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Removal of Uranium from Acidic Solution Using Activated Carbon Impregnated with Tri Butyl Phosphate

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Abstracte: In this work, the recovery of uranium from phosphate ore (El Sibaiya area, Egypt) requires applying some hydrometallurgical processes, leaching and extraction. To study the leaching of uranium ions from its ores, the ore material was first crushed and grinded to the liberation size (200 mesh ≡ 0.075 mm), amenable for U dissolution. The acid leaching process depends largely on a number of factors; these factors include acid type and its concentration, oxidizing agent concentration, leaching time, temperature, and solid/liquid ratio (S/L). These parameters have been investigated and optimized conditions was determined (1g of phosphate ore contact with 4ml of H_2SO_4 (200g/l) and H_2O_2 (5%) for 90min. at 70°C. The adsorption of uranium(VI) from acidic leach liquor onto activated carbon (AC) and impregnated AC by tributyl phosphate (TBP) have been studied using a batch adsorber. The parameters that affect the uranium(VI) adsorption, such as contact time, solution pH, initial uranium(VI) concentration, concentration of TBP, amount of AC and modified AC, and temperature, have been investigated and optimized conditions was determined (0.03g of AC, modified AC contact with 50 ml of leach liquor for 45min. at pH 4 and at room temperature). The maximum loading of uranium ions on AC and TBP/AC are 24.3 mg/g (243 mg/l), and 58.2 mg/g (582 mg/l), respectively. And it was analyzed by the Fourier Transform Infrared Spectroscopy (FTIR) and the Scanning Electron Microscopy (SEM). Both the kinetic and the sorption isotherm modeling have been applied upon the obtained data. Thus, it was found that the uranium sorption obeys a pseudo-second order reaction while the Freundlich sorption isotherm model is most suitable to describe the studied sorption reaction.

Key words: Standard uranium solution, El Sibaiya phosphate ore, Activated carbon (AC) and Tri butyl phosphate (TBP).

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1. Introduction

Uranium (U) is an important source of energy at present and in the future. It is a natural, radioactive and chemo toxic heavy metal. It is a trace in nature and is found in rocks, soils, plants and water as trace element [1]. As the most common radionuclide, uranium is considered to be not only an irreplaceable raw material for nuclear energy, but also a serious long-term potential environmental hazard because of its long half-life and high radiological and biological toxicity [2-4]. Since the 1950s, great efforts have been focused on new materials and technologies for separation of uranium (VI) from aqueous solution. Although liquid–liquid extraction (LLE) has been widely used in separation and/or recovery of uranium (IV) from U-containing aqueous solution so far [5-7], this technology is being applied with its insurmountable limitations due to heavy use of organic extractants and solvents and so on [8-10]

In this paper, the recovery of uranium from phosphate ore requires applying some hydrometallurgical processes, leaching and extraction. The great efforts have been focused on new materials and technologies for the separation of uranium (VI) from its aqueous solutions. In spite of a large number of versatile extractants that are commercially available, solvent extraction suffers from the limitations of labor intensiveness of the technique, third phase formation, large-scale use of organic solvents and problems related to the disposal of wastes. Also, ion exchange resins have lower extraction selectivity for transition metals with respect to alkali metals. Impregnated resins have thus emerged as a technological alternative to liquid–liquid extraction and ion-exchange as they overcome these drawbacks. This technology is based upon modification of a solid support for separation of metal ions from complex matrices. Two methodologies have indeed been adopted for the preparation of the solid phase; one is based upon the physical impregnation or modification of a suitable reagent on the solid support while the second involves binding of a chelating ligand to the support material. For selective adsorption, separation, preconcentration and recovery of uranium, various solid phase extraction methods were developed using different types of solid supports such as activated carbon, naphthalene, benzophenone, octadecyl bonded silica membrane disks and polymeric resins, etc [11]. The activated carbon has been chosen for its chemical, radiation, and thermal stability [12, 13]. In fact, the activated carbon can be considered as the most effective and economic process. In view of the above, the current paper has focused on the uptake behavior of uranium from leach liquor by solid phase extraction using activated carbon (AC) as a supporting material anchored with TBP. The extraction behavior of the uranium on the applied TOA impregnated activated carbon was studied under varying experimental conditions using batch operation mode in order to determine the optimum loading conditions. In the mean time, the latter was interpreted via sorption kinetic and adsorption isotherm modelings [14].

2. Experimental

2.1. Material Preparations

2.1.1. Preparation of Activated Carbon (AC)

A commercial activated carbon was dried in muffle furnace at 500 °C for 4 h. The dried powder was soaked in 10% (v/v) hydrochloric acid solution for 24h in order to remove the metal ions and other impurities adsorbed on it. The insoluble residue was filtered and rinsed with double distilled water until to neutral. The purified activated carbon was immersed in 3M HNO_3 with stirring for 8h and solid/liquid (S/L) ratio 1/10 at 60 ºC. The resultant was filtered and washed with deionized water to neutral pH. The oxidized product was dried in a drying furnace at 110 ºC for 24h to enhance the hydroxyl capacity on AC, and therefore the products with abounding hydroxyl (HO-AC) was obtained [15].

2.1.2. Preparation of Tributyl Phosphate Modified Activated Carbon

To preparation of this working material, a series of different volumes (1- 10 ml) 20 % of tributyl phosphate (TBP) were used to modify activated carbon by dry technique which was widely used. In this technique, 1 g of activated carbon was contacted with different volumes of TBP in diethyl ether or benzene solution by changing the S/L ratio from 1/1 to 1/10 under fixed conditions of 60 min. contact time at room temperature until complete homogenization followed by leaving the slurry till organic diluent was evaporated. The different samples of modified activated carbon then dried at 60 °C till complete dryness to complete modification [16].

2.1.3. Preparation of Uranium Stock Synthetic Solution

A standard stock solution of 1000 mg/l U(VI) has been prepared by dissolving 1.782 g uranyl acetate ($UO_2(CH_3COO)_2.2H_2O$) of BDH Chemicals Ltd. Poole, England in 1L distilled water. This solution was actually used to determine the relevant factors of uranium adsorption by the prepared materials.

2.2. Material characterization

a-The Scanning Electron Microscopy (SEM) images were taken using a Jeol (Tokyo, Japan) JSM 5600 LV Scanning Electron Microscope equipped with an Oxford Instruments 6587 EDX microanalysis detector. The images have been taken under low vacuum conditions where samples do not show charging effects; in this

way, it is possible to avoid the coating of the samples with a high conductance thin film (gold or graphite films).

b- Absorption spectra in the IR region are collected using a Fourier Transform Infrared spectrometer (FT-IR) (Thermo Scientific - NICOLET iS10 USA) spectrometer. This technique is used to characterize the major functional groups of activated carbon modified with solvents. Samples were mixed with KBr and the mixture was ground and then pressed with a special press to give a disc of standard diameter in KBr pellet (IR grade, Merck).

2.3. Experimental Procedures

2.3.1. Leaching studies

Leaching can be defined as a process of dissolving valuable constituents from an ore by suitable reagents. In the present work the leaching is studied by batch technique. The ore material is first crushed and grinded to the liberation size (200 mesh). In all cases, 1gm of the phosphate ore, 4 ml of hydrogen peroxide (5%) and acid solution (200g/l) were mixed and shaken using a batch technique for 90 min at 70°C which it was sufficient for equilibrium attainment. After filtration, the concentration of uranium ions in the aqueous phase is determined spectrophometrically using The Perkin Elmer lambda 3b (USA). These concentrations are used to obtain the leaching efficiency (L %) [17]:

$$L\% = \left(\frac{C_{a,e}}{C_{s,i}} \right) X\, 100 \tag{1}$$

Where $C_{a,e}$ (mg/l) and $C_{s,i}$ (mg/g) are aqueous uranium concentrations at equilibrium and initial solid phases uranium concentrations, respectively.

2.3.2. Adsorption studies

Several batch experiments were performed to study the different relevant adsorption factors. Except otherwise cited, each experiment was performed by shaking 1 g of the TBP impregnated activated carbon with 50 ml of the prepared synthetic uranium solution 84 mg/l at 25 °C±1 for 30 min. The solution was then filtered and the concentration of uranium was spectrophotometrically determined before and after equilibration.

The amount of metal ion loaded on the impregnated activated carbon was calculated using the following equation [14]:

$$q_e = (C_0 - C_e)\frac{V}{m} \quad (2)$$

Where qe is the metal loaded (mg g^{-1}), Co and Ce are the initial and equilibrium metal concentrations in the solution (mg l^{-1}), respectively, v is the solution volume (l), and m is the mass of the adsorbent (g) (impregnated solid phase).

The removal percent of ions from the aqueous phase is calculated from the relation [14]:

$$A\% = \left(\frac{C_0 - C_e}{C_0}\right)? \ 00 \quad (3)$$

2.4. Analytical procedures

2.4.1. Chemical Analysis of Phosphate Rock

In the present study, composite phosphorite sample was collected from El Sibaiya area, this sample is yellowish brown colour. Minerallogically, composed of dahllite and hydroxyl apatite as phosphatic minerals. As well as non phosphatic minerals such as pyrite (FeS_2), Quartz (SiO_2), Hematite (Fe_2O_3) and Dolomite ($Ca,Mg(CO_3)_2$).

This sample was prepared for analysis and leaching by crushing about 2Kg using a laboratory jaw crusher into pea – size, followed by grinding using a blending mill to 60 mesh size, about 50 g was separated by quartering before being ground to 200 mesh size, the pulverized sample was then analyzed using the suitable techniques.

Where the major oxides SiO_2, Al_2O_3, TiO_2, and P_2O_5 were analyzed using spectrophotometric methods (Table 1). The content of Na and K were determined by the flame photometric technique. Total Fe as Fe_2O_3 was determined by titration with EDTA using sulphosulcylic acid as indicator from which was subtract the amount of ferrous which was determined by titration against standard potassium permanganate solution.

MgO + CaO were determined by titration with EDTA using Eriochrome black T as indicator from which the amount of calcium was subtracted after being determined using Muruxide as indicator [18]. Trace elements were also determined using ICP-OES.

Table (1): Analysis of interested components of Sibaiya phosphate rock sample

Constuents	Conc. %	Constuents	Conc. ppm
SiO_2	7.0	Zn	186
Al_2O_3	1.6	Zr	52
Fe_2O_3	4.0	Th	2
CaO	45.0	U	100
MgO	1.0	V	87
P_2O_5	28.0	Pb	9
TiO_2	0.03	Cu	12
Na_2O	1.2	Cr	151
K_2O	0.14	Y	87
MnO	0.06	Ba	183
F^-	1.5	Ni	15
L.O.I	9.0	Sr	1314

2.4.2. Control Chemical Analysis of Uranium

Uranium concentration in the different aqueous stream solutions was measured via its arsenazo (III) complex using Perkin Elmer lambda 3b (USA) double-beam UV-Visible programmable spectrophotometer at a wavelength of 655 nm. The arsenazo (III) reagent solution was prepared by dissolving 0.25 g of arsenazo(III) and 0.5 g of sodium acetate in 100 ml of water. A digital pH meter (Misura Line 1010) was used for pH adjustment [19].

3. Results and Discussion

3.1. Uranium Leaching from Phosphate Ore

We have investigated the parameters which affect uranium leaching, such as acid type and its concentration, oxidizing agent concentration, leaching time, temperature, and solid/liquid ratio (S/L).

3.1.1. Effect of Acid Type

The effect of acid type upon uranium leaching efficiency of the ore material was studied using mineral acids such as H_2SO_4, HCl and HNO_3 while the other factors were fixed at 200 mesh ore size, 30 min. agitation

time, room temperature, 1/4 solid/liquid (S/L) ratio and concentration of both leaching agents is 200 g/l. Under these mentioned conditions, uranium leaching efficiencies using H_2SO_4, HCl and HNO_3 were 66.1, 64.3 and 65.0 % respectively. From the obtained results, it is clear that all the mineral acids can dissolve uranium ions from the studied sample with acceptable efficiencies. The leach liquors of HCl and HNO_3 have been highly metal impurities but H_2SO_4 has been a moderate metal impurities. Also, sulfuric acid is an inexpensive and easy to use. According, sulfuric acid is the best leaching agent of uranium from the studied sample. The latter has thus been used for studying the other relevant parameters that have been applied in this study; namely the concentration of sulfuric acid, the concentration of oxidizing agent (hydrogen peroxide), solid/liquid ratio, leaching time and leaching temperature.

3.1.2. Effect of Sulfuric Acid Concentration

The effect of H_2SO_4 concentration upon the leaching efficiency of uranium ions from the studied sample was studied at the concentrations ranging from 50 to 400 g/l while the leaching conditions were kept constant at 200 mesh ore size, 2.5% hydrogen peroxide concentration, 1/5 solid/liquid (S/L) ratio and 60 min. leaching time at room temperature. The leaching efficiency of uranium ions is given in Figure (1). From the obtained results, the leaching efficiency is gradually increased to 72.2 % with increasing the acid concentration until 200 g/l. After the latter concentration, the leaching efficiency is sharply decreased. This decreasing behavior of the uranium leaching efficiency after 200 g/l acid concentration due to the formation rate of the gypsum is increased which adsorb the uranium ions on the surface of calcium sulfate precipitate [17]. Thus, 200 g/l is considered as optimum acid concentration and is selected for subsequent experiments.

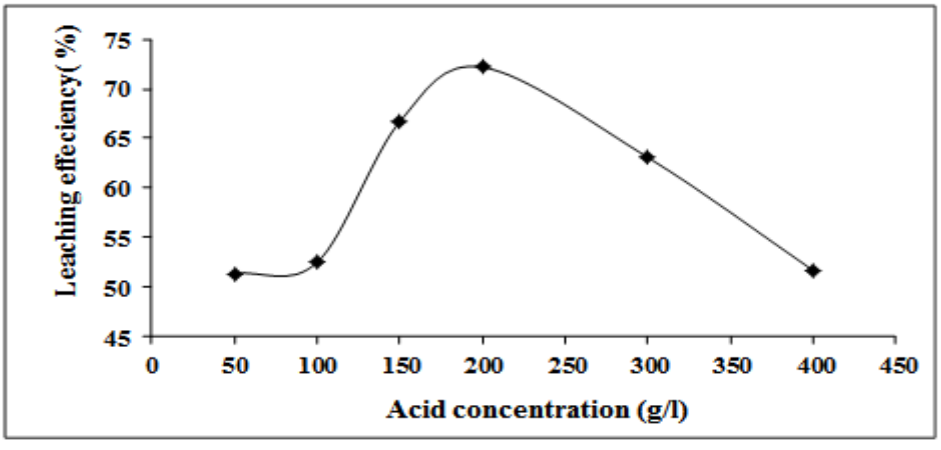

Figure (1): Effect of of sulfuric acid concentration upon leaching efficiency of uranium ions from the ore sample.

3.1.3. Effect of Hydrogen Peroxide Concentration

Generally, most of the uranium mills are used sulfuric acid to extract uranium from its ore. Simple hexavalent uranium oxides and its compounds are readily soluble, but uranium(IV) is insoluble in H_2SO_4 and hence must be oxidized for its dissolution to occur. Uranium which exists in tetravalent form in natural uranium ore, require oxidizing conditions to convert uranium(IV) in the ore to the uranium(VI) to enhance the leaching efficiency of uranium ions. Generally the oxidant used in this study is hydrogen peroxide (H_2O_2) due to the cost and case of availability.

Several leaching experiments have been performed to investigate the effect of hydrogen peroxide concentration upon uranium leaching efficiency in the range from 2.5 up to 20.0 % and without oxidizing agent case. In these experiments the other leaching conditions were fixed at 200 mesh ore size, 200 g/l sulfuric acid concentration, 1/5 solid/liquid (S/L) ratio and 60 min. leaching time at room temperature. The obtained data are given in Figure (2), it is clear that the leaching efficiency increases from 66.35 to 84.76% with increasing the hydrogen peroxide concentration from 2.5 up to 5 % of H_2O_2. After the latter concentration, the leaching efficiency is constant at 84.76 %. Accordingly, the best concentration of hydrogen peroxide is 5 %.

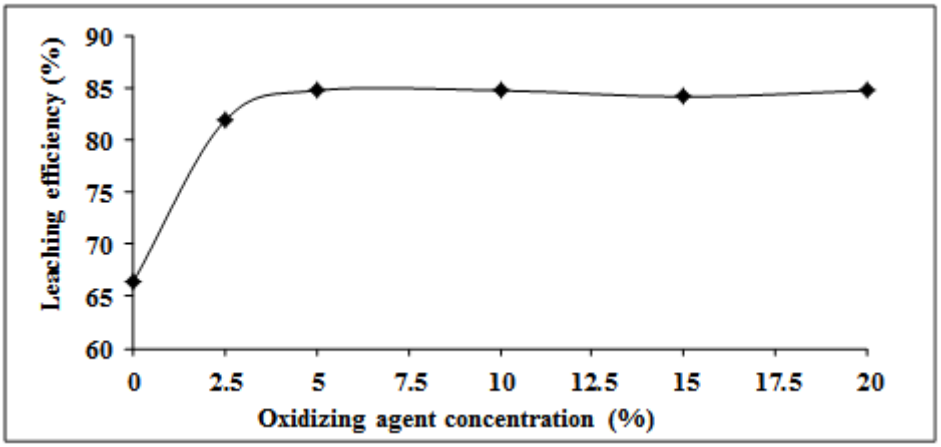

Figure (2): Effect of hydrogen peroxide concentration (%) upon leaching efficiency of uranium (%) from the ore sample.

3.1.4. Effect of Solid/Liquid Ratio

To study the effect of solid/liquid ratio, first, the preparation of liquid solution is performed by 200 g/l sulfuric acid and 5 % hydrogen peroxide as stock solution. A set of experiments was carried out to examine the effect of ore amount (g) to liquid (ml) ratio upon the leaching efficiency of uranium ions by varying S/L ratio

from 1/1 to 1/7 while the other factors were kept constant at 200 mesh ore size, 200 g/l sulfuric acid concentration, 5 % hydrogen peroxide concentration and 60 min. leaching time at room temperature. The obtained data was gives in Figure (3), indicated that uranium leaching efficiency is gradually increased from 18.03 to 98.31 % at the S/L ratio from 1/1 to 1/4 while the leaching efficiency is constant from 1/4 to 1/7. It is clear that decreasing the pulp density and acid consumption was beneficial for uranium extraction. Thus, the best solid/liquid ratio is 1/4.

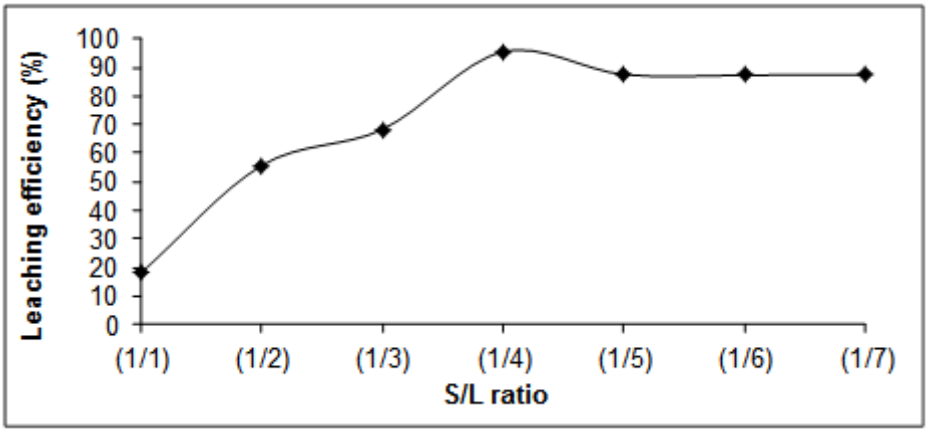

Figure (3): Effect of solid/liquid ratio upon uranium leaching efficiency (%) from the ore sample.

3.1.5. Effect of Agitating Time

The effect of leaching time upon the uranium leaching efficiency was studied in the range from 15 to 240 minutes while the other leaching conditions were fixed at 200 mesh ore size, 200 g/l sulfuric acid concentration, 5 % hydrogen peroxide concentration and 1/4 S/L ratio at room temperature. The obtained results shown in Figure (4) revealed that the uranium leaching efficiency increased from 72.77 % after 15 min. to 97.53 % after 90 min. with no further increase in recovery of uranium with more time. Thus 90 min is the optimum leaching time.

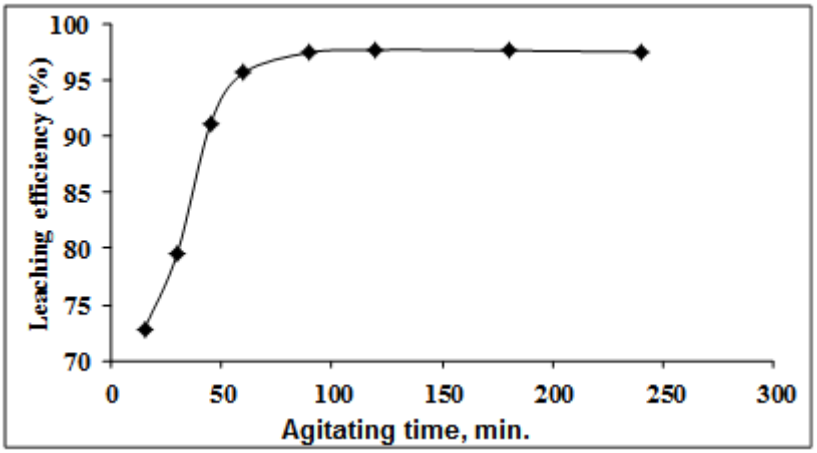

Figure (4): Effect of agitating time upon uranium leaching efficiency (%) from the ore sample.

3.1.6. Effect of Temperature

To study the effect of temperature upon the uranium leaching efficiency, it was found that temperature has a great effect on the leaching efficiencies of uranium. Several experiments were carried out the leaching temperature in the range from 25 to 90 ºC while the other factors were kept constant at 200 mesh ore size, 200 g/l sulfuric acid concentration, 5% hydrogen peroxide concentration and 1/4 solid/liquid (S/L) ratio at 90 min. leaching time. From the obtained results in Figure (5), it is clear that increasing temperature leads to slightly increase from 97.77 to 99.21 %.

Increasing the leaching temperature may improve leaching of uranium but this will also increase the dissolution of gangue minerals and acid consumption. This means that the reaction is endothermic and an increase of temperature favors the leaching of uranium. Therefore, 70 °C was selected as the optimum temperature for leaching.

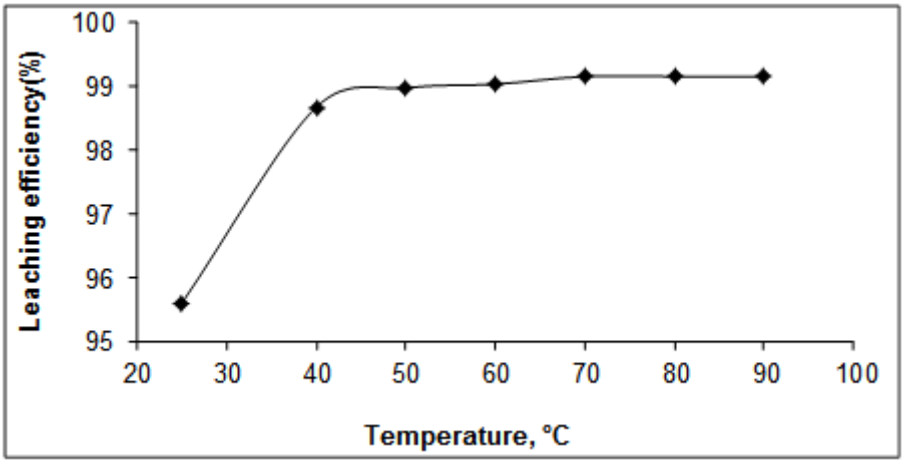

Figure (5): Effect of leaching temperature upon uranium leaching efficiency from the ore sample.

3.2. Characteristics of the Activated Carbon and Modified Activated Carbon

3.2.1. Scanning Electron Microscope Characterization

Scanning Electron Microscope (SEM) is the most reliable and convenient tool for the study of physical structure of modified resin beads with solvent [20]. Accordingly, the surface of modified activated carbon was observed using SEM in order to illustrate the change in its surface feature after modification and after loading of uranium. The activated carbon has been individually modified with tributyl phosphate which fills nearly all the pores of the AC. Scanning Electron Microscope photographs of the surface of the activated carbon before and after are given in Figures (6-8). The micrograph apparently shows that the original activated carbon possesses many vacant pores before modification (Figure 6). On the other hand, the rough surface turned to be relatively bright after modification with tributyl phosphate which suggests that the individual extractants filled out most of the vacant pores (Figures 7). Uranium seems to appear as brilliant spots on the surface of the activated carbon and modified activated carbon as shown in Figures (8) which emphasizes its adsorption on the surface of AC or modified activated carbon.

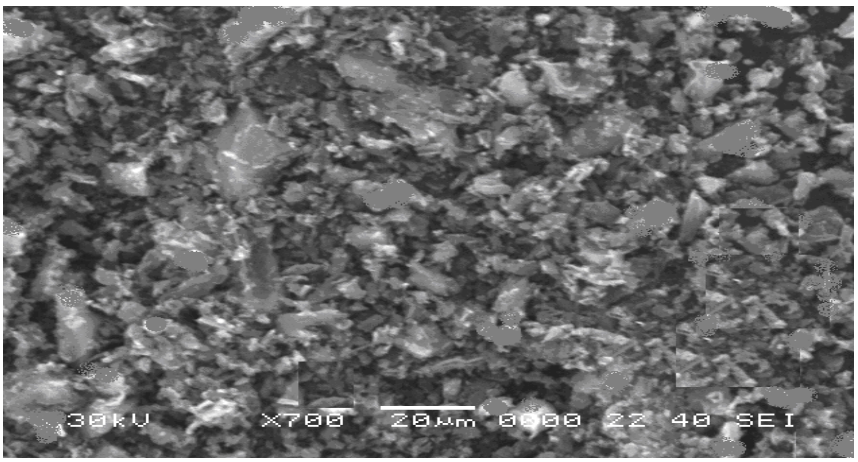

Figure (6): SEM photograph of the AC surface before modification.

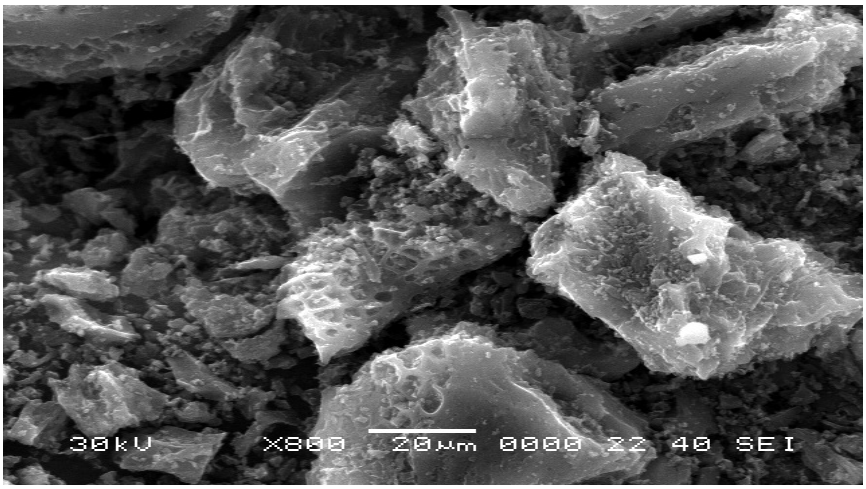

Figure (7): SEM photograph of the AC surface after modification with TBP.

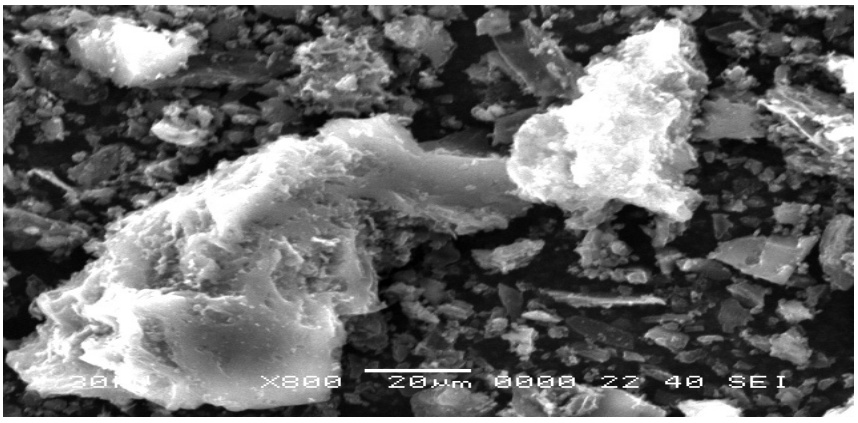

Figure (8): SEM photograph of the modified AC by TBP after loaded with U(VI).

3.2.2. Fourier Transform Infrared Spectrometer Characterization

Fourier Transform Infrared (FT-IR) spectroscopy is an important analysis technique which detects various characteristic functional groups present on surface of activated carbon (AC) or modified activated carbon. On interaction of an infrared light with activated carbon or modified activated carbon surface, chemical bond will stretch, contract or bend, and as a result each functional group tends to absorb infrared radiation in a specific wave number range regardless of the structure of the rest of the molecules. The FTIR spectra were collected in the range of 4000-400 cm^{-1} region. Evaluation of the interaction between the extractant and the beads of the activated carbon has been characterized by Fourier Transform Infrared spectrometer. FTIR has been applied to the activated carbon before and after modification and adsorption of uranium(VI) ions. The IR spectra for activated carbon are given in Figure 9. The spectrum exhibits two strong bands at 3335.2, and 2366.1 cm^{-1} attributed to the O–H stretching band and C≡C stretching, singlet and medium band respectively. Also the spectrum shows five bands at 1565.7, 1450.1, 1210.1, 1030.1 and 522.3 cm^{-1} corresponding to C=C–H stretch, C–H bending, C–O–C ether linkage, C–O bending band and C–C also bending band [21]. While the IR absorbance spectrum for AC modified with tributyl phosphate (TBP) is obtaind in Figures 10. The presence of C–P stretching band at ≈1150 cm^{-1} and P=O stretching band at 960.8 cm^{-1} [22]. From the obtained data which are given in Figures 11. These results shown that, the main differences between the above data in case of absence of uranium ions and the adsorption of uranium ions on the AC and modified AC with TBP were the appearance of U=O stretching band at ≈ 920 cm^{-1} and also, two weak bands of U–O at ≈ 475 and ≈ 415 cm^{-1} [23].

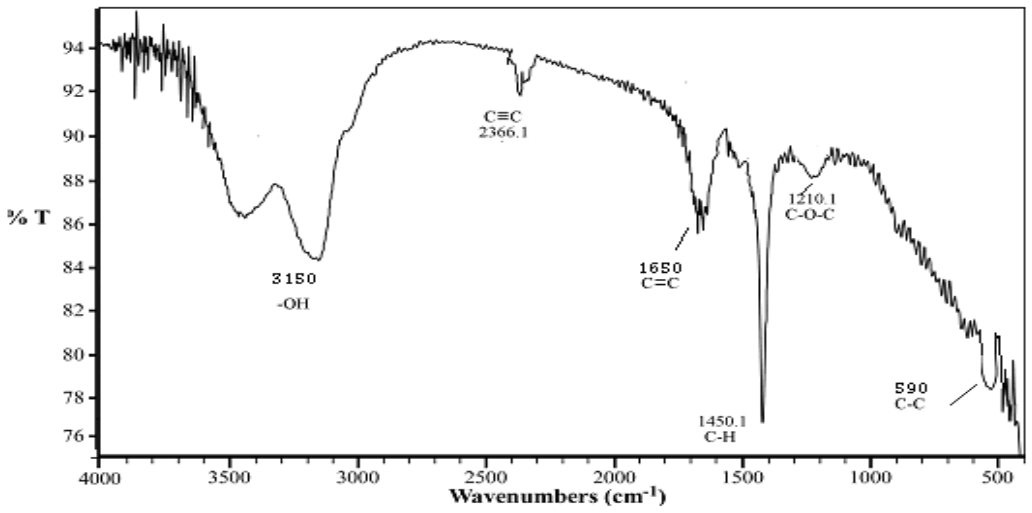

Figure (9): FT-IR spectrum of the AC.

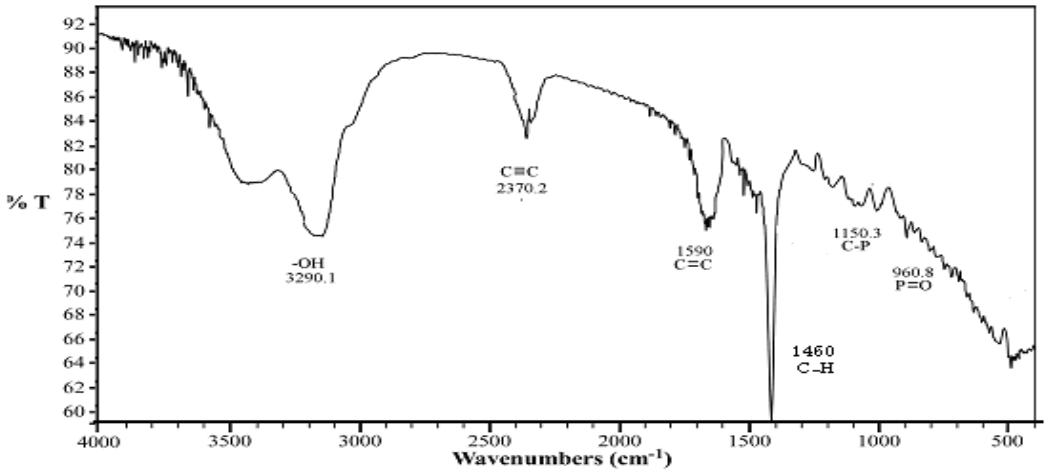

Figure (10): FT-IR spectrum of the AC modified with TBP.

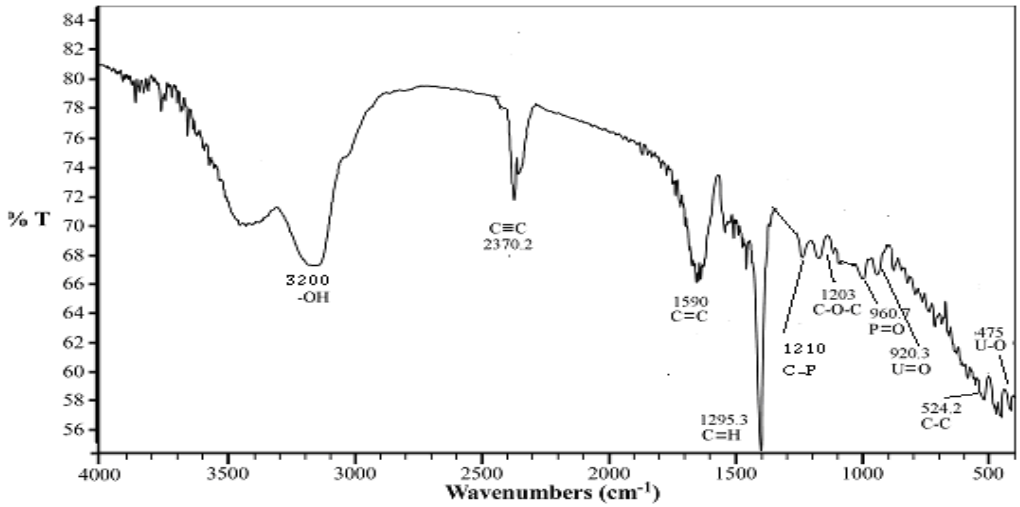

Figure (11): FT- IR spectrum of the AC modified with TBP loaded with uranium(VI) ions.

3.3. Uranium Adsorption Behavior using Activated Carbon (AC) and Modified Activated Carbon

We have investigated the parameters which affect uranium sorption, such as pH, contact time, concentration of TBP, amount of AC and modified AC, initial uranium concentration, and temperature using the leach liquor.

From the above studies of leaching, the applied leach liquor was prepared by mixing a powdered phosphorite sample weighing 250 g with 1 litre of 200 g/l sulfuric acid and 5 % hydrogen peroxide solution (1/4, S/L ratio). The obtained slurry was agitated for 90 min. at 70 ºC and the insoluble residue was separated

by filtration. The obtained leach liquor thus mainly contains uranium ions besides some metal impurities. Also, the prepared leach liquor has similarly been subjected to complete chemical analysis for both the major and trace elements (Table 2). The leach liquor has then been treated for uranium(VI) extraction using AC and modified AC with TBP. Extraction by adsorption of uranium ions from this actual solution was then carried out. The adsorption parameters such as pH, contact time, concentration of TBP, amount of AC and modified AC, and temperature are studied with the leach liquor.

Table (2): Chemical composition of the prepared pregnant solution

Constituents	**Conc. (g/l)**
P_2O_5	6.410
Fe^{3+}	0.98
Ti^{4+}	0.007
U^{6+}	0.025
V^{5+}	0.0217
Al^{3+}	0.910
SO_4^{2+}	40.810
Na^{+}	0.210
Ca^{2+}	0.24
Si^{4+}	0.18
Mg^{2+}	0.11
Zn^{2+}	0.046
K^{+}	0.087

3.3.1. Effect of pH

According to Ritcey and Ashbrook [24], extraction of uranium as an anionic or else as a neutral species from sulfuric acid media depends upon the nature of the present uranium species and which depends in turn upon the sulfate concentration and the solution pH, a matter which is due to the fact that sulfuric acid is a dibasic acid which gives rise to sulfate - bisulphate equilibria. Thus at acidic pH, a high concentration of HSO_4^- would be formed and which would hinder uranium extraction since the uranyl bisulfate is not extractable.

The most important parameter for the adsorption experiments was pH. In order to obtain the optimum pH value for uranium adsorption, several experiments were carried out at different pH values ranging from 0.5

to 7.0 and the other factors were kept constant at 0.03 g of AC or modified AC for 30 min. contact time at room temperature. The pH was adjusted to the required value with either concentration of 2 M H_2SO_4 and 2 M NaOH solutions. Figure (12) shows that the adsorption uranium efficiencies increased by increasing the pH value until 2.5 and the adsorption efficiencies at the interval 2.5 to 5 were constants 50.11 and 94.15% for AC and AC modified with TBP, respectively. At the lower of the pH value for the U(VI) solution, the uptake capacities were decreased upon the AC or modified AC. This is due to the electrostatic repulsion of the protonated active sites with the positively charged uranyl species.

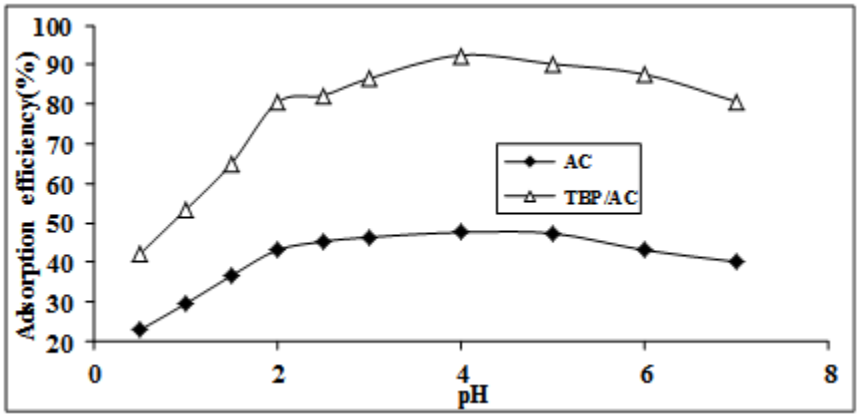

Figure (12): Effect of pH on uranium adsorption efficiency upon AC and modified AC (50 ml of leach liquor containing 25 mg/l uranium concentration, 0.03 g of AC and modified AC, and 30 min. contact time, at room temperature)

3.3.2. Effect of Contact Time

In order to study the effect of contact time of uranium adsorption on activated carbon or modified activated carbon with TBP, a series of adsorption experiments were performed under fixed conditions at 50 ml of leach liquor containing 25 mg/l uranium concentration, 0.03 g of AC or modified AC, and pH 4 at room temperature. The applied contacting time was ranged from 5 up to 120 min. The obtained results show that the uranium adsorption efficiencies were increased rapidly until 50.2 and 94.7% for AC and TBP impregnated AC, respectively at 45 min and then becomes constant (Figure 13). This relatively rapid attainment of equilibrium may be related to the large surface area and adequate active sites of the AC and modified AC. Accordingly, the best contact time is 45 min.

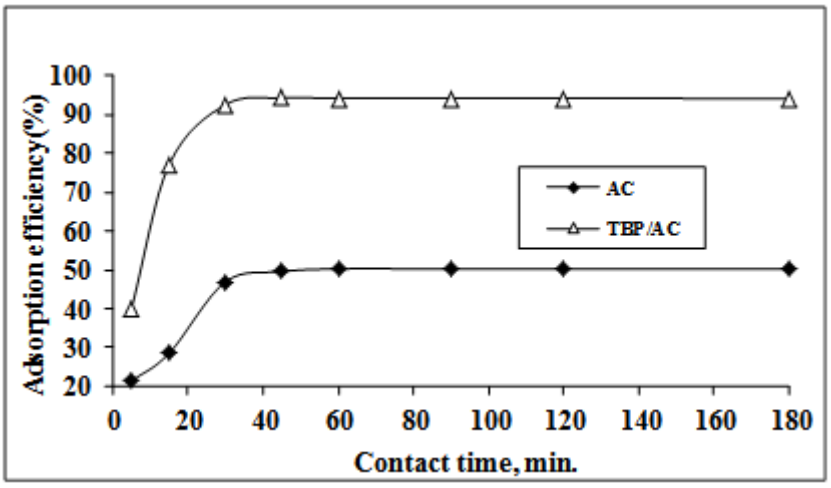

Figure (13): Effect of contact time on uranium adsorption efficiency upon AC and modified AC (50 ml of leach liquor containing 25 mg/l uranium concentration, 0.03 g of AC and modified AC, and pH 4 at room temperature)

3.3.3. Effect of TBP Concentrations

The effect of TBP concentrations impregnated upon 1 g of AC on uranium adsorption efficiency percentage was studied. A series of experiments were performed by using different concentrations of TBP ranging from 5 to 30 %, and stirred with 1 g of AC for 1 h at room temperature and then dried at 60 ºC for 2 h. Adsorption efficiencies of uranium from leach liquor were done with 0.03 g modified AC from the above preparation of different concentration of TBP while other factors were fixed at 50 ml of leach liquor containing 25 mg/l uranium concentration, pH 4 and 45 min. contact time at room temperature (Figure 14). The obtained results indicated that, the uranium adsorption efficiencies have been increased with increasing of the concentrations of the three solvents until reaching maximum values at 20 % of TBP in suitable diluents.

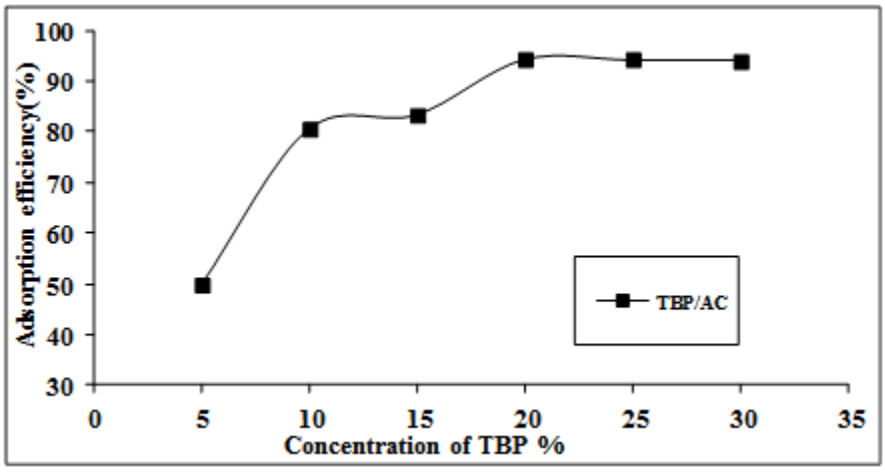

Figure (14): Effect of TBP concentrations on uranium adsorption efficiency upon AC (50 ml of leach liquor containing 25 mg/l uranium concentration, 0.03 g of the prepared modified AC, pH 4 and 45 min. contact time at room temperature)

3.3.4. Effect of Amount of AC and Modified AC

The Effect of amounts of AC and modified AC on the adsorption efficiency of U(VI) ions was applied within the range from 0.005 to 0.05 g to achieve a high adsorption capability. These experiments were performed by stirring of 20 ml leach liquor containing 25 mg/l of uranium ions with different amounts of AC or modified AC by TBP (20 %) at pH 4 and 45 min contact time at room temperature (Figure 15). The obtained results shown that the adsorption of uranium increase as the amount of adsorbents increase until 0.03 g while the uranium adsorption efficiencies were constants with increasing the amounts of adsorbents from 0.03 to 0.05 g. Finally, the suitable amount of the studied individually adsorbent is 0.03 g to obtain the highly uranium adsorption efficiency from its solution.

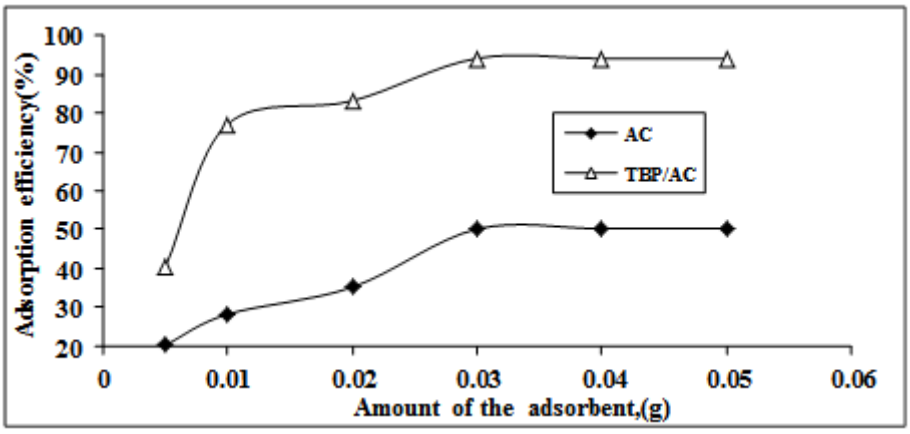

Figure (15): Effect of amount of AC and modified AC on uranium adsorption efficiency (50 ml of leach liquor containing 25 mg/l uranium concentration, pH 4 and 45 min. contact time at room temperature)

3.3.5. Effect of Initial Uranium Concentration

Effect of initial uranium concentration is the most important parameters on the sorption system, which can influence the sorption behavior of U(VI) ions. The effect of initial uranium concentrations on its extraction upon AC or modified AC with TBP were studied by 60min. contacting time, (1 g) mass of the working adsorbents (AC and modified AC) with a solution volume of 100 ml and pH 4 at room temperature (25 °C±1) using a range of initial uranium concentration varying from 100 mg/l (0.42 mmole/l) to 1000 mg/l (4.20 mmole/l). The results are given in Figure (16), revealing that increasing the initial uranium concentration, the amount of uranium loaded on the working adsorbents (mg/g) have increased and reached a maximum loading at 600 mg/l initial uranium concentration. The maximums loading efficiencies at 600 mg/l initial uranium concentration for AC and TBP/AC are 40.5 and 97.0 %, respectively. These mean that, the

maximum loading of uranium ions on AC, and TBP/AC are 24.3 mg/g (243 mg/l), and 58.2 mg/g (582 mg/l), respectively. After that, the loaded uranium amounts have remained constant expressing that the working adsorbents have reached to its maximum loading capacity (saturation capacity). Because the mobility of uranyl ions $(UO_2)^{2+}$ in the solutions is the highest and the interactions of these ions with the adsorbents are increased [25].

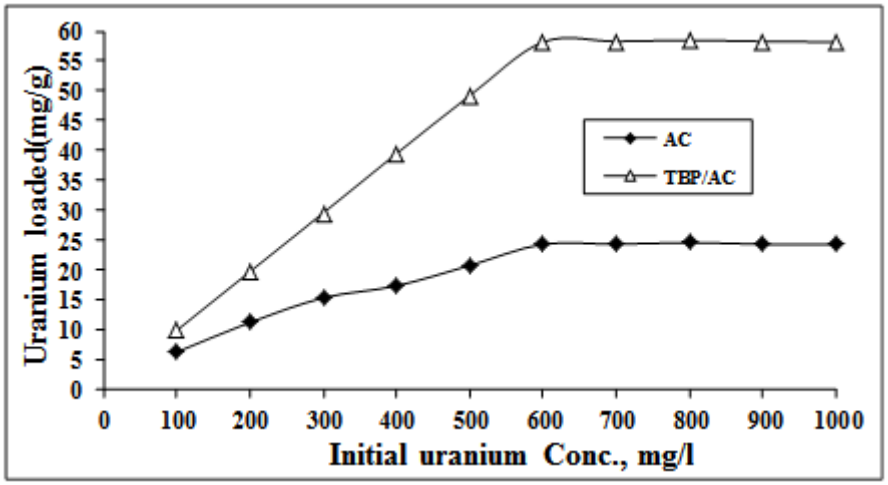

Figure (16): Effect of initial uranium concentration (mg/l) on its loading (mg/g) upon AC, modified AC (100 ml uranium solution, 1 g of AC or modified AC, pH 4 and 60 min. contact time at room temperature)

3.3.6. Effect of Temperature

By using a uranium solution after leaching of phosphate rock sample, the effect of temperature upon uranium adsorption on AC or modified AC by TBP was studied from 25 to 90 ºC under the previous optimum conditions. From the obtained results in reported Figure (17) it can be observed that the adsorptions efficiencies of uranium decreased with the increase of temperature, this due to the dissolution of the bonds between adsorbent and adsorbate.

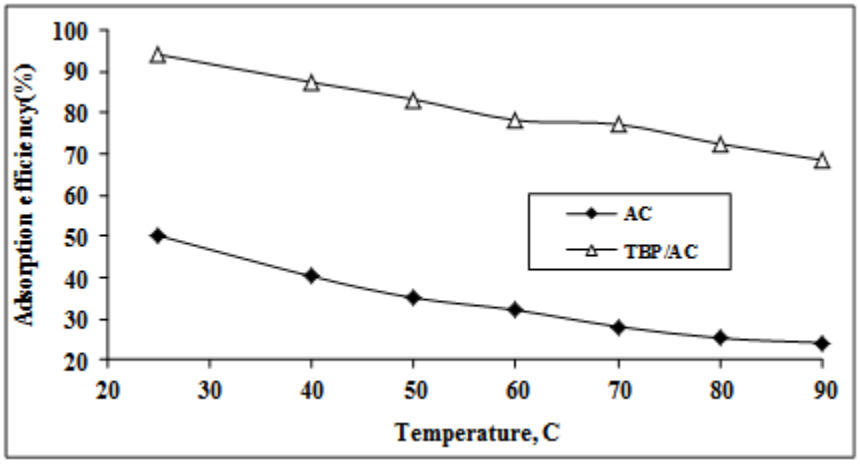

Figure (17): Effect of temperature on uranium adsorption efficiency upon AC, modified AC (50 ml of leach liquor containing 25 mg/l uranium concentration, 0.03 g of AC and modified AC, pH 4 and 45 min. contact time)

3.4. Adsorption Kinetics

An important characteristic influencing the possibility of the commercial use of the sorbent is the sorption rate. It is well recognized that the characteristic of the sorbent surface is a critical factor that affect the sorption rate parameters and that diffusion resistance plays an important role in the overall transport of the ions. To describe the changes in the sorption of metal ions with time, simple kinetic models such as simple first order model, pseudo first-order model and pseudo second-order rate model were tested [26].

According to Alkan et al. [27], most sorption processes take place by a multi-step mechanism comprising (i) diffusion across the liquid film surrounding the solid particles (a process controlled by an external mass transfer coefficient), (ii) diffusion within the particle itself assuming a pore diffusion mechanism (intraparticle diffusion), and (iii) physical or chemical adsorption at a site. On the other hand, the transient behavior of the batch sorption process of each of the studied metal ions was analyzed using both the Lagergren pseudo first-order kinetics model and the pseudo second-order model [28].

The Lagergren pseudo first order model is given by the equation:

$$Log\left(q_e - q_t\right) = Logq_e - \left(\frac{K_1}{2.303}\right)t \tag{4}$$

Where q_e and q_t are the concentrations of the ion sorbed at equilibrium and at time t (mg/g) respectively and K_1 is the pseudo first order rate constant (min^{-1}).

From the obtained data, the kinetic plots of $Log(q_e-q_t)$ versus t for the obtained uranium(VI) ions sorption upon the working adsorbents (AC or modified AC) have indicated a deviation between the

experimental and the calculated q_e values; a matter which confirms that it is not appropriate to apply the Lagergren kinetic model to predict the sorption kinetic of the studied system. From figures (18-19), the latter system do not follow a pseudo first order reaction ($R^2 < 0.85$).

The obtained kinetic data were thus analyzed using the pseudo second-order model within the form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (5)$$

Where K_2 is the rate constant of the pseudo second-order equation(g/mg. min). From the obtained data, the kinetic plots of t/q_t versus t for uranium sorption onto the working adsorbents (AC or modified AC with TBP) were represented in Figures (20-21), the obtained relations are linear and the values of the correlation coefficient (R^2) suggest a strong relationship between the parameters and also explain that the processes of ion sorption follow the pseudo second-order kinetic model. The product $K_2 q_e^2$ is the initial sorption rate represented as $h = K_2 q_e^2$. The kinetic parameters of this model are calculated from the slope and intercept of the linear plot. The correlation coefficient (R^2) has an extremely high value (≥ 0.97) as shown from Figures (20-21). So, it is possible to suggest that the sorption of uranium complex ions onto the working adsorbent would follow the pseudo second-order kinetic model and that the pseudo second-order equation rate constant of the sorption process appears to be controlled by the chemical sorption process [29].

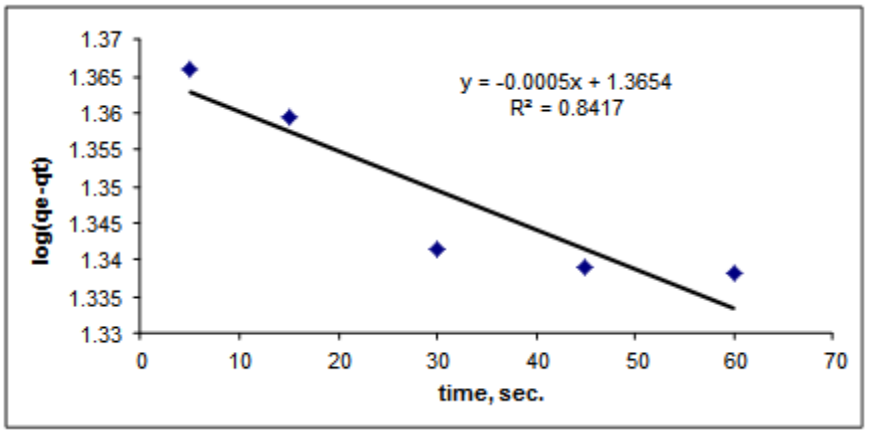

Figure (18): Pseudo first-order plot for uranium(VI) loading upon the AC from sulfate leach liquor

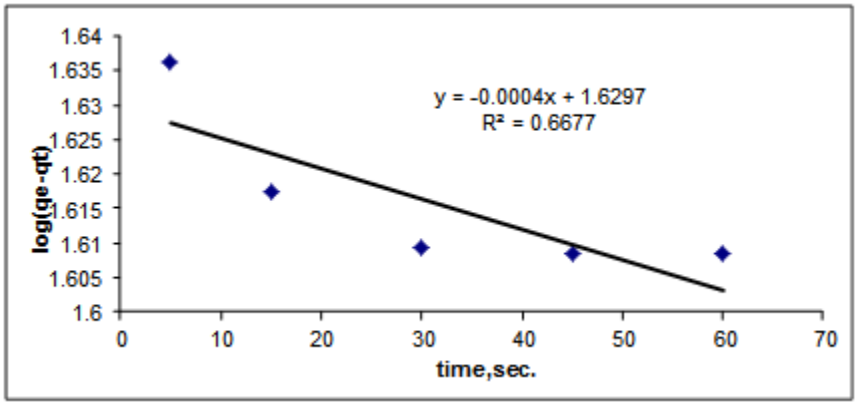

Figure (19): Pseudo first-order plot for uranium(VI) loading upon the modified AC with TBP from sulfate leach liquor.

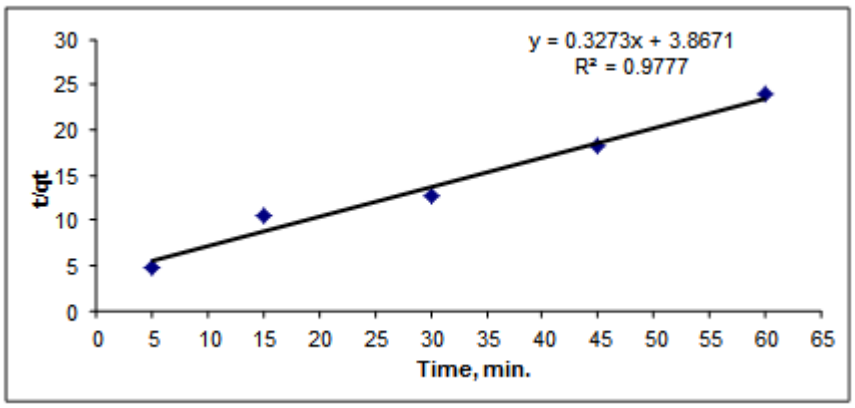

Figure (20): Pseudo second-order plot for uranium(VI) loading upon the AC from sulfate leach liquor

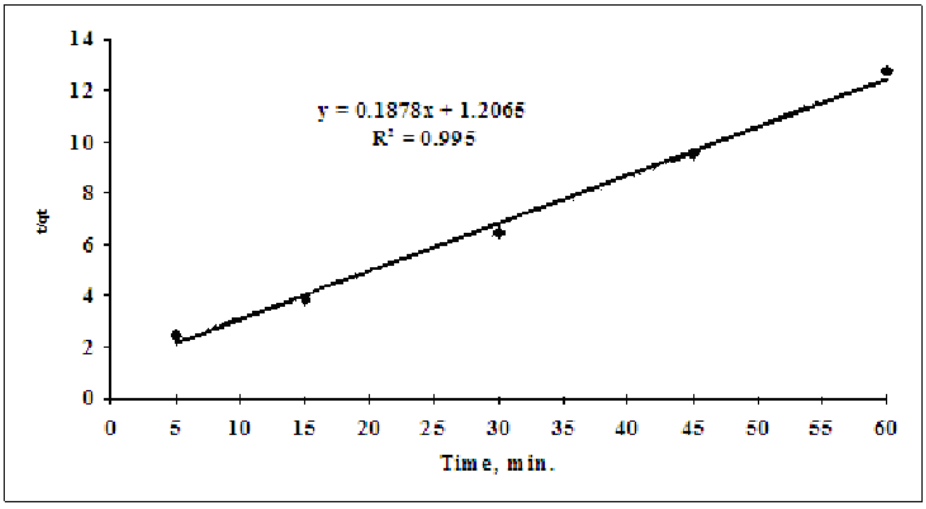

Figure (21): Pseudo second-order plot for uranium(VI) loading upon the modified AC with TBP from sulfate leach liquor

3.5. Adsorption Isotherms

The common sorption isotherm models indicating those of Freundlich and Langmuir were used to study the fitness of the obtained isotherm data.

3.5.1. Freundlich Isotherm Model

The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface [30]. Freundlich equation was derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. In the logarithmic form of the Freundlich equation:

$$Logq_e = LogK_f + \frac{1}{n} LogC_e \quad (6)$$

Where K_f is the constant indicative of the relative adsorption capacity of the activated carbon (mg/g), C_e the equilibrium concentration of the metal ion in the equilibrium solution (mg/l) and 1/n is the constant indicative of the intensity of the adsorption process. The illustration of Log q_e versus Log C_e, from the obtained adsorption data are shown in Figures (22-23) and from which it can be suggested that the sorption of the uranium complex ions obeys Freundlich isotherm over the entire range of the studied sorption concentration. The numerical values of the constants 1/n and K_f are computed from the slope and intercept by means of a linear least square fitting method and are given in Table (3). It can be seen from these data that the Freundlich intensity constant (n) is greater than unity for the studied uranium ion. This has physicochemical significance with reference to the qualitative characteristics of the isotherms, as well as to the interactions between metal ion species and modified activated carbon.

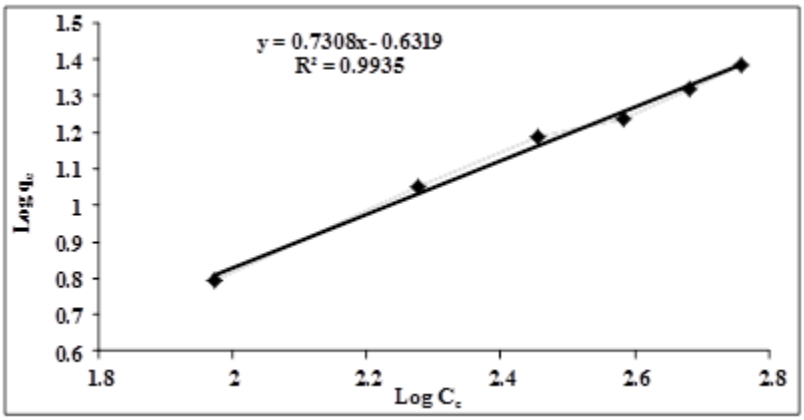

Figure (22): Freundlich equilibrium isotherm model for the sorption of the U(VI) ions from aqueous solution using AC as an adsorbent.

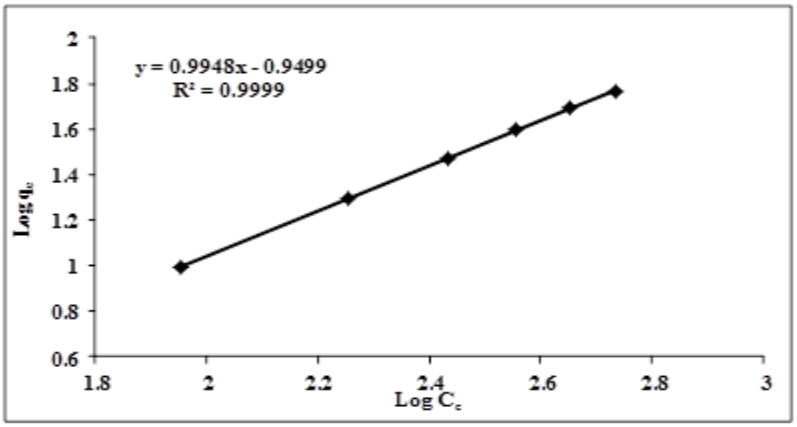

Figure (23): Freundlich equilibrium isotherm model for the sorption of the U (VI) ions from aqueous solution using modified AC with TBP as an adsorbent.

Table (3): Freundlich equilibrium constants for U(VI) ions by AC or modified AC with TBP in aqueous solution at 25 °C

Freundlich parameters	AC	TBP/AC
Freundlich isotherm K_f (mg/g)	0.2334	0.1908
n	1.368	1.119
R^2	0.9935	0.9999

3.5.2. Langmuir Isotherm Model

The adsorption of uranium (VI) as a function of AC and modified AC with TBP is studied by equilibrating for 60 min. contact time, pH 4 at room temperature. The amount of uranium (VI) loaded onto AC and modified AC is determined by following the general procedure described above. Adsorption data for a wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Langmuir isotherm, which relate adsorption density (q_e) (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase (C_e) [31]. Langmuir sorption isotherm models the monolayer coverage of the sorption surfaces and assumes that sorption occurs on a structurally homogeneous adsorbent and all the sorption sites are energetically identical. The linearized form of the Langmuir equation is given by:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^0 b}\right) + \left(\frac{1}{Q^0}\right) C_e \tag{7}$$

Where Q^0 and b, the Langmuir constants related to the saturated sorption capacity and the sorption equilibrium constant respectively. From the obtained data a plot of C_e/q_e versus C_e of AC and modified AC with TBP resulted in a straight lines with a slope of $[1/Q^0]$ and an intercept of $[1/Q^o b]$ show that adsorption obeys Langmuir adsorption model (Figures 24-25). The correlation coefficient, Q^0 and b for the linear regression fits of the Langmuir plots determined from the Langmuir plot were found in Table (15).

The Langmuir parameters given in Table (4) can be used to predict the affinity between the sorbate and the sorbent using the dimensionless separation factor R_L [32]:

$$R_L = \frac{1}{(1 + bC_0)} \tag{8}$$

Where C_0 is the highest initial metal ion concentration (mg/l).The value of R_L indicates the type of isotherm to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1), or unfavorable (R_L>1). The R_L value (Table 6) was found to be less than 1 and greater than 0 indicating the favorable sorption isotherms of metal ions.

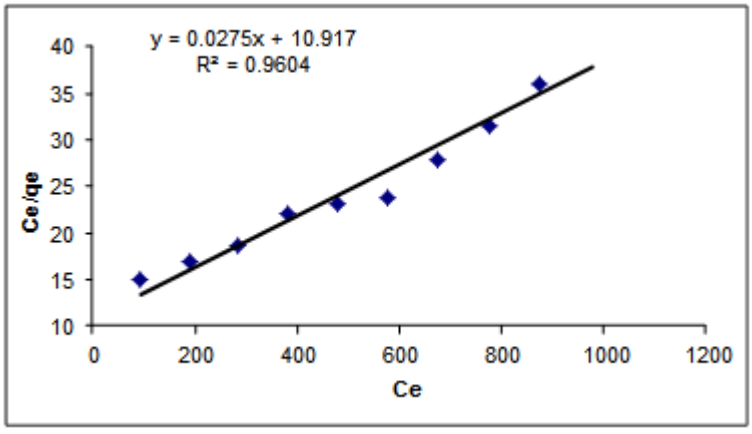

Figure (24): Langmuir equilibrium isotherm model for the sorption of the U(VI) ions from aqueous solution using AC as an adsorbent.

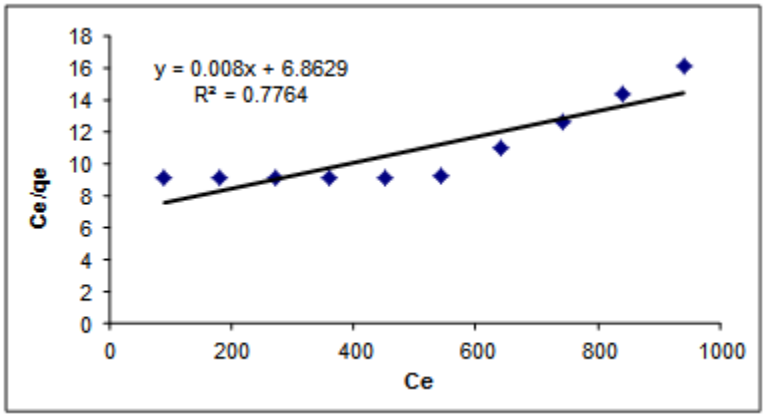

Figure (25): Langmuir equilibrium isotherm model for the sorption of the U(VI) ions from aqueous solution using modified AC with TBP as an adsorbent.

Table (4): Langmuir equilibrium constants for U(VI) ions by AC and modified AC with TBP in aqueous solution at 25 °C.

parameters	AC	TBP/AC
Langmuir isotherm Q_0 (mg/g)	35.014	121.14
b (l/mg)	0.00317	0.001179
R^2	0.9604	0.7764
R_L	0.90	0.8750

4. Conclusion

The parameters of uranium leaching have been investigated and optimized conditions determined (1g of phosphate ore contact with 4ml of H_2SO_4 (200g/l) and H_2O_2 (5%) for 90min. at 70°C.and The parameters that affect the uranium(VI) adsorption have been investigated and optimized conditions determined (0.03g of AC, modified AC contact with 50 ml of leach liquor for 45min. at pH 4 and room temperature). While the maximum loading of uranium ions on AC and TBP/AC are 24.3 mg/g (243 mg/l), and 58.2 mg/g (582 mg/l), respectively.

Both the kinetic and the sorption isotherm modeling have been applied upon the obtained data. Thus, it was found that the uranium sorption obeys a pseudo-second order reaction while the Freundlich sorption isotherm model is most suitable to describe the studied sorption reaction.

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