



Laser Fluorimetric Determination of the Extracted Uranium from Industrial Grade Phosphoric Acid and Phosphate Rocks Using Natural Adsorbent, EWS

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ABSTRACT

Laser Fluorimetric determination of the complete reduced U(IV) using Zn metal was applied on industrial grade phosphoric acid and phosphate rocks after separation using a low cost natural cationic adsorbent of Egyptian white silica sand (EWS). The determination process was performed after prior separation of cationic uranyl complex. This method was applied to overcome the interfering problems of P(V), Fe(III) and Ca(II). For maximum loading efficiency, the adsorption parameters such as pH, amount of adsorbent, contact time, temperature and initial U(IV) concentrations were investigated via batch process. On the other hand the effective elution factors such as eluting agents, ratio of NaCO₃ with NaHCO₃, volume of 30% H₂O₂, contact time and temperature were also investigated. A selective elution of oxidized U(VI) was carried out by using 1M mixture of NaCO₃ and NaHCO₃ solution in the presence of (0.8 mL/10 mL) of 30% H₂O₂ as an oxidizing agent. The maximum U loading capacity (75 mg g⁻¹) was attained at the resulted optimum loading and elution conditions.

Keywords: U(IV), U(VI), Egyptian white silica sand (EWS), Industrial grade phosphoric acid, Phosphate rocks, Loading and Elution.

INTRODUCTION

U recovery from phosphate deposits is generally agreed to be a very reliable and long term source of U. As a consequence of an increased demand of U on the world market, new mineral resources are always welcome. One of these is the phosphate rock used in the fertilizer industry, which has a U content of 0.01-0.02%. Therefore, large amounts of U are lost in the wet processing of the phosphate rock. In the sulfuric acid route, the resulted phosphoric acid has a U content of 0.1-0.2 g L⁻¹. There are now several processes based on solvent extraction which permit this uranium recovery [1, 2]. Phosphoric acid contains also other impurities in higher concentration than U such as Fe(II) and Fe(III). The U valence state was affected by the presence of Fe(II) which might reduce it to U(IV) [3].

Wet process phosphoric acid (WPPA) derived from the dissolution of phosphate rock is an important secondary source of U. Exhaustive work in the field of solvent extraction has been carried out for the recovery of U from various industrial grades of phosphoric acid employing different synergistic extracting mixtures [4]. Approximately 13 tons of U₃O₈ could be recovered each year and there were many reasons

that make the recovery of U from WPA attractive, especially in countries without of conventional U ore bodies [5]. At current global rate of consumption, phosphatic U can meet the global demand for 440 years as against a life of 86 years for known U resources [6]. Recovery from secondary sources was important for the conservation of resources. Separation of U from fertilizer products also serves the objective of controlling its release into the human environment, including the food chain [7].

The determination of U at various stages of the nuclear fuel cycle with a high degree of precision and accuracy is one of the essential requirements in nuclear materials accounting and chemical quality control of fuel materials. Several important aspects should be considered while judiciously selecting the method for the determination of U and reprocessing streams; (1) the method should be simple, rapid and precise and accurate; (2) the sample size required for the analysis should be small to reduce difficulties in handling radioactivity and (3) the analytical waste generated should be small in volume and should be amenable to easy recover U [8].

Fluorimetric determination of U is very popular due to its high sensitivity and specificity [9], and it is widely used for the determination of U in a variety of geological samples [10]. Majority of the reported works [11] deals with the determination of U in igneous rocks after selective separation of U because many elements quench the fluorescence. Few reports were available for the determination of U in phosphoric acid, phosphorites and refractory minerals like ilmenite, rutile, zircon and monazite, and the procedure given was cumbersome and dealt the minerals separately, involving separation and preconcentration of U [10].

The major problems in the U determination of these minerals were the preparation of a clear sample solution, presence of interfering elements with high concentrations and the accurate determination of U at trace levels ($\leq 10 \mu\text{g/g}$). WPPA contains a number of organic and inorganic impurities that affect the grade of the acid. Some of these inorganic impurities are heavy ions such as U, Th, Zn, Cr and Cd which are considered as hazardous substances besides possible recovery of U as a secondary resource, while U causes environmental problems due to its radioactive properties, it is considered in the meantime as a strategic element with a high inherent value. The presence of these impurities is indeed the reason behind which 95% of the acid produced by the wet process is directly used as fertilizers and not in other applications as food stuff, pharmaceuticals and sugar industries [12].

Solvent extraction solely was found to be a successful process for industrial recovery of U from phosphates, although other methods such as ion-exchange [13], membrane separation [14] and precipitation [15] were also investigated. Synergistic mixtures of D2EHPA and TOPO or D2EHPA and DBBP were reported as suitable for extraction of U from WPA [16].

U in phosphate rock was determined spectrophotometrically using arsenazo I. In this case the rock was dissolved in HNO_3 , then U was extracted with tributyl phosphate, stripped with hot water and then determined. For the determination of U in technical phosphoric acid, the fluorosilicate ion present as impurity must first be precipitated, the U was separated on Amberlite IRA-400 in the sulfate form, and determined in the eluate spectrophotometrically by arsenazo I [17].

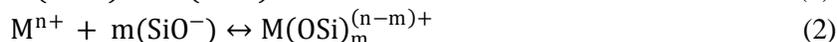
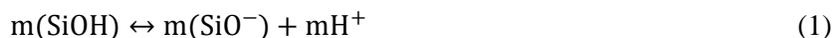
A selective anion-exchange separation and spectrophotometric method was developed for the determination of U and Th in phosphate rocks. About 0.2 g of rock sample was decomposed with nitric acid U and Th were adsorbed by anion-exchange on Amberlite CG 400 (NO_3^-) column from the sample solution adjusted to 2.5M in magnesium nitrate and 0.1M in nitric acid. U and Th are eluted consecutively with 6.6M nitric acid and 0.1M nitric acid, respectively. U and Th in the respective effluents were determined spectrophotometrically with Arsenazo III. Results were quoted on U and Th in NBS standard phosphate rock [18].

An extraction spectrophotometric method for determination of trace amounts of U in phosphate fertilizers was described. It was based on the extraction of U with trioctylphosphine oxide in benzene and the spectrophotometric determination of uranium with Arsenazo III in buffer-alcoholic medium. The maximum absorbance occurs at 655 nm with a molar absorptivity of $1.2 \times 10^4 \text{ mmol}^{-1} \cdot \text{cm}^{-1}$. Beer's law was obeyed from 0.6 to $15.0 \mu\text{g mL}^{-1}$ U (VI). This method was applied successfully to the analysis of phosphate fertilizers with concentration of 45% P_2O_5 [19].

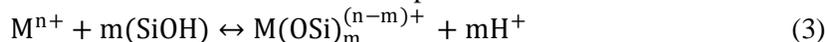
A method for the quantitative determination of U in wet phosphoric acid containing 0.001 – 0.02% U was developed. After reduction with Fe metal or $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, U (IV) was extracted with kerosene solution of an equimolar mixture of mono and di-nonylphenyl phosphoric acids. The U was stripped with an oxidizing medium consisting of 10 M H_3PO_4 containing NaClO_3 . The stripped U was determined spectrophotometrically using Arsenazo III [20].

The U present in the leach liquors obtained by addition of sulphuric acid on phosphate rock can be extracted with D2EHPA and TBP after oxidation of any Fe(II), and then stripped at 65°C with Fe(II) in 8.6 M phosphoric acid. The U was finally determined with Arsenazo III [21]. U was present in industrial grade phosphoric acid and phosphate rocks in the tetravalent and hexavalent states and their ratio was highly variable [22]. The U in the rock appears fundamentally as an element substituting the principle constituents in the crystal lattice. The most abundant form of this substitution is by tetravalent U [23].

Silica is an adsorbent widely used in the purification and separation due to its adsorption properties, high surface area and porosity [24]. A surface functional group in silicates plays a significant role in adsorption process. It is a plan of oxygen atoms bound to silica tetrahedral layer and hydroxyl groups that are associated with the edge of the silicate structure units. These functional groups provide surface sites for the chemisorption of transition and heavy metals. The surface hydroxyl groups dissociate in water and serve as Lewis bases towards metal cations M^{n+} . The metal surface bonding (adsorption) reaction was favored by the metals properties that its hydrolysis. Such properties include high charge, small radius and polarizability [25]. The sorption of metal ions can take place by the cation exchange reaction through the substitution of protons from silanol groups on the surface by the metal ions from the solution, as follows in equations (1, 2 and 3).



The overall reaction can thus be represented as:



where M^{n+} is the metal ion with $n+$ charge, SiOH is the silanol group on SiO_2 surface, $m\text{H}^+$ is the number of protons released. Although the ion exchange reaction was able to explain the sorption process, metal sorption on the white silica sand may also take place through complex formation on the cell surface after interaction between the metal and active groups present on surface of white silica sand [26]. Finally, the main target of this work is the usage of EWS as a natural cationic exchanger which is a low cost adsorbent for U (IV) separation from industrial grade phosphoric acid and phosphate rocks to overcome the effect of interfering elements such as P(V), Fe(III) and Ca(II) which are present at high concentration compare with low concentration of U (IV).

MATERIALS AND METHODS

Materials: The chemicals used are $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, CaCl_2 , Na_2CO_3 , NaHCO_3 , H_3PO_4 , H_2SO_4 , HCl , NaCl , NH_4OH , $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NH_4VO_3 are analytical reagent grade. A stock solution of 10000 mg/L U solution was prepared by dissolving 2.11 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt in a 100mL volumetric flask and completed with double distilled water. The latter was treated with 0.5-1 g of Zn metal to reduce

all U(VI) to U(IV) with addition of few drops of 1 M HNO₃ to 0.1 M free acidity solution. A mixed stock solution assaying 20% of P (V), 2% Fe (III), 30% Ca (II), 0.02% Cr (III) and 0.02% V(V) was prepared. The controlled reference materials required for the present work were a commercial wet-process phosphoric acid (P₂O₅ = 39.5%), which was kindly received from Abu-Zaabal, Cairo, Egypt, two standard samples [phosphate (1) and phosphate (2) [27]] and the phosphoric acid sample already analyzed in ACME laboratories in Canada using ICP-MS as an advanced analytical tool [28]. On the other side, unknown phosphate samples were collected from Abu Tartur Western Desert, El Sibaiya West Nile Valley, El Hamarwin Red Sea and Wadi Mishash East Luxor area for application of the studied method. The natural EWS adsorbent was brought from Sinai, Egypt. It was ground and sieved to a particle size of 200 μm using standard Tyler screen series. A weight of 10 g from the later prepared sample was washed with hot double distilled water and then filtered. The precipitate was immersed in 50 mL 6M HCl solution for 24 h to remove any gangue materials. After filtration and washing with suitable volume of double distilled water, it was dried at 110°C for 2 h and then stored under vacuum for several days at room temperature. The chemical composition of EWS was shown in table1 [29].

Table 1. Chemical analysis of natural Egyptian white silica sand (EWS)

Elements Oxide	Concentrations, %
SiO ₂	98.5
TiO ₂	0.12
Al ₂ O ₃	0.31
Na ₂ O	0.11
Fe ₂ O ₃	0.22
H ₂ O	0.11
Total	99.37

Preparation of the activated EWS: A weighed 5 g portion of the treated and dried EWS was activated by washing with a 50mL mixed solution of the following; 5mL of 0.5M NaCl, 3mL of 0.3M NH₄Cl, 2mL of 0.015M EDTA and 2mL of 0.015M tartaric acid [30].

Instrumentations: N₂-Laser Fluorimetric Technique, (UA-3), model Scintrex, Canada was used for U determination. An intense excitation source, N₂-Laser, at 337 nm was applied for exciting U. This instrument was periodically calibrated, starting from 0.01 mg/L U. Double Beam UV-Visible Spectrophotometer, model UNICAM, England was used with 1×1 cm cells. The optical system was checked automatically and the instrument was periodically calibrated, using Arsenazo III [31]. A pH-meter, model SCHOTT GERATE, Germany was applied for all experiments in the present work. Calibration of the pH meter was carried out before each experiment by using two successive buffer solutions (pH 4 and 7 or pH 7 and 10).

Extraction procedures

Determination of U loading capacity of EWS, (mg g⁻¹): Several 50 mL of different concentrations ranged from 200 to 500 mg L⁻¹ U(IV) of standard solutions were mixed separately with 1g of the activated EWS in four beakers and stirred for 30 minutes after filtration and determination of U in the effluent the maximum loading capacity of U(IV)/g EWS was calculated as shown in equation (4).

Efficiency of EWS (loading capacity) of adsorbed U(IV) per gram of EWS, Q_e, was calculated from:

$$Q_e (\text{mg/g}) = \frac{(C_{\text{int}} - C_{\text{fin}}) \times V}{m} \quad (4)$$

Where V and m are the volumes of the solutions (mL) and the mass of adsorbent (g) or cationic exchanger EWS respectively [32]. The extraction procedures of synthetic U solutions using activated EWS for its analysis required to subsequent steps loading and elution.

Loading step: Different parameters; pH values from 0.1 to 2.0, the amount of adsorbent from 0.2 to 1.0 g 50 mL⁻¹, the contact time varied from 10 to 90 min, temperature from 25-60°C and the initial U(IV) concentration from 20 to 200 mg L⁻¹ were studied to optimize the loading of U. After the achieving of the optimum loading conditions the interfering elements assaying 20% of P (V), 2% Fe (III), 30% Ca (II), 0.02% Cr (III) and 0.02% V(V) were add to the synthetic solution to observe the influence of these metal ions on the determination of U through the elution process. The contents of the flask were filtered where the U (IV) ions in each effluent solution was then determined and the concentrations of the loaded U (IV) ions were calculated as shown in equation (5). The loading efficiency (%) of U was calculated as follows:

$$\text{Loading efficiency of U(IV), \%} = \frac{(C_{\text{int}} - C_{\text{fin}})}{C_{\text{int}}} \times 100 \quad (5)$$

where C_{int} and C_{fin} are the initial and final U concentrations (mg L⁻¹), respectively.

Selective elution step using oxidized NaCO₃ with NaHCO₃ mixture: To optimize the U elution step several effective parameters; NaCO₃ with NaHCO₃ mixture concentration, ratio of NaCO₃ to NaHCO₃, volume of 30% H₂O₂, contact time and temperature were studied. U(VI) in the elute (desorbed) solution was determined using N₂-Laser Fluorimetric Technique (UA-3) to calculate its elution efficiency (%) as shown in equation (6).

$$\text{Elution efficiency of U(VI), \%} = \frac{C_{\text{fin}}}{C_{\text{int}}} \times 100 \quad (6)$$

where C_{int} and C_{fin} are the initial and final U concentrations (mg L⁻¹), respectively.

Determination method: U(VI) determined using N₂-Laser Fluorimetric Technique (UA-3) as follows: A specific sample volume ranged from 10-50 µL depending mainly on U concentration on the aqueous solution was mixed with the alternative buffer solution (500 g of NH₄H₂PO₄ + 50 ml H₃PO₄ in 2L) by the ratio buffer to sample = 2/3, completed up to 7 mL with distilled water and mixed well. The fluorescence of the measured uranyl solution in the cell was compared with the sample and internal standard measurements [33, 34].

RESULTS AND DISCUSSION

Studying the effect of interfering elements on direct determination of U on synthetic phosphate solutions: The effect of different interfering ions on direct determination of U in aqueous phosphate solutions was shown in table 2.

Table 2. Effect of interfering metal ions on the direct determination of 100 mg/L U(IV) using N₂-Laser Fluorimetric Technique (UA-3)

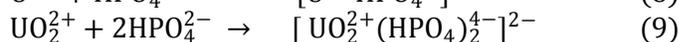
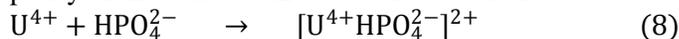
Effect of Phosphorus		Effect of Iron		Effect of Calcium		Effect of Mixture	
P(V), % added	U(IV) conc., mg/L	Fe(III), % added	U(IV) conc., mg/L	Ca(II), % added	U(IV) conc., mg/L	20% P(V) 2% Fe(III) 30% Ca(II) 0.02% Cr(III) 0.02% V(V)	U(IV) conc., 25.8 mg/L
10	165	1	71	20	80		
15	188	1.5	50	25	74		
20	210	2	22	30	66		

This table shows that increasing P(V) metal ion concentrations from 10-20 % enhanced U concentration from 100 to 165, 188 and 210 mgL⁻¹, respectively. While the addition of Fe(III) metal ion concentrations from 1-2 % leads to quenched U concentration from 100 to 71, 50 and 22 mg L⁻¹, respectively. On the other hand the addition of Ca(II) metal ion concentrations from 20-30 % leads to quenched U concentration from 100 to 80, 74 and 66 mg L⁻¹, respectively. It was also observed from the table that the addition of mixture of these interfering metal ions as a matter of phosphoric acid and phosphate rocks has a considerable quenching effect on U concentration which decreased from 100 mg L⁻¹ up to 25.8 mg L⁻¹. The mixture quenching effect was similar to that occurs during direct determination of U in both phosphoric acid and phosphate rocks which decreased by 75% less than the real concertation. The presence

of P(V), Fe(III) and Ca(II) ions leads to the formation of $[\text{CaUO}_2(\text{PO}_4^{3-})_2]^{2-}$ as illustrated in equation (7) which inhibit the fluorescence of U causing quenching effect. So U determination in phosphate solutions should be performed after extraction.



For this purpose, a natural cationic exchanger EWS was used during the investigation of both loading and elution process. The usage of cationic resin required the reducing of total U in phosphoric acid and phosphate rocks to U(IV) the tetra valent U which formed in aqueous solutions cationic complexes, on the other side U(VI) formed in aqueous solution anionic complexes as shown in the following equations (8 and 9) [17, 35, 36]. Thus, the prepared U synthetic solution required for optimization the extraction process should be treated with zinc metal to convert all U to the tetra valent form. In the meantime, the total U capacity of the activated EWS would be calculated.



Determination of U loading capacity of EWS, (mg g^{-1}): A volume of 50 mL of different concentrations ranged from 200 to 500 mg L^{-1} U(IV) of standard solution were mixed separately with 1g of the activated EWS in four beakers and stirred for 30 min. After filtration and determination of U in the filtrates it was shown that the average U capacity was 75mg g^{-1} of EWS as shown Table (3).

Table 3. Loading capacity of EWS, (mg g^{-1})

Initial U(IV) conc., mg/L	Loading capacity (mg/g)
200	70
250	75
300	75
500	80

Optimization of U loading process: To optimize the U loading process several effective parameters were studied; pH, the amount of adsorbent, the contact time, temperature and the initial U(IV) concentration.

Effect of pH value: This factor was studied by changing the pH values of the present U solution from 0.1 to 2 where the other parameters were kept constant at 0.5 of EWS, stirring time 30 minutes at room temperature. After filtration and determination of U, the obtained data in figure 1 indicated that increasing the adsorption of U(IV) from lower pH values till reaches maximum at pH 0.2 after which it decreases again. At the later pH, the number of negatively charged groups on the adsorbent matrix increases and enhances the adsorption of the U(IV) species by coulombic attraction. Generally, U(IV) was better adsorbed at low pH values. This could be due to the fact that at low pH, U exist as U(IV) and can therefore be better adsorbed by the C=O functional group on the adsorbent since oxygen is electronegative and can attract ions that are positively charged [37].

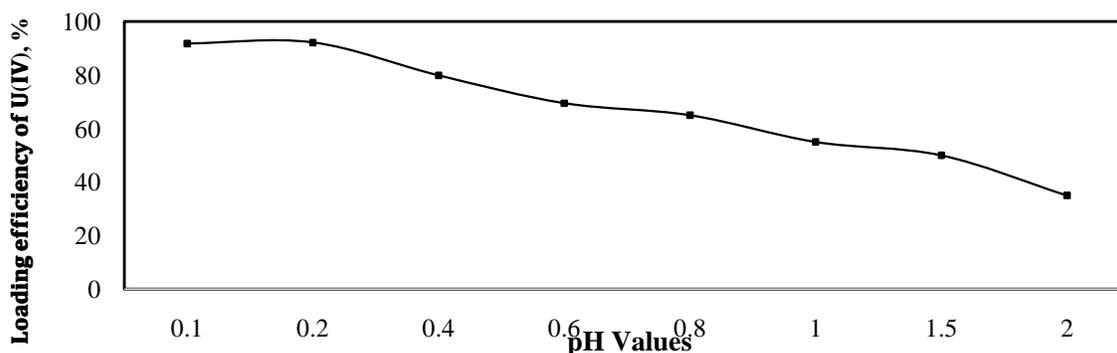


Figure 1. Effect of pH values on loading efficiency of U(IV), %

Effect of EWS amount: Figure 2 shows the effect of using different amounts of EWS on U loading efficiency (%) from 0.2 to 1 g by using 50 mL of U standard solution adjusted to pH 0.2 and stirring for 30 minutes at room temperature. The obtained results showed that the best U loading efficiency 94.5% was attained by using 0.8 g of EWS. This may be attributed to increased surface of area and hence the availability of more adsorption active sites. Further increasing in EWS weight more than 0.8g has a very limited effect due to the formation of clusters of adsorbent particles resulting in decreased surface area [38].

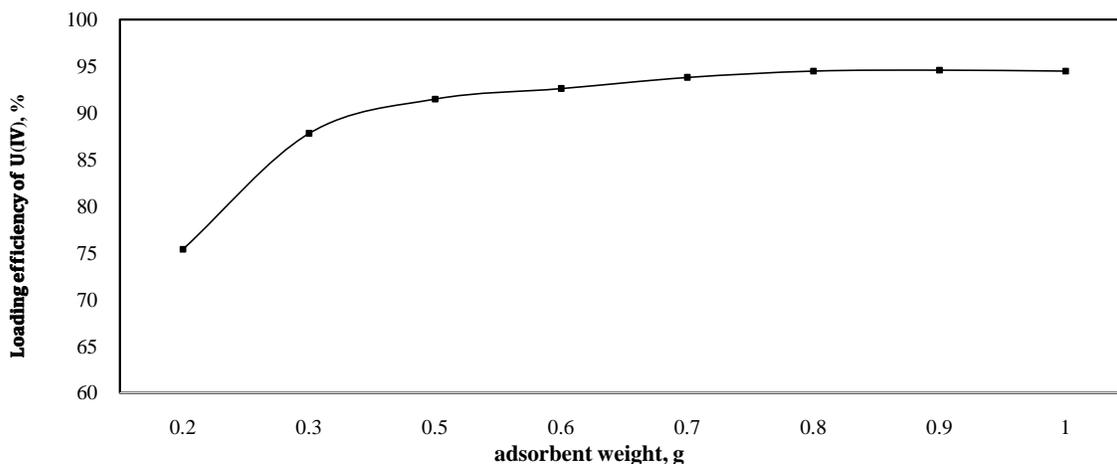


Figure 2. Effect of adsorbent weight (g) on loading efficiency of U(IV), %

Effect of contact time: This effect was studied by mixing 0.8g of EWS with 50 mL of U standard solution adjusted to pH 0.2 and stirring for different periods of time ranging from 10 to 90 min. Obtained data illustrated in figure 3 revealed that increasing the stirring time from 10 to 40 min increases U percentage loading efficiency up to 98.2% while further increasing up to 90 min decreases the latter up to 70.3%. This may be due to regeneration of some loaded U by increasing the contact time.

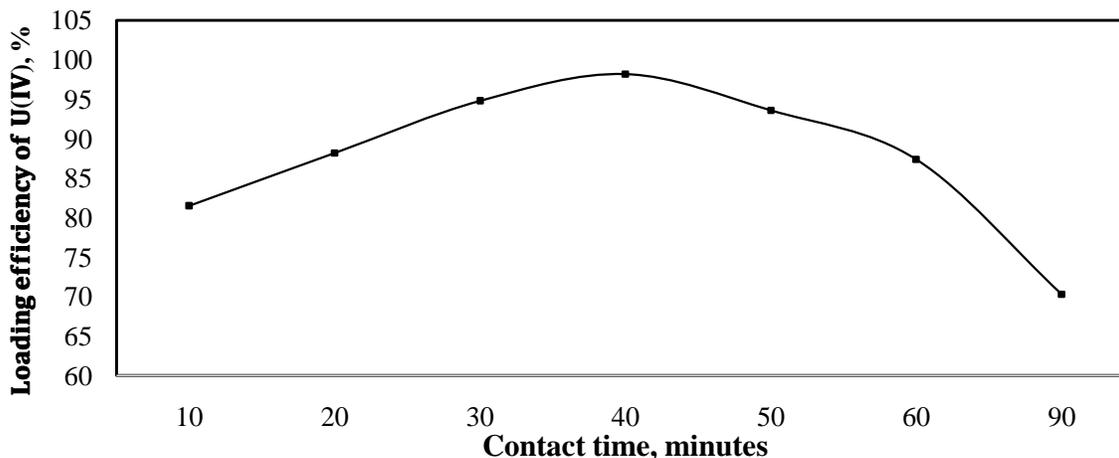


Figure 3. Effect of contact time on loading efficiency of U(IV), %

Effect of temperature: The effect of different temperatures from 25 to 60°C on the percentage of uranium efficiency was studied while keeping the other studied factors fixed; pH 0.2, 0.8 g EWS and 40 min contact time. Figure 4 showed that the maximum loading efficiency of 98.8% was attained at room temperature while increasing the temperature leads to increasing in the escaping tendency of the metal ions

from the solid phase (EWS) to the aqueous phase due to the weakness of adsorptive forces between the active sites of the adsorbents and the adsorbate species [39].

From the foregoing loading study, it can be concluded that, the effective loading conditions for loading efficiency about 98.8% of U(IV) content from the U synthetic solution was summarized as follows:

pH value	:	0.2
EWS amount	:	0.8g 50 mL ⁻¹
Contact time	:	40 min
Temperature	:	25°C

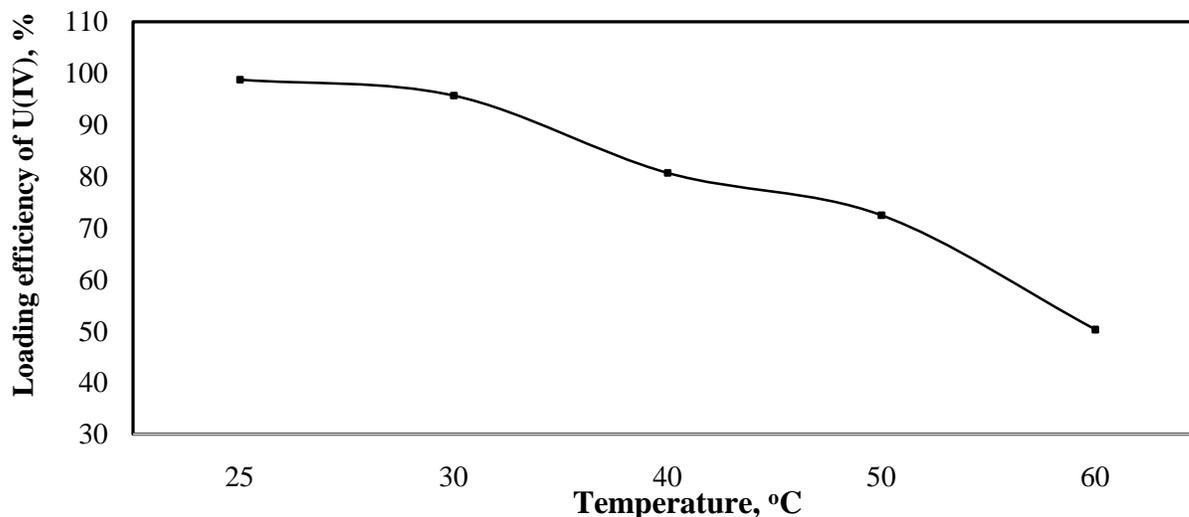
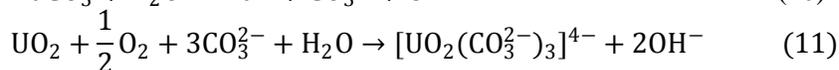


Figure 4. Effect of Temperature on loading efficiency of U(IV), %

Selective elution using oxidized alkaline NaCO₃ + NaHCO₃ mixture: The mentioned optimum loading conditions were applied on U synthetic solution containing some interfering elements. Those interfering elements should be a simulation to the concentrations found in studied phosphoric acid and phosphate rock; 20% of P (V), 2% Fe (III), 30% Ca (II), 0.02% Cr (III) and 0.02% V(V). After filtration and analysis, it was observed that U(IV) and Fe(II) which formed the cationic complexes, [U⁴⁺HPO₄²⁻]²⁺ and [Fe²⁺H₂PO₄¹⁻]¹⁺ respectively, were loaded in a percentage of 98.8 and 95, respectively. Where both of PO₄³⁻ and Ca²⁺ were not adsorbed by EWS. Thus, an oxidized alkaline solution [(NaCO₃+ NaHCO₃)/H₂O₂] was used for selective elution of U(VI) free from Fe(III) [40, 41]. Several effective parameters were studied to optimize the latter selective elution process such as, NaCO₃ concentration, NaCO₃ with NaHCO₃ mixture concentration, ratio of NaCO₃ with NaHCO₃, volume of 30% H₂O₂, contact time and temperature.

The effect of NaCO₃ concentration: This factor was studied by using 10 mL of Na₂CO₃ solution of different concentrations ranged from 0.5 M to 2.0 M and stirring for 10 minutes with addition of H₂O₂ in v/v (0.5mL10mL⁻¹) at room temperature. Data obtained in Figure 5 showed that U elution efficiency increased from 75.4% to 86.8%, in the meantime the maximum Fe elution efficiency did not exceed 0.2%. U elution efficiency by using NaCO₃ only cannot be increased more than 86.8% due to the liberation of OH⁻ anion which precipitates a portion of the eluted U as shown in equations (10 & 11) [42]. Thus NaHCO₃ should be added to remove OH⁻ to prevent the precipitation of U.



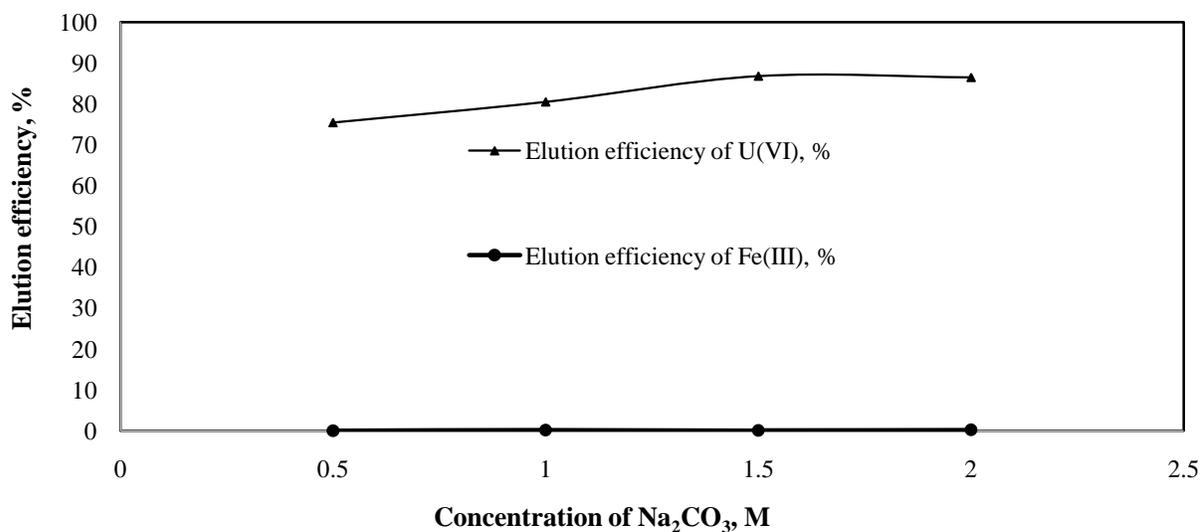


Figure 5. Effect of Na₂CO₃ concentration on elution efficiency, % U(VI) from EWS

Effect of [NaCO₃ + NaHCO₃] concentration: This factor was studied by using 10 mL of [NaCO₃+NaHCO₃] in addition ratio 3:1 solution of different concentrations ranged from 0.5 M to 2.0 M and stirring for 10 min with addition of H₂O₂ in v/v (0.5mL 10mL⁻¹) at room temperature. Data obtained in Figure 6 showed that U elution efficiency increased up to 92.4% at mixture solution concentration of 1M. On the other side there was no Fe eluted. The following equations (12, 13 and 14) explained why the addition of NaHCO₃ increased the U elution efficiency where its H⁺ ion in hydrolysis will equilibrium the OH⁻ anion liberated from the hydrolysis of NaCO₃ [42].

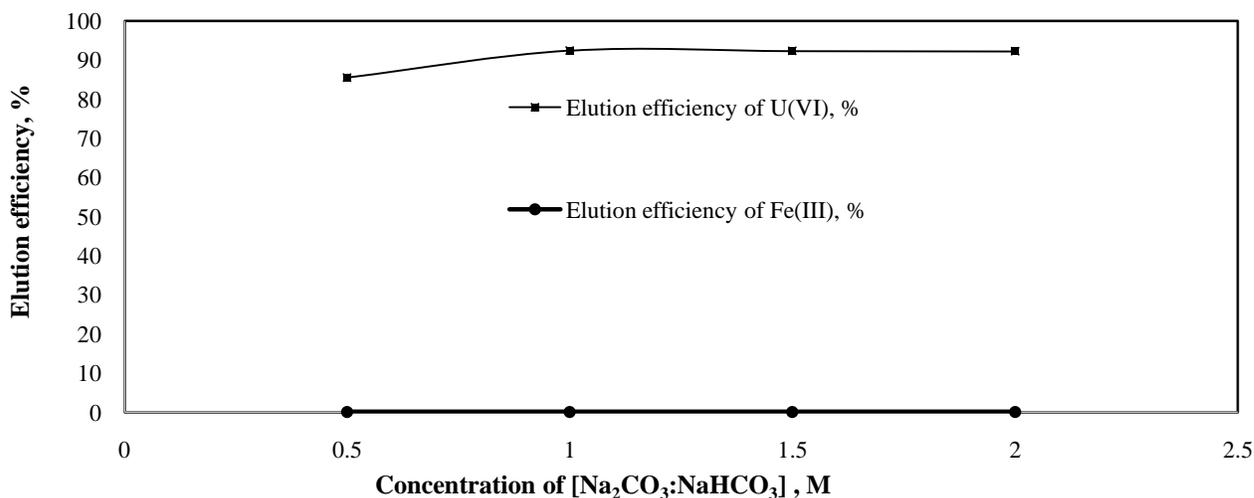
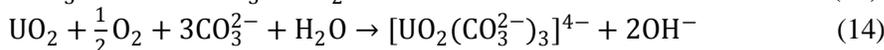


Figure 6. Effect of [NaCO₃+NaHCO₃] concentration on U(VI) elution efficiency (%) from EWS

Effect of $[\text{NaCO}_3 + \text{NaHCO}_3]$ addition ratio: This factor was studied by using 10 mL solution of 1M $[\text{NaCO}_3 + \text{NaHCO}_3]$ mixture with different addition ratios ranging from 1:1 to 4:1 and stirring for 10 minutes with addition of H_2O_2 in v/v ($0.5\text{mL } 10\text{mL}^{-1}$) at room temperature. Data obtained in Figure 7 showed that the most effective percentage U elution efficiency 93.4% was given at $[\text{NaCO}_3 + \text{NaHCO}_3]$ mixture ratio of 2:1 where further decreasing up to 4:1 has an opposite effect.

Effect of H_2O_2 addition v/v: This factor was studied by using 10 mL solution of 1M $[\text{NaCO}_3 + \text{NaHCO}_3]$ mixture and addition ratio of 2:1 and stirring for 10 minutes with addition of 30% H_2O_2 in different v/v ranged from (0.2 to 1 mL) 10mL^{-1} at room temperature. Data obtained in figure 8 indicated that increasing H_2O_2 addition v/v from (0.2 to 0.8 mL) 10mL^{-1} increases U elution efficiency from 91.4% to 96.5 while further increasing to ($1\text{mL } 10\text{mL}^{-1}$) has no effect.

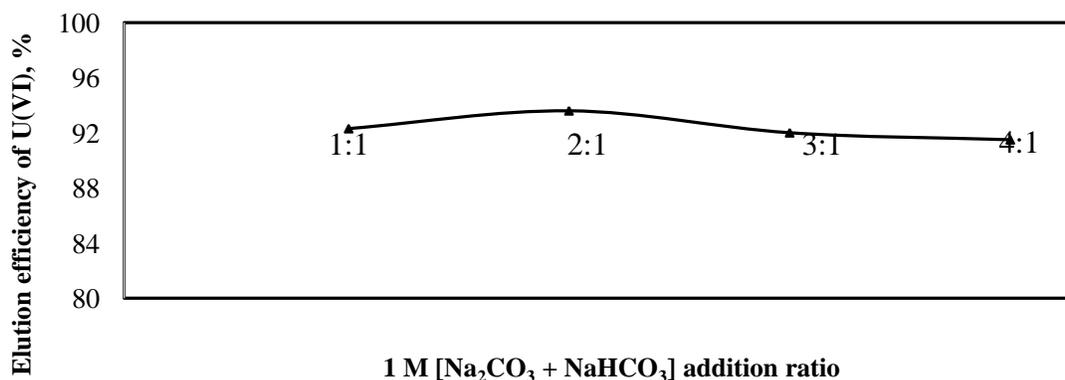


Figure 7. Effect of $[\text{NaCO}_3 + \text{NaHCO}_3]$ ratio on U(VI) elution efficiency (%) from EWS

Effect of contact time: At the optimum conditions boundary changing the contact time from 5 to 20 minutes, figure 9 reflected that increasing contact time up to 15 minutes increases U elution efficiency up to 97.8%. On the other hand further increasing in contact time decrease in the percentage elution efficiency of U(VI) was observed.

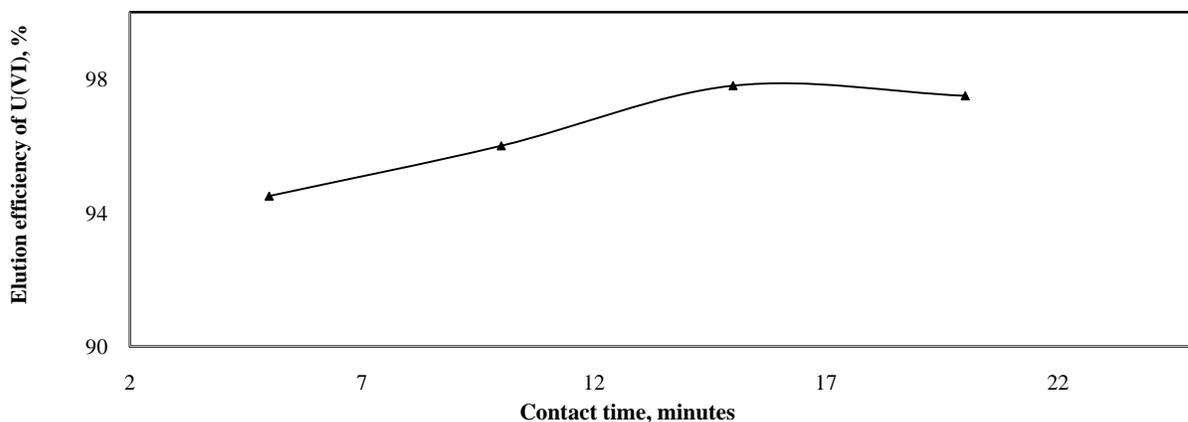


Figure 8. Effect of H_2O_2 addition v/v on U(VI) elution efficiency (%) from EWS

Effect of temperature: At the previous studied optimized the effect of temperature from $25\text{ }^\circ\text{C}$ to $55\text{ }^\circ\text{C}$ was studied. It was found that the maximum value of U elution efficiency 98.5% was reached at $45\text{ }^\circ\text{C}$, as shown in Figure 10. Increasing temperature more than $45\text{ }^\circ\text{C}$ leads to decrease in U elution efficiency due

to the conversion of NaHCO_3 to NaCO_3 a matter which leads to the liberation of OH^- anion which precipitates a portion of the eluted U [43].

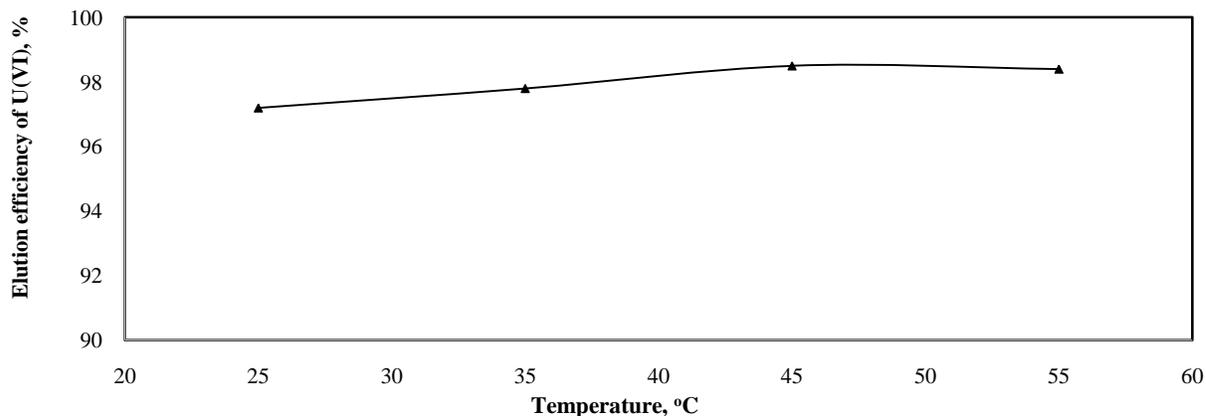


Figure 10. Effect of Temperature on U(VI) elution efficiency (%) from EWS

From the above study, a value 98.5% of the loaded U(VI) was eluted at the following summarized optimum conditions

$[\text{Na}_2\text{CO}_3 + \text{NaHCO}_3]$ concentration	:	1 M
1 M $[\text{Na}_2\text{CO}_3 + \text{NaHCO}_3]$ addition ratio	:	2:1
30% H_2O_2 addition ratio v/v	:	(0.8 mL 10 mL ⁻¹)
Contact time	:	15 min
Temperature	:	45°C

Standard application curve: By applying the above studied U(VI) extraction optimum conditions (loading and elution) upon different standard U(VI) solutions of concentrations ranging from 20 to 200 mg L⁻¹, it could be constructed a standard application curve, figure 11. From this curve it could be concluded the determination of U(VI) after extraction from phosphate solutions was succeeded in a percentage of 97.5% to 98% at U(VI) concentrations ranging from $\leq 10 \geq 100$ mg L⁻¹. on the other hand this successful percent decreased by using U(VI) solutions more than 100 mg L⁻¹ where it decreased to 85.7, 65 and 59% at 140, 180 and 200 mg L⁻¹, respectively. It was also concluded from this curve that the U(VI) detection limit by this method achieved 10 mg L⁻¹.

APPLICATIONS

After optimizing the factors affecting on both loading and elution of U from activated EWS to reach the maximum loading and elution efficiency to overcome the effect of the major of interfering elements P(V), Fe(III) and Ca(II) found in phosphoric acid and phosphate rocks after that the extracted U(VI) was determined using N₂-Laser Fluorimetric (UA-3) instrument. The controlled reference materials required for the present work are a commercial wet process phosphoric acid and two standards samples phosphate (1) & phosphate (2), and the other sample was already analyzed in ACME laboratories in Canada using ICP-MS as an advanced analytical tool. On the other side, the unknown application samples were collected from Abu Tartur Western Desert, El Sibaiya West Nile Valley, El Hamarwin Red Sea and Wadi Mishash East Luxor area. The present samples were treated as the following:

- (1) A weight of 0.5g of the quartered phosphate sample is placed in a glass beaker.
- (2) 20mL of 4M HNO_3 were added and the beaker was covered with watch glass.
- (3) The whole content was heated for 2 hours on a water bath at 70°C.
- (4) After filtration the filtrate is completed to a proper volume in a 100 mL volumetric flask.

- (5) An aliquot of 5mL was diluted up to volume 50 mL with the addition of 0.5 to 1 g of Zn metal to have a complete reduced U solution and adjusted to pH 0.2. The latter was directed to apply the extraction by using 0.8g of activated EWS with stirring for 40 min at 25°C. After saturation the U loaded EWS was mixed with 10 ml of 1M [Na₂CO₃+NaHCO₃] 2:1 addition ratio with adding 30% H₂O₂ solution in v/v % of 8% (0.8 mL/10 mL) and stirring for 15 minutes at 45°C.
- (7) U(VI) concentration on the eluted solution was determined by using N₂-Laser fluorimetric (UA-3) instrument, where the results were shown in Table (4).

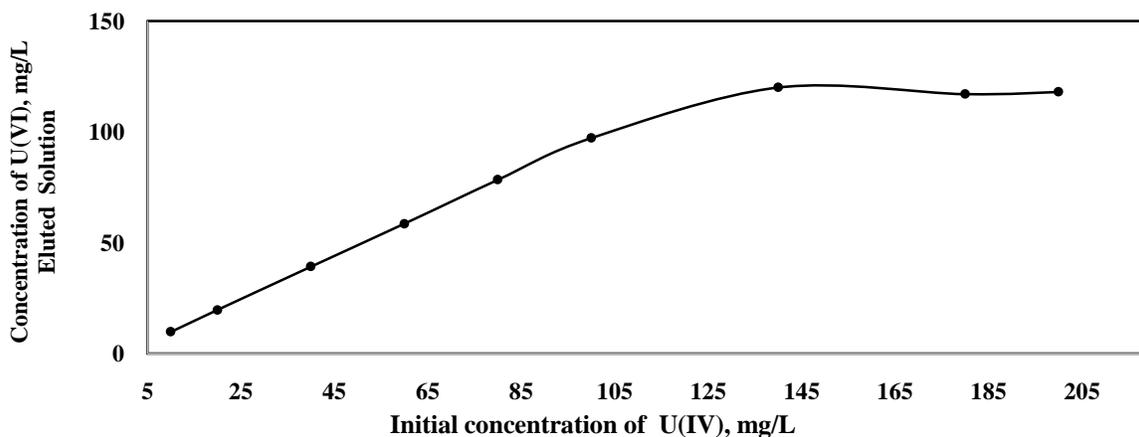


Figure 11. Standard application curve

Table (4): Application of Laser Fluorimetric determination of U(VI) in industrial grade phosphoric acid and phosphate rocks.

Samples	U concentration, (mg/L) (Published data)	Without separation, EWS	With separation, EWS		Reference
		U concentration, determined, (mg/L)	U(VI) concentration, (mg/L) with Zn metal	% Error	
Industrial Grade H ₃ PO ₄	73.5	25.2	71.5	2.7	[44]
Phosphoric acid (ACME) (ICP-MS)	125.9	55.5	123.5	1.9	[28]
Standard Phosphate (1)	88.6	32.6	85.3	3.7	[27]
Standard Phosphate (2)	87.7	34.8	85.8	2.16	[27]
Abu Tartur, Western Desert	20	6.8	18.7	6.5	[45]
El Sibaiya West, Nile Valley	54	18.5	50.5	6.48	[46]
El Hamarwin, Red Sea	94	32.4	91.4	2.76	[47]
Wadi Mishash, East Luxor	95	33.5	92.5	2.6	[48]

From the data gathered in table 4, it was concluded that the separation of U(IV) from phosphoric acid and phosphate rock samples using activated EWS after reduction of U(IV) with Zn metal for the determination of U using laser Fluorimetric technique UA-3 which give a good values of accuracy and precision compare with the results obtained without separation. Statistical calculations were carried out for Phosphate (ACME) (ICP-MS) and results obtained are: Sd (Standard Division) = 0.364, SE (Standard Error) = 0.163 and (Relative Standard Division) RSD = 0.294.

High Lights:

- 1- Laser Fluorimetric determination of the complete reduced U(IV) using Zn metal.
- 2- Applied on industrial grade phosphoric acid and phosphate rocks.
- 3- Separation using a low cost natural cationic adsorbent of Egyptian white silica sand (EWS).
- 4- The determination process was performed after prior separation of cationic uranyl complex.
- 5- This method was applied to overcome the interfering problems of P(V), Fe(III) and Ca(II). For maximum loading efficiency.
- 6- The adsorption parameters such as pH, amount of adsorbent, contact time, temperature and initial U(IV) concentrations were investigated via batch process.
- 7- On the other hand the effective elution factors such as eluting agents, ratio of NaCO₃ with NaHCO₃, volume of 30% H₂O₂, contact time and temperature were also investigated.

A selective elution of oxidized U(VI) was carried out by using 1M mixture of NaCO₃ and NaHCO₃ solution in the presence of (0.8 mL 10 mL⁻¹)

CONCLUSIONS

This method for U determination showed be in good accuracy and selectivity, thus the U(IV) selective adsorbent EWS was used. The optimum loading conditions for U(IV) loading efficiency of 98.8% were 0.8g of activated EWS with stirring for 40 minutes at 25°C from the phosphoric acid and phosphate rocks leaving behind P(V), Fe(III) and Ca(II). After saturation the U(IV) loaded EWS was mixed with 10 ml of 1M [Na₂CO₃+NaHCO₃] 2:1 addition ratio with adding 30% H₂O₂ solution in v/v % of 8% (0.8mL 10mL⁻¹) and stirring for 15 min at 45°C to achieve 98.5% of U(VI) elution efficiency. The maximum experimental U loading capacity (75 mg/g) was attained at the resulted optimum loading and elution conditions. Application on different standard phosphate samples of concentration ranging from ≤ 10 ≥ 100 mg/L reflects an accuracy ranging from 97.5% to 98%. The relative standard deviation (RSD) for U(VI) determination of 10 and 100 mg L⁻¹ was found to be 0.75 and 0.7 respectively after 5 repeated determinations; percent error for U determination from phosphoric acid and phosphate rocks was 3.6%.

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