



RESEARCH ARTICLE

Advanced Method for Extraction of Uranium (VI) From Synthetic and Egyptian Phosphoric Acid using Modified Carbon

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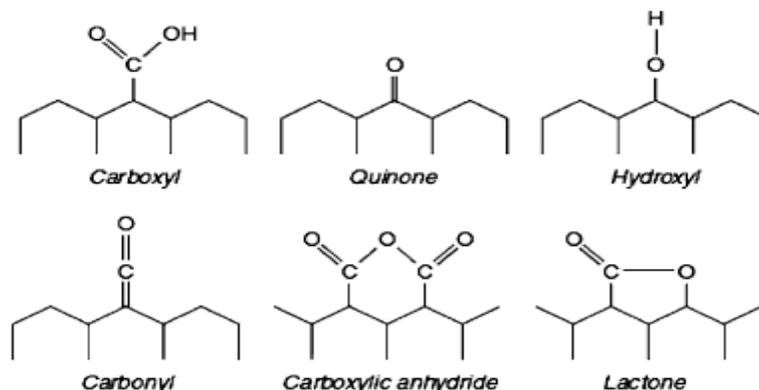
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The adsorption of uranium (VI) from phosphoric acid onto modified carbon has been investigated using a batch adsorber. The parameters that affect the uranium adsorption such as stirring time, carbon pH, solution pH, phosphoric acid concentration, temperature, modified carbon to phosphoric acid phase ratio and uranium oxidation state have been studied. Also, the factors affect on the modification of carbon such as the solvent concentration and soaking time were investigated. The thermodynamic parameters ($\Delta H_{ads.} = -51.60$ and $-53.70 \text{ kJ mol}^{-1}$ while $\Delta S_{ads.} = -166.07$ and $-170.03 \text{ J mol}^{-1}\text{K}^{-1}$) showed the exothermic heat of adsorption and the feasibility of the process.

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1-Introduction

Nuclear power is derived from uranium, which has no significant commercial use other than as a fuel for electricity generation. For this reason the recovery, concentration and purification of uranium are of great importance. Because of the expected shortage of uranium in the near future, further research is to be directed to the recovery of uranium from non conventional resources such as sea water, industrial waste waters and phosphoric acid (Kabay. N and Egawa. H, 1993; Mellah. A, 2006). Therefore, many processes have been proposed for uranium (VI) removal from solutions. Chemical precipitation, ion exchange, solvent extraction and adsorption are the most commonly used methods; each has its merits and limitation in application. The adsorption of uranium from Egyptian crude phosphoric acid was investigated (Morsy. A. M. A. and Hussein A. E. M., 2011) it was found that treatment with nitric acid oxidized the surface of the activated carbon and significantly increased the adsorption capacity for uranium in acidic solutions. The surface groups play a key role in the surface chemistry of activated carbon as they are important for adsorption from aqueous solutions (Noh. J. S. and Schwarz. J. A., 1990) the acidic surface shows cation exchange properties in aqueous solutions. The surface groups shown in the following figure are acidic groups.



The separation and purification processes based on adsorption technique are important in nuclear industry (Othmer Kirk, 1997) where activated carbon is often used for the separation of ions from the solutions due to its selective adsorption stability and high purity. Adsorption of uranium (VI) onto various solids is important from purification, environmental and radioactive waste disposal points of view (Mellah. A. et al., 1992; Saleem. M., 1992). Contributions in this regard have been made by many researchers who have utilized a number of materials such as activated charcoal (Kutahyali. C. and Eral. M., 2004), olivine rock (Aamrani. F. Z. El, L. Duro and Pablo. J. de, 2002), coir pith (Parab. H. and Joshi. S., 2005), smectites (Chrisholm. C. J. et al., 2004), bentonite (Missana. T., 2004; Chegrouche. S., 1997), montmorillonite (Boualia. A., 1993; Mellah. A. and Chegrouche. S., 2005; Catalano., J. G et al., 2005), biomass (Psareva. T. S. et al., 2005; Kalin. M. et al., 2004), goethite (Missara. T. et al., 2003) and polymeric materials (Walters. M., 2008) The purpose of this work is to study the feasibility of uranium (VI) adsorption onto modified carbon from both synthetic and Egyptian wet process phosphoric acid.

2- Experimental

2.1- Activated carbon

The granular activated carbon used was supplied by Ubichem Limited, UK, size of 3-6 mm. It was modified by soaking it in D2EHPA 2.86 M for 60 min and then filtered before use for extraction of uranium from phosphoric acid solutions.

2.2- Reagents

Stock solution of uranium (1000 ppm) was supplied from AccuStandard, USA. Two types of phosphoric acid were used in this work, first is a standard stock of uranium (60 ppm) dissolved in pure phosphoric acid (44 % P_2O_5), second type is Egyptian wet process phosphoric acid which has the following components ($P_2O_5 = 44.0\%$, U = 40 ppm, Fe = 2.6%, Cu = 0.0012%, Cd = 0.001%, F = 0.7%) was supplied from Abu-Zaabal Co., Cairo, Egypt. Abu Tartur bentonite was used. All chemicals and reagents were of A.R. grade and used without further purification. Fe was determined by GBC 932- AAS.

2.3- Batch adsorption experiments

The experiments were carried out by batch technique. Adsorption experiments were carried out in mechanically agitated beakers containing 50 mL of phosphoric acid containing uranium 60 mg U/L with modified carbon to aqueous phase ratio ranged from 2.0 to 0.2, the vessel was immersed in a water bath controlled at different temperatures. The content was agitated with a constant stirring rate of 400 rpm, at preset times after stirring the modified carbon was separated from the supernatant aqueous samples (3 mL) were taken, and the concentration was analyzed. The amount of adsorbed uranium was determined from the difference between the initial and final concentrations of uranium in aqueous solution using spectrophotometer.

2.4- Calculations

The percent adsorption (Y%) and the distribution coefficient D were calculated from the equations:

$$\text{Yield (Y \%)} = \frac{[U]_{\text{feed acid}} - [U]_{\text{raffinate}}}{[U]_{\text{feed acid}}} \times 100$$

The distribution ratio (D) was calculated from the equation:

$$D = \frac{\text{Total concentration of uranium in organic phase}}{\text{Total concentration of uranium in aqueous phase}}$$

3- Results and discussion

We have investigated the parameters which affect the uranium adsorption such as carbon pH and soaking time for carbon modification with D2EHPA, also factors affect the uranium adsorption from both synthetic solution and Egyptian phosphoric acid such as phosphoric acid concentration, modified carbon to aqueous phase ratio, organic solvent concentration, stirring time, uranium oxidation state, adsorption temperature, uranium isotherm and solution pH.

3.1- The factors affect the modification of the carbon with D2EHPA

3.1.1- Effect of carbon pH

In practice, carbon pH presumably affects the adsorption of uranium. The uranium adsorption is markedly suppressed at carbon pH higher than 8.0, however by decreasing the carbon pH, adsorption of uranium decreases and reaches its minimum at pH 2.0. Hence it can be demonstrated that, the combination of D2EHPA solvent with the basic carbon surface (pH = 8.0) leaving the free hydrogen ions is more suitable than its combination with the acidic carbon (pH = 2.0) due to the positive charge nature of the basic carbon which combined with the negative charge present on the solvent. On the other hand, the uranium adsorption efficiency reached 68.8 % by using modified basic carbon while it reached 5.0% only using modified acidic carbon.

3.1.2- Effect of soaking time

The effect of soaking time on the adsorption process was studied in the range 1.0 – 60 min. The operating conditions used were [U] =30 ppm for synthetic phosphoric acid, modified carbon to aqueous phase ratio =1 and the adsorption temperature was room temperature. From (Fig. 1) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}$, %) increases by increasing the soaking time of carbon in the organic solvent reached 68.8% adsorption efficiency at 60 min.

3.2- The factors affect the uranium adsorption from both synthetic and Egyptian phosphoric acid

3.2.1- Effect of phosphoric acid concentration

The effect of phosphoric acid concentration on the extraction process was studied in the range 0.77 – 9.2M. The operating conditions used were [U] =30 and 20 ppm for synthetic and Egyptian phosphoric acid respectively, modified carbon to aqueous phase ratio =1, stirring time= 30 min and the adsorption temperature was room temperature. From (Fig. 2) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}$, %) decreased by increasing the phosphoric acid concentration reached 16.7 and 21.3% adsorption efficiency at 9.2M phosphoric acid for synthetic and Egyptian phosphoric acid respectively, while the uranium $E_{\text{adsorption}}$, % reached 68.8 and 76.9% for synthetic and Egyptian phosphoric acid respectively using 3.36M phosphoric acid.

3.2.2- Effect of modified carbon to aqueous phase ratio

Modified carbon to aqueous phase ratio has pronounced effects on the adsorption of uranium from synthetic (20 ppm U) and Egyptian phosphoric acid (30 ppm U). Fig. (3) shows the effect of modified carbon to aqueous phase ratio. It is obviously indicated that, by increasing the modified carbon to aqueous phase ratio the uranium adsorption markedly increases. The uranium adsorption efficiency reached 78.7 and 82.0% for synthetic and Egyptian phosphoric acid respectively by modified carbon to aqueous phase ratio equal to 2.0, while the uranium adsorption efficiency decreased to 16.7 and 20.1% for synthetic and Egyptian phosphoric acid respectively by applying modified carbon to aqueous phase ratio 1:5.

3.2.3- Effect of D2EHPA concentration

The effect of D2EHPA concentration on the uranium adsorption process was studied in the range 0.10 – 2.86M. The operating conditions used were [U] =30 and 20 ppm for synthetic and Egyptian phosphoric acid respectively, modified carbon to aqueous phase ratio =1, stirring time= 30 min and the adsorption temperature was room temperature. From (Fig. 4) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}$, %) increased by increasing the D2EHPA concentration reached 68.8 and 76.9% adsorption efficiency at 2.86M D2EHPA for synthetic and Egyptian phosphoric acid respectively, while the uranium $E_{\text{adsorption}}$, % reached 15.0 and 20.0% for synthetic and Egyptian phosphoric acid respectively using 3.36M phosphoric acid.

3.2.4- Effect of stirring time

The effect of stirring time on the adsorption of uranium was studied in the range 1.0 – 120.0 min. The operating conditions used were [U] =30 and 20 ppm for synthetic and Egyptian phosphoric acid respectively, modified carbon to aqueous phase ratio =1 and the adsorption temperature was room temperature. From (Fig. 5) it is

noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}$, %) increased by increasing the stirring time reached 68.8 and 76.9% adsorption efficiency at 30 min for synthetic and Egyptian phosphoric acid respectively.

3.2.5- Effect of oxidation state

The oxidation state was varied from 100 to 650 mv to study the effect of uranium adsorption from synthetic and Egyptian phosphoric acid. The operating conditions used were $[U] = 30$ and 20 ppm for synthetic and Egyptian phosphoric acid respectively, modified carbon to aqueous phase ratio =1 and the adsorption temperature was room temperature. From (Fig. 6) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}$, %) increased by increasing the uranium oxidation state reached 71 and 80% for synthetic and Egyptian phosphoric acid respectively, while it $U E_{\text{adsorption}}$, % decreased to reach 12.8 and 22% for synthetic and Egyptian phosphoric acid respectively. On the other hand, the adsorption of uranium hexavalent is more suitable than tetravalent one.

3.2.6- Effect of adsorption temperature

The effect of temperature on the adsorption of uranium was studied from 25 to 60 °C. The operating conditions used were $[U] = 30$ and 20 ppm for synthetic and Egyptian phosphoric acid respectively, modified carbon to aqueous phase ratio =1. Fig. 7 indicates that, the percentage of uranium adsorption decreased with increasing the temperature indicating that the process is exothermic in nature so, the adsorption of uranium from synthetic and Egyptian phosphoric acid is preferred at room temperature.

3.2.7- Effect of modified carbon size

The size particle of modified carbon has an important effect on the uranium adsorption. The influence of this parameter was studied in the range of 0.075, 0.85, 1.7 and 3.0 mm. The operating conditions used were $[U] = 30$ and 20 ppm for synthetic and Egyptian phosphoric acid respectively, modified carbon to aqueous phase ratio =1 and the adsorption temperature was room temperature. From (Fig. 8) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}$, %) increased by decreasing the size particle of modified carbon reached 68.8 and 76.9% uranium adsorption efficiency by using modified carbon particle size of 3.0 mm for synthetic and Egyptian phosphoric acid respectively, while the uranium adsorption efficiency increased to 90.8 and 95.6% by using small size of modified carbon particle (0.075 mm).

3.2.8- Effect of phosphoric acid pH

The most important parameter for the adsorption experiments, effect of pH was examined. The pH values were varied between 0.5 and 6.0 ± 0.2 keeping the other parameters constant. The pH was adjusted to the required value with diluted H_2SO_4 and NaOH. Fig. 9 shows the influence of pH on the uranium adsorption from synthetic phosphoric acid on the modified carbon. The percentage of adsorption increases with increasing pH to a maximum value ($pH 3.0 \pm 0.2$) and then declines with further increase in pH. The influence of pH on uranium adsorption can be explained in the following way, hydrolysis of uranyl ion takes place as the pH varies from 0.5 to 3.0 and the availability of free uranium ions is maximum at pH 3.0 and hence maximum adsorption. Uranium exists in hydrolyzed form and the following ionic species have been identified, UO_2^{2+} , $[(UO_2)_2(OH)_2]^{2+}$ dimer, $[(UO_2)_3(OH)_5]^+$ trimer. It is these species that are exchanged at the functional groups on the surface of modified carbon [20,24,25]. When pH increases beyond 3.0 precipitation starts due to the formation of complexes in aqueous solution and adsorption decreases, thus, the optimum adsorption of uranium took place at $pH 3.0 \pm 0.2$.

3.3- Stripping of uranium

Sodium carbonate solution was used for achieving the uranium stripping process from loaded modified carbon. For achieve this purpose, many factors were studied such as: sodium carbonate concentration, temperature and stirring time.

3.3.1- Effect of sodium carbonate concentration

The effect of sodium carbonate concentration on the uranium stripping process was studied in the range of 1.0– 20% wt/v. From (Fig. 10) it is noticed that the uranium stripping efficiency ($U E_{\text{stripping}}$, %) increased by increasing the concentration of sodium carbonate reached 87.6.0% using 15.0% (wt/v) solution of sodium carbonate.

3.3.2- Effect of stripping temperature

The effect of temperature on the stripping process of uranium was studied from 25 to 60 °C. Fig. 11 indicates that, the stripping temperature has a small positive effect on the uranium stripping from loaded modified carbon, the uranium stripping efficiency reached 87.6% at room temperature and increased to 91.7% by increasing the temperature to 60 °C. The temperature indicating that the process is endothermic in nature so, the stripping of uranium from loaded modified carbon is preferred at room temperature from economic point of view.

3.3.3- Effect of stirring time

The effect of stirring time on the stripping of uranium was studied in the range 1.0 – 60.0 min. From (Fig. 12) it is noticed that the uranium stripping efficiency ($U_{E_{stripping}}$ %) increased by increasing the stirring time reached 87.6 % at 30 min. Uranium was stripped from the loaded modified carbon with 15% wt/v sodium carbonate solution. Uranium precipitation was carried out using hydrogen peroxide to bring down the pH of the stripped solution, an addition of sulfuric acid to the solution with a slight excess of hydrogen peroxide was added. At pH of 3, the uranium will precipitate then uranium can be filtered as a peroxide hydrate, washed, dried and calcined at 400°C to obtain UO_3 powder.

3.4- Thermodynamics studies

The thermodynamics parameters obtained for the adsorption process were calculated using the equation:

$$\ln K_D = \Delta S_{ads}/R - \Delta H_{ads}/RT$$

Where, K_D is the distribution coefficient (ml/g), ΔS_{ads} is standard entropy ($J mol^{-1}K^{-1}$), ΔH_{ads} is the standard enthalpy ($kJ mol^{-1}$), T is the absolute temperature (K) and R is the gas constant ($8.314 J mol^{-1}K^{-1}$).

The experiments were carried out at 298, 313, 323 and 333 K for uranium concentration 30 and 20 ppm for synthetic and Egyptian phosphoric acid respectively, the values of ΔH_{ads} and ΔS_{ads} were calculated from the slopes and intercepts of linear regression of $\ln K_D$ versus $1000/T$ (Fig. 13). The values of ΔH_{ads} and ΔS_{ads} are reported in Table 1. The negative value of enthalpy change ΔH_{ads} for the processes further confirms the exothermic nature of the process and negative entropy of adsorption ΔS_{ads} reflects the affinity of the adsorbent material toward uranium.

table 1- The thermodynamic parameters

$\Delta H_{ads} \text{ kJ mol}^{-1}$		$\Delta S_{ads} \text{ J mol}^{-1}K^{-1}$	
ΔH_{ads} synthetic acid	ΔH_{ads} Egyptian acid	ΔS_{ads} synthetic acid	ΔS_{ads} Egyptian acid
-51.6	-53.7	-166.07	-170.03

Fig. 1- Effect of soaking time on the uranium extraction efficiency

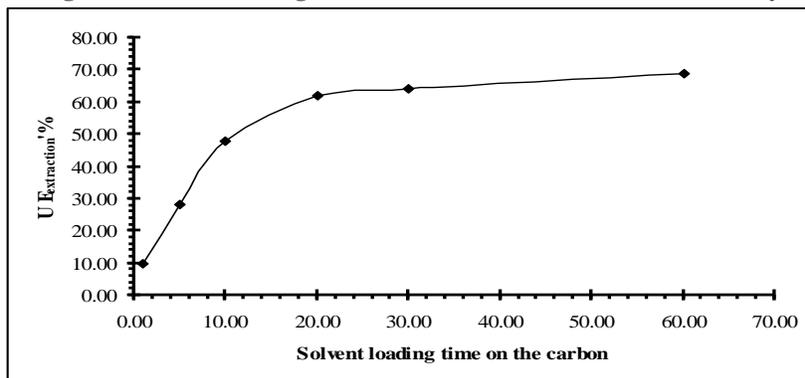


Fig. 2- Effect of phosphoric acid concentration on the uranium extraction efficiency

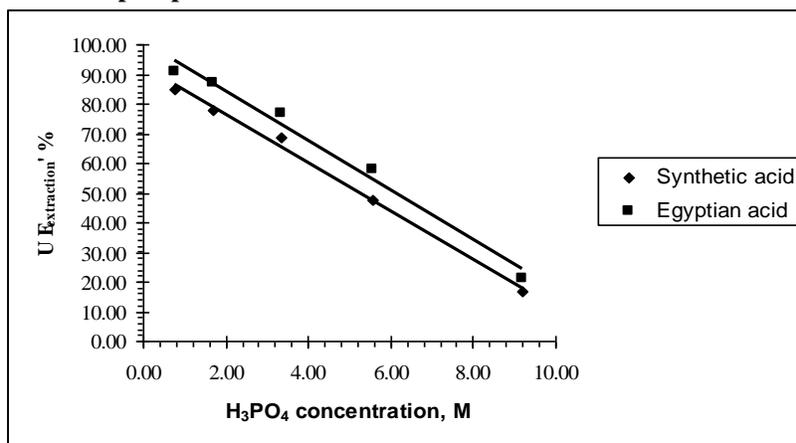


Fig. 3- Effect of modified carbon to aqueous phase ratio on the uranium extraction efficiency

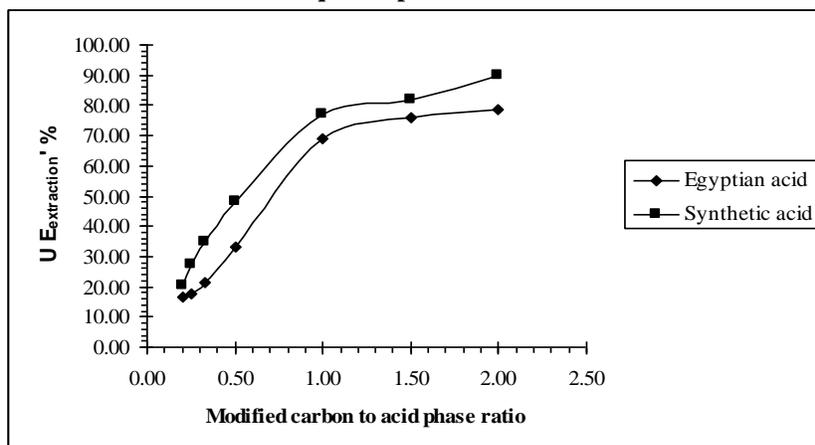


Fig. 4- Effect of D2EHPA concentration on the uranium extraction efficiency

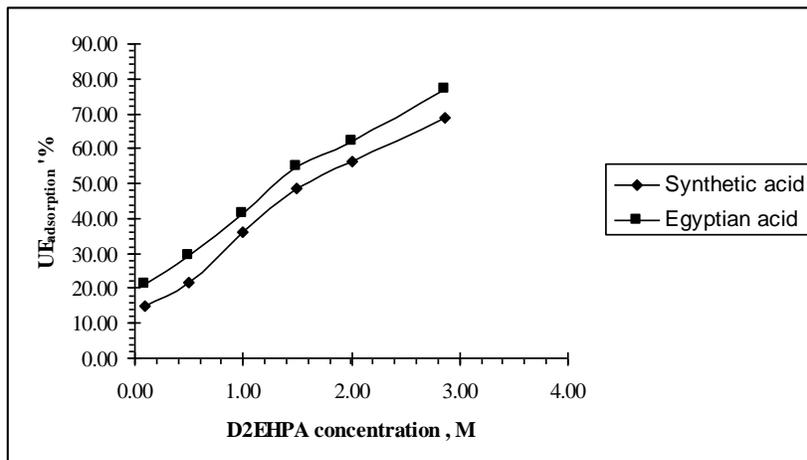


Fig. 5- Effect of stirring time on the uranium extraction efficiency

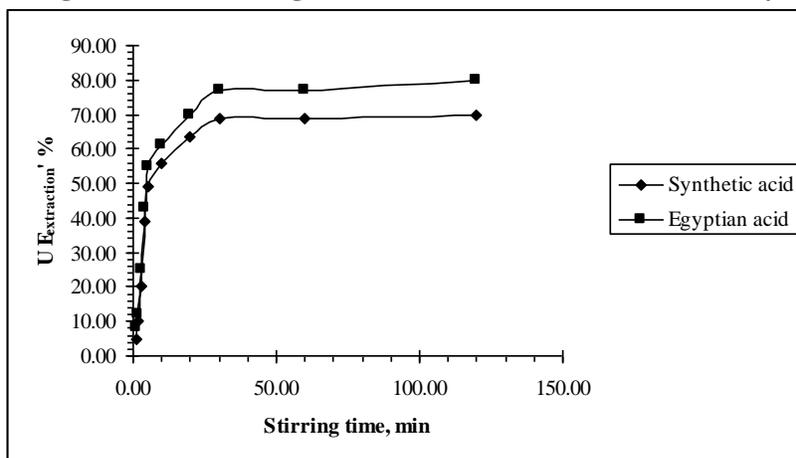


Fig. 6- Effect of uranium oxidation state on the uranium extraction efficiency

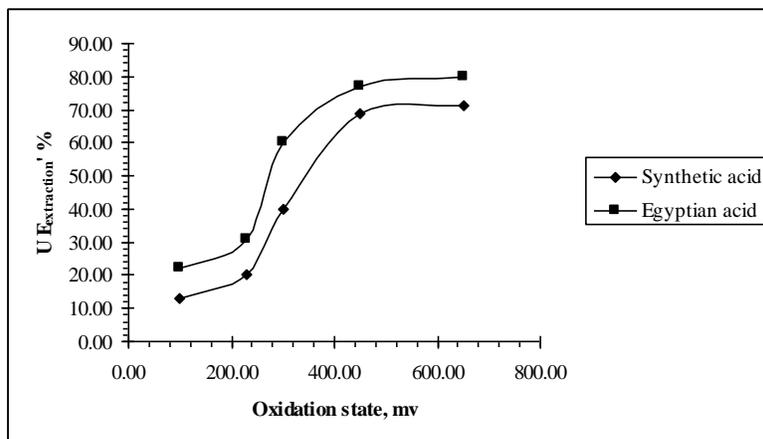


Fig. 7- Effect of temperature on the uranium extraction efficiency

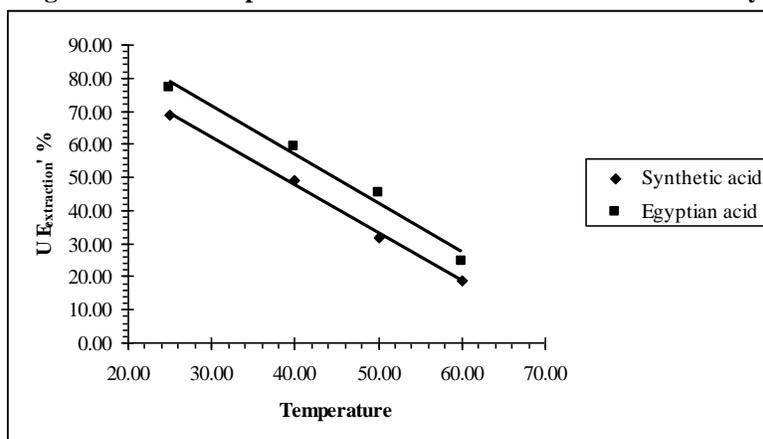


Fig. 8- Effect of modified carbon size on the uranium extraction efficiency

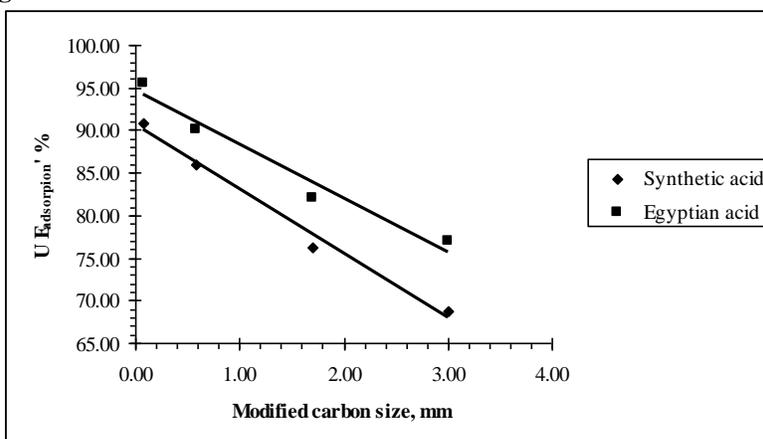


Fig. 9- Effect of phosphoric acid pH on the uranium extraction efficiency

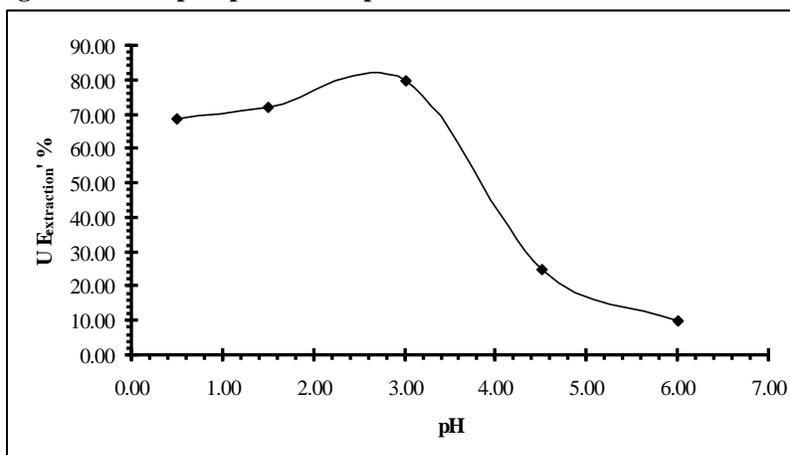


Fig. 10- Effect of sodium carbonate concentration on the uranium stripping efficiency

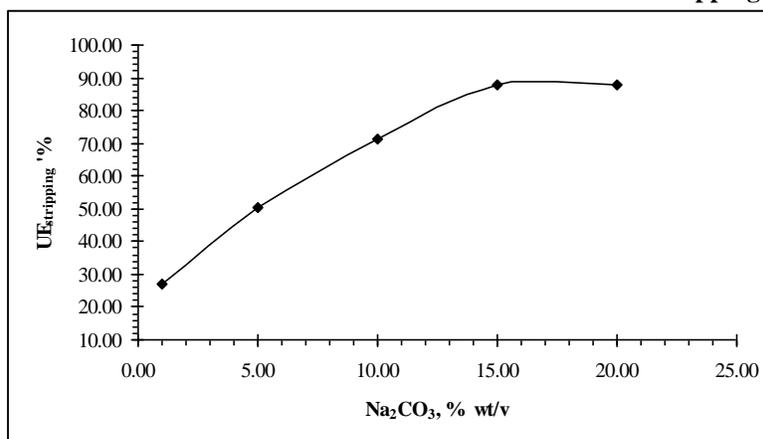


Fig. 11- Effect of temperature on the uranium stripping efficiency

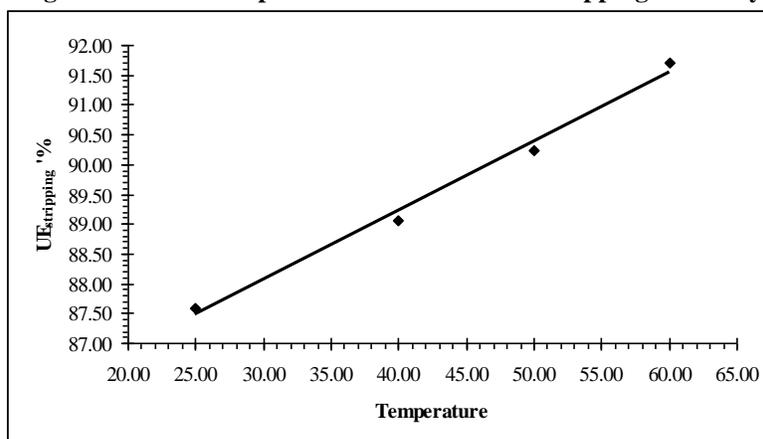


Fig. 12- Effect of stirring time on the uranium stripping efficiency

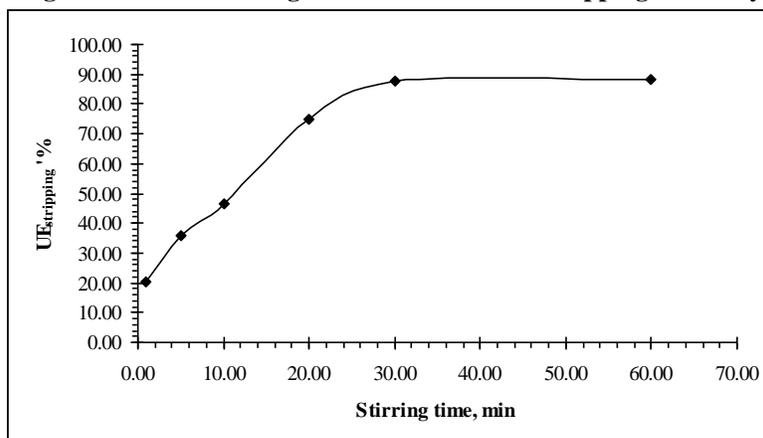
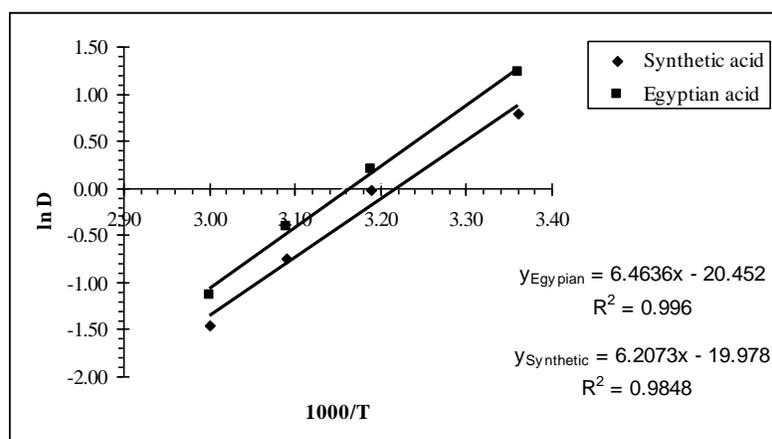


Fig. 13- ln D as a function with temperature (T)

Conclusion

According to the results obtained in this study of extraction of uranium from both synthetic and Egyptian phosphoric acid using modified carbon with di-ethyl hexyl phosphoric acid, we can concluded that:

- The modified carbon can be used as an efficient extracting material for uranium from phosphoric acid.
- Carbon pH must be in the range of 8-9 to be more suitable to loaded with D2EHPA organic solvent and hence give satisfactory results.
- The obtained optimum conditions for adsorption process were: phosphoric acid concentration 3.36M, modified carbon to aqueous phase ratio equal to 2.0, the uranium extraction increased by increasing the D2EHPA concentration at an optimum stirring time 30.0 min under room temperature. It is noticed that U (VI) was more suitable for adsorption by modified carbon than U (IV), so that H_2O_2 must be added to the phosphoric acid before applying the uranium adsorption process. The phosphoric acid pH must be adjusted to be in the range of 3-4 to give highly uranium adsorption efficiency.
- The results of uranium stripping revealed that: stirring of 10% wt/v of sodium carbonate for 30.0 min under room temperature re-extracted 87.6% of uranium from loaded modified carbon.
- The negative value of enthalpy change ΔH_{ads} for the processes further confirms the exothermic nature of the process and negative entropy of adsorption ΔS_{ads} reflects the affinity of the adsorbent material toward uranium.

From all the above data we can concluded that the modified carbon can be a useful tool in the uranium recovery from both synthetic and Egyptian phosphoric acid with highly efficiency and cheap cost.

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