Research on the adsorption of Cr\(^{3+}\) and Cr\(^{6+}\) by the cracked products of β-cyclodextrin

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Abstract. β-cyclodextrin (β-CD) was used as raw material at different temperatures (300°C, 500°C and 700°C) the adsorption properties of β-cyclodextrin on Cr\(^{3+}\) and Cr\(^{6+}\) were researched by kinetic adsorption and isothermal adsorption. The maximum adsorption capacity and adsorption rate of β-cyclodextrin on Cr\(^{3+}\) and Cr\(^{6+}\) were compared, which provided a theoretical basis for the preparation of efficient adsorbents and the prediction of their adsorption properties on Cr\(^{3+}\) and Cr\(^{6+}\). The results show that the adsorption rate of Cr\(^{3+}\) and Cr\(^{6+}\) by β-cyclodextrin cracking products is in accordance with the Quasi First-order Kinetic model. The adsorption rate of Cr\(^{3+}\) by β-CD300 and β-CD500 is the same and higher than that by β-CD700. The adsorption rate of Cr\(^{6+}\) by β-CD300 is faster. The isotherm adsorption curves of Cr\(^{3+}\) and Cr\(^{6+}\) on β-cyclodextrin cracking products are in accordance with the Langmuir equation. The maximum adsorption capacity of Cr\(^{3+}\) is higher than that of Cr\(^{6+}\), and the maximum adsorption capacity of β-CD500 for Cr\(^{3+}\) and Cr\(^{6+}\) is 1151.77 mg/g and 440.78 mg/g.

1. Introduction

Heavy metal pollution has a serious impact on the ecosystem, agricultural production and human health, so in recent years, it has aroused widespread concern. Because of the application of Cr in metallurgy, electroplating, metal processing and other industrial fields, Cr enters the soil and water body through waste water and solid waste. When Cr enters the environment, it exists in the stable state of Cr\(^{3+}\) and Cr\(^{6+}\). Cr\(^{3+}\) is slightly less toxic, and excessive intake will affect people's health, especially the skin and lungs. Compared with Cr\(^{3+}\), Cr\(^{6+}\) is more toxic in nature, more carcinogenic and mutagenic. It has high mobility in soil and aquatic system, and is also a strong oxidant, which can be absorbed by skin\(^{[1]}\). Among various treatment technologies for Cr removal, the most commonly used are reduction precipitation, ion exchange and reverse osmosis\(^{[2]}\), and most commercially prepared adsorbents can effectively remove various heavy metal ions\(^{[3]}\).

At present, activated carbon is widely used in the field of environmental protection because of its good adsorption performance\(^{[4-5]}\). However, due to the cost limitation of the use of activated carbon, people began to use low-cost materials to prepare adsorbents, such as rice straw\(^{[6]}\), sludge\(^{[7]}\), starch and starch derivatives\(^{[8]}\). As a natural molecule extracted from starch, β-cyclodextrin has an outer hydrophilic internal hydrophobic cavity, in which it can form inclusion complexes with a variety of organic and inorganic compounds\(^{[9]}\). Although there are few reports on the environmental application of β-cyclodextrin in the removal of heavy metals, there is evidence that cyclodextrin can achieve the effect of metal adsorption through the complexation of -OH and metal. Biomass is prepared into stable solid-state carbon-rich product by limiting oxygen cracking\(^{[10]}\). Due to its rich oxygen-containing functional groups and microporous structure, it can absorb heavy metals in water body, which has
been widely used in the field of water restoration in recent years. However, there are little research on the preparation of cracking products from β-cyclodextrin. At the same time, β-cyclodextrin can effectively adsorb heavy metals in the environment due to its slightly tapered hollow cylinder stereoscopic ring structure, and its derivatives may have better characteristics than their own cyclodextrins, so as to achieve efficient heavy metal adsorption.

2. Experimental materials and methods

2.1. Experimental instruments and materials
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 (provide Cr³⁺), sodium chromate (provide Cr⁶⁺), sodium nitrate, nitric acid, sodium hydroxide, all reagents used in the test are analytical pure.

2.2. Preparation of β-cyclodextrin cracking products
The β-cyclodextrin was packed in crucible, and then put into muffle furnace after being compacted and sealed. The cracking products of cyclodextrin were prepared by heating rate of 10℃/min. The products were kept at each final cracking temperature (300℃, 500℃ and 700℃) for 4h. After cracking, it will be naturally reduced to room temperature and taken out. After grinding, it will pass through 100 mesh screen and be sealed for preservation. The prepared products are labeled as β-CD300, β-CD500 and β-CD700, respectively, in which β-CD is the abbreviation of β-cyclodextrin, and the following figures represent the final temperature during pyrolysis.

2.3. Determination of adsorption of Cr³⁺ and Cr⁶⁺ by β-cyclodextrin cracking products
Accurately weigh 1mg of β-cyclodextrin cracking product in a glass bottle with a precision balance, and add 40mL of solution containing Cr ion. Cr ion solution is prepared with 0.01 mol/L sodium nitrate solution as the background solution. The pH of the solution was adjusted to 4.5 with 0.1 mol/L nitric acid and 0.1 mol/L sodium hydroxide solution. There were 10 measurement time settings (5min, 30min, 1h, 4h, 8h, 12h, 24h, 36h, 48h and 72h), and three parallel settings were set at each time point. The initial concentration of Cr ion used in the isotherm adsorption curve determination is 5, 10, 20, 40, 100, 200, 400 and 800 mg /L, and the solution pH is 4.5. There are 8 concentration points in total. The experimental time is 48h. Each concentration point is set with three parallel points. Put the glass bottle into an air constant temperature shaker at (25 ± 0.5)℃, set the rotating speed of 180r /min to vibrate horizontally for 24h, and then take it out. After passing the 0.22 μm filter membrane, it is to be tested. The concentration of Cr³⁺ and Cr⁶⁺ after adsorption was determined by ICP-OES. The standard solution for the determination is made up of 800mg / L chromium nitrate (Cr³⁺) and sodium chromate (Cr⁶⁺), The concentration of standard solution was 5, 10, 30, 40, 100, 200, 400 and 800mg/L respectively. According to the concentration of Cr³⁺ and Cr⁶⁺ in equilibrium, the adsorption capacity was calculated, and the relevant parameters were fitted according to the relevant equation by using Origin9.1 software.

3. Experimental results and discussion

3.1. Adsorption kinetics of Cr³⁺ and Cr⁶⁺ by β-cyclodextrin cracking products
In the process of adsorption, the atoms, ions or molecules of the adsorbed substance diffuse to the solid surface, combine with the solid surface or be adsorbed by the weak intermolecular force on the solid surface. Electrostatic, chemical adsorption and functional group interaction determine the affinity of adsorbent to specific substances. In this research, β-cyclodextrin cracking product was used as adsorbent to remove Cr³⁺ and Cr⁶⁺ from aqueous solution. The research on the adsorption kinetics of
heavy metal ions in wastewater is of great significance to understand its adsorption mechanism. The adsorption amount of Cr\(^{3+}\) and Cr\(^{6+}\) by β-cyclodextrin cracking product changes with time as shown in Figure 1 and Figure 2. It can be seen from Figure 1, that in the first 30h, the adsorption rate of Cr\(^{3+}\) by β-cyclodextrin cracking product is faster, and then it tends to balance quickly; after 40h, the adsorption amount of Cr\(^{3+}\) is no longer significantly increased. It can be seen from Figure 2, that in 20h, the adsorption rate of Cr\(^{6+}\) by β-cyclodextrin cracking product is faster, and the apparent equilibrium is reached in 25h. The results of adsorption kinetics are fitted with Quasi First-order and Quasi Second-order Kinetic equations respectively. The equations are shown in formula (1) and (2). The fitting parameters of relevant kinetic models are shown in Table 1 and Table 2.

\[
\log (Q_e - Q_t) = \log Q_e - Q_e - k_1/2.303 \\
t/Q_e = 1/ (k_2 Q_e^2) + t/Q_e
\]

Compared with the adsorption of Cr\(^{3+}\), the adsorption of Cr\(^{6+}\) by β-cyclodextrin cracking products is faster, and the adsorption mechanism of Cr ion on its surface includes the following three steps: (1)
Cr ion diffuses around β-cyclodextrin cracking products; (2) from β-cyclodextrin cracking products to its surface; (3) from the surface of β-cyclodextrin cracking products to the internal site, Cr ion and active site point combination. The rate of the general adsorption process is controlled by step (2) or step (3). Under the same adsorption site, the kinetic adsorption of Cr$^{6+}$ first reaches the apparent equilibrium state, which indicates that Cr$^{6+}$ needs more adsorption sites on β-cyclodextrin cracking products. When Cr$^{6+}$ combines with available adsorption sites, the adsorption kinetics reaches equilibrium.

Table 1. Regression parameters of kinetic models for the adsorption of Cr$^{3+}$ by β-cyclodextrin pyrolysis product

| Sample  | Initial concentration (mg·L$^{-1}$) | Quasi First-order Dynamics model | Quasi Second-order Dynamics model |
|---------|-----------------------------------|---------------------------------|----------------------------------|
|         |                                   | $Q_e$ (mg·g$^{-1}$) | $K_1$ (h$^{-1}$) | $R^2$ | $Q_e$ (mg·g$^{-1}$) | $K_2$/(mg·g$^{-1}$·h$^{-1}$) | $R^2$ |
| β-CD300 | 40                                 | 144.39±3.13 | 0.064±0.004 | 0.996 | 182.97±11.07 | 0.00033±0.00007 | 0.985 |
| β-CD500 | 40                                 | 219.10±4.43 | 0.064±0.004 | 0.996 | 277.49±16.40 | 0.00022±0.00004 | 0.986 |
| β-CD700 | 40                                 | 161.55±3.48 | 0.063±0.003 | 0.995 | 205.03±12.07 | 0.00029±0.00006 | 0.986 |

Table 2. Regression parameters of kinetic models for the adsorption of Cr$^{6+}$ by β-cyclodextrin pyrolysis product

| Sample  | Initial concentration (mg·L$^{-1}$) | Quasi First-order Dynamics model | Quasi Second-order Dynamics model |
|---------|-----------------------------------|---------------------------------|----------------------------------|
|         |                                   | $Q_e$ (mg·g$^{-1}$) | $K_1$ (h$^{-1}$) | $R^2$ | $Q_e$ (mg·g$^{-1}$) | $K_2$/(mg·g$^{-1}$·h$^{-1}$) | $R^2$ |
| β-CD300 | 40                                 | 135.43±1.42 | 0.0894±0.0031 | 0.998 | 161.66±5.27 | 0.00061±0.00008 | 0.993 |
| β-CD500 | 40                                 | 210.19±2.03 | 0.0893±0.0028 | 0.999 | 251.13±8.05 | 0.00039±0.00005 | 0.993 |
| β-CD700 | 40                                 | 161.55±3.48 | 0.0891±0.0027 | 0.999 | 176.80±5.60 | 0.00055±0.00007 | 0.993 |

It can be seen from Table 1. and Table 2. that the adsorption of Cr$^{3+}$ and Cr$^{6+}$ by β-cyclodextrin cracking products conforms to the Quasi First-order Kinetic model. And the correlation coefficient $R^2$ is above 0.995, which shows that the fitting effect is preferably. In the Quasi First-order Kinetic equation, the adsorption rate constant $K_1$ indicates the speed of adsorption. The larger the value of $K_1$ is, the faster the adsorption rate is. The adsorption rate of Cr$^{6+}$ is faster and it can reach the dynamic equilibrium earlier. Among them, the adsorption rate of Cr$^{6+}$ by β-CD300 is the fastest, and its adsorption rate constant is 0.0894.
3.2. Isothermal adsorption of Cr$^{3+}$ and Cr$^{6+}$ by β-cyclodextrin cracking products

The isotherm adsorption curves of Cr$^{3+}$ and Cr$^{6+}$ by β-cyclodextrin cracking products are shown in Figure 3. and Figure 4. The isothermal adsorption curve was fitted by the Langmuir and the Freundlich equations, and the specific equations are shown in equations (3) and (4). See Table 3. and Table 4. for regression parameters.

$$Q_e = b \cdot Q_m \cdot C_e / \left(1 + b \cdot C_e\right)$$

$$Q_e = K_f \cdot C_e N$$

It can be seen from Figure 3, that the adsorption of Cr$^{3+}$ by β-cyclodextrin cracking products basically reaches equilibrium when the concentration of Cr$^{3+}$ reaches 500mg/L, with the continuous increase of Cr$^{3+}$ concentration, the isotherm adsorption curve gradually becomes flat and the maximum
adsorption capacity no longer continues to increase. It can be seen from Figure 4, that the isotherm adsorption curve of Cr$^{6+}$ by β-cyclodextrin cracking product is basically in equilibrium when the concentration of Cr$^{6+}$ is 250mg/L, and the relationship between equilibrium concentration and adsorption capacity is basically linear. At the same time, by comparing the slope between the equilibrium concentration and the adsorption capacity, it can be seen that the adsorption rate of Cr$^{6+}$ by β-cyclodextrin cracking product is faster, which is consistent with the conclusion of adsorption kinetics experiment.

| Sample  | The Langmuir equation | Freundlich equation |
|---------|-----------------------|--------------------|
|         | $Q_m$ (mg·g$^{-1}$)   | $b$ (L·mg$^{-1}$)  | $R^2$ | $K_f$ (mg$^{1-N}$·g$^{-1}$·L$^{-N}$) | $N$ | $R^2$ |
| β-CD300 | 932.86±38.88          | 0.00027±0.00031    | 0.988 | 978.91±79.76               | 1.19±0.22 | 0.977 |
| β-CD500 | 1151.77±67.09         | 0.00077±0.00088    | 0.980 | 1250.56±78.51              | 1.01±0.20 | 0.966 |
| β-CD700 | 954.67±43.57          | 0.00037±0.00042    | 0.986 | 1016.80±89.88              | 1.14±0.22 | 0.974 |

It can be seen from Table 2. and Table 3, that the correlation coefficient $R^2$ of Cr$^{3+}$ the Langmuir fitting is greater than that of the Freundlich fitting, so the adsorption of β-cyclodextrin cracking product to Cr$^{3+}$ is more in line with the Langmuir equation. For Cr$^{6+}$, the Langmuir fitting correlation coefficient $R^2$ is also greater than that of the Freundlich equation, and all of them are above 0.990, which indicates that there is good consistency among the parameters, and the adsorption capacity of β-CD500 reaches the maximum, reaching 1151.77mg/g and 440.78mg/g. It can be seen that the adsorption of Cr ion by β-cyclodextrin cracking product is not only the surface adsorption. When the concentration of Cr ion reaches a certain level, Cr ion will fill in the pores of β-cyclodextrin cracking product, and the pore size structure of β-CD500 is more in line with the filling conditions of Cr ion. At the same time, it was found that the maximum adsorption capacity of Cr$^{3+}$ by β-cyclodextrin cracking products was much greater than that of Cr$^{6+}$. Because more adsorption sites are needed for Cr$^{6+}$ adsorption, the maximum adsorption capacity is less than Cr$^{3+}$.

4. Conclusion

(1) The adsorption rate of Cr$^{3+}$ and Cr$^{6+}$ on β-CD300, β-CD500 and β-CD700 was lower than that on β-cyclodextrin. In β-CD300, β-CD500 and β-CD700, the adsorption rate of β-CD300 and β-CD500 to Cr$^{3+}$ is the same and higher than that of β-CD700, and the adsorption rate of β-CD300 to Cr$^{6+}$ is faster.

(2) The isotherm adsorption curves of Cr$^{3+}$ and Cr$^{6+}$ by β-cyclodextrin cracking products are consistent with the Langmuir equation, and the maximum adsorption capacity of Cr$^{3+}$ by β-cyclodextrin cracking products is higher than that of Cr$^{6+}$.

(3) The adsorption capacity of β-CD500 to Cr$^{3+}$ and Cr$^{6+}$ is the largest, reaching 1151.77mg/g and 440.78mg/g.

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