Preparation of Hawaii nut shell biochar/graphene sponge and study on uranium adsorption properties

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Abstract. The composite sponge of Hawaii nut shell biochar and graphene oxide was prepared by using polyvinyl alcohol as three-dimensional composite carrier (BC/GO/PVA). The characterization analysis found that the composite sponge material has a good specific surface area of pore structure, and improved the plasticity of biochar, overcoming the stacking problem of graphene sheets, and proposed a reasonable material cross-linking composite mechanism. The optimum adsorption capacity and adsorption mechanism were analyzed by batch adsorption experiments. The results showed that the removal of uranium by BC/GO/PVA materials was beneficial under weakly acidic conditions. The maximum adsorption capacity of the experiment is 14.3 mg/g.

1. Introduction
Uranium is a kind of natural radionuclide and typical nuclear fuel in nuclear power plants. With the continuous increase of people's demand for electricity, nuclear power is developing as an efficient and clean energy. However, uranium is gradually released into the environment from uranium processing, refining and nuclear power plant accident pollution, becoming the most common radioactive nuclide pollutants in soil and groundwater [1]. Even at low concentrations, uranium has been reported to cause chemical toxicity and internal radiation [2]. Therefore, the removal of uranium from waste liquid is a problem worthy of attention. At present, the main methods for treating uranium-containing wastewater are chemical precipitation method, ion exchange method, membrane separation method and adsorption method[3-6]. Considering the available methods for the treatment of contaminated water, adsorption is one of the most attractive, highly efficient and cost-effective method and used most widely [7].

At present, the commonly used adsorbent materials mainly include attapulgite [8], sepiolite [9], bentonite [10], carbon materials [11] and graphene oxide[12] etc. Carbon material has become an important adsorption material for adsorption and removal of uranium from water because of its large specific surface area, high porosity, high temperature resistance, radiation resistance, high stability to all kinds of acid-base environment, and its own non-toxic, environmentally friendly and so on[13]. The fruit of Hawaiian fruit is popular, the remaining Hawaii nut shell is hard, the surface is compact...
and the carbon content of the shell is high, and is the preferred material for making the biochar [14, 15]. What’s more, biochar was prepared from Hawaii nut shell and food waste was treated effectively at the same time.

Graphene oxide (GO) has excellent adsorption properties. In addition to its mechanical properties, it is also highly hydrophilic, with abundant functional groups (hydroxyl, carboxyl and carbonyl) on the surface, base and edge, and has a high affinity for water molecules. Graphene as an adsorbent also has its drawbacks. Most of the research is carried out by using two-dimensional GO and its composite materials [16]. The high affinity between graphene sheets makes it easy to randomly and uniformly aggregate and disperse in aqueous solution. This defect limits the full realization of its high surface area and is not conducive to adsorption [17]. In addition, the disadvantages of GO flake separation and recovery from solution greatly limit its practical application.

In this study, in order to improve the adsorption energy of U(VI), Hawaii nut shell biochar with high specific surface area was prepared by KOH activation, GO was prepared by Hummers method, polyvinyl alcohol sponge (PVA) was used as the composite carrier, and graphene oxide composite sponge (BC/GO/PVA) was prepared by foaming crosslinking method. The adsorption performance of biochar and graphene oxide in BC/GO/PVA materials overcomes the shortcomings of poor plasticity and difficulty in recycling. The effects of initial concentration, the value of pH and other factors on the absorption behavior of U(VI) ions were studied. The adsorption mechanism was discussed through adsorption isotherm and calculation of thermodynamic parameters.

2. Experiment

2.1. Material
Hawaiian nut shells were taken from Hengyang city, Hunan province, China, cleaned several times with ultra-pure water and dried for later use. Carbon, KOH, azo arsenic III H2SO4(98%), ethanol, HCl, FeCl3 and other experimental material were purchased from Tianjin Tiangan Chemical Technology Development. Different concentrations of uranium solution are diluted with uranium standard solution(1g/L). Mix the pH value with hydrochloric acid and sodium hydroxide.

2.2. Preparation of BC/GO/PVA
Graphene oxide (GO) solution concentration was 2mg/mL. 5g Hawaii nut shell biochar was mixed with 50mL GO moisture dispersion. The mixture was then vigorously stirred for 4 hours to form a uniform graphene/biochar solution. Meanwhile, 3.0 g polyvinyl alcohol (PVA) particles were stirred vigorously in 30mL distilled water at 90℃ until completely dissolved. After that, the graphene/biochar mixture was gradually dropped into the prepared polyvinyl alcohol solution and stirred for 1 hour. Subsequently, 7.5 g soluble starch was added to the mixed solution by foaming crosslinking method. Add formaldehyde (12 mL) and pentane (7 mL) into the GO/BC/PVA mixture and stir it vigorously. After full reaction, pour 8.5 mL H2SO4 into the foam at room temperature, pour the foam into the mold, and solidify in the oven at 60 °c for 1.5 hours. Rinse the original sample with clean water at least 3 times to remove impurities. Biochar sponge (BC/PVA) and biochar modified graphene composite sponge (BC/GO/PVA) were prepared by the same method and dried for later use[18].

2.3. Characterization
The morphology of the material was studied by scanning electron microscope (SEM). The types and contents of microelements in the material were analyzed by energy dispersive spectrometer (EDS). Analysis of the structure and functional groups of organic compounds before and after modified adsorption by Fourier transform infrared spectroscopy (FT-IR)
3. Results and discussions

3.1. Characteristic analysis

3.1.1. Characterization of biochar and modified go sponge. The morphology of P-C, BC, and BC/GO/PV was revealed by scanning electron microscopy. The elements of BC/GO/PV and U were revealed by EDS. The results are shown in Figure 1. The morphological difference between P-C and BC can be clearly seen. The P-C image in Figure 1(a) shows a relatively smooth surface shape, which conforms to the characteristics of better carbonization degree, and the surface is smooth, indicating that the degree of opening before activation was general. The surface in Figure 1(b) has obvious traces of corrosion, adding a lot of holes, making the smooth surface bumpy, which greatly improves its specific surface area, which may also be the key to improve its adsorption capacity. Figure 1 (c) shows the sponge structure after uranium adsorption with obvious pore structure and compact structure. This porous and cohesive structure reduces the accumulation of go layers and significantly increases the surface area of GO. The morphology images after U(VI) adsorption showed no obvious structural degradation, which reflected the good structural stability of the modified graphene sponge material. At the same time, the remaining oxygen functional groups on go flakes also facilitate the formation of porous go[19]. EDS analysis of selected areas (Figure 1(c)) shows that the modified material is mainly composed of carbon and oxygen elements, and the weight percentage of U(VI) is 4.18, indicating the effectiveness of uranium adsorption. The higher Au content is due to the scanning electron microscope gold spraying pretreatment.

![Figure 1. SEM images of P-C (a), BC (b), BC/GO/PV-U(C) and EDS of BC/GO/PV-U (d).](image-url)
3.1.2. Infrared spectra analysis. The surface active groups of polyvinyl alcohol biochar (BC/PVA) and graphene biochar sponge material were studied by infrared spectra(FT-IR). The results are shown in Figure 2. Figure 2a shows the infrared spectrum of BC/PVA. It is known from the literature that BV/PVA mainly contains active groups such as \( \text{CO}^-, \text{-CH}_3, \text{C}=\text{O}[11,20]\).

Figure 2b shows the infrared spectrum of BC/GO/PVA which is different from figure 2a, at 1687 cm\(^{-1}\). There is an absorption peak caused by C = C stretching vibration in the graphene structure, indicating the presence of graphene SP\(_2\) structure. The stretching vibration peak of C=O on the carboxylate carboxylate at 1793 cm\(^{-1}\) is not obvious, indicating that the oxidation of graphene is better. The stretch peak at 2513 cm\(^{-1}\) is S-H, which should be the impurity peak of hydrogen sulfide; the stretch peak at 2923 cm\(^{-1}\) is the anti-scaling stretch peak of alkane CH\(_2\), which is the residual peak of formaldehyde[21].

![Figure 2. FT-IR spectra of BC/ PVA(a), BC/GO/PVA (b).](image)

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

3.2. effects

The effect of different initial uranium solution pH on the removal of U(VI) by BC/GO/PVA was investigated. The results are shown in Figure 3. Neutral conditions are most conducive to the adsorption and removal of uranium ions, while acidic and alkaline conditions are not conducive to the removal of uranium. This may be because at a low pH the uranium is predominantly uranyl divalent cation (UO\(_2\))\(^{2+}\) form exists. And as the pH increases further, (UO\(_2\))\(^{2+}\) while the proportion of uranyl hydrolyzed ions, such as UO\(_2\)(OH)\(^{+}\), begins to increase. UO\(_2\)(OH)\(^{+}\), (UO\(_2\))\(_2\)(OH)\(_2\), [UO\(_2\)]\(_2\)(OH)\(_3\) decrease.

The removal rate was increased by the stronger adsorption of these monovalent cations with the modified graphene sponge materials. When the pH value exceeds 6.0 and moves towards 7.0, two precipitates, uranyl hydroxide (UO\(_2\)(OH)\(_2\)) and uranium hydrate (UO\(_2\cdot2\)H\(_2\)O), are produced, which will reduce the dissolution of U(VI). Therefore, the removal rate decreases with the decrease of adsorbable U(VI) concentration. Therefore, at pH 7.0, U(VI) removal rate decreases slightly[22].

3.3. Effect of release quality on uranium adsorption capacity

The effect of different dosages of BC/GO/PVA on the removal of U(VI) with an initial concentration of 20 mg/L was studied. The experimental results are shown in Figure 4. It can be clearly seen from Figure 4 that the removal rate increases simultaneously with the increasing amount of adsorbent, but the adsorption capacity decreases. This is because the total amount of uranium removal (mg) increases with the increase of adsorbent surface and adsorption sites. However, the adsorbent's ability to remove contaminants is expressed in milligrams per gram of adsorbed material. Due to the overlap or aggregation of adsorption sites, the adsorption capacity decreases with the increase of the amount of modified graphene sponge.
3.4. Effect of initial concentration on uranium adsorption capacity

The effects of 20-100mg/L initial uranium concentration on the removal rate and adsorption capacity of BC/GO/PVA were studied. The result is shown in Figure 5. When the initial U(VI) concentration increases, the adsorption capacity increases significantly. With the initial concentration of U(VI) increasing from 20 mg/L to 100mg/L, the adsorption capacity per unit mass of BC/GO/PVA increased from 6.5 mg/g to 14.97 mg/g, and the relative removal efficiency of U(VI) decreased from 97.5% to 44.9%. With the increase of initial U(VI) concentration, the adsorption capacity of uranium increases significantly. When the initial uranium concentration is more than 80mg/L, the adsorption capacity of uranium remains almost unchanged. This phenomenon suggests that the adsorption sites are saturated at later stages because only a limited number of active sites are available at high uranium concentrations.

3.5. Effect of temperature on uranium adsorption capacity

The adsorption effect of BC/GO/PVA on U was studied at different temperatures. The results are shown in Figure 6. It can be seen from Figure 6 that different temperature conditions will produce different adsorption curves. The higher the temperature, the higher the adsorption capacity, but the growth rate after 35 °C was not obvious, basically it will not reach the adsorption amount of 14.9 mg/g. Increased with increasing temperature. From this we can speculate that the adsorption of uranium ions by modified graphene sponge was mainly chemical adsorption. Since physical adsorption was generally an exothermic process, the rate of adsorption decreases with increasing temperature. For
chemisorption, an increase in temperature increases the rate of molecular collision and adsorption reactions. When the temperature is raised to 35 °C, the adsorption rate is lowered. The reason may be that the high temperature hinders the adsorption of uranium ions on the sponge, leading to desorption, and physical reactions occur during the adsorption process. [23].

4. Conclusion
In summary, the BC/GO/PVC sponge material was prepared by waste Hawaii nut shell biochar combined with foaming crosslinking method. The sponge was used as the three-dimensional carrier to make the material have a rich three-dimensional pore structure, which overcomes the problem of stacking graphene sheets. The loading of biochar and graphene increases the number of carbon-oxygen functional groups in the material, which was beneficial to the adsorption of uranium. The adsorption mechanism analysis showed that proper temperature increase was beneficial to the adsorption of uranium by materials, endothermic reaction and chemical adsorption of multi-molecular layers. Experiments by batch showed that the maximum adsorption capacity of the material was 14.9 mg/g.

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Author contributions
Yong Liu,Xiaoyan Wu and Mi Li conceived and designed the experiments; Shoufu Yu,Keyou Shi,Chunxue Lv and Peng He performed the experiments; Xiaoyan Wu and Shoufu Yu analyzed the data; Xiaowen Zhang,Qiucai Zhang and Yong Liu contributed reagents/materials/analysis tools; Shoufu Yu wrote and revised the paper. All authors read and approved the manuscript.

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