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Properties of Uranium(VI) Adsorption by Methyl 3-*O*-Acetyl-5,6-dideoxy-(*S*)-1,2-trichloroethylidene-α-D-xylo-hept-5(E)-eno-1,4-furano-uronate

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ABSTRACT: In this study the effect of adsorption parameters such as pH, concentration of uranium(VI), shaking time, and temperature on methyl 3-*O*-acetyl-5,6-dideoxy-(*S*)-1,2-trichloroethylidene-α-D-xylo-hept-5(E)-eno-1,4-furano-uronate (MOADDTCEXHEFU) for U(VI) ions have been investigated. The adsorption data for uranium(VI) were well-fitted by the Langmuir isotherm. Thermodynamic analysis showed that the value of ΔG° is negative and ΔH° and ΔS° are positive. These results and a Fourier transform infrared (FTIR) spectrum analysis show that uranium(VI) ions were successfully bonded to this molecule. The affinity of MOADDTCEXHEFU to Th^{4+}, Ba^{2+}, and also Mg^{2+} is about 10 times higher than uranium(VI).

INTRODUCTION

In an effort to develop useful scavengers for the removal of metal ions from contaminated sources, examinations have been carried out with respect to the uptake of inorganic metal ions by a variety of synthetic and natural polymers. Although no universal adsorbent has yet been found, nor has a perfect adsorbent for any given purpose been developed, many scientists show that natural and synthetic polyamine polymers such as chitosan, tannin-rich agricultural byproduct and proteins such as wool and silk fibroin, and inorganic−organic composites all are effective adsorbents for uranium(VI). In addition it has also been observed that chelating resins generally have the greatest potential for cation selective adsorption; however, most chelating resins (for example, those on iminocarboxylate binding sites) are limited by slow complexation kinetics and high proton affinities.[1−8] Solid organic compounds are able to bind metals due to their reactive terminals. Therefore, they can be used as an alternative adsorbent material for adsorption of metals in separation techniques. The monoen structures of unsaturated carbohydrate skeletons and their derivatives are very useful molecules for the synthesis of complex and derivative sugars (disaccarides, antibiotics, and amino sugars), natural products (such as prostanoids and sex phores, etc.), and carboxylic systems in organic chemistry. On account of this, using these kind of molecules which have ester carbonyl groups on their skeletons will be useful in adsorption techniques.

No study has been found which focuses on the behavior of uranium(VI) ions on the adsorption characteristics of methyl 3-*O*-acetyl-5,6-dideoxy-(*S*)-1,2-trichloroethylidene-α-D-xylo-hept-5(E)-eno-1,4-furano-uronate (MOADDTCEXHEFU). This paper describes the attempts to find the optimum adsorption conditions of uranium(VI) from diluted aqueous solution on MOADDTCEXHEFU. To provide information on the adsorption mechanism, the well-known isotherms, thermodynamic properties, and also Fourier transform infrared (FTIR) analysis of the adsorbent (along with uranium(VI)) were carried out.

MATERIALS AND EXPERIMENTAL SECTION

Materials. All chemical reagents used in the experiments were of analytical reagent grade, used without further purification, and were purchased from Merck. The synthesis procedure and structural formation of MOADDTCEXHEFU, which is an unsaturated sugar derivative, were reported elsewhere.[9] To use an insoluble form of this material for the adsorption process, this unsaturated molecule was methylated.[10,11] This material was stored in a refrigerator.

The stock solution of uranium was prepared by dissolving an appropriate quantity of uranium(VI) nitrate hexahydrate $[UO_2(NO_3)_2 \cdot 6H_2O]$ in a diluted solution of HNO_3 so as the uranium concentration in the resulting solution was 1000 $mg \cdot L^{-1}$. The pH of the initial solution was adjusted using $NaHCO_3/Na_2CO_3$ or HNO_3 solutions in such a way that the required pH was achieved from the acid side. The pH measurements were made on an Ai-On digital ion analyzer (model MI 8100) combination with a glass pH electrode and a reference electrode.

Adsorption Studies. To conduct adsorption experiments colorless polypropylene (PP) tubes (13 × 120 mm) with a stopper were used. The adsorption experiments for uranium on the MOADDTCEXHEFU were carried out by the batch equilibrium adsorption technique by using a G.F.L shaking water bath (model 1083). MOADDTCEXHEFU having particles of size 0.25 mm was used for this procedure. A total of 0.01 g of this monoen and the 10 mL of uranium solution were placed in a 15 mL PP tube. Each tube was shaken which allowed the sample to equilibrate with the uranium ions. The supernatant solutions were then filtered through Whatman No. 42 filter papers. The solution phase was sampled and analyzed. The total concentration of U(VI) was determined with a spectrophotometric analysis

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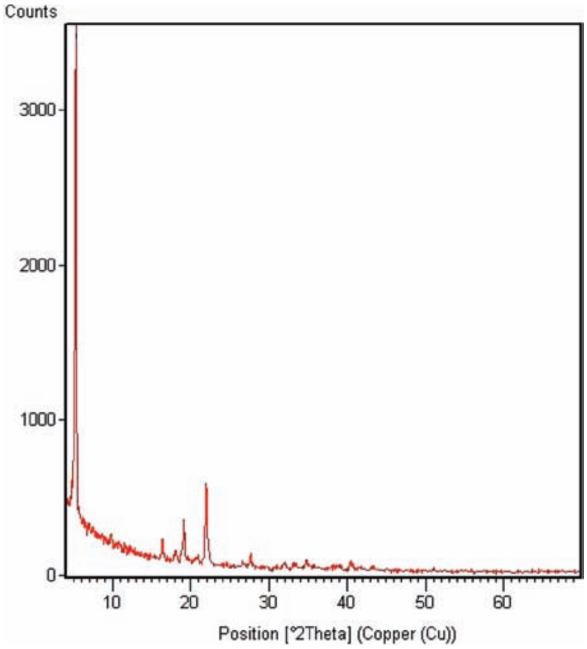

Figure 1. XRD pattern of MOADDTCEXHEFU.

method with dibenzoyl methane-tri-*n*-octyl phosphine oxide (DBM-TOPO) as a chromogenic reagent using a Shimadzu UV−vis 1601 model spectrophotometer at 405 nm.[12]

To determine the effect of other metal ions on the uranium uptake, an artificial mixture solution containing 50 mg·L^{-1} of Mg^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Ba^{2+}, Pb^{2+}, Th^{4+}, and U^{6+} each was prepared from their nitrate salts and treated with MOADDTCEXHEFU. Inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin-Elmer Optima 2000 DV) was used for the determination of the concentration of each metal ion except thorium and uranium.

To analyze thorium and uranium, a γ-ray spectrometry system was used with the components of a $3'' \times 3''$ NaI(Tl) scintillation detector, CANBERRA-802 model spectroscopy amplifier, and Canberra DSA 1000 multichannel analyzer and also the GenieTM 2000 version 3.0 software. To reduce the background, the detector was fitted in a 5 cm thick cylindrical lead shield of 20 cm in radius. The energy calibration of the γ spectrometer system was carried out with ^{137}Cs and ^{60}Co (Amersham) γ sources, and also the obtained data were compared with IAEA-384 reference material. The concentration of these two elements was measured by a γ spectrometry system with the selection of the (1001 and 2620) keV peaks due to the γ rays of ^{234m}Pa and ^{208}Tl for uranium and thorium, respectively.[13]

The adsorption yield and the solid phase concentration were computed from the difference between the initial concentration and the equilibrium concentration of the supernatant, using the following equation;

$$\text{adsorption yield}(\%) = \left(\frac{(C_i - C_e)}{C_i}\right) \cdot 100 \qquad (1)$$

where C_i and C_e are the initial and equilibrium concentration of uranium in solution. All experimental data were the average of duplicate experiments, and the adsorption yields within each pair were different by less than 5 %.

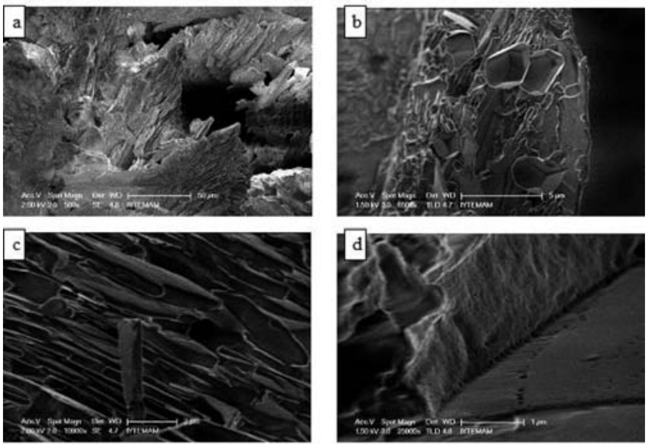

Figure 2. Intra structure of MOADDTCEXHEFU.

RESULTS AND DISCUSSION

Structural Studies. Powder X-ray diffraction (XRD) data were collected on a Phillips X'Pert Pro X-ray diffractometer with Cu Kα radiation (λ = 1.5405 Å). The data were collected at room temperature in the range of 2θ between 5° and 70°. The X-ray diffraction pattern of synthesized MOADDTCEXHEFU show that this adsorbent has strong crystallinity as shown in Figure 1.

To know the structure of MOADDTCEXHEFU, morphological analysis of the MOADDTCEXHEFU was performed by scanning electron microscopy using a Phillips XL-30S FEG. The working voltage was 20 kV. Figure 2 indicates that MOADDTCEXHEFU has an extensive surface area and may be used as a sorbent material.

To make a structural identification of the adsorbent material and clarify the situation of adsorbed uranium IR analysis was performed with a Fourier transform infrared (FTIR) spectrometer (PerkinElmer, Spectrum BX System version 5.0.1). Each 1 mg dried sample was mixed with 200 mg of KBr and pressed under vacuum. The tablet was recovered with a clip and was immediately analyzed in the range of (4000 to 400) cm^{-1} with a resolution of 4.0 cm^{-1}. The influences of atmospheric water and CO_2 were always subtracted.

The FTIR spectra of MOADDTCEXHEFU before and after adsorption of uranium(VI) were used to determine the vibrational frequency changes of the functional groups in the adsorbent. The spectra of adsorbents were measured within the range of (4000 to 400) cm^{-1} wave numbers. The spectra were plotted using the same scale on the transmittance axis for the adsorbent before and after adsorption. The FTIR spectra of the MOADDTCEXHEFU displayed a number of absorption peaks, indicating the complex nature of the studied adsorbent. Figure 3 presents the fundamental peaks of the adsorbent before and after use as spectra A and B, respectively. The information extracted from these figures is also summarized in Table 1.

Weak stretching vibration signals which are shown in spectrum A of Figure 3 at around (3014.0, 2997.2, and 1669.6) cm^{-1} reveal that the configuration of the molecule is a *s-trans* formation. The observed sharp peaks at (1756.3 and 1729.3) cm^{-1} which are more characteristic stretching vibration signals for both ester groups on the skeleton. C—O vibration signals can be seen at (1049.6, 1117.5, and 1224.9) cm^{-1} and also at 1164.2 cm^{-1} related with the —O—CH_3 group. For the C−Cl bond, the bending vibration signals can be easily seen at (620.4 and 813.4) cm^{-1} from

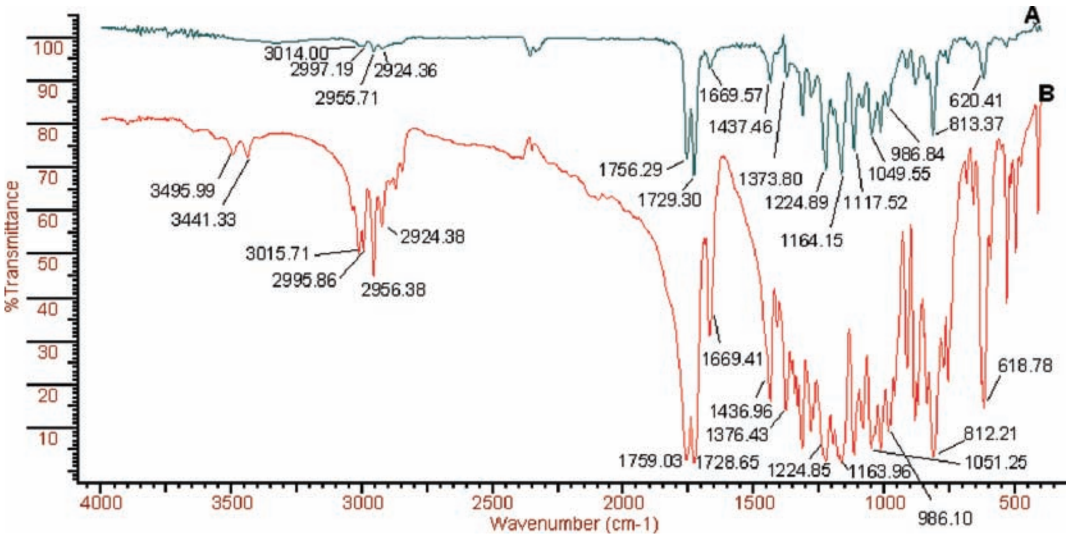

Figure 3. FTIR spectra of MOADDTCEXHEFU molecule before (A) and after (B) adsorption of uranium.

Table 1. IR Spectra of MOADDTCEXHEFU and Uranium(VI) Linked MOADDTCEXHEFU

function group	before binding of uranium (VI) ions, $\lambda/(\text{cm}^{-1})$	after binding of uranium (VI) ions, $\lambda/(\text{cm}^{-1})$
hydroxyl groups on the uranium(VI) ion		3495.9 and 3441.3
=C—H stretching vibration	3014.0 and 2997.2	3015.7 and 2995.9
C=C stretching vibration	1669.6	1669.4
C=C bending vibration	986.8	986.1
C—H stretching vibration	2955.7 and 2924.4	2956.4 and 2924.4
C—H bending vibration	1437.5 and 1373.8	1437.0 and 1376.4
C=O ester groups (stretching vibration)	1756.3 and 1729.3	1759.0 and 1728.7
C—O stretching vibration	1049.6, 1117.5, and 1224.9	1051.3, 1117.7, and 1224.9
OCH_3	1164.2	1163.9
C—Cl bending vibration	620.4 and 813.4	618.8 and 812.2

each spectra. As for comparing the two IR spectra, it is clear that the stretching vibration intensity of the C=C bond observed at 1669.4 cm^{-1} is increased in spectrum B of Figure 3. The intensity of C—H stretching and bending vibrations observed at (2956.4, 2924.4, 1437.0, and 1376.4) cm^{-1} also increased while the intensity of carbonyl groups decreased. The sharpness of the —O—CH_3 peak observed at 1163.9 cm^{-1} also decreased at the same time. These changes and minor shifting values of whole signals between IR spectra may be due to the bonding of uranium(VI) to the MOADDTCEXHEFU skeleton. The additional peaks around (3495.9 and 3441.3) cm^{-1} can be characterized as the formation of intermolecular bonding of the hydroxyl groups on the uranium(VI). These data obtained from the IR spectrum of the molecule agree with the literature.[14,15]

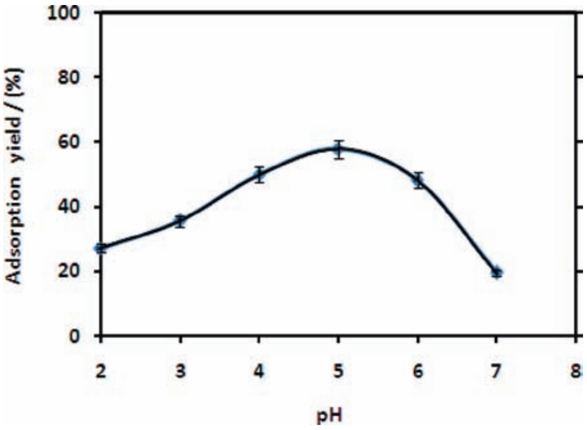

Figure 4. Effect of pH on U(VI) adsorption (c: 50 ppm, v: 10 mL, m: 0.01 g, t: 2 h, T: 25 °C).

Effect of pH Variation. Ren et al. (2010) explained that the adsorption of U(VI) is dominated by ion exchange and surface complexation due to the dependence of adsorption phenomena to pH values.[16] Adsorption of U(VI) on MOADDTCEXHEFU as function of pH value is shown in Figure 4. It is clear that U(VI) adsorption on MOADDTCEXHEFU is strongly dependent on pH value. The adsorption of U(VI) increases quickly with pH values over pH 3 to 4, reaches a maximum adsorption at pH ~5, and then decreases with increasing pH at pH > 6.0. The adsorption of uranium below pH 4 is low. It may be considered that the available sites on the surfaces of the adsorbent are protonated. In solution, protons can adsorb to surfaces. Hence, the solution pH affects the overall surface charge of the solid;

$$\equiv \text{R—OH} + \text{H}^+ \leftrightarrow \equiv \text{R—OH}_2{}^+$$

$$\equiv \text{R—OH} \leftrightarrow \equiv \text{R—O}^- + \text{H}^+$$

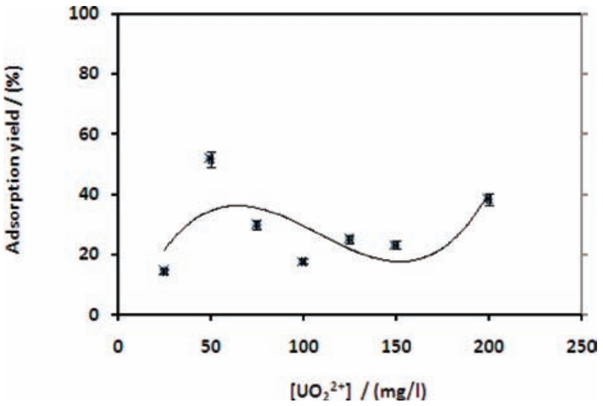

Figure 5. Effect of U(VI) concentration on adsorption (*v*: 10 mL, *m*: 0.01 g, *t*: 2 h, *T*: 25 °C, pH: 5).

where ≡ denotes a surface of the adsorbent. Therefore, the adsorbent has a net-positive surface charge at low pH and a net-negative surface charge at high pH.[17] On the other hand, according to Sorg (1990), the dominant species of uranium ions is UO_2^{2+} in the pH range from 1 to 4. The species of uranium carbonate such as $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ in carbonate media form with increasing pH. Since both adsorbent surface and adsorbate are negatively charged above pH 4 and 5, respectively, the adsorption yield is decreased.[18] As Wazne et al. mentioned, the affinity of uranium(VI) carbonate complexes to surface sites is low above pH 5, and also the competitive adsorption of carbonate on the surface could occur.[19] These confirm that the pH effects on the adsorption of uranium which compete with protons of solution for adsorption on the active sites of the adsorption surface.[20−22]

Effect of U(VI) Concentration. Adsorbents used in uranium adsorption are mostly in particulate shape. Comprehensive types of polymers having a range of adsorption capacities for uranium(VI) have been reported. Say et al. reported that the maximum uranium(VI) adsorption capacity of P(MAGA-$[UO_2]^{2+}$−co-EGDMA) microbeads was found to be 181 mg·g^{-1}.[23] The adsorption capacity of *N*,*N*′-dimethyl-*N*,*N*′-dibutyl malonamide (DMDBMA) for uranium was found to be 18.78 mg·g^{-1} by Ansari et al.[24] Egawa et al. introduced amidoxime-type resin (RNH) containing acrylonitrile−divinylbenzene copolymer beads to adsorb uranium(VI) and determined that the adsorption capacity was 191.7 mg·g^{-1}.[25]

As seen from Figure 5, the adsorption yield is increased rapidly from 14.52 % to 51.80 % for (25 and 50) mg·L^{-1} uranium(VI) concentrations from aqueous solution, respectively. Then, the adsorption yield decreased with increasing initial metal cation concentration up to 100 mg·L^{-1}. These results show that the adsorbent has a good performance in diluted solutions and could adsorb approximately 26 mg·L^{-1} of uranium(VI) on 0.01 g of adsorbent. The adsorption data indicate that the maximum adsorption capacity is governed by the amount of active sites on the adsorbent surface. As mentioned in the next section and also shown in Table 2 the adsorption capacity of this material was found to be 40.82 mg·g^{-1} which is in good agreement with data available in the literature.

Effect of Shaking Time. The treatment periods of uranium with the adsorbent were chosen in the range of (15 to 300) min at ambient temperature. Figure 6 shows the variation of adsorption efficiency with contact time for U(VI) at pH 5. According to obtained data, the highest value of adsorbed uranium(VI) on the adsorbent was reached at 30 min (58.4 %).

Table 2. Langmuir and Freundlich Isotherm Parameters and Error Analysis Results[a]

Langmuir parameters				Freundlich parameters			
Q	b			K			
mg·g^{-1}	L·g^{-1}	χ^2	R^2	mg·g^{-1}	n	χ^2	R^2
26.32	0.006	0.66	0.96	0.05	0.69	101.81	0.88

[a] χ^2: nonlinear chi-square test.

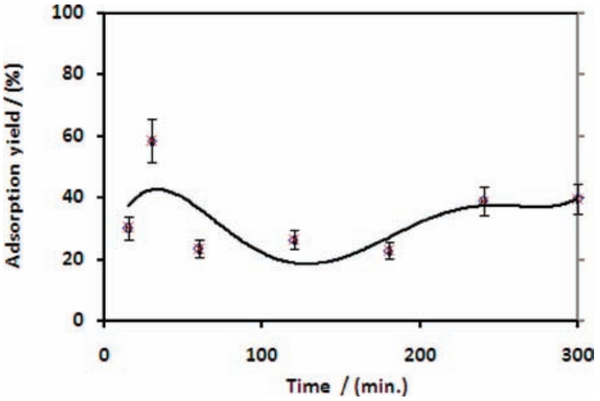

Figure 6. Effect of retention time (*v*: 10 mL, *m*: 0.01 g, *c*: 50 ppm, *T*: 25 °C, pH: 5).

As can be seen from Figure 6, the adsorption amount of U(VI) rapidly increased at the beginning of adsorption due to the adsorption of the adsorbent on the surface sites of MOADDT-CEXHEFU; then it becomes slow due to the diffusion of uranium from the surface sites to the interlayer of the solid. It means sorption of U(VI) ions on the adsorbent was very fast and the equilibrium was reached after only 30 min. The maximum adsorption percentages of U(VI) ions decrease with time until 180 min and then increase again slightly with time. Therefore, a 30 min shaking time was found to be appropriate for the maximum adsorption and was used in all subsequent measurements. This property agreed with the literature as reported by Demirbas, Liu et al., and Chaari et al.[26−28]

Isotherms. To examine the relationship between sorbed (q_e) and aqueous concentration (C_e) of uranium(VI) at equilibrium, adsorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are mostly used. The Langmuir model assumes that the uptake of metal ions occur on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.[29] To gain the equilibrium data, initial uranium(VI) concentrations were varied, while the adsorbent mass in each sample was kept constant. Equilibrium periods of 30 min for adsorption experiments were used to ensure equilibrium conditions. The Langmuir model takes the linear form:

$$\frac{1}{q_e} = \frac{1}{Q} + \left(\frac{1}{Qb}\right)\frac{1}{C_e} \qquad (2)$$

where C_e (g·L^{-1}) is the solution phase metal ion concentration, q_e (mg·g^{-1}) is the amount of uranium(VI) adsorbed onto the unit mass of adsorbent to form a complete monolayer on the surface,

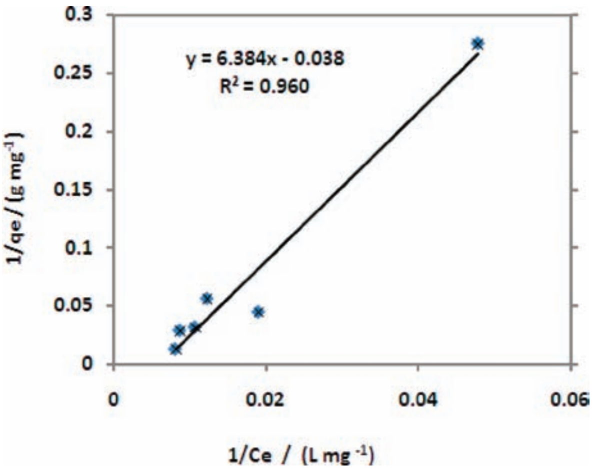

Figure 7. Langmuir adsorption isotherm.

b is the Langmuir constant, being the ratio of adsorption and desorption rate coefficients ($\mathrm{L \cdot g^{-1}}$), and Q is the maximum adsorption capacity ($\mathrm{mg \cdot g^{-1}}$). At low concentrations, this equation model is reduced to a linear relationship, while the maximum adsorption capacity Q is attained at concentrations corresponding to monolayer coverage. As the value of b becomes larger, the limiting adsorption capacity is attained at a lower solution phase concentration.[30] Adsorption data were expressed as the amount of uranium(VI) sorbed per unit weight of sorbent (C_e/q_e) versus the concentration of uranium(VI) in the solution phase at equilibrium (C_e). The adsorption data were fitted to the linear form of eq 2 to obtain the values of Q and b as shown in Figure 7 where the amounts of uranium(VI) were available in the range from (25 to 110) $\mathrm{mg \cdot L^{-1}}$.

The Freundlich adsorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentration. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.[31] The adsorption data were tested on the following linearized form of Freundlich adsorption isotherm by plotting log C_{ads} versus log C_e, as shown in Figure 8.

$$q_e = KC_e^{1/n} \tag{3}$$

where C_{ads} is the amount of adsorbed at equilibrium ($\mathrm{mg \cdot g^{-1}}$ adsorbent), C_e is the equilibrium concentration of adsorbate ($\mathrm{mg \cdot L^{-1}}$), and n and K are the Freundlich constants characteristic of the system, indicating the extent of the adsorption and the degree of nonlinearity between metal solution concentration and adsorption, respectively. From the slope and intercept of the plot, the value of the Freundlich parameters, $1/n$ and K are found to be 1.43 and 0.05 $\mathrm{mg \cdot g^{-1}}$, respectively. These values signify the adsorption intensity and capacity, respectively. The correlation factors computed for the linear regression analysis of this isotherm come out to be 0.88, being close to unity. The numerical value of $1/n > 1$ indicates that the adsorption capacity is only slightly suppressed at higher equilibrium concentrations. The value of the multilayer Freundlich capacity K is smaller than the value of the monolayer Langmuir maximum adsorption capacity Q (Table 2). This confirms that the adsorption of uranium(VI) on MOADDTCEXHEFU occurred on a homogeneous surface without any interaction between uranium(VI) ions.

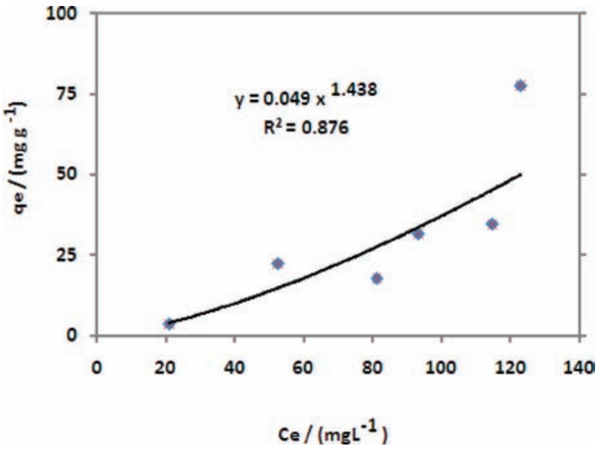

Figure 8. Freundlich adsorption isotherm.

The chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculation from models, with each squared difference divided by the corresponding data obtained from the model. The equivalent mathematical statement is:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{4}$$

where $q_{e,m}$ is the equilibrium capacity obtained from the model ($\mathrm{mg \cdot g^{-1}}$) and q_e is the experimental data of the equilibrium capacity ($\mathrm{mg \cdot g^{-1}}$). If data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ, χ^2 will be a bigger number. Therefore, it is necessary to also analyze the data set using the nonlinear chi-square test to confirm the best-fit isotherm for the sorption system.[32]

Also the results of the application of the linear coefficient of determination, R^2, and nonlinear chi-square test on experimental data, q_e, for two adsorption isotherms are shown in Table 2. The Langmuir model appears to be the better fitting model for U(VI) adsorption on the adsorbent due to its high regression coefficient, R^2 (0.96) and lowest chi-square, χ^2 (0.66) values. The Freundlich model has a lower value of R^2 (0.88) and higher value of χ^2 (101.81).

Thermodynamics of Adsorption. The influence of temperature variation was examined on the adsorption of U(VI) using 0.01 g of MOADDTCEXHEFU at 30 min equilibration time, and 50 $\mathrm{mg \cdot L^{-1}}$ of initial concentration of uranium(VI) over the temperature range from (30 to 50) °C. Thermodynamic parameters, entropy and enthalpy, for the adsorption of uranium(VI) on this adsorbent were calculated by using the following equation:

$$\ln K_d = \left(\frac{\Delta S^o}{R}\right) - \left(\frac{\Delta H^o}{RT}\right) \tag{5}$$

(R is the gas constant, 8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$).[33] The thermodynamic equilibrium constant K_d is defined as eq 6 for adsorptive reactions:

$$K_d = \alpha_s/\alpha_e = \nu_s q_e/\nu_e C_e \tag{6}$$

where α_s and α_e refer to the activity of adsorbed uranium(VI) and the activity of uranium(VI) in solution at equilibrium and ν_s and ν_e denote the activity coefficient of the adsorbed uranium(VI) and the uranium(VI) in solution, respectively. As the uranium(VI)

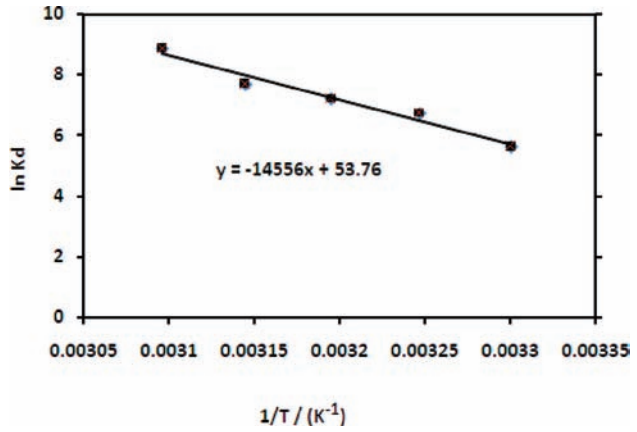

Figure 9. Plot of ln K_d against T^{-1}.

Table 3. Thermodynamic Parameters of Adsorption Process

ΔH^0	ΔS^0	$\Delta G^0/(\text{kJ}\cdot\text{mol}^{-1})$				
$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	303 K	308 K	313 K	318 K	323 K
121.02	0.45	−14.41	−16.65	−18.88	−21.11	−23.35

concentration in the solution decreases and approaches zero, K_d can be obtained by plotting q_e/C_e versus q_e and extrapolating q_e to zero.[34] The plot of ln K_d against $1/T$ for uranium(VI) is shown in Figure 9. The values of ΔH^o and ΔS^o are obtained from the slope and the intercept of plot, which were calculated by curve-fitting. The Gibbs energy for the specific adsorption ΔG^o was calculated by using the following well-known equation;

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (7)$$

The values of the thermodynamic parameters for the adsorption of uranium(VI) on MOADDTCEXHEFU are given in Table 3.

The negative values of ΔG^o indicate feasibility and spontaneity with the high preference of U(VI) for MOADDTCEXHEFU. The positive value of ΔH^o indicated that the adsorption phenomenon is endothermic. Since the adsorption is endothermic, the amount adsorbed at equilibrium must increase with increasing temperature, because ΔG^o decreases with increasing temperature of the solution. The positive value of entropy ΔS^o (0.45 $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) reveals that the complex formation is favored and adsorption process is stable.[35−37] In addition, a direct interaction might occur between the U(VI)-functional group complex and adsorbent materials at the positive value of entropy.[38,39]

Studies on the Effect of Competing Ions. With a view to studying the separation of uranium from barium, copper, iron, magnesium, nickel, lead, and thorium ions, 50 $\text{mg}\cdot\text{L}^{-1}$ of each metal ion in the same solution was prepared. The established optimum condition (v: 10 mL, T: 25 °C, pH: 5, and t: 30 min) was used with 0.01 g of adsorbent. The adsorbent particles and ion solution mixture was filtered off from the fine crystalline Whatman filter paper. The filtrate was then analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin-Elmer Optima 2000 DV). It has found that the degree of adsorption with MOADDTCEXHEFU diminishes in the sequence $\text{Th}^{4+} > \text{Ba}^{2+} > \text{Mg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{U}^{6+}$. The small adsorption of uranium(VI) could be related to its size (3.54 Å) or its ionic complexes, which are too large to be sorbed, in competing with the other metal ions. The results again show that there is significant adsorption of Th^{4+}, Ba^{2+}, and also Mg^{2+} on MOADDTCEXHEFU, about 20.51 %, 18.54 %, and 13.27 %, respectively.

■ CONCLUSIONS

The feasibility of using MOADDTCEXHEFU for the preconcentration/separation of uranium(VI) was assessed by varying parameters such as pH, uranium(VI) concentration, temperature, and shaking time.

The Langmuir and Freundlich adsorption models were used for the mathematical description of the adsorption equilibrium of uranium ions to MOADDTCEXHEFU, and the obtained results showed that the adsorption equilibrium data fitted well to the Langmuir model. That the value of linear regression (R^2) of the Langmuir isotherm is less than unity is an indication that significant adsorption takes place at low uranium(VI) concentrations.

Various thermodynamic parameters, such as ΔG^o, ΔH^o, and ΔS^o, were calculated from the experimental data. The thermodynamics of the U(VI) ion/MOADDTCEXHEFU system indicate the spontaneous and endothermic nature of the process.

The experimental studies showed that MOADDTCEXHEFU could be used as an economic and low-risk sorbent material to remove toxic and radioactive U(VI) ions from wastewaters.

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