

Adsorption of U(VI) from Aqueous Solution by Chitosan Grafted with Citric Acid via Crosslinking with Glutaldehyde

Nguyen Van Suc Ho Thi Yeu Ly*

Ho Chi Minh City University of Technical Education, Vietnam

Abstract

This paper reports on the studied results of the sorption ability of the grafted chitosan with citric acid via crosslinking with glutaldehyde (C-Gch). The results obtained shown that after grafting citric acid on crosslinked chitosan, the adsorption capacity for U(VI) was significantly enhanced. Effects of the adsorption process including contact time, pH, initial concentration and some of metal ions were investigated. It was found that the maximum capacity obtained was 172 mg/g after 300 min of contact time and at pH 4. In the presence of cations such as Cu (II), Zn (II), Pb (II) and Cd (II), the adsorption capacity for U(VI) was reduced. The effect of these metals on the adsorption of U(VI) by C-Gch was arranged in the order: Cu (II) > Zn (II) > Cd (II) > Pb (II). The experimental data good fitted the pseudo second order model with correction coefficients $R^2 \geq 0.995$ for all U(VI) concentrations ranging from 10 to 80 mg/L. The Langmuir model was found to be an appropriate model for describing the equilibrium adsorption process. Based on the Langmuir model, the maximum adsorption capacity was found to be 172 mg U(VI)/g adsorbent.

Keywords: Crosslinked chitosan; Grafted chitosan; Citric acid; Uranium; Adsorption; Kinetic model; Isothermal model

Introduction

Recently, the development of nuclear industry along with activities in the mining, fertilizer production, combustion of fossil fuels, the water sources in many parts of the world has been contaminated by uranium [1-3]. Because of its toxic and radioactive, uranium exposure can cause adverse effects to human health [4,5]. Therefore, the need to remove uranium from the polluted water to the permitted level is essential.

Adsorption is a process that has been widely used to remove heavy metals including uranium from contaminated water environment [6,7]. Particularly, adsorption is a very effective process when dealing with low concentrations of pollutants. One of the critical components in the adsorption process is the adsorbent that is crucial to the efficiency of the process as well as treatment cost. In generally, active carbon, zeolite, etc. are adsorbents that have been commonly used in the adsorption. However, these adsorbents are relatively expensive. Therefore, finding alternative materials with reasonable cost to use in the adsorption is an urgent task for investigators [8,9].

Recent researches have been focused on studying alternative materials including agriculture by products for expensive materials in the adsorption. The results obtained have been proved that materials from agriculture by-products are capable of adsorbing heavy metals and shows great potential as adsorbent utilizing in the adsorption [7-13].

One of the byproducts of agriculture has been identified for the adsorption material is chitosan which is a natural product derived from chitin, a polysaccharide foundation in the exoskeletons of shellfish like shrimps and crabs. Because of owning different functional groups such as amino group (NH₂), hydroxyl group (OH), the major sites for adsorption, chitosan has very large adsorption capacity for metal ions [14,15].

To increase the applicability of chitosan which has been modified by cross linking with a number of chemical agents such as epichlorohydrin (EPI), glutaraldehyde [14-17]. In the most crosslinking case, chitosan

becomes stability in an acidic environment. However, crosslinked chitosan with such agents was varied adsorption properties, its adsorption capacity can be reduced by blocking various functional groups in the polymer network.

To overcome this problem, crosslinked chitosan was grafted with new function groups which can be changed pH range for metal sorption and uptake mechanism in order to increase sorption selectivity for target metal. For example, sulfur compounds were grafted on chitosan via a cross-linking agent such as glutaraldehyde or epichlorohydrin to enhance the adsorption efficiency of mercury and noble metals [14,18].

Recently, low ionic carboxylic acid such as citric acid and its salts have been widely used to modify chitosan for pharmaceutical application [19,20]. In this study, we used citric acid, a chemical compound containing hydroxyl and carboxylic groups to graft onto chitosan by two steps consisting of pre-reaction of chitosan with glutaraldehyde followed by reaction with citric acid. The resulting adsorbent was used to adsorb uranyl ions in contaminated water environment. The results reported here including effects of parameters such as pH, contact time, adsorbent dose and co-ions. Characteristics of U(VI) adsorption process described using the adsorption kinetic and isotherm models were also include.

Materials and Method

Chemicals

Commercial chitosan, 80% deacetylation from Center of Irradiation

*Corresponding author: Nguyen Van Suc Ho Thi Yeu Ly, Ho Chi Minh City University of Technical Education, 01 Vo Van Ngan, Thu Duc dist. Ho Chi Minh City, Vietnam, Tel: 08-04-8 38968641; Fax: 08-04-838964922, E-mail: sucnv@hcmute.edu.vn

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Technology, VINAGAMMA, Ho Chi Minh City, Vietnam was used to prepare the adsorbent. All chemicals used in this work were analytical grade. The standard uranium solution ($1.0 \text{ mg}\cdot\text{mL}^{-1}$) was prepared by dissolving 0.10 g of uranium metal (99.99%) in 15 mL of conc. HNO_3 and evaporated to dryness on a water bath. The residue was dissolved with 10 mL of 0.1M HNO_3 and transferred to a 100 mL measuring flask. The solution was diluted with water to the mark and shaken well. The arsenazo III solution (0.07%) was prepared by dissolving 0.07g arsenazo III (Merck Co.) in 100 ml of 0.05M HCl solution and kept in a polyethylene vessel.

Preparation of adsorbent

Chitosan (5g) was dissolved in 2 % (w/v) acetic acid and reprecipitated by adding dropwise of 2N NaOH solution into the mixture until pH of the solution reached to 6.5 -7. The pure mass precipitate of chitosan was washed with distilled water and air-dried. The obtained chitosan was further dried under vacuum at 60°C and crushed in an agate mortar to fine powder. Crosslinking reactions were performed by adding 0.5 molar ratios of glutaraldehyde. Reactions were performed for a period of 24h under pH value of 3-5. The crosslinked chitosan was washed several time with distilled water and dried at room temperature and labeled as Gch. Citric grafted chitosan was obtained by immersing the Gch in aqueous 5.0% (w/v) citric acid solution at pH 5 and 4°C for 24 hrs. After grafting, modified chitosan was repeatedly washed with deionized water, thoroughly dried in air and under vacuum at 60°C and labeled as C-Gch. The FT-IR spectra of C-Gch and Gch samples were recorded by FT-IR -8400S-SHIMADU.

Uranium analysis

Determination of U(VI) in the liquid phase after equilibriums was based on measuring the color complex of U(VI) with arsenazo III in the medium of 10^{-3} M HClO_4 [21]. The procedure for determination of U(VI) can be briefly described as follows:

A test solution containing U(VI) was placed into a 50 mL measuring flask. 1 mL of 0.07 % arsenazo III and 10 mL of 3M HClO_4 were added. The mixture was shaken for two min and 3M HClO_4 solution was then added to the measuring volume. The mixture was shaken for three min. The absorbance of the absorbing solution was measured at 650 nm using a Libra S32 Perking Elmer spectrophotometer. Uranium content in the test solution was determined from a calibration curve, which was constructed using a uranium standard solution.

Adsorption experiment

For determination of contact time required for adsorption equilibrium, batch experimental mode was conducted. A desired amount of adsorbent were added to each 50 ml of solution containing a desired amount of U(VI). pH values of reaction solutions was adjusted to 4. The adsorption solutions were shaken at speed 200 rpm by mechanical shaker for 300 min at room temperature ($30 \pm 1^\circ\text{C}$). A series of 0.5mL were taken from the adsorption solutions at predefined time intervals for analysis of the U(VI) residual. For evaluation of pH effect, adsorption experiments were carried out as above mentioned but variation of pH of the adsorption solution and retaining the equilibrium time which was obtained from the first experiment. pH of the adsorption solutions was varied from 1 to 6 and adjusted by diluted solution of HNO_3 or NaOH. The obtained pH value at which the adsorption efficiency reached to maximum value was taken for the

next experiments. To investigate the effect of co-ions including Cu (II), Zn(II), Pb(II) and Cd(II), the experiments were conducted under optimum conditions such as pH, contact time. The amount of U(VI) was kept constants (50 mg/L) while variation of co-ion concentrations ranging from 100 to 900 mg/L. Similarly, the adsorption isothermal of U(VI) by C-Gch were studied by adding a desired amount of adsorbent into each 50 ml of solution containing U(VI) concentration in the range of 30, 50, 100, 150, 200, 250, 300 mg/l.

Concentration of U(VI) in the liquid phase of all experiment was determined by spectrophotometric method following the procedure which was mentioned above. The adsorption capacity for U(VI) in each experiment was calculated using the following equations:

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

Where q_e is adsorbent capacity, mg/g, %; C_0 is initial concentration of U(VI), mg/l; m is weigh of adsorbent, g; C_e is final concentration of U(VI) at equilibrium adsorption, mg/l; V is volume of U(VI) used for adsorption reaction, L.

Results and Discussion

FT-IR spectra of C-Gch

The FTIR spectra of chitosan (Ch), crosslinked chitosan with glutaraldehyde (Gch) and crosslinked chitosan grafted with citric acid (C-Gch) are shown in Figure 1a, 1b and 1c, respectively. From the FTIR spectra of chitosan (Figure 1a), it can be observed the band amide 1 around 1634 cm^{-1} stretching frequency, characteristic of acetylated units. The FTIR spectra of Gch (Figure 1b) shows the more adsorption band in the region from $1600\text{-}1700 \text{ cm}^{-1}$ for the crosslinked chitosan which is a characteristic of C=O groups from aldehyde proving the presence of glutaraldehyde in crosslinked chitosan [15]. The appearance of adsorption 1717 cm^{-1} peak and more intensity of adsorption peaks at 1388 cm^{-1} (Figure 1c) indicated that citric acid was grafted into chitosan network [22].

Adsorption rate and kinetic model

Figure 2 is a graph represents the relationship of the adsorption capacity and contact time of C-Gch for U(VI). As can be seen from results, it was found that the U(VI) adsorption rate at the beginning increased up 300 min of contact time. After that, the adsorption rate was slowly increased and reached plateau values. These adsorption behaviors can be explained by adsorption mechanisms which are governed by the surface adsorption on the pore wall of adsorbent for the rapid adsorption rate or by the membrane transport of U(VI) ions onto adsorbent for the slow adsorption rate [23]. Such a variation of the adsorption rate is also observed in the most case of biosorption studies for metal ions. The obtained results suggested that 300 min of contact time were sufficient to achieve equilibrium condition and would be applied for subsequent experiments.

For chemical adsorption, the kinetic model used for fitting the time-dependent experimental adsorption data is pseudo-second-order model [24]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (2)$$

The equation (2) can be integrated and the linear form of this model equation is given as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (3)$$

$$h = kq_e^2 \quad (4)$$

Where q_e is the amount of U(VI) adsorbed at equilibrium (mg/g), k is the equilibrium rate constant (g/mg.min), q_t is the amount of U(VI) adsorbed at time t (mg/g). h is the initial adsorption rate as $t \rightarrow 0$. The plot of t/q_t against t from Eq. (3) gives a linear relationship, which allows calculated of k , h and predicted q_e . The linear plots for pseudo-second-order model at different initial concentration of U(VI) are presented in Figure 3. The parameter values of pseudo-second-order model are shown in Table 1. The regression coefficients R^2 values were found to be near 1 for all concentration ranging from 10 to 80 mg/L indicating that the experimental data good fitted the pseudo-second-order model.

Effect of pH

pH is one of the important parameters for the adsorption of metal ions because pH controls the charge of the adsorbent surface as well

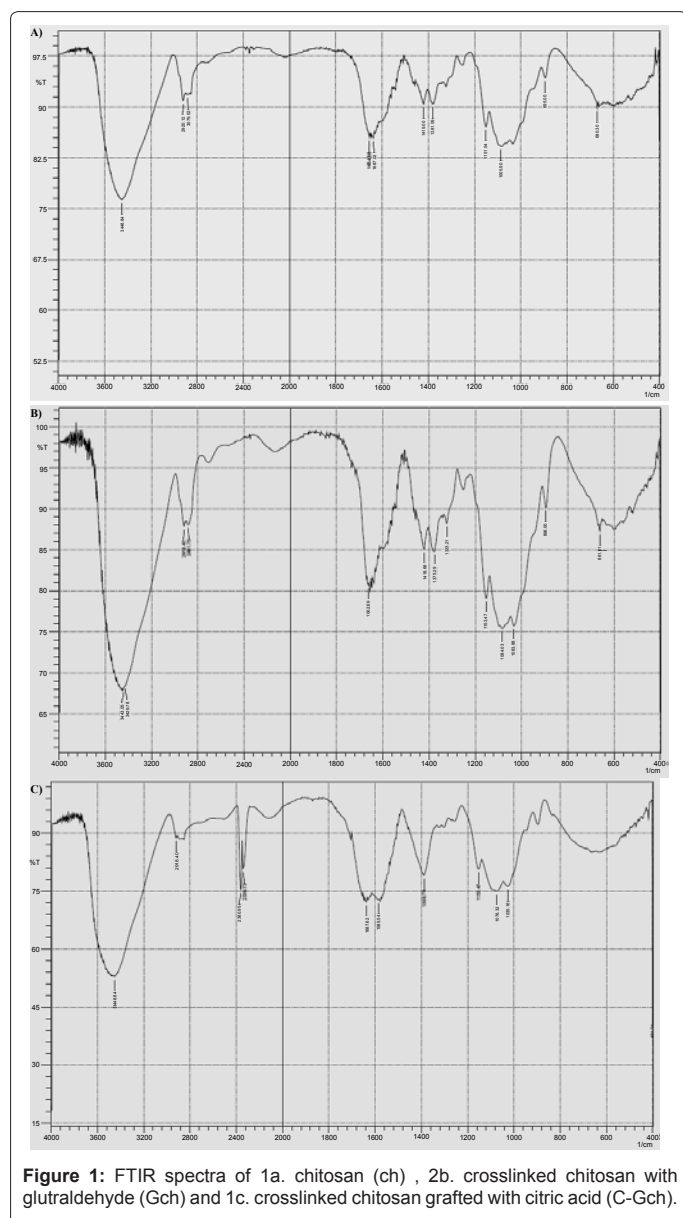


Figure 1: FTIR spectra of 1a. chitosan (ch), 1b. crosslinked chitosan with glutraldehyde (Gch) and 1c. crosslinked chitosan grafted with citric acid (C-Gch).

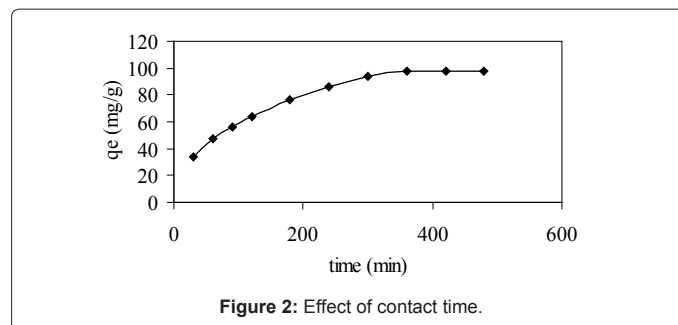


Figure 2: Effect of contact time.

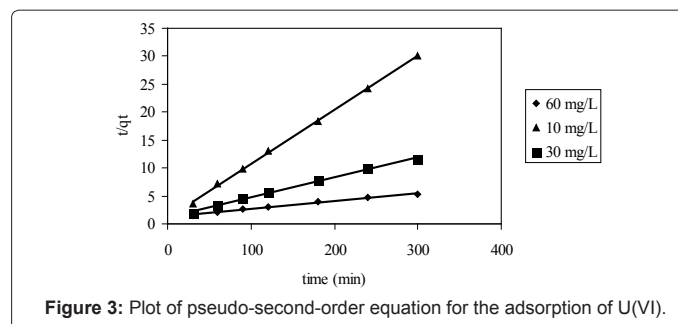


Figure 3: Plot of pseudo-second-order equation for the adsorption of U(VI).

as the existence in various forms of the sorbate in the solution. The effect of pH on the U(VI) adsorption by C-Gch is shown in Figure 4. For U(VI), the presence of different hydrolyzed species in the wide range of pH will be affected to the adsorption efficiency. In the range of acid to neutral of the solution, U(VI) ions are mainly exist in the hydrolyzed forms such as UO_2^{2+} , $(UO_2)(OH)_2^{2+}$, $UO_2(OH)^+$ and $(UO_2)_3(OH)_5^+$ [23, 25]. Thus, the negative charge sites on the adsorbent surface play an important role in the adsorption process of U(VI). As results obtained showing in Figure 3, the adsorption capacity for U(VI) by C-Gch increased with increasing pH and reached the maximum value at pH 3.5 - 4 and then gradually reduced when pH reached the value more than 4.5. The low capacity value at $pH < 3$ can be explained that hydrolyzed ions of U(VI) are strongly competed against with H^+ ions for protonation of negative charge sites on the adsorbent surface. At $pH \geq 3-4.5$, the competition of H^+ ions is reduced leading the adsorption capacity increase. On the other hand, the presence of carboxylic groups in C-Gch leading to increasing adsorption sites on the adsorbent surface. According to Memon et al. [26], at pH from 3 to 4.5, the carboxylic group is deprotonated and became negatively charged, hence, increasing the availability of binding sites for positively charged of U(VI) ions. At $pH > 5$, U(VI) begins partly forming the anionic complexes with OH^- and CO_3^{2-} (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 slightly reduce adsorption capacity of U(VI).

Effect of initial U(VI) concentration

Results obtained in study of an effect of initial U(VI) concentration were illustrated in Figure 5. As can be seen from the Figure 5, the adsorption capacities were increased with increasing initial U(VI) concentration. At higher concentration of U(VI) (≥ 100 mg/L), the adsorption capacities slowly go to near a constant value. This phenomenon can be explained that at initial state, a large number adsorption vacant site were available on the adsorbent surface leading to increase the adsorption capacity. At near equilibrium, most vacant adsorption sites were filled resulting in slowdown of adsorption capacity.

Concentration (mg/L)	Equation	K (g/mg.min)	R ²	h (g/mg.min)	q _e (mg/g)	q _{e-exp} (mg/g)
10	y = 0.096x + 1.085	8.59 · 10 ⁻³	0.999	0.921	10.35	9.94
30	y = 0.036x + 1.107	1.18 · 10 ⁻³	0.995	0.90	27.70	25.79
60	y = 0.014x + 1.303	1.46 · 10 ⁻⁴	0.995	0.767	72.46	68.87

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

Effect of adsorbent dose

Figure 6 shows results of the effect of the adsorbent dose on the adsorption capacity. The results showed that the adsorption capacity was reduced with increasing the adsorbent dose. It was found that at low dosage of C-Gch from 0.05 -0.1 g/ 50mL, the adsorption capacity reduced from 43.4 mg/g to 18.5 mg/g and rapidly reduced to 7.32 mg/g at dosage ranging from 0.1 to 0.4 g/5mL. This phenomenon is due to the fact that at higher dosage of adsorbent, the vacant adsorption sites on the adsorbent are remained constants resulting in reduced metal uptake.

Effect of other metal ions

Effects of cations including Cu (II), Pb(II), Zn(II) and Cd(II) on the adsorption of uranium (VI) by C-Gch are shown in Figure 7. It

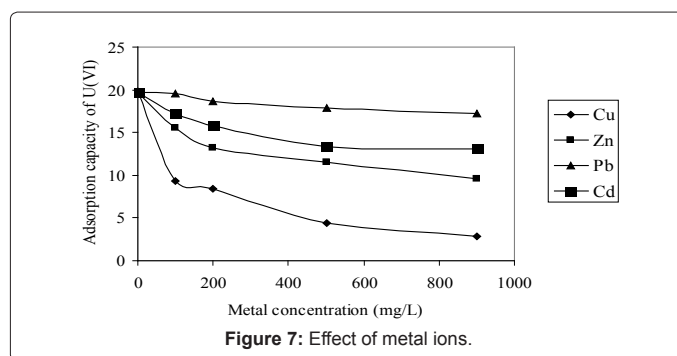


Figure 7: Effect of metal ions.

was found that the adsorption capacity of U(VI) was reduced with increasing concentrations of cations. As can be seen from results, in the presence of cations with concentration ranging from 100 to 900 mg/L, the adsorption capacity of U(VI) reduced from 20mg/g to 4.3, 11.6, 15.1 and 17.5 mg/g in the presence of Cu(II), Zn(II), Cd(II) and Pb(II), respectively. The effect of metal ions on the adsorption of uranium (VI) can be arranged in the order: Cu (II) > Zn (II) > Cd (II) > Pb (II).

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 [10,11]. In this study, two famous adsorption isotherm models were used to describe the adsorption process including Langmuir and Freundlich models [27].

Langmuir model:

$$q_{eq} = \frac{K_L q_{max} C_{eq}}{1 + q_{max} C_{eq}} \quad (5)$$

The linear equations of Langmuir model is presented as following:

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_{max}} + \frac{1}{K_L q_{max}} \quad (6)$$

Where:

q_{eq} – amount of U(VI) adsorbed per gram of dry adsorbent at equilibrium (mg/g)

C_{eq} – equilibrium concentration of U(VI) in solution (mg/L)

K_L – Langmuir constant (L/g)

q_{max} – maximum U(VI) to adsorb per gram of dry adsorbent (mg/g)

Freundlich model:

$$q_{eq} = K_F C_{eq}^{1/n}$$

The linearised form of the Freundlich model was used:

$$\log q_{eq} = \log K_L + 1/n \log C_{eq}$$

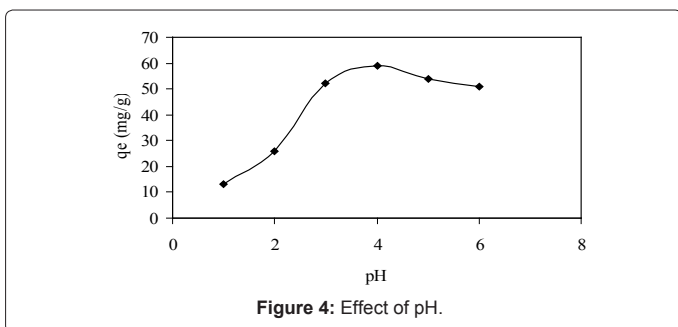


Figure 4: Effect of pH.

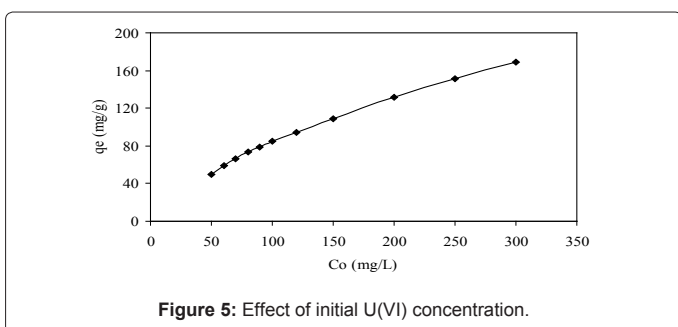


Figure 5: Effect of initial U(VI) concentration.

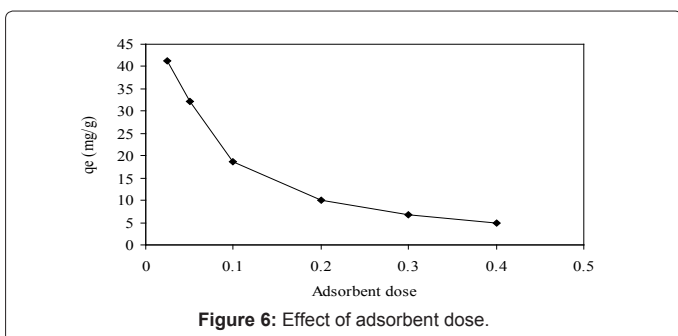


Figure 6: Effect of adsorbent dose.

Where:

q_{eq} – amount of U(VI) adsorbed per gram of dry adsorbent (mg/g)

C_{eq} – equilibrium concentration in solution (mg/L)

$1/n$ – Freundlich constant (mg/g)

K_F – Freundlich constant (g/L)

The plots of the linear Langmuir and Freundlich models were presented in Figure 8 and 9. The parameters in two models were calculated from slope and interpreted of the plots. The results obtained were given in Table 2. From the results in Table 2, the correction values R^2 of Langmuir equation and Freundlich equation were found to be 0.9693 and 0.9353, respectively. Based on the R^2 values, It suggested that the adsorption process of U(VI) by C-Gch was fixed to both models. However, the used of Langmuir model for description of U(VI) adsorption by C-Gch is better than that of Freundlich model due to higher value of R^2 . Based on Langmuir model, the maximum adsorption capacity of U(VI) was found to be 172 mg/g for C-Gch. The high value of adsorption capacity of C-Gch shows that carboxyl groups of citric acid grafted on crosslinked chitosan could significantly contribute to the adsorption process of U(VI).

Conclusion

Research results on adsorption U(VI) by C-Gch showed that grafting citric acid on crosslinked chitosan with glutraldehyde was improved the adsorption capacity. The equilibrium adsorption was

reached at 300 min of the contact time and maximum adsorption capacity was obtained at pH 4. Effect of co-ion such as Cu (II), Zn (II), Cd(II) and Pb(II) was studied. The results show that the presence of metal ions significantly affected on the adsorption of U(VI). Adsorption kinetic study of U(VI) on C-Gch showed that experimental data good fitted the pseudo second order. This means that the adsorption process of U(VI) is the chemical sorption. Two adsorption isothermal models were used to describe the adsorption equilibrium. It was found that the Langmuir model with correction value $R^2 = 0.9963$ was appropriate to use for description of the adsorption of U(VI) by C-Gch. Based on the Langmuir model, the maximum capacity of C-Gch for U(VI) was found to be 172mg/g. From the results obtained, it could be concluded that this material is potential adsorbent to use in the adsorption technology for remove U(VI) from contaminated water environment.

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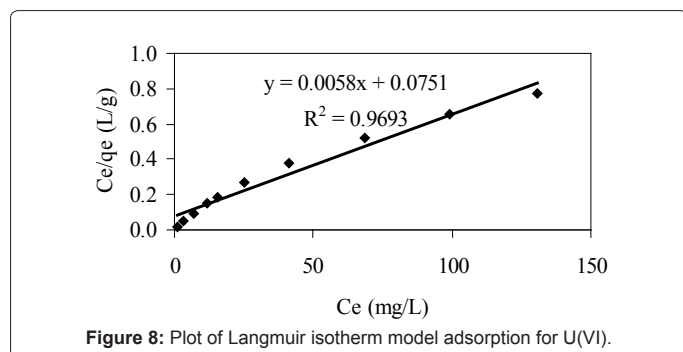


Figure 8: Plot of Langmuir isotherm model adsorption for U(VI).

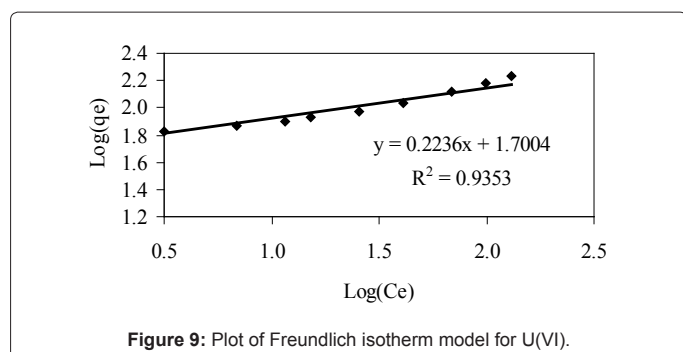


Figure 9: Plot of Freundlich isotherm model for U(VI).

Langmuir model			Freundlich model		
K_L (L/mg)	q_{max} (mg/g)	R^2	K_F (mg/g)(mg/l) ⁿ	$1/n$	R^2
0.07	172	0.969	50.16	0.223	0.935

Table 2: The Langmuir and Freundlich adsorption parameters for uranium adsorption.

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