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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 Na_2CO_3 *with* $NaHCO_3$*, volume of 30%* H_2O_2*, contact time and temperature were also investigated. A selective elution of oxidized U(VI) was carried out by using 1mol* L^{-1} *mixture of* Na_2CO_3 *and* $NaHCO_3$ *solution in the presence of (0.8 mL 10* mL^{-1}*) of 30%* H_2O_2 *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 Elution.

INTRODUCTION

Uranium 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 sources 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].

The determination of U at various stages of the nuclear fuel cycle is one of the essential requirements in 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, 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 [4].

Fluorimetric determination of U is very popular due to its high sensitivity and specificity [5], and it is widely used for the determination of U in a variety of geological samples [6]. Majority of the reported works [7] 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 [6]. 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 ($\leq 10\ \mu g\ g^{-1}$).

The presence of impurities in WPPA is the essential reason behind at least 95% of the produced acid is directly used as fertilizers and not in other important applications as food stuff, pharmaceutics and sugar industries [8].

Solvent extraction solely was found to be a successful process for industrial recovery of U from phosphates, although other methods such as ion-exchange [9], membrane separation [10] and precipitation [11] were also investigated. Synergistic mixtures of D2EHPA and TOPO or D2EHPA and DBBP were reported as suitable for extraction of U from WPA [12].

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 2.5mol L^{-1}in magnesium nitrate and 0.1mol L^{-1}in nitric acid. U and Th are eluted consecutively with 6.6molL^{-1}nitric acid and 0.1mol L^{-1}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 [13].

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 $1.2\ x10^4\ l\cdot mol^{-1}\cdot cm^{-1}$. Beer's law was obeyed from 0.6 to 15.0 µg mL^{-1}U (VI). This method was applied successfully to the analysis of phosphate fertilizers with concentration of 45% P_2O_5[14].

Recently silica is a widely used uranium extractant especially the white sand due to its adsorption properties, high surface area and porosity [15]. 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 chemisorptions of transition and heavy metals [16].

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).

$$m(SiOH) \leftrightarrow m(SiO^-) + mH^+ \qquad (1)$$

$$M^{n+} + m(SiO^-) \leftrightarrow M(OSi)_m^{(n-m)+} \quad (2)$$

The overall reaction can thus be represented as:

$$M^{n+} + m(SiOH) \leftrightarrow M(OSi)_m^{(n-m)+} + mH^+ \quad (3)$$

Where M^{n+} is the metal ion with n+ charge, SiOH is the silanol group on SiO_2 surface, mH^+ is the number of protons released.

Finely, the main target of this work is the usage of EWS as a natural cationic exchanger which is a low cost adsorbent for the reduced U (IV) from industrial grade phosphoric acid and phosphate rocks. As well as 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 $UO_2(NO_3)_2.6H_2O$, $FeCl_3.6H_2O$, $CaCl_2$, Na_2CO_3, $NaHCO_3$, H_3PO_4, H_2SO_4, HCl, NaCl, NH_4OH, $Cr(NO_3)_3.9H_2O$ and $NH_4VO_3$are analytical reagents grade. A stock solution of 10000 mg L^{-1} U solution was prepared by dissolving 2.11 g of $UO_2(NO_3)_2.6H_2O$ salt in a 100 mL 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 mol L^{-1} HNO_3 to 0.1 mol L^{-1} free acidic solution. A mixed stock solution containing 20% of P (V), 2% Fe (III), 30% Ca (II), 0.02% Cr (III) and 0.02% V(V) was prepared.

The natural Egyptian white silica sand (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 6 mol L^{-1}HCl solution for 24 hours to remove any gangue materials. After filtration and washing with suitable volume of double distilled water, it was dried at 110°C for 2 hours and then stored under vacuum for several days at room temperature. The chemical composition of EWS was shown elsewhere [17].

Preparation of the activated EWS: A weighed 5 g portion of the treated and dried EWS was activated by washing with a 50 mL mixed solution of the following; 5 mL of 0.5 mol L^{-1} NaCl, 3mL of 0.3mol L^{-1} NH_4Cl, 2 mL of 0.015mol L^{-1} EDTA and 2 mL of 0.015 mol L^{-1} tartaric acid [18].

Instrumentations: N_2-Laser Fluorimetric Technique, (UA-3), model Scintrex Canada, was used for U determination. An intense excitation source, N_2-Laser, at 337 nm was applied for exciting U. This instrument was periodically calibrated, starting from 0.01 mg L^{-1}U. Double Beam UV-Visible Spectrophotometer, model UNICAM, England was used. The optical system was checked automatically and the instrument was periodically calibrated, using Arsenazo III [19]. ApH-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}): 50 mL standard solutions of different concentrations ranged from 200 to 500 mg L^{-1}U(IV) 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:

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

Where V (mL) and m(g) are the volumes of each solutions and the mass of adsorbent or cationic exchanger EWS respectively [20].
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, the contact time varied from 10 to 90 minutes, temperature from 25-60^{o}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 added 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:

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

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

Selective elution step using oxidized Na_2CO_3 with $NaHCO_3$ mixture: To optimize the U elution step several effective parameters; Na_2CO_3 with $NaHCO_3$ mixture concentration, ratio of Na_2CO_3 to $NaHCO_3$, volume of 30% H_2O_2, contact time and temperature were studied. U(VI) in the elute (desorbed) solution was determined using N_2-Laser Fluorimetric Technique (UA-3) to calculate its elution efficiency (%) as shown in equation (6).

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

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

Determination method: U(VI) determined using N_2-Laser Fluorimetric Technique (UA-3) as follow: 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 $NH_4H_2PO_4$ + 50 mL H_3PO_4 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 [21, 22].

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 are shown in table 1.

This table shows that increasing P(V) ion concentrations from 10-20 % enhanced U concentration from 100 to 165, 188 and 210 mg L^{-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},

Table 1. Effect of interfering metal ions on the direct determination of 100 mg L^{-1} U (IV) using N_2-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^{-1}	Fe(III), % added	U(IV) conc., mg L^{-1}	Ca(II), % added	U(IV) conc., mg L^{-1}	20% P(V) 2% Fe(III) 30% Ca(II) 0.02% Cr(III) 0.02% V(V)	U(IV) conc., 25.8 mg L^{-1}
10	165	1	71	20	80		
15	188	1.5	50	25	74		
20	210	2	22	30	66		

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 concentration. The presence of P (V), Fe(III) and Ca(II) ions leads to the formation of $[CaUO_2(PO_4^{3-})_2]^{2-}$as illustrated in equation (7) which inhabit the fluorescence of U causing quenching effect. So, U determination in phosphate solutions should be performed after extraction.

$$UO_2^{2+} + Ca^{2+} + PO_4^{3-} \rightarrow [CaUO_2(PO_4^{3-})_2]^{2-} \qquad (7)$$

For this purpose a natural cationic exchanger EWS was used during the investigation of both loading and elution process. The use 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 & 9) [25-27].

$$U^{4+} + HPO_4^{2-} \rightarrow [U^{4+}HPO_4^{2-}]^{2+} \qquad (8)$$

$$UO_2^{2+} + 2HPO_4^{2-} \rightarrow [\,UO_2^{2+}(HPO_4)_2^{4-}]^{2-} \qquad (9)$$

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 minutes. After filtration and determination of U in the filtrates it shows that the average U capacity is 75mg g^{-1} of EWS as shown table 2.

Table 2. Loading capacity of EWS, (mg g^{-1})

Initial U(IV) conc., mg L^{-1}	**Loading capacity (mg g^{-1})**
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 present100 mg L^{-1} 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 (Fig.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 [28].

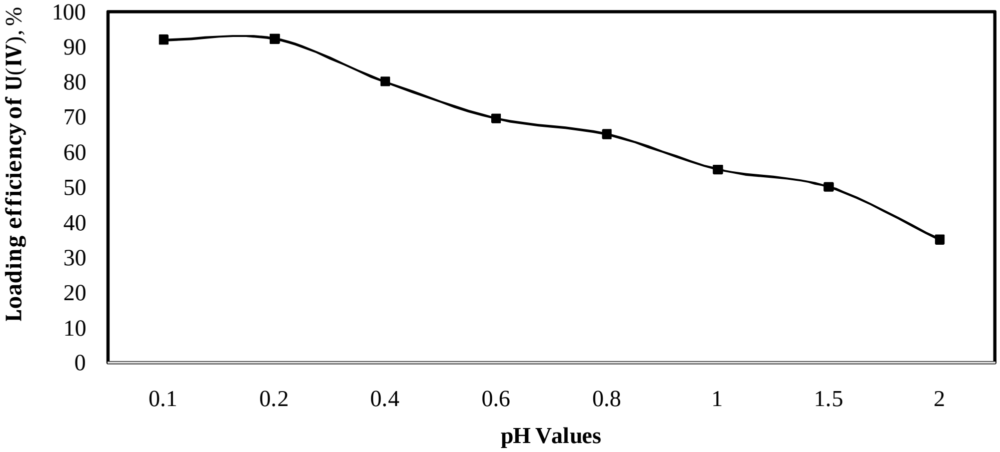

Figure 1. Effect of pH values on loading efficicency of U(IV), %

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 100 mg L^{-1}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 [29].

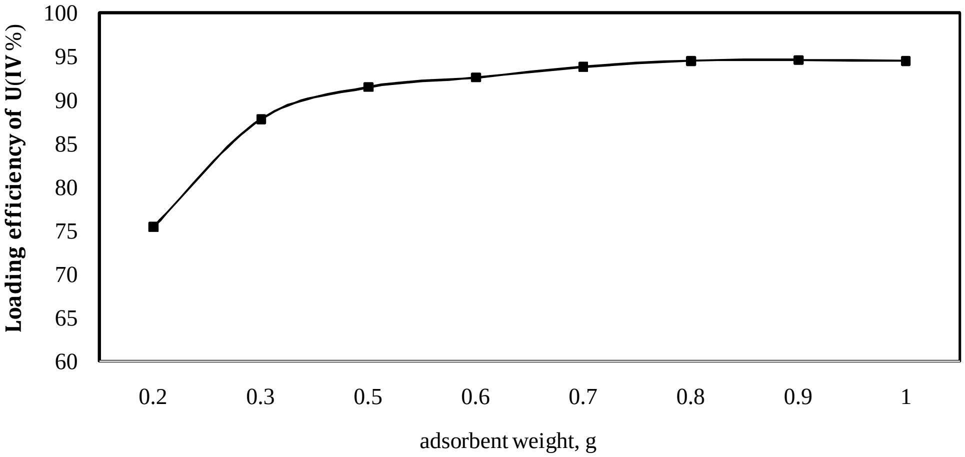

Figure 2. Effect of adsorbent weight (g) on loading efficiency of U(IV), %

Effect of contact time: This effect was studied by mixing 0.8g of EWS with 50 mL of100 mg L^{-1} U standard solution adjusted to pH 0.2 and stirring for different periods of time ranging from 10 to 90 minutes. Obtained data illustrated in (Fig.3) revealed that increasing the stirring time from 10 to 40 minutes increases U percentage loading efficiency up to 98.2%; while further increasing up to 90 minutes decreases the latter up to 70.3%. This may be due to regeneration of some loaded U by increasing the contact time.

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 minutes contact time. (Fig.4) shows 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 [30].

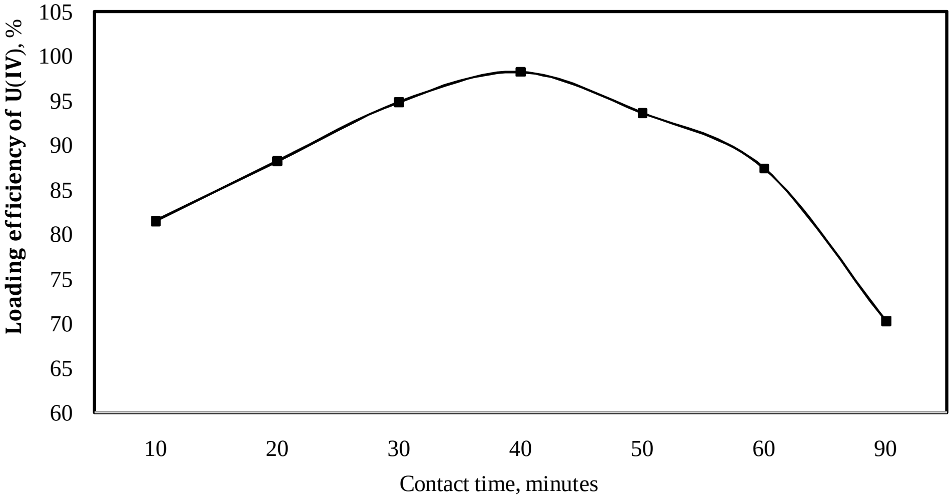

Figure 3. Effect of contact time on loading efficiency of U(IV), %

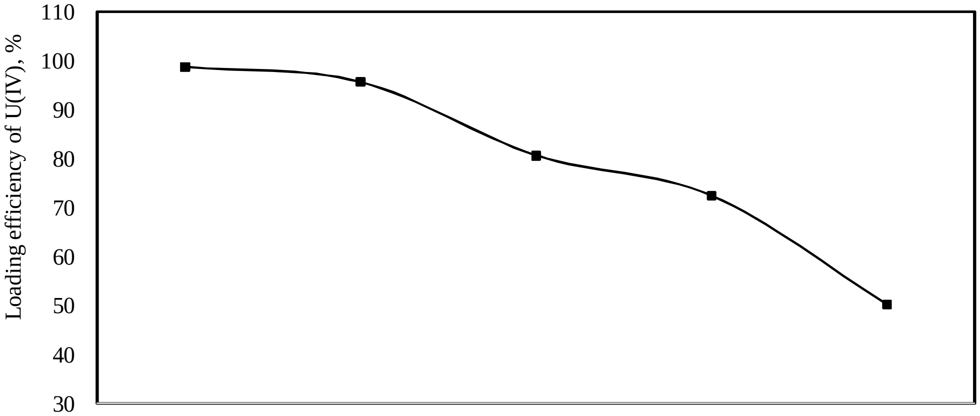

Figure 4. Effect of Temperature on loading efficiency of U(IV), %

After filtration and analysis, it was observed that U(IV) and Fe(II) which formed the cationic complexes, $[U^{4+}HPO_4^{2-}]^{2+}$ and $[Fe^{2+}H_2PO_4^{-}]^{+}$ respectively, were loaded in a percentage of 98.8 and 95, respectively. Where both of $PO_4^{3-}$and Ca^{2+} were not adsorbed by EWS. Thus an oxidized alkaline solution $[(NaCO_3+ NaHCO_3)/H_2O_2]$ was used for selective elution of U(VI) free from Fe(III) [31, 32].The optimum loading conditions are a pH value of 0.2, EWS amount of 0.8g/50 mL, a contact time of 40 minutes at room temperature.

Selective uranium elution using oxidized alkalineNa_2CO_3 + $NaHCO_3$ mixture: Several effective parameters were studied to optimize the selective uranium elution process such as,Na_2CO_3 concentration,Na_2CO_3 with $NaHCO_3$ mixture concentration, ratio of Na_2CO_3 with $NaHCO_3$, volume of 30% H_2O_2, contact time and temperature.

Effect of Na_2CO_3 concentration: This factor was studied by using 10 mL of Na_2CO_3 solution of different concentrations ranged from 0.5 mol L^{-1} to 2.0 mol L^{-1} and stirring for 10 minutes with addition of H_2O_2 in v/v (0.5mL/10mL) 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 Na_2CO_3 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) [33**]**. Thus $NaHCO_3$ should be added to remove OH^- to prevent the precipitation of U.

$$Na_2CO_3 + H_2O \rightarrow 2Na^+ + HCO_3^- + OH^- \qquad (10)$$

$$UO_2 + \frac{1}{2}O_2 + 3CO_3^{2-} + H_2O \rightarrow [UO_2(CO_3^{2-})_3]^{4-} + 2OH^- \qquad (11)$$

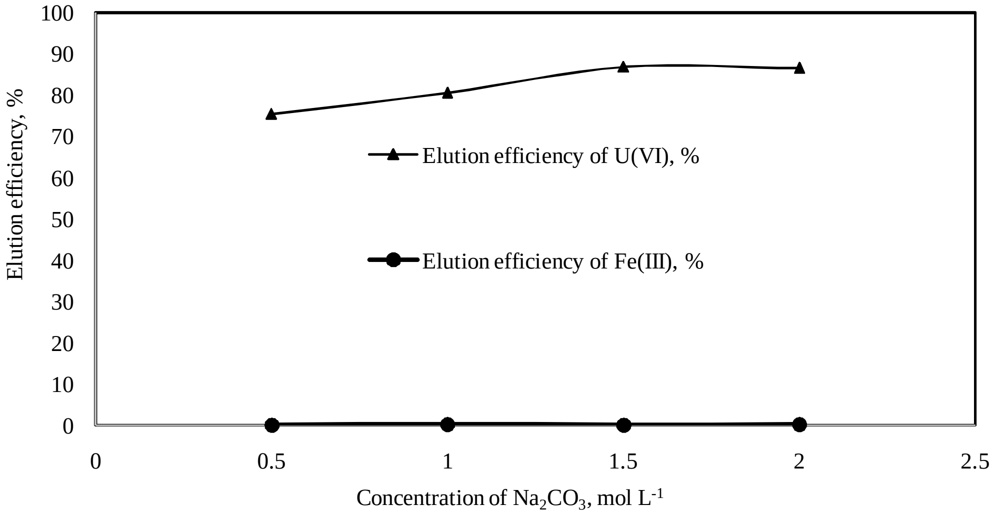

Figure 5. Effect of Na_2CO_3 concentration on elution efficiency, % U(VI)from EWS

Effect of [Na_2CO_3 + $NaHCO_3$] concentration: This factor was studied by using 10 mL of [Na_2CO_3+$NaHCO_3$] in addition ratio 3:1 solution of different concentrations ranged from 0.5 mol$L^{-1}$to 2.0 mol $L^{-1}$and stirring for 10 minutes with addition of H_2O_2 in v/v (0.5mL/10mL) at room temperature. Data obtained in (Fig.6) showed that U elution efficiency increased up to 92.4% at mixture solution concentration of 1molL^{-1}. On the other side there was no Fe eluted. The following equations (12, 13 & 14) explained why the addition of $NaHCO_3$ increased the U elution efficiency where its H^+ ion in hydrolysis will equilibrium the OH^- anion liberated from the hydrolysis of Na_2CO_3 [33].

$$NaHCO_3 + H_2O \rightarrow Na^+ + HCO_3^- \qquad (12)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad (13)$$

$$UO_2 + \frac{1}{2}O_2 + 3CO_3^{2-} + H_2O \rightarrow [UO_2(CO_3^{2-})_3]^{4-} + 2OH^- \quad (14)$$

Effect of [Na_2CO_3 + $NaHCO_3$] addition ratio: This factor was studied by using 10 mL solution of 1mol L^{-1}[Na_2CO_3+$NaHCO_3$] 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 (0.5mL/10mL) at room temperature. Data obtained in figure.7 showed that the most effective percentage U elution efficiency 93.4% was given at [Na_2CO_3+ $NaHCO_3$] 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 10mL solution of 1mol L^{-1} [Na_2CO_3+$NaHCO_3$] mixture and addition ratio of 2:1and stirring for 10 minutes with addition of 30% H2O2 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)/10 mL increases U elution efficiency from 91.4% to 96.5% while further increasing to (1mL 10mL^{-1}) has no effect.

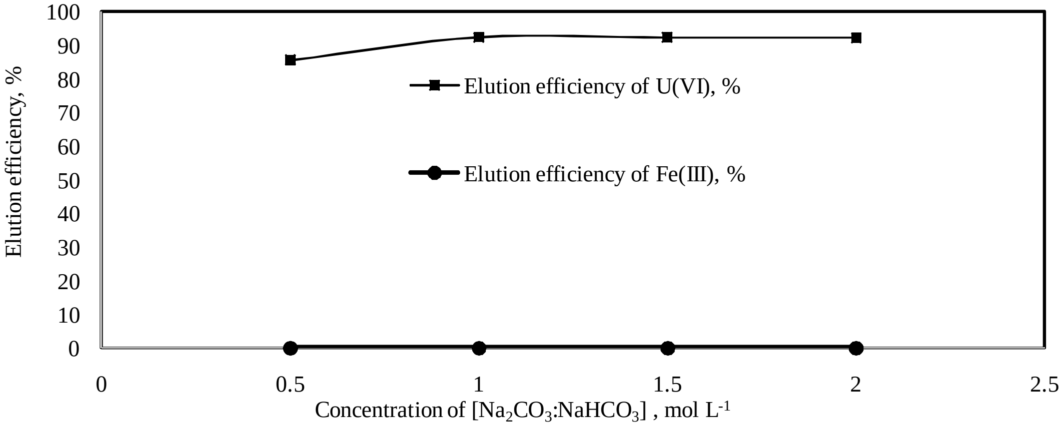

Figure 6. Effect of [Na_2CO_3+$NaHCO_3$] concentration on U(VI)elution efficiency (%)from

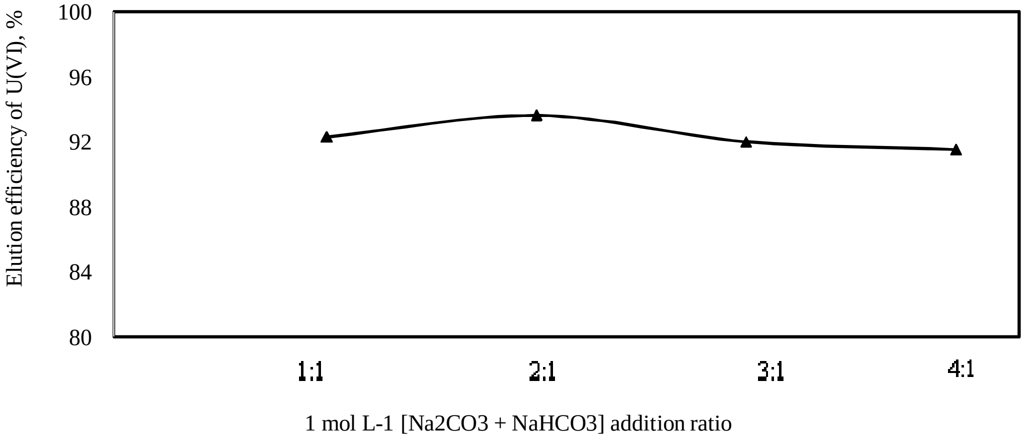

Figure 7. Effect of [Na_2CO_3 + $NaHCO_3$] addition ratio on U(VI)elution efficiency (%)from EWS

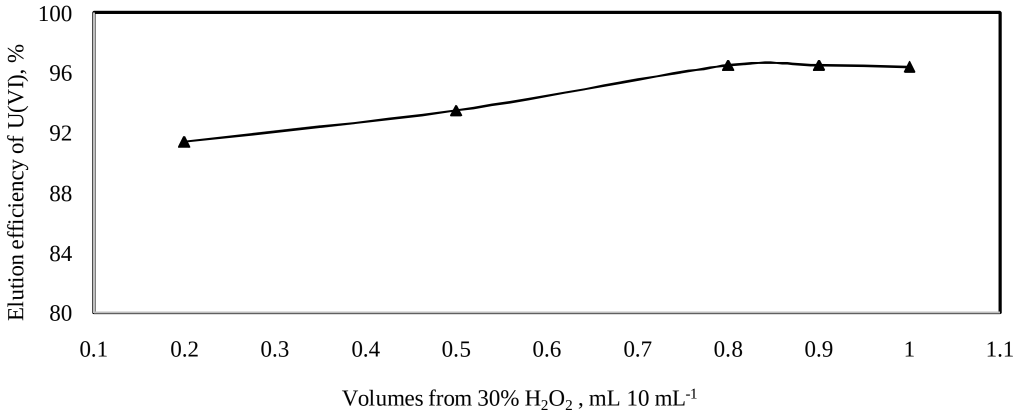

Figure 8. Effect of H_2O_2 addition v/v on U(VI)elution efficiency (%)from EWS

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.

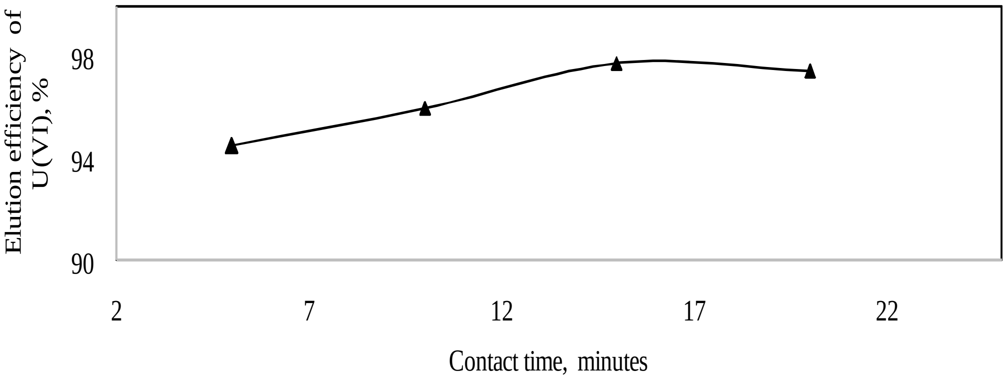

Figure 9. Effect of contact time on U(VI) elution efficiency (%)from EWS

Effect of temperature: At the previous studied optimized the effect of temperature from 25ºC to 55ºC was studied. It was found that the maximum value of U elution efficiency 98.5% was reached at 45ºC, as shown in figure.10. Increasing temperature more than 45^{o}C leads to decrease in U elution efficiency due to the conversion of $NaHCO_3$ to Na_2CO_3 a matter which leads to the liberation of OH^- anion which precipitates a portion of the eluted U [34]. From the above study, the value 98.5% of the loaded U(VI) is eluted by 1molL^{-1} [Na_2CO_3+$NaHCO_3$] (mixed ratio) 2:1, 30% H_2O_2 oxidizing solution in v/v % of 8% and stirring time of 15 minutes at 45^{o}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.

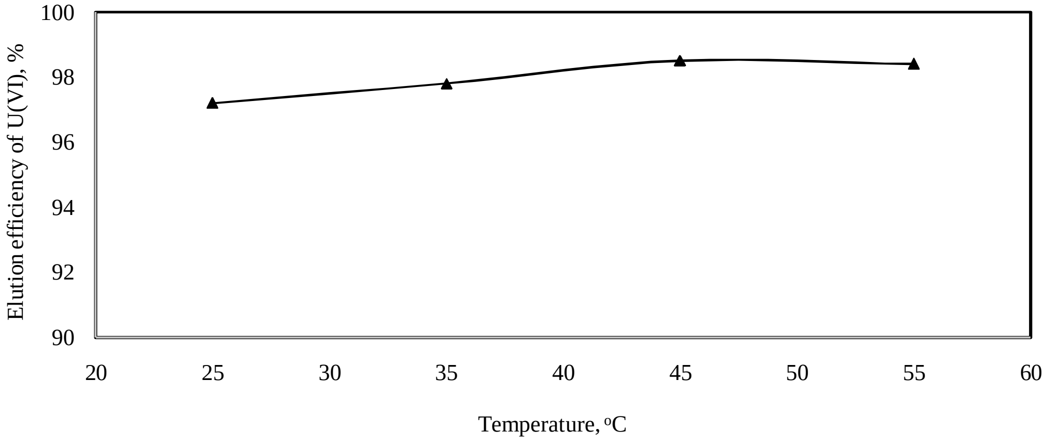

Figure 10. Effect of Temperature on U(VI)elution efficiency (%)from EWS

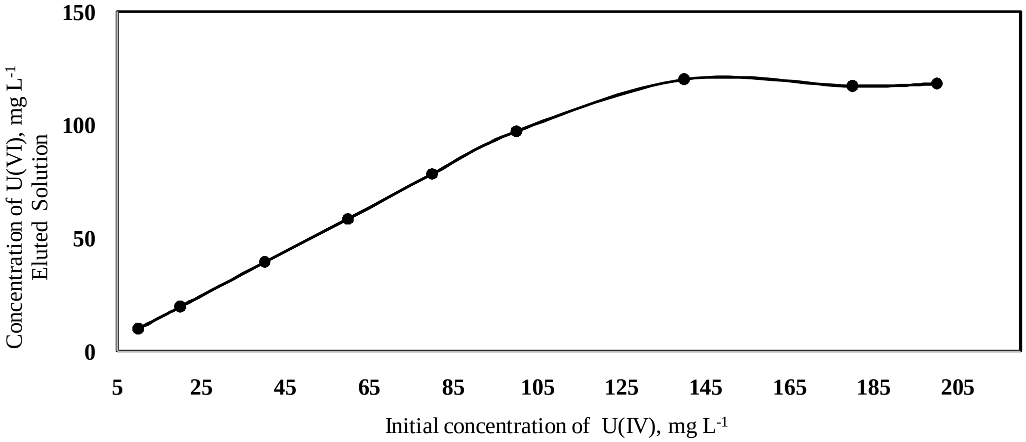

Figure 11. Standard application curve

APPLICATIONS

By application of this method on different standard and unknown phosphoric acid and phosphate rock samples the data gathered in table.3 shows that the separation of U(IV) using activated EWS after reduction of U(VI) 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.

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 N_2-Laser fluorimetric (UA-3) instrument.

Table 3. Application of Laser fluorimetric determination of U(VI) in industrial grade phosphoric acid and phosphate rocks.

Samples	U concentration, (mg L^{-1}) (Published data)	Without separation, EWS	With separation, EWS		Reference
		U concentration, determined, (mg L^{-1})	U(VI) concentration, (mg L^{-1}) with Zn metal	% Error	
Industrial Grade H_3PO_4	73.5	25.2	71.5	2.7	[35]
Phosphate (ACME) (ICP-MS)	125.9	55.5	123.5	1.9	[24]
Standard Phosphate (1)	88.6	32.6	85.3	3.7	[23]
Standard Phosphate (2)	87.7	34.8	85.8	2.16	[23]
Abu Tartur, Western Desert	20	6.8	18.7	6.5	[36]
El Sibaiya West, Nile Valley	54	18.5	50.5	6.48	[37]
El Hamarwin, Red Sea	94	32.4	91.4	2.76	[38
Wadi Mishash, East Luxor	95	33.5	92.5	2.6	[39]

The controlled reference materials required for the present work were a commercial wet-process phosphoric acid (P_2O_5 = 39.5%), which was kindly received from Abu-Zaabal, Cairo, Egypt, two standard samples [phosphate (1) & phosphate (2) [23] and the phosphate sample already analyzed in ACME laboratories in Canada using ICP-MS as an advanced analytical tool [24] 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.

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). 20 mL of 4mol L^{-1} 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 with10 mL of 1molL^{-1}[Na_2CO_3+$NaHCO_3$] 2:1 addition ratio with adding 30% H_2O_2 solution in v/v % of 8%(0.8 mL/10 mL) and stirring for 15 minutes at 45°C.
(6). U(VI) concentration on the eluted solution was determined by using N_2-Laser flourimetric (UA-3) instrument.

CONCLUSIONS

Determination process of U(VI) from phosphoric acid and phosphate rocks aqueous solutions should be in good accuracy and more selectivity, thus the selective U(VI) adsorbent EWS was used in the present study. The obtained data emphasized that the optimum loading conditions for the loading efficiency of 98.8% were 0.8 g of activated EWS with the stirring time of 40 minutes and temperature of 25°C. While the applied optimum elution conditions were 1mol L^{-1} [Na_2CO_3+$NaHCO_3$] (mixed ratio) 2:1, 30% H_2O_2 oxidizing solution in v/v % of 8% and stirring time of 15 minutes at 45°C to achieve 98.5% of U(VI) elution efficiency. The maximum experimental Uranium loading capacity

(75 mg g^{-1}) was attained at the resulted optimum loading and elution conditions. Application of this U(VI) determination method on different standard phosphate solutions of concentration $\leq 10 \geq 100$ mg L^{-1} reflects an accuracy ranging from 97.5% to 98%. The (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. The percent error for this U(VI) determination process when applied on different phosphoric acid and phosphate rocks aqueous solutions not exceed 3.6%.

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