pseudo-second order rate constant, K_2 and equilibrium capacity, Q_e were calculated from the values of intercept ($1/K_2Q_e^2$) and slope ($1/Q_e$) of the straight lines and are given in Table (2). Obviously, a satisfactory agreement was obtained between calculated and experimental values of Q_e. This implies that the adsorption process proceeds according to pseudo second order kinetic mechanisms and depends upon these metal ion concentrations and active site concentrations and the rate of each ion is controlled by the chemisorption process.

Table (2): Kinetic parameters for adsorption of uranium, hafnium and zirconium onto anion Dowex resin

Metal ion	**Q_e(mg/g)**		**K_2 g/(mg.min)**	**R^2**
	Experimental	**Calculated**		
U	2.31	2.33	0.312	0.9997
Hf	4.2	4.01	1.0096	0.99994
Zr	3.77	3.335	0.4954	0.9971

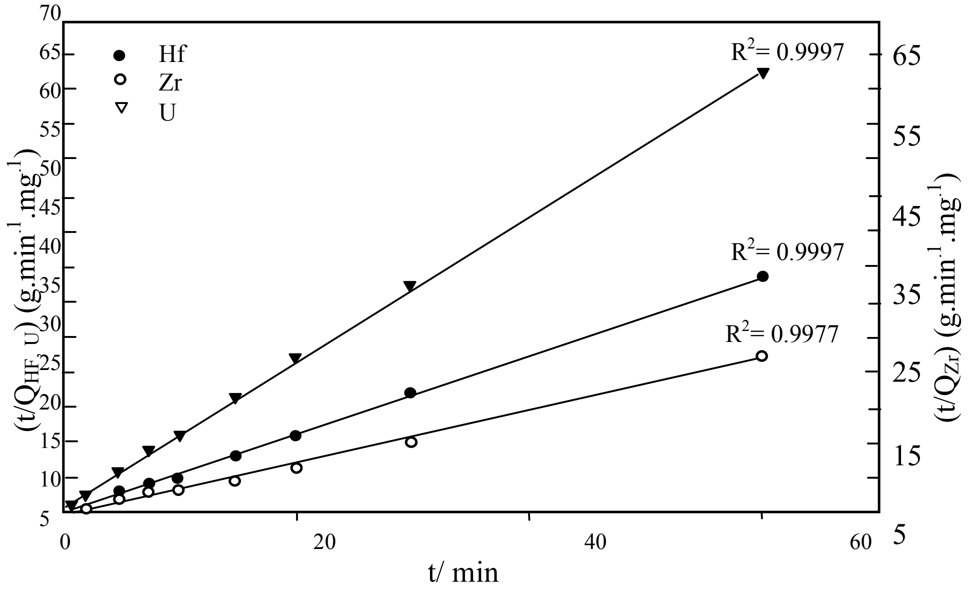


Fig. (3): Experimental kinetic curves of adsorption of hafnium, zirconium and uranium onto anion Dowex resin

1.3. Adsorption Isotherms

The adsorption isotherms were studied at different initial total concentrations of uranium, hafnium and zirconium at pH 1.5 upon anion Dowex resins. The obtained results (Fig. 4) show that the adsorption capacities of uranium, hafnium and zirconium increase with the increase of the total initial concentration of these metal ions until reaching the equilibrium adsorption capacity. The Q_e of uranium, hafnium and zirconium are 2.31, 4.2 and 3.77 mg/g, respectively, theses values reflect the higher uptake efficiency of the concerned resin toward hafnium relative to zirconium and uranium. The adsorption data are analyzed according to Langmuir and Freundlich isotherm models. In this respect,

The Langmuir isotherm model is represented by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{K_L \quad Q_{max}} + \frac{C_e}{Q_{max}}$$

Where Q_{max} is the maximum adsorption capacity, (mg/g); and K_L is the Langmuir isotherm constant which relates to the adsorption energy, (L/g). By plotting C_e/Q_e against C_e gives straight lines for zirconium and uranium with slope and intercept equals $1/Q_{max}$ and $1/K_LQ_{max}$ respectively, (Fig. 5). The obtained values of Q_{max} were 5.556 and 10.053 mg/g while, the values of K_L were -0.344 and 0.5258 L/g for uranium and zirconium, respectively. The lower value of K_L for uranium refers to the lower binding affinity relative to zirconium. This indicates that the adsorption process is a monomer adsorption and is preceded according an ideal Langmuir model.

Hafnium, on the other hand showed significant deviation from the Langmuir isotherm model.

The essential features of Langmuir adsorption isotherm can be expressed in terms of dimensionless constant (RL), which is defined by the following relationship [15]:

$$R_L = \frac{1}{1 + \quad K_L \quad C_o}$$

Where C_o is the initial total concentration of uranium, hafnium and zirconium, mol/L; and K_L is the Langmuir isotherm constant. The R_L calculated by the latter equation is 0.77 for zirconium, which indicates that the zirconium adsorption onto Dowex resin is favorable adsorption.

On the other hand, the Freundlich isotherm model is represented by the following equation [16]:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where K_F is the Freundlich isotherm constant, mg/g; and n is the adsorption intensity. By plotting log Q_e against log C_e of uranium, hafnium and zirconium gives straight lines for all metal ions, this indicates that all the metal ions are fitted perfectly with the Freundlich isotherm model (Fig. 6). The K_F of uranium, hafnium and zirconium are calculated from the intercept of these lines and represented by 0.14, 0.20 and 0.17 mg/g, respectively. The slopes (1/n) of uranium, hafnium and zirconium lines reached 0.8253, 0.8142 and 0.7284 respectively. Thus, the adsorption process is favourable when the value of 1/n lies between 0.1 and 1.

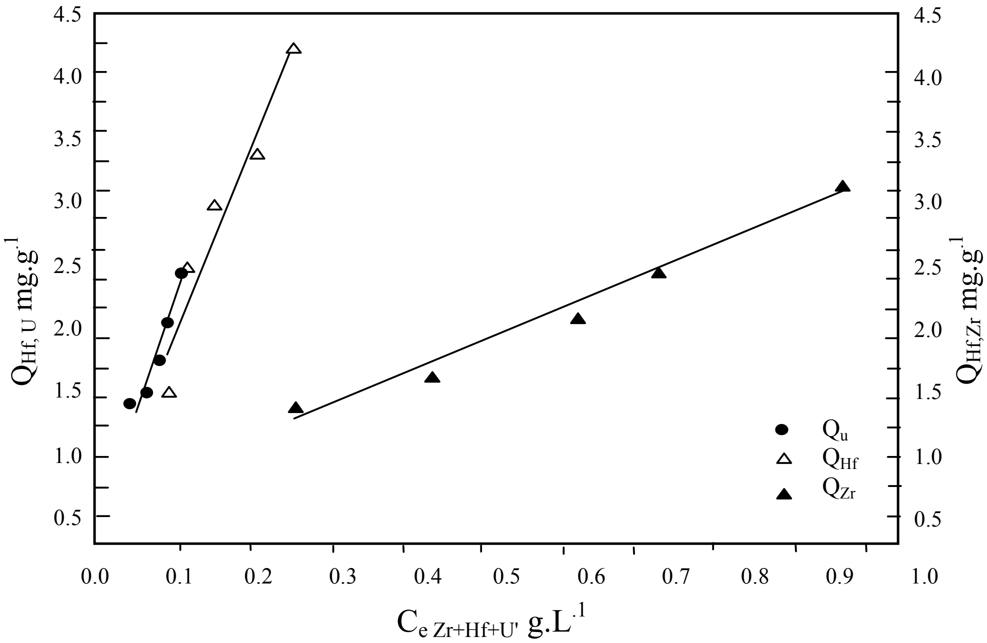


Fig. (4): Adsorption isotherms of hafnium, zirconium and uranium onto anion Dowex resin at pH 1.5

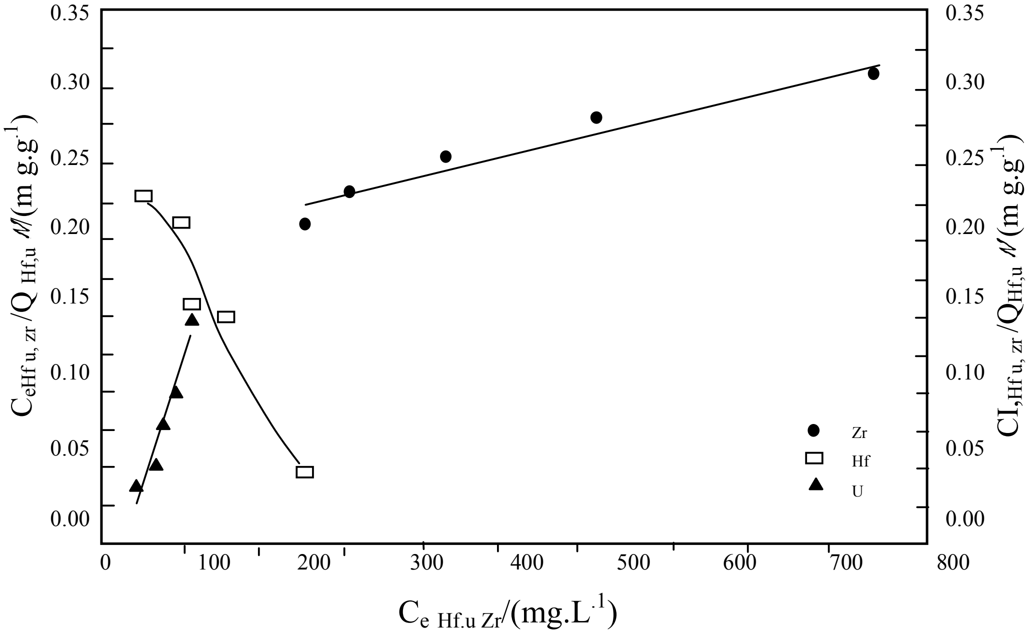


Fig. (5): Langmuir adsorption isotherms of hafnium, zirconium and uranium onto anion Dowex resin

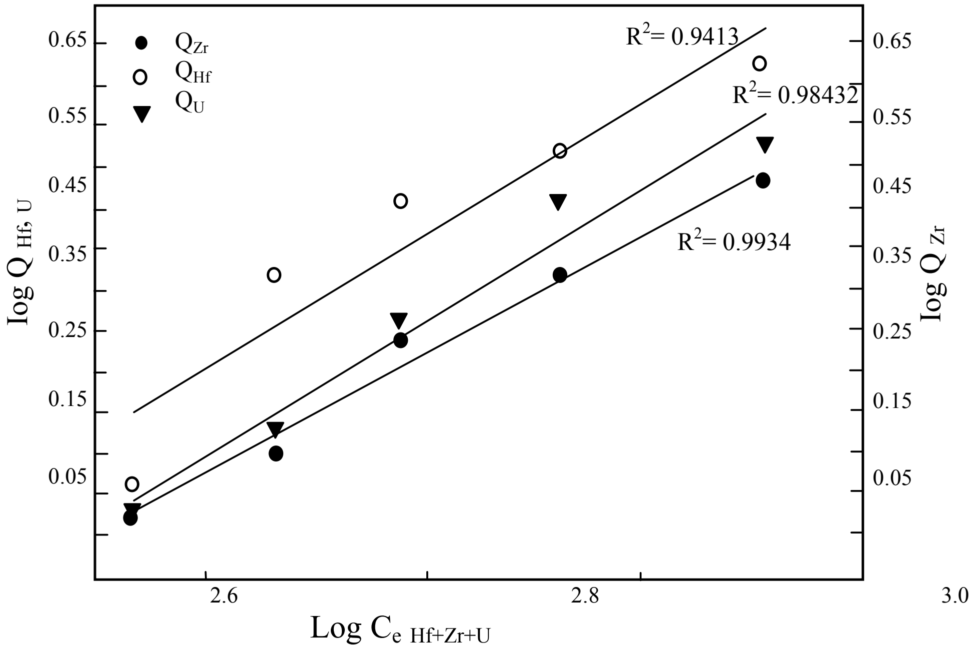


Fig. (6): Freundlich adsorption isotherms of hafnium, zirconium and uranium

1.4. Thermodynamic Studies

The obtained results (Fig. 7) according to the study of the temperature effect on the distribution ratios of uranium, hafnium and zirconium showed that these ratios decrease with increasing the temperature from 25 to 75 ^{o}C, which basically mean that the adsorption of the three elements under consideration by the anion exchange Dowex resin is exothermic. The effect of temperature on the adsorption process of zirconium and uranium by the resin are relatively stronger than that of hafnium.

According to Van't Hoff equation [17]:

$$\left|\frac{\partial \mathrm{Lg}\, D}{\partial T^{-1}}\right|_{p} = -\ \frac{\Delta H}{2.303\, R}$$

Where D is the distribution ratio, T is the absolute temperature, R is the ideal gas constant and ΔH is the enthalpy change. Straight lines were obtained by plotting lg$D$ for uranium, hafnium and zirconium vs T^{-1}, respectively. The slope line for hafnium (39.0961) is greater than for uranium (20.7857) and zirconium (8.0209). The enthalpy changes of adsorption for uranium, hafnium and zirconium onto Dowex anion exchange resin as calculated from the slopes of the Van't Hoff equation and they are - 398.005, -748.61, and -153.584 kJ/mol, respectively. The negative value of ΔH indicates the exothermic nature of the adsorption process of the concerned elements. Furthermore, the values of ΔH are in the order of Zr > U > Hf which indicates that the adsorption capacities are in the order of Hf > U > Zr. This is in agreement with the results of adsorption rate constant study.

The free energy of adsorption equation can be calculated from the following equation [18]**:**

$$\Delta G = -\mathrm{n}RT$$

Where ΔG is the adsorption free energy and n is the adsorption intensity of Freundlich isotherm equation. The values of ΔG for uranium, hafnium and zirconium are calculated by the latter equation and they were found to be - 3.0036, -3.45 and -3.4033 kJ/mol at 298.15 K, respectively, indicating that the adsorption of zirconium is slightly thermodynamically favorable than hafnium and uranium. The negative values of ΔG at 298.15 K indicate the feasibility of the adsorbent and spontaneity of the adsorption process. Also, according to Gibbs-Helmholtz equation:

$$\Delta S = (\Delta H - \Delta G)/T$$

Where ΔS is the entropy change.

The values of ΔS for uranium, hafnium and zirconium are calculated and found to be -1.33, - 2.499, and – 0.504 kJ/(mol.K) at 298.15 K, respectively. This confirmed that, the adsorption capacities are in the order of Hf > U > Zr which also is in agreement with the results of adsorption rate constant study.

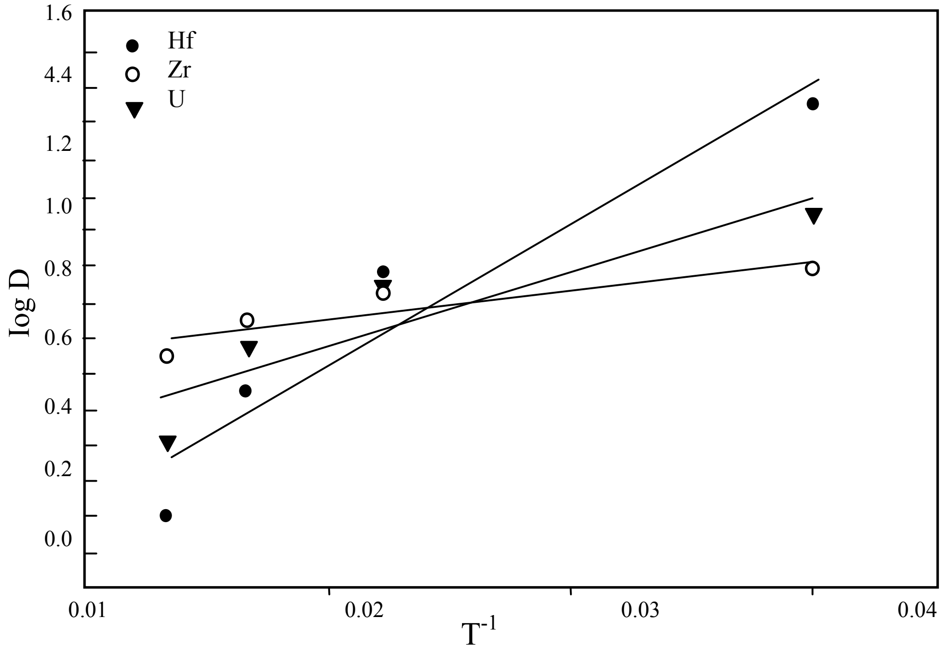


Fig. (7): Van't Hoff plots for adsorption of uranium, hafnium and zirconium onto Dowex anion resin

2. Adsorption by Column System

2.1. Effect of Flow Rate on Adsorption Efficiency

The leach liquor flow rate is an important parameter in the column adsorption system to achieve favorable adsorption conditions. The flow rate was studied in the column tests in the range from 0.3 to 30 ml/min. The obtained data (Fig. 8) showed that the adsorption of uranium decreases after flow rate higher than 5 ml/min due to insufficient contact between uranium and the Dowex resin. On the other hand, the adsorption efficiency of hafnium and zirconium increases with the increase of the flow rate. The flow rate of 5 ml/min was enough to remove all the hafnium and zirconium content of the liquor within the studied time. Therefore, the value 5 ml/min was selected as the optimum flow rate. It should be noted that the adsorption of other contamination ions from the mineral liquor was avoided by an initial reduction step using sulfur dioxide or iron dust as reducing agents [19].

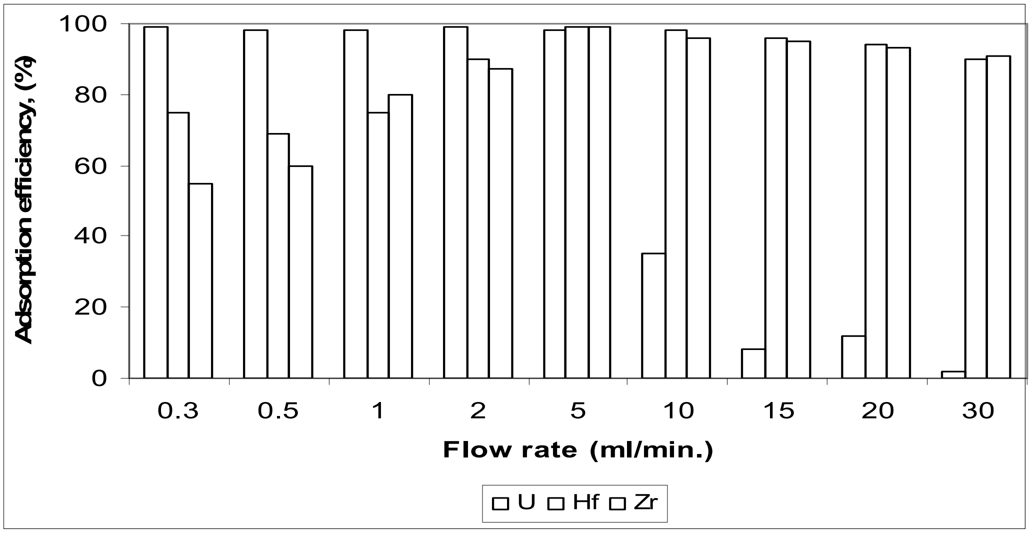
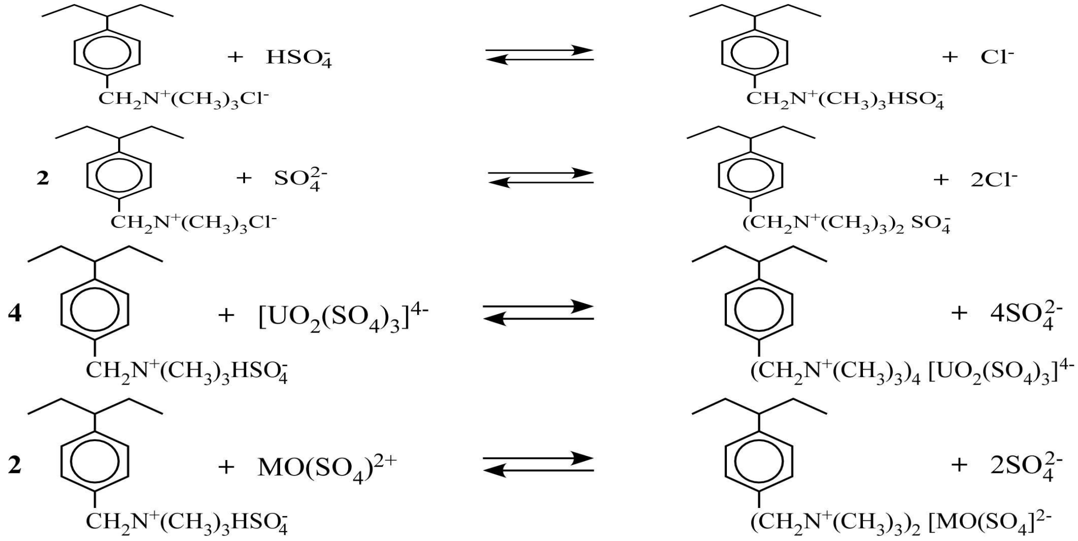


Fig. (8): Effect of flow rate upon hafnium, zirconium and uranium adsorption efficiency onto Dowex anion resin from initial leach liquor at pH 1.5

2.2. Adsorption of Uranium, Hafnium and Zirconium

About 20 liters of the feed leach liquor were passed downward through the previously prepared resin column twice. The downstream effluent was collected at different volume fractions (200 ml). After the adsorption of total the three metal concentrations namely hafnium, zirconium and uranium they were determined in the collected fractions by *ICP-OES*. The loading capacities efficiencies of them were determined (Fig. 9), the results reveal that the column backed with Dowex 1x8 anion exchange resin was completely saturated with the concerned elements after about 9 liter with flow rate of 5 ml/min. Also, the obtained results are in accordance with the results of the batch study experiments where zirconium was adsorbed firstly upon the anion exchange resin faster than hafnium. Then hafnium was adsorbed steadily and replaces zirconium upon the resin. The extraction mechanisms can be shown as in the following equations:



Where M = Hf and Zr.

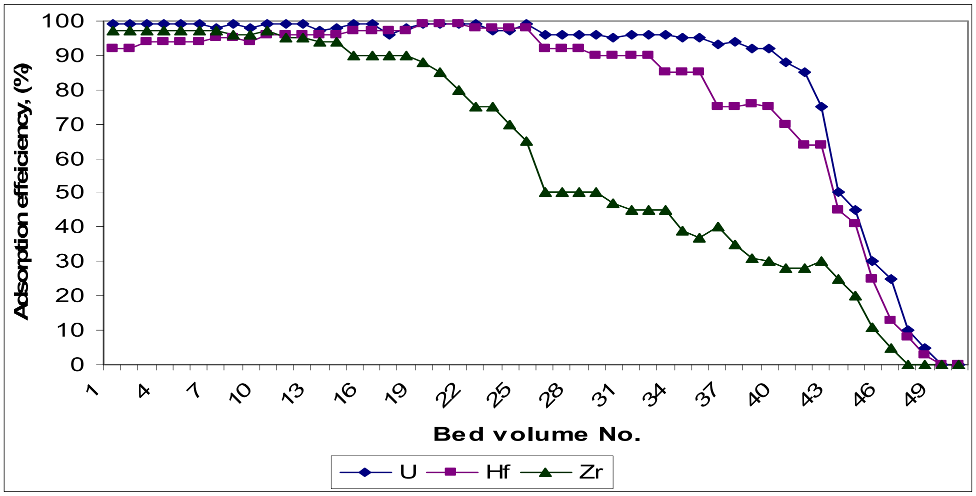


Fig. (9): Column adsorption curves for hafnium, zirconium and uranium onto anion Dowex resin at 5 ml/min. flow rate and pH 1.5

3. Elution Procedures

The elution trials of U, Hf and Zr were performed by using either an eluant mixture formed of 1 M acetic acid and 2 M HCl or a mixture of 2 M HCl and 0.01 HF at different flow rates. The acetic acid-HCl solution did not show significant separation between hafnium, zirconium and uranium. On the other hand, the eluant that contains a mixture of 10 M HCl and 0.05 M HF acids at a flow rate of 10 ml/min seems promising. The obtained results (Fig. 10) show that this eluant can separate the three elements successfully. The hafnium and zirconium were firstly eluted together (fractions from 1 to 10) then uranium was eluted completely at (fractions from 14 to 27). However, three fractions containing all the three metals were also obtained. These fractions could be directed to the loading step again upon the resin in new adsorption cycle or else they could be separated by the precipitation technique. Thus, the elution mechanism of the extracted elements can be presented by the following equations:

Where M = Hf and Zr.

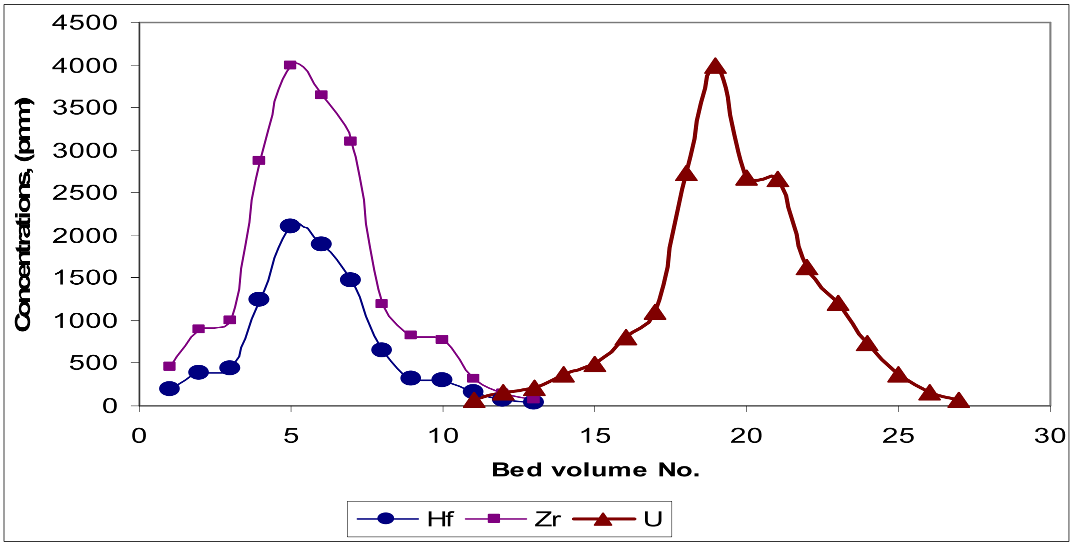


Fig. (10): Elution curves of the loaded elements upon Dowex resin by 10 M HCl + 0.05 M HF

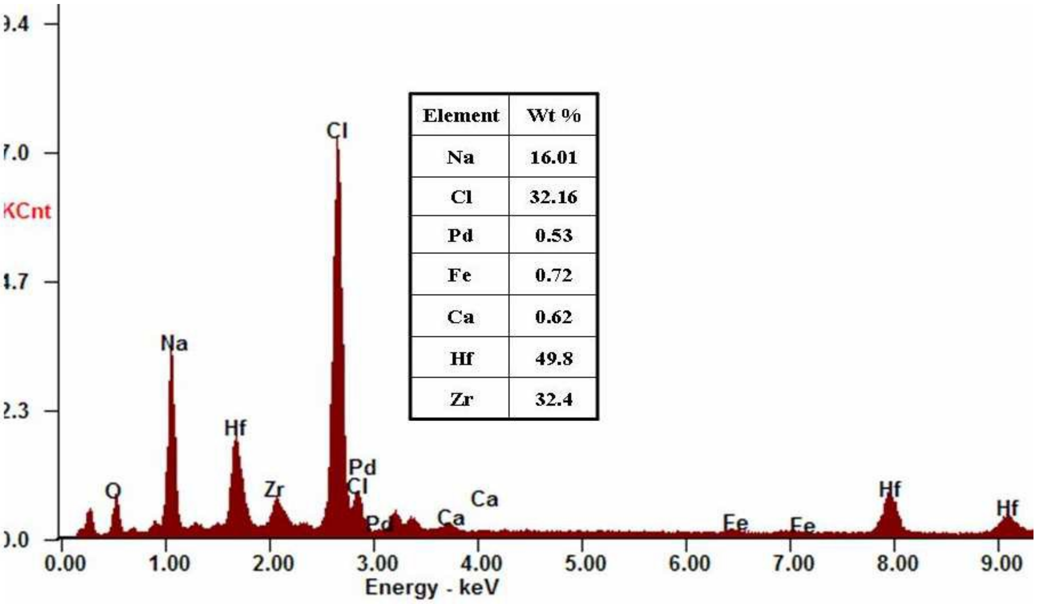
4. Precipitations Procedures

4.1. Hafnium and Zirconium Precipitation

The rich eluted fractions in Hf and Zr (1 to 10), were mixed and used in the precipitation of hafnium and zirconium concentrate. This was achieved either by sodium hydroxide at pH 4 or by evaporation till dryness. The analysis of such precipitate by using *ICP-OES* (Table 3), revealed that the precipitate has about 20 % hafnium together with about 34 % Zr. This was introduced as due to the low precipitation efficiency of zirconium. Thus, the evaporation step may be preferred. However, it may needs more detailed study. It should be mentioned herein also that, these results differ to some extent from those results obtained from *EDAX* analysis pattern (Fig. 11), because, the *EDAX* area analyses revealed that the concentration of hafnium reached (49.8 %) which is higher than the concentration of zirconium (32.4 %) by *ICP-OES*. Both analysis show that the concentrate of hafnium and zirconium seems to be relatively pure from any other impurities except sodium chloride. The chloride salt can be removed by several washing. Another alternative is to precipitate hafnium, zirconium and uranium together reducing uranium by using a reducing agent such as CO_2 while hafnium and zirconium are precipitate by using sodium hydroxide at low pH (about 4) the reduced uranium (IV) could be precipitated at a higher pH (about 12) by using sodium hydroxide.

Table (3): Complete analysis of hafnium and zirconium concentrate precipitate using *ICP.OES*

Elements	Conc. (ppm)	Elements	Conc. (ppm)
Hf	201621.5	**Zr**	320992.4
V	599.8	**U**	Undetected
Co	999.8	**Fe**	3673.3
Ni	193.4	**As**	Undetected
Cu	9786.7	**Mg**	1126.7
Zn	458.7	**Al**	Undetected
Ba	273.4	**Ca**	10733



Element	Wt %
Na	16.01
Cl	32.16
Pd	0.53
Fe	0.72
Ca	0.62
Hf	49.8
Zr	32.4

Fig (11): Semi quantitative *EDAX* analysis pattern of hafnium and zirconium concentrate precipitate

4.2. Uranium Precipitation

The uranium rich eluant fractions (14 to 27), were mixed together and were applied for the precipitation of uranium by NaOH solution at pH 7.2. The obtained yellow cake (sod. diuranate) was dried at 110 °C firstly then 0.1 g was dissolved in 100 ml of acidified water and completely specified by analyzing its impurities by using *ICP.OES* (Table 4). The analysis by *ICP.OES* revealed that the precipitate contains 47.8 % uranium oxide with a purity of 68.5 %. The main impurities of such yellow cake are magnesium, aluminum and calcium. The dried precipitate was then analysed by X-ray diffraction (*XRD*) technique (Fig. 13) as well as by Environmental Scanning Electron Microscope model FEI Insect S (*ESEM-EDAX*) (Fig. 12). The pattern obtained from *XRD* shows that at temperature till 400 °C, the precipitate is being completely amorphous. However, the crystals began to be build at 600 °C and were developed completely at 800 °C. The X-Ray diffraction pattern has similar to the Clarkeite uranium mineral (ASTM card No. 50-0-1586), sodium uranyl oxide hydroxide hydrate, $Na[(UO_2)O]OH.H_2O$. In fact, the formed sodium urinate precipitate is crystallized in general at about 500 °C but the late crystallization of this precipitate at higher temperature may be due to the presence of magnesium in the obtained precipitate as shown in *XRD* pattern with form of magnesium silicate (Forsterite Mg_2SiO_4), mineral (about 3.5 %) (*ASTM* card No. 34-0-0189) which was confirmed by the *ICP.OES* about 4.5 %.

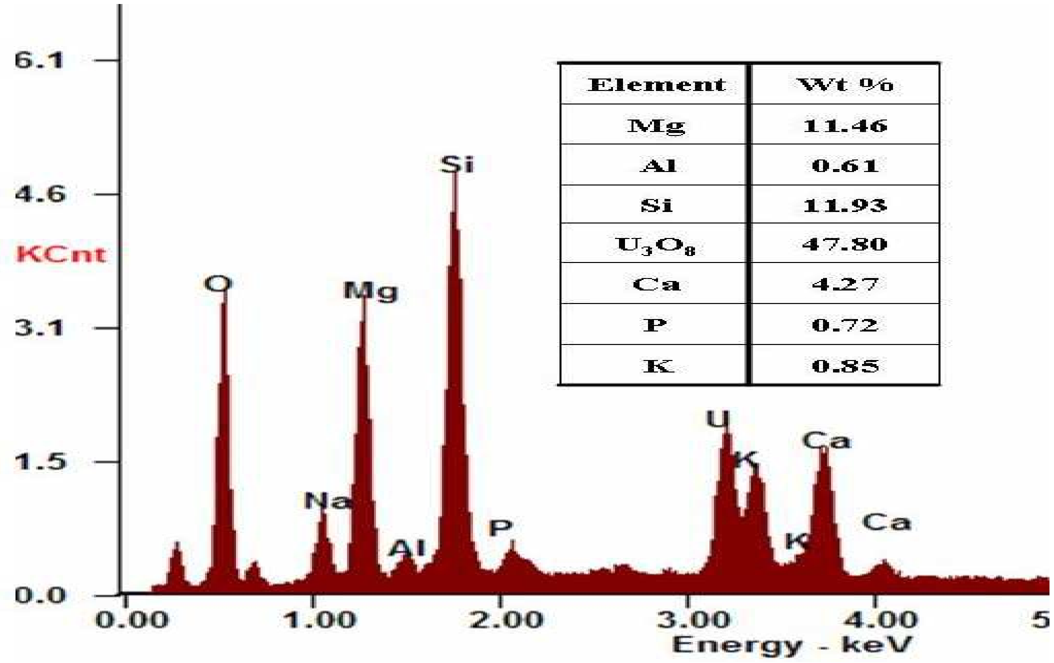
Uranium was also precipitated as peroxide concentrate by adding hydrogen peroxide (28 % in amount more than needed by the stoichiometric amount) [20], at pH range from 1.5-3.5, the precipitate was formed after 4h and was calcined at 500 °C then analyzed by *EDAX* (Fig. 14):

$$UO_2^{2+} + O_2^{2-} + 2H_2O \rightarrow UO_4.2H_2O \quad (4.20)$$

The analytical data revealed that the precipitate is formed as uranium peroxide 78.73 % with total purity of 94.7 %.

Table (4): Complete analysis of uranium precipitate using *ICP.OES*

Elements	Conc. (ppm)	Elements	Conc. (ppm)
Mn	74	**Th**	799.4
V	1981.5	**Ti**	204.5
Co	288.7	**Fe**	509.5
Ni	300.5	**As**	17.8
Cu	600	**Mg**	48268.4
Zn	85.1	**Al**	2057.5
Ba	163.4	**Ca**	1909.2
Cd	33.5	**K**	1280



Element	Wt %
Mg	11.46
Al	0.61
Si	11.93
U_3O_8	47.80
Ca	4.27
P	0.72
K	0.85

Fig (12): Semi quantitative *EDAX* analysis pattern of the uranium precipitate

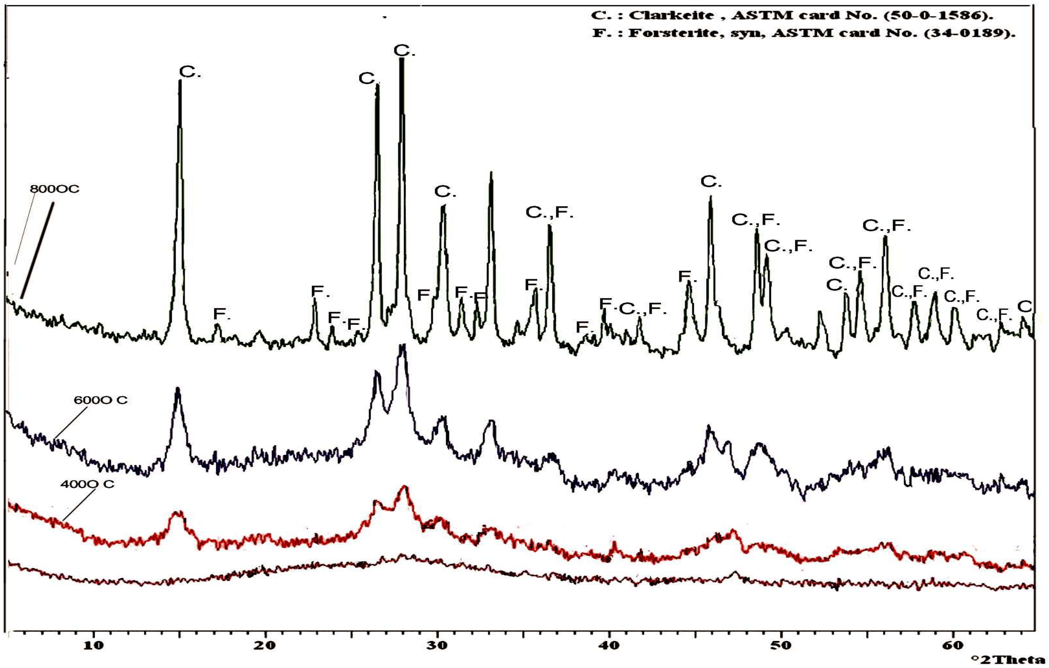
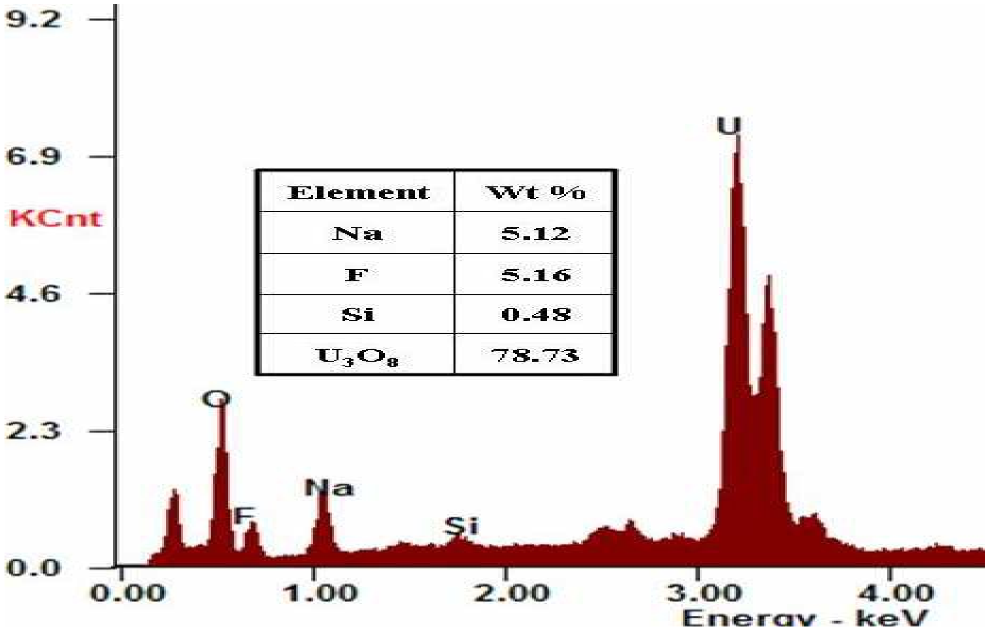


Fig. (13): X-ray diffraction pattern of the calcined uranium precipitate



Element	Wt %
Na	5.12
F	5.16
Si	0.48
U_3O_8	78.73

Fig (14): Semi quantitative *EDAX* analysis pattern of the uranium peroxide precipitate

5. Individual Separation of Hafnium and Zirconium

Individual separation of hafnium and zirconium from their concentrate was conducted via solvent extraction technique using Alamine 336 extractant (N,N-dioctyloctan-1-amine of molecular weight 353.67 and 0.8 specific gravity), from chloride media, as suggested by **Banda *et al.,*** [21]. . Briefly, about one gram of concentrate was dissolved in 200 ml of 9 M HCl solution.

The applied extraction conditions involve 0.1 M Alamine 336 diluted in kerosene as diluent with organic/aqueous ratio of 1/1 and shaking the mixture for about 30 min at room temperature. Zr and Hf were loaded upon Alamine 336 solvent. However, hafnium was scrubbed from the loaded solvent using 0.5 M H_2SO_4 with aqueous/organic ratio of 5/1. Zirconium was finally stripped from the loaded organic phase by simple contact with dilute 1 M HCl. Batch simulation of counter-current extraction indicates that the extraction efficiencies of Zr and Hf reached 98.7 % and 20.5 % respectively and the stripping efficiency of the loaded zirconium on the solvent reached 95.2 %. The concentration of zirconium in the raffinate was about 5133 ppm while hafnium concentration in the strip solution was 18000 ppm (1.8 % of the zirconium precipitate). The strip solution and the raffinate were evaporated till dryness and the yields were analyzed by *EDAX* (Fig. 15 and 16). From the obtained data, it is clear that the concentration of hafnium in its precipitate is about 74.5 % while zirconium does not appear in the area analysis pattern. On the other hand, the concentration of zirconium in its precipitate reached 62.3 % however, the concentration of hafnium reached 11.5 %.

Table (5): Complete analysis of hafnium precipitate using *ICP.OES*

Elements	Conc. (ppm)	Elements	Conc. (ppm)
Hf	753759.6	**Zr**	5133.4
V	240	**U**	Undetected
Co	72	**Fe**	979.8
Ni	323.4	**As**	Undetected
Cu	Undetected	**Mg**	2445.7
Zn	322	**Al**	Undetected
Ba	306.7	**Ca**	2021.98

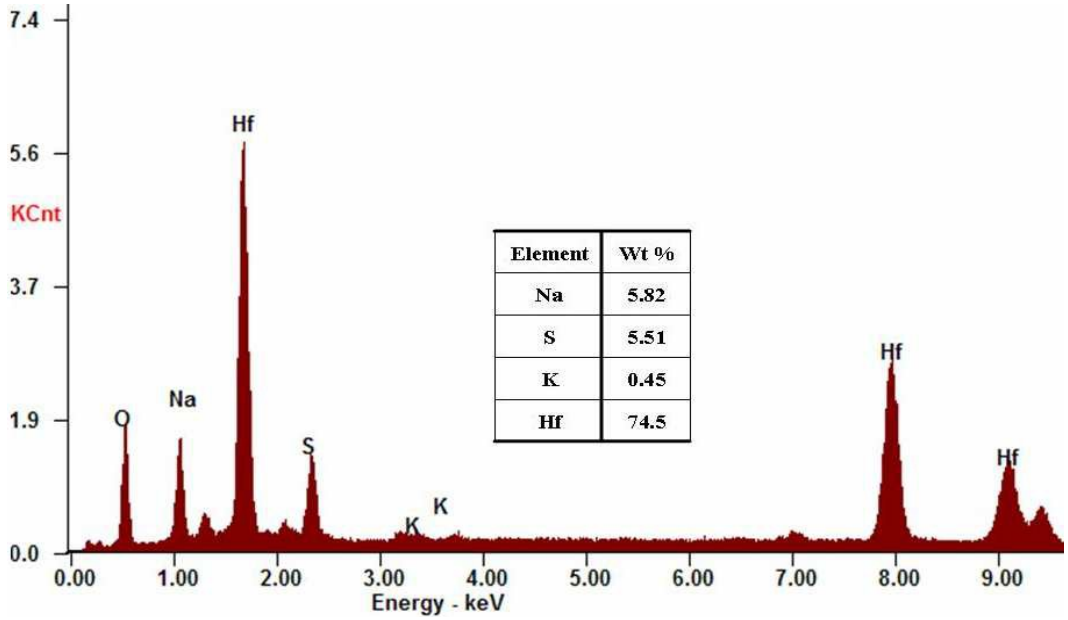


Fig (15): Semi quantitative *EDAX* analysis pattern of hafnium precipitate from raffinate solution

Table (6): Complete analysis of zirconium precipitate using *ICP.OES*

Elements	Conc. (ppm)	Elements	Conc. (ppm)
Hf	18000.2	**Zr**	659742.5

V	173.4	**U**	undetected
Co	100	**Fe**	399.8
Ni	73.4	**As**	Undetected
Cu	793.4	**Mg**	2433.4
Zn	779.8	**Al**	Undetected
Ba	133.4	**Ca**	2153.34

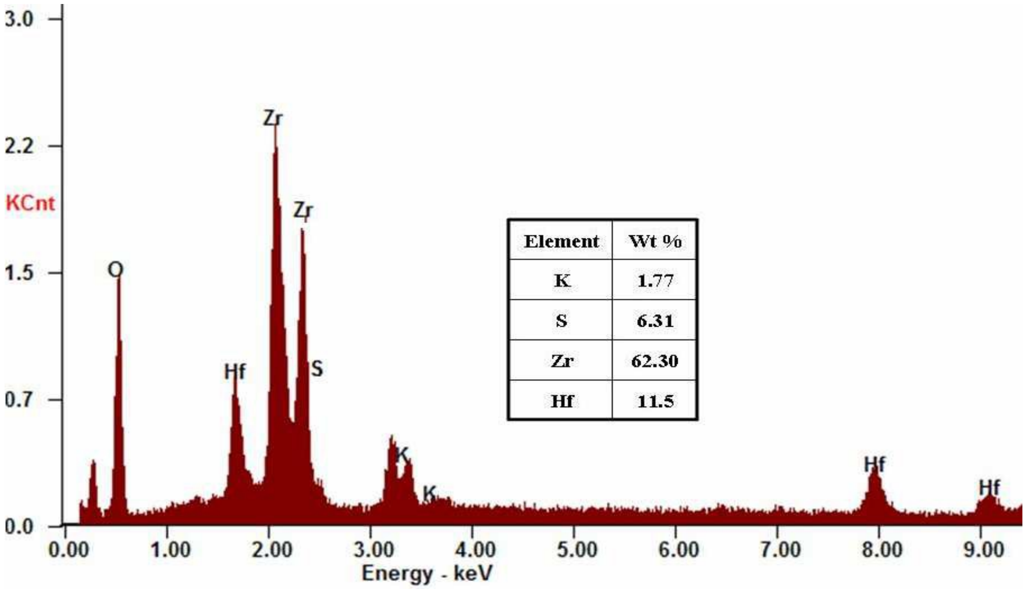


Fig (16): Semi quantitative *EDAX* analysis pattern of zirconium precipitate from strip solution

Conclusions

The obtained results showed that; the optimum adsorption conditions of the concerned elements (Hf, Zr and U), from the petroleum fly ash leach liquor by using Dowex 1 x 8 as strong basic anion exchange resin are 5 ml/min flow rate at pH of 1.5 while using a reducing agent to eliminate the adsorption of iron and vanadium. The eluant containing a mixture of 10 M HCl and 0.05 M HF acids at a flow rate of 10 ml/min was applied to separate firstly hafnium and zirconium elements then uranium was eluted completely. Uranium was precipitated by using either NaOH or H_2O_2 solutions at different pH, while the concentrate containing hafnium and zirconium was firstly precipitated by using NaOH solution then it was dissolved in HCl to separate hafnium and zirconium individually separated from each other by solvent extraction technique using Alamine 336 extractant. When applying the extraction conditions of 0.1 M Alamine 336 diluted in kerosene as diluent with organic/aqueous ratio of 1/1 and shaking for about 30 min at room temperature, the extraction efficiencies of Zr and Hf reached 98.7 % and 20.5 % respectively. The 20.5 % hafnium was scrubbed from the loaded solvent by using 0.5 M H_2SO_4 with aqueous/organic ratio of 5/1 and finally zirconium stripped from loaded organic phase by simple contact with dilute 1 M HCl while the stripping efficiency of zirconium from the loaded solvent was 95.2 %. The other elements such as vanadium, nickel and iron were separated by direct precipitation.

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