Extraction and Pre-concentration of Uranium Using Activated Carbon Impregnated Trioctyl Phosphine Oxide

Hassanien Gomaa Abdien [1,*], Mohamed Farid Mohamed Cheira [2,*], Mohamed Abd-Elmottaleb Abd-Elraheem[1], Tarek Ahmed Saef El-Naser[1] and Ibrahim Hashem Zidan[2]

[1]Chemistry Department Faculty of Science, Al-Azhar University, Assiut, Egypt.

[2]Nuclear Materials Authority, Cairo, Egypt.

ABSTRACT

This paper focused on the recovery of uranium from solutions. The adsorption of uranium(VI) from standard uranium solution using activated carbon AC and AC impregnated by trioctyl phosphine oxide (TOPO) was studied using a batch system. The parameters that affect the uranium(VI) adsorption, such as contact time, solution pH, initial uranium(VI) concentration, concentration of TOPO, amount of AC and modified AC, and temperature were investigated and optimized conditions determined (0.03g of AC and modified AC contact with 20ml of standard uranium solution (100 mg/l) at pH4 and room temperature for 45min.). The maximum loading of uranium ions on AC and TOPO/AC are 23 mg/g (230 mg/l) and 57.6 mg/g (576 mg/l), respectively. Uranium (VI) could be conveniently recovered by elution by H_2SO_4 this allows recycling of adsorbent. And it's 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.

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1. Introduction

Uranium is a radioactive element and above all chemically toxic [1]. Overexposure to it can cause important health problems such as kidney and other organ failures leading to death [2]. The maximum acceptable concentrations (MAC) limit of uranium for drinking water is 30 ppb [3]. Uranium disposed into the environment can eventually reach the top of the food chain, which can possibly be ingested, causing severe kidney or liver damage and even death, therefore, it is necessary to treat wastewater containing uranium to prevent radioactive contamination of the environment [4].

Several methods are available for removal and recovery of uranium from radioactive aqueous solution, such as chemical precipitation, evaporation, reverse osmosis, ion exchange, solvent extraction, micellar ultrafiltration [5, 6]. Among of these methods, adsorption is an important technique in separation and purification processes which is used in water and waste water industry to the removal of color, odor, and organic pollution [7]. Only adsorption is the most effective method due to the low cost, ease of regeneration, eco-friendly nature and has high efficiency, especially when the uranium concentration is over the allowable limit in nature [8, 9]. To date, numerous adsorbents have been developed including activated carbon, kaolinite, mesoporous silica, cellulose, metal oxides goethite, olivine rock, coir pith, bentonite and polymers [10-15]. Among the numerous adsorbents, activated carbon is one of the most widely used in underdeveloped countries in treatment of various industrial effluents [16]. The activated carbon has been chosen for its chemical, radiation, and thermal stability.

In fact, the activated carbon can be considered as the most effective and economic process [17]. In view of the above, the current paper has focused on the uptake behavior of uranium from uranium solution by solid phase extraction using activated carbon (AC) as a supporting material anchored with TOPO and elution of uranium ions from the adsorbent. In the same time, the latter was interpreted via sorption kinetic and adsorption isotherm modeling.

2. Experimental

2.1. Materials

All of the chemical reagents used in this experiment were analytically pure. Nitric acid and Sulphuric acid (Analar BDH laboratory supplies Poole, England), Hydrochloric acid (Merck, Germany), Ammonia hydroxide (ADWIC, Prolabo), Sodium acetate trihydrate (Pratap PVT.LTD, India), Activated carbon and Sodium hydroxide (ADWIC, Prolabo), Arsenazo(III) and Urea(Sigma), Uranyl acetate dehydrate (BDH Chemicals Ltd. Poole, England), and Trioctyl phosphine oxide (TOPO) (Sigma-Aldrich),

2.2. Preparation of Activated Carbon (AC) and Trioctyl Phosphine Oxide Modified Activated Carbon

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.

Tele:
E-mail address: ch_h.gomaa22@yahoo.com

The oxidized product was dried in a drying furnace at 110 °C for 24h to enhance the hydroxyl capacity on AC, and therefore the products with abounding hydroxyl (HO-AC) was obtained [18]. The preparation of trioctyl phosphine oxide (TOPO) modified activated carbon was carried out by wet method. In this method, the solution of 1 g of TOPO in 25 ml acetone (diluent) was added to a suspension of 10 gm of activated carbon in 500 ml of deionised water with constant stirring at room temperature. The resulting mixture was stirred and refluxed for 5 h and was allowed to settle for 30 min. Then it was filtered through filter paper placed in a Buchner funnel by suction, washed with deionised water, dried in an oven at 60°C for 24h and then stored in an amber coloured bottle. 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.

2.3. 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).

2.4. Experimental Procedures: 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 [19]:

$$q_e = (C_0 - C_e) \times \frac{V}{m} \tag{1}$$

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:

$$A\% = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \tag{2}$$

2.5. 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 [20].

3. Results and Discussion

3.1. Scanning Electron Microscope Characterization

Scanning Electron Microscope (SEM) is the most reliable and convenient tool for the study of physical structure of materials [21]. 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 trioctyl phosphine oxide which fills nearly all the pores of the AC. Scanning Electron Microscope photographs of the surface of the activated carbon before and after is given in Figure (1a, b and c). The micrograph apparently shows that the original activated carbon possesses many vacant pores before modification (Figure 1a). On the other hand, the rough surface turned to be relatively bright after modification with trioctyl phosphine oxide which suggests that the individual extractants filled out most of the vacant pores (Figure 1b). Uranium seems to appear as brilliant spots on the surface of the activated carbon and modified activated carbon as shown in Figures (1c) which emphasizes its adsorption on the surface of AC or modified activated carbon.
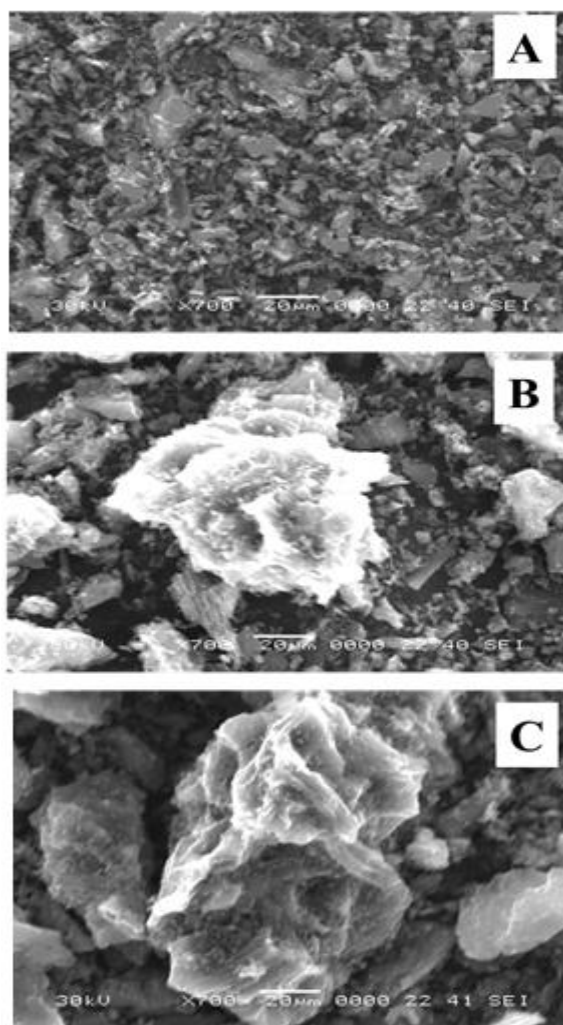

Figure 1. A. SEM photographs of the AC surface before modification. B. AC surface after modification with TOPO. C. The modified AC by TOPO after loaded with U(VI).

3.2. 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 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 spectrum for activated carbon are given in Figure 2a 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 [22]. While the IR absorbance spectra for AC modified with trioctyl phosphine oxide (TOPO) are obtaind in Figure 2b. The main differences between the AC and the modified with TOPO were obtained because of the prescence of C–P stretching band at ≈1150 cm^{-1} and P=O stretching band at 960.8 cm^{-1} [23]. From the obtained data which are given in Figure (2c). 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 TOPO 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} [24].
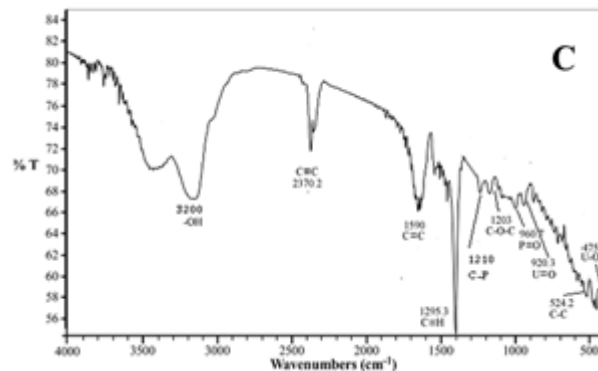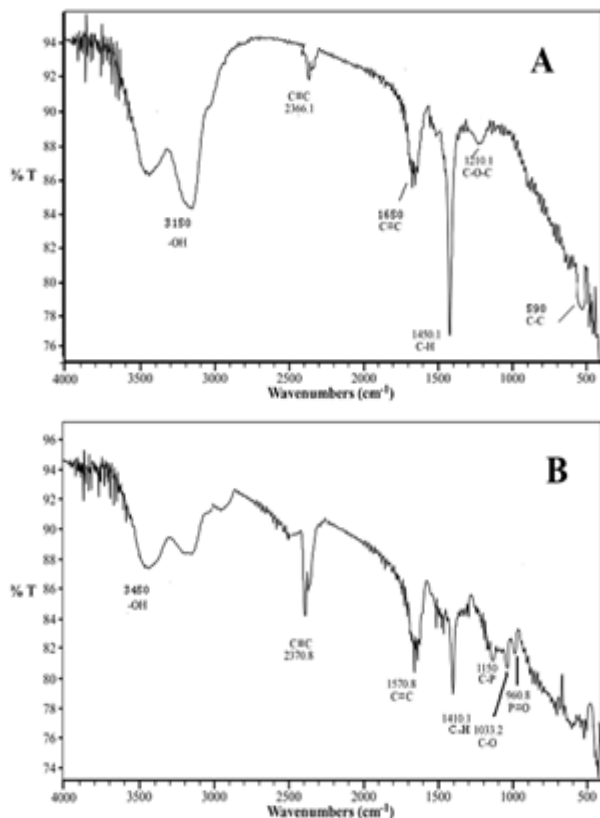

Figure 2. A. FT-IR spectra of the AC. B. AC modified with TOPO. C. the AC modified with TOPO loaded with standard uranium(VI) ions.

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

Several batch experiments were performed to study the different relevant adsorption factors. Each experiment was performed by stirring 0.03 g of AC and modified AC with 20 ml of uranium solution, at room temperature (25 °C ±1) for 30 minute. The solution was then filtered and uranium concentration was spectrophotometrically determined with arsenazo(III) before and after of experiment. In this study, the adsorption parameters such as pH, contact time, concentration of TOPO, amount of AC and modified AC, initial uranium concentration, and temperature are studied with the standard uranium solution. Also, studying the factors that affected on the elution process of uranium. Figure 3 show scheme illustration of major steps involved adsorption and recovery of uranium using AC and modified AC
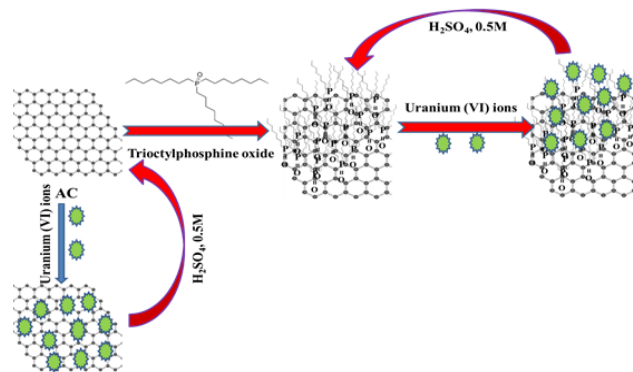

Figure 3. Scheme illustration of major steps involved adsorption and recovery of uranium using AC and modified AC.

3.3.1.Effect of pH

The most important parameter that would control uranium extraction is the pH. In order to obtain the optimum pH value for uranium extraction, several batch tests were performed at different pH values ranging from 0.5 to 7 and the other parameters were kept constant (0.03 g of AC or modified AC, 20 ml of 100 mg/l standard uranium solution for 30 minute at room temperature). The pH was adjusted to the required value with 2 M H$_2$SO$_4$ and 2 M NaOH solutions. The obtained results in Figure (4a) show that the uranium loading efficiency was increased by increasing the pH value until pH 2.5 while the pH from 2.5 to 5, the uranium loading efficiencies were constant at 50.12, and 98 % for AC and modified AC with TOPO respectively. At the lowering pH value of the U (VI) solution was decreased the uptake capacity of the AC or modified AC.

This is due to the electrostatic repulsion of the protonated active sites with the positively charged uranyl species [25]. Accordingly, maximum adsorption efficiencies occur at pH range 2.5 - 5. The pH dependence of metal ion adsorption is a complex phenomenon and strongly influences the metal ions adsorption. The pH has two kinds of influence on metal sorption an effect on the solubility and speciation of metal ions in solution, and on the overall charge of the sorbent. Uranium exists in hydrolyzed form and the following ionic species have been identified UO_2^{2+}, $[(UO_2)_2(OH)_2]^{2+}$ dimmer, $[(UO_2)_3(OH)_5]^+$ trimmer. These species are exchanged at the functional groups on the surface of AC, when pH increases beyond 5 precipitation starts due to the formation of complexes in aqueous solution and adsorption decreases since micropores are not formed [26].

3.3.2. Effect of Contact Time

The effect of contact time was investigated for the adsorption of U (VI) on activated carbon and modified activated carbon as a function of contact time ranging from 5 to 180 min. while other factors were kept constant at 0.03 g of AC or modified AC contact with 20 ml of standard uranium solution (100 mg/l) and pH 4 at room temperature. From the obtained results, it was found that the time required for uranium loading efficiencies at 50.1 and 98% for AC and AC modified with TOPO respectively, is achieved within 45 min. and then it becomes nearly constant (Figure 4b). This relatively rapid attainment of equilibrium may be related to the large surface area and adequate active sites of the AC and modified AC. This relatively rapid attainment of equilibrium may be related to the large surface area and adequate active sites of the modified activated carbon besides the relatively low initial uranium concentration of the applied solution [27]. Therefore, 45 min. contact time was chosen as optimum contact time for adsorption of uranium ions upon AC and modified AC.

3.3.3. Effect of TOPO Concentrations

The effect of TOPO concentrations impregnated upon 1 g of AC on uranium adsorption efficiency percentage was studied. For this purpose, a series of experiments were carried out using different concentrations of TOPO ranging from 5 to 30%, and stirred with 1 g of AC for 1 h at room temperature then dried at 60 ℃ for 2 h. Adsorption experiments were performed by 0.03 g of modified AC which previously prepared to obtain the suitable concentration of TOPO while the other factors were fixed at 20 ml of standard uranium solution (100 mg/l), pH 4 and 45 min. contact time at room temperature. From the obtained results reported in Figure (4c), it can be observed that the uranium adsorption efficiencies have been increased with increasing of the concentrations of the three solvents until reaching maximum values at 20 % of TOPO in suitable diluents.

3.3.4. Effect of Amount of Adsorbents

The Effect of amounts of AC or modified AC on the adsorption percent of U(VI) ions was studied within the range from 0.005 to 0.050 g to achieve a high adsorption capability. These experiments were carried out by stirring of 20 ml of standard uranium solution (100 mg/l) with different amounts of AC or modified AC by TOPO (20%) at pH 4, 45min contact time and room temperature. The results in Figure (4d) shown that the adsorption of uranium increases as the amount of adsorbents increase until 0.03 g while the uranium adsorption efficiencies were constant 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.

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 TOPO 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 pH4 at room temperature (25 ℃±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 (4e), 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 TOPO/AC are 40.5 and 96.0 %, respectively. These mean that, the maximum loading of uranium ions on AC and TOPO/AC are 23.0 mg/g (230 mg/l) and 57.6 mg/g (576 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].

3.3.6. Effect of Temperature

The effect of temperature upon uranium adsorption on the AC or modified AC by TOPO was studied by varying from 25 to 70 ℃ while the other parameters were kept constant under the 20 ml of 100 mg/l uranium concentration, 0.03 g of AC or modified AC, pH 4 and 45min. contact time. From the obtained results shown in Figure (4f), indicates that the adsorption uranium percentage decreased with the increase of temperature, this due to the dissolution of the bonds between adsorbent and adsorbate [25]. The reducing of the adsorption efficiency by stepping up the temperature is due to the higher temperature inactivates the metal ions for enhancing adsorption at the coordinating sites of the adsorbent. The percentage of metal ions adsorption decreased with increasing temperature indicating that the process is exothermic in nature [28]. Accordingly, the maximum efficiencies of uranium uptake by AC and modified AC by TOPO are 50.1 and 98 % respectively, which are equivalent to 33.39 and 65.32 mg uranium per 1 g of AC and modified AC by TOPO respectively, and so the adsorption processes are clearly favored at room temperature (25 ℃±1).

3.4. Uranium Elution Behavior and Recycibility of Adsorbent

Elution of the interested analytes is performed by an appropriate solvent, without removing retained matrix components. The solvent volume must be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution. The adsorbed uranium(VI) onto AC and modified AC with TOPO was eluted with suitable eluant such as H_2SO_4. The solution was then filtered and the concentration of uranium was spectrophotometrically determined with arsenazo(III). The effect of eluent concentration (H_2SO_4) on elution of uranium upon AC or modified AC loaded by standard uranium was studied.
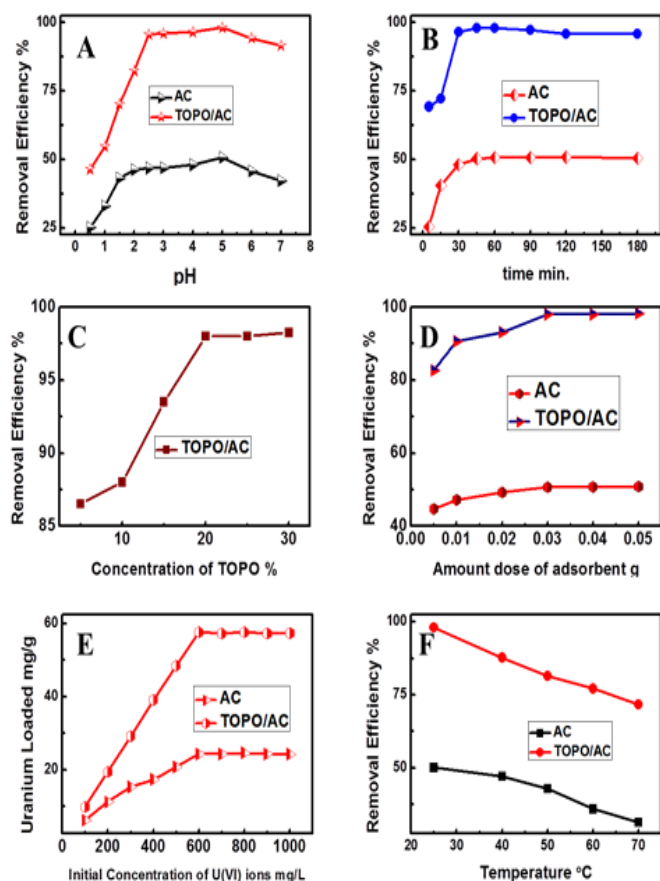
Figure 4. A. Effect of pH on uranium adsorption efficiency upon AC and modified AC (20 ml of 100 mg/l uranium concentration, 0.03 g of AC and modified AC, and 30 min. contact time, at room temperature). B. Effect of contact time on uranium adsorption efficiency upon AC and AC modified. C. Effect of TOPO concentration. D. Effect of amount of AC and modified AC on uranium adsorption efficiency. E. Effect of initial uranium concentration (mg/l) on its loading (mg/g). F. Effect of temperature on uranium adsorption efficiency upon AC, modified AC (20 ml of 100 mg/l uranium concentration, 0.03 g of AC and modified AC, pH 4 and 45 min. contact time).

For this purpose, elution experiments were carried out using different concentration of H_2SO_4 (10 ml) ranging from 0.05 to 1M while other factors were kept constant at 0.5 g of AC or modified AC loaded with uranium for 30 min. contact time at room temperature. The obtained results in Figure (5a) indicated that, the uranium elution efficiency increased with increasing concentration of eluent until reaching maximum value at 0.5M H_2SO_4 and the uranium elution efficiency steady stable after 0.5M of H_2SO_4. Effect of contact time on elution of the loaded uranium onto the AC or modified AC with TOPO was carried out by varying contact time from 10 to 120 minutes, while the other parameters were kept constant at 0.5 g of AC or modified AC loaded with standard uranium contact with 10 ml of 0.5 M H_2SO_4 at room temperature. The results in Figure (5b) clear that, the time required for maximum elution efficiency of uranium is achieved within 60 min. and then it becomes nearly constant. The effect of solid/liquid ratio (weight of AC or modified AC/volume of 0.5 M H_2SO_4) on the elution of uranium loaded on AC or modified AC was studied by varying the S/L ratio from 1/5 to 1/30 under the optimum conditions at room temperature for 60 min. contact time. A series of 0.5 g of AC or modified AC loaded by standard uranium was contacted with different

volumes of 0.5 M H_2SO_4 ranging from 2.5 to 15 ml. The results indicate that, the best solid/liquid ratio is 1/20 (Figure 5c). The most important parameter that would control uranium elution percent is temperature. Under the previous optimum conditions, the effect of temperature upon uranium elution from AC or modified AC loaded by standard uranium was studied from 25 to 70 °C. From the obtained results reported in Figure (5d) it can be observed that the uranium elution percent increased with the increase of temperature, this is due to the dissolution of the bonds between adsorbent and adsorbate.
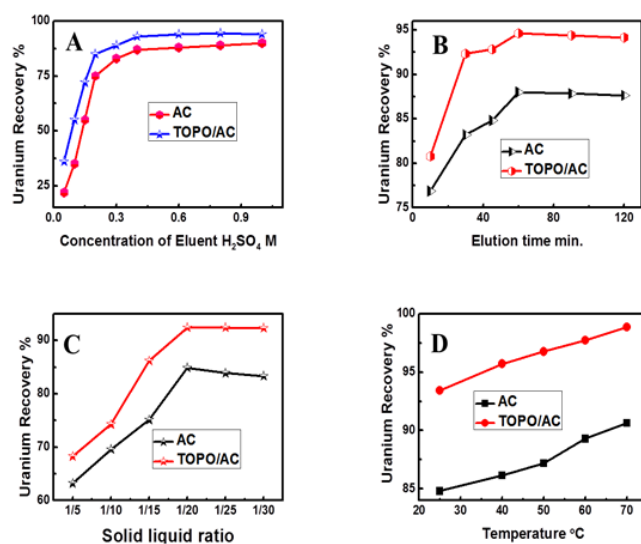

Figure 5. A. Effect of eluent concentration on the eluted uranium efficiency % of the loaded uranium upon AC or modified AC (10 ml of sulfuric acid, 0.5 g of AC or modified AC adsorbed with U(VI), 30min. contact time at room temperature). B. Effect of contact time on the eluted uranium efficiency % .C. Effect of solid/liquid phase ratio on the eluted uranium efficiency %. D. Effect of temperature on the eluted uranium efficiency % of the loaded uranium upon AC, modified AC (10 ml of 0.1 M concentration of sulfuric acid, 0.5 g of AC or modified AC adsorbed with U(VI) at 60 min. contact time).

3.5. Adsorption Kinetics and Isotherm:

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 [29]. According to Alkan et al. [30], 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 pseudo first-order kinetics model and the pseudo second-order model [31]. The pseudo first order model is given by the equation:

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

(3)

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 kinetic model to predict the sorption kinetic of the studied system. From figures (6a), the latter systems 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:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{4}$$

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 TOPO) were represented in Figures (6b), 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 (6b). 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 [32].

The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface [33]. Freundlich equation was derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. In the logarithmic form of the Freundlich equation:

$$ln\ q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

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 Ln q_e versus Ln C_e, from the obtained adsorption data are shown in Figure (6c) 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 (1). 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. The adsorption of uranium (VI) as a function of AC and modified AC with TOPO is studied by equilibrating for 60 min. contact time, pH4 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) [34]. 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:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^0 b}\right) + \left(\frac{1}{Q^0}\right) C_e \tag{6}$$

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 TOPO resulted in straight lines with a slope of [$1/Q^0$] and an intercept of [$1/Q^0 b$] show that adsorption obeys Langmuir adsorption model (Figure 6d). 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 (1). The Langmuir parameters given in Table (1) can be used to predict the affinity between the adsorbate and the adsorbent using the dimensionless separation factor R_L [35]:

$$R_L = \frac{1}{(1 + bC_0)} \tag{7}$$

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 1) was found to be less than 1 and greater than 0 indicating the favorable sorption isotherms of metal ions.
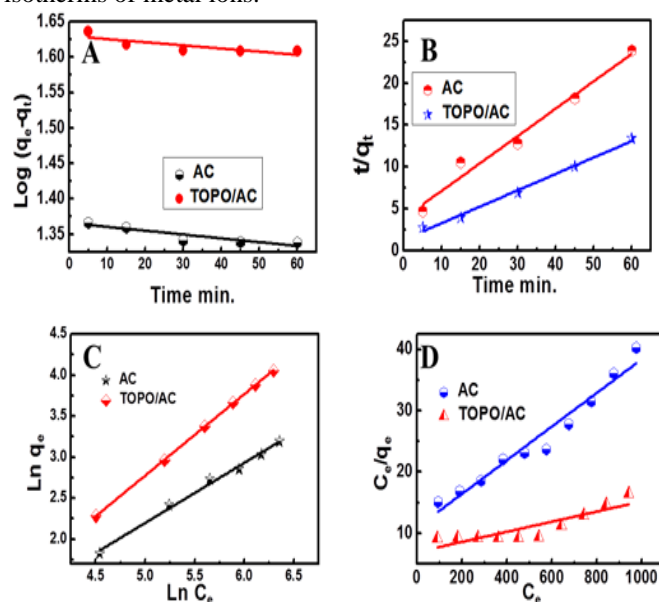

Figure 6. A, B. Pseudo first-order and Pseudo second-order plots for uranium(VI) loading upon the AC and modified AC respectively. C, D. Freundlich and Langmuir isotherm model for uranium(VI) loading upon the AC and modified AC respectively.

Table 1. Freundlich and Langmuir equilibrium constants for U(VI) ions by AC or modified AC with TOPO in aqueous solution at 25 °C.

Freundlich parameters			Langmuir parameters		
Parameters	AC	TOPO/AC	Parameters	AC	TOPO/AC
K_f	0.2334	0.1926	q_m mg/g	35.014	118.1
n	1.368	1.125	K_L l/mg	0.00317	0.00121
R^2	0.9935	0.9999	R_L	0.90	0.8751
			R^2	0.9604	0.7813

4. Conclusion

The parameters that affect the uranium(VI) adsorption have been investigated and optimized conditions determined (0.03g of AC, modified AC contact with 20 ml of uranium solution for 45min. at pH 4 and room temperature).While the maximum loading of uranium ions on AC and TOPO/AC are 23.0 mg/g (230 mg/l), and 57.6 mg/g (576 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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