

Advanced method for extraction of uranium (VI) from synthetic and Egyptian phosphoric acid using modified carbon

M.I.Amin*, El.A.Nouh, M.Gouda
Nuclear Materials Authority, Cairo, (EGYPT)
E-mail: Mostafa_nma@yahoo.com

ABSTRACT

The adsorption of uranium (VI) from phosphoric acid onto modified carbon has been investigated. 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 kJ/mol while $\Delta S_{ads} = -166.07$ and -170.03 kJ/mol) showed the exothermic heat of adsorption and the feasibility of the process.

© 2014 Trade Science Inc. - INDIA

KEYWORDS

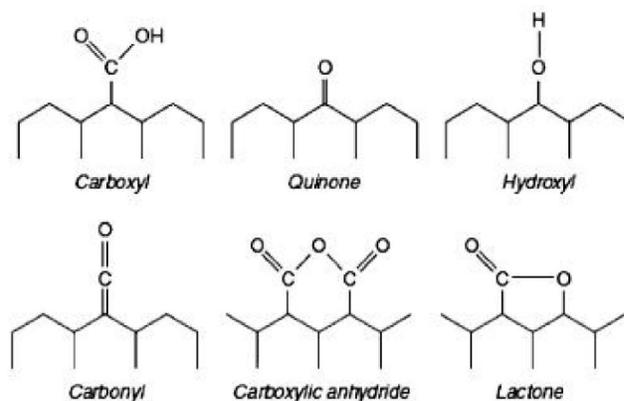
Extraction of uranium (VI);
Phosphoric acid;
Modified carbon.

INTRODUCTION

Uranium is present in the environment as a result of leaching from natural deposits, discharge from mill tailings, emissions from the nuclear industry, combustion of coal and other fossil fuels, and use of uranium containing phosphate fertilizers. Naturally occurring uranium is a mixture of three radioisotopes (^{234}U , ^{235}U and ^{238}U), but majority of them are ^{238}U isotope (99.27%). Uranium is a radioactive heavy metal that can cause cancer. Its primary toxic effect when consumed in water is that of heavy metals^[1,2]. 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^[3] 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^[4] the acidic surface shows cation exchange properties in aqueous solutions. The surface groups shown in the following figure are acidic groups.

Adsorption of uranium (VI) on a natural clinoptilolite zeolite from Sweetwater County, Wyoming was inves-



tigated^[5]. The general methods developed for the recovery or removal of uranium ions from aqueous solutions are extraction^[6,7], precipitation^[8,9], ion exchange^[10] and sorption^[11,12]. Among those approaches, sorption is commonly used for the recovery of uranium ions because of its high efficiency, ease of handling, and the availability of different adsorbents. Various kinds of new adsorbents for removing and recovering uranium have been reported^[13-18]. However, the separation process of adsorbents from aqueous solution after saturated sorption is usually complex and time-consuming.

Rapid removal of U(VI) from aqueous solutions was investigated^[19] using magnetic Fe₃O₄@SiO₂ composite particles as the novel adsorbent. Batch experiments were conducted to study the effects of initial pH, amount of adsorbent, shaking time and initial U(VI) concentrations on uranium sorption efficiency as well as the desorbing of U(VI). The sorption of uranium on Fe₃O₄@SiO₂ composite particles was pH dependent, and the optimal pH was 6.0. In kinetics studies, the sorption equilibrium can be reached within 180 min, and the experimental data were well fitted by the pseudo-second-order model and the equilibrium sorption capacities calculated by the model were almost the same as those determined by experiments.

EXPERIMENTAL

Activated carbon

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

Reagents

Stock solution of uranium (1000 ppm) was supplied from Accu Standard, USA. Two types of phosphoric acid were used in this work, first is a solution of pure phosphoric acid (44% P₂O₅) containing standard solution of uranium (60 ppm) and the second type is impure Egyptian wet process phosphoric acid which have the following components (P₂O₅ = 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. Iron and other heavy metals were determined by atomic adsorption spectrometer of model GBC 932- AAS.

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 with uranium concentration of 60 mg /L agitated with different amount of modified carbon, 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.

Calculations

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

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

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

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

RESULTS AND DISCUSSION

The parameters which affect the uranium adsorption such as carbon pH and soaking time for carbon modification with D2EHPA were investigated, 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 and solution pH.

The factors affect the modification of the carbon with D2EHPA

Full Paper

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 reached its minimum value 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 basic modified carbon while it reached 5.0% only using acidic one.

Effect of soaking time

The effect of soaking time on the adsorption process was studied in the range of 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 (Figure 1) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}^{\text{adsorption}}$, %) increases by increasing the soaking time of carbon in the organic solvent reached 68.8% adsorption efficiency at 60 min.

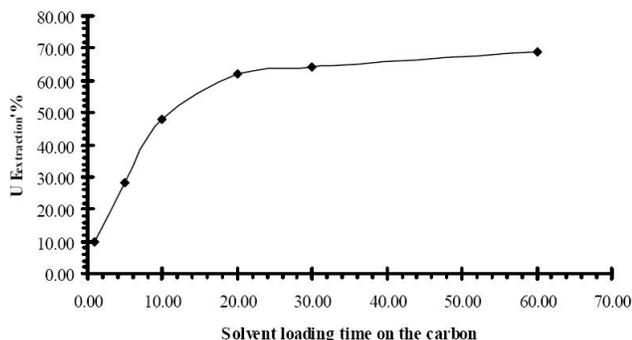


Figure 1 : Effect of loading time on the uranium extraction efficiency

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

Effect of phosphoric acid concentration

The effect of phosphoric acid concentration on the extraction process was studied in the range of 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 (Figure 2) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}^{\text{adsorption}}$, %) 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 $E_{\text{adsorption}}^{\text{adsorption}}$, % reached 68.8 and 76.9% for synthetic and Egyptian phosphoric acid respectively using 3.36M phosphoric acid.

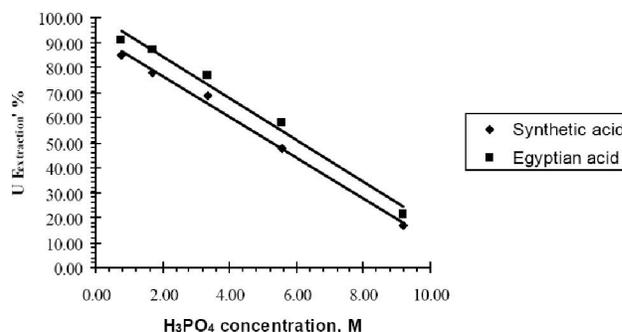


Figure 2 : Effect of phosphoric acid concentration on the uranium extraction efficiency

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). Figure 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 phos-

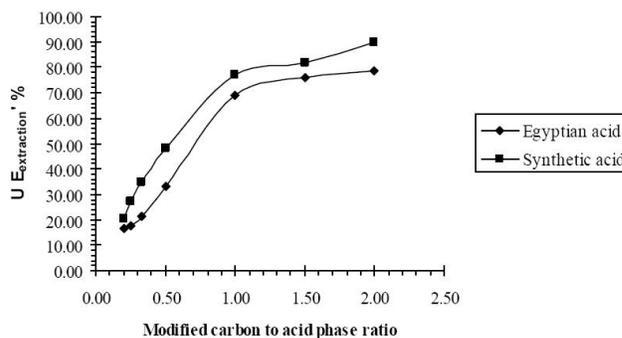


Figure 3 : Effect of modified carbon to aqueous phase ratio on the uranium extraction efficiency

phoric acid respectively by applying modified carbon to aqueous phase ratio 1:5.

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 (Figure 4) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}^{\text{?}}$, %) 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 $E_{\text{adsorption}}^{\text{?}}$, % reached 15.0 and 20.0% for synthetic and Egyptian phosphoric acid respectively using 3.36M phosphoric acid.

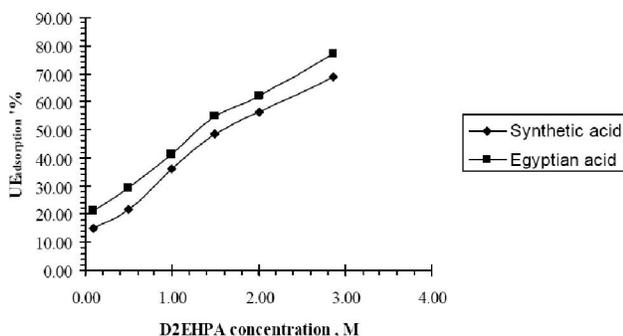


Figure 4 : Effect of D2EHPA concentration on the uranium extraction efficiency

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 (Figure 5) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}^{\text{?}}$, %) increased by increasing the stirring time reached 68.8 and 76.9% adsorption efficiency at 30 min for synthetic and Egyptian phosphoric acid respectively.

Effect of oxidation state

The oxidation state was varied from 100 to 650 mv to study the effect of uranium adsorption from syn-

thetic 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 (Figure 6) it is noticed that the uranium adsorption efficiency ($U E_{\text{adsorption}}^{\text{?}}$, %) increased by increasing the uranium oxidation state reached 71 and 80% for synthetic and Egyptian phosphoric acid respectively, while it $U E_{\text{adsorption}}^{\text{?}}$, % 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.

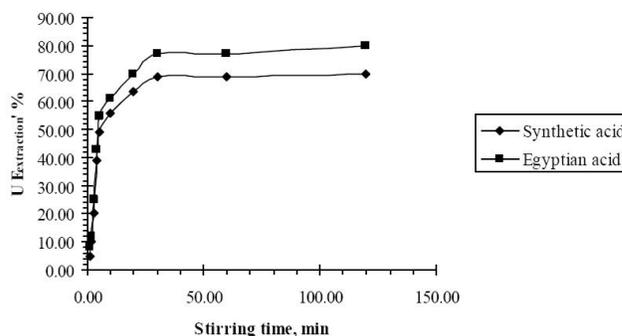


Figure 5 : Effect of stirring time on the uranium extraction efficiency

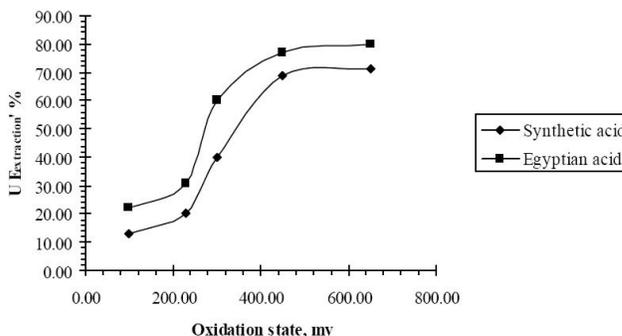


Figure 6 : Effect of uranium oxidation state on the uranium extraction efficiency

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. Figure 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

Full Paper

room temperature.

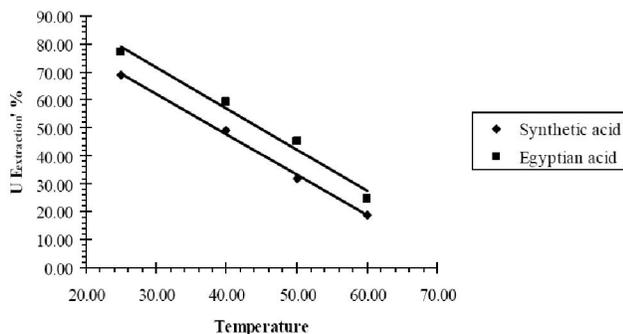


Figure 7 : Effect of temperature on the uranium extraction efficiency

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 (Figure 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).

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

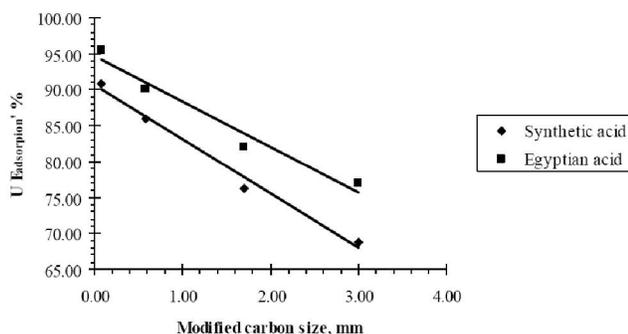


Figure 8 : Effect of modified carbon size on the uranium extraction efficiency

the required value with diluted H_2SO_4 and NaOH. Figure 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]. 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 $pH 3.0 \pm 0.2$.

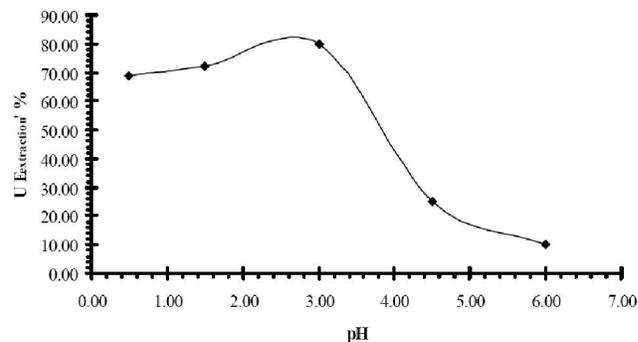


Figure 9 : Effect of phosphoric acid pH on the uranium extraction efficiency

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.

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 (Figure 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.

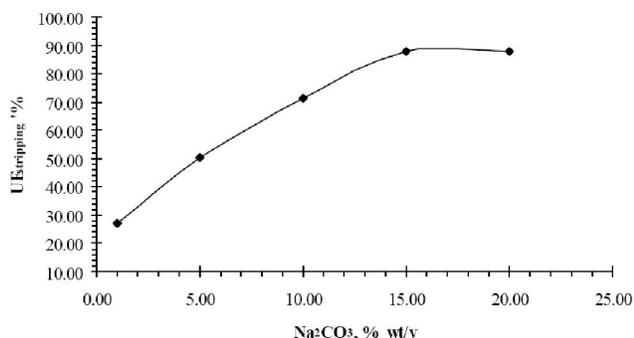


Figure 10 : Effect of sodium carbonate concentration on the uranium stripping efficiency

Effect of stripping temperature

The effect of temperature on the stripping process of uranium was studied from 25 to 60 °C. Figure 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.

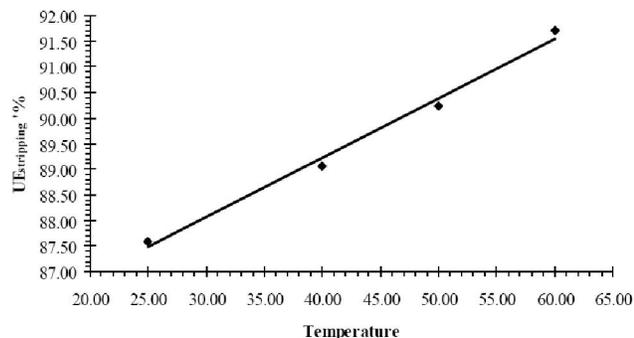


Figure 11 : Effect of temperature on the uranium stripping efficiency

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 (Figure 12) it is noticed that the uranium stripping efficiency ($U E_{\text{stripping}}$, %) 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.

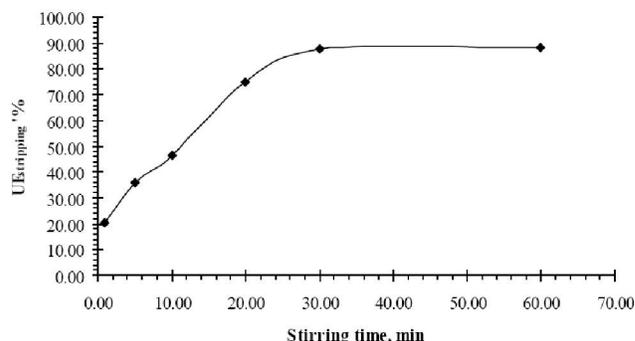


Figure 12 : Effect of stirring time on the uranium stripping efficiency

Thermodynamics studies

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

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

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

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 $1000/T$ (Figure 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 ad-

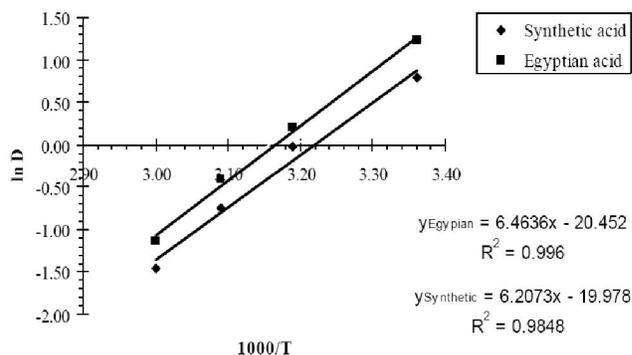


Figure 13 : ln D as a function with temperature (T)

Full Paper

TABLE 1 : The values of ΔH_{ads} and ΔS_{ads}

ΔH_{ads} kJ mol ⁻¹		ΔS_{ads} J mol ⁻¹ K ⁻¹	
ΔH_{ads}	ΔH_{ads}	ΔS_{ads}	ΔS_{ads}
synthetic acid	Egyptian acid	synthetic acid	Egyptian acid
-51.6	-53.7	-166.07	-170.03

sorbent material toward uranium.

CONCLUSION

According to the results obtained in this study of extraction of uranium from both pure synthetic and impure 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 H₂O₂ 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.

REFERENCES

- World Health Organization (WHO); Uranium in Drinking water: Background document for development of WHO guidelines for drinking water quality (WHO/SDE/WSH/03.04/118), World Health Organization, 26 (2005).
- A.C.Hakonson-Hayes, P.R.Fresquez, F.W.Whicker; J.Environ.Radioact., **59**(1), 29–40 (2002).
- A.M.A.Morsy, A.E.M.Hussein; Adsorption of uranium from crude phosphoric acid using activated carbon, J.Radioanal Nucl.Chem., **346**, 288 (2011).
- J.S.Noh, J.A.Schwarz; Effect of HNO₃ treatment on the Surface acidity of activated carbons, Carbon New York, **28**, 675 (1990).
- L.M.Camachoa, S.Denga, R.R.Parra; Uranium removal from groundwater by natural clinoptilolite zeolite: Effects of pH and initial feed concentration, Journal of Hazardous Materials, **175**, 393–398 (2010).
- J.L.Lapka, A.Paulenova, M.Y.Alyapyshev, V.A.Babain, R.S.Herbst, J.D.Law; Extraction of uranium(VI) with diamides of dipicolinic acid from nitric acid solutions. Radiochim.Acta, **97**, 291-296 (2009).
- R.S.Praveen, P.Metilda, S.Daniel, T.P.Rao; Solid phase extractive preconcentration of uranium(VI) using quinoline-8-ol anchored chloromethylated polymeric resin beads. Talanta, **67**, 960-967 (2005).
- C.Riordan, M.Bustard, R.Putt, A.P.McHale; Removal of uranium from solution using residual brewery yeast: Combined biosorption and precipitation. Biotechnol.Lett., **19**, 385-387 (1997).
- R.Ganesh, K.G.Robinson, L.L.Chu, D.Kucsmas, G.D.Reed; Reductive precipitation of uranium by desulfovibrio desulfuricans: Evaluation of cocontaminant effects and selective removal. Water Res., **33**, 3447-3458 (1999).
- K.Vaaramaa, S.Pulli, J.Lehto; Effects of pH and uranium concentration on the removal of uranium from drinking water by ion exchange. Radiochim.Acta, **88**, 845-849 (2000).
- S.B.Xie, C.Zhang, X.H.Zhou, J.Yang, X.J.Zhang, J.S.Wang; Removal of uranium(VI) from aqueous solution by adsorption of hematite. J.Environ.Radioact., **100**, 162-166 (2009).
- T.S.Anirudhan, C.D.Bringle, S.Rijith; Removal of

- uranium(VI) from aqueous solutions and nuclear industry effluents using humic acid-immobilized zirconium-pillared clay. *J. Environ. Radioact.*, **101**, 267-276 (2010).
- [13] G.Wang, X.Wang, X.Chai, J.Liu, N.Deng; Adsorption of uranium (VI) from aqueous solution on calcined and acid-activated kaolin. *Appl. Clay. Sci.*, **47**, 448-451 (2010a).
- [14] J.Wang, S.Zheng, Y.Shao, J.Liu, Z.Xu, D.Zhu; Amino-functionalized $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal. *J. Colloid Interf. Sci.*, **349**, 293-299 (2010b).
- [15] A.M.Donia, A.A.Atia, E.M.M.Moussa, A.M.El-Sherif, M.O.Abd El Magied; Removal of uranium(VI) from aqueous solutions using glycidyl methacrylate chelating resins. *Hydrometallurgy*, **95**, 183-189 (2009).
- [16] T.S.Anirudhan, S.S.Sreekumari; Synthesis and characterization of a functionalized graft copolymer of densified cellulose for the extraction of uranium(VI) from aqueous solutions. *Colloids Surf.A: Physicochem.Eng.Aspects*, **361**, 180-186 (2010).
- [17] Y.Zhao, C.Liu, M.Feng, Z.Chen, S.Li, G.Tian, L.Wang, J.Huang, S.Li; Solid phase extraction of uranium(VI) onto benzoylthiourea-anchored activated carbon. *J.Hazard.Mater.*, **176**, 119-124 (2010).
- [18] K.Oshita, A.Sabarudin, T.Takayanagi, M.Oshima, S.Motomizu; Adsorption behavior of uranium(VI) and other ionic species on cross-linked chitosan resins modified with chelating moieties. *Talanta*, **79**, 1031-1035 (2009).
- [19] F.Li. Fan, Z.Qin, J.Bai, W.D.Rong, F.Y.Fan, W.Tian, X.L.Wu, Y.Wang, L.Zhao; Rapid removal of uranium from aqueous solutions using magnetic $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ composite particles, *Journal of Environmental Radioactivity*, **106**, 40-46 (2012).
- [20] A.Mellah, S.Chegrouche, M.Barakat; The removal of uranium (VI) from aqueous solutions onto activated carbon: Kinetic and thermodynamic investigations, *Journal of Colloid and Interface Science*, **296**, 434-441 (2006).