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Adsorption of Cr(VI) from wastewater by iron-modified coconut shell biochar

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Abstract. This study is aimed to investigate the effect of raw and Fe-modified coconut shell biochar on the adsorption of Cr(VI) in the wastewater. Fe-modified biochar was obtained from the impregnation with $FeNO_3$ solutions and the surface functional groups of two biochars were examined by infrared spectrometer.The result showed that the Fe-modified biochar had lower abundance of the surface functional groups than that of raw biochar, and had the group of Fe-O.The removal rate of Cr(VI) increased by 94.89% compared with the raw biochar because of existing of the group of Fe-O . The removal rate of Cr(VI) by modified biochar could reach more than 99.0% when the concentration of Cr(VI) was 12μg/ mL, pH 4.0, adsorbent dosage was 0.2g and adsorption time was 2h.

1 Introduction

Cr(VI) in wastewater mainly comes from leather preparations, chromium plating , industrial pigments, etc. Cr(VI) has strong toxicity, carcinogenicity and mutagenicity, which can actively migrate and transform among water, soil, atmosphere and biology[1-2].The treatment methods of Cr(VI) in wastewater mainly includes chemical precipitation, electrolysis, reverse osmosis, adsorption, ion exchange and biological methods[3-4]. The adsorption method has good adaptability and effect, which is the main treatment method. Biochar is paid attention to researcher in the study of adsorption materials because of its huge specific surface area and functional groups[[5]]. Biochar's adsorption efficiency can be improved by modifying owing to changing its surface properties. The modification methods mainly include oxidation, reduction, metal ion loading, microwave treatment and so on.Metal ion-loaded modification is usually used because of simple and low cost. Metal ions are adsorbed on the surface of biochar, and the adsorption capacity of biochar to target adsorbents is improved through the mutual adsorption[6]. In this study, the influence of biochar modified by iron nitrate on the adsorption removal effect of Cr(VI) by changing concentration of Cr(VI) , adsorption time, pH value and other factors was studied.

2 Materials and methods

2.1 Reagents and instruments

Coconut shell biochar, iron nitrate, potassium dichromate, pH meter, atomic absorption spectrophotometer(AAS, Shimazu AA7000), Infrared spectrometer(IR, PerinElmer Frontier).

2.2 Experiment of biochar modified by iron nitrate

20g of coconut shell biochar was weighed into 100ml $FeNO_3$ solution of 0.5mol /L, placed in a water bath at 100 ℃ , and constantly stirred until the solution evaporating. Then, the biochar was taken out, washed with deionized water repeatedly until the lotion was colorless, and put into the oven to dry for 10h.

2.3 Adsorption test

The adsorption experiment was conducted in a volume of 25ml solution. The effect of raw and modified biochar on the adsorption of Cr(VI) in the solution was studied when the concentration of Cr(VI) was 10μg/ml, pH value was 4, absorption time was 2h, and dosage was 0.2g. The effects of the pH, adsorbent dosage,adsorption time, and Cr(VI)concentration on removal rate and adsorption capacity were also studied by changing a single factor of the above experiment conditions.

The content of Cr(VI) in the filtrate was determined by AAS. The removal rate η and adsorption capacity q were calculated according to the reference[7-8].

The calculation formula is as follows:

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$

In the formula: C_0 -- Cr(VI) concentration in water before adsorption (μg/ml);

C -- Cr(VI) concentration in the filtrate after filtration (μg/ml)

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$$q(mg/g) = \frac{C_0 - C}{W} \cdot \frac{V}{1000}$$

In the formula: W--weight of modified biochar, g;
V -- Cr(VI) solution volume, mL

3 Results and analysis

3.1 Infrared spectra of coconut shell biochar

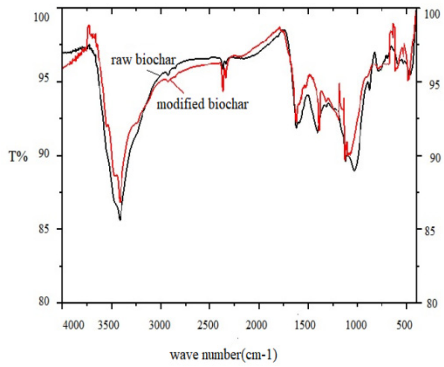

Fig. 1 Fourier infrared spectrum of biochar

It can be seen from Figure 1 that both biochar had almost same absorption peaks. The broad adsorption peak at 3500cm^{-1}-3000cm^{-1} was formed by stretching vibration of hydroxyl O-H , the adsorption peak around 1700cm^{-1} was formed by C=O and C=O, and the peaks at 1500cm^{-1}-1000cm^{-1} represented the bend vibration peak of C-H.The overall absorption strength of modified biochar was a little lower than that of raw biochar, which indicates that the surface functional groups decreased because of iron materials. There were some differences around 750cm^{-1}-500cm^{-1}. This indicated that there was the bending vibration of Fe-O, which further verified the successful loading of iron materials on the surface of the biochar[9].

3.2 The effect of raw and modified biochar on Cr(VI) removal rate

The Comparison effect of raw and modified biochar on Cr(VI) removal rate was conducted. The result showed that the raw biochar had only 4.66% removal rate of Cr(VI) in solution and 0.0622mg/g adsorption capacity. However, using modified biochar, the removal rate could be increased to 99.55%, the adsorption capacity increased to 1.27mg/g. The removal rate of the modified biochar was 94.89% higher than that of the raw biochar. The surface of raw biochar was loaded with a large number of negative group, and most of Cr(VI) existed in the form of anion such as $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$, and $HCrO^{4-}$ in the solution. The electrostatic repulsion between the negative group and the anion on the surface of raw biochar leaded to the poor adsorption capacity. Modified biochar carried lots of iron ion, formed more cationic group center on the biochar surface, and it was conducive to adsorb Cr(VI) [10]. So the removal rate of Cr(VI) in water was improved largely.

3.3 Effect of pH in the solution on Cr(VI) removal rate

The effect of pH on adsorption of Cr(VI) in the solution by modified biochar was studied .

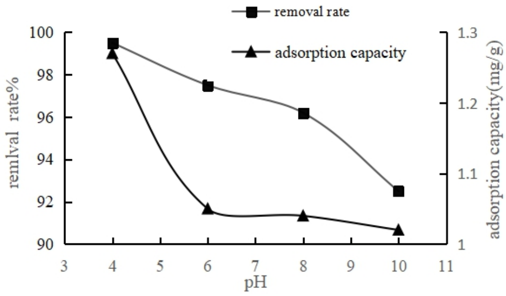

Fig. 2 Effect of pH on adsorption of Cr(VI)

As can be seen from Figure 2, adsorption rate was 99.5% when pH was 4, and then decreased with pH increasing. This was because the negative groups like -OH and -C=O on the biochar surface occured protonation reaction at low pH which was beneficial to adsorb $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the solution. However, because of deprotonation with the increase of pH , the number of positive adsorption centers decreased, resulting in the decrease of electrostatic adsorption and low removal rate[11].

3.4 Effect of adsorbent dosage on Cr(VI) removal rate

As can be seen from Figure 3, the removal rate of Cr(VI) increased with the amount of adsorbent increasing, reached the maximum of 99.2% at 0.2g and then kept stable. The adsorption capacity increased slowly and reached the maximum of 1.30mg/g at 0.15g and then decreased. The adsorbent sites were fully utilized by Cr(VI) in the solution at low dosage, which resulted in a higher adsorption capacity and improved removal rate. However, when the amount of adsorbent increased to a certain extent, the absorption equilibrium achieved between the modified biochar and the solution. So the removal rate kept stable and the adsorption capacity decreased with the adsorbent dosage improved.

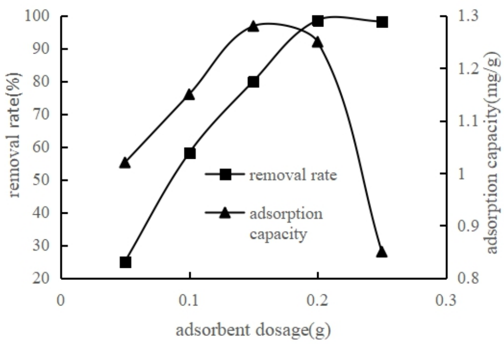

Fig. 3 Effect of dosage on adsorption of Cr(VI)

3.5 Effect of adsorption time on Cr(VI) removal rate

As can be seen from Fig. 4, the removal rate and adsorption capacity increased rapidly during 0.5~1h, and the growth slowed down during 1h ~2h, and reach the peak at 2h, and then maintained a relative balance during 2h ~ 4h. At the beginning of adsorption experiment, there were lots of adsorption sites on the surface of the modified biochar, which could be occupied by Cr(VI) rapidly, and the removal rate and adsorption capacity both showed an obvious upward trend. Cr(VI) could enter inside the modified biochar slowly during 1-2h , which resulted in low growth in removal rate and adsorption capacity until equilibrium at 2h. The removal rate and adsorption capacity changed little during 2-4h, even slightly decreased owing to desorption. This was consistent with the three-stage adsorption described by Peng Fang et al[12-13].

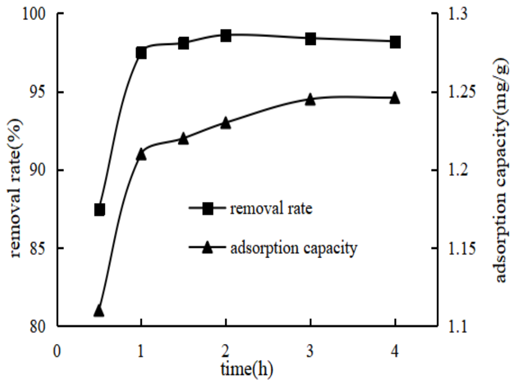

Fig.4 Effect of time on adsorption of Cr(VI)

3.6 Effects of Cr(VI) concentration on removal rate

As can be seen from Figure 5, the removal rate basically stabilized at about 99% and the

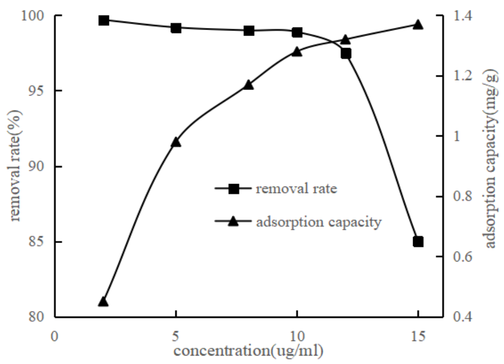

Fig. 5 Effect of concentration on adsorption of Cr(VI)

adsorption capacity gradually increased during 2 μg/mL~12μg/mL because of the sufficient adsorption sites. When the concentration was more than 12μg/mL, there were not so many adsorption sites and the adsorption capacity was close to the maximum , so the removal rate reduced.

4 Conclusion

Coconut shell biochar was modified by using iron nitrate solution. The removal rate and adsorption capacity of Cr(VI) in wastewater by modified biochar were studied by changing certain factors, such as pH, adsorbent dose, adsorption time and concentration of Cr(VI). The results showed that:

(1)The removal rate and adsorption capacity of Cr(VI) in wastewater by modified coconut shell biochar was 99.55% and 1.27mg/g, which were much higher than that by raw biochar, indicating that the adsorption effect of Cr(VI) by modified biochar could be improved largely.

(2)The optimum conditions for adsorption of Cr(VI) in wastewater by modified biochar were as follows: The removal rate of Cr(VI) in wastewater reached above 99.0% when pH was 4, the dosage was 0.2 g, the adsorption time was 2h, and the initial concentration of Cr (VI) was 12μg/ml.

Acknowledgments

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