Removal of U (VI) From Aqueous Solution By Effective Bio-Adsorbent From Walnut Shell And Cellulose Composites Stabilized Iron Sulfide Nanoparticle

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9
10 **Abstract**

11 FeS nanoparticles were easily aggregated and oxidized in the natural environment due
12 to van der Waals forces between nanoparticles. Biochar could be used as a carrier to
13 inhibit the agglomeration and oxidization of FeS nanoparticles. An efficient
14 bio-adsorbent (CFeS-WS) from walnut shell (WS) and cellulose composites stabilized
15 iron sulfide nanoparticle was synthesized by the modified method. It also was
16 determined by SEM, EDS, XRD and FT-IR, respectively. The removal of U(VI) ions
17 from aqueous solution by CFeS-WS were conducted. The reaction mechanism
18 between CFeS-WS and U(VI) ions also were discussed in details. The experimental
19 results were showed that the biochar successfully was supported with cellulose/FeS
20 composites (CFeS). CFeS-WS exhibited an excellent removal performance for U(VI)
21 ions in solution. The adsorption process of U(VI) ions by CFeS-WS was more
22 consistent with pseudo second-order kinetic model and Langmuir isotherm model.
23 The proposed reaction mechanism of U(VI) ions removal by CFeS-WS mainly
24 consisted of ion exchange reaction, reduction reaction, hydrogen bonding and
25 functional group, and pore of adsorbent filling. Recycle experiment indicated that
26 CFeS-WS was a cost-effective bio-adsorbent.

27 **Keywords: Removal; U(VI); Iron sulfide nanoparticle; Cellulose; Walnut shell**

Introduction

For nuclear energy, uranium is the main fuel in the nuclear industry and the main component of nuclear waste (Ma et al. 2015, Sun et al. 2016, Zhang et al. 2021). Because of its low price and non-polluting advantages, it is considered to be one of the potential substitutes for fossil fuels in the future (Pegg 2015; Hao et al. 2021). However, Uranium also is radioactive and carcinogenic for a long time. Even a small amount of uranium may cause serious harm to human health and environment (Sun et al. 2014, Xu et al. 2015, Troyer et al. 2016). Therefore, the disposal of nuclear waste is a very challenging problem and an urgent problem that needs to be solved (Sheng et al. 2012, Qiu et al. 2021). According to the perspective of economic and practical efficiency advantages, adsorption technology has gradually attracted the attention of researchers (Tan et al. 2009, Wang et al. 2015, Qiu et al. 2018, Hu et al. 2019). Various adsorbents are applied into the treatment of radioactive wastewater (Chen et al. 2007, Yu et al. 2008, Sheng et al. 2014, Sun et al. 2015, Popel et al. 2016, Yao et al. 2018). Many adsorbents (such as carbon fibers, carbon nanotubes and graphene oxide et al.) have been applied into the removal of U(VI) from environment (Senanayake & Idriss 2006, Hedhili et al. 2000, Hyun et al. 2012, Yu et al. 2016). In recent years, the application of iron-based materials was studied because of their environmental friendliness and high treatment processing efficiency. Therefore, they have attracted the attention of many scholars (He et al. 2010). More and more researchers have begun to develop a variety of different iron-based materials to remove the radioactive uranium from wastewater (Shi et al. 2015, Sun et al. 2016, Qiu & Huang 2017, Li et al. 2019). Ferrous sulfide (FeS) is one of the iron-based materials (Bostick et al. 2000). Compared with other iron-based materials, it is more effective in treating U(VI) wastewater due to the presence of Fe^{2+} ions and S^{2-} ions (Duan et al. 2016, Rehmana et al. 2018, Maity & Agrawal 2007, Hussain et al. 2017, Hua & Deng 2008). Because of their large volume ratio and high reactivity, nanoparticles are widely used to treat pollutants in sewage and soil (Cao et al. 2018, Wang et al. 2021). However, FeS nanoparticles are easily aggregated and oxidized in the natural environment due to van der Waals forces between nanoparticles. This

reduces the reactivity between nanoparticles and pollutants. This reduces the contact area between nanoparticles and pollutants and thus affects the reactivity between them. This problem has become an important factor limiting the application of FeS nanoparticles into pollution treatment. It was very important to look for a suitable stabilizer to modify FeS nanoparticles.

Various techniques have been tested to overcome the shortcoming of FeS nanoparticles, such as silica, sepiolite, activated carbon and biochar et al. (Liu et al. 2011, Oliveira et al. 2014, Liang et al. 2016, Zhang et al. 2016, Wang et al. 2018). Compared with other materials, biochar presented some advantages. They were large specific surface area, high stability, low bulk density, strong adsorption capacity, low cost and simple operation (Qiu et al. 2017). As an emerging adsorbent, biochar had the advantages of wide sources of raw materials and low price, so it had huge application potential in uranium (VI) adsorption (Amuda et al. 2007, Veeramani et al. 2011, Yang et al. 2016). Biochar was a carbon-rich solid material, which was obtained under anoxic conditions. Biochar had attracted more and more attention due to its high efficient removal rate, novel porosity, high specific surface area and low cost. It had been proved that biochar could be considered as an effective material to eliminate U(VI) from aqueous solution (Zou et al. 2013, Hu et al. 2021). Additionally, biochar could be used as a carrier to inhibit the agglomeration and oxidization of FeS nanoparticles. Therefore, it was important to stabilize iron sulfide nanoparticle composite with a stabilizer before being supported by biochar. Furthermore, the removal of U(VI) ions in solution by biochar stabilized iron sulfide nanoparticle composite are reported relatively few.

The overall objective of this work was to synthesize an efficient bio-adsorbent(CFeS-WS) from walnut shell(WS) and cellulose composites stabilized iron sulfide nanoparticle(FeS), and elaborate the reaction mechanism between CFeS-WS and pollutant. The characterization of CFeS-WS was determined by SEM, EDS, XRD and FT-IR, respectively. The U(VI) ions were selected as contaminant to test the removal rate. The specific objectives were to: (1) synthesize and characterize of CFeS-WS; (2) assess the influences of operating parameters on the removal rate of

U(VI) in solution; (3) describe reaction mechanism between U(VI) ions and CFeS-WS.

Materials and methods

Chemical reagents

The walnut shell(WS) was obtained from the farm Fuzhou City, Jiangxi Province, P.R. China. In this experiment, chemical reagents all were analytical grade and used without further purification. Chemical reagents, such as cellulose, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, were purchased at Shanghai McLin Chemical Reagent Co. Ltd. (Shanghai, China). Moreover, they all were analytical grade. Under the magnetic stirring condition, the deionized water was aerated by nitrogen for about 30 min. Then, the anaerobic deionized water was obtained.

Preparation of adsorbents

According to the modified method (Lyu et al. 2018), the preparation of biochar from walnut shell, FeS nanoparticle and CFeS-WS were prepared, respectively. Preparation of biochar derived from walnut shell, FeS nanoparticles and CFeS-WS were shown in Supporting Information. In a word, biochar from walnut shell were added into 250 mL Erlenmeyer flask containing of FeSO_4 . They were stirred for 30 min. Then, cellulose and Na_2S were added, mixed with them, stirred for 30 min again. In the process of preparation, they were conducted under magnetic stirring condition and continuous aerating nitrogen. Next, the mixture solution was placed at the temperature of 25°C for 48 h, freeze-dried for 12 h, washed for three times with anaerobic deionized water, and freeze-dried for 12 h. The efficient bio-adsorbent of CFeS-WS was obtained.

Characterization

SEM (SIGMA, Germany) was used for observing the surface morphology and structure of adsorbents. FT-IR spectrometer (Nexus 670, Madison) in the wave number range of $400\text{--}4000\text{ cm}^{-1}$ was used for testing the surface functional groups of

adsorbents. D/Max-III A Powder X-ray Diffractometer (Rigaku Corp., Japan) was used to analyze XRD of adsorbents.

Batch experiments

The batch experiments were conducted at a shaker. Added 100 mL U(VI) ions solution into 250 mL of Erlenmeyer flask. Then, adsorbents were put into 250 mL of Erlenmeyer flask. The pH in solution was adjusted by 0.2 mol/L NaOH or 0.2 mol/L HCl, respectively. Next, flask was sealed by bottle cap, which was placed in the shaker at 150 rpm and constant temperature. After the entire experimental process reached equilibrium, the supernatant was sampled by filter filtration. The U(VI) ions in solution was analyzed by method of UV-vis spectrophotometry (Liu et al. 2018). Then, the residual solution was centrifuged at 5000 rpm for 10 min. The obtained sediment also was determined.

In order to describe the removal mechanisms and the characteristic of adsorption process, the influences parameters (for example, initial of pH value in solution, initial concentration of U(VI) ions, reaction time and temperature) on the removal rate of U(VI) ions in solution by adsorbents were tested. The calculation of the removal rate ($R(\%)$) and uptake capacity ($q(\text{mg/g})$) were shown in Supporting Information.

Results and discussion

Characterization of composites

The SEM images of biochar, FeS nanoparticle, FeS-WS and CFeS-WS were showed in Fig.1. From Fig.1A, it could be seen that biochar was irregular shape and rough surface. However, there were very few pores on the surface of biochar. FeS nanoparticles were aggregated flocculent shape and looked like snowflake or flower (Fig.1B). Fig.1C showed clearly that the discrete FeS nanoparticles were observed on the irregular and rough surface of biochar. It also indicated that the like snowflake FeS nanoparticles were appeared on the surface of biochar, and were connected with biochar. The existence of biochar could inhibit the agglomeration of FeS

nanoparticles in a certain extent. However, it also could be found that the amount of FeS nanoparticles loaded on biochar was small. The SEM image of CFeS-WS was shown in Fig.1D. It depicted that the surface of biochar was covered by a large number of fine particles. It could be concluded that the particles on the surface of biochar were FeS nanoparticles. The biochar successfully was loaded with cellulose and FeS nanoparticles composites. The cellulose and biochar effectively prevent the agglomeration of FeS nanoparticles. It would improve the ability to remove pollutants.

Fig.1 SEM images of biochar(A), FeS nanoparticles(B), FeS-WS(C) and CFeS-WS(D)

EDS layered images and EDS spectrum of biochar, FeS nanoparticles, FeS@biochar and CFeS-WS were depicted in Fig.2. It clearly indicated that FeS nanoparticles were embedded inside cellulose-FeS@biochar composites. For biochar, there were two obvious peaks corresponding to two elements of C (61.77%) and O (38.23%). Furthermore, the two elements of Fe (4.68%) and S (0.71%) were observed for

CFeS-WS (Fig.2D). This result revealed that biochar as a skeleton material was loaded by Fe and S elements evenly. There were some FeS nanoparticles on the surface of biochar. The FeS nanoparticles were attached on the surface of biochar uniformly due to the large surface area of the biochar and the dispersibility of CFeS-WS. In other words, the preparation of CFeS-WS successfully was obtained again. This result was consistent with the results of Fig.1. FT-IR spectra and XRD patterns of biochar, FeS nanoparticles, FeS-WS and CFeS-WS were shown in Fig.3.

For biochar, five characteristic peaks were appeared at wavelengths of 563, 1051, 1373, 2330 and 3435 cm^{-1} , respectively (Fig.3A). They were attributed to the vibration of alkoxy C-O, carboxyl O=C-O, C=C, C $\equiv$ C and -OH functional groups (Devi & Saroha 2014). For FeS-WS and CFeS-WS, the other functional groups were observed except for C $\equiv$ C functional groups. It might be the reason that biochar interacted with FeS nanoparticles. XRD patterns (B) of biochar, FeS nanoparticles, FeS-WS and CFeS-WS were depicted in Fig.3B. For biochar, a characteristic diffraction peak was appeared at 22.1°. It should be characteristic peak of biochar (Yen et al. 2011, Nguyen & Pho, 2014, Zhang et al. 2015). For FeS nanoparticle, eight characteristic diffraction peaks were observed. They were assigned to the (101), (004), (200), (110), (204), (205), (303) and (222) planes of the FeS (JCPDS No. 23-1120). It could be proved that the pure crystalline was formed during the preparation process (Bacik et al. 2012, Lyu et al. 2016).

Fig.2 EDS layered images and EDS spectrum of biochar (A), FeS nanoparticles (B), FeS-WS (C) and CFeS-WS (D)

Fig.3 FT-IR spectra (A) and XRD patterns (B) of biochar, FeS nanoparticles, FeS-WS and CFeS-WS

Effects of operational parameters on removal of U(VI) ions

The value of pH was an important operational parameter in the adsorption process of U(VI) ions by CFeS-WS. The influence of pH in solution on U(VI) ions removal was

tested with a different pH ranged from 2 to 12. As shown from Fig.4A, it depicted that the removal rate of U(VI) ions was increasing with the increasing of pH at first stage. When pH in solution was ranged from 4 to 8, the removal rate of U(VI) ions reached maximum adsorption. Subsequently, the removal rate of U(VI) ions began to decrease along with the increasing of pH in solution. This result was related to the species distribution of U(VI) ions in aqueous solution. The species distribution of U(VI) ions at different pH were shown in Fig.7 of Supplement materials. When value of pH in solution was less than 2.0, the main form of U(VI) ions in solution was UO_2^{2+} ions. Along with the value of pH in solution increased, the concentration of UO_2^{2+} ions began to decrease. The concentration of $(UO_2)_2(OH)_2^{2+}$ and $UO_2(OH)^+$ in solution were increasing slowly. When pH was 7.0, the main form of U(VI) ions in solution was $(UO_2)_2(OH)_2^{2+}$, $UO_2(OH)^+$ and $UO_2(OH)_2$, respectively. When the value of pH>7.0, the main form of U(VI) ions in solution was $UO_2(OH)_2$, $UO_2(OH)_3^-$, $(UO_2)_3(OH)^{7-}$ and $UO_2(OH)_4^{2-}$, respectively. The value of pH in solution had an important influence on the species distribution of U(VI) ions.

The contact time played a role in the adsorption process of U(VI) ions in solution (Fig.4B). It could be found that the removal rate of U(VI) ions increased quickly with the increasing of contact time. However, the removal rate of U(VI) ions began to increase very slowly as contact time reached 100 min. Subsequently, the removal rate of U(VI) ions increased very little. This might be the reason that there were a lot of vacancies on the surface of the adsorbent at the beginning of adsorption process. As the adsorption process progressed further, the vacancy available for adsorption decreased gradually. The initial concentration of U(VI) ions in solution had an important effect on the removal rate (Fig.4C). It depicted that the removal rate decreased with the increasing of initial concentration. This might be this reason that the adsorption sites on the surface of adsorbent were not saturated at low concentration. Furthermore, under the driving force of the concentration gradient, the adsorption capacity of adsorbent also was increased (Nguyen & Pho 2014, Zhang et al. 2016). These experimental results confirmed that concentration of U(VI) had an important effect on the removal rate of U(VI) ions in solution. The reaction

temperature was benefit to enhance the removal rate of U(VI) ions by CFeS-WS (Fig.4D). The removal rate was increasing with an increase of the reaction temperature.

Fig.4 Effects of operational parameters on U(VI) ions removal in solution (A: pH; B: contact time; C: concentration of U(VI) and temperature)

Adsorption kinetics, adsorption isotherms and thermodynamic

In this study, pseudo first-order kinetic model and pseudo second-order kinetic model were used for the calculation of kinetic data (Leite et al. 2017). Pseudo first-order kinetic model and Pseudo second-order kinetic model were shown Supporting Information. Kinetics curves of U(VI) ions in solution onto CFeS-WS were described as Fig.5A-B.

The results were shown that the correlation coefficient of pseudo second-order kinetic model ($R^2=0.9937$) was higher than that of pseudo first-order kinetic model ($R^2=0.9792$). It was suggested that the order of adsorption process of U(VI) ions by CFeS@biochar should be a chemical reaction.

Adsorption isotherms could describe the relationship between the degree of accumulation of adsorbate onto an adsorbent surface to the concentration of adsorbate at constant temperature. In this research, the Langmuir isotherm model and Freundlich isotherm model were used to fit the adsorption data in order to display the adsorption behavior of U(VI) ions in solution onto CFeS-WS. Langmuir isotherm model and Freundlich isotherm model were shown Supporting Information.

Fig.5 The kinetic adsorption and the adsorption isotherm for U(VI) by CFeS-WS (pseudo first-order kinetic model (A), pseudo second-order kinetic model (B), Langmuir isotherm model (C) and Freundlich isotherm model (D)).

The adsorption isotherms of U(VI) ions in solution onto CFeS-WS were given in Fig.5C-D. According to the correlation coefficients, it was showed that the adsorption process of U(VI) ions by CFeS-WS was more consistent with Langmuir isotherm model ($R^2=0.9848$). It also indicated that the value of q fitted by Langmuir isotherm model was closer to the adsorption experimental data.

In order to explore further mechanism of U(VI) uptake, thermodynamic parameters

are evaluated to determine the spontaneity of the reaction. Calculation of thermodynamic parameters was shown in Supporting Information. ΔH^0 and ΔS^0 were calculated from the slope and the intercept respectively. The results of calculation were listed in Table 1.

Table 1 Thermodynamic parameters of U(VI) removal by CFeS-WS

ΔG^0 (kJ/mol)			ΔH^0 (kJ/mol)	ΔS^0 (J/mol/K)	R^2
298 (K)	308 (K)	318 (K)			
-3.48	-5.45	-8.11	231.15	60.65	0.9912

It showed that the values of ΔG^0 were all negative. It indicated that the adsorption process of U(VI) ions in solution onto CFeS-WS was a spontaneous process under experimental conditions. The value of ΔG^0 decreased as the reaction temperature increased. It depicted that the increase of reaction temperature was conducive to the reaction. The value of ΔH^0 was 231.15 kJ/mol and the value of ΔS^0 was 60.65 J/mol/K. It indicates that the adsorption process of U(VI) ions was an endothermic process. The system had a higher level of confusion.

Proposed reaction mechanism

According to the characterization of CFeS-WS, it could be concluded that there were a lot of FeS nanoparticles on the surface of CFeS@biochar composites. Additionally, there also were a lot of alkoxy C-O, carboxyl O=C-O, C=C, C $\equiv$ C and -OH functional groups on the surface of CFeS-WS. Furthermore, they also were irregular shape and rough surface. Therefore, the following reaction mechanism in this research could be suggested. It could be depicted at Fig.6.

Fig.6 The proposed reaction mechanism

As shown from Fig.6, it indicated that the reaction mechanism of U(VI) removal by CFeS-WS mainly consisted of ion exchange reaction, reduction reaction, hydrogen bonding and functional group, and pore of adsorbent filling. The related chemical reactions were as following (Hyun et al. 2012).

Eqn.10-13 indicated that UO_2^{2+} could be adsorbed on the surface of FeS nanoparticles through an ion exchange reaction. Then, U(VI) ions were reduced by S^{2-} ions and HS^- ions, respectively. S^{2-} ions and HS^- ions all were released from the dissolution of FeS(s).

There were a lot of alkoxy C-O, carboxyl O=C-O, C=C, C≡C and -OH functional

groups on the surface of CFeS@biochar composites. U(VI) ions in solution could be adsorbed through hydrogen bonding and functional groups. Additionally, a lots of adsorption location could be observed on the surface of CFeS-WS composites. It could be adsorb the U(VI) through pore of adsorbent filling.

In a word, the reaction mainly mechanism of U(VI) removal by CFeS-WS consisted of ion exchange reaction, reduction reaction, hydrogen bonding and functional group, and pore of adsorbent filling.

Recycle experiment

The ability of recycle was very important for the efficient bio-adsorbent in order to improve the economic value of the reaction process. The adsorption experiment was carried out at pH 6.0, 40 mg/L of U(VI) concentration, 0.05 g of CFeS-WS, contact time of 6 h, temperature of 318 K and 150 rpm. The 0.1 mol/L H₂SO₄ was used to desorb U(VI) ions from the surface of the adsorbent. Performance of CFeS-WS was evaluated according to five consecutive recycles of adsorption-desorption. The experimental results were shown in Fig.7.

Fig.7 The recycle time of CFeS-WS for removal of U(VI) ions in solution

As from Fig.7, it could be found that during the five consecutive recycles of adsorption-desorption, the removal rate of U(VI) ions was 68.12%, 66.03%, 62.83%, 61.27% and 59.06%, respectively. It could be concluded that the chemical stability of CFeS-WS was very well. CFeS-WS was a cost-effective bio-adsorbent.

Conclusions

An efficient bio-adsorbent from walnut shell stabilized iron sulfide nanoparticle composites were prepared. The biochar of walnut shell successfully was loaded by cellulose and FeS nanoparticles composites. The cellulose and biochar could prevent effectively the agglomeration of FeS nanoparticles. The adsorption process of U(VI) ions by CFeS-WS was more consistent with Langmuir isotherm model and pseudo second-order kinetic model. The adsorption process of U(VI) ions in solution onto CFeS-WS was a spontaneous process under experimental conditions. The adsorption process of U(VI) ions was an endothermic process. The system had a higher level of confusion. The proposed reaction mechanism of U(VI) ions removal by CFeS-WS mainly consisted of ion exchange reaction, reduction reaction, hydrogen bonding and functional group, and pore of adsorbent filling. CFeS-WS was a cost-effective bio-adsorbent.

Ethical Approval

This section is “not applicable” for this study.

Consent to Participate

Not applicable.

Consent to Publish

All authors reviewed and approved the manuscript for publication.

Authors Contributions

Huifang Huang and Renrong Liu designed the experiment, and Li Han performed the

experiment. Muqing Qiu processed the experimental data and wrote this article.
Baowei Hu revised this paper.

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Competing Interests

The authors declare no competing interests.

Availability of data and materials

The data and materials presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy restrictions.

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