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Adsorption of uranium (VI) from aqueous solution onto cross-linked chitosan

Guanghui Wang[a,*], Jinsheng Liu[a], Xuegang Wang[a], Zhiying Xie[a], Nansheng Deng[b]

[a] Department of Civil and Environmental Engineering, East China Institute of Technology, Fuzhou, 344000, Jiangxi, PR China
[b] School of Resources and Environmental Science, Wuhan University, Wuhan, 430079, PR China

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ABSTRACT

Cross-linked chitosan (CCTS) was synthesized by the reaction of chitosan with epichlorohydrin under alkaline conditions. Adsorption of uranium (VI) from aqueous solution onto cross-linked chitosan was investigated in a batch system. Adsorption isotherm and adsorption kinetic studies of uranium (VI) onto cross-linked chitosan were carried out. The influence factors on uranium (VI) adsorption were also investigated and described in detail, such as contact time, pH value and initial uranium (I) concentration. Langmuir and Freundlich adsorption models were used for the mathematical description of the adsorption equilibrium. Equilibrium data agreed very well with the Langmuir model. Adsorption kinetics data were tested using pseudo-first-order and pseudo-second-order models. Kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model, indicating that the chemical adsorption was the rate-limiting step. Results also showed that cross-linked chitosan was favourable adsorbent.

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1. Introduction

Uranium is a toxic radioactivity element. It is usually found in the environment in the hexavalent form. Excessive amounts of uranium have entered into environment through the activities of nuclear industry [1]. Uranium disposed into the environment can eventually reach the top of the food chain and be ingested by humans, causing severe kidney or liver damage and even death [2]. The World Health Organization has determined that uranium (VI) is a human carcinogen and its concentration level in water should not exceed 50 mg/L. The U.S. Environmental Protection Agency has recommended a drinking water standard of 20 mg/L for ^{238}U [3]. Therefore, it is necessary to treat wastewaters containing uranium in order to prevent radioactive contamination of the environment.

Various techniques are employed for the removal of uranium ions from wastewaters and radioactive wastes. Chemical precipitation, membrane processes, ion exchange, solvent extraction, photocatalysis and adsorption are the most commonly used methods [4–9]. Adsorption of uranium (VI) onto various solids is important from purification, environmental, and radioactive waste disposal points of view [10,11].

In recent years, attention has been focused on various adsorbents with metal-binding capacities and low cost, such as chitosan, zeolites, clay or certain waste products [12]. Chitosan is a kind of polymer made up of glucosamine, which is prepared from chitin by partially deacetylating its acetamido groups with a strong alkaline solution. Chitosan has been reported to have high potential for adsorption of metal ions due to its high contents of amino and hydroxy functional groups [13]. However, chitosan is soluble in aqueous organic acids such as acetic acid, formic acid, etc., as well as inorganic acids, to give a viscous solution. In order to enhance the resistance of chitosan against acid, alkali and chemicals as well as increasing chitosan adsorption ability and mechanical strength, cross-linking reaction is a crucial step [14]. Different kinds of cross-linking agents such as glutaraldehyde [15], epichlorohydrin and ethylene glycol diglycidyl ether have been used in cross-linking reaction of chitosan. However, an advantage of epichlorohydrin is that it does not eliminate the cationic amine function of chitosan [16,17].

In this work, cross-linked chitosan was synthesized by the reaction of chitosan with epichlorohydrin under alkaline conditions. The uranium (VI) adsorption behavior on cross-linked chitosan was investigated. The influence of experimental conditions such as contact time, pH value and initial uranium (VI) concentration were studied. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The adsorption rates were determined quantitatively and compared by pseudo-first-order and pseudo-second-order model. This information will be useful for further applications of system design in the treatment of practical radioactivity waste effluents.

* Corresponding author. Tel.: +86 794 8258287; fax: +86 794 8258828.
E-mail address: wgh68611@163.com (G. Wang).

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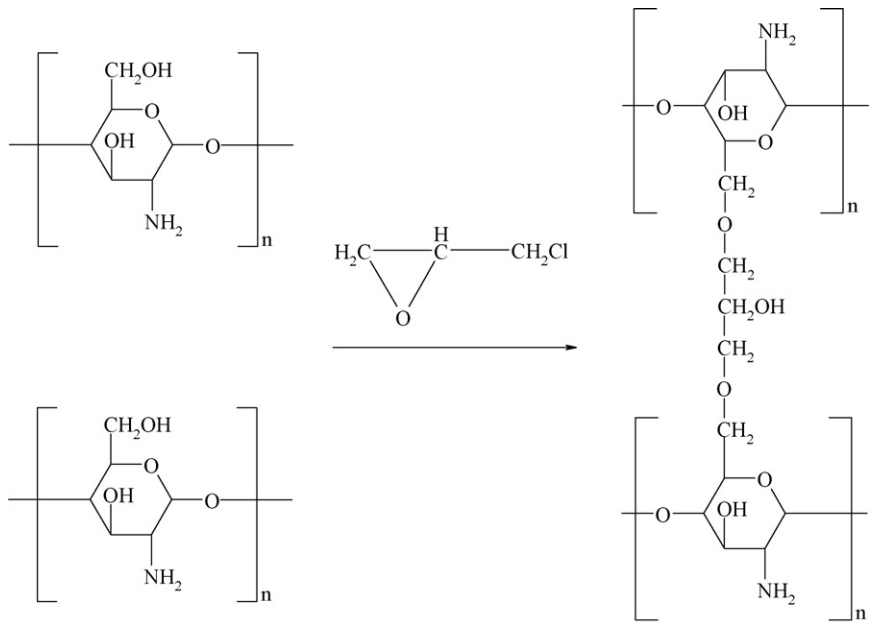

Fig. 1. Schematic representation for the cross-linking reaction of chitosan with epichlorohydrin.

2. Materials and methods

2.1. Materials

Chitosan with 40 mesh, 92% degree of deacetylation and molecular weight of 6×10^5 was purchased from Yuhuan Ocean Biology Company (Zhejiang, China). A stock solution of 1000 mg/L uranium (VI) was prepared by dissolving an appropriate amount of $UO_2(NO_3)_2 \cdot 6H_2O$ in deionized water. The initial pH of the working solutions was adjusted by addition of HNO_3 or NaOH solution. 0.1% Arsenazo-III solution was prepared by dissolving 1 g of the reagent in 1000 mL of deionized water. All other reagents and solvents used were of analytical reagent grade unless otherwise stated. The water was used throughout the work was deionized by a Milli-Q Water Purification system.

2.2. Preparation of cross-linked chitosan

Chitosan solution was prepared by dissolving 6.0 g of chitosan flakes in 60 mL of 5% (v/v) acetic acid solution. To this, 6 mL of epichlorohydrin was slowly added with rigorous stirring, and then 50 mL of 5% (w/v) NaOH was added in drops. After about 18 h of reaction at room temperature, a white solid was precipitated. The precipitate was filtered off, washed thoroughly with water and then with a little propanol, dried in vacuo, milled, and sieved (200 mesh). The reaction of chitosan with epichlorohydrin in an acidic condition might be cross-linked at hydroxyl groups to form the epichlorohydrin cross-linked chitosan product, as shown in Fig. 1. The cross-linked chitosan was confirmed by Nicolet FT-IR 5700 infrared spectrophotometer (Thermo, Madison, USA).

2.3. Determination of uranium (VI) in solution

Concentration of uranium (VI) was analyzed with the Arsenazo-III spectrophotometric method [18] on a Shimadzu UV-1601 spectrophotometer (Tokyo, Japan). 1 mL uranium (VI) solution sample, 5 mL chloroacetic acid ($ClCH_2COOH$)–sodium acetate (CH_3COONa) buffer solution (pH 2.5) and 1.0 mL 0.1% Arsenazo-III aqueous solution were added to a glass flask, respectively, the final solution volume was filled up to 25 mL by adding deionized water. After 10 min, the absorbance of the mixture liquid was measured at 652 nm. The calibration curve equation for uranium (VI) detection was absorbance = 0.01276 + 0.2268C (R = 0.9987), where C was the concentration of uranium (VI). Measurements were made in double for each experiment with errors less than 5%.

2.4. Adsorption experiments

The uranyl nitrate solution of given concentration, pH value and volume was added to a conical flask containing the cross-linked chitosan. The mixture was shaken for 3 h at 25 °C in a shaker. The mixture solution was centrifuged at 4000 rpm for 10 min at room temperature. The uranium (VI) concentration in the solution was determined by UV–vis spectrophotometer at 652 nm as described above. The amount of adsorption at equilibrium time t, q_e (mg/g), was calculated by:

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

where C_0 and C_e are the liquid-phase concentrations of uranium (VI) at initial and equilibrium time, respectively; V the volume of the solution (L); W is the mass of dry adsorbent used (g).

The adsorption removal efficiency of uranium (VI) from aqueous solution was calculated as follows:

$$\text{removal efficiency}\,(\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (2)$$

where C_f is the final uranium (VI) concentration.

3. Result and discussion

3.1. Characterization of chitosan and cross-linked chitosan

The infrared spectra of chitosan (CTS) and cross-linked chitosan (CCTS) are shown in Fig. 2. A characteristic strong and broad band appeared at around 3441 cm^{-1}; corresponding to the stretching vibration of $-NH_2$ group and –OH group in CTS spectra. However, the absorption intensity of $-NH_2$ group and –OH group from CCTS is obviously lower than that of $-NH_2$ group and –OH group from CTS, which indicates cross-linked reaction occurred between chitosan and epichlorohydrin. The peaks at 2920 and 2869 cm^{-1} can

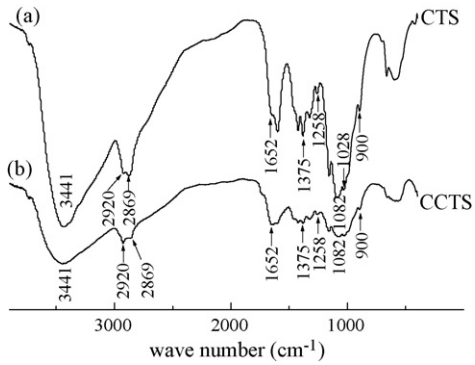

Fig. 2. FT-IR spectra (a) CTS and (b) CCTS.

be assigned to asymmetric and symmetric $-CH_2$ groups. The peak at 1258 cm^{-1} can be attributed to the C–O–C stretching. The absorption bands at 1082 and 1028 cm^{-1}, corresponding to the stretching vibration of the primary –OH group and the secondary –OH group, respectively. The absorption band at 900 cm^{-1}, corresponding to the characteristic absorption of β-D-glucose unit. The bands at 1652 and 1375 cm^{-1} was attributed to the stretching vibration of C=O of amide group and the C–H deformation of the CH_3 group, associated with few remaining acetamide groups present in the polymeric chain, as a result of the incomplete deacetylation of chitosan (92%).

3.2. Effect of contact time on the adsorption

Under the conditions of 10 mg adsorbent amount, pH 3.0, 25 °C and 50 mg/L uranium (VI), the adsorption experiments were carried out for contact times ranging from 30 to 180 min. The results are shown in Fig. 3. It is clear that the adsorption capacity of uranium (VI) onto CCTS increases with an increase of contact time and reaches adsorption equilibrium within 120 min. Kinetics of adsorption of uranium (VI) consisted of two phases: an initial rapid phase where adsorption was fast and contributed significantly to equilibrium uptake, and a slower second phase whose contribution to the total metal adsorption was relatively small. The first phase is interpreted to be the instantaneous adsorption stage or external surface adsorption. The second phase is interpreted to be the gradual adsorption stage where intraparticle diffusion controls the adsorption rate until finally the metal uptake reaches equilibrium. After 120 min, the change of adsorption capacities for uranium (VI) did not show notable effects. As a consequence, the adsorption equilibrium time considered for the further work has been taken as 180 min.

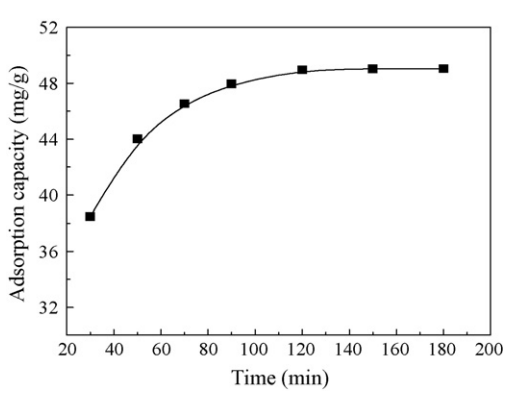

Fig. 3. Effect of contact time on the adsorption of uranium (VI) ([UO_2^{2+}] = 50 mg/L, CCTS = 10 mg, pH = 3, and T = 25 °C).

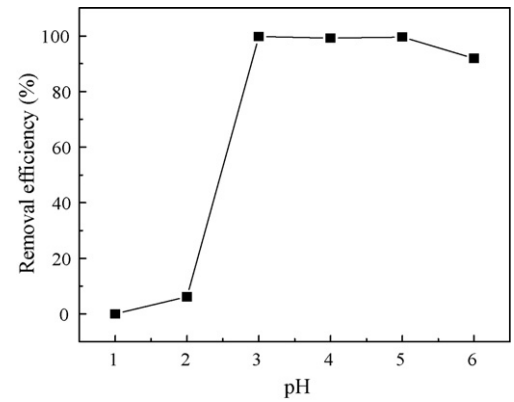

Fig. 4. Effect of pH on the adsorption of uranium (VI) ([UO_2^{2+}] = 50 mg/L, CCTS = 10 mg, and T = 25 °C).

3.3. Effect of initial pH values

The effect of pH on the adsorption of uranium (VI) onto CCTS was investigated using 100 mL of uranium (VI) 50 mg/L for a pH range of 1.0–6.0 at 25 °C for 180 min. The results are shown in Fig. 4. The uranium (VI) removal efficiency by CCTS was strongly depended on variations of the solution pH, the adsorption removal efficiency increased with increasing pH to a maximum value (pH 3.0) and then declines slowly with further increase in pH. In strong acidic solutions (pH < 3.0), more protons will be available to protonate amine groups to form groups $-NH_3^+$, reducing the number of binding sites for the adsorption of UO_2^{2+}, therefore, the removal efficiency of uranium is lower in strong acidic solutions (pH < 3.0). However, the availability of free uranium (VI) ions is maximum at pH 3.0 and hence maximum adsorption, when pH value increase beyond 3.0; hydrolysis precipitation starts due to the formation of complexes in aqueous solution [19]. The hydrolysis of uranyl ions play significant role in determining the equilibrium between uranium (VI) in solution and on adsorbent. Hydrolysis products occur, including $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^{3+}$, $(UO_2)_2(OH)_2$, which results in decline of adsorption removal efficiency of uranium (VI), similar results were also observed [20].

3.4. Effect of initial uranium (VI) concentration

The effect of the initial uranium (VI) concentration on the adsorption removal efficiency was studied by contacting a fixed mass of CCTS (10 mg) at a fixed temperature (25 °C) and initial pH (3.0) using a range of initial uranium (VI) concentrations (10, 20, 30, 50, 60, 70, 80 and 90 mg/L). The results are shown in Fig. 5. It is clear that the adsorption removal efficiency of uranium (VI) decreased with increasing the initial uranium (VI) concentration

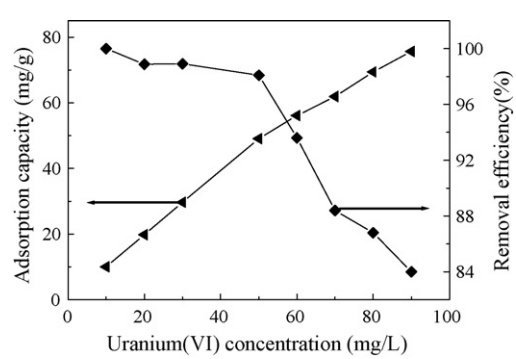

Fig. 5. Effect of initial concentration on the adsorption of uranium (VI) (CCTS = 10 mg, pH = 3, and T = 25 °C).

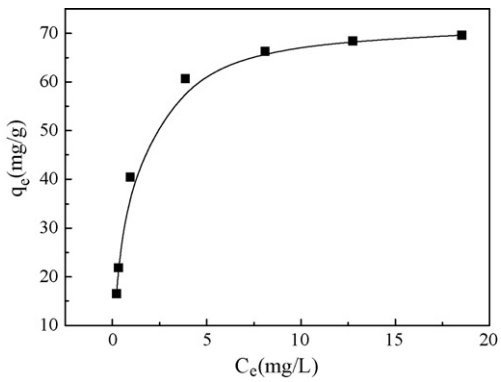

Fig. 6. Adsorption isotherm of uranium (VI) on CCTS (CCTS = 10 mg, pH = 3, and T = 25 °C).

in the aqueous solution. On one hand, this is because more mass of uranium is put into the system with increasing the initial uranium (VI) concentration in the aqueous solution, but the same mass of adsorbent. On the other hand, because of the higher mobility of uranyl ions $(UO_2)^{2+}$ in the diluted solutions, the interaction of this ion with the adsorbent also increases. However, the adsorption capacity of CCTS for uranium increased with increase in the initial uranium concentration. This result is similar to that reported by Ceren Kütahyalı et al. in their study on selective adsorption of uranium from aqueous solutions using activated carbon prepared from charcoal by chemical activation [21].

3.5. Adsorption isotherm

The adsorption isotherm is the most important information, which indicates how the adsorbent molecules distribute between the liquid and the solid phase when the adsorption process reaches an equilibrium state [22]. Fig. 6 shows the adsorption isotherm of uranium (VI) on the cross-linked chitosan. The Langmuir and Freundlich models are often used to describe equilibrium adsorption isotherms. The Langmuir isotherm considers the adsorbent surface as homogeneous with identical sites in terms of energy. Eq. (3) represents the Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{3}$$

where b is a constant of adsorption equilibrium (L/mg), and Q_0 is the saturated monolayer adsorption capacity (mg/g). A linearized plot of C_e/q_e against C_e gives a Q_0 and b.

The empirical Freundlich equation based on adsorption on a heterogeneous surface is given as follows [23]:

$$q_e = K_F \times {C_e}^{1/n} \tag{4}$$

This expression can be linearized to give:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

where K_F and n are Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively. K_F and n can be determined from a linear plot of $\ln q_e$ against $\ln C_e$. The calculated results of the Langmuir and Freundlich isotherm constants are given in Table 1. It is found that the adsorption of uranium (VI) on the cross-linked chitosan correlated well (R > 0.99) with the Langmuir equation as compared the Freundlich equation under the concentration range studied, Langmuir model is suitable for adsorption equilibrium of uranium (VI) onto CCTS. The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L which is used to predict if an adsorption system is 'favourable' or 'unfavourable'. The separation factor, R_L is given by [24]:

Table 1
Langmuir, Freundlich isotherm model constants and correlation coefficients.

Isotherm model	Value
Langmuir model	
Q_0 (mg/g)	72.46
b (L/mg)	1.33
R	0.9983
Freundlich model	
K_F (mg/g)	37.31
n	3.98
R	0.9377

Table 2
R_L values based on the Langmuir equation.

Initial uranium (VI) concentration (mg/L)	R_L value
1.0	0.42955
4.0	0.15843
8.0	0.08603
13.0	0.05475
19.0	0.03812

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where C_0 is the initial uranium (VI) concentration (mg/L) and b is the Langmuir adsorption constant (L/mg). Table 2 lists the calculated results. Based on the effect of separation factor on isotherm shape, the R_L values are in the range of $0 < R_L < 1$, which indicates that the adsorption of uranium (VI) on CCTS is favourable [21]. Thus, CCTS is favourable adsorbent.

3.6. Adsorption kinetics

In order to investigate the kinetic mechanism, which controls the adsorption process, the pseudo-first-order and pseudo-second-order models were used to test the experiment data [25,26]. The pseudo-first-order kinetic model is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e is equilibrium adsorption capacity (mg/g), and k_1 is the pseudo-first-order rate constant (min^{-1}). A straight-line plot (Fig. 7) with correlation coefficient of 0.9897 suggests the applicability of pseudo-first-order kinetics model to fit the experimental data (Table 3). The calculated value of adsorption capacity, $q_{e,cal}$ (35.23 mg/g) is lower than the value of experimental adsorption capacity, $q_{e,exp}$ (49.05 mg/g).

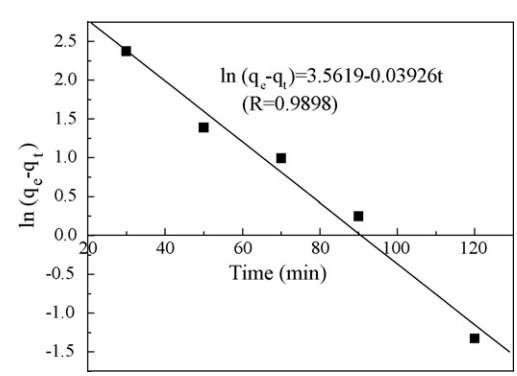

Fig. 7. Pseudo-first-order kinetics of uranium (VI) adsorption on CCTS ($[UO_2{}^{2+}]$ = 50 mg/L, CCTS = 10 mg, pH = 3, and T = 25 °C).

Table 3
Kinetic parameters of uranium (VI) adsorbed onto cross-linked chitosan.

Kinetic model	Value
Pseudo-first-order	
k_1 (min^{-1})	0.03926
$q_{e,cal}$ (mg/g)	35.23
R	0.9898
Pseudo-second-order	
k_2 (g mg^{-1} min^{-1})	0.00202
$q_{e,cal}$ (mg/g)	52.63
R	0.9997
$q_{e,exp}$ (mg/g)	49.05

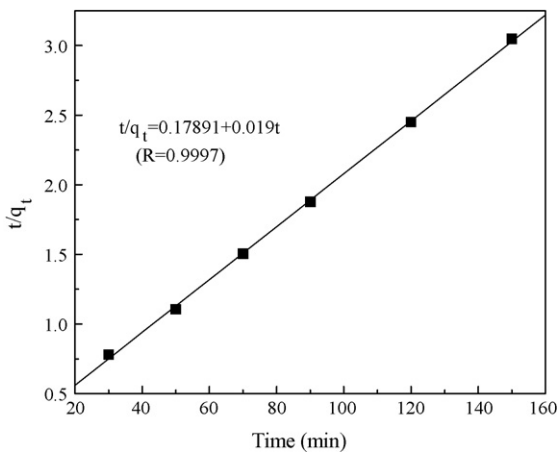

Fig. 8. Pseudo-second-order kinetics of uranium (VI) adsorption on CCTS ([UO_2^{2+}] = 50 mg/L, CCTS = 10 mg, pH = 3, and T = 25 °C).

The pseudo-second-order kinetic model is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where k_2 is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The pseudo-second-order plot (Fig. 8) is also linear with correlation coefficient of 0.9997 (Table 3), however the calculated value of adsorption capacity, $q_{e,cal}$ (52.63 mg/g) is close to the value of experimental adsorption capacity, $q_{e,exp}$ (49.05 mg/g). Therefore, it could be suggested that adsorption of uranium (VI) on CCTS follows pseudo-second-order better than pseudo-first-order model, thus, pseudo-second-order equation is suitable for adsorption of uranium onto CCTS. The pseudo-second-order kinetic model assumes that the rate-limiting step may be chemical adsorption [27]. It is more likely to predict that the adsorption behavior may involve valency forces through sharing of electrons between metal cations and adsorbent.

4. Conclusions

The uranium (VI) adsorption capacity by CCTS was strongly dependent on contact time, pH, and initial uranium (VI) concentration. The adsorption capacity of uranium (VI) onto CCTS increases with an increase of contact time and reaches adsorption equilibrium within 120 min, the adsorption removal efficiency increased with increasing pH to a maximum value (pH 3.0) and then declines slowly with further increase in pH. Langmuir and Freundlich adsorption models were used for the mathematical description of the adsorption equilibrium. It is found that the adsorption of uranium (VI) onto CCTS correlated well with the Langmuir equation as compared the Freundlich equation under the concentration range studied, Langmuir model is suitable for adsorption equilibrium of uranium (VI) onto CCTS. Adsorption kinetics data were tested using pseudo-first-order and pseudo-second-order models. Kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model, indicating that the chemical adsorption was the rate-limiting step. CCTS was favourable adsorbent for uranium (VI) removal from aqueous solutions.

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