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Adsorption of U(VI) from aqueous solution onto Modified Chitosan

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Abstract : The chitosan grafted with citric acid via crosslinking with glutraldehyde (C-Gch) has been studied for removal of U(VI) from aqueous solution by batch method. The results showed that after grafting, its adsorption capacity for U(VI) was significantly enhanced. The effects on the adsorption including the contact time, the solution pH were investigated. The time dependent experimental data well fitted the pseudo- second-order model and the adsorption rate was controlled by intraparticle and boundary layer diffusion mechanisms. Langmuir Freundlich and Redlich-Peterson models were found to be the appropriate model for describing the adsorption equilibrium. From the results obtained, it could be concluded that, C-Gch is a potential adsorbent for removal of uranium from contaminated water sources.

Keyword: Modified chitosan, Uranium, Adsorption, Kinetic models, Isothermal models.

I. Introduction

In recent years, much attention has been focused on the pollution of the water sources by uranium. Because of a radioactive and toxic element, long-term internal exposure to uranium can cause adverse effects to human health. The major health concern is kidney damage and bone cancer as a result of the ionizing radiation associated with its radioactive decay products [1-6].

Concentration of uranium in drinking water under the guidance of USEPA[7] is 30µg/l. However, some the natural water sources which even directly utilizing for running water had recorded levels of uranium with most values exceeding the USEPA limit. This is a very urgent problem requiring a appropriate technology solution for removal of this metal to protect human health.

Adsorption process has been widely used to remove heavy metals including uranium from contaminated water environment [8-11]. In general, adsorption is a very effective process in contaminated water treatment, especially, when the pollutants are at low concentration. The most important component in a adsorption process is the adsorbent that is crucial to the efficiency of the process as well as treatment cost[10,12]. Recently, natural products have been studied as novel and alternative absorbent materials for removal of heavy metals from contaminated water. The results obtained have been proved that certain materials from natural products have great potential as adsorbents for the adsorption process [9,13,14]. Chitosan which is derived from chitin, a polysaccharide foundation in the exoskeletons of shellfish like shrimps and crabs has been identified as a potential absorbent material. The presence of large number of functional groups such as amino group (NH_2) and hydroxyl group (OH) that acts as active sites on the surface of chitosan allow to have a high adsorption capacity for metal ions [15,16].

Several studies have reported that the applicability of chitosan could be improved by crosslinking with a chemical agent such as epichlorohydrin (EPI) or glutaraldehyde[17,18]. In the most cases, crosslinked chitosans were found to be stable in an acidic environment. However, the absorption capacities of those crosslinked chitosans were reduced, primarily because the active functional groups on chitosan surface became inaccessible in the cross linked polymer network.

The possible solution for this problem is to grafted on the crosslinked chitosan with new active functional groups, which can be tailored so that the grafted materials become compatible with the optimal pH range for metal sorption, as well as the interactions between those functional groups are controllable. These two effects have been shown to to increase sorption selectivity for target metal. For example, when chitosan was grafted with sulfur containing functional groups by using glutaraldehyde or epichlorhydrin as crosslinking agents, its adsorption efficiency of mercury and noble metals was enhance[17,19]. Other grafting agents have been reported are low ionic carboxylic acids such as citric acid and its salts, especially for chitosan materials used in pharmaceutical application [20,21]. The functional groups on citric acid, when grafted on chitosan, could potentially become active site for heavy metal ions absorption. However, up to date, the use of chitosan grafted with citric acid for the uranium adsorption is not interested.

In this study, we explore this potential by investigating the absorption properties of crosslinked chitosan grafted with citric acid using glutaraldehyde as crosslinking reagent. The grafting process was conducted by pre-reaction of chitosan with glutaradehyde then followed by reaction with citric acid. The resulting adsorbent was used to study it adsorption ability for U(VI) ions, The results report here including effects of parameters such as pH, contact time on the adsorption of U(VI). Characteristics of U(VI) adsorption process by the modified chitosan are also described using the adsorption kinetic and isotherm models.

2. Materials and method

2.1. Chemicals

Commercial chitosan, 80 % deacetylation from the Center of Irradiation Technology, VINAGAMMA, Ho Chi Minh City, Vietnam was used to prepare as starting material. All chemicals used in this work were analytical grade. The standard uranium solution (1.0 mg·mL^{-1}) was prepared by dissolving 0.10 g of uranium metal (99.99%) in 15 mL of conc. HNO_3 then evaporated to dryness on a heating water bath. The residue was dissolved in 10 mL of 0.1M HNO_3 and transferred to a 100 mL volumetric flask, distilled water was added to the mark. The arsenazo III solution (0.07 %) was prepared by dissolving 0.07 g of arsenazo III (Merck Co.) in 100 mL of 0.05M HCl solution and kept in a polyethylene vessel.

2.2. Preparation of adsorbent

About 5 g of Chitosan (ch) were dissolved in 2 % (w/v) acetic acid and reprecipitated by adding dropwise of 2 N NaOH solution into the solution until pH of the solution reached to 6 -7. The chitosan precipitate was washed with distilled water, dried in air, then further dried under vacuum at 60 °C. The dried chitosan was ground in an agate mortar to fine powder. Crosslinking reactions were carried out by adding 0.5 molar ratios of glutaraldehyde for 24 h under pH value of 3-5. The crosslinked chitosan (Gch) was washed several time with distilled water the dried at room temperature. Acid citric grafting process was conducted by immersing the Gch in aqueous 5.0 % (w/v) citric acid solution at pH 5, temperature of 4 °C for 24 hrs. The acid citric grafted chitosan (C-Gch) was repeatedly washed with deionizer water, thoroughly dried in air and under vacuum at 60 °C. The FT-IR spectra of ch, C-Gch and Gch samples were recorded by FT-IR -8400S-SHIMADU.

2.3. Uranium analysis

The concentration of U(VI) in the liquid phase was determined by using a spectrophotometric method [22]. A specific volume of the solution containing U(VI) was added to a 50 mL volumetric flask. One mL of 0.07 % arsenazo III and 10 mL of 3 M $HClO_4$ were added, the mixture was shaken for two min. 3 M $HClO_4$ solution was then added to the measuring volume. The mixture was shaken for additional three min. The absorbance at 650 nm of the final solution was measured using a Libra S32 Perking Elmer spectrophotometer. Uranium concentration in the test solution was determined from a calibration curve, which was constructed using a uranium standard solution.

2.4. Adsorption procedure

The contact time required for the adsorption process to reach adsorption equilibrium was determined by batch experiments. 0.1 g of the adsorbent was added to 50 mL of solution containing 100 mg/L of U(VI). The pH of the solution was adjusted to 4.5 by adding appropriate volume of diluted HNO_3 or NaOH solutions. The flask containing the mixture were shaken at 200 rpm by mechanical shaker for 400 min at room temperature (30 ± 1 °C). 0.5 mL of the sample were taken from the adsorption solutions at predefined time intervals to analyze the U(VI) concentration in the liquid phase. The effect pH on the adsorption process was evaluated by experiments at different pH values, ranging from 1 to 6. For equilibrium study, 50 mg of C-Gch were added in to stopper flacks containing 100 ml of U(VI) solution with concentration ranging from 30 to 300 mg/l. pH of the solution was adjusted to 4.5. The solutions were shaken at 30 ± 1^0 for 400 min.

The adsorption capacity, q_e, defined as amount of adsorbate per unit mass of adsorbent (mg/g) is calculated by formula:

$$q_e = \frac{C_i - C_e}{C_i} \times \frac{V}{m} \qquad (1)$$

where, V is volume of adsorbate (dm^3), m is the mass of adsorbent (g), C_i is initial concentration of U(VI) in mg/L and C_e is concentration of U(VI) at equilibrium (mg/L).

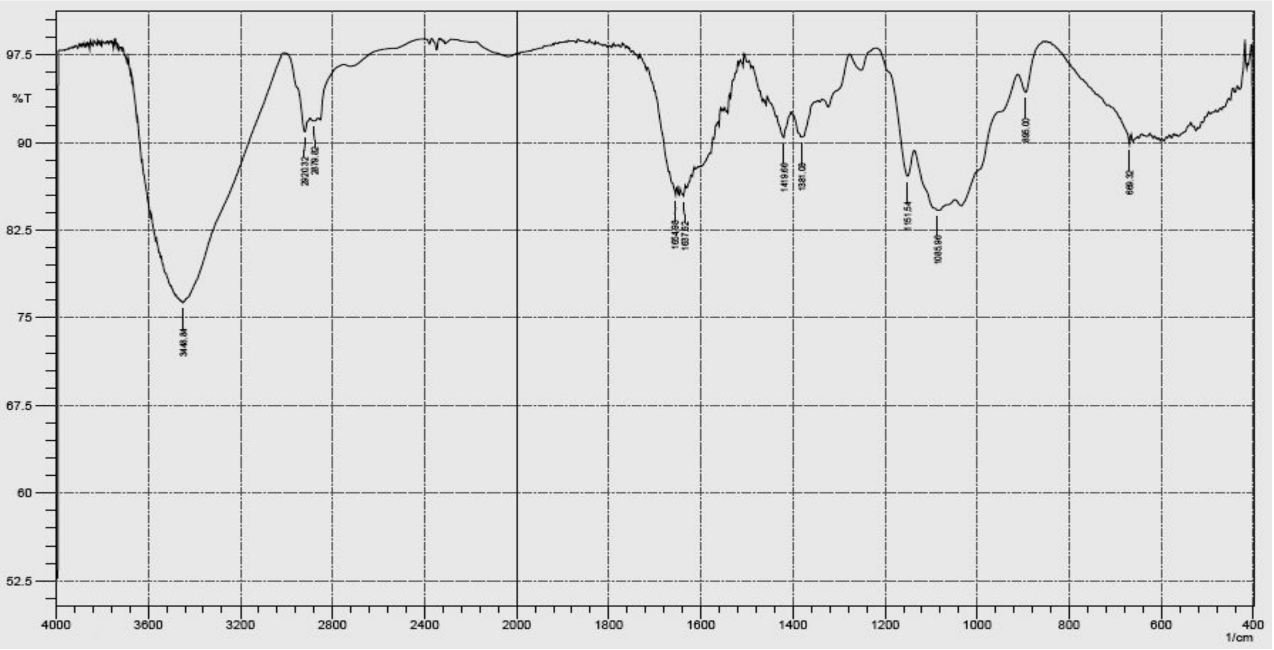
3. Results and discussion

3.1. FT-IR spectra

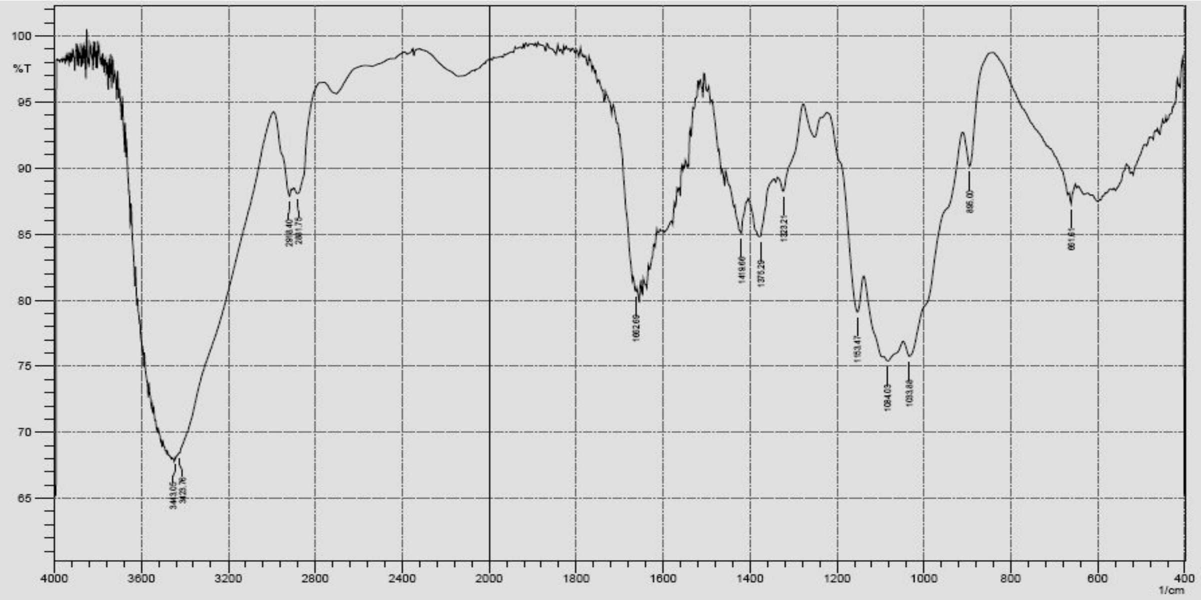
The FTIR spectra of chitosan (Ch), crosslinked chitosan with glutraldehyde (Gch) and crosslinked chitosan grafted with citric acid (C-Gch) are shown in Fig. 1. In FTIR spectra of chitosan (Fig. 1a), the absorbance band around 1634 cm^{-1} stretching frequency (amide) characterize the presence of acetylated units. The FTIR spectra of Gch (Fig. 1b) shows the more adsorption band in the region from 1600 – 1700 cm^{-1} for the crosslinked chitosan which is a characteristic of C=O groups from aldehyde, providing evidence for the presence of glutaradehyde in crosslinked chitosan[20]. The appearance of absorbance peak at 1717 cm^{-1} and the increasing in intensity of absorbance peak at 1388 cm^{-1} (Fig.1c) indicate that citric acid was grafted into chitosan network [21].

Figure 1: FTIR spectra of a) chitosan (ch), b) crosslinked chitosan with glutraldehyde (Gch) and c) crosslinked chitosan grafted with citric acid (C-Gch)

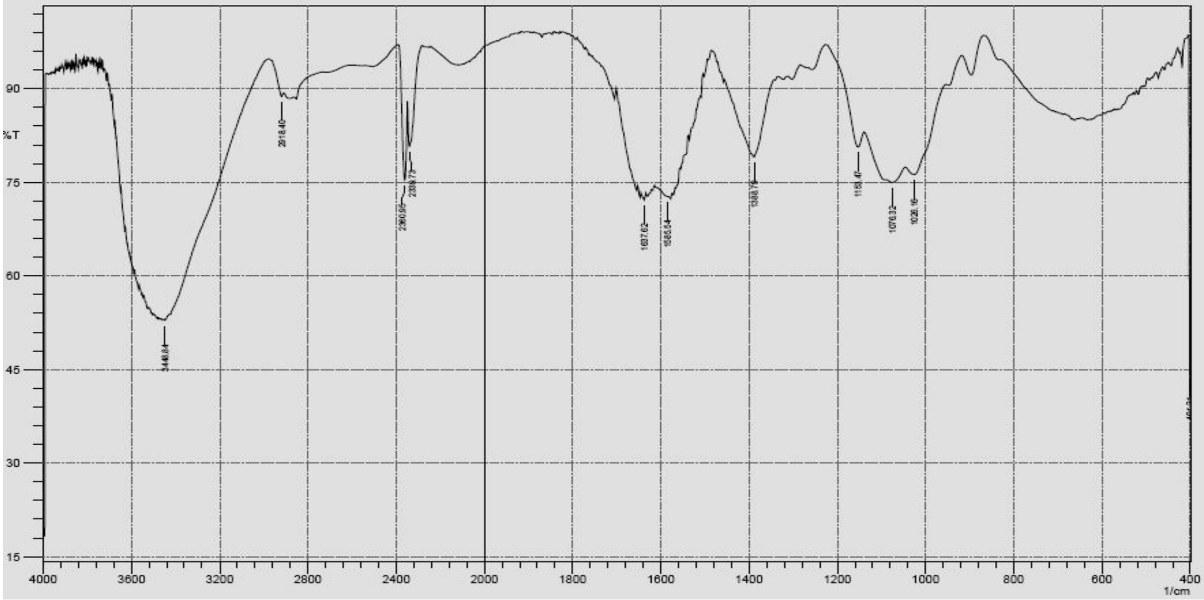
a)



b)



c)



3.2. Effect of pH

The pH of the solution in the adosprtion process is one of the important parameters to be considered because it controls the charge of the adsorbent surface as well as the the sorbate species in the adsorption solution. The effect of pH on the U(VI) adsorption by C-Gch material is shown in Fig. 2. For U(VI), the presence of different hydrolyzed species at different pH values will affect the adsorption efficiency. In the range of pH from acidic to neutral (≤7) of the solution, U(VI) ions mainly exist in the hydrolyzed forms such as UO_2^{2+}, $(UO_2)(OH)_2^{2+}$, $UO_2(OH)^+$ and $(UO_2)_3(OH)_5^+$ [30]. Thus, the negative charge sites on the adsorbent surface are important in the adsorption process of U(VI). As results shown in Fig. 2, the adsorption capacity for U(VI) by C-Gch increases and reaches maximum value at pH 3.5 – 4, then gradually decreases when pH is greater than 4.5. The low adsorption capacity at pH less than 3 is probably because hydrolyzed ions of U(VI) have to compete with H^+ ions, which protonation of negative charge sites on the adsorbent surface. At pH from 3 to 4.5, the the lower concentration of H^+ ions reduces this type of competition, leading the increasing in the adsorption capacity. Further, the presence of carboxylic functional groups in C-Gch leads to the increasing in the number of adsorption sites on the adsorbent surface. Memon et al.[23] reported that, at pH from 3 to 4.5, the carboxylic group is mostly at deprotonated states (i.e, negatively charged), which increase the availability of binding sites for positively charged of U(VI) ions. At pH greater than 5, U(VI) begins partly forming multiple anionic complexes with the available OH^- and CO_3^{2-} species (formed by dissolution of CO_2 from air) such as $(UO_2)CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, leading to the slightly reducing in the adsorption capacity of U(VI).

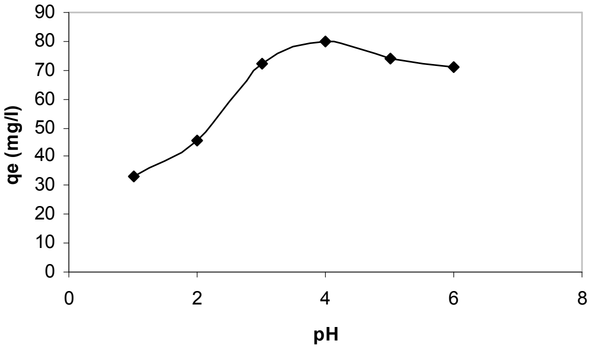


Fig.2: Effect of pH on U(VI) adsorption

3.2. Effect of contact time

The results of the adsorption capacity of Cr(VI) at pH 4.5 with increasing contact time are presented in Fig 3. It was observed that the adsorption rate rapidly occurred in the first 110 - 150 min and thereafter the adsorption rate was found to be slow and reached equilibrium at 400 min. The initial faster rate observed for concentrations of U(VI) can be explained by the presence of the available uncovered surface areas of the adsorbent. According to Memon et al.[23], the active site on the adsorbent surface are gradually filled and the adsorption process becomes more difficult. Hence, the adsorption capacity almost did not increase and it is represented as a flat line in the plot . Such a variation of the adsorption rate is also observed in the most case of bio-sorption studies for metal ions[23,24] . The obtained results suggested that 400 min of contact time are sufficient to achieve equilibrium condition and would be applied for subsequence experiments.

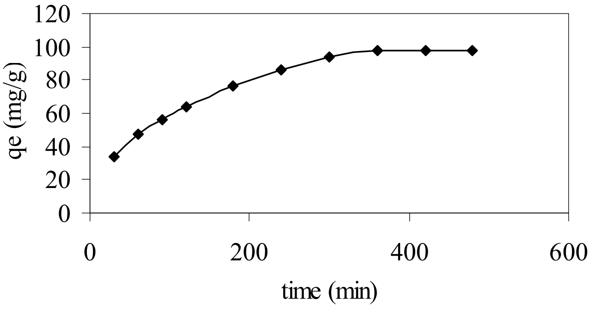


Fig.3: Effect of contact time on U(VI) adsorption

3.3. Kinetic models

Adsorption kinetic investigation is to find out the stage which plays a decisive role to the adsorption reaction rate. Therefore, the use of kinetic models to fit the time dependent experimental data is one of important steps for the adsorption study. In this research, kinetic models used for fitting experimental data are pseudo-first-order, pseudo-second order and intraparticle diffusing model[25-27].

Pseudo-first order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (2)$$

where, k_1 is the pseudo-first-order constant (min^{-1}), q_t is amount adsorbed at time t (mg/g), and q_e is the amount adsorbed at equilibrium (mg/g).

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (3)$$

where, q_e k_2 is the pseudo-second-order constant (g/mg.min).

The plots of $\log(q_e\text{-}q_t)$ from Eq.(2) and t/q_t from Eq.(3) against t give a linear relationship, which allow to calculate k_1, k_2, and predict q_e. The linear plots for the pseudo-first -odder and the pseudo-second-order models at different initial concentration of U(VI) are presented in Figs.4 and 5, respectively. It can be seen in the Fig. 4 that, the plots for the pseudo-first-order model were not good linearity and with large discrepancy. The correlation coefficients values, R^2, of the pseudo-first-order model were found to be 0.743, 0.865 and 0.957 at initial concentrations of 80, 100 and 140 mg/l, respectively. These values are very pure comparing with those obtained from the pseudo-second-oder model.Therefore, the results of parameters of pseudo-first-order model were rejected and are not included here. The parameter values of the pseudo-second-order model are shown in Table 1. The correlation coefficient values,R^2, were found to be near unity for all concentrations ranging from 80 to 140 mg/L, indicating that the experimental data are good fitted with the pseudo–second-order model. From the results in table 1, it can be seen that the larger concentration of U(VI) the higher is obtained value of q_e. These results are very significant in the adsorption of polluted water containing high concentrations of U(VI) by using the C-gch.

Table 1 Parameters of pseudo-second-order model for the adsorption of U(VI)

Concentration (mg/L)	Equation	K (g/mg.min)	R^2	q_e (mg/g)	$q_{e\text{-}exp}$ (mg/g)
10	y = 0.096x + 1.085	$8.59\ 10^{-3}$	0.999	10.35	9.94
30	y = 0.036x + 1.107	$1.18.10^{-3}$	0.995	27.70	25.79
60	y =0.014x +1.303	$1.46.10^{-4}$	0.995	72.46	68.87

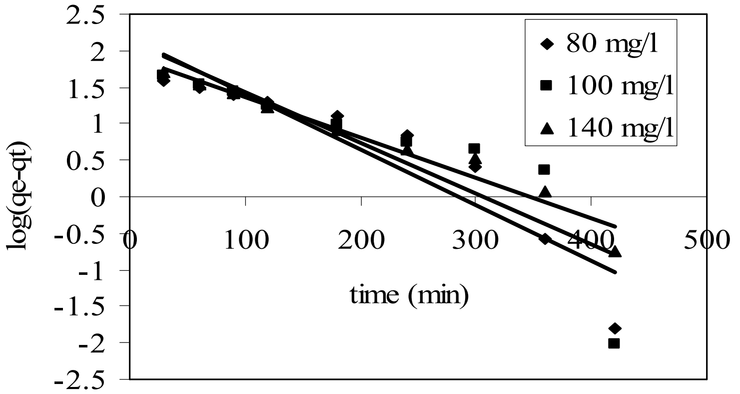


Fig. 4: Plots of pseudo-first-order equation for U(VI) adsorption

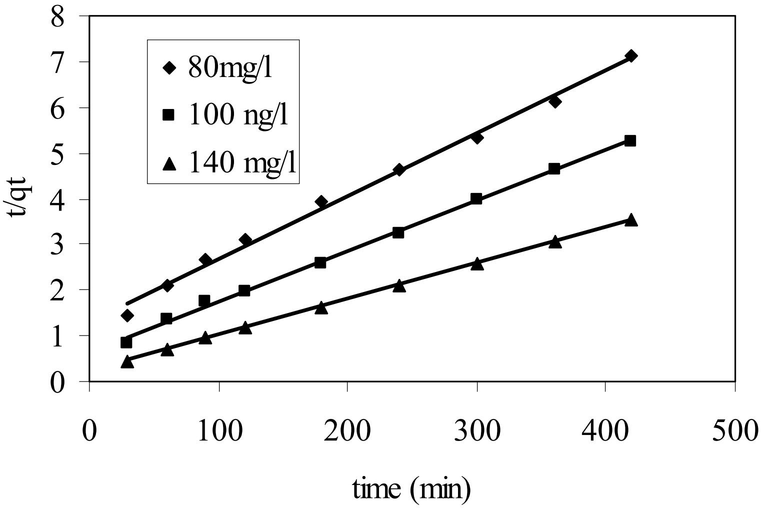


Figure 5. Plots of pseudo-second-order equation for U(VI) adsorption

Intraparticle diffusion model:

The adsorption process of solute onto the solid surface is a process of mass transfer characterized by either external mass transfer or intraparticle diffusion or both. Thus, the adsorption rate will be determined by one or both process. However, for experiments carrying out by the batch method with a good mixing condition, the rate of the external mass transfer usually is negligible. Therefore, the adsorption rate is determined primarily by intraparticle diffusion. The relation between the amount of adsorbate on the adsorbent surface varies proportionally with a function of retention time is given by Weber and Morris [26]:

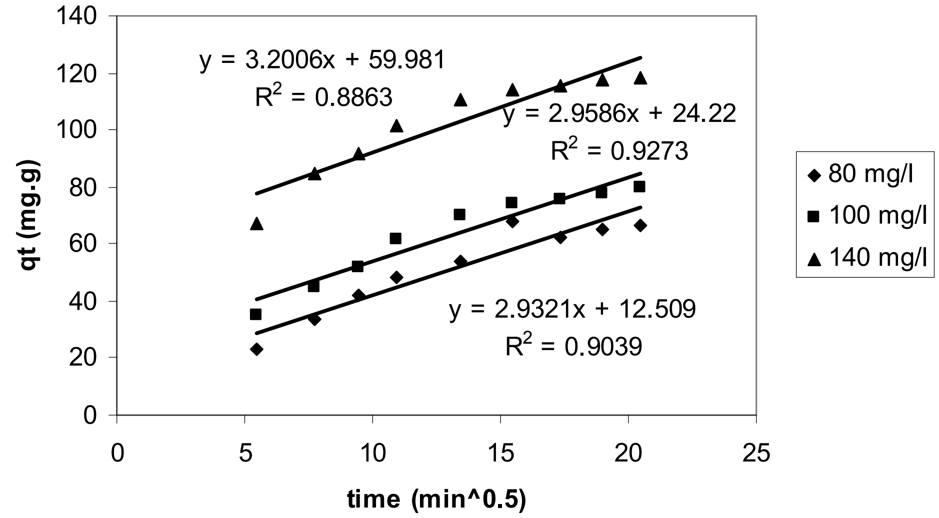


Fig. 6: Plots of intraparticle diffusing for U(VI) adsorption

$q_t = kt^{1/2}$ (4)

where, k is the rate constant of intraparticle diffusion (mg/g.min).

The plot of q_t against $t^{1/2}$ in the Eq.(6) is presented in Fig 5 that will yield a straight line and should pass through the origin. The diffusion constant, *k*, is calculated by the slope of the plot. It was found that the *k* values obtained from the plots are 3.206, 2.96 and 2.93 mg/g.min for U(VI) concentration of 80, 100 and 140 mg/l, respectively. However, the intercept of the plots in the Fig.5 did not pass through the origin. It indicates that besides the intraparticle diffusion, the adsorption rate of U(VI) by C-Gch was contributed by the mass transport mechanic of U(VI) ions from the solution through liquid film to the adsorbent exterior surface [27].

3.4. Adsorption isotherm

The adsorption isotherm is the most important information, which indicates how the adsorbent molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state (Abdel-Ghani et. 2007; Jeon and Holi et al. 2003). It is also helpful in model prediction for analysis and design of an adsorption process. In this study, three widely adsorption isotherm models were used to describe the adsorption process including Langmuir model, Freundlich model and Redlich-Peterson[27-29].

The Langmuir model:

$$q_e = \frac{K_L q_{\max} C_e}{1 + q_{\max} C_e} \quad (5)$$

where: q_e is the amount of U(VI) adsorbed per gram of dry adsorbent at equilibrium (mg/g),C_e is the equilibrium concentration of U(VI) in solution (mg/L), K_L is the Langmuir constant (L/g), and q_{max} is the maximum U(VI) to adsorb per gram of dry adsorbent (mg/g).

the Freundlich model:

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

where, q_{eq} is the amount of U(VI) adsorbed per gram of dry adsorbent (mg/g), n and K_F is the Freundlich constants. K_F is a measurement of the adsorption capacity, n is a measure of the adsorption intencity.

The Redlich-Peterson model:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \quad (7)$$

where, K_R and a_R are the Redlich-Peterson isotherm constant and β is the Redlich-Peterson isotherm exponent which lies between 0 and 1.

The correlation coefficient, R^2 was used to test the best-fitting isotherm to the experimental data [28]:

$$R^2 = \frac{\sum (q_m - \bar{q}_e)^2}{\sum (q_m - \bar{q}_e)^2 + \sum (q_m - q_e)^2} \quad (8)$$

where, q_m is the equilibrium capacity from the isotherm model, q_e has the same definition as described in equation 5. $\bar{q}_e$ is the average of q_e

The isotherm equation parameters in Eqs 6, 7 and 8 were determined by the method of Ho [28]. The solver add-in of Microsoft Excel was used for optimization to maximize the coefficient of determination between the experimental data and isotherms.

The parameters of Langmuir, Freundlich and models obtained are given in Table 2. The plots of isoterms obtained from the non-linear models are presented in Fig. 7. By comparing the values of correlation coefficient, R^2, it was found that Langmuir, Freundlich and Redlich-Peterson are well fitted the experimental data . However, the best fit was achieved by the Langmuir model.

The maximum adsorption capacity for U(VI) was found to be 191 mg /g. This value was also much higher comparing with those obtained using the crosslinked chitosan with glutaraldehyde (Gch) for U(VI) adsorption. By our experiments, the maximum adsorption capacity for U(VI) by Gch was determined to be only 22.3 mg U(VI) per gram Gch. It was obvious that the carboxyl groups of citric acid grafted on crosslinked chitosan significantly enhaned the the adsorption capacity for f U(VI).

Table 2 Parameters of isotherms for U(VI) adsorption

Langmuir model			Freundlich model			Redlich-Peterson			
K_L (L/mg)	q_{max} (mg/g)	R^2	K_F (mg/g)(mg/l)^n	1/n	R^2	K_R (L/mg)	a_R (L/g)	β	R^2
0.075	191	0.989	49.16	0.243	0.945	69.5	1.75	0.770	0.950

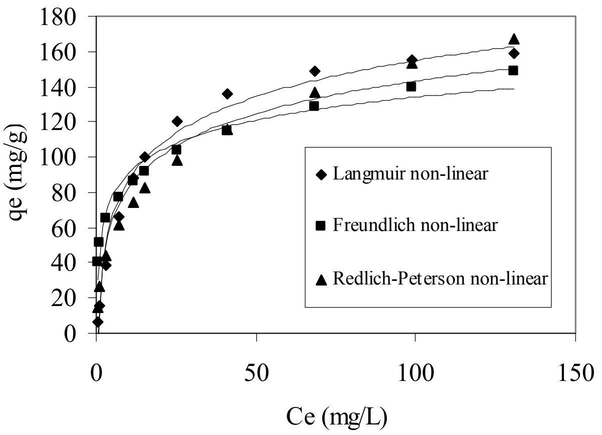


Fig. 7: Adsorption isotherms of Cr(VI) on C-Gch at 30 ± 1^{0}C

3.5. Uranium recovery and reusable of adsorbent

To avoid the decomposition of the adsorbent and release uranium back into the environment duration storing the exhausted adsorbent, it is necessary to recover uranium from the exhausted adsorbent. The experiment was conducted in each 20 ml $NaHCO_3$ solution with concentrations of 0.1, 0.3 and 0.5 M. 1.0 g of the exhausted adsorbent were added into each solutions. The mixtures were shaken for 10 min. After shaking, a volume aliquot of the adsorption solution were drown and the liquid phase was separated from solid phase by centrifugation. Determination of U(VI) concentration in the liquid phase by method mentioned above. The recovery yield (%) was determined by the formula:

$$E(\%) = \frac{C_R}{C_{Ex}} \times 100 \quad (9)$$

where, E is recovery efficiency (%), C_R is amount of U(VI) from solid phase entering into the solution (mg/g), C_{Ex} is initial amount of U(VI) in the solid phase, i.e. in the exhausted C-Gch (mg/g).

Recovery efficiencies of uranium with different concentrations of $NaHCO_3$ are given in Table 3. From the results obtained, the solution of $NaHCO_3$ 0.1 M was selected as an elution for recovery of uranium.

Three the adsorption/de-adsorption cycles were carried out to evaluate the reusable adsorbent. In each cycle, U(VI) was removed from the exhausted adsorbent, using the solution of $NaHCO_3$ 0.1 M then the adsorbent was washed several times with distilled water to pH 6-7. The resulting adsorbent was pre-equilibrated with the solution of pH 4.5. the adsorption process for U(VI) was repeated. Results showed that after three cycles, the adsorption efficiency of C-Gch was found to be not significantly change (Table 4). This indicates that C-Gch can be multiple used for removal of U(VI) from aqueous solution.

Table 3: Recovery efficiency of U(VI) from the exhausted C-Gch using different concentration of $NaHCO_3$ solution as an elution

Reagent	Concentration (M)	Recovery (%)
$NaHCO_3$	0.1	99.78
$NaHCO_3$	0.3	99.78
$NaHCO_3$	0.5	99.77

Table 4: Effect of C-Gch desorption/ sorption recycles on U(VI) adsorption efficiency

Cycle number	Adsorption efficiency (%)
1	99.85
2	99.73
3	99.67

IV. Conclusions

Research results on adsorption U (VI) by C-Gch showed that grafting citric acid on crosslinked chitosan with glutradehyde improved in the adsorption capacity. The equilibrium adsorption reached at 400 min of the contact time and maximum adsorption capacity was obtained at pH 4.5. Adsorption kinetic study of U(VI) on C-Gch showed that experimental data well fitted the pseudo-second-order and the adsorption rate was controlled by intraparticle and boundary layer diffusion mechanisms. Adsorption isotherm models were used to describe the adsorption equilibrium. It was found that the Langmuir, Freundlich and Redlich-Peterson models are appropriate to use for description of the adsorption equilibrium of U(VI) onto C-Gch.

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