Research on Adsorption of Cr(VI) in Water by Potassium Chloride Modified Peanut Shell Carbon

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Abstract: In order to remove Cr (VI) in water effectively, peanut shell carbon was modified by potassium chloride. The results showed that the removal rate of modified peanut shell carbon was 50.3%, increasing by 17.73% compared with peanut shell carbon. The removal and adsorption effects of modified shell carbon on Cr (VI) under different adsorption conditions were investigated and which including pH, adsorbent dosage, adsorption time and the ion concentration. The results showed that the best adsorption removal efficient of Cr (VI) in water can be obtained with pH of 4, adsorption dosage of 0.3g, the adsorption time of 150 min, and the Cr (VI) concentration of 8μg/ml. The removal rate of modified peanut shell carbon reached 99.86% under the condition. The adsorption process fitted the Freundlich adsorption isotherm and conformed to the quasi-second order kinetic equation.

1. Introduction

The accumulation of heavy metals in the environment is a serious problem through artificial pollution such as mining, metal smelting and processing, discharge of chemical wastewater, abuse of pesticides and fertilizers, and disposal of various kinds of garbage. Chromium pollution mainly comes from leather preparations, chromium plating parts of metal, industrial pigments, rubber and ceramic raw materials, etc. Chromium mainly exists in the form of Cr(III) and Cr (VI) in the environment. Among them, Cr(VI) has strong toxicity, carcinogenicity and mutagenicity, which can actively migrate and transform among water, soil, atmosphere and biology. It is one of the priority heavy metals monitored on the blacklist of environmental priority pollutants in China, and is also listed as one of the internationally recognized carcinogenic metals[1-2].

Heavy metal pollution has the characteristics of concealment, long-term and irreversibility, so the treatment of heavy metal in wastewater has been highly valued by scientific researchers. There are many methods to treat heavy metals in wastewater. Traditional methods mainly include chemical precipitation, ions exchange, electrochemical method, and membrane filtration method, etc. Adsorption method has attracted wide attention because of its simple operation and strong adsorption capacity. Biochar is a stable carbon rich product synthesized through pyrolysis of biomass. Due to its abundant pore structure and adsorption capacities, biochar has been widely applied to study heavy-metal wastewater treatment[3-4].

Peanut shells are by-products of peanut production. With the exception of a small amount of raw materials used as roughage and fiberboard, most of them are discarded, which not only causes great waste of resources, but also easily leads to environmental pollution. The conversion of peanut shell into activated carbon can improve its application value and solve environmental pollution [5]. There-
fore, biochar produced by peanut shell and modified by potassium chloride were selected as adsorbent to study the adsorption properties of Cr (VI) in wastewater.

2. Materials and methods

2.1 Reagents and instruments
potassium chloride; hydrochloric acid; sodium hydroxide; potassium dichromate; diphenylcarbazide; acetone; alcohol; nitric acid; phosphate; sulfuric acid; all the above reagents are analytically pure.

Electronic balance (ME104/02), electronic thermostat blast dryer (DHG-9070A), full temperature oscillatory incubator (HZQ-F100), ultraviolet visible spectrophotometer (UV-5100), pH meter (pHS-25).

2.2 Preparation of Peanut Shell carbon and modified by potassium chloride
The peanut shells were carbonized in a continuous vertical biomass carbonization kiln, and the reaction temperature was adjusted to 110-120°C for 2 hours and 350°C-450°C for 2 hours. And then peanut shell carbon was prepared and removed from the kiln, and grinded, passed through 80 mesh screen. This product was called the original bichar. And then took the original bichar and modified by 0.3mol/L potassium chloride solution[6]. This product was called the modified bichar. The characteristics of organic carbon, specific surface area, cation exchange capacity, alkaline functional group and pH of the original bichar was analyzed[7].

2.3 Adsorption experiments
When modified peanut shell carbon were added into Cr(VI) solution, the effects of change of the solution pH, absorption time, adsorbent dose and concentration of Cr(VI) on removal rate and adsorption capacity of Cr(VI) were studied.

Use diphenylcarbazide (DPC) spectrometry to determine the content of Cr(VI) in the filtrate. The removal rate and adsorption capacity q were calculated according to the formula as follows:

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

In the formula: $C_0$—the concentration of Cr(VI) in solution before adsorption(μg/ml); $C$—concentration of Cr(VI) in solution after adsorption (μg/ml)

$$q(\text{mg/g}) = \frac{C_0 - C}{W} \times 100 \quad (2)$$

In the formula: $W$—dosage of adsorbents, g; $V$—volume of solution, ml

3. Results and discussion

3.1 Analysis of basic Properties of Peanut shell carbon

| Peanut shell carbon | Organic carbon (g·kg⁻¹) | Specific surface area (m²·g⁻¹) | Cation exchange capacity (cmol·kg⁻¹) | Alkaline functional group (cmol·kg⁻¹) | pH/H₂O |
|---------------------|--------------------------|--------------------------------|-----------------------------------|--------------------------------------|--------|
| 558.16              | 11.08                    | 9.54                           | 1.80                              | 9.16                                 |

According to the results in Table 1, peanut shell carbon contained high specific surface area, organic carbon and CEC, as well as rich functional groups. The pH of peanut shell carbon was more than 9, which was alkaline. These properties indicated that peanut shell carbon contained more adsorption sites and had ion exchange capacity.

3.2 Comparison the effect of original and modified biochar on Cr(VI) removal rate
The effect of original and modified biochar on the adsorption of Cr(VI) in water was studied when pH value was 4, absorbent time was 120 min, the concentration of Cr(VI) was 10μg/ml, and absorbent
dosage was 0.1g. The removal rate of Cr(VI) in solution of original and modified biochar was 32.6% and 50.3% respectively. The modification of peanut shell carbon by potassium chloride had certain effect. The peanut carbon had negative surface charge which generated electrostatic repulsion to Cr (VI) in solution with CrO$_4^{2-}$ mostly, Cr$_2$O$_7^{2-}$ and HCrO$_4^-$. Peanut carbon modified by potassium chloride made its structure loose, which was advantageous to the Cr (VI) adsorption. Meanwhile, the adsorption of potassium changed the surface charge property of peanut shell carbon and increased the adsorption capacity of Cr (VI).

3.3 Effect of pH on Cr(VI) removal rate
The pH value of the solution was adjusted to be 2, 4, 5 and 7 respectively with 0.5g of modified peanut shell carbon added into Cr (VI) concentration of 10μg /ml of 25ml in conical bottles. And then the conical bottles were oscillated at 150r/min for 2 h at the temperature of 25°C, filtering, measuring Cr (VI) concentration of the filtrate, and calculating the removal rate of Cr (VI).

The results showed that in the process of increasing pH from 2 to 7, the adsorption removal rate of Cr (VI) in the solution decreased from 95.63% to 43.64%. Cr(VI) in water on biochar adsorption was mainly due to physical adsorption because biochar had a large specific surface area, and these disordered structures had a high surface energy, which can well absorb metal ions in wastewater[9]. Apart from the physical adsorption, there existed electrostatic adsorption[9]. When the pH value was in the range of 1–6, the Cr (VI) in the solution was mainly in the form of CrO$_4^{2-}$ and HCrO$_4^-$. A large amount of H$^+$ in solution combined with amino, hydroxyl and other functional groups on the surface of modified peanut shell carbon to form -NH$_3^+$ and -OH$_3^+$, and adsorbed the CrO$_4^{2-}$ and HCrO$_4^-$ in the solution. When pH > 6, the number of positive adsorption centers on biochar surface decreased, resulting in the decrease of electrostatic adsorption. Although the Cr (VI) removal rate was the best at pH 2, the following experiment of solution pH was controlled at 4 because of saving the reagents and the difficulty in treating acidic solution.

3.4 Effect of adsorbent dosage on Cr(VI) removal rate
The modified peanut shell carbon of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0g were added into Cr (VI) solution with concentration of 10μg /ml and volume of 25ml, adjusting the pH value of the solution to 4, oscillating at 150r/min for 2 h at the temperature of 25°C, filtering, measuring Cr (VI) concentration of the filtrate, and calculating the removal rate and the adsorption capacity.

The effect of adsorbent dosage was shown in figure 1. The fig.1 showed that when the dosage of adsorbents was the range of 0.1g– 0.3g, the adsorption removal rate of Cr (VI) in the solution increased from 49.32% to 80.23%, and when it was more than 0.3g, the removal rate decreased from 80.23% to 40.76%. The adsorption capacity had been declining from 1.19 mg·g$^{-1}$ to 0.09 mg·g$^{-1}$.

As the amount of adsorbent increased, the total number of adsorption sites increased too, leading to increase in adsorption capacity. However, when the amount of adsorbent increased to a certain extent, the effective adsorption sites decreased due to contact and combination between the adsorbents.
Therefore, modified peanut shell carbon of 0.3 g was selected as the best dosage for adsorption of Cr (VI) in the following experiment.

3.5 Effect of adsorption time on Cr(VI) removal rate
The modified peanut shell carbon of 0.3 g was added into Cr (VI) solution of 10 ug / mL of 25 ml, adjusting the pH value of the solution to 4, oscillating at 150 r/min for 30, 60, 90, 120, 150 and 180 min at the temperature of 25°C, filtering, measuring Cr (VI) concentration of the filtrate, and calculating the removal rate and the adsorption capacity.

![Figure 2. Effects of adsorption time on Cr(VI) removal rate and adsorption capacity](image)

Figure 2 showed that when the adsorption time was in the range of 0~90 min, the removal rate and adsorption capacity increase rapidly. The growth rate became slowly in 90~150 min period, reached the peak at 150 min, and began to show a downward trend in 150 min~180 min period.

The adsorption surface area changed with the adsorbent dosage. At beginning of adsorption process, the removal rate and adsorption capacity were on the rise because the adsorption kinetics was obvious. With the increase of adsorbent time, most of the adsorption sites on the surface of the adsorbents were occupied by Cr(VI), and it gradually entered the micropores. So the increase of removal rate and adsorption capacity became slowly. When the adsorption time was 150 min, the removal rate reached 85.95%. Therefore, 150 min was selected as the best absorbent time for adsorption of Cr (VI) by modified peanut shell carbon in the following experiment.

3.6 Adsorption isotherm
The adsorption isotherm is an important basis for studying the adsorption process. It is often used to describe the equilibrium relationship, affinity and adsorption capacity [10]. The adsorption isotherm experiment was carried out by fixing the modified peanut shell carbon of 0.3 g and changing the initial content of Cr(VI) solution. The obtained data were fitted by Langmuir linear isotherm and Freundlich linear isotherm, respectively. The results were shown in table 2.

| Modified peanut shell carbon | q_0   | K_L  | R^2  | K_F  | I/n  | R^2  |
|------------------------------|-------|------|------|------|------|------|
| Langmuir                     | 0.4302| -1.0030| 0.8592| 0.7191| -0.3214 | 0.9643 |
| Freundlich                   |       |       |      |      |      |      |

Table 2 showed that the adsorption isotherm of Cr(VI) by the modified carbon was fitted by Langmuir model and Freundlich model. The adsorption of Cr (VI) by modified peanut shell carbon was more suitable to be described by Freundlich isotherm model because R^2 was closer to 1. As the Freundlich model is half empirical equation, which is based on the adsorption equilibrium model established on the polyphase surface. So it can be inferred that there was physical adsorption during the adsorption
process of modified peanut shell carbon, and the physical adsorption process was multi-molecular layer\textsuperscript{[11]}

3.7 Adsorption kinetics studies
In order to better describe the kinetic characteristics of Cr(VI) adsorption by modified peanut carbon, quasi-level 1 kinetic equation and quasi-level 2 kinetic equation were used to fit the experimental data, and the kinetic parameters were shown in table 3.

| Modified peanut shell carbon | Quasi-first-order | Quasi-second-order |
|-----------------------------|------------------|--------------------|
|                             | $k_1$   | $q_e$  | $R^2$  | $k_2$   | $q_e$  | $R^2$  |
|                             | 0.0071  | 0.0044 | 0.1766 | 0.0889  | 0.6880 | 0.9931 |

The table 3 showed that the adsorption of Cr (VI) by modified peanut shell carbon was more in accordance with the quasi-second-order kinetic equation which meant the adsorption of Cr(VI) had two process. At the first process, adsorption speed was fast with Cr(VI) diffusion to the surface of adsorbent and adsorption on the surface. At the second process, Cr(VI) entered into the mesopore and micropore of the adsorbent and the adsorption speed was slow\textsuperscript{[12]}

4. Conclusions
Biochar was prepared from peanut shells and modified by 0.3mol/L potassium chloride solution. The removal rate and adsorption capacity of Cr(VI) in water by modified peanut shell carbon were studied by controlling factor, such as pH, adsorbent dose, adsorption time and concentration of Cr(VI). Some conclusions can be drawn as follows:

(1) The removal rate of Cr(VI) in the solution of peanut shell carbon and modified by potassium chloride was 32.6% and 50.3% respectively. The modification of potassium chloride had certain effects on remove of Cr(VI) in water.

(2) The optimum conditions for adsorption of Cr(VI) in water by modified peanut shell carbon were as follows: The removal rate of Cr(VI) in water reached 99.86% when pH was 4, the dosage was 0.3 g, the adsorption time was 150 min, and the initial concentration of Cr(VI) ion was 8μg/ml.

(3) Adsorption models showed that the removal behaviors of Cr(VI) by modified peanut shell carbon followed Freundlich and quasi-second-order kinetic equation, and the linear correlation coefficient was 0.96 and 0.99 respectively, which meant the adsorption was physical process and had multi-molecular layer.

Acknowledgments:
This research was supported by funding from Nanjing Educational Committee with Grant 2018ZHHDXXK1; Jiangsu university student innovation project 201811460048X; Laboratory of Environmental monitoring, Nanjing Xiaozhuang University

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