

Preparation of carboxymethyl chitosan microspheres and the adsorption of heavy metal cadmium

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Abstract. Cadmium pollution is a serious environmental and agricultural issue. As such, an adsorbent material with convenient recovery must be used to adsorb excess cadmium. In this study, carboxymethyl chitosan (CMCS) microspheres were prepared under controlled conditions. The structure, acid/alkali resistance, and thermal properties of these microspheres were assessed. The adsorption properties of the prepared CMCS microspheres were also studied through graphite furnace atomic absorption spectrometry. Factors affecting adsorption efficiency were discussed. Results showed that the optimum preparation conditions included the following: 5% CMCS solution, 0.15 mol·L⁻¹ hydrochloric acid solution, and 0.625% glutaraldehyde cross-linking solution with bathing beads in a 40 °C water bath for 1 h and in a 60 °C water bath for 2 h. The optimal dosage, adsorption time, and pH of the fabricated CMCS microspheres are 5 g, 2 h, and 5, respectively. The initial concentration of cadmium chloride is 0.2 g·L⁻¹. The adsorption rate of CMCS microspheres on the simulated cadmium ions in aqueous solution is higher than 64% under the optimal condition.

Keywords: carboxymethyl chitosan; bead; heavy metal; cadmium; adsorption.

1 Preface

With rapid industrial and agricultural development, cadmium pollution of surface and industrial wastewater has intensified, leading to accumulate of this heavy metal in agricultural products. Excessive cadmium in the body can disrupt the normal physiological function of kidney, liver, and lung, resulting in organ lesions [1–3]. Although water protection in China has achieved good advances, the issue of water pollution has not been resolved yet [4–6]. Adsorption is an effective method used to dispose excess cadmium in water [7,8]. Traditional adsorbents, such as activated carbon and ion-exchange resin, can absorb large amounts of cadmium; however, the applications of these adsorbents become restricted because of their high price resulting from unforeseen reuse.

Chitosan (CTS), a polysaccharide with low price, can absorb excess cadmium in water through flocculation [9]. However, CTS application is limited because this compound only dissolves in dilute acids [10]. In this regard, carboxymethyl chitosan (CMCS) is prepared by chemical modifying OH⁻ and NH₂ in CTS to improve its water solubility. Huang [11] showed that compared with CTS solubility, CMCS solubility in alkaline solutions is improved significantly when the substitution

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degree reaches 1.36. As a kind of ideal green adsorbents [12], CMCS microspheres, which exhibit polycation characteristics, are prepared through ionic gelation under acidic conditions. These microspheres can be easily recycled after chelating cadmium. The natural characteristics and solution conditions of CMCS microspheres evidently influence their cadmium adsorption rate.

In this study, CMCS microspheres were prepared using a constant flow pump. The physical properties of these microspheres were characterized by analyzing their quality and structure, determining their alkali resistance through swelling behavior, and evaluating their thermal stability through DSC/TG. Conditions (i.e., adsorbent dosage, reaction time, pH, and initial cadmium concentration) affecting CMCS microsphere removal rate were studied and optimized to prepare highly efficient and environment friendly heavy metal adsorbents.

2 Materials and methods

2.1 Reagents and instruments

2.1.1 Main materials

The main materials included food grade CMCS (80% or higher) and A. R. grade glutaraldehyde, formaldehyde, and cadmium chloride.

2.1.2 Main instruments

The main instruments included a constant flow pump (HL-2 type), astral construct (TMS-Pro), synchronous thermal analyzer (STA409PC), and flame atomic absorption spectrophotometer (TAS-990).

2.2 Methods

2.2.1 CMCS microsphere preparation

Briefly, 1, 1.5, 2, and 2.5 g of CMCS was dissolved in 50 mL of water to prepare 2%, 3%, 4%, and 5% CMCS solution, respectively. The solution was added into 100 mL of 0.1, 0.15, and 0.15 mol·L⁻¹ hydrochloric acid solution at a constant speed by using a constant flow pump under constant stirring. The microspheres were washed with distilled water until pH 7 was obtained.

Two portions of 8 g of microspheres were weighed in 100 mL beaker. The first portion was mixed with 25 mL of 1.25% cross-linking agent (0.625% glutaraldehyde: 0.625% formaldehyde = 1:1). The remaining portion was mixed with the same volume of 0.625% glutaraldehyde. The two suspensions were placed in a water bath at 40 °C for 1 hour and at 60 °C for 2 h to cross link. The cross-linked CMCS microspheres were washed until the pH became neutral and preserved under wet condition.

2.2.2 Determination of physical and chemical properties of CMCS microspheres

(1) Structure profile analysis

The two kinds of CMCS microspheres were obtained, and the microspheres were uncross-linked in seven pieces. These microspheres were constantly shoved twice with TM-Pro type texture analyzer with a compression probe (D 35 mm). The following conditions and parameters were followed: instrument parameters, 120 mm/min; deformation of the component, 50%; trigger force, 0.50 N; residence time, 5 s; and data acquisition rate, 200 pps. The hardness and elasticity of CMCS microspheres were evaluated through quality and structure profile analysis using the texture profile analysis curves [13].

(2) Resistance to acid/alkaline

Briefly, 1 g of CMCS microspheres were placed in 40 mL solutions with pH values of 0.5, 1, 1.5, 1, 2.5, 3, 8.5, 8.75, 9, 9.25, 9.5, 9.75, 10, 10.25, 10.5, 10.75, 11, and 11.5. Ten CMCS microspheres were obtained every 1 h in the first 5 h, and their resistance to acid/alkaline was evaluated. The microspheres were then immersed for 24 h, and their resistance to acid/alkaline was evaluated again.

(3) DSC/TG thermal analysis

The sample (85 µg) was accurately weighed in alumina crucible. DSC/TG analysis [14] was conducted under nitrogen atmosphere at a flow rate of 40 ml/min, heating rate of 10 °C·min⁻¹, and temperature range of 30 °C to 500 °C.

2.2.3 Effect of cadmium adsorption by CMCS microspheres and influencing factors

Cadmium determination was conducted according to the standard procedures (GB 5009.15-2014).

(1) Dosage of CMCS

First, 1, 2, 3, 4, 5, and 6 g of wet CMCS microspheres were added in 20 mL of 0.2 g·L⁻¹ cadmium chloride at room temperature and oscillated for 2 h. Residual Cd²⁺ concentration was then determined.

(2) Reaction time

At room temperature, 80 mL of the cadmium chloride solution (0.2 g·L⁻¹) and 15 g of wet CMCS microspheres were added to 150 mL reaction bottle for oscillation. A sample was obtained every 5 min in the first 20 min, once every 20 min once, and every hour for 2 h thereafter. The sampling was discontinued after 8 h. Residual Cd²⁺ concentration was determined.

(3) Solution pH

Cadmium chloride solution (0.089 g·L⁻¹) was prepared with pH gradients of 1, 2, 3, 4, 5, 6, 7, and 8. Briefly, 20 mL of the solution was taken “in each”, and added with equal amount of wet CMCS microspheres. Residual Cd²⁺ concentration was determined after 2 h of oscillation.

(4) Initial concentration of cadmium

Briefly, 5 g of CMCS microspheres were weighed in 100 mL beaker flask with six replicates. The microspheres were added with 20 mL of 0.1, 0.15, 0.20, 0.25, 0.30, and 0.35g·L⁻¹ cadmium chloride solution. Residual Cd²⁺ concentration was determined after 2 h of oscillation.

2.2.4 Experiment data processing methods

A flame atomic absorption spectrophotometer was used to measure Cd²⁺ concentration. The adsorption rate of CMCS microspheres for cadmium was determined using Formula 1.

$$\text{Adsorption rate} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are the concentration of the adsorbed Cd²⁺ in the solution before and after adsorption, respectively (µg·mL⁻¹).

All of the tests were repeated three times. Statistics and data processing were implemented using MATLAB.

3 Results and discussion

The experiments were performed to select stable CMCS microspheres that could adsorb Cd²⁺ under various conditions. The microspheres were evaluated in terms of ballability, acid and alkali resistance, and thermal stability.

3.1 Basic properties of CMCS microspheres

3.1.1 CMCS microsphere structure

The following regression surfaces were obtained by applying triangle-based cubic interpolation method on discrete simulation data.

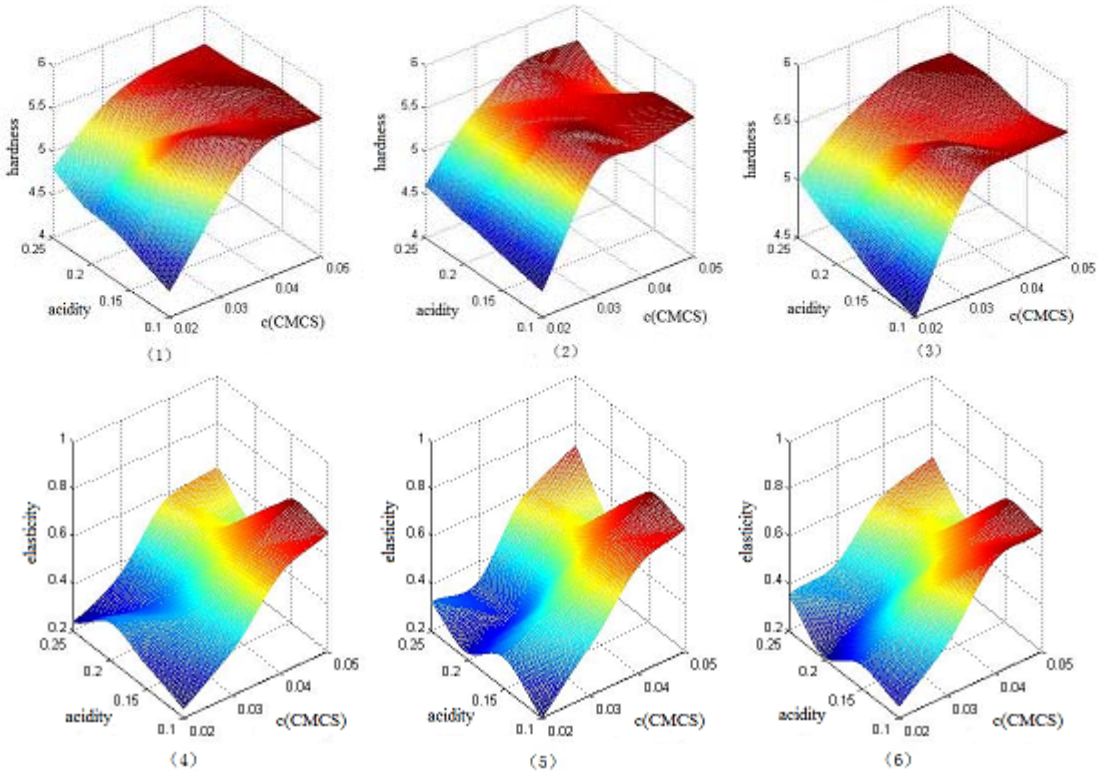


Figure 1. Regression surfaces of hardness and elasticity of CMCS microspheres.

(1)/(4) Uncross-linked CMCS microspheres; (2)/(5) 1.25% mixed cross-linking agent CMCS microspheres (3)/(6) 0.625% glutaraldehyde cross-linked CMCS microspheres.

Figures 1(1)–(3) show that the hardness of CMCS microspheres was not correlated with acidity but associated with concentration. Thus, 5% CMCS solution was selected to prepare high-quality CMCS microspheres^[15,16]. In 5% CMCS solution, glutaraldehyde cross-linked microspheres were harder than CMCS microspheres cross-linked with mixed agents. Figures 1(4) to 1(6) shows that glutaraldehyde cross-linked CMCS microspheres were the most elastic at HCl concentration of 0.15 mol·L⁻¹.

2.1.2 Acid/alkaline proof of CMCS microspheres

The pH sensitivity of CMCS microspheres can be determined by swelling behavior [17,18]. The results are shown as follows.

Table 1. CMCS pellets acid experimental results

pH \ time	1h	2h	3h	4h	5h	24h
0.50	—	—	—	—	—	smaller particle size
1.01	—	—	—	—	—	—
1.52	—	—	—	—	—	—
2.01	—	—	—	—	—	—
2.50	—	—	—	—	—	—
3.00	—	—	—	—	—	—
8.50	—	—	—	—	—	—
8.75	—	—	—	—	—	—
9.01	—	—	—	—	—	—
9.24	—	—	—	—	—	—
9.50	—	—	—	—	—	recover after swelling
9.75	—	—	—	—	—	recover after a little swelling
10.02	—	—	recover after swelling	recover after a little swelling	swell with a little dissolving	swell
10.24	swell with a little dissolving	swell with dissolving	swell with dissolving	swell with dissolving	swell with dissolving	swell with dissolving
10.50	swell with a little dissolving	swell with dissolving	swell with dissolving	swell with dissolving	swell with dissolving	swell with dissolving
10.74	swell with a little dissolving	swell with dissolving	swell with dissolving	swell with dissolving	swell with dissolving	swell with dissolving
10.97	swell with a little dissolving	swell with dissolving	swell with dissolving	swell with dissolving	swell with dissolving	swell with dissolving
11.52	a little dissolve	a little dissolve	dissolve	dissolve	dissolve	dissolve

Note: the above table “—” indicates no obvious change

CMCS microspheres were stable under acid or weak alkali conditions but begun to swell at pH > 9.5. Hence, CMCS microspheres are acid proof, not alkaline proof. The CMCS microspheres reacted with OH⁻ to produce salt (Figure 2). The suitable pH for preparing CMCS microspheres should be less than 9.5.

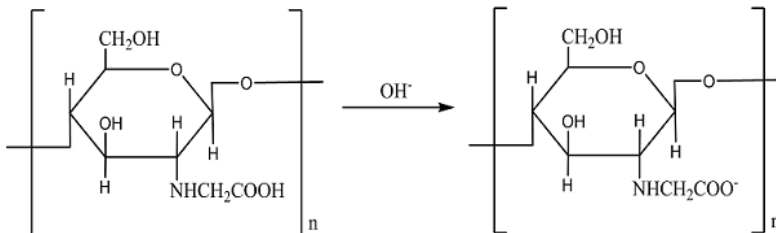


Figure 2. Schematic diagram of CMCS and OH⁻ reaction.

3.1.3 Thermal behavior of CMCS microspheres

The thermal analysis curves were obtained using the DSC/TG thermal analysis data. (1)CMCS, (2) 1.25% mixed cross-linking agent, cross-linked CMCS microspheres, (3)0.625% glutaraldehyde cross-linked CMCS microspheres.

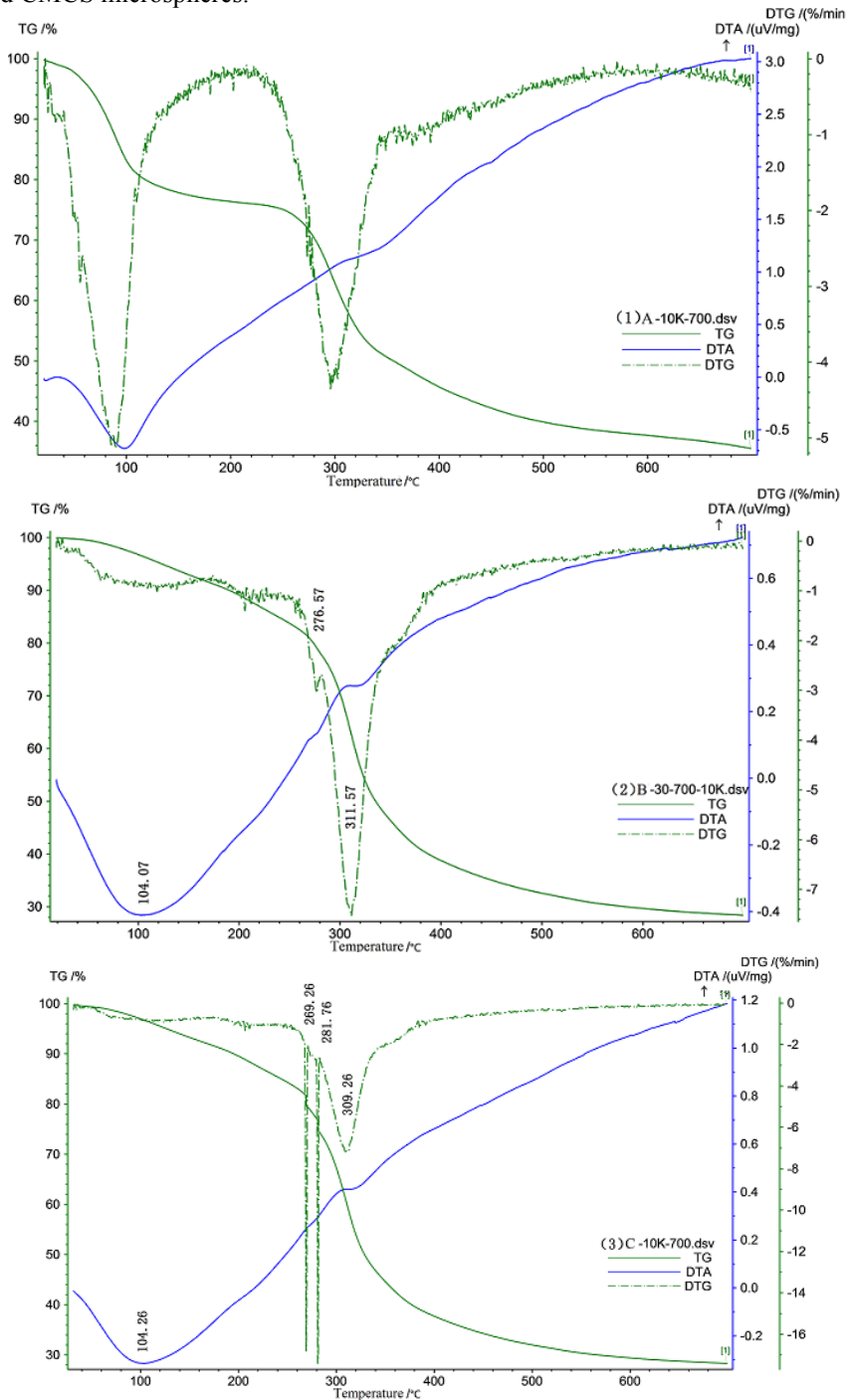


Figure 3. CMCS pellet thermograms.

Comparison of Figure 3(1) with Figure 3(3) showed differences among DTA, TG, and DTG curves of each sample. Figure 3(1) shows that the TG–DTG curve had two peaks. The peak at 91.26 °C is caused by water evaporation, and the peak at 296.26 °C is due to rupture of the main chain of CMCS and release of small molecular fragments. Figure 3(2) shows that the TG–DTG curve had two peaks at 276.57 °C and 311.57 °C. Figure 3(3) shows the three peaks of the TG–DTG curve at 269.26 °C, 281.76 °C, and 309.26 °C. This observation indicated that 0.625% glutaraldehyde cross-linked CMCS microspheres have denser structures than 1.25% mixed agent cross-linked CMCS microspheres. After cross-linking reaction, the structure of the CMCS microspheres changed from linear to reticular. The corresponding bond strength, number, and temperature of chain rupture also changed [19]. The conclusion supported the analysis results of the CMCS microsphere structure.

3.2 Factors affecting cadmium adsorption of CMCS microspheres

In addition to the properties of microspheres, solution conditions affect the cadmium adsorption effect.

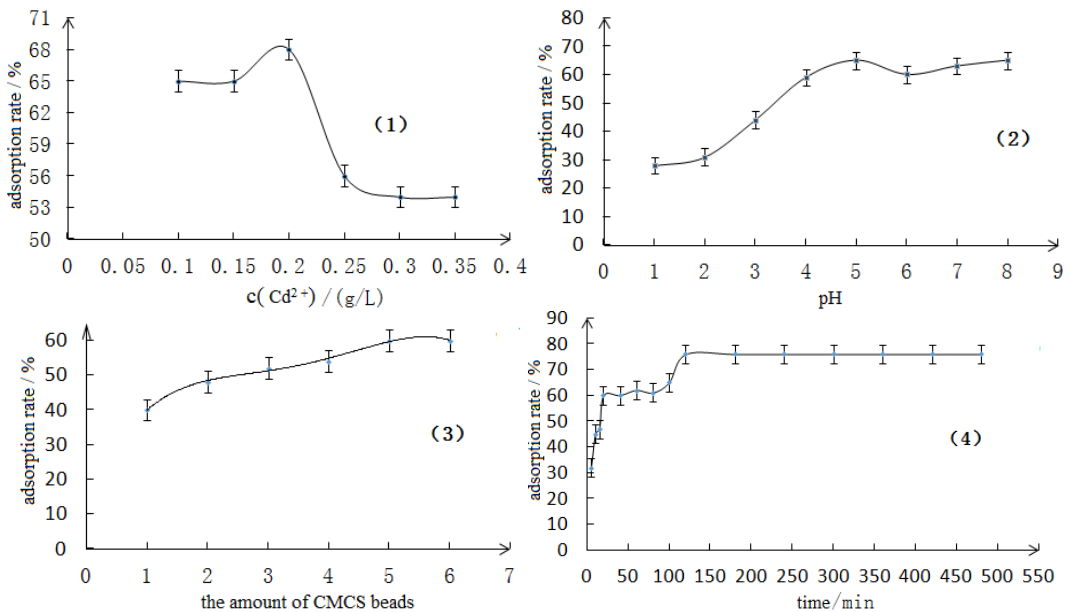


Figure 4. Effect of various factors on the adsorption rate of cadmium.

(1) Amount of balls, (2) Adsorption time, (3) pH, (4) Initial concentration of cadmium ion.

The Cd²⁺ adsorption rate of CMCS microspheres was positively correlated with the amount of microspheres added. The adsorption rate improved by adding CMCS microspheres for carboxyl groups and by increasing the reticular adsorption area [20]. The optimal amount of CMCS microspheres to be added was 5 g based on the cost of CMCS microspheres and Cd²⁺ adsorption rate. This finding is similar to that reported by Sankaramakrishnan [21], who showed that the adsorption is saturated upon addition of 4 g of CMCS.

Figure (2) shows that the Cd²⁺ adsorption rate increased with increasing time. The adsorption rate was constant 120 min after reaching the equilibrium. The equilibrium adsorption rate of CMCS microspheres was 64%, which is significantly higher than the 32% Cd²⁺ adsorption by CTS according to the research of Shan-shan Cheng [22].

The adsorption of Cd²⁺ by CMCS microspheres increased as the pH increased from pH 1 to 5. A turning point existed in pH 5, and then a rising trend occurred when the solution had pH 6. This research showed that the increase of pH resulted in the increase of the negatively charged carboxymethyl chelating ability of Cd²⁺ [23–25] because of the release of hydrogen ions. However, the adsorption rate decreased in pH 7 for Cd²⁺, which began to precipitate. Moreover, CMCS

microspheres could not be stabilized in alkaline conditions. The result is similar to that obtained by Muzzarelli et al. [26]. Thus, the optimal pH was 5.

Figure 4 shows that the adsorption of Cd^{2+} by CMCS microspheres in cadmium chloride reached the highest adsorption rate when the initial concentration was $0.2 \text{ g}\cdot\text{L}^{-1}$. The reaction rate was limited according to Arrhenius formula when the concentration was lower than $0.2 \text{ g}\cdot\text{L}^{-1}$. Limited CMCS microspheres reached the saturated adsorption of Cd^{2+} when the concentration was higher than $0.2 \text{ g}\cdot\text{L}^{-1}$, which was consistent to the findings by Liu B [27]. The best initial cadmium chloride concentration was $0.2 \text{ g}\cdot\text{L}^{-1}$.

4 Conclusions

Two kinds of CMCS microspheres were prepared with glutaraldehyde cross-linking agent and mixed cross-linking agent. After the comprehensive analysis of the physical and chemical properties of the two types microspheres, the optimal preparation condition involved dripping 5% CMCS solution into $0.15 \text{ mol}\cdot\text{L}^{-1}$ hydrochloric acid. The cross-linking reaction in 0.625% glutaraldehyde was conducted for 1 h in $40 \text{ }^\circ\text{C}$ water and in $60 \text{ }^\circ\text{C}$ water for 2 h. Under this condition, the elasticity, hardness, and thermal stability of CMCS microspheres were higher than those of CMCS.

In consideration of the effect of the medium conditions on CMCS carboxyl adsorption site groups and Cd^{2+} concentration, the best beginning cadmium chloride concentration was $0.2 \text{ g}\cdot\text{L}^{-1}$, the ideal dosage of CMCS beads was 5 g, the ideal pH was 5, and the ideal adsorption time was 2 h. Under these conditions, the adsorption rate of cadmium was higher than 64%.

CMCS microspheres had relatively stable structures in adsorbing cadmium when prepared under the optimized condition. Thus, CMCS microspheres had a certain advantage in recycling and have a wide application prospect. However, "the problem" remains to be studied after the CMCS microsphere saturated adsorption of Cd^{2+} .

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