A study of adsorption of Cu$^{2+}$ on magnetic β-cyclodextrin pyrolysis products

Liu Jun-Hong¹, Liu Ying², Li Jin³, GUO Jian-Hua¹*,
School of Water Conservancy and Hydroelectric Power, Hebei University of Engineering, Hebei Handan 056038, China

Abstract. Magnetic β-cyclodextrin pyrolysis products at 500°C were prepared from β-cyclodextrin pyrolysis products as raw materials, and the adsorption performance of magnetic β-cyclodextrin pyrolysis products on Cu$^{2+}$ was studied by nitrogen nitriding. This study provided a theoretical basis for the preparation of highly effective adsorbents and the prediction of their adsorption performance on Cu$^{2+}$. The results show that the adsorption behavior of Cu$^{2+}$ by magnetic β-cyclodextrin pyrolysis products conforms to the pseudo-second-order kinetic equation. The isothermal adsorption curve conforms to the Langmuir equation, and the maximum adsorption capacity is 405.99 mg·g$^{-1}$.

1. Introduction
In recent years, the use of magnetic adsorption materials for heavy metal adsorption has become a research hotspot[1]. Most magnetic adsorbent materials are prepared by adding magnetism to the original adsorbents[2-3]. However, the current research pays little attention to the improvement of β-cyclodextrin pyrolysis products. As a starch derivative, β-cyclodextrin is a non-toxic and non-polluting polymer[4]. β-cyclodextrin is made from starch through the fermentation of enzymes. It is a cone-shaped cylindrical structure. The outside of the cylinder is hydrophilic because of the hydroxyl groups. The guest molecule, therefore β-cyclodextrin has the reputation of molecular capsule[5]. Although there are few reports on the environmental applications of β-cyclodextrin to remove heavy metals, there is evidence that β-cyclodextrin can complex metal with hydroxyl groups to achieve the effect of metal adsorption[6]. The pyrolysis products also have good adsorption properties.

In this paper, magnetic β-cyclodextrin pyrolysis products at 500°C were prepared by using cyclodextrin pyrolysis products with hexahydrate and ferric chloride. It mainly includes the preparation process of magnetic β-cyclodextrin pyrolysis products at 500°C, the kinetic adsorption process fitting of Cu$^{2+}$ and the isothermal adsorption curve fitting. The pyrolysis products of magnetic β-cyclodextrin at 500°C were obtained by experiments and the adsorption process was preliminarily understood.

2. Experimental materials and methods

2.1. Experimental materials and instruments
The experimental instruments used in the experiment are shown in Table 1.
Table 1. Experimental instruments

| Serial number | Instrument          |
|---------------|---------------------|
| 1             | Agilent 5100 ICP-OES|
| 2             | AY-BF-666-170       |
| 3             | 101-1A              |
| 4             | KYC-100B            |
| 5             | Mettler S210        |
| 6             | SD                  |
| 7             | Mettler XSE205      |

2.2. Experimental reagent

Table 2. Experimental instruments

| Serial number | Reagent            | Purity            |
|---------------|--------------------|-------------------|
| 1             | FeCl₃·6H₂O         | Analytically pure |
| 2             | Cu(NO₃)₂·3H₂O      | Analytically pure |
| 3             | NaNO₃             | Analytically pure |
| 4             | HNO₃              | Analytically pure |
| 5             | NaOH              | Analytically pure |

2.3. Method for preparing magnetic β-cyclodextrin pyrolysis product

Take 10g of FeCl₃·6H₂O was dissolved in 50mL deionized water, and the FeCl₃·6H₂O was fully stirred and melted with ultrasonic wave until FeCl₃·6H₂O was completely dissolved. FeCl₃ solution was obtained. Dissolve 50g of β-cyclodextrin in FeCl₃ solution and oscillate for 24 hours. The mixture of solid β-cyclodextrin and FeCl₃ was obtained by drying the solution in a drying oven at 80°C for 72 hours. The solid-state β-cyclodextrin FeCl₃ mixture was pyrolysis under continuous nitrogen flow at a flow rate of 50mL/min. The heating process was as follows: from room temperature to 500°C at 15°C/min and maintained for 120min. After cooling, magnetic cyclodextrin pyrolysis products were obtained.

3. Experimental determination method

The mass difference subtraction method was used to measure the adsorption amount of Cu²⁺. The adsorption experiment was carried out under the condition of (25 ± 0.5) °C, avoiding light, 180r / min horizontal vibration, and pH value of 4.5. Different concentrations of Cu(NO₃)₂ solutions were prepared using 0.01 molꞏL NaNO₃ solution as the background solution. The pH of the solution was adjusted to 4.5 using 0.1 molꞏL HNO₃ and 0.1 molꞏL NaOH solution. Put 1mg 500 °C magnetic β-cyclodextrin lysate in a 40m sample bottle and add 40mL Cu(NO₃)₂ solution. The initial concentration of Cu²⁺ used in the kinetic experiment is 40mgꞏL, the initial pH of the solution is 4.5, and the measurement time is set to 10 (5min, 30min, 1h, 4h, 8h, 12h, 24h, 36h, 48h, 72h) Point to set two parallel. The initial concentration of Cu²⁺ used in the measurement of isotherm adsorption curve is 5, 10, 20, 40, 100, 200, 400, 800 mgꞏL, the solution pH is 4.5, a total of 8 concentration points are set, the experiment time is 48h, each concentration Both points are set parallel. The concentration after adsorption was measured using ICP-OES.

4. Experimental results and analysis

4.1. Adsorption kinetics experiment

Adsorption time has a certain effect on the amount of adsorption. In the first 10h, the adsorption of Cu²⁺ by the magnetic β-cyclodextrin pyrolysis product at 500 °C increased rapidly, and the adsorption speed gradually decreased with the increase of the adsorption time. This adsorption process gradually stabilized after 10h. At the beginning of the adsorption process, there are a large number of adsorption
sites on the surface of the magnetic β-cyclodextrin pyrolysis product at 500℃. The concentration of Cu²⁺ in the solution is high, so the adsorption amount is relatively large. After reaching the equilibrium stage, that is, after 10 hours, the decrease of the adsorption sites and the decrease of the concentration of Cu²⁺ in the solution cause the adsorption process to become slow. At this time, the adsorption of Cu²⁺ by the magnetic β-cyclodextrin pyrolysis product at 500℃ gradually reaches saturation. The kinetic equations of pseudo-first-order and pseudo-second-order are used to fit the adsorption kinetics, the equations are as follows:

pseudo-first-order:

\[ \log\left( \frac{Q_e - Q_t}{Q_e} \right) = \log Q_e - \frac{k_1 t}{2.303} \]  

pseudo-second-order:

\[ \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \]  

Qt and Qe are the adsorption amount (mg·g⁻¹) of Cu²⁺ at time t and adsorption equilibrium respectively; t is the adsorption time (h); k₁ and k₂ are the rate constants of the pseudo-first-order and pseudo-second-order kinetic equations, respectively. The unit of which is h⁻¹, mg·g⁻¹·h⁻¹.

![Fig1 Kinetics of Cu²⁺ adsorption onto 500 ℃ magnetic β-cyclodextrin pyrolysis product](image)

It can be seen from Table 3 that the R²(0.996) of the quasi-second-order kinetic model is larger than that of the pseudo-first-order kinetic model (0.980). Therefore, the adsorption of Cu²⁺ by the pyrolysis products of magnetic β-cyclodextrin at 500℃ is more consistent with the pseudo-second-order kinetic model. The equilibrium adsorption capacity obtained by fitting with the pseudo-second-order kinetic model is 189.73 mg·g⁻¹, and more closer to the measured value of 182.47 mg·g⁻¹, which indicates that the adsorption of Cu²⁺ by the magnetic β-cyclodextrin pyrolysis product at 500 ℃ is a chemical process. The reaction process is related to the ion exchange and surface precipitation between the active sites on the surface of the magnetic β-cyclodextrin cleavage product at 500 ℃ and the adsorbate.

The fitted adsorption rate constant k reflects the speed of the adsorption process. The larger the value k is, the faster the adsorption process reaches equilibrium. As can be seen from Table 3, the k₂ value of magnetic β-cyclodextrin pyrolysis products at 500℃ is 0.00205 mg·g⁻¹·h⁻¹, which indicates that the adsorption rate of Cu²⁺ by adsorbent is slow. Compared with many other adsorbents, the adsorption of Cu²⁺ by magnetic β-cyclodextrin pyrolysis products at 500℃ is a slow process.
Table 3. Regression parameters of kinetic models for the adsorption of Cu$^{2+}$ by 500℃ magnetic β-cyclodextrin pyrolysis products

| Sample                                      | Initial concentration / (mg/L$^{-1}$) | $Q_e$ / (mg/g$^{-1}$) | $K_1$ /h$^{-1}$ | $R^2$ | $Q_e$ / (mg/g$^{-1}$) | $K_2$ /((mg/g$^{-1}$)/h$^{-1}$) | $R^2$ |
|---------------------------------------------|--------------------------------------|-----------------------|-----------------|-------|-----------------------|----------------------------------|-------|
| 500 ℃ magnetic β-cyclodextrin pyrolysis     | 40                                   | 170.88±3.71           | 0.304±0.030     | 0.980 | 189.73±10.80          | 0.00205±0.00006                   | 0.996 |

4.2. Isothermal adsorption experiment of Cu$^{2+}$

In order to further understand the adsorption mechanism of Cu$^{2+}$ adsorbed by magnetic β-cyclodextrin at 500 ℃, Langmuir and Freundlich equations were used to fit the adsorption. The fitting equation is as follows:

Langmuir:

$$Q_e = \frac{b \cdot Q_m \cdot C_e}{(1 + b \cdot C_e)} \quad (3)$$

Freundlich:

$$Q_e = K_f \cdot C_e^N \quad (4)$$

$Q_m$ is the maximum adsorption capacity (mg·g$^{-1}$), $C_e$ is the concentration of Cu$^{2+}$ in the solution at adsorption equilibrium (mg·L$^{-1}$); $b$ is the affinity parameter (L·mg$^{-1}$) that characterizes the adsorbent and adsorbate, $K_f$ is Freundlich Adsorption capacity parameter (mg$^{-1}$·N / g$^{-1}$·L$^{-N}$), $N$ is the index of Freundlich equation. The regression parameters are shown in Table 4. It can be seen from Fig2, with the increase of the concentration of Cu$^{2+}$ in the solution, the adsorption amount of Cu$^{2+}$ by magnetic β-cyclodextrin pyrolysis products at 500℃ gradually increases. In the phase when the initial concentration of Cu$^{2+}$ was 0~200 mg/L, the adsorption amount of Cu$^{2+}$ from β-cyclodextrin pyrolysis products of magnetic adsorbents at 500℃ increased rapidly, indicating that there were more active sites on the adsorbents at this stage, and the more active sites, the more favorable it was for Cu$^{2+}$ adsorption from β-cyclodextrin pyrolysis products of magnetic adsorbents at 500℃. When the concentration of Cu$^{2+}$ was further increased to 200~800 mg·L$^{-1}$, the adsorption amount of Cu$^{2+}$ on the β-cyclodextrin pyrolysis products at 500℃ tended to balance.

![Fig2 Adsorption isotherms of Cu$^{2+}$ by 500℃ magnetic β-cyclodextrin pyrolysis product](image)

It can be seen from Table 4 that the R2 value of the fitting results of the Langmuir equation, that is,
the value of the fitting phase relation is 0.996, which is greater than the R2 value of the fitting correlation coefficient of the Freundlich equation, 0.986, indicating that the adsorption of Cu2+ by β-cyclodextrin pyrolysis products at 500°C is more consistent with the Langmuir adsorption isothermal equation. It can be known from the Table 4 that the maximum adsorption capacity of Cu2+ on the pyrolysis products of magnetic β-cyclodextrin at 500°C is 405.99mg/g.

| Sample | Langmuir | Freundlich |
|--------|----------|------------|
|        | Qm/(mg·g⁻¹) | b'/(L·mg⁻¹) | R² | Kf/(mg¹·N·g⁻¹·L⁻¹·N) | N | R² |
| 500 ℃ magnetic β-cyclodextrin pyrolysis products | 405.99±8.66 | 0.0027±0.00106 | 0.996 | 425.03±21.60 | 1.21±0.14 | 0.986 |

5. Conclusion
In this paper, 500°C magnetic β-cyclodextrin pyrolysis products were prepared using β-cyclodextrin and FeCl₃·6H₂O as raw materials, and nitrogen pyrolysis method was used in high-temperature pyrolysis furnace. The results show that:
(1) The adsorption of Cu²⁺ of the magnetic β-cyclodextrin pyrolysis product at 500 ℃ conforms to pseudo-second-order kinetics. The pseudo-second-order kinetics gives an equilibrium adsorption of 189.73 mg/g, which is closer to the measured value of 182.47 mg/g, indicating that the adsorption process is chemical adsorption.
(2) The maximum amount of Cu²⁺ adsorbed by the magnetic β-cyclodextrin pyrolysis product at 500 ℃ is 405.99mg/g, and the isothermal adsorption curve conforms to the Langmuir fitting equation.
(3) The 500 ℃ magnetic β-cyclodextrin pyrolysis product is used to adsorb the heavy metal Cu²⁺ in the water, and the magnet can be used to separate the adsorbent and the heavy metal Cu²⁺ from the water to avoid secondary pollution.

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