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RESEARCH ARTICLE

Novel Sorbent for Uranium Sorption from Crude Phosphoric Acid

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Abstract

Novel sorbent prepared from the dispersion of phosphate ore into a phenolic resin was investigated. Uranium sorption behavior from crude phosphoric acid using this novel sorbent (PhP) was compared to the host phenolic resin (Ph).The experimental data showed that, the sorption capacity was 135 mg g^{1-} and 390 mg g^{1-} for PhP and Ph, respectively. Considering the amount of effective material in both sorbents, the sorbent (PhP) contains 2.5 % of the phenolic sorbent (Ph), the theoretical capacity of the new sorbent (PhP) would be decreased by 40 times of the phenolic one (Ph). Actually its uptake capacity decreased only by about three times, this may be attributed to high dispersion of the phosphate ore.

1. Introduction

Uranium is essential element in the atomic energy program. In spite of its low concentration in the phosphate ores, its recovery is significant for environmental and economical point of view [1]. It is assessed that adequate uranium remains for 70 years of nuclear-power generation if the present rate of spending is continued [2], making the recovery of uranium from alternative sources important for long-term resource availability. In general, several technologies have been currently used in industry for uranium recovery from crude phosphoric acid such as chemical precipitation [3], liquid-liquid extraction [4, 5], ion-exchange resin [6] and more notably, adsorption [7]. Multi - stage solvent extraction (SE) technique was proposed for many decades; however, the extractants was costly and the procedures are labor intensive [8]. In addition, the technical problems associated in terms of third phase formation and the flammability hazards make this technique not preferred [9]. Recently, the chemically modified chelating sorbents with high selectivity was developed [10, 11]. However, the weak acidic properties of its ligand moiety make these sorbents ineffective in extracting uranium from a high-strength acidic medium such as crude phosphoric acid [12, 13]. In the past few years, great interest has been shown lately in organic modified inorganic compounds such as silicates due to the remarkably range of possible applications for such hybrids [14]. These applications include the use of the hybrids to improve the extraction properties of uranium ions from highly acidic mediums [15]. Taking in the consideration the aforementioned factors into account for our investigation, a novel sorbent containing phenolic resin dispersed in phosphate ore has been synthesized using a simple and non costly procedure. As a sorbent for uranium ions, many advantages of this sorbent make it, particularly attractive. First, it is manufactured using a simple synthetic route. Second, it has large adsorptive sites of the sorbent. Third, it can be used for impressive sorption and recovery of uranium ions from crude phosphoric acid. The integrated properties of the novel sorbent hold great promise in a wide range of recovery fields.

2. Experimental

Chemical studies on sorption behavior of uranium using batch method for its recovery from crude phosphoric acid using novel synthesized sorbent are discussed in this work.

2.1. Chemicals

All chemicals and reagents used in the present work were of analytical grade and purchased from Aldrich. All experiments were carried out using double distilled water and Whatman filter paper No. 40. The stock solution containing uranium was prepared by dissolving its corresponding nitrate salt in water. Crude phosphoric acid was kindly provided by Abu Zaable Company, Egypt, and its chemical composition shown in Table 1. Phosphate ore having low uranium content was obtained from Abu Tartur area, New Valley, Egypt, and its chemical composition shown in Table 2.

Table 1: The chemical composition of the crude phosphoric acid.

Major constituent	Conc., %	Trace constituent	Conc., ppm
P_2O_5	40.00	Cr	120.0
Fe_2O_3	02.20	Ni	42.00
Al_2O_3	00.66	Pb	20.00
SiO_2	00.98	Zn	200.0
MgO	00.50	V	35.00
CaO	00.30	Mn	800.0
SO_4	01.30	Na	400.0
F	00.85	K	200.0
T.O.C*	00.51	U	55.00

* Total organic carbon

Table 2: The chemical composition of Abu Tartor phosphate ore**.**

Major constituent	Conc., %	Trace constituent	Conc., ppm
P_2O_5	27.00	Cr	200.0
Fe_2O_3	06.20	Ni	220.0
Al_2O_3	03.00	Pb	40.00
SiO_2	05.00	Zn	400.0
MgO	03.00	V	50.00
CaO	45.00	Mn	900.0
F	03.00	Na	450.0
RE_2O_3	00.20	K	250.0
L.O.I*	08.00	U	25.00

* Lose on ignition

2.2. Instruments

Holland Inolab pH meter was used for pH measurement. Barnstead water purifying was used for supplying double distilled water. Metertech UV/VIS SP 8001 Spectrophotometer was used for uranium determination by Arsenazo III method [16].

2.3. Synthesis of the sorbent

2.3.1. Phenolic sorbent (Ph)

Mix 2.0 g of nonyl phenol ethoxylate with 0.1 g amino sulfonic naphthanol, 0.25 g para formaldehyde, 0.1 g salicyldhyde, 1.0 g sodium hydroxide then adds 10 ml water. The mixture was warmed to 40 ^oC for 1.0 hour. After cooling, add 4.0 g resorcinol, 1.0 g para formaldehyde then heat to 90 – 120 ^oC for 3.0 hour under reflux until formation reddish brown precipitate.

2.3.2. Phenolic-phosphate sorbent (PhP)

The novel phenolic-phosphate sorbent (PhP) under study was prepared by adding 0.5 g of the Phenolic sorbent (Ph) to the molten mixture of resoin and bee wax followed by addition 20 g of Abu Tartor phosphate ore (-200 to -250 mesh size) then heating with stirring until formation uniform pellets.

2.4. Performance of the novel sorbent for uranium sorption

2.4.1 The studied factors

Sample of each sorbent weighing 0.05 g was added to a 25 mL of crude phosphoric acid (strength 60 %) in 50 mL glass beaker. The acid was initially spiked by 1.5 g/L uranium concentration. To ensure the sorption equilibrium, the phases were agitated at the ambient temperatures (25 ^{o}C) for 25 minutes using a hot plate magnetic stirrer. The phases were separated by filtration, and the residual uranium concentration was determined. Uranium uptake was calculated according to the following equation:

$$\mathbf{q_e = (C_i - C_e) V / m} \qquad \mathbf{(1)}$$

Where: q_e = uranium uptake at equilibrium, mg / g,
C_i = initial uranium concentration, mg / L,
C_e = uranium concentration at equilibrium, mg / L,
V / m = phases ratio, L / g

The studied factors involve sorption time, liquid to solid (L/S) ratio, phosphoric acid concentration, sulfuric acid addition, temperature and initial uranium concentration.

2.4.2 Uranium recovery from the loaded sorbent

Sample of dry loaded phenolic-phosphate sorbent (PhP) weighing 100 g was digested using concentrated sulphuric acid (90 %). The aim was to attack the uranium in phosphate ore itself as well as desorption that was extracted by the sorbent and producing phosphoric acid having high concentration of uranium. The acid to the sorbent ratio of 2.6 was agitated for 10 min. at 80 ^{o}C.

2.4.3 Uranium thermodynamic and sorption isotherm

Thermodynamic and sorption isotherms for uranium from crude phosphoric acid by the sorbents Ph and PhP were calculated as follows:
Thermodynamic parameters involving the heat of sorption (ΔH°) and entropy change (ΔS°) were calculated according to van’t hoff equation [17]:

$$\mathbf{\log K_d = (\Delta S° / 2.303R) - (\Delta H° / 2.303RT)} \qquad \mathbf{(2)}$$

The values of ΔH° and ΔS° were derived from intercept and slope of the resultant straight line after plotting log K_d versus 1/T. On the other hand, the free energy for the specific sorption (ΔG°) was calculated from the following relation:

$$\mathbf{\Delta G° = \Delta H° - T\Delta S°} \qquad \mathbf{(3)}$$

Sorption isotherm was investigated according to Langmuir equation [18] as follows:

$$\mathbf{C_e/q_e = C_e/q_s + 1/Kq_s} \qquad \mathbf{(4)}$$

Where: C_e = uranium concentration at equilibrium, mg/l,
q_e = quantity of the adsorbed uranium at equilibrium, mg/g,
q_s = maximum uranium uptake quantity by the sorbent, mg/g,
K = equilibrium constant.

The values of $1/Kq_s$ and $1/q_s$ were derived from intercept and slope of the resultant straight line after plotting C_e/q_e versus C_e, where the values of K and q_s for the sorption of uranium by Ph and PhP were then calculated from the corresponding slopes and intercepts.

3. Results and discussion

It is worthy to mention that, the novel sorbent phenolic-phosphate (PhP) containing only 2.5 % by weight of the phenolic sorbent (Ph). Accordingly, the predicted uranium uptake by the sorbent Ph would be 40 times more than that of the novel PhP sorbent for the same weight.

3.1. Effect of contact time

Sorption of uranium by the prepared sorbents Ph and PhP was shown in Fig. 1 as a function of time in the range of 5 – 30 minutes. It is clear from results that, the sorption equilibrium of uranium for the sorbent PhP, and the sorbent Ph reached after 15 min. and 20 min., respectively. The faster sorption of the two sorbents may be due to the hydrophilic (–OH) group which in turn increased the chelating site accessibility of uranium, which providing better surface contact with the aqueous phase.

3.2. Effect of liquid to solid ratio L/S

The results of phase's ratio (L/S) effect in the range of 100 – 500 on uranium uptake were shown in Fig. 2. The data reveal that uranium uptake for the sorbent; PhP was slightly increased from ratio 400 to 500, which means approaching saturation while uptake of the sorbent Ph was increased steadily, which means the saturation would be achieved with a ratio more than 500. Considering the same weight of Ph in the novel sorbent PhP, we can notice that the sorbent PhP was powerful than Ph. This is due to the addition of the phosphate ore material in addition to the chelating power of introducing the phenolic groups that achieves better coordination with the metal ions and its compactness.

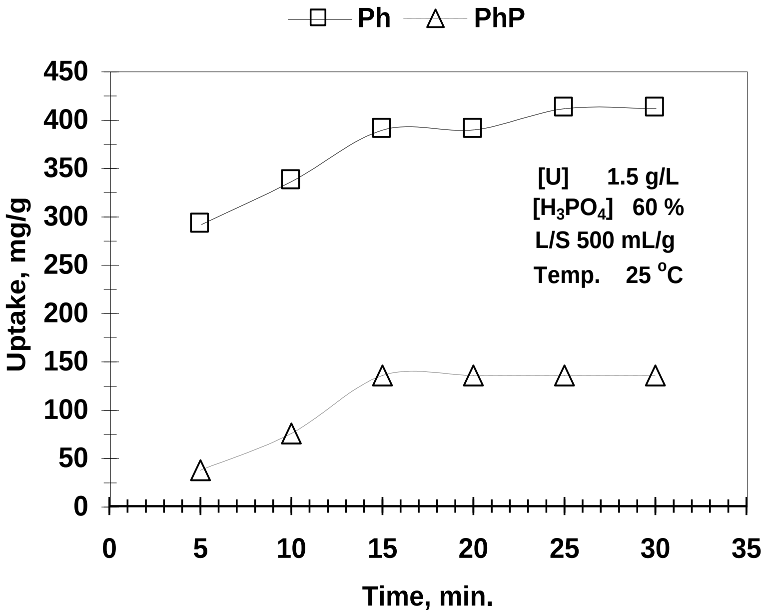

Fig. 1. Effect of contact time on the sorption of uranium by the prepared sorbents

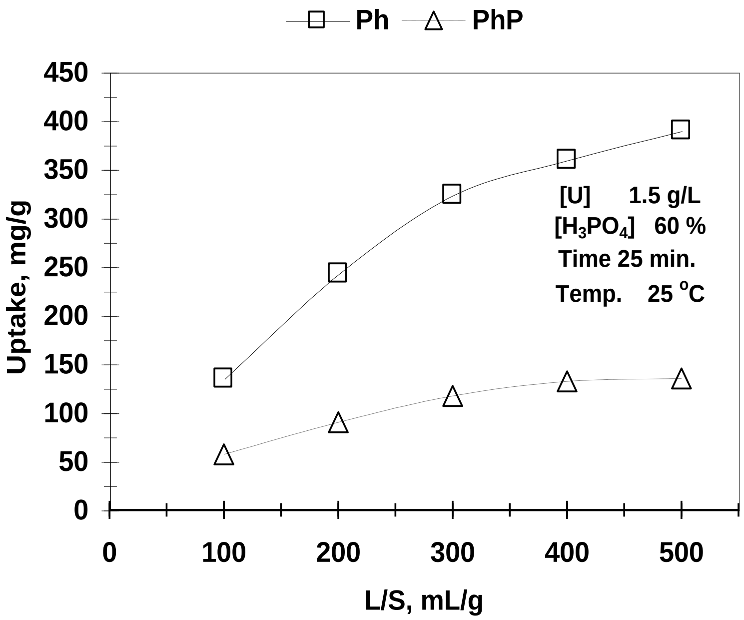

Fig. 2. Effect of liquid to solid ratio (L/S) on the sorption of uranium

3.3. Effect of crude phosphoric acid concentration

The effect of crude phosphoric acid concentration (10 – 60%) upon uranium uptake by the prepared sorbents' Ph and PhP was illustrated in Fig. 3. Clearly uranium uptake was increased by decreasing the phosphoric acid concentration from 50% to 10% for both sorbents. In this regard, uranium uptake for the sorbents' Ph and PhP was increased by 1.6 and 2.0 times, respectively at 10% phosphoric acid concentration. The prepared sorbents may serve as a quantitative extracting media for uranium as a neutral metal chelator in the concentrated phosphoric acid mediums while in diluted phosphoric acid; the uranium sorption was also carried out by chelating-action exchanger.

3.4. Effect of sulfuric acid concentration

Depending on the fact that crude phosphoric acid containing free un-reacted sulphuric acid from 1 to 5 %, the effect of this concentration range on uranium uptake was studied upon ortho phosphoric acid by the prepared sorbents Ph and PhP. The results were indicated in figure 4, which revealed that uranium uptake increased by decreasing sulphuric acid concentration. In this regard, uranium uptake was increased by 1.4 and 2.3 times for the sorbents Ph and PhP respectively at the 1% sulfuric acid concentration.

3.5. Sorption thermodynamics

The influence of temperature variation ranged from 303 – 373 K was studied upon the uptake of uranium by Ph and PhP sorbents. The results were shown in Fig. 5, which indicates that uranium uptake was dramatically decreased with the increase of temperature. Thermodynamic parameters, i.e., heat of sorption ($\Delta H°$), entropy change ($\Delta S°$) and the free energy ($\Delta G°$) for the sorption of uranium on Ph and PhP sorbents were shown in Fig. 6 and the calculations for this system according to the previously mentioned equations were reported in Table 3. From these results it is obvious that negative value of $\Delta H°$ corresponds to the exothermic sorption process while the positive values of $\Delta G°$ indicate non spontaneous nature of uranium sorption on the sorbents and more favorable at lower temperature whereas the negative value of $\Delta S°$ indicate favors ion exchange.

3.6. Effect of initial uranium concentration

Effect of initial uranium concentration in the range 0.25 - 1.5 g/L on the sorbents uptake capacity under experiment conditions was shown in Fig.7. The results show that the sorbents uptake capacity increases as the initial concentration of uranium increases. At initial uranium concentration of 1.5 g/L, the maximum uptake capacity of Ph and PhP are 390 and 135 mg/g, respectively. However, inspect the new phosphate phenolic sorbent (PhP) contains 2.5 % of the parent phenolic sorbent (Ph), its uptake capacity decreased by about three times only. The predicted capacity of phosphate phenolic sorbent (PhP) would be decreased by 40 times of the phenolic sorbent (Ph), this assures the high effect of dispersion phosphate ore into the phenolic sorbent.

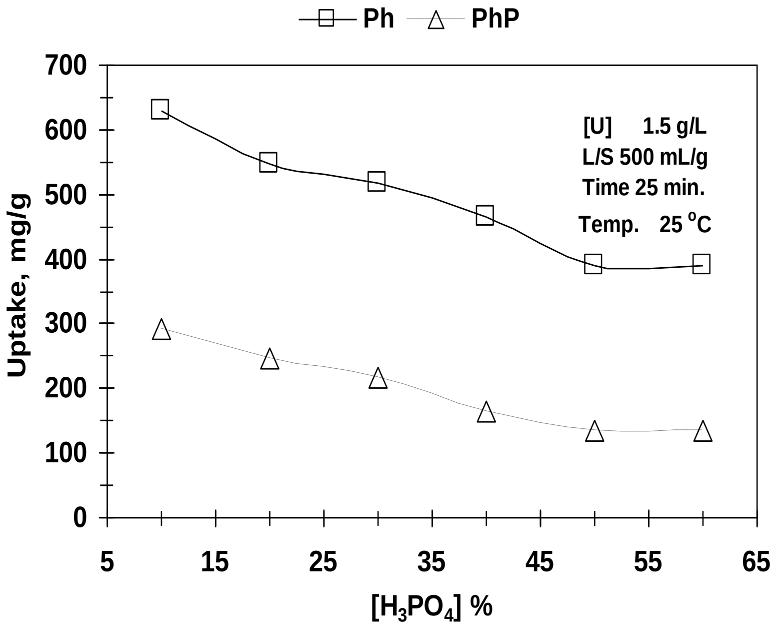

Fig. 3. Effect of phosphoric acid concentrations on the sorption of uranium

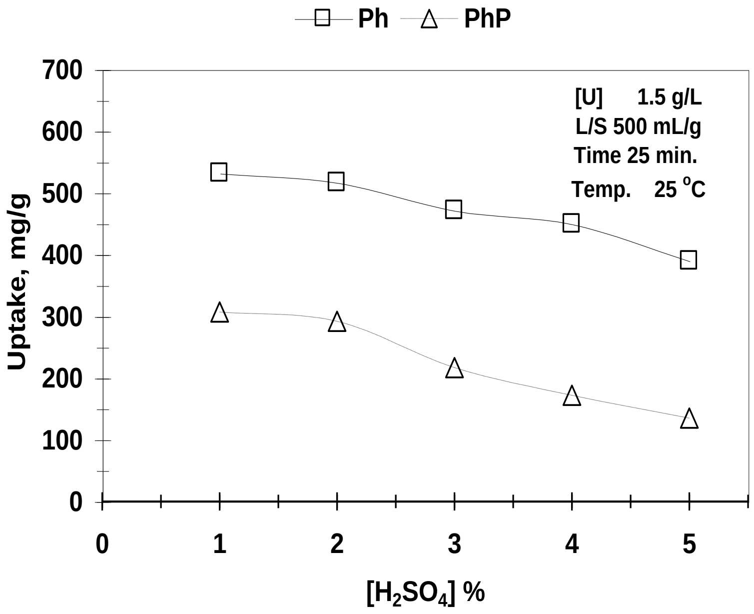

Fig. 4. Effect of sulfuric acid concentrations on the sorption of uranium

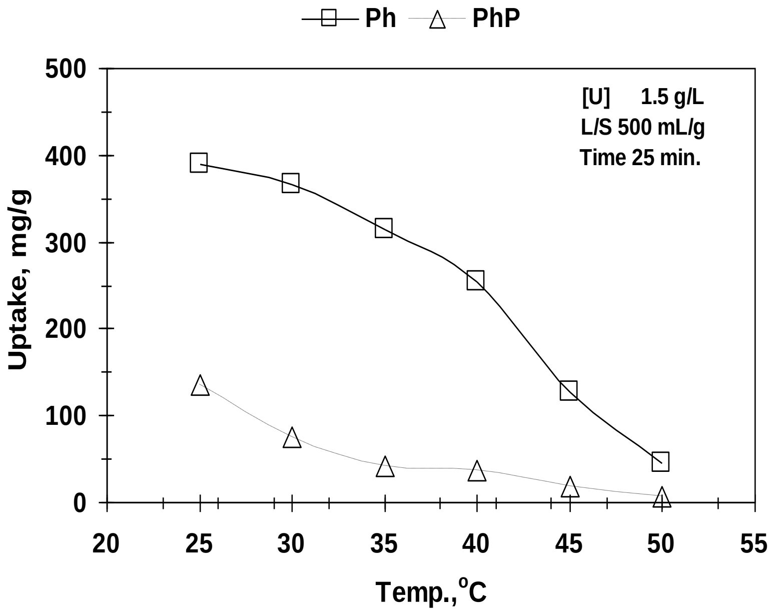

Fig 5. Effect of temperature on the sorption of uranium

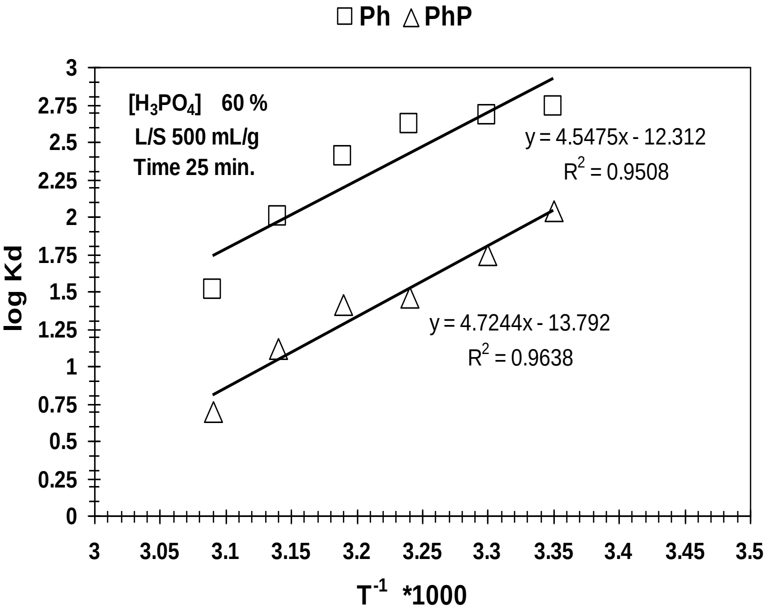

Fig. 6. Thermodynamics of the sorption of uranium

Table 3: Thermodynamic data of uranium sorption.

Sorbent	Thermodynamics data, KJ /mole		
	ΔH°	ΔS°	ΔG°
Ph	- 43	- 118	358
PhP	- 45	- 132	403

3.7. Sorption isotherm

Langmuir isotherm was constructed according to the sorption data of uranium in the concentration range from 0.25 to 1.5 g/L and the corresponding uptake for the two sorbents phenolic (Ph) and phosphate phenolic (PhP). The resultant straight line from plotting C_e/q_e vs. C_e was shown in Fig. 8. The intercept and slope values of the straight-line equivalent $1/Kq_s$ and $1/q_s$, respectively. Accordingly, the values of K and q_s for uranium sorption on Ph and PhP were calculated and reported in Table 4. The values of K for uranium sorption on PhP are higher than that of Ph; this referred to stronger interaction between metal ions and the active sites of the sorbent PhP [19]. In another ward, this implies that uranium ions bind strongly with the active chelating sites of PhP due to the addition of the phosphate ore to the parent phenolic sorbent (Ph).

Table 4: Isotherm data of uranium sorption.

Sorbent	Isotherm data		
	Qs, mg/g	K	r^2
Ph	390	0.564	0.98
PhP	135	1.036	0.95

3.8. Uranium recovery from the loaded Phenolic-phosphate

Results of digestion the dry loaded phenolic-phosphate sorbent (PhP) sample which weighing 100 g was illustrated in Table 5. The produced phosphoric acid by this method having high concentration of both P_2O_5 and uranium. Clearly, uranium concentration was increased about 230 fold of that present in the normal phosphoric acid produced from Abu Tartur phosphate ore.

Table 5: The chemical composition of the phosphoric acid produced after PhP loaded sorbent**.**

Major constituent	Conc., %	Trace constituent	Conc., ppm
P_2O_5	**18.00**	Cr	54.00
Fe_2O_3	01.30	Ni	13.00
Al_2O_3	00.31	Pb	07.00
SiO_2	00.10	Zn	120.0
MgO	00.20	V	15.00
CaO	00.10	Mn	460.0
SO_4	01.20	Na	200.0
F	00.90	K	110.0
T.O.C*	00.70	**U**	**5750.0**

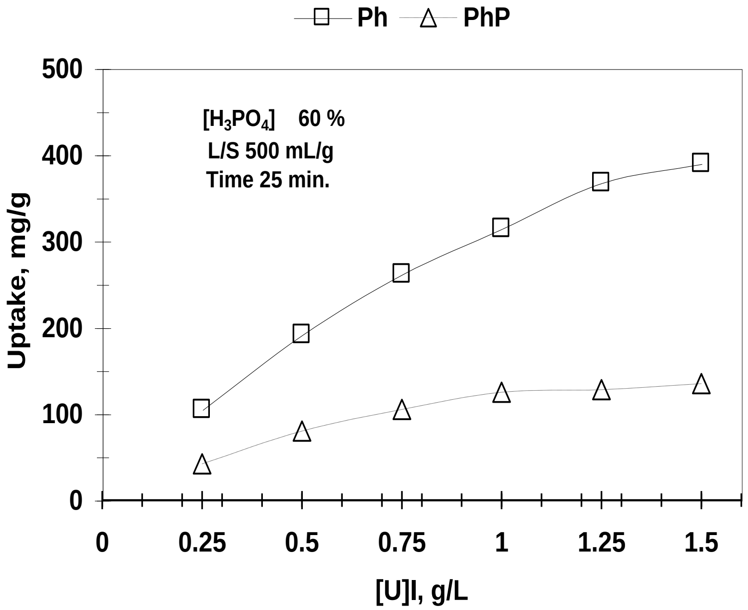

Fig. 7. Effect of uranium initial concentration on the sorption process

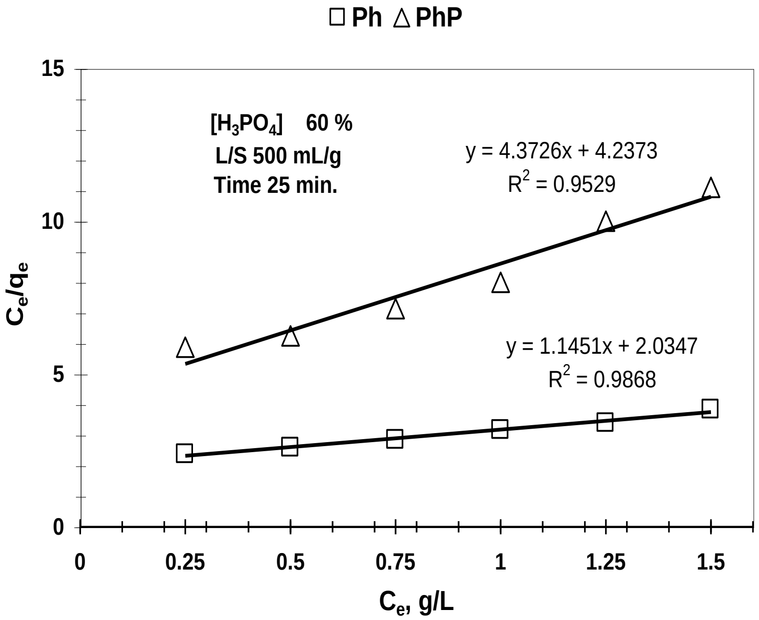

Fig. 8. Langmuir isotherm of the uranium sorption

4. Conclusions and recommendations

The present work describes the uranium sorption from crude phosphoric acid onto a phenolic sorbent (Ph) as well as novel phosphate phenolic sorbent (PhP) which contains only 2.5% of the parent phenolic sorbent (Ph). Performance of the sorbents revealed that the equilibrium sorption of uranium reached after 15 min. for the sorbent PhP and after

20 min. for the sorbent Ph. The extraction phase's ratio (L/S) proved that the sorbent PhP was powerful than Ph. This may due to the addition of the phosphate ore material in addition to the chelating power of introducing the phenolic groups that achieves better coordination with the metal ions and its compactness. However, uranium uptake was increased for the two sorbents by decreasing both the phosphoric (from 50% to 10%) and sulfuric (from 5% to 1%) acid's concentrations. In this regard, the prepared sorbents may serve as a quantitative extracting media for uranium. Thermodynamic studies indicate that negative value of ΔH° corresponds to the exothermic sorption process. The positive values of ΔG° indicate non spontaneous nature of uranium sorption on the sorbents and more favorable at lower temperature whereas the negative value of ΔS° reveal favors ion exchange. On the other hand, sorption isotherm for uranium sorption on PhP was higher than that of Ph; this referred to stronger interaction between metal ions and the active sites of the sorbent PhP .Finally, phosphoric acid produced from digestion of dry loaded phenolic-phosphate sorbent (PhP) sample revealed that uranium concentration was increased about 230 fold of that present in the normal phosphoric acid produced from Abu Tartor phosphate ore material. Accordingly, it was recommended to use the novel phenolic-phosphate sorbent (PhP) in direct sorption of uranium from crude phosphoric acid.

5. References

[1] Nriagu J.O., Pacyna, J.M. Quantitative assessment of worldwide contamination of air, water and soils by trace metals, Nature 333 (1988) 134–139.

[2] Gupta, C.K., Singh, H. Uranium Resource Processing: Secondary Resources, Springer-Verlag, Berlin, 2003.

[3] Navarro, R.R. Wada, S. Tatsumi, K. J. Hazard. Mater. 123 (2005) 203–209.

[4] Lee, B.G. Lee, H.J. Shin, D.Y. Mater. Sci. Forum 486 (2005) 574–577.

[5] Amaral, J.C.B.S. Morais, C.A. Miner. Eng. 23 (2010) 498–503.

[6] Woodberry, P. Stevens, G. Snape, I. Solvent Extr. Ion Exc. 24 (2006) 603–620.

[7] Miretzky, P. Cirelli, A.F. J. Hazard. Mater. 180 (2010) 19 –21

[8] Mowafy, E.A. Aly, H.F. Solvent Extr. Ion Exch. 20 (2003) 177 –194.

[9] Hennion, M.C. J. Chromgr. A 856 (1999) 3-10.

[10] Zhao,Y. Liu, C. Feng, M. Chen, Z. Li, S. Tian, G. Wang, L. Huang, J. J. Hazard. Mater. 176 (2010) 119–124.

[11] Bo Li, Lijian Ma,YinTian,XiaodanYang, Juan Li,Chiyao Bai, Xiaoyu Yang, Shuang Zhang, Shoujian Li, Yongdong Jin,. J. Hazard. Mater. 271(2014)41– 49

[12] Maheswari,M.A. Subramanian,M.S. Anal. Lett. 36 (2003) 2875-2892.

[13] . Prabhakaran, D. Subramanian, M.S. Talanta 61 (2003) 423- 430.

[14] Lebeau, B. Sanchez, C. Current Opinion in Solid State Materials Science,. 4 (1999)11-23

[15] Kouraim, M. N. Sheta, M. E. Abd Elaal, M. M. European Journal of Chemistry 5 (2014) 446- 450.

[16] Marczenko, Z.: "Spectrophotometric Determination of Elements", John Wiley and Sons, Inc., New York, (1986).

[17] Jia, Q. Wang, Z. H. Li, D. Q. Niu, C.J. J Alloys and Compounds 374 (2004) 434 – 437.

[18] Qi, T. Sonoda, A. Maketa, Y. Kanoh, H. Ooi, K. Hirotsu, T.Industrial and Engineering Chemistry Research 41(2002)133– 138.

[19] Boonamnuayvitaya, V. Chaiya, C. Tanthapanichakoon, W. Jarudilokkul, S. Separation and Purification Technology 35 (2004) 11 – 22.