Removal of uranium(VI) by adsorption onto peanut activated shell carbon powder

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Abstract. In this paper, we investigated the possibility of using peanut shell activated carbon (PSAC) as an adsorbent to remove U(VI) pollution from wastewater. Batch tests were carried out to study the influence of solution pH, contact time, temperature and initial metal concentration on the U(VI) adsorption process. The experimental results indicated 35 °C was the optimal temperature for U(VI) adsorption over the temperature range from 20 to 45 °C. Moreover, the adsorption process was highly pH dependent in the pH range of 2.0 – 6.0. The pH 5.5 was found to be most beneficial to U(VI) removal. The U(VI) uptake followed pseudo-first-order kinetics and reached equilibrium within 60 min. Isotherm adsorption data exhibited good correlation with Langmuir equation with a maximum monolayer adsorption capacity of 387.57 mg/g dry weight of PSAC. In conclusion, PSAC can be used as an efficient adsorbent for uranium-bearing wastewater treatment.

1. Introduction
Uranium mining and milling for nuclear power stations and for nuclear weapon manufacture have brought about the production large amounts of uranium-containing wastewater. Because uranium is very toxic and has a long half-life, its influence on environment is great. Uranium released into the environment would ultimately get into the food chain and be absorbed by humans, resulting in severe kidney or liver damage [1, 2]. Hence treating uranium-containing wastewater is in great need. Moreover, radioactive uranium which often exists in the form of uranyl cations under oxidizing conditions is extremely soluble and mobile and is hard to be eliminated. Common treating methods, including precipitation, ion exchange, reduction, reverse osmosis, membrane filtration, electrochemical treatment and solvent extraction are not only very prohibitive [3], but can also be restricted by poor extraction efficiency, inhibitory competing ions and massive waste generation. In consideration of the high cost and technical limitations of traditional approaches, it is necessary to look for cheap alternatives to remove U(VI) pollution.

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. Adsorption has proved to be a promising method to treat uranium-containing wastewater because of its simple operation, mature technology and extensive applicability. Many investigations have been conducted to
develop cheap and effective uranium adsorbents. In the past thirty years, much research focused on some agricultural and forestry residues such as chaff [4], wheat straw [5], corn cob [6], rice husk [7], poplar leaves [8] and tea waste [9] due to their low cost, low secondary pollution and easy recycling. Every year lots of peanut shells are disposed of owing to the lack of uses for these materials. The shells are biodegradable and can be utilized as animal food filler, absorbents, or carriers for pesticides or fertilizers, although they are often landfilled. In the southern United States, the application of peanut shells as mulch has been associated with the spread of southern blight and other fungal diseases. Peanut shell can also be processed into peanut shell activated carbon (PSAC) via chemical activation through ZnCl₂ and H₃PO₄ as well as high-temperature steam activation. PSAC has porous structures with large surface area, thereby enabling the use of PSAC as a high-performance adsorption material. To the best of our current knowledge, little research has been done on the adsorption of hexavalent uranium (U(VI) or UO₂²⁺) by PSAC, although other wood activated carbon materials have been used in the removal of radionuclide. In this study, PSAC was used to adsorb uranyl cations in the solution. The optimal adsorption conditions were discussed as a function of temperature, contact time, pH and initial U(VI) concentration. The objective of this study is to evaluate the feasibility of its use as a U(VI) adsorbent.

2. Materials and methods

2.1 Chemicals and U(VI) stock solutions

Peanut shells from Hunan province of China were ground to the size between 10 and 20 mesh. The milled peanut shells were mixed with ZnCl₂ solution (wt%: 60%) at a ratio of 1 : 2 by mass (shells : ZnCl₂ solution). The mixture was stirred well for 2 h and then was filtered to obtain the solid residues remaining in the filter paper. The solid residues were heated in a tube heating furnace at a heating ramp of 10 °C/min in a N₂ atmosphere and was held at 500 °C for 3 h. The peanut shell carbon materials were washed with 0.2 mol/L HCl to remove surface ash after natural cooling to room temperature. Then the activated carbons were rinsed using deionized water to remove the remaining HCl and dried in a vacuum dryer at 120 °C overnight. The obtained PSAC powder was cooled to room temperature for the following adsorption experiment. The microstructure of PSAC was characterized via scanning electron microscopy (SEM, Model S-4800 Hitachi, Tokyo, Japan). The sample was gold coated prior to SEM observation.

A stock solution of U(VI) (1 mg/mL) was prepared was prepared by dissolving U₃O₈ in a mixture of HCl, H₂O₂ and HNO₃ [10]. The other concentrations were obtained from the stock solutions by appropriate dilution. The U₃O₈ was supplied by School of Nuclear Resources and Nuclear Fuel Engineering, University of South China. The other chemicals were purchased from Sinopharm Chemical Reagent Company, Shanghai, China. All chemicals used in this study were of analytical grade. All experimental solutions were prepared using distilled water.

2.2 Adsorption experiments

For all adsorption experiments, 100 mL U(VI) solution was mixed with a known amount of dry PSAC in a series of 250 ml conical flasks. The pH of the U(VI) solution was adjusted as required using 1.0 M NaOH and 1.0 M HNO₃ before mixing with the PSAC. Then the experiments continued on a rotary shaker (140 r/min). A sample of solution was withdrawn at suitable time intervals, centrifuged at 10000 ×g for 15 min and U(VI) was determined in the supernatant. The U(VI) removal efficiency and equilibrium adsorption capacity of U(VI) onto the biomass (mg U/g dry PSAC weight) were obtained by using the following expressions:

\[
U (V I) \text{ uptake } (\%) = \frac{C_0 - C}{C_0} \times 100
\]

\[
Q = \frac{(C_0 - C)V}{M}
\]
where \( Q \) (mg/g) is the amount of U(VI) adsorbed onto the unit amount of the adsorbent, \( C_0 \) and \( C \) (mg/L) are the concentrations of the U(VI) in the solution before and after adsorption, respectively. \( V \) (L) is the volume of the aqueous solution and \( M \) (g) is the dry weight of the adsorbent. Uranium-free and sorbent-free blanks were used as controls. Each of the experiment was repeated twice and the average values were obtained. The U(VI) concentrations in samples were determined using a standard spectrophotography method [11].

### 2.3 Adsorption kinetic models

Pseudo-first-order and pseudo-second-order kinetic models are usually adopted in kinetic investigations. The pseudo-first-order equation is a simple kinetic model describing the kinetic process of liquid-solid phase adsorption which was put forward by Lagergren [12]. Its nonlinear formula is given as follows:

\[
Q_t = Q_e (1 - e^{-k_1 t})
\]

where \( k_1 \) is the rate constant of the pseudo-first-order sorption (min\(^{-1}\)). Obviously, \( Q_e \) and \( k_1 \) can be figured out by plotting \( Q_t \) versus \( t \) and by further nonlinear regression analysis.

The pseudo-second-order model based on the adsorption equilibrium capacity may be expressed as the following linear form [13]:

\[
\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2}
\]

where \( k_2 \) is the rate constant of pseudo-second-order adsorption \([\text{g/(mg}\cdot\text{min}]\). Obviously, \( Q_e \) and \( k_2 \) can be determined experimentally by plotting \( t/Q_t \) versus \( t \).

### 2.4 Adsorption isotherm models

Langmuir and Freundlich equations are commonly adopted to describe the adsorption isotherms. Langmuir model assumes adsorption homogeneity, such as uniformly energetic adsorption sites, monolayer surface coverage, and no interactions between adsorbate molecules on adjacent sites. Freundlich isotherm is applicable to nonideal adsorption onto heterogeneous surfaces involving multilayer adsorption. In this study, the Langmuir and Freundlich adsorption equations were both used to correlate the obtained isotherm data.

The linear Langmuir equation can be expressed as follows:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{bQ_{max}}
\]

where \( Q_{max} \) represents the maximum monolayer adsorption capacity (mg/g), and \( b \) represents the Langmuir adsorption constant which is related to the adsorption bonding energy (L/mg).

The linear Freundlich equation can be described as follows:

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \( K_F \) is the Freundlich constant indicative of the adsorption capacity of the adsorbent \((\text{mg}/(\text{L/mg})^{1/n})\), and \( n \) is the Freundlich exponent depicting adsorption intensity (dimensionless). In the Freundlich model, both monolayer and multiple-layer adsorptions are considered to take place during the adsorption process.

### 3. Results and discussion

#### 3.1 PSAC surface morphology observation

The surface feature of PSAC was shown in Fig. 1. Apparently, the PSAC surface displayed a non-uniform macroporous structure with the pore diameter of approximately 10–20 nm. Actually, this pore size could accommodate many U(VI) in that the diameter of U(VI) ion is only about 350 pm. In short, the porous structure could be favorable to the adsorptive removal of uranyl cations.
3.2 Effect of temperature

Because the final removal efficiency is affected by temperature, the study of its influence on the adsorption process is important for wastewater treatment. In this study, the U(VI) adsorption capacity increased slightly with temperature when the temperature was less than 35°C (Fig. 2). By contrast, when the temperature was greater than 35°C, the U(VI) adsorption capacity remained. An increase in U(VI) uptake with increasing temperature may be explained that the adsorption reaction is an endothermic reaction and the temperature rise is beneficial to U(VI) uptake. In addition, the phenomenon that a higher adsorption at the higher temperature also indicated that the adsorption process belongs to chemisorption rather than physical adsorption. Generally speaking, if the process is a physical adsorption, the higher temperature would have a negative effect on adsorption.

![Figure 1. SEM pictures of PSAC surface (Magnification: left, ×200; right: ×100).](image)

![Figure 2. Effect of temperature on U(VI) adsorption.](image)

3.3 Adsorption kinetics

The adsorption time between the adsorbate and adsorbent is a key parameter for designed adsorption process. The removal of U(VI) increased with time and reached equilibrium within 60 min. Besides, the removal of U(VI) was relatively quick in the first 30 min, but it gradually decreases with time until it reached equilibrium. Therefore, the equilibrium time of 60 min was selected for all further studies. As shown in Table 1, although the correlation coefficients ($R$) of pseudo-first-order and pseudo-second-order model are both reasonable, the calculated $Q_{e,cal}$ value does not agree with the experimental data $Q_{e,exp}$ for the latter model. In other words, only the pseudo-first-order model gives an reasonable $Q_{e,cal}$ value, which is much closer to $Q_{e,exp}$. This result suggested that the U(VI)
adsorption onto PSAC could be described very well by the pseudo-first-order model rather than the pseudo-second-order model.

### Table 1. Kinetic parameters of the U(VI) adsorption onto PSAC.

| Model               | Parameter       | Value    |
|---------------------|-----------------|----------|
| Pseudo-first-order  | $k_1$ (min⁻¹)   | 0.0905   |
|                     | $Q_{e, \text{cal}}$ (mg/g) | 181.14   |
|                     | $R$             | 0.9975   |
| Pseudo-second-order | $k_2$ (g/(mg·min)) | 0.0007   |
|                     | $Q_{e, \text{cal}}$ (mg/g) | 196.07   |
|                     | $R$             | 0.9976   |
|                     | $Q_{e, \exp}$ (mg/g) | ca. 180  |

#### 3.4 Effect of pH

Adsorption of U(VI) on the adsorbent was investigated at varying pH values (Fig. 3). It was found that the initial solution pH significantly affected the equilibrium U(VI) adsorption capacity. In the pH range studied, acid medium (pH 2.0~3.0) is not beneficial to the adsorption of U(VI). Along with the increase of pH, the U(VI) uptake increased and a maximum of U(VI) adsorption capacity was achieved at pH 5.5. An increase in pH beyond the optimum caused a decline in U(VI) adsorption. This result can be interpreted as follows. The non-ion dissolved solid schoepite began forming in the solution at higher pH values [14], thereby decreasing the availability of U(VI) and retarding the uranium adsorption.

![Figure 3. Effect of pH on U(VI) adsorption.](image)

#### 3.5 Adsorption isotherm models

The equilibrium data were fitted using the Langmuir and Freundlich isotherms over the initial U(VI) concentration range of 50–250 mg/L and the corresponding parameters are listed in Table 2. The $R$ value of Freundlich isotherm deviates from 1.0, indicating that the adsorption onto PSAC did not follow Freundlich isotherm. By contrast, the $R$ value of Langmuir isotherm model is much nearer to 1.0. This result suggested that Langmuir isotherm is more appropriate to describe the adsorption process. Because Langmuir isotherm is a monolayer adsorption equation, the adsorption of U(VI) onto PSAC belongs to monolayer adsorption rather than multilayer one.
Table 2. Isotherm parameters for adsorption of U(VI) onto PSAC.

| Model      | Parameter       | Value   |
|------------|-----------------|---------|
| Langmuir   | $Q_{\text{max}}$ (mg/g) | 387.57  |
|            | $b$ (L/mg)     | 0.0026  |
|            | $R$            | 0.9962  |
| Freundlich | $K_F$ (mg⋅(L/mg)$^{1/n}$) | 63.43   |
|            | $n$            | 2.2401  |
|            | $R$            | 0.9846  |

4. Conclusions

Batch experiments were performed to investigate the effects of several operational parameters on the U(VI) adsorption onto PSAC. In the temperature range examined, 35 °C was the optimal temperature for U(VI) adsorption. Besides, the adsorption process relied highly on pH and the pH 5.5 was most favorable to U(VI) removal over the pH range from 2.0 to 6.0. The U(VI) adsorption agreed with pseudo-first-order kinetics and Langmuir model with the $Q_{\text{max}}$ of 387.57 mg/g. In summary, PSAC could be used as a promising adsorbent for U(VI) removal.

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