Synthesis of Eco-Friendly Adsorbent Based on Chitosan-Tannic Acid *via* Solution Mixing Technique with High Uranium Adsorption Performance

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ABSTRACT: *One of the main challenges in uranium extraction treatment is how to improve the adsorption performance of uranium with high adsorption capacity by using a simple and environmentally friendly technique. To tackle this challenge, in this study, effective eco-friendly adsorbents were synthesized based on chitosan-tannic acid (TACH) via a solution mixing technique. The chemical structures of the obtained adsorbents were characterized using Fourier transmutation InfraRed (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray (EDX) analysis. The effect of pH, temperature, adsorbent dosage, contact time, and initial U(VI) concentration on the removal capacity of the made adsorbents was investigated. The thermodynamic behavior and kinetic properties were studied. The adsorption data fit with the Lagergren equation, the sorption reaction is more favorably to be pseudo-second order sorption. The adsorption capacity of uranium achieved 155 mg/g which accords with Langmuir isotherm (150 mg/g). The synthesized TACH adsorbent showed the highest absorbance at PH 3, contact time 90 minutes, and temperature 25°C. These features make the prepared adsorbents in this study applicable as eco-friendly biopolymers with high uranium adsorption performance.*

KEYWORDS: *Chitosan; Adsorbent; Tannic acid; Uranium adsorption; Kinetic model.*

INTRODUCTION

Chitosan consider as a one of the best appropriate and promising sorbent in the extraction of impurities [1- 6]. Chitosan is real in the heavy metals absorption due to the biggest content of terminal amino groups which act as absorbent [5-6]. Chemical change of chitosan without shifting its central basic is a good target for it brings new and better-quality physical and chemical investments and more applications. Chitosan is a moderately deacetylated chitin biopolymer that happens in wide range of uses as anti-bacterial and anti-fungi [1, 2]. Chitosan has many of constructions through its applications as biodegradability, anti-bacterial stuff and high hydrophobicity [3, 4]. Enhanced chitosan complexes by fixing new function groups were produced to generate improved extracting

properties in metal elimination technique from manufacturing waste population. The new terminal groups are prepared to growth the density of sorption locations, to improve the products in a wide range of pH for extraction of metal and to optimized the sorption sites and metal extraction choosiness [7-10]. Enhancement of chitosan was a goal to increase the metal separation performance and improve the stability in low pH intermediate as in this work application. The reactions mostly targeted the NH_2 group on the location of C2 or the OH groups in locations C3, C5 of the Aco(Acetylated) and DAco (deacetylated) parts [11]. Improved chitosan approves the founding of functional products by covalent mandatory of a molecule [11, 12]. Crosslinking materials are usually ended with function groups divided by some spaced molecules that can be controlled in many structures. Crosslinking can increase the extraction performance, dependent on the terminal groups in the cross-linking parts [13- 25]. Various adsorbents have been investigated for metal ion extraction [26]. Contaminations of the environment by uranium have a high risk in environmental impact. The presence of uranium is of great concern because of toxicity and the tendency for bioaccumulation even at relatively low concentrations. In addition, as the most abundant radioactive element in nature, uranium is widely applied in nuclear power plants. It's important to meet future energy needs. Currently, about 15% of the world's electricity is generated by over 400 nuclear power plants. The treatment should reduce the quantities of contaminants to a level that allows safe discharge according to national and international regulations. Chitosan shows lower stability in weak acids, which limits their adsorption character. Therefore, the modification of chitosan by inserting more active adsorption sites into amino and hydroxyl groups could improve its stability and adsorption performance. Tannic acid has a large number of hydroxyl groups, a biocompatible surface, and it has an affinity towards uranium extraction. Consequently, fabrication of tannic acid-chitosan adsorbent (TACH) via solution mixing technique could enhance the stability and extraction performance of chitosan. The solution mixing technique is a facile and economic method that does not need a complex system or a large number of chemicals. Moreover, there is no additional energy required, and high amounts of products are precipitated within a short reaction time. In this study, tannic acid-chitosan (TACH) biopolymer was prepared by mixing chitosan and tannic acid using the solution mixing method. The applicability of the prepared eco-friendly biopolymer was valued for uranium removal from its aqueous solutions. The effect of pH, temperature, adsorbent dosage, contact time, and initial U (VI) concentration on the uranium adsorption performance of the produced adsorbents were considered.

EXPERIMENTAL SECTION
Materials
The chitosan flakes (CH, 110 kDa and 85% grade of DAc (deacetylation)) was acquired authorizing to the distributed techniques [27]. Tannic acid (TA) (≥ 99% purity) was provided from Sigma Aldrich chemicals, Germany.

Characterizations
Spectrophotometric analysis and FT-IR spectroscopy were achieved using: Buck 200 Series AA and ATI Mattson model Genesis Series (USA) infrared spectrophotometer, respectively [27, 28]. Uranium was detected spectrophotometrically using Arzenazo III at 655 nm [29].

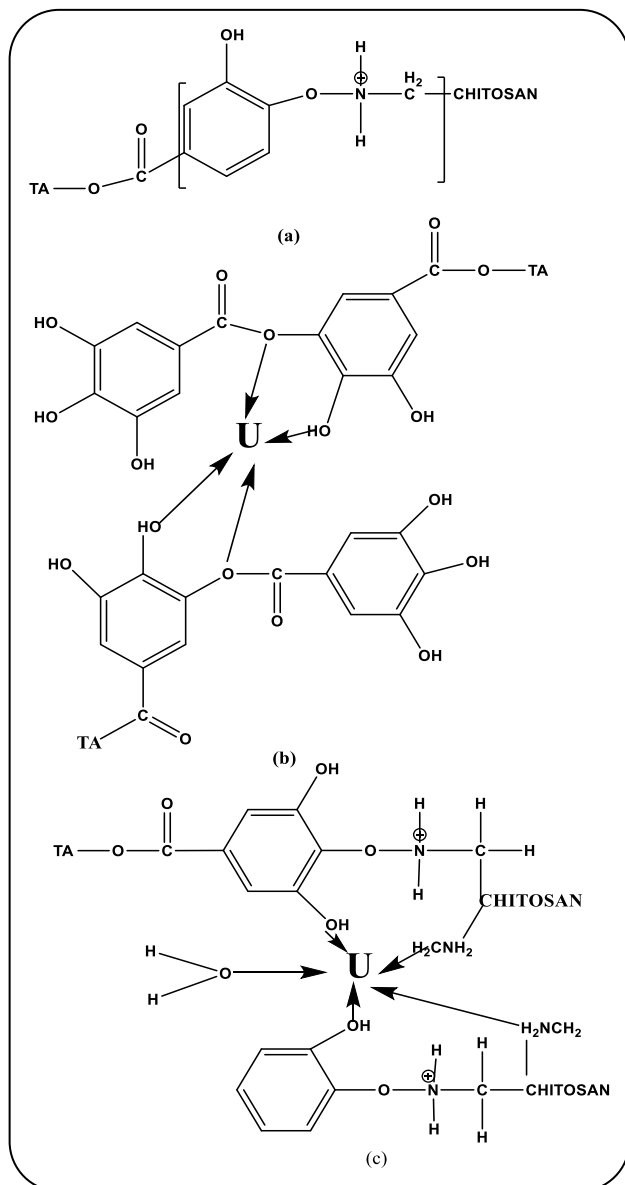## Fabrication of chitosan -tannic acid adsorbent (TACH)
TACH adsorbent was synthesized by mixing Tannic Acid (TA) with chitosan (CH) in a ratio of 1:5. CH solubilized in distilled water (DW, 100 mL) at pH 4 by using glacial acetic acid and the solution temperature was increased to 60°C and mixed well for 3 hr. TA in DW (100 mL) was prepared and added to the CH solution. The obtained mixture mixed well for 4 at 60°C until the adsorbent was formed. It is filtered off and washed with DW and dried till the powder is obtained [30].

Uranium Adsorption performance
The TACH was used for U (VI) adsorption from sulfate solution by batch produced. Weighted TACH (0.1g) contacted with (10 mL) uranium synthetic solution of 600 mg/L for famous period at ambient temperature U concentration was determined according to Eq. 1.

$$U \text{ adsorption efficiency\%} = \frac{U_o - U_e}{U_o} \times 100 \qquad (1)$$

Where U_o and U_e are the initial and equilibrium U concentration in solution (mg/L), respectively [31].

Scheme 1: a) interaction between CH and TA, b) adsorption of U by TA and c) adsorption of U by TACH adsorbent.

Result of U adsorption quantity qe (mg/g) has been passed at the equilibrium time by Eq. 2.

$$q_e = (U_o - U_e) \times \frac{V}{m} \qquad (2)$$

Where *V* is the solution volume (L), m is the resin weight (g). The *U* distribution coefficient (K_d) between the aqueous bulk phase and the solid phase was designed by Eq. (3).

$$K_d = \frac{U_O - U_e}{U_e} \times \frac{V}{m} \qquad (3)$$

Elution Performance

To desorb U from the loaded TACH, various eluents have been examined namely; HCl, H_2SO_4, HNO_3, NaOH, Na_2CO_3, NaCl, Na_2SO_4 and CH_3COONa. Desorption experiments were performed by shaking the loaded uranium-TACH (0.1 g) with 10 mL of the eluent solution (1.0 M) for 60 min.

RESULTS AND DISCUSSION
Synthesis and characterization of chitosan -tannic acid adsorbent (TACH)

In this study, TACH adsorbent was synthesized by mixing Tannic Acid (TA) with chitosan (CH) via solution mixing technique (Scheme 1). Controlling the chemical compositions of TACH is critical to improving their active adsorption sites that effectively lead to enhancing their stability and adsorption properties as well [32-40].

Fourier Transform Infrared (FT-IR)

The surface functionality of tannic acid-chitosan (TACH) before and after loading with U was detected by FT-IR as shown in Fig. 1. The peak at 3320 cm^{-1} for a strong band of the N–H stretching was detected. The presence of the ring C–H stretching band of the tannic acid (cross-linked chitosan) was confirmed by a peak at 2923 cm^{-1}. The observed peaks were detected at 1720 cm^{-1} (C=O stretching of secondary amide bonds), 1635 cm^{-1} (C=C stretching of skeletal vibration of aromatic ring), 1569 cm^{-1} (N-H bending vibrations of 1° amine). The ring C–C stretching and the scissoring of the methylene groups (bending -CH_2) were observed at 1468 cm^{-1} and 1376 cm^{-1} (Vinyl and Vinylidene of C–H in-plane bend). After adsorption, most peaks were shifted 5 cm^{-1}, which confirmed of the interaction between U and TACH as uranyl ion complex. The new peaks 1161 cm^{-1} and 925 cm^{-1} appeared after adsorption suggesting the uptake of U (VI) by TACH [36, 37].

Scanning Electron Microscope (SEM)

The morphology of tannic acid-chitosan (TACH) before and after the adsorption process was investigated using a Scanning Electron Microscope (SEM) (Fig. 2 A and B). It was obvious, that the surface morphology of TACH after the adsorption process was altered from that of the surface before U adsorption. The tannic acid-chitosan showed loose aggregates with a porous structure,
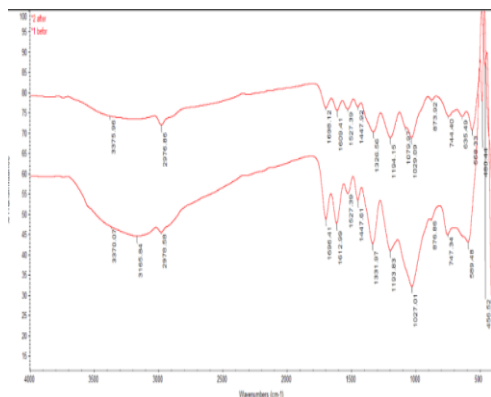
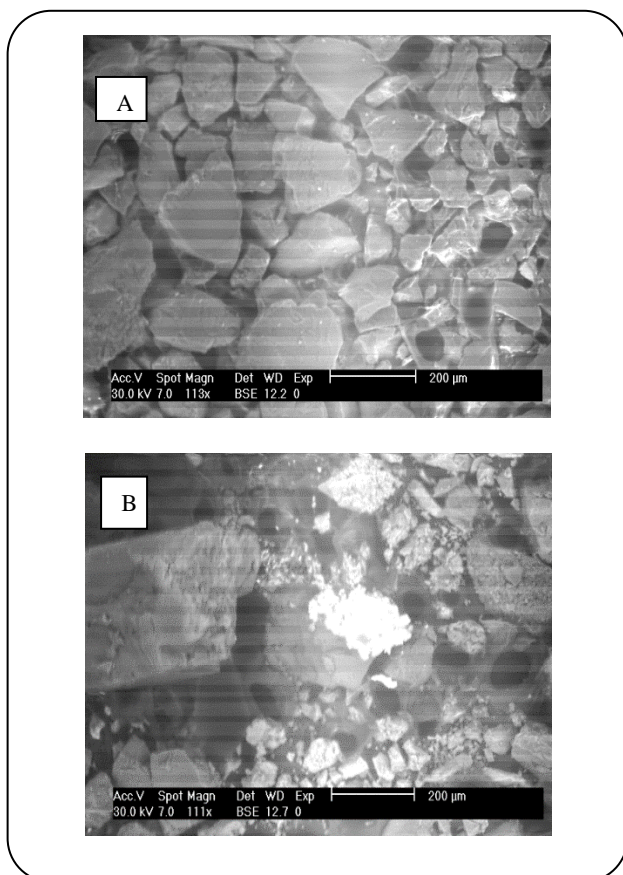**Fig. 1: FT-IR of TACH before and after U adsorption.**

Fig. 2: SEM of TACH (A) before and (B) after U adsorption.

while after adsorption the surface shows compacted aggregates. The morphology of the tannic acid-chitosan surface changed interface occurred during the experiment. The visible change of the surface morphology in the U adsorbed confirmed that the sorption of U occurred onto the tannic acid-chitosan sorbent [38].

EDX Analysis

The elemental analysis of tannic acid-chitosan (TACH) before and after the adsorption process was investigated using EDX analysis (Fig. 3). As seen in Fig. 3 A, B. TACH particles are spherical with a uniformly planar surface. However, the surface converted rough and high wrinkled after the adsorption process as shown in Fig. 3 B. The change in surface topography can be recognized by the diffusion of ions from the solution and adsorbed on the adsorbent surface. The elemental analysis formed by EDX detection for TACH before and after sorption of U is represented in Table 1. The reference TACH does not contain uranium ions according to Fig. 3 A. After contact with the solution containing uranium ions, one can detect the presence of U in the sample [39].

Uranium adsorption performance of chitosan -tannic acid adsorbent (TACH)

The efficiency of U adsorption from sulfate solution via solid-liquid batch method was investigated in function of initial U concentration, contact time, temperature, and pH.

pH effect

The effect of pH on the adsorption performance of U from aqueous solution by TACH was investigated at the range from 0.5 to 4.0 at 25 °C (above the pH 4.0 value, U become precipitate) using 0.1g TACH with a U solution (10 mL) with concentration of 500 mg/L at room temperature. Fig. 4 shows the adsorption performance of the fabricated TACH for U by changing pH of the medium. From the results it can be concluded that pH 3 is optimal.
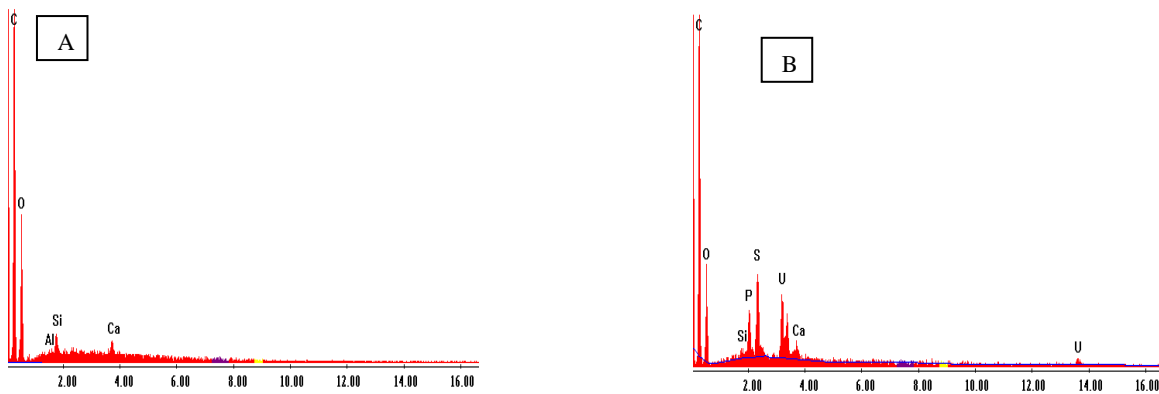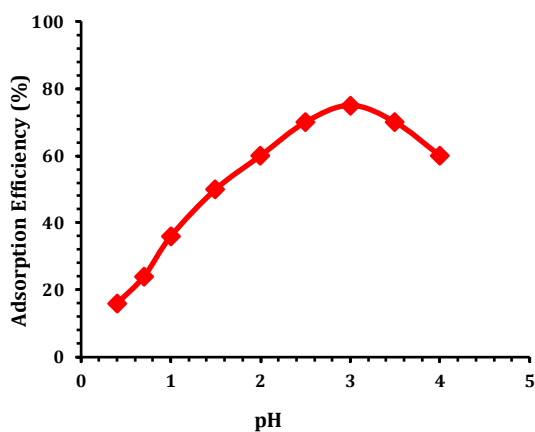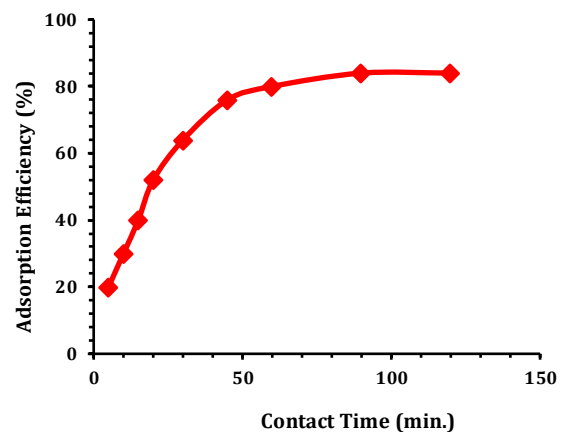
Contact time effect

Contact time represents the time of interface between the TACH adsorbent and the metal ions in the solution [32]. Commonly, increasing the contact time increases the amount of U ions uptake from their solution as shown in Fig. 5. Using weight of TACH was (0.1g) with U solution (10 mL) with concentration 500 mg/L and pH 3.0 at room temperature for contact time from 5.0 to 120 minutes. From the results, it can be concluded that 90 min contact time is optimal

Initial uranium concentration effect

To examine the effect of initial U concentration upon its adsorption efficiency on to TACH, a series of experiments were accomplished by contacting a fixed

Table 1: EDX elemental analysis of TACH (A) before and (B) after U adsorption.

Before adsorption		After adsorption	
Element	Wt. %	Element	Wt. %
C	66.00	C	61.42
O	32.71	O	22.14
Al	0.14	Al	--
Si	0.60	Si	0.32
Ca	0.54	Ca	0.58
P	-	P	1.46
S	-	S	2.37
U	-	U	11.71
Total	100		100

Fig. 3: EDX of TACH (A) before and (B) after U adsorption.

Fig. 4: Effect of adsorption capacity of U(VI) as a function of equilibrium pH using TACH sorbent (C_0: 500 ± 5 mg/L; contact time:30 min; T:25 ± 1 ºC, (rpm: 250).

Fig. 5: Contact time effect upon the U adsorption performance on TACH (TACH weight = 0.1 g, volume = 10 mL, pH = 3.0, U conc. = 500 mg/L, rpm: 250).

weight (0.1 g) of the studied TACH with 10 mL U stock solution and pH 3.5 for 90 min at room temperature (˜ 25 ºC). The studied initial U concentrations ranged from 400 up to 4000 mg/L. The attained results were plotted in Fig. 6. From the attained data, it was found that the adsorption efficiency is inversely proportional to its initial concentration. In contrast, the adsorption capacity is directly proportional to initial U concentration till maintenance after 2000 mg/L where at this point experimental adsorption capacity of the adsorbent was about 152 mg U /g TACH.

Phase ratio (S/L) effect

The effect of dose concentration (S/L) has been studied in the range of 0.01-0.1 g of TACH /10 mL solution under the circumstances of U initial concentration of 2000 mg/L, pH of 3.5 at ambient temperature for 90 minutes, the results were graphically plotted in Fig. 7. The results revealed that the U adsorption increases progressively by increasing the S/L ratio from 0.01/10 to 0.1/10 for the TACH without further increase. As a result, TACH/aqueous ratio of 0.1/10 was the more favorable ratio for the TACH.

The effect of the temperature

The effect of the temperature on adsorption performance of tannic acid-chitosan (TACH) adsorbent for U (VI) was investigated at TACH weight = 0.1 g, volume = 10 mL, pH=3.5, 90 min U conc. = 2000 mg/L). The results are clarified in Fig. 8. It can be concluded that the adsorption performance of the TACH adsorbent is smoothly increased from 97.4% to 99.4% by elevating the temperature of the tests from 25 to 50 ℃. So, no requirement to increase the temperature overhead room temperature [33].

Adsorption Isotherm

Several public adsorption isotherm models were measured to fit the achieved isotherm data under the equilibrium adsorption of the TACH. Examples of these models are Langmuir and Freundlich.

A- Langmuir Isotherm

Langmuir model assumes that the adsorption happens homogeneously on the active sites of the sorbent, and once a sorbet occupies a site, no additional sorption can take place at this site [34].
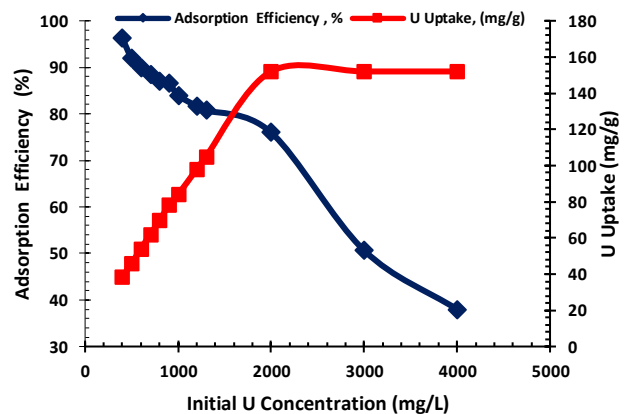

Fig. 6: Initial U concentration effect on U adsorption efficiency and U uptake (TACH weight = 0.1 g, volume = 10 mL, pH=3.5, 90 min, 25 ^{0}C).
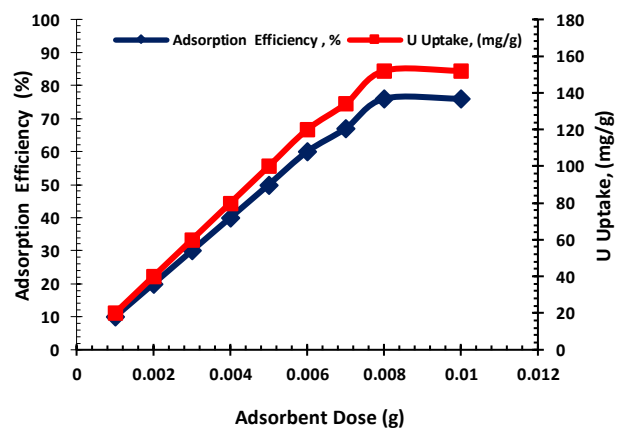

Fig. 7: Phase ratio (S/L) effect on U adsorption efficiency and U uptake (U initial Conc. 2000 mg/L, volume = 10 mL, pH=3.5, 90 min, 25 ^{0}C).
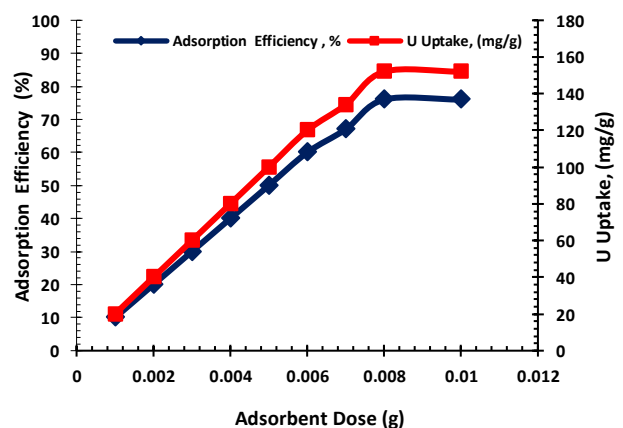

Fig. 8: Effect of temperature on U adsorption efficiency onto TACH (TACH weight = 0.1 g, volume = 10 mL, pH = 3.5, U conc. = 2000 mg/L, time 90 min.)
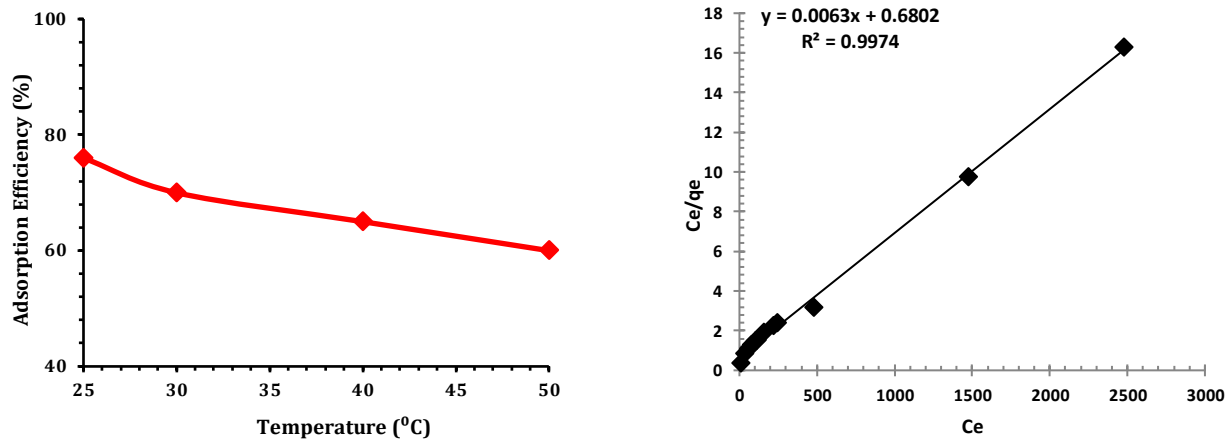
Fig. 9: Langmuir isotherm plot for adsorption of uranium onto TACH.

Langmuir model is given by the subsequent equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \qquad (4)$$

Where K_L is the adsorption equilibrium constant (L/mg), q_{max} is the adsorption capacity (mg/g) of saturated monolayer while q_e and C_e are the U uptake capacity (mg/g) of adsorbent and the residual U concentration (mg/L) at equilibrium respectively. The linearized plot of C_e/q_e versus C_e provides q_{max} and K_L as revealed in Fig. 9. The Langmuir factors are described in Table 2. Langmuir model is thus suitable for the description of the adsorption equilibrium of U onto the adsorbent.

The vital Langmuir isotherm characteristics can be stated in terms of a dimensionless constant separation factor, R_L, which is used to expect if an adsorption system is favorable or not. The separation factor, R_L, is given by Eq. (5):

$$R_L = \frac{1}{1 + K_L C_o} \qquad (5)$$

Where C_0 is the initial U concentration (mg/L) and, K_L is the constant of Langmuir adsorption (L/mg). Calculations show that R_L value for U concentration of 500 mg U/L is 0.17 which was in the range of 0.0 to 1.0, and indicates that the adsorption of U on TACH material is appropriate.

B- Freundlich Isotherm

The Freundlich model identified that the ratio of solute adsorbed to the solute concentration is a function of the solution. The experimental model was revealed to be consistent with the exponential distribution of active centers, characteristic of heterogeneous surface [37]. The amount of solute adsorbed at equilibrium, qe, is associated with the concentration of solute in the solution, Ce, by the following

$$q_e = K_F C_e^{1/n} \qquad (6)$$

This expression can be linearized to give:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (7)$$

Where K_F and n are the constants of Freundlich isotherm, which characterize sorption capacity and sorption intensity. A plot of $(\log q_e)$ versus $(\log C_e)$ would result in a straight line with a slope of $(1/n)$ and intercept of $(\log K_F)$ as given in Fig. 10. Freundlich constant is assumed in Table 2.

By comparing the isotherms applied with the experimental data, Langmuir gave fit well, while Freundlich isotherms did not fit well.

Adsorption kinetics and mechanism

The obtained results from batch experiments which were accomplished at various temperatures (25–65 ^{0}C) were estimated by using the simple Lagergren Eq.(8) [35]. To define the rate of the sportive interactions assuming pseudo first order kinetics. Thus, the Lagergren model is assumed by the Relation (8):

$$\text{Log}(q_e - q_t) = \text{Log} q_e - \left(\frac{K_1}{2.303}\right) t \qquad (8)$$

Table 2: Langmuir and Freundlich parameters for U adsorption onto TACH.

Langmuir model parameters			Freundlich model parameters		
q_{max}, (mg/g)	K_L,	R^2	K_f (mg/g)	n	R^2
155	0.0092	0.997	12.33	3.45	0.919

Fig. 10: Freundlich isotherm plot for U adsorption onto TACH.

Fig. 11: Lagergren plot for U adsorption (TACH weight = 0.1 g, volume = 10 mL, pH 3.0, U Conc. = 2000 mg/L)

Where qt and qe are the quantities of U adsorbed (mg/g) at the time, t (min) and equilibrium time (90 min), one-to-one, and $K1$ is the pseudo-first-order Lagergren adsorption rate constant (min $^{-1}$). The K_1 value can be revealed by plotting log (qe – qt) versus t for adsorption of U at various temperatures as shown in Fig. 10. The value of the first-order rate constant (K_1) and correlation coefficient (R^2) found from these plots are described in Table 3. The value of K_1 shows that the rate of the adsorption process decreases with temperature. The pseudo-first-order plots in link with the experimental qe values are described in Table 3. The experimental qe values differed from the parallel theoretical values. Thus, the interaction of uranium with the TACH amounts does not follow the first-order kinetics see Fig. 11.

To cover the description of the kinetics, second-order kinetic equation was applied by the linear equation (9) [39]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{9}$$

Where K_2 is the rate constant of second-order (g/mg.min). The kinetic plot of t/qt versus t for U is shown in Fig. 12. The plot show straight lines with good linearity temperatures. In the case of the pseudo-second-order
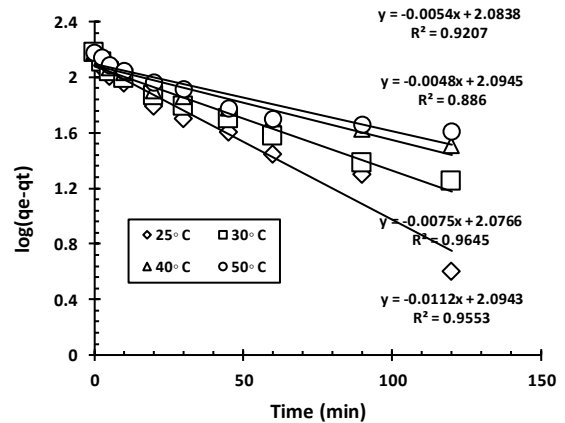
kinetic model, the correlation coefficient is closer to unity. The estimated equilibrium adsorption capacity (qe) is matched with the experimental results. The K_2 value shows the applicability of the equation for the adsorbent. The values of the second-order rate constant (K_2) and correlation coefficient (R^2) gained from these plots are stated in Table 3. Hence, the sorption reaction is following pseudo-second-order sorption other favorable as the predominant technique.

Adsorption Thermodynamics

Thermodynamic data of U adsorption process on TACH adsorbent was considered with Van's Hoff equation (10):

$$Ln\,K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

K_d (mL/g), ΔH (kJ/mol), ΔS (kJ/mol K), T (Kelvin) and R (J/K mol) are the distribution coefficient, the enthalpy, the entropy, the temperature in Kelvin and the molar gas constant respectively. LnK_d versus 1/T for U adsorption was shown in Fig. 13. The enthalpy and the entropy values were calculated from the slope and intercept of the latter plot, while the Gibbs free energy (ΔG (KJ/mol)) was calculated from the subsequent Equation (11):

Table 3: Kinetic parameters data for U adsorption onto TACH.

Temp. (°C)	Lagergren pseudo first-order				Pseudo second-order			
	K_1 (min^{-1})	q_{ecal} (mg/g)	q_{eexp} (mg/g)	R^2	K_2 (min^{-1})	qe_{cal} (mg/g)	qe_{exp} (mg/g)	R^2
25	0.021	124.2	152	0.955	0.00018	158.8	152	0.990
30	0.019	119.2	140	0.964	0.00016	148.5	140	0.990
40	0.014	124.3	130	0.886	0.00016	138.1	130	0.985
50	0.013	121.2	120	0.920	0.00014	129.9	120	0.985

Table 4: Thermodynamics data for the uranium adsorption on adsorbent.

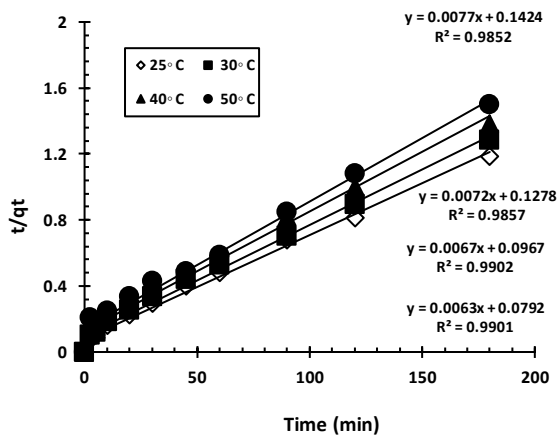| ΔH (KJ/mol)	ΔS (KJ/mol K)	ΔG (KJ/mol)			
		298 K	303 K	313 K	323 K
-22.59	-0.086	-3.03	-3.46	-4.32	-5.18

Fig. 12: Pseudo second-order plots for U adsorption (TACH weight = 0.1 g, volume = 10 mL, pH 3.0, U Conc. = 2000 mg/L).

Fig. 13: relation between Ln K_d and 1000/T for U adsorption onto TACH.

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

The evaluated values of the thermodynamic limitations for U adsorption were revealed in Table 4. The negative value of ΔH and ΔS confirmed that uranium adsorption is an exothermic behavior with lower randomness at the solid-liquid interface during the adsorption process. Additionally, the negative values of Gibbs free energy of activation ΔG showed that the adsorption reaction takes place spontaneously at the various reaction temperatures.

Elution experiments

Various eluents (HCl, H_2SO_4, HNO_3, NaOH, Na_2CO_3, NaCl, Na_2SO_4 and CH_3COONa) have been used to investigate the regeneration and reusability efficiency of the fabricated TACH adsorbent [40]. Desorption performance was measured as shown in Fig. 14. Loaded TACH was observed to desorb U to the greatest extent with HCl, while desorbing to a large extent was observed with H_2SO_4, HNO_3, NaOH, Na_2CO_3, and NaCl, Na_2SO_4.. TACH desorbing was the least with CH_3COONa. It was obvious that 1.0 M HCl was a good eluent to desorb U from the loaded TACH and recover 92.3% for 60 min contacting time.

CONCLUSION

Tannic acid-chitosan adsorbent (TACH) was fabricated by mixing tannic acid with chitosan via solution mixing technique as a facile and economic method. The adsorption efficiency of uranium (U) achieved 155 mg/g
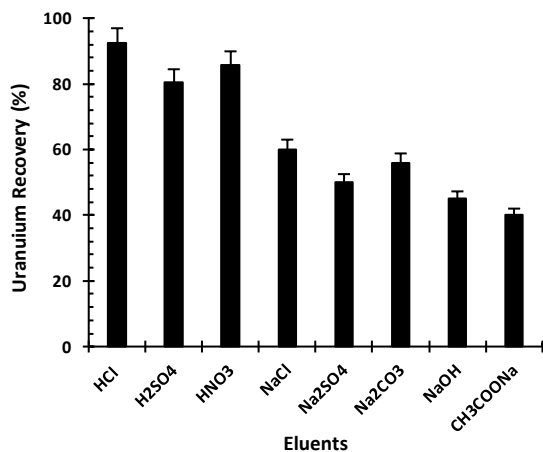
Fig. 14: Desorption performance in various eluents.

which accords with Langmuir isotherm (150 mg/g). Capacity was accomplished at pH 3 for 90 min contact time and with TACH to Liquor ratio of 0.1/10 at ambient temperature. According to Lagergren equations, the sorption reactions are more likely to be pseudo-second-order; this is due to predominate mechanism and the values of K2 "second-order rate constant" indicate that the rate of the process decreases with increasing temperature. Langmuir isotherm model is found to be more favorable for the adsorption equilibrium of U onto TACH. The distinguished dimensionless constant separation factor "RL" value is small which indicates that the adsorption of U on TACH is perfected. From the thermodynamic data, -ΔH displays that uranium adsorption is exothermic, and -ΔS factor recommends decreasing the system randomness at the solid-liquid interface during the adsorption process. The -ΔG value means that the reaction is spontaneous and proper at room temperature.

Acknowledgment

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