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STUDIES ON URANIUM RECOVERY BY ACTIVATED CARBON IMPREGNATED WITH TRIDODECYLAMINE AND TRIBUTYL PHOSPHATE

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ABSTRACT

Two solvent impregnated activated carbon materials were prepared for uranium recovery from its aqueous sulfate solutions using tridodecylamine (TDA) and tributyl phosphate (TBP). This was achieved by direct adsorption of each extractant onto the solid phase (dry method). The obtained adsorbents demonstrated that the loading capacity of TDA and TBP have attained 0.69g and 0.85g per 1g activated carbon (AC) respectively which were characterized by means of Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). For the two materials, the relevant factors such as contact time, solution pH, initial uranium ion concentration, volume of aqueous solution to the weight of the impregnated activated carbon ratio and the extraction temperature were optimized by equilibrium batch experiments using uranium synthetic sulfate solution. The obtained uranium loaded from the latter on 1g of each of TDA-AC and TBP-AC was 45mg and 89mg respectively. Desorption of the loaded uranium was carried out using hydrochloric acid which was found to be 66% for TDA-AC and 93.5% for TBP-AC respectively. Based on the obtained optimum factors, the practical applicability of the two developed impregnated solid phases was then examined upon a uranium sulfate leach liquor prepared from Abu Zeneima uraniferous mineralization.

INTRODUCTION

Extraction chromatography is a solid-liquid extraction process, in which metal ions are extracted upon solid particles (support) loaded with an extractant or a mixture of extractants (stationary phase). This procedure is available not only as a separation and/or concentration technique in the field of analytical chemistry (Takeshita and Nakano, 2000) but also as a new technology for waste water treatment (El Dessouky et al., 2008), the recovery of useful metals from industrial waste water (Yanaguchi et al., 1996) or the removal of radioactive elements from nuclear wastes (Diaz, 1996; Horwitz et al., 1997; Rogers et al., 1997; Mathur et al., 1995). The application of liquid extrac-

tion chromatography to process scale separations in hydrometallurgy, water treatment, and nuclear fuel reprocessing has also been reported (Warshawsky et al., 1981; Eschirch and Ochsenfeld, 1980; Faubel and Ali, 1989). Different solvents are used as extractants in such studies including acidic extractants e.g. di(2-ethyl hexyl) phosphoric acid (HDEPA), cyanex 272, PC-88A, neutral extractants e.g. tri-n-butyl phosphate (TBP) as well as basic extractants e.g. tri-n-octylamine (TOA) and tridodecylamine (TDA). These extractants are generally impregnated on different supports like XAD resins, silica gel and activated carbons. The stability of impregnated resins depends principally on the type of the support

used and the nature of the organic reagent retained. Among the numerous adsorbents, activated carbon is one of the most widely used in developed countries for treatment of various industrial effluents (Qadeer and Hanif, 1994; Abbasi and Streat, 1994; Chegrouche et al., 1996). Activated carbon is also an important support material preferred by many investigators due to its high surface area and radioactive stability compared with most polymeric materials (Marzal et al., 1996). In fact, the activated carbon can be considered as the most effective and economic support. Charcoals impregnated with organophosphorus compounds (Byler and Maclain, 1995; Noble et al., 1958; Maclain et al., 1958) and organic amines (Goren, 1967) were investigated for the recovery of uranium from acid leach liquors.

In this contribution, a study has been oriented to evaluate the efficiency of TDA and TBP impregnated activated carbon for the recovery of uranium ions from a synthetic sulfuric acid solutions and applying the obtained optimum conditions on a sulfate leach liquor of Abu Zeneima uraniumiferous ore material. The experimental data were investigated by batch equilibrium studies. This work is actually justified by the fact that uranium loaded from its synthetic solution upon activated carbon itself is relatively low (10mg/g).

EXPERIMENTAL

Materials

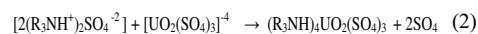
Two extractants are used for impregnation of activated carbon to test their efficiency for uranium recovery from sulfate solutions. The two extractants TDA and TBP have been provided by Sigma Aldrich of Germany with density of about 0.82 and 0.97 kg/L and an assay of 95 and 99% respectively. Benzene is used as a diluent for both extractants.

Synthesis of solvent impregnated activated carbon

The process of impregnation was per-

formed using 1g. solid phase (activated carbon) as mentioned by Ahmed et al., 2013. In this concern, a series of experiments was performed to optimize the maximum loading of TDA and TBP onto the activated carbon. Thus 1 g sample portions of the activated carbon were contacted with different volumes of 10% of each of TDA and TBP solutions in benzene till equilibrium was reached. The amount of TDA and TBP taken up by the activated carbon were determined by measuring the increase in the weight of the activated carbon after proper treatment. In each experiment, the impregnated solution was gently stirred with the activated carbon (at room temperature of $25^{\circ}\text{C}\pm 1$) for a period of time until complete homogenization followed by leaving the slurry till benzene (diluent) is evaporated. The impregnated activated carbon was then dried at 40°C till complete dryness and a powder form was obtained.

The tertiary amine should be first converted to the appropriate polar ion pair $(\text{R}_3\text{NH}^+)_2\text{SO}_4^{2-}$ (Eq. 1) in order to undergo the exchange mechanism with the metal ion species (Eq. 2) while the alkyl phosphate would react as a neutral species (Eq. 3).



Characteristics of the studied geological material

The geological material under study represents a sample from Abu Zeneima mineralized in Um Bogma Formation which is assigned to the middle carbonate series of the Paleozoic sequence in south west Sinai, Egypt (Kora, 1984; El Aassy et al., 1986). This sample represents one of the uranium occurrences related to the dolostone of Um Bogma formation. The main mineral constituents of the dolostone faces are calcite, ankerite, kaolinite, limonite, goethite besides arsenopyrite, chalcopyrite and framboidal pyrite.

Preparation of synthetic and Abu Zeneima leach liquor uranium solutions

A uranium synthetic stock solution (1000 ppm) was prepared by dissolving $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ in deionized water followed by its acidification with sulfuric acid to avoid possible hydrolysis. From this solution, the required uranium concentration (84 ppm), for optimizing the adsorption factors upon the prepared solvent impregnated AC, was prepared by proper dilution. On the other hand, a representative sample (50 g) of the provided ore material was treated with 50 ml of 15% H_2SO_4 acid and stirred in a glass beaker for about 4 hours at room temperature. The slurry was then left to settle and after filtration its pH was adjusted using Na_2CO_3 powder (Merck, Germany).

Batch Experimental Procedure for Uranium Adsorption

Several series of experiments have been carried out to investigate the sorption characteristics of both TDA-AC and TBP-AC towards uranium in a batchwise equilibrium process. For this purpose the initial and equilibrium uranium concentration was measured under different conditions. Except otherwise cited, these experiments were conducted in 100 ml glass beaker by mixing a working volume of 50 ml of 84 mg/l uranium solution with 1 g of each of the impregnated solid phases. The solutions were shaken at $25^\circ\text{C} \pm 1$ for 1 hr and 2 hr for TDA-AC and TBP-AC respectively. A digital pH meter (Jenway, UK) was used for pH adjustment by adding NaOH (1 mol, Fixanal, Germany) or H_2SO_4 (Tedia, USA) to the working solutions as required.

Analytical Procedures

Characterization of the solvent impregnated AC

Scanning electron microscope (SEM)

The SEM instrument (model Philips XL 30 ESEM) is considered as the most reliable and convenient tool for studying the physi-

cal structure of the solvent impregnated solid phases (Warshawsky et al., 1981) as well as for mineralogical investigation. The analytical conditions are 25-30 kv accelerating voltage, 1-2 mm beam diameter and 60-120 second counting time. The minimum detectable weight concentration ranges from 0.1 to 1 wt%.

Fourier transform infrared spectrometer (FTIR)

The FTIR model Thermo Scientific Nicolet IS10, Germany is used for evaluating the interaction between the extractant and the beads of the activated carbon.

Uranium control analysis

Uranium control in the synthetic solutions

In all the stream solutions obtained during optimization of the relevant factors of adsorption and desorption using the prepared solvent impregnated AC, uranium was spectrophotometrically analyzed using the arsenazo (III) complex. For this purpose SP-8001 UV-VIS Spectrophotometer was used at the wavelength 655 nm (Marczenko, 1976).

The uranium loading capacity (q_e in mg g^{-1}) was calculated according to its mass balance; viz;

$$q_e = (C_o - C_e) \times V/m$$

where C_o and C_e are the initial and equilibrium uranium concentrations in the solution in (mg l^{-1}) respectively while V is the solution volume in (L) and m is the adsorbent impregnated solid phase mass in (g).

On the other hand, the uranium removal percent or its extraction efficiency was calculated as follow:

$$R\% = [(C_o - C_e)/C_o] \times 100$$

Analysis of Abu Zeneima uraniumiferous ore material and its leach liquor

A representative sample of the provided Abu Zeneima uraniumiferous ore material and the

prepared sulfate leach liquor were analyzed for both the major oxides as well as for some economic and heavy metals. For the former, the rapid analysis procedure of the silicate analysis of the Shapiro and Brannock, 1962, was used while for uranium [Ahmed, 2015] and both the economic and heavy metals, the Dionex Ion Chromatograph (DX-500) (Dionex Corporation, Sunnyvale, California, USA) was used. This was found necessary to overcome the interference of the complex matrix when using the UV-VIS Spectrophotometric analysis of these latter metals. The ion chromatography technique has indeed the ability to separate the ion before its determination and is then considered as indispensable tool in modern analytical chemistry (Fritz and Gjerde, 2009). The used DX-500 Ion Chromatograph in the present work is equipped with AD20 UV-Visible wavelength detector and GP40 gradient pump. Prior to their analysis, uranium and other mentioned metals were separated using an IonPac CS5A analytical column and IonPac CG5A guard column.

Batch Experiment Procedure for Uranium Desorption

In order to achieve successful metal elution from the two loaded working sorbents, a number of elution tests were carried out to elute the uranium ions from the amine and the alkyl phosphate impregnated activated carbon. For this purpose, hydrochloric acid with variable concentrations ranging from 0.001 to 0.2 mol/l and at different contact time intervals varying from 15-120 minutes was applied to obtain the maximum elution efficiency. These metal elution experiments were performed using the batch method at room temperature upon a fixed mass of the loaded TDA and TBP impregnated activated carbon.

The elution efficiency can be determined through the following equation:

$$\text{Elution \%} = [C_i / (C_i - C_e)] \times 100 \quad (4)$$

where C_i and C_e are the initial and equilibrium metal concentrations in the aqueous phase before and after sorp-

tion process respectively and C_e is the concentration of the studied metal in the aqueous phase after elution step.

RESULTS AND DISCUSSION

Preliminary Testing

In a preliminary test experiment, 1g from activated carbon was stirred with about 200ml of 1000 ppm (200mg U) standard U sulfate solution with pH of 3.43 for about 2 hours at room temperature. It was found that the amount of uranium loaded on 1g AC was estimated as 10 mg. So, it was recommended to impregnate this activated carbon with two different extractants and to study their effect on activated carbon improvement for uranium recovery. One of these extractants was TDA (basic extractant) while the other was TBP (neutral extractants).

Impregnation of TDA and TBP on Activated Carbon

The obtained impregnation data using 1g activated carbon were shown in Table (1). From the obtained data, the resulting optimum conditions for maximum loading of TDA and TBP involved contact of 1 g AC with 8.93 ml of each of the prepared 10% solution and which were found to be equivalent to 0.69g TDA and 0.85g TBP respectively. Increasing the volume of the two working extractants solutions beyond 8.93 ml have resulted in a viscous mixture with the AC.

Table 1: Amount of extractant impregnated upon activated carbon

10% Extractant/1g AC (ml)	Impregnated Extractant, g/1g AC	
	TDA	TBP
2.7	0.21	0.26
5.5	0.42	0.53
6.8	0.53	0.65
7.5	0.58	0.72
8.2	0.63	0.79
8.93	0.69	0.85

Characteristics of the Solvent Impregnated AC

Scanning electron microscope characteristics

The scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the activated carbon (Warshawsky et al., 1981). Figure (1) shows the SEM photographs of the activated carbon before solvent impregnation while Figures (2,3) show the SEM photographs of both TDA and TBP impregnated activated carbon before and after loading with uranium at the determined optimum operating conditions. The micrograph of Fig. (1) apparently shows that the original activated carbon possesses many vacant pores before impregnation. On the other hand, the rough surface was turned to be relatively bright (Figs. 2a,3a) after having been impregnated with TDA and TBP; a

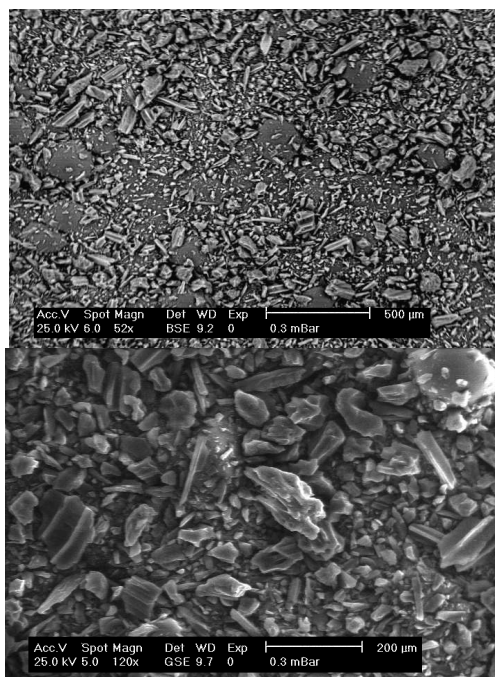


Fig. 1: SEM photographs of the activated carbon surface before impregnation

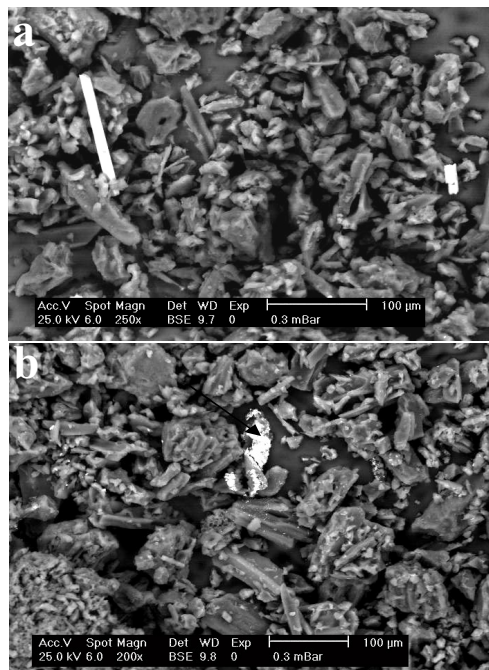


Fig. 2: SEM photographs of the TDA impregnated activated carbon (a) before and (b) after loading with uranium

matter which suggests that the extractants have filled up most of the vacant pores. The adsorbed uranium seems to appear as brilliant spots on the surface of the impregnated activated carbon (Figs. 2b,3b); a matter which emphasizes its adsorption.

Fourier transform infrared spectrometer characteristics

The infrared spectroscopy is generally used to obtain the necessary information about the chemical structure and functional groups of the activated carbon and the working impregnated solid phases (Gomez-Serrano et al., 1996; Pastor-Villesgas et al., 1993; Zawadki, 1989). The FTIR spectrum of the activated carbon used in the present work is shown on Fig.(4). From the latter, the two adsorption bands observed at 3428.81 and 2356.59 cm^{-1} are assigned to the O-H stretching band and $\text{C}\equiv\text{C}$ respective-

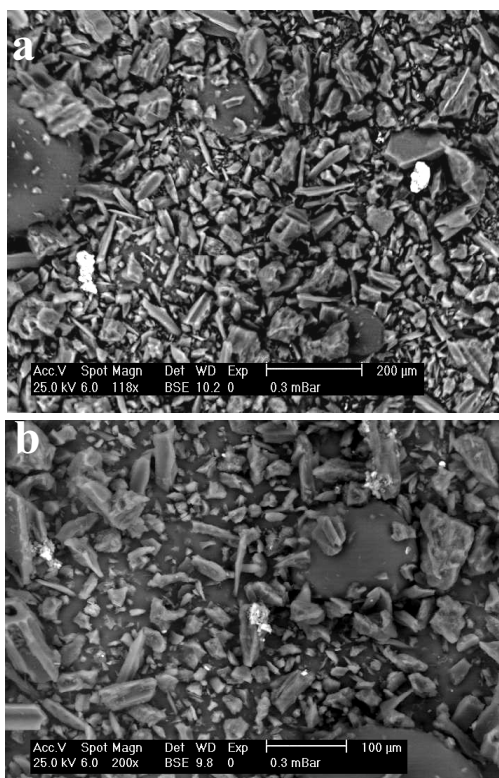


Fig. 3: SEM photographs of the TBP impregnated activated carbon (a) before and (b) after loading with uranium

ly. The bands in the region ($1613\text{-}1244\text{ cm}^{-1}$) were associated to C=C stretch, C-H bending and C-O-C ether linkage. Comparing the FTIR spectra of the TDA and TBP impregnated activated carbon with the original activated carbon, it has been observed an existence of two additional peaks at wave numbers 1155.15 and 1053.91 cm^{-1} corresponding to C-N stretching band bending aliphatic amine for TDA (Fig. 5) while the two bands at 1263.15 and 1025.94 cm^{-1} indicating the formation of P=O and P-O-C bonds related to TBP extractant (Fig. 6).

Optimization of Uranium Adsorption Factors

In order to obtain maximum recovery of uranium from aqueous sulfate solution, it was necessary to optimize the experimental parameters such as contact time, pH, initial metal ion concentration, v/m ratio and temperature.

Effect of contact time

The changes in sorption of U(VI) onto 1g of either TDA impregnated AC and TBP impregnated AC as a function of contact time at a solution pH of 3.43 ± 0.01 , concentration of 84 ppm and using a loading solution volume of 50 ml at a room temperature of $25^\circ\text{C} \pm 1$ are repre-

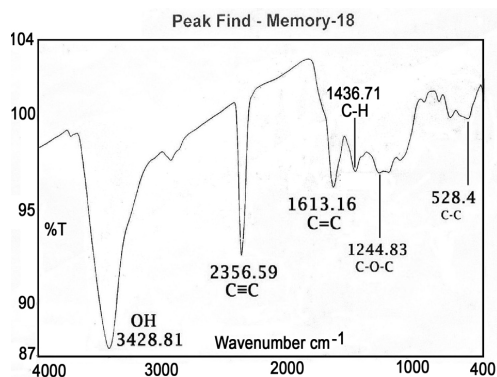


Fig. 4: FTIR spectrum of the activated carbon before solvent impregnation

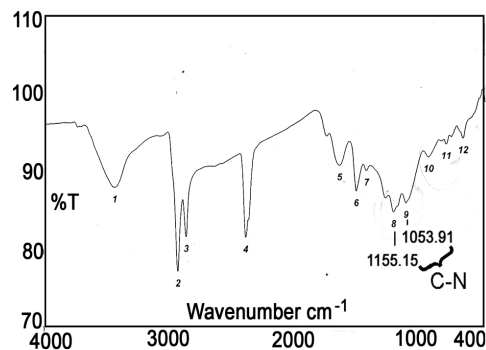


Fig. 5: FTIR spectrum of the activated carbon after impregnation with TDA

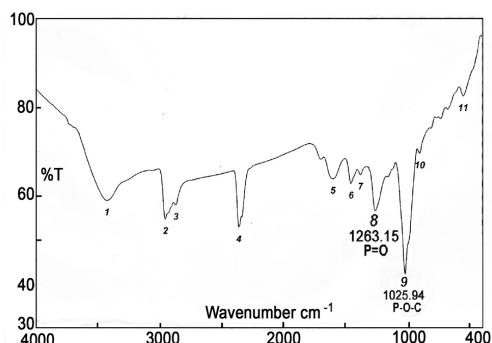


Fig. 6: FTIR spectrum of the activated carbon after impregnation with TBP

sented in Figures (7a,b). The latter show that in case of TDA impregnated AC, the sorption efficiency increases with increasing the contact time till reaching equilibrium at about 1 hr and after which it remained constant. On the other hand, in case of TBP impregnated AC, the uranium sorption efficiency was found to attain about 80% at 1 hr and increased to about 85% at 120 minutes whereas thereafter, it has been partially decreased. In the light of these data, it can be concluded that the time required for maximum uranium loading onto TDA impregnated AC (99.12%) was achieved within 60 minutes as compared to that onto TBP impregnated AC (85.01%) that was achieved within 120 minutes. This means that TDA-AC has not only higher sorption efficiency but also kinetically faster than TBP-AC.

Effect of pH

Sorption of U(VI) from aqueous solution as a function of pH was studied using a solution concentration of 84ppm, a v/m ratio of 50 at room temperature of $25^{\circ}\text{C}\pm 1$ and at the previously optimized contact time for the two sorbents under study. The revealed data are illustrating in Figures (8a,b). For TDA impregnated AC, the extraction efficiency was investigated varying the initial pH of the solution from 0.5 to 7. The results clarify that uranium sorption increases with raising the pH value

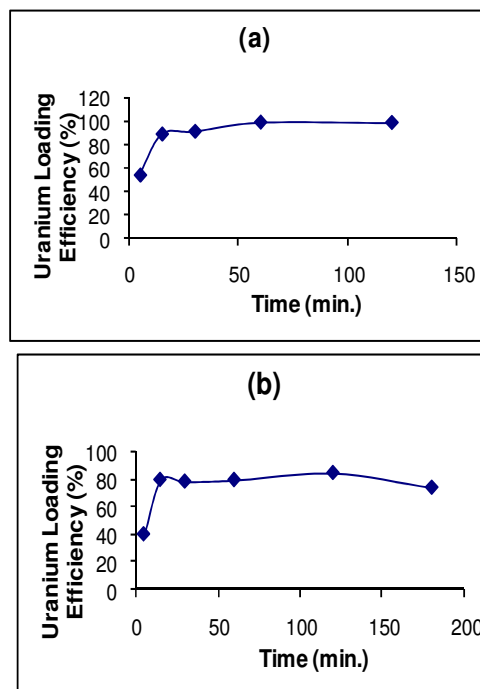


Fig. 7: Effect of contact time on uranium loading efficiency upon (a) TDA impregnated AC and (b) TBP impregnated AC.

up to about 2.1 to 5.1 in a manner to record a maximum loading efficiency of 99.12% at pH 3.43. Beyond the pH value of 5.1, the uranium extraction efficiency was found to have been subjected to a partial decrease. On the other hand, the uranium extraction efficiency for TBP impregnated AC was investigated using an initial pH ranging also from 1 to 7. It was thus found that uranium adsorption increased with increasing the pH value to a maximum loading efficiency of 91.37% at pH 5.2. This behavior can be discussed in the light of the exchangeable properties of hydrogen ions and their effect on the solubility equilibria. At low pH values, the hydrogen ions compete for the available active sites on the sorbent surface protonating their functional groups and this would negatively affect the sorption of U(VI) and where the electrostatic interaction

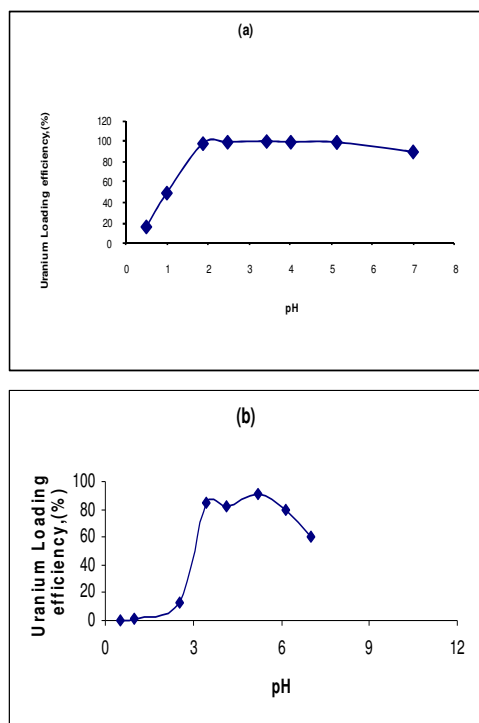


Fig. 8: Effect of pH on uranium loading efficiency upon (a) TDA impregnated AC and (b) TBP impregnated AC

would be electrically unfavorable (Somedra and Sheha, 2006). Also acidification with H_2SO_4 forms a high concentration of HSO_4^- which would hinder uranium extraction since the uranyl bisulfate is not extractable (Ritcey and Ashbrook, 1984). The increase in metal ion removal as the pH increases can be explained on the basis of a decrease in H^+ on the surface sites and by a decrease in positive charge, which result in less repulsion in adsorbing metal ions (Kadirvelu and Namasiyayam, 2003). This may explain the gradual increase in sorption with increasing pH up to 5 and 5.2 for TDA and TBP impregnated AC respectively. The decrease in uranium loading efficiency after pH 5 and 5.2 for both sorbents is probably due to the precipitation of uranium ions as their corresponding hydroxides. In

addition, the amines convert free salts up to pH 5 (Merritt, 1971; Ölmez and Eral, 1994). Accordingly, it can be mentioned that the pH range of 2 to 5 can be considered to be the optimum and the chosen value is actually 3.43 for TDA impregnated AC while a pH of 5.2 is chosen as an optimum value for the TBP impregnated AC.

Effect of initial uranium concentration

The effect of initial uranium concentration upon the extent of uranium extraction by 1 g of the two working impregnated AC was tested using synthetic sulfate solutions of concentrations varying from 84 up to 940 mg/l at room temperature of $25^\circ C \pm 1$, a v/m ratio of 50 and at the previously optimized contact time and pH. From the obtained results, it was indicated that the uranium extraction increases steadily with increasing the uranium concentration reflecting the moderate capacity of the impregnated activated carbon at this stage (Figs. 9a,b). The obtained uranium capacity of the working sorbents was thus found to attain 22.48 mg/g at 600 mg/l initial uranium concentration and to attain 38.67 mg/g at 784 mg/l initial uranium concentration for TDA and TBP impregnated AC respectively.

Effect of solution volume to sorbent mass (v/m ratio)

The adsorption of uranium from different volumes of aqueous sulfate solutions containing varying amounts of the metal ion is shown in Table (2). The batch experiments were carried out at a room temperature of $25^\circ C \pm 1$ and at the previously optimized contact time, pH and initial uranium concentration of 600 and 784 ppm for TDA and TBP impregnated AC respectively. The results indicate an extraction amount of 45mg/g from a solution volume of 300ml (600 ppm U) for TDA impregnated AC while an extraction amount of 89.76mg/g was obtained from a solution volume of 200ml (784 ppm) for TBP impregnated AC.

Accordingly, it can be concluded that the

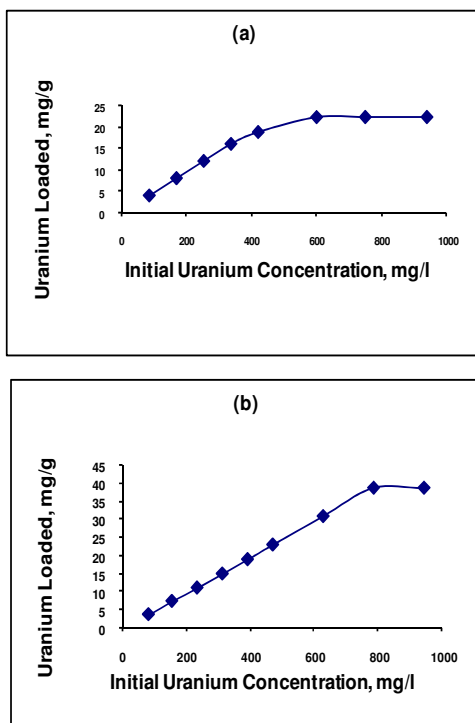


Fig. 9: Effect of initial uranium concentration on its loading capacity upon (a) TDA impregnated AC (b) TBP impregnated AC

Table 2: Effect of solution volume to sorbent mass (v/m ratio) upon their loading capacity

v/m ratio	Amount of Uranium Loaded (mg/g)	
	TDA-AC	TBP-AC
25	14.79	----
50	22.48	38.67
100	31.04	76.25
200	-----	89.76
300	45.00	89.63
500	45.93	----
700	----	86.61
800	38.40	----
1000	----	89.61

---: not performed

achieved uranium adsorption capacity of the two working TDA and TBP impregnated AC [0.69g TDA/1g AC and 0.85g TBP/1g AC (Table 1)] was found to attain 45 and 89.76 mg U/1g solvent impregnated AC respectively. Referring to the adsorption reactions (Eqs.2,3), it can be calculated that the theoretical capacity of 1 g of both the working TDA and TBP impregnated AC should attain 79 and 382 mg uranium respectively. However, the practical capacities that have been realized in the present work under the mentioned conditions have only attained 45 mg and 89.76 mg per 1g working TDA and TBP impregnated AC representing 56.94 and 23.49 % of the theoretical capacity respectively. The difference between the theoretical and the practical capacities as determined under the chosen conditions might be due to partial adsorption that has most probably been limited to the external surface of the solvent impregnated AC. On the other hand and according to equilibrium conditions, the UO_2SO_4 neutral complex is present in sulfuric acid in association with the uranyl cation (UO_2^{2+}) and the uranyl sulphate complex species; namely $[\text{UO}_2(\text{SO}_4)_2]^{2-}$ and $[\text{UO}_2(\text{SO}_4)_3]^{4-}$. Presence of these uranyl species in sulfuric acid media might interpret its low adsorption efficiency of only 23.49 % of the theoretical capacity of the neutral TBP impregnated AC.

Effect of temperature

To investigate the effect of the temperature range of 25 to $60^\circ\text{C} \pm 1$ on uranium adsorption upon the working sorbents, two series of extraction experiments were conducted using 1g of each of the sorbents at the previously optimized contact time, pH, initial uranium concentration and v/m ratio. The results are given on Fig. (10a,b) and from which it can be seen that the loaded amount of uranium and in turn the loading efficiency were decreased for both sorbents as the temperature increased. This decrease in adsorption capacity indicated that low temperature is favorable for uranium adsorption on the working sorbents. This may

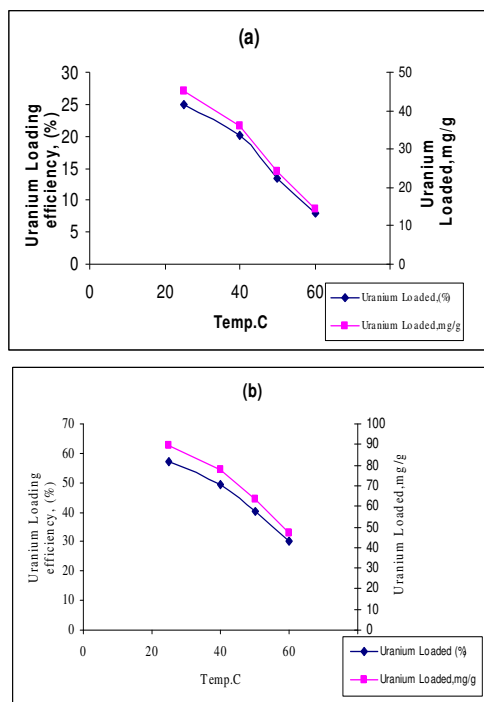


Fig. 10: Effect of temperature on uranium loading efficiency and loading capacity upon (a) TDA impregnated AC and (b) TBP impregnated AC

be due to a tendency for the adsorbed uranium to desorb from the solid phase to the aqueous phase with increasing temperature of the solution. This effect suggests that the adsorption mechanism associated with uranium species removal from the two working sorbents involves a physical process, in which it can be mentioned that adsorption arises from an electrostatic interaction which is usually associated with low adsorption heat (Karaca et al., 2006). This means that the adsorption process is actually of an exothermic character. So room temperature of $25^{\circ}\text{C} \pm 1$ was chosen as the appropriate temperature.

Optimum conditions of uranium extraction by the working sorbents

From the above results, it is clearly evident

that the optimum extraction conditions for TDA impregnated AC were found to involve a uranium concentration of 600 ppm, a pH solution of 3.43, a v/m ratio of 300, a contact time of 1 hr and a temperature of $25^{\circ}\text{C} \pm 1$. At these optimum conditions, the amount of uranium adsorbed on 1g of the sorbent was found to be 45 mg. On the other hand, the optimum extraction conditions for TBP impregnated AC were found to include a uranium concentration of 784 ppm, a pH solution of 5.2, a v/m ratio of 200, a contact time of 1 hr and a temperature of $25^{\circ}\text{C} \pm 1$. At these optimum conditions, the amount of uranium adsorbed on 1g of the sorbent was found to attain 89.76 mg. The relatively low uranium extraction efficiency obtained under such equilibrium conditions and which has attained 56.94 % and 23.49 % of the theoretical capacity of the TDA and TBP impregnated AC respectively can indeed be increased by applying a countercurrent extraction system.

As observed from the above results that 45mg/1g sorbent was adsorbed on TDA impregnated AC from original uranium solution of 180 mg which means that about 135mgU was still present in solution and not extracted so we have increased the quantity of the working sorbent used to be 4.5g and the achieved result was about 122mgU adsorbed on 4.5g of TDA impregnated AC. In case of TBP impregnated AC 2g of the working sorbent was used instead of 1g to adsorb about 142.8mg U from solution of original amount of 156.8mg.

Uranium Desorption

According to Attallah et al.,2008, it was found that hydrochloric acid has high efficiency than nitric acid for uranium desorption from tertiary amines and phosphate impregnated solid phases. Using the batch experimental procedure, a uranium elution efficiency of 66.10 % for TDA impregnated AC and 93.52 % for TBP impregnated AC could be accomplished during 1 hr by using 0.009mol/l and 0.1 mol/l HCl respectively (Table 3). On the

other hand, using the applied HCl concentration for these efficiencies, a trail was made to test the effect of the contact time. However, a lower or a high contact time than 1 hr was found to have an adverse effect upon the elution efficiency of uranium (Table 4). In the meantime, an almost complete uranium elution can be accomplished by a countercurrent extraction system.

APPLICATION

As previously mentioned, it was found necessary to apply the obtained optimized conditions of uranium recovery from the sulfate synthetic solution by the prepared TDA and TBP impregnated activated carbon upon an actual leach liquor. For this purpose, both

the provided uraniferous dolostone ore material (1500ppm) of Um Bogma Formation of Abu Zeneima area and the prepared sulfate leach liquor were subjected to chemical analysis using Shapiro and Brannock wet procedure and the DX-500 Ion Chromatograph (IC). The obtained results are shown in Table (5). From the latter, it is clearly evident that the working ore sample is mainly composed of about 44 % SiO_2 together with about 11% Al_2O_3 . It is also shown that the working sample assays up to 2.64% Cu whose recovery during processing (80% leaching efficiency) would improve the economy of working this ore material. On the other hand, it was shown that the working ore sample assays 5.33, 0.50 and 0.47% Fe, Ni and Mn respectively while Zn and Cd were shown to attain 0.48 and 0.93% respectively. Under the applied leaching conditions, the uranium assay in the leach liquor attained 1035 ppm equivalent to a leach efficiency of about 70%.

Table 3: Results of uranium elution from TDA and TBP impregnated activated carbon as a function of hydrochloric acid concentration

HCl Concentration (mol/l)	Uranium Elution Efficiency from TDA-AC (%)	Uranium Elution Efficiency from TBP-AC (%)
0.001	36	9.5
0.009	66.1	---
0.005	---	65
0.024	58.7	---
0.05	52.1	75
0.1	42	93.52
0.2	---	28.31

Table 4: Results of uranium elution from TDA and TBP impregnated activated carbon as a function of contact time

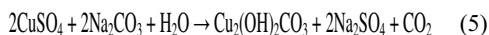
Contact Time (min)	Uranium Elution Efficiency from TDA-AC (%)	Uranium Elution Efficiency from TBP-AC (%)
15	20	40
30	45	56.6
60	66.1	93.52
120	40	56.6

Table 5: Chemical analyses of the major oxides, the heavy metals and uranium in working Abu Zeneima uraniferous sample and its sulfate leach liquor

Major Elements (Oxides)	Abu Zeneima Uraniferous Sample (%)	Leach Liquor Sample (g/l)
SiO_2	43.62	55.60
Al_2O_3	11.34	21.30
TiO_2	1.71	5.00
CaO	1.12	0.20
MgO	0.80	1.20
Na_2O	1.48	1.07
K_2O	1.47	1.15
P_2O_5	0.18	0.70
Heavy Metals [IC]	Abu Zeneima Ore Sample (%)	Leach Liquor Sample (ppm)
Fe	5.33	398
Cu	2.64	2.14 g/l
Ni	0.49	139
Zn	0.47	Nil
Cd	0.93	371
Mn	0.47	198
U^{+6} , [IC]	1500 ppm	1035

Sodium Carbonate Addition

The prepared leach liquor of the study uraniferous material obtained was characterized by a blue-green colour due the presence of Cu ions in a relatively high concentration (2.14 g/l). However to avoid Cu extraction by the working solvent impregnated AC, it was found necessary to introduce sodium carbonate (as a powder) in the leach liquor. This addition would have actually two advantages; first was to raise the pH of the solution and second was to complex the Cu ions in the leach liquor according to Eq. (5) and where the colour of the leach liquor was turned from the blue green to the yellow colour of uranium ions. Indeed, capturing Cu ions with carbonate is greatly advantageous in allowing uranium ions to be almost selectively recovered onto the two working sorbents.



Uranium Adsorption from Abu Zeneima Leach Liquor and its Desorption

Two sample solutions of uranium concentration 403.8ppm and pH 3.33 were prepared from the Abu Zeneima sulphate leach liquor assaying 1035ppm and were stirred with both of the prepared impregnated sorbents (TDA-AC and TBP-AC) using the recommended optimum conditions. The pH of the sample solution contacting with TBP-AC was however adjusted from 5.2 (optimum condition) to 3.33 to avoid uranium precipitation resulted from matrix effect. The leached uranium recovered on 4.5g TDA-AC and 2g TBP-AC was found to attain 66.65mg from original 121.19mgU and 40.98mg from original 80.79mgU respectively.

Another important experiment was done to report the behavior of the activated carbon alone towards uranium recovery from the sulfate leach liquor solution under study. The data resulted from the latter shown the loading of about 1.9 mg uranium on 1 g AC when mixing activated carbon mass with 200 ml

of 1035 ppm (207 mgU) of the sulfate leach liquor for 2 hours at room temperature after adjusting the sample pH to 3.33. Comparing this experiment result with that obtained for the two working impregnated AC (calculated; 14.81mg and 20.49 mg per 1g of TDA-AC and TBP-AC respectively), it is obvious that the prepared two materials provided a significant improvement for uranium recovery. On the other hand, the low uranium loaded in sample application would reflect the matrix effect on uranium recovery.

Finally, the loaded uranium was eluted with efficiency 61.1% (40.72 mgU) using 0.009mol/l HCl from TDA-AC impregnated solid phase while uranium elution from TBP-AC sorbent was achieved with efficiency 90.52 % (37.09 mgU) using 0.1mol/l HCl.

CONCLUSION

Two impregnated solid phases (TDA-AC and TBP-AC) have been prepared and their application to recover uranium ions from sulfate media has been studied. Optimum conditions achieved at uranium equilibrium adsorption from synthetic solutions were 1 hour at pH of 3.43 for a 300ml uranium solution of concentration 600 ppm at room temperature which resulted in loading of about 122 mg U on 4.5g of TDA impregnated AC while 142.8 mg U was loaded on 2g TBP impregnated AC at the studied optimum conditions of 2 hours at pH of 7 for a 200 ml uranium solution of concentration 784 ppm at room temperature. The sorbed uranium was eluted in 1 hour using 0.009 mol/l HCl which has achieved an elution efficiency of 66.10% in case of TDA-AC while an efficiency of 93.52% was obtained using 0.1 mol/l HCl as the eluent in case of TBP-AC. A uraniferous material sample was collected from Abu Zeneima area for application studies of the developed optimum conditions. The assay of uranium in the prepared leach liquor from this ore material was found to attain 1035ppm. From the latter, a 400ppm uranium solution was prepared and from which uranium was loaded on both 4.5g TDA-AC and 2g TBP-AC

and was found to be 66.65mg from 121.19mg and 40.98mg from 80.79mg respectively. Uranium was eluted with efficiency of 61.1% (40.72mgU) from TDA-AC while from TBP-AC, the achieved efficiency attained 90.52 % (37.09mgU).

RECOMMENDATION

As observed from the results of applying the two impregnated sorbents to the two solution samples prepared from the sulfate leach liquor under study, it was found that their behavior was changed to low uranium recovery which is emphasized by matrix effect. So, it was recommended to undergo pretreatment of the Abu Zeneima sulfate leach liquor to somehow prevent the effect of the present interfering ions before applying to the prepared sorbents in order to enhance their behavior towards uranium recovery.

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دراسات عن استرجاع اليورانيوم باستخدام الكربون النشط المحمل بمذيبى دوديساسل الامين وثلاثى بيوتيل الفوسفات

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تم تحضير عينتين لمذيبين عضويين دوديساسل الامين وثلاثى بيوتيل الفوسفات عن طريق ادمصاصهما المباشر على الفحم النشط وذلك بهدف استخلاص اليورانيوم من محاليله الكيريتية. وقد اتضح ان الكمية المدمصة تبلغ ٠,٦٩ جرام بالنسبة لمذيب دوديساسل الامين لكل جرام من الفحم النشط و ٠,٨٥ جرام بالنسبة لمذيب ثلاثى بيوتيل الفوسفات لكل جرام من الفحم النشط والتي تم توصيفهم باستخدام كلا من المجهر الالكترونى الماسح وطيف الاشعة تحت الحمراء. هذا وقد تم دراسة العوامل المؤثرة على ادمصاص اليورانيوم على كلا منهما والتي شملت وقت التقليل، درجة الاس الهيدروجينى، تركيز اليورانيوم ونسبة حجم المحلول الى وزن عينة الفحم النشط الحامل للمذيب العضوى علاوة على درجة الحرارة وذلك من خلال تجارب الاتزان باستخدام محلول يورانيوم قياسى فى حامض الكيريتيك. وقد وجد ان كمية اليورانيوم المحملة من التجارب السابقة على واحد جرام من كلا من مذيب دوديساسل الامين المحمل على الكربون النشط ومذيب ثلاثى بيوتيل الفوسفات المحمل على الكربون النشط تقدر بـ ٤٥ مللجرام و ٨٩ مللجرام متتابعين. تم ازالة اليورانيوم المدمص باستخدام حامض الهيدروكلوريك والتي اتضح انها تمثل نسبة ٦٦% لمذيب دوديساسل الامين المحمل على الكربون النشط ونسبة ٩٣,٥% لمذيب ثلاثى بيوتيل الفوسفات المحمل على الكربون النشط. واستنادا على العوامل المثلى التى تم الوصول اليها قد تم اختبار المادتين الصلبيتين المحملتين المتطورين للتطبيق العملى على محلول كيريتيك اذابة اليورانيوم من تمعدن ابو زنيمه.