



Adsorption of U(VI) in Solution by Biochar and FeS Nanoparticles

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ABSTRACT

Uranium (U) is a common radionuclide in soil and groundwater. Uranium contamination often results from uranium mining and processing, nuclear energy power plants, nuclear weapon tests and nuclear accidents. Due to its toxicity and bioaccumulation, it was necessary to treat it effectively. Biochar and FeS nanoparticles were prepared for the treatment of U(VI) in solution. The characteristics of biochar and FeS nanoparticles were determined by Scanning Electron Microscopy, Energy Dispersive Spectrum and Fourier Transform Infrared Spectroscopy and BET adsorption method. The results showed that a large number of functional groups were present on the surface of biochar and FeS nanoparticles. The influencing factors, such as contact time, pH of the solution, initial concentration U(VI) and solution temperature, had an important influence on the adsorption capacity of U(VI) by biochar and FeS nanoparticles.

INTRODUCTION

The development of new energy has become a requirement for sustainable economic development and national defence construction. As a green energy source, nuclear energy has attracted extensive attention from countries around the world (Liu et al. 2010, Vogel et al. 2010). Among them, uranium as the main nuclear fuel needs to increase its development and smelting efforts. However, a large amount of uranium wastewater will be generated during the development, smelting and use of uranium. The direct discharge of uranium wastewater will cause water and soil pollution causing serious harm to the environment and humans (Lovering et al. 2016, Veliscek-Carolan 2016). Therefore, the treatment of uranium wastewater is urgent. The treatment of uranium wastewater usually adopts coagulation-filtration method, evaporation-concentration method, ion exchange method, biological method, adsorption method, etc. (Li et al. 2012). The coagulation-filtration method is a simple process and low cost. However, the concentration of uranium in the effluent of the wastewater treated by this method is relatively high and needs further treatment. The evaporative concentration method is simple, effective and has a high removal rate and high cost. The ion exchange method has good removal rate and low concentration of uranium in the effluent. However, the treatment cost is high, and it is easy to bring secondary pollution. The biological method has a high removal rate, but its practical application is difficult. Adsorption method is a

simple and efficient wastewater treatment method. In recent years, it has been widely used in the treatment of wastewater containing uranium (Feng et al. 2016, Sun et al. 2016, Li et al. 2019, Ma et al. 2019).

At present, the commonly used adsorbents are montmorillonite, kaolin, chitosan, graphene, nano-zero iron, biochar, etc. (Li et al. 2012, Decker et al. 2017, Qiu & Huang 2017). Biochar has become the main application and research adsorbent for pollutant removal in the water environment due to its wide source, economical and environmental protection (Jin et al. 2018). FeS nanoparticles are effective fixatives for the removal of heavy metals with low solubility of metal sulphide (Liu et al. 2008). FeS is a natural sulphide mineral and an excellent fixative for heavy metals for its unique molecular structure, compositions, and surface chemical properties (Maxim et al. 2007, Milad et al. 2018). Heavy metals can be immobilized by FeS through adsorption, ion exchange, and/or chemical precipitation of highly insoluble metal sulphides (Feng et al. 2008). Numerous studies have reported on the remediation of heavy metal contaminated water prepared in the laboratory by FeS (Hua & Deng 2008, Hyun et al. 2012, Lyu et al. 2017).

In this study, biochar and FeS nanoparticles were prepared. The characteristic of biochar and FeS nanoparticles are discussed. Adsorption experiments are carried out. The effect of the operational parameters (such as contact time, initial concentration of U(VI), pH in solution and temperature) on

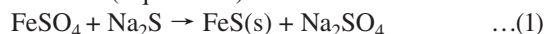
adsorption capacity by biochar and FeS nanoparticles were evaluated in details.

MATERIALS AND METHODS

Materials

Peanut shell was obtained from a farm in the city of Jinan, Shandong province, P.R. China. It was washed three times with water, then dried at 105°C for 24 h, and then milled into powder of 2 mm as the feedstock biomass for biochar production. Ten grams of peanut shell powder was pyrolyzed in a porcelain crucible under the oxygen-limited conditions at 450°C for 2 h in a muffle furnace. The biochar from peanut shell was obtained.

FeS nanoparticles were prepared through co-precipitation of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ in the aqueous phase under anoxic conditions (Equation 1).



All chemicals used in this study were of analytical grade. Sodium sulphide nonahydrate, iron sulphate heptahydrate, NaOH, H_2SO_4 , uranium nitrate hexahydrate ($\text{UO}_2\text{NO}_3\cdot 6\text{H}_2\text{O}$) were obtained from Fengchuan Chemical Technology Co. Ltd. (Tianjin, China).

Adsorption Experiments

Adsorption experiments were carried out on a shaker at 200 rpm under a constant temperature condition. Typically, an amount of the adsorbent was added into 100 mL U(VI) of initial concentration in a 250 mL Erlenmeyer flask. Flask was sealed by a bottle cap and placed in the shaker at 200 rpm and constant temperature. The anaerobic deionized water was used in adsorption experiments. The pH in the solution was adjusted by 0.1 mol/L HCl or NaOH solution. The entire adsorption process reached equilibrium and the supernatant was collected after filtration. The residual sample was centrifuged at 4000 rpm for 5 min. All the experiments

were carried out in duplicate and the data were analysed by the mean and standard deviation.

Analytical Methods

The U(VI) concentration in the supernatant was analysed by UV-vis spectrophotometry. The characteristics of biochar and FeS nanoparticles were determined by Scanning Electron Microscopy (SEM), Energy Dispersive Spectrum (EDS) and Fourier Transform Infrared Spectroscopy (FT-IR), respectively. The specific surface area, pore size and pore volume of biochar and FeS nanoparticles were determined by the BET adsorption method. The amount of adsorption was calculated using the following formula:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad \dots(2)$$

Where, q_e (mg/g) is the amount of adsorption per unit mass of adsorbent at the end of adsorption. C_0 (mg/L) and C_e (mg/L) are the initial concentration of the adsorbate in the solution and the concentration at the equilibrium of adsorption. V (mL) is the volume of solution and m (g) is the dosage of the modified biochar.

RESULTS AND DISCUSSION

Characterization of Biochar and FeS Nanoparticles

SEM images of biochar and FeS nanoparticles were determined by SEM. As shown in Fig. 1A, the morphology of biochar was smooth and a few small fragments were present. While the surface of FeS was compact and aporate (Fig. 1B). The shape was cotton wool. The surface area of biochar ($52.17 \text{ m}^2/\text{g}$) was greater than that of FeS nanoparticles ($18.25 \text{ m}^2/\text{g}$). Some related researches have proved that surface area had an important role in the adsorption capacity.

From Fig. 2A, it could be concluded that biochar included a large number of elements, such as C, O, Si, Mg, K and Ca. Among them, elements of C and O for biochar

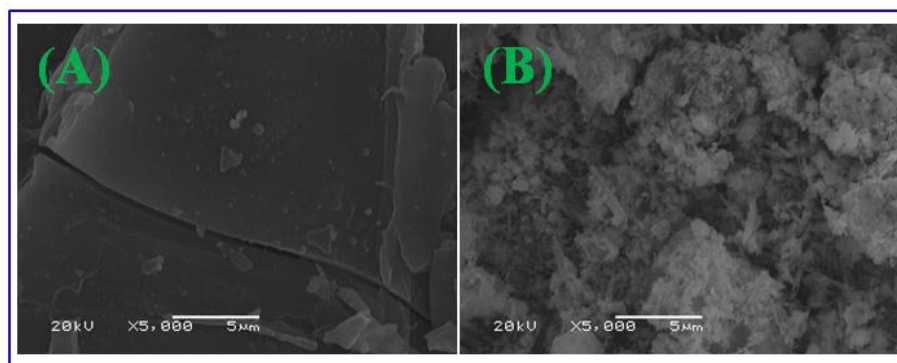


Fig. 1: SEM images of biochar (A) and FeS nanoparticles (B).

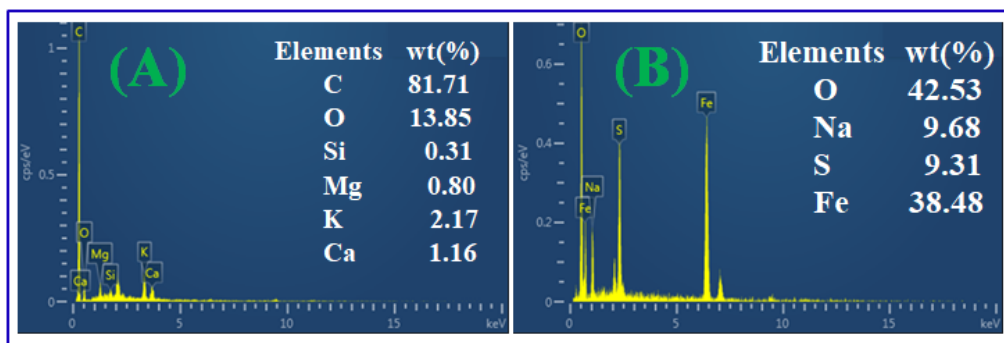


Fig. 2: EDS spectrum of biochar (A) and FeS nanoparticles (B).

were the main elements. Their weights were 81.71% and 13.85%, respectively. The weights of Si, Mg, K and Ca were 0.31%, 0.80%, 2.17% and 1.16%, respectively. For FeS nanoparticles (Fig. 2B), elements of O, Na, S and Fe were observed. Their weights were 42.53%, 9.68%, 9.31% and 38.48%, respectively. The elements of O and Fe were the main elements.

Fig. 3 displayed the characteristic stretching frequencies of biochar and FeS nanoparticles. Six peaks were observed for biochar at 3363, 2021, 1608, 1379, 1061 and 571 cm^{-1} , respectively. They were attributed to the vibrations of -OH, C-C, C=C, O=C-O, C-O and Si-O functional groups. These functional groups benefited for the adsorption of U(VI). For biochar, possible removal mechanisms consisted of electrostatic attraction and surface complexation (Ahmad et al. 2014). For FeS nanoparticles, four peaks were appeared at 3373, 1601, 1375 and 1074 cm^{-1} , respectively. They were attributed to -OH, O=C-O and C-O functional groups.

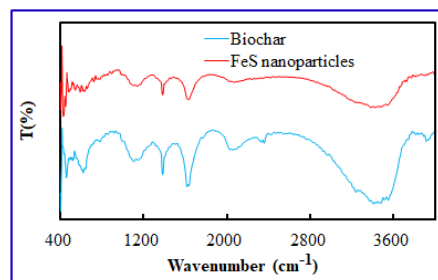


Fig. 3: FT-IR spectrum of biochar and FeS nanoparticles.

Adsorption Experiments

Adsorption experiments were carried out on a shaker at 200 rpm under a constant temperature condition. The effect of operation parameters (such as pH, contact time, initial concentration U(VI) and temperature) on adsorption capacity by biochar and FeS nanoparticles were tested. The experimental results are shown in Fig. 4.

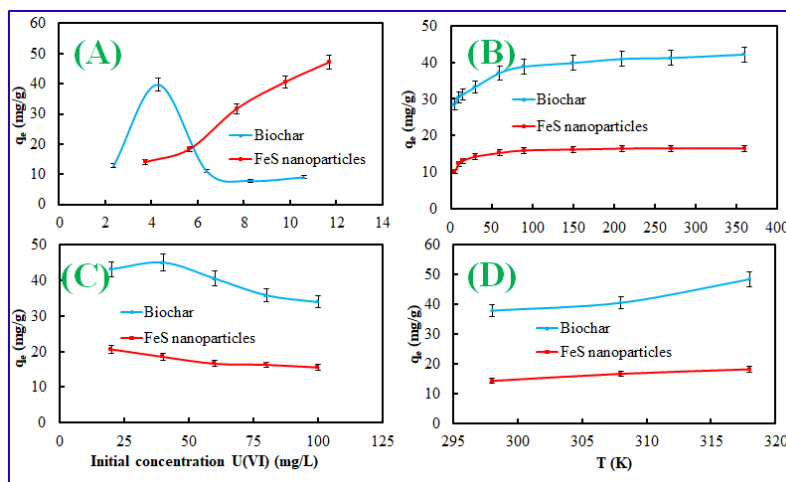


Fig. 4: Effect of operation parameters on adsorption capacity by biochar and FeS nanoparticles (A: pH, B: contact time, C: initial concentration of U(VI), D: temperature).

Effect of pH: pH in solution could affect the stability, surface potential and reactivity of biochar and FeS nanoparticles. Therefore, it was important to evaluate the effect of pH. Experimental conditions were as following: Initial concentration U(VI) was 60 mg/L, contact time was 360 min, dosage of biochar or FeS nanoparticle was 0.1 g, and temperature was 308 K. The initial pH in solution ranged from 2.0 to 12.0. Fig. 4A displayed the effect of initial pH in solution on the adsorption capacity of U(VI) by biochar and FeS nanoparticles. It suggested that the initial pH in solution influenced the adsorption capacity of U(VI) by biochar and FeS nanoparticles. It might be the reason that formation of U(VI) in solution varied with initial pH value in the solution. At alkaline pH, the dominant U(VI) species shifted from positively charged $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_4(\text{OH})_7^+$ to negatively charged $(\text{UO}_2)_3(\text{OH})_7^-$, $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$ (Zhu et al. 2019). Therefore, the initial pH in solution was an important operation parameter for adsorption of U(VI) by biochar and FeS nanoparticles.

Effect of contact time: Experimental conditions were: initial concentration of U(VI) was 60 mg/L, pH was 4.5, the dosage of biochar or FeS nanoparticle was 0.1 g and temperature was 308 K. The contact time was 5, 10, 15, 30, 60, 90, 150, 210, 270 and 360 min, respectively. Fig. 4B described the effect of contact time on the adsorption capacity of U(VI) ions in solution by biochar and FeS nanoparticles. As shown in Fig. 4B, the adsorption capacity of U(VI) increased quickly at the first stage. Then adsorption capacity of U(VI) increased slowly as the contact time increased. The adsorption capacity of U(VI) increased very less when the adsorption process reached adsorption equilibrium. For biochar and FeS nanoparticles, the adsorption equilibrium of contact time was 360 min. At the first stage, U(VI) could be very rapidly adsorbed by biochar or FeS nanoparticles because of many adsorption sites. As the initial concentration of U(VI) increased, adsorption sites were utilized fully and the adsorption process reached saturation gradually.

Effect of initial concentration U(VI): Experimental conditions were: contact time was 360 min, pH was 4.5, the dosage of biochar or FeS nanoparticle was 0.1 g and the temperature was 308 K. The initial concentration U(VI) was 20, 40, 60, 80 and 100 mg/L, respectively. The effect of initial concentration U(VI) on adsorption capacity of U(VI) by biochar and FeS nanoparticles is shown in Fig. 4C. It suggested that adsorption capacity decreased as the initial concentration U(VI) increased. When the initial concentration U(VI) was 100 mg/L, the adsorption capacity for biochar and FeS nanoparticles reached 34.12 and 15.52 mg/g, respectively. The adsorption capacity of biochar was better than that of FeS nanoparticles.

Effect of temperature: Experimental conditions were: initial concentration U(VI) was 60 mg/L, pH was 4.5, the dosage of biochar or FeS nanoparticle was 0.1 g and the contact time was 360 min. The temperature was 298, 308 and 318 K, respectively. It was found that the removal efficiency of U(VI) ion in aqueous solution increased with increasing solution temperature from 293 K to 313 K. It also indicated that the adsorption process is endothermic. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of adsorbate molecules into the pores of biochar or FeS nanoparticles at higher temperatures (Cho et al. 2011, Nethaji et al. 2013).

CONCLUSIONS

The biochar from the peanut shell and FeS nanoparticles was prepared. The characteristics of biochar and FeS nanoparticles were determined by SEM, EDS, FT-IR and BET adsorption method. The adsorption capacity and influencing factors of U(VI) in aqueous solution by the biochar and FeS nanoparticles were studied in detail by the adsorption experiments. The experimental results showed that the influencing factors, such as contact time, pH in solution, initial concentration U(VI) and solution temperature, had an important influence on the adsorption capacity of U(VI) by biochar and FeS nanoparticles.

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