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, 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 by the BET adsorption method. The amount of adsorption was calculated using the following formula:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

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 m²/g) was greater than that of FeS nanoparticles (18.25 m²/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 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:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

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

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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 were carried out in duplicate and the data were analysed by the mean and standard deviation.
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 \(-\text{OH}, \text{C-C}, \text{C=C}, \text{O=C-O}, \text{C-O and Si-O}\) 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 \(-\text{OH}, \text{O=C-O and C-O}\) functional groups.

**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.
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 positively charged (UO\(_2\))\(_5\)(OH)\(_7\)^+ and (UO\(_2\))\(_4\)(OH)\(_7\)^+ to negatively charged (UO\(_2\))\(_5\)(OH)\(_7\)^-, UO\(_2\)(OH)\(_5\) and UO\(_2\)(OH)\(_4\)^+ (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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**REFERENCES**

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S. and Ok, Y.S. 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere, 99: 19-33.

Cho, D.W., Chon, C.M., Kim, Y.J., Jeon, B.H., Schwartz, F.W., Lee, E.S. and Song H. 2011. Adsorption of nitrate and Cr (VI) by cationic polymer-modified granular activated carbon. Chem. Eng. J., 175: 298-305.

Decker, J.D., Folems, K., Clercq, J.D., Meledina, M., Tendeloo, G.V., Laing, G.D. and Voort, P.V.D. 2017. Ship-in-a-bottle CMPO in MIL-101(Cr) for selective uranium recovery from aqueous streams through adsorption. J. Hazard. Mater., 335: 1-9.

Feng, J., Zhu, B.W. and Lim, T.T. 2008. Reduction of chlorinated methanes with nano-scale Fe particles: effects of amphiphiles on the dechlorination reaction and two-parameter regression for kinetic prediction. Chemosphere, 73: 1817-1823.
Feng, M.L., Sarma, D., Qi, X.H., Du, K.Z., Huang, X.Y. and Kanatzidis, M.G. 2016. Efficient removal and recovery of uranium by a layered organic-inorganic hybrid thiostrannate. J. Am. Chem. Soc., 138: 12578-12585.

Hua, B. and Deng, B. 2008. Reductive immobilization of uranium(VI) by amorphous iron sulfide. Environ. Sci. Technol., 42: 8703-8708.

Hyun, S.P., Davis, J.A., Sun, K. and Hayes, K.F. 2012. Uranium (VI) reduction by iron(II) monosulfide mackinawite. Environ. Sci. Technol., 46: 3369-3376.

Jin, J., Li, S.W., Peng, X.Q., Liu, W., Zhang, C.L., Yang, Y., Han, L.F., Du, Z.W., Sun, K. and Wang, X.K. 2018. HNO₃ modified biochars for uranium(VI) removal from aqueous solution. Biore. Technol., 256: 247-253.

Liu, J., Valsaraj, K.T., Devai, I. and DeLaune, R. 2008. Immobilization of aqueous Hg(II) by mackinawite (FeS). J. Hazard. Mater., 157: 432-440.

Liu, M.X., Dong, F.Q., Yan, X.Y., Zeng, W.M., Hou, L.Y. and Pang, X.F. 2010. Biosorption of uranium by Saccharamonosces cerevisiae and surface interaction under culture conditions. Biore. Technol., 101: 8573-8580.

Li, Z.D., Zhang, H.Q., Xiong, X.H. and Luo, F. 2019. U(VI) adsorption onto covalent organic frameworks-TpPa-1. J. Solid State Chem., 277: 484-492.

Li, Z.J., Chen, F., Yuan L.L., Zhao, Y.L., Chai, Z.F. and Shi, W.Q. 2012. Uranium(VI) adsorption on graphene oxide nanosheets from aqueous solution. Chem. Eng. J., 210: 539-546.

Lovering, J.R., Yip, A. and Nordhaus, T. 2016. Historical construction costs of global nuclear power reactors. Energy Policy, 91: 371-382.

Lyu, H.D., Tang, J.C., Huang, Y., Gai, L.S., Zeng, E.Y., Liber, K. and Gong, Y.Y. 2017. Removal of hexavalent chromium from aqueous solutions by a novel biochar supported nanoscale iron sulfide composite. Chem. Eng. J., 322: 516-524.

Ma, F.Q., Nian, J.R., Bi, C.L., Yang, M., Zhang, C.H., Liu, L.J., Dong, H.X., Zhu, M.X. and Dong, B. 2019. Preparation of carboxylated graphene oxide for enhanced adsorption of U(VI). J. Solid State Chem., 277: 9-16.

Maxim, I.B., Edward, J.O., Jeremy, B.F. and Kenneth, M.K. 2007. Adsorption of Fe(II) and U(VI) to carboxyl-functionalized microspheres: The influence of speciation on uranyl reduction studied by titration and XAFS. Geochim. Cosmochim. Ac., 71: 1898-1912.

Milad, M., Reza, T., Abolghasem, F. and Joel, T.M. 2018. Fe(III), Cu(II) and U(VI) binuclear complexes with a new isothiosemicarbazon ligand: Syntheses, characterization, crystal structures, thermal behavior and theoretical investigations. Inorg. Chim. Acta, 4821: 643-653.

Nethaji, S., Sivasamy, S. A. and Mandal, A.B. 2013. Preparation and characterization of corn cob activated carbon coated with nano-sized magnetite particles for the removal of Cr(VI). Biore. Technol., 134: 94-100.

Qiu, M.Q. and Huang, P. 2017. Kinetic and thermodynamic studies on the adsorption of zinc ions from aqueous solution by the blast furnace slag. Nature Environ. Poll. Technol., 16: 639-642.

Sun, Y.B., Zhang, R., Ding, C.C., Wang, X.X., Cheng, W.C., Chen, C.L. and Wang, X.K. 2016. Adsorption of U(VI) on sericite in the presence of Bacillus subtilis: A combined batch, EXAFS and modeling techniques. Geochim. Cosmochim. Ac., 180: 51-65.

Veliscek-Carolan, J. 2016. Separation of actinides from spent nuclear fuel: A review. J. Hazard. Mater., 318: 266-281.

Vogel, M., Günther, A., Rossberg, A., Li, B., Bernhard, G. and Raff, J. 2010. Biosorption of U(VI) by the green algae Chlorella vulgaris in dependence of pH value and cell activity. Sci. Total Environ., 409: 384-395.

Zhu, W., Lei, J., Li, Y., Dai, L., Chen, T., Bai, X., Zhou, J., Wang, L. and Duan, T. 2019. Procedural growth of fungal hyphae/Fe₃O₄/graphene oxide as ordered-structure composites for water purification. Chem. Eng. J., 355: 777-783.