Adsorption properties of β-cyclodextrin cracking products for Cd$^{2+}$

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Abstract. B-cyclodextrin can react with metals through hydroxyl groups, which has a certain contribution to the removal of heavy metals. However, the application of β-cyclodextrin in heavy metal adsorption is limited because of its slow adsorption speed and low adsorption capacity. In this paper, β-cyclodextrin was pyrolyzed under oxygen limitation to prepare β-cyclodextrin pyrolysis product, and its adsorption performance of Cd$^{2+}$ in water was studied. The adsorption of Cd$^{2+}$ by the β-cyclodextrin cracked product conforms to the quasi-first-order kinetic model, and the Langmuir fitting effect is better. The maximum adsorption capacity of Cd$^{2+}$ by β-cyclodextrin cracking products prepared at 300 ℃, 500 ℃ and 700 ℃ is 1029.04mg/g, 1237.42mg/g and 829.06mg/g, respectively.

1. Introduction
Cadmium is one of the highly toxic environmental harmful substances. As a heavy metal, cadmium has been widely used in many industrial productions. As a result, cadmium enters the water directly through industrial waste water, and the concentration of cadmium in the water increases significantly. When its concentration in drinking water exceeds the limit value of 0.005 mg/L, it will have a toxic effect on human body. It can lead to various types of acute and chronic diseases, such as kidney damage, emphysema, hypertension and so on[1]. Cadmium polluted water and food are harmful to human body, and metabolism is slow in human body. Japan suffered from "itai— itai Disease" due to cadmium poisoning[2]. The conventional methods of treating cadmium containing wastewater include alkaline precipitation and ion exchange. However, due to the high maintenance cost, these methods are not suitable for large-scale use. At present, we have tried to develop a cheap, simple, easy to operate and maintain method. Among all available methods, adsorption method has a good prospect. Many adsorbents, such as waste activated carbon, waste automobile tires, agricultural products and agricultural by-products, and starch xanthate, have been used to remove cadmium[3]. By recycling and reusing conventional adsorbents (such as activated carbon) or using low-cost adsorbent materials (one-time use, then destruction or retention), cadmium adsorption can achieve economic and efficient results. In this paper, β-cyclodextrin cracking products were selected as adsorbents to remove cadmium from water, hoping to get a cheap and efficient adsorbent material.

2. Experimental materials and methods

2.1. Experimental materials and instruments
Test instruments: Agilent 5100 ICP-OES inductively coupled plasma emission spectrometer, program intelligent temperature control muffle furnace KSMF-2000), electric blast drying oven (101-1A), air constant temperature shaker (KYC-100b), pH meter and precision balance.

Test materials and reagents: β-cyclodextrin, chromium nitrate (Cd^{2+}), sodium nitrate, nitric acid, sodium hydroxide, all reagents used in the test are analytical pure.

2.2. preparation of cracking products of cyclodextrin
In this experiment, crucible was used as the container, and an appropriate amount of cyclodextrin was taken and put into the crucible. At the rate of 10℃/min, cyclodextrin cracking products were prepared at 300℃, 500℃ and 700℃, respectively. The cracking time was 4h. After the furnace temperature is reduced to room temperature, the carbonized cracked products of cyclodextrin are taken out from the crucible, ground thoroughly with a mortar, screened with a 100-mesh screen, and sealed. The cracking products of cyclodextrin were labeled as β-CD300, β-CD500, and β-CD700, respectively. Among them, β-CD is the abbreviation of β-CD, and the Numbers behind represent the final temperature during pyrolysis.

2.3. Determination of Cd^{2+} adsorption experiment by β-cyclodextrin cracking products
Using a precision balance, accurately weigh 1 mg of β-cyclodextrin lysate into a glass bottle and add 40 mL of a solution containing Cd^{2+}. Carry out kinetic and isothermal adsorption experiments. All chemical reagents are analytically pure, and all solutions are prepared using ultrapure water. The concentration of Cd^{2+} after adsorption was measured using ICP-OES. By comparing the concentration of Cd^{2+} before and after adsorption, the amount of heavy metal Cd^{2+} adsorbed by β-cyclodextrin cracking products was obtained.

3. Experimental results and discussion

3.1. adsorption kinetics of Cd^{2+} by β-cyclodextrin
The kinetic experiments were carried out under the condition of 25±0.5 ℃ in dark and 180r/min horizontal oscillation. Cadmium nitrate solution was prepared with 0.01 mol/L sodium nitrate solution. Adjust the pH to 4.5 with 0.1 mol/L nitric acid and 0.1 mol/L sodium hydroxide solution. Accurately weigh 1mg of β-cyclodextrin cracking product into a 40ml sample bottle, and add 40ml of cadmium nitrate solution. The initial concentration of cadmium ion used in the kinetic experiment is 40mg/L (calculated as the concentration of Cd^{2+}), the initial pH of the solution is 4.5, and the measurement time is set to 5min, 30min, 1h, 4h, 8h, 12h, 24h, 36h, 48h 72h, set two parallels at each time point. After the test is completed, Quasi-First Order and Quasi-Second Order kinetic equations are used to fit the adsorption kinetics results. The equations are as follows:

Quasi First Order kinetic equation:

$log(Qe - Q_t) = logQe - \frac{k_1 t}{2.303}$

Quasi-Second-Order kinetic equation:

$t / Q_t = \frac{1}{k_2 Q_e^2} + t / Q_e$

Where, Qt and Qe are water adsorption capacity (g/g) at time t and adsorption equilibrium, respectively; t is adsorption time (h); k1 and k2 are the rate constants of the Quasi-first order rate constant and Quasi-second order rate constant (h^{-1}, mg·g^{-1}·h^{-1}), respectively.

The adsorption kinetics of Cd^{2+} by β-cyclodextrin at different cracking temperatures is shown in Figure 1. The order of Cd^{2+} adsorption capacity of β-cyclodextrin cracking products in 72 hours was β-CD500 > β-CD300 > β-CD700. At 25 h, the adsorption capacity of β-CD500 was about 175mg / g, while that of β-CD300 was about 100mg/g. However, the adsorption rate of Cd^{2+} by β-cyclodextrin cracking products and the time to reach the apparent equilibrium state are relatively consistent. In the first 15 hours, the adsorption rate of Cd^{2+} by the three temperature treated β-cyclodextrin cracking products is faster, and the relationship between adsorption time and adsorption capacity is basically
linear. When the adsorption time reaches 25h, β-CD300, β-CD500 and β-CD700 all reach the apparent equilibrium state. At this time, with the increase of the adsorption time, the adsorption capacity basically does not change, and the adsorption reaches the apparent equilibrium state.

The adsorption kinetics fitting parameters of β-cyclodextrin cracking products to Cd\(^{2+}\) are shown in Table 1. Both kinetics have a good fitting effect on the adsorption process of β-cyclodextrin cracking product Cd\(^{2+}\). Compared with the quasi-second-order kinetic correlation coefficient R\(^2\), the quasi-first-order kinetic correlation coefficient R\(^2\) is greater than 0.99, indicating that the quasi-first-order kinetics can better fit the adsorption process of β-cyclodextrin cracking products for Cd\(^{2+}\).

![Fig1 Kinetics of Cd\(^{2+}\) adsorption onto β-cyclodextrin pyrolysis product](image)

3.2. Isothermal adsorption of Cd\(^{2+}\) by β-cyclodextrin
Weigh 1mg of β-cyclodextrin cracking product into a 40ml sample bottle, add 40ml of Cd\(^{2+}\) solutions with different initial concentrations (5, 10, 20, 40, 100, 200, 400, 800 mg / L), and set two parallel solutions for each concentration. The background solution of Cd\(^{2+}\) is 0.01mol/l sodium nitrate solution, and the pH of the background solution is adjusted to 4.5 using 0.1mol/l nitric acid and 0.1mol/l sodium hydroxide solution.

The isothermal adsorption experiment was carried out under the condition of 25 ± 0.5 ℃ in dark and 180r / min horizontal oscillation. After equilibrium, a certain amount of supernatant was taken and filtered through 0.22 μm water phase membrane. The concentration of Cd\(^{2+}\) after adsorption was determined by ICP-OES. The adsorption capacity was calculated by mass difference subtraction, and the isotherm adsorption curve was drawn by equilibrium concentration and adsorption capacity. The isotherm adsorption curve is fitted by Langmuir and Freundlich equation, and the equation is as follows:

**Langmuir equation:**

\[
Q_e = \frac{(b \cdot Q_m \cdot C_e)}{(1 + b \cdot C_e)} \quad (1)
\]
Freundlich equation

\[ Q_e = K_f \cdot C_e^N \]  

In the formula, \( Q_m \) is the maximum adsorption capacity (mg / g), \( C_e \) is the concentration of Cd\(^{2+}\) in the solution at adsorption equilibrium (mg / L); \( b \) is the affinity parameter (L/mg) characterizing the adsorbent and adsorbate, and \( K_f \) is Freundlich Adsorption capacity parameter (mg\(^{1-N}/g\)·L\(^N\)). \( N \) is the index of Freundlich equation. The curve fitted by the Langmuir and Freundlich equations is shown in Figure 2, and the fitted regression parameters are shown in Table 4.

The isotherm adsorption curve of Cd\(^{2+}\) by β-cyclodextrin cracking product is shown in Figure 2. It can be seen from the figure that when the concentration of Cd\(^{2+}\) is in the low concentration range (0-500mg/ L), the adsorption capacity of β-cyclodextrin cracking product to Cd\(^{2+}\) increases rapidly with the increase of concentration. When the concentration further increases (500-1500mg/L), it tends to balance. The isothermal adsorption curve is fitted by Langmuir and Freundlich equations, and the relevant fitting parameters are shown in Table 2. It can be seen from Table 2 that the adsorption amounts of β-cyclodextrin cracking products prepared at 300°C, 500°C, and 700°C cracking temperatures are: 1029.04 mg / g, 1237.43 mg / g, and 829.06 mg / g, respectively. β-CD500 has a high adsorption capacity for Cd\(^{2+}\), which may be due to its rich oxygen-containing functional groups, which can complex with Cd\(^{2+}\) to achieve the effect of adsorbing heavy metals.

The fitting parameters of the isotherm adsorption of Cd\(^{2+}\) by β-cyclodextrin cracking products are shown in Table 2. It can be seen from the table that the fitting effect of Langmuir is better, and the correlation coefficient R2 is greater than 0.95. For β-cyclodextrin cracking products, the adsorption affinity parameter \( b \) is the largest when the cracking temperature is 500°C, followed by 300°C, and the smallest is 700°C. The change trend corresponds to the maximum adsorption capacity. Compared with the previous literature, the maximum adsorption capacity of different adsorbents for Cd\(^{2+}\) is shown in Table 5. The maximum adsorption capacity of β-cyclodextrin cracking products for Cd\(^{2+}\) is larger. It can be seen from the comparison that the cleavage products of β-cyclodextrin have great advantages in the adsorption of Cd\(^{2+}\) and have great application prospects.
Table 2 Langmuir and Freundlich fitting parameters of isothermal adsorption curve of Cd\(^{2+}\) by β-CD

| Sample       | Langmuir     | Freundlich   |          |          |          |          |
|--------------|--------------|--------------|----------|---------|---------|---------|
|              | \(Q_m\) (mg·g\(^{-1}\)) | \(b\) (L·mg\(^{-1}\)) | \(R^2\)  | \(K_f/(mg^{1/N}·g^{-1}·L^{-N})\) | \(N\)       | \(R^2\)  |
| β-CD300     | 1029.04±17.17 | 0.00014±0.00006 | 0.997   | 1053.11±32.36 | 1.55±0.16 | 0.993   |
| β-CD500     | 1237.43±22.31 | 0.00019±0.00012 | 0.996   | 1270.02±45.87 | 1.46±0.17 | 0.991   |
| β-CD700     | 829.06±14.37  | 0.00013±0.00008 | 0.997   | 849.38±27.56 | 1.52±0.16 | 0.992   |

Table 3 Maximum adsorption capacity of Cd\(^{2+}\) with different adsorbents

| Number | Adsorption material                                      | \(Q_e\) (mg/g) |
|--------|----------------------------------------------------------|----------------|
| 1      | reed-derived biochar                                     | 206.18[4]      |
| 2      | KMnO4 impregnation straw biochars                        | 90.32[5]       |
| 3      | biochar-supported magnetic MnFe2O4 nanocomposite          | 127.83[6]      |
| 4      | magnetic rice husk biochar by KMnO4 modification         | 79[7]          |
| 5      | tea waste biochar                                        | 42.01[8]       |
| 6      | CaCO3 nanoparticle modified sewage sludge biochar        | 36.5[9]        |
| 7      | KMnO4 impregnation corn straw biochars                  | 68.87[10]      |

4. Conclusion

In this paper, the adsorption properties of β-cyclodextrin cracking products for Cd\(^{2+}\) are mainly studied, and the following conclusions are drawn through the analysis of experimental results:

1. The kinetic adsorption of β-cyclodextrin cracked products to Cd\(^{2+}\) conforms to the quasi-first-order kinetic model, the adsorption rates of β-CD300, β-CD500, and β-CD700 are 0.0839 h\(^{-1}\), 0.0823 h\(^{-1}\), and 0.0815 h\(^{-1}\), respectively.

2. The isotherm adsorption of Cd\(^{2+}\) by β-cyclodextrin cracked product is in accordance with Langmuir equation. The maximum adsorption capacity of β-CD300, β-CD500 and β-CD700 are 1029.04 mg/g, 1237.43 mg/g and 829.06 mg/g respectively.

3. The adsorption rate of Cd\(^{2+}\) by β-cyclodextrin cracking products at different cracking temperatures is different. The low-temperature β-cyclodextrin cracking product (β-CD300) has a faster adsorption rate for Cd\(^{2+}\), and the high-temperature β-cyclodextrin cracking product (β-CD700) has a slower adsorption rate for Cd\(^{2+}\).

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