Effect of Modified Peanut Shell on the Removal of Cu(II) in Aqueous Solution

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Abstract. The effective resource utilization of agricultural and forestry waste has always been a core issue in the field of environmental protection. In this study, nitric acid-potassium hydroxide (HNO₃-KOH) was used to modify the peanut shell, and the effects of different adsorption time, initial concentration and exogenous Cr(III) addition on the adsorption of Cu(II) were investigated. The results show that the adsorption of Cu(II) on peanut shell raw material (HS-YL) and acid-base modified peanut shell (HS-SJ) was in accordance with the pseudo-second-order kinetic model. Isotherm study shows that HS-YL fitted Langmuir adsorption model, mainly exhibiting monomolecular and chemical adsorption. HS-SJ conformed to the Freundlich adsorption model, which was mainly controlled by multi-layer adsorption. Additionally, when Cr(III) and Cu(II) coexisted, HS-SJ could simultaneously adsorb two heavy metals in a large amount, showing stronger adsorption performance compared to HS-YL. Therefore, the acid-base combined modification method is one of the important ways to recycle peanut shells.

1. Introduction

With the rapid pace of urbanization and industrialization, heavy metal pollution has spread broadly over the world [1]. Although copper (Cu) is classified as essential to metabolism for humans and animals, excessive Cu intake can lead to poisoning, such as nausea and abdominal pain, even in severe cases, gastrointestinal mucosal ulcers, kidney damage, and shock death [2]. The main sources of Cu pollution are the mining and smelting of copper-zinc mines, steel production, machinery manufacturing, etc. Once heavy metals enter the environment, they will migrate and transform, and in natural water bodies, they will not be eliminated by self-purification, and they can hardly be decomposed [3]. If they are not treated properly, they will cause secondary pollution.

Usually, porous solid materials can remove heavy metal ions in wastewater by adsorption. The critical point lies in the choice of adsorbent. In recent years, researchers have gradually turned to the use of natural resources to prepare efficient and cheap adsorbents, especially agricultural and forestry wastes [4]. They have a large specific surface area, high porosity and a large specific surface area. Meanwhile, if more active functional groups are added through chemical modification, its adsorption performance can be further improved [5]. An et al. (2019) found that the adsorption ability of peanut shell biochar based on KMnO₄ and KOH modification to Ni(II) significantly increased [6]. Peanut shell contains a lot of cellulose (C₆H₁₀O₅)n and polyphenols, but due to the few functional groups, with
limited adsorption capacity. Modification can be used to destroy the surface cellulose structure and increase the specific surface area, pores and surface active sites, which has a great effect on improving the adsorption performance of peanut shell [7]. Using peanut shells as adsorbent raw materials not only greatly improves the utilization rate of natural resources, but also contributes to environmental protection, being an effective way to use waste resources.

2. Materials and methods

2.1. Preparation of modified peanut shell

The peanut shell was washed with tap water and deionized water, dried in a drying oven at 55°C, crushed and passed through an 18-mesh sieve (HS-YL). 20 g of the above peanut shell was weighed into a 500 mL beaker with 200 mL of 7mol·L⁻¹ HNO₃ solution, stirred for 2 h on a magnetic stirrer under 180 r·min⁻¹ conditions, and then soaked for 24 h. Thereafter, the soaked liquid was filtered by suction filter device, and the filter cake was placed in the beaker again, and repeatedly washed with distilled water until the filtrate was neutral. Then, the peanut shell modified by nitric acid was dried in an oven at 55°C to a constant weight. The nitric acid modified peanut shell was put into a 500 mL beaker, added 200 mL of 25% KOH solution, stirred for 2 h on a magnetic stirrer under the same conditions. After soaking for 24 h, the mixture was through suction filtration-washing-suction filtration until the filtrate was neutral. Then put the peanut shell (HS-SJ) modified by nitric acid-potassium hydroxide joint modification in an oven at 55°C to be dried to constant weight, and store it in a dry box.

2.2. Adsorption experiment

For the kinetic study, briefly, according to a batch experiment, 0.1 g of the modified or unmodified peanut shell was transferred into a 50 mL centrifuge tube, then 20 mL of 60 mg·L⁻¹ Cu(II) solution (pH 7.0) was added into the tube. The study was carried out on a shaker for 5 min, 10 min, 20 min, 40 min, 1h, 2h, 3 h, 6 h, 8 h, 10 h, 12h, respectively. After the reaction, all samples were centrifuged and filtered through 0.45 μm filter membrane, and then analyzed by atomic absorption spectrophotometer (AAS).

For the adsorption isotherm study, a weight of 0.1 g modified or unmodified peanut shell was placed into a 50 mL centrifuge tube, and then 20 mL of 5 mg·L⁻¹, 10 mg·L⁻¹, 20 mg·L⁻¹, 30 mg·L⁻¹, 40 mg·L⁻¹, 50 mg·L⁻¹, 60 mg·L⁻¹ Cu(II) solution (pH 7.0) were added and shaken for 6 h in a constant temperature oscillator. Thereafter, all samples were centrifuged, filtered through 0.45 μm filter membrane, and then analyzed by AAS.

For competitive adsorption study, accurate 0.1 g modified or unmodified peanut shell was weighed and placed in a 50 mL centrifuge tube, then 20 mL of 30 mg·L⁻¹ Cu(II)-Cr(III) composite solution (pH 7.0) was added and placed on a shaker for 6 h. After that, all samples were centrifuged, filtered through 0.45 μm filter membrane, and determined the remaining Cu(II) or Cr(III) concentrations by AAS.

2.3. Statistical analysis

\[ q = \frac{v(C_0 - C_t)}{m} \]

Where, \( q \) is the adsorption capacity, mg·g⁻¹; \( C_0 \) and \( C_t \) are the initial and equilibrium concentrations of metal ions before and after adsorption respectively, mg·L⁻¹; \( v \) is the volume of adsorption solution, L; \( m \) is mass of adsorbent, g. All data were performed for model fitting and graph drawing of adsorption kinetics and isotherms by Origin 9.0.
3. Results and discussion

3.1. Effect of time and adsorption kinetics

The effect of time on the adsorption of Cu(II) by the absorbents is shown in Figure 1. The adsorption of Cu(II) increased rapidly within the first 20 min, and gradually tended to equilibrium after 1 h and 6 h for HS-YL and HS-SJ, respectively. Due to some degree of concentration and pressure differences between the solid-liquid interface, and numbers of active sites on the peanut shell surface, the adsorption rate was faster at the beginning. However, as the adsorption progresses, the diffusion resistance of Cu(II) in the pores increased, so the adsorption gradually reached equilibrium. The adsorption capacity of Cu(II) on HS-YL and HS-SJ in the solution at equilibrium are 8.930 mg·g⁻¹ and 11.047 mg·g⁻¹, respectively. The peanut shell modified by acid-alkali combination has a removal rate of 92% for Cu(II) in the solution. The kinetic adsorption equation showed that the adsorption of Cu(II) by the two adsorbents were most in line with the pseudo-second-order kinetic model (Table 1). The equilibrium adsorption capacity \( q_e \) of HS-SJ fitted by pseudo-second-order kinetic model was higher than HS-YL, which was consistent with the actual measured value. The ideal intra-particle diffusion model was a straight line passing through the origin, but Fig.1 showed that they were obviously not, thus the adsorption rate is not only affected by diffusion, also mainly controlled by the chemical adsorption mechanism.

![Figure 1. Adsorption kinetics of HS-YL and HS-SJ for Cu(II)](image)

| Absorbents | Intra-particle diffusion model | Pseudo-first-order kinetic model | Pseudo-second-order kinetic model |
|------------|--------------------------------|---------------------------------|---------------------------------|
| HS-YL      | \( k_i \) = 0.030 | \( C \) = 8.293 | \( R^2 \) = 0.503 | \( q_e \) = 8.777 | \( k_1 \) = 0.994 | \( R^2 \) = 0.575 | \( q_e \) = 9.003 | \( k_2 \) = 22.424 | \( R^2 \) = 1.000 |
| HS-SJ      | \( k_i \) = 0.090 | \( C \) = 9.053 | \( R^2 \) = 0.755 | \( q_e \) = 10.475 | \( k_1 \) = 0.673 | \( R^2 \) = 0.419 | \( q_e \) = 11.164 | \( k_2 \) = 59.053 | \( R^2 \) = 0.9998 |

3.2. Effect of initial metal ion concentration and adsorption isotherms

The adsorption capacity of Cu(II) on HS-YL and HS-SJ increased with the increase of the initial Cu(II) concentration (Figure 2). The higher the Cu(II) concentration in the initial solution, the greater the mass transfer motive force, which promoted Cu(II) diffusion in the pores. In Table 2, the adsorption thermodynamic equation showed that the adsorption of Cu(II) in solution by HS-YL kept in line with the Langmuir adsorption model, mainly exhibiting monomolecular and chemical adsorption. Meanwhile, HS-SJ fitted the Freundlich adsorption model best, which was mainly uneven multi-layer
adsorption on the surface. As the initial concentration of Cu(II) increased, the adsorption rate of HS-SJ to Cu(II) gradually increased, so HS-SJ was more suitable for high-concentration adsorption, which was related to the Freundlich adsorption model referring to the conclusion of ‘limited by low concentration’.

![Figure 2](image)

**Figure 2.** Adsorption isotherm of HS-YL and HS-SJ for Cu(II)

**Table 2. Isothermal parameters of Cu(II) adsorption on HS-YL and HS-SJ**

| Absorbents | Langmuir | Freundlich | Temkin |
|------------|----------|------------|--------|
|            | \( K_L \) | \( q_m \) | \( R^2 \) | \( K_F \) | \( n \) | \( R^2 \) | \( A \) | \( B \) | \( R^2 \) |
| HS-YL      | 0.127    | 13.678     | 0.960  | 1.919   | 1.707   | 0.931  | 1.673   | 2.650   | 0.923  |
| HS-SJ      | 5.474 × 10^{-6} | 2.576 × 10^{5} | 0.851  | 0.338   | 0.536   | 0.996  | 0.663   | 6.110   | 0.841  |

3.3. Effect of competitive adsorption

When Cr(III) is present, the adsorption of Cu(II) and Cr(III) by HS-SJ were significantly higher than those of HS-YL by approximate 30% (Figure 3). In order to further evaluate the effect of Cr(III) on Cu(II) adsorption, the ratio of the adsorption capacity \( Q_{\text{mix}} \) of the metal in the composite system to the adsorption amount \( Q_{\text{single}} \) in the single system was calculated and compared with 1. The appearance of Cr(III) weakened the adsorption of HS-YL to Cu(II) (\( Q_{\text{mix}} / Q_{\text{single}} < 1 \)), but promoted the adsorption of HS-SJ to Cu(II) (\( Q_{\text{mix}} / Q_{\text{single}} > 1 \)) (Table 3). The results showed that in the Cu(II)-Cr(III) composite solution, the selectivity of HS-YL to Cr(III) was better than that of Cu(II). HS-SJ could adsorb simultaneously two heavy metal ions, and the effect was even better than that of in single system.
Figure 3. The adsorption of adsorbents for Cu(II)-Cr(III) composite solution
(Note: The letters in the figure indicates the significant difference of different
Adsorbents for Cu(II) and Cr(III) adsorption)

Table 3. The Q_{mix}/Q_{single} values of Cu(II) and Cr(III) adsorption by different adsorbents

| Metal ions | HS-YL  | HS-SJ  |
|------------|--------|--------|
| Cu(II)     | 0.883  | 1.094  |
| Cr(III)    | 0.967  | 1.075  |

4. Conclusions
The adsorption capacity of peanut shell was significantly increased after HNO₃-KOH combined modification. The adsorption of Cu(II) by both HS-YL and HS-SJ fitted the pseudo-second-order kinetic model, mainly controlled by chemical adsorption. HS-YL most conformed to the Langmuir adsorption model, while HS-SJ most fitted the Freundlich adsorption model, and the adsorption mechanism needed further study. HS-SJ could simultaneously remove Cu(II) and Cr(III) in a composite solution system to avoid competitive adsorption. Therefore, peanut shell modified by acid-alkali combination is a relatively good adsorbent material and an effective approach for waste resource utilization.

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