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Low-Cost magnetic adsorbent for efficient Cu(II) removal from water

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Abstract

Selective adsorption using magnetic adsorbent is supposed as one of the most effective methods for heavy metal removal from water for the advantage of efficient solid-liquid separation. However, the application of this technique is hindered by the high cost, unfavorable environmental effects of the chemical synthesis of magnetic adsorbents. In this study, the industrial waste coal-fly-ash magnetic sphere (CMS) were carefully processed to prepare cheap and green magnetic core material. Then, a composite bioadsorbent using CMS as core and chitosan (CS) as the shell (CMS@CS for short) was fabricated via an extrusion-dripping method. Structural investigations indicate that the obtained CMS@CS samples are hollow microsphere with a solid wall or porous solid microsphere depending on the preparation conditions. CMS particles are evenly distributed in both microspheres. The porous sample has an 81.49 m² g⁻¹ special surface area, 96 times larger than the hollow. The highest Cu(II) adsorption of the porous sample is measured as 22.41 mg g⁻¹, 3.6 times larger than that of the hollow. The Cu(II) adsorption of the CMS@CS samples is closely related to the internal structure, surface chemical modification, and solution pH. The adsorption mechanism could be explained by a two-step procedure model. The CMS@CS adsorbents have an average magnetism of 10.07 emu g⁻¹, thus could be magnetically separated efficiently. The density of CMS@CS is tested as 1.45–1.65 g cm⁻³. A similar density with water would improve its suspend ability in the water. The used CMS@CS adsorbent could be recycled several times after appropriate treatment.

1. Introduction

Heavy metal pollution has been attracted worldwide attention for its high toxicity and non-biodegradability. Removal of heavy metal ions, e.g., Cu(II), from water is of great significance to human health and water purification [1, 2]. Various techniques, including chemical precipitation, ion exchange, adsorption, electrochemical separation, and biological treatment, have been developed to get rid of Cu(II) from wastewater. Adsorption of Cu(II) using biomaterial chitosan (CS) as adsorbent has been hotly studied owing to the advantages of low cost, green operation, and little secondary pollution [3–7]. Owing to abundant amino and hydroxyl groups in molecular structure, CS has a strong selective adsorption capacity for Cu(II) adsorption. The adsorption capacity of CS adsorbents has been further improved by graft modification, surface modification, and increasing the specific areas [8–10]. However, CS is soluble in a weak acid condition. Thanks to the hard work of the researchers, this problem has been solved by the crosslinking technique [2, 7, 11–13]. One of the challenges in CS adsorbent application is the inefficient solid-liquid separation, and bad suspend ability (the density of CS is 0.75–0.85 g cm⁻³) in water. To increase the solid-liquid separation efficiency, a magnetic separation technique was developed, and various magnetic CS adsorbents were synthesized. However, most of these magnetic CSs used nano-sized Fe₃O₄ or another ferrite as magnetic cores [14–18]. Given that nano-magnetic cores need to be chemically synthesized, the application of these magnetic adsorbents has been limited.
followed by a continuous 4 h stirring. Then, CMS particles with a mass ratio of 3:1 to CS was added into the CS in order to improve their magnetic property and enhance their adsorption capacity. The CMS@CS samples were fabricated by an extrusion-dripping method. The overall processing is diagrammed in figure 2. Brieﬂy, a CS solution (2 wt.%) was prepared by dissolving CS in an acetic acid solution (1 wt.%) followed by a continuous 4 h stirring. Then, CMS particles with a mass ratio of 3:1 to CS was added into the CS.

by their high cost, agglomeration, and signiﬁcant environmental impact. In addition, possible oxidation of the Fe²⁺ in nano-sized magnetite requires a hypercritical preservation condition. Finding a cheap and green substitute for the nanomagnetic core is essential for the wide application of magnetic CS. Coal-ﬂy-ash magnetic sphere (CMS) is supposed as one of the most promising candidates. Coal ﬂy ash is a bulk industrial waste with tremendous output and widespread distribution, especially in developing countries where coal acts as a major energy source [19]. There are some 2–23 wt.% CMS in coal ﬂy ash depending on the mining environment and burning condition. CMS can be separated easily from CFA by magnetic separation. Since CMS is a recycled resource extracted from industrial waste, it is cheap, in ample supply, and eco-friendly. The primary component of CMS is ferrous oxide. Thus CMS has strong magnetism [20, 21]. The density of CMS is 3.1–4.5 g cm⁻³. Therefore, if CMS combined with CS, it will increase the density of CS adsorbent and improve the suspend ability in the water. All these suggest CMS could be a promising magnetic core material. However, raw CMS cannot be used directly. CMS has a typical diameter of 20–100 μm, too large for water-treatment applications. CMS also contains some nonmagnetic impurities, which reduce the magnetism. Furthermore, some CMSs contain heavy metals or toxic components that may dissolve. Therefore, careful processing is needed before its application.

In this study, CMS was carefully ball-milled, followed by multiple magnetic separations, to produce cheap and green magnetic core material. Then two types of CMS@CS magnetic microspheres were fabricated by a simple extrusion dripping method. The structure, magnetism, and Cu(II) adsorption of the samples were systematically investigated, and the mechanism of the Cu(II) adsorption was discussed in detail.

### 2. Materials and methods

#### 2.1. Apparatus and analysis method

The particle size distribution of the CMS particle samples was examined using an SALD-7101 laser diffraction particle size analyzer (LDPAZ, Japan). The scanning electron microscope (SEM) images, element-distribution mapping, and element composition of the samples were obtained with a JEOL JSM-4990LV SEM (Japan) equipped with an Oxford energy dispersive spectrometer (EDS, England). The structure of the samples was characterized by a Rigaku D/Max-2200 x-ray diffractometer (XRD, Japan) with Cu (Kα1) (1.54 Å) radiation. The thermodynamic stability was tested by a thermogravimetry (TG, SETAMAR, France). The magnetic properties were characterized by a vibrating sample magnetometer (VSM, Lake Shore 7410, USA) at 300 K. The surface characterization was carried out using pore structure analysis (BET, Autosorb-IQ-MP, Quantachrome Instruments). The infrared spectra were acquired using an FTIR-Vector33 instrument (FTIR, Germany).

#### 2.2. Processing of the CMS

The coal ﬂy ash was collected by an electrostatic precipitator from a typical pulverized-coal–fired power plant in Huainan city, China. CMS was separated from the coal ﬂy ash using a two-step magnetic separation process [22]. Briefly, a high-ﬁeld dry magnetic separation is followed by a low-magnetic-ﬁeld wet magnetic separation. The obtained CMS was ball-milled by a planetary ball miller using steel balls as ball milling media with a rotate speed of 280 r m⁻¹. After 8 h ball-milling, the particle size was reduced below 9.6 μm. After an additional low-magnetic-ﬁeld wet magnetic separation, CMS particles obtained. The CMS particles were dried at 110 °C in vacuum for 2 h. The mineral composition and the particle size distribution of the CMS particles are shown in Table 1 and Figure 1, respectively.

#### 2.3. Synthesis of the magnetic chitosan microspheres

The CMS@CS samples were fabricated by an extrusion-dripping method. The overall processing is diagrammed in figure 2. Briefly, a CS solution (2 wt.%) was prepared by dissolving CS in an acetic acid solution (1 wt.%) followed by a continuous 4 h stirring. Then, CMS particles with a mass ratio of 3:1 to CS was added into the CS.

| Samples    | Output (%) | Particle diameter (μm) | Element percentage (%) | Saturation magnetization (emu g⁻¹) |
|------------|------------|------------------------|------------------------|-----------------------------------|
|            | Output (%) | Diameter               | Φ₅₀                    |                          |
| Coal flyash| 100        | 0.4–196.3              | 38.1                   | 7.63                  | 55.35                   | 27.19                   | 9.82                  | /                     |
| CMS        | 7.32       | 0.9–116.2              | 41.6                   | 65.18                 | 15.65                   | 11.13                   | 8.14                  | 23.71                 |
| CMS particle| 5.63      | 0.4–8.1                | 3.7                    | 78.04                 | 8.84                    | 6.79                    | 6.35                  | 31.12                 |

Table 1. Output and mineral composition of coal fly ash, raw CMS, and processed CMS particles (with the elements below number 10 not taken into account). ‘Others’ refers to Ca, Mg, K, Na, Ti, and trace elements.

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*Note: The table and figures are not included in this text. The content is extracted and formatted for readability.*
solution to form a stable CS/CMS mixture. The CS/CMS mixture was divided equally into two parts. Then, 20 ml ethanol, 1 ml foaming agent (FA), and 5 ml carbon disulphide (CDS) was added into one of the CS/CMS mixture. After 6 h stirring at 40 °C, the CS/CMS/FA-CDS solution was obtained. Two types of CS@CMS microspheres were fabricated by the extrusion-dripping method using CS/CMS and the CS/CMS/FA-CDS solution, respectively. For convenience, the latter was named as CS@CMS-F. The extrusion dripping was driven by a syringe pump with a controllable flow rate ranges 0.002–100 ml min\(^{-1}\) (see figure S1 is available online at stacks.iop.org/MRX/7/105503/mmedia) at a flow rate of 0.5 ml min\(^{-1}\). A hypodermic needle with an inner diameter of 0.3 mm was used for dripping the CS/CMS or CS/CMS/FA-CDS mixture into the 2 M NaOH solution (water: ethanol = 4:1) and stirred at 500 r m\(^{-1}\). The obtained microspheres were magnetically separated from the solution. After 2 times of washing by ethanol, the samples were dried entirely by freeze-drying at –30 °C [23].

2.4. Adsorption experiments

The Cu(II) containing solution used in this study was prepared in the laboratory by dissolve CuSO\(_4\) into deionized water. The Cu(II) concentration was 20.0 mg l\(^{-1}\), and the original pH value was examined as 5.1. To test the adsorption performance, 0.5 g of CMS, CMS@CS, and CMS@CS-F were added into 250 ml Cu(II) solution in a 500 ml conical flask, respectively. The mixtures were electrically stirred for 4 h using a six-linkage electric stirrer. 5 ml solution was extracted every 15 min to test the Cu(II) concentration. To study the effect of the pH on the adsorption, the pH of Cu(II) solution was tuned to 3–7 by dilute hydrochloric acid and ammonia. After the equilibration time had elapsed, the magnetic adsorbents were separated using an external magnet. The
concentration of Cu(II) ion was measured using the sodium diethyl dithiocarbamate spectrophotometric method, which was described in support information section 1 and figure S2.

2.5. Desorption and recycling

The reusability of the CMS@CS-F was investigated using Na₂EDTA as desorbent. Briefly, 0.5 g of the CMS@CS-F was added to 100 ml of 0.1 M Cu(II) solution, and then the mixture was electrically stirred for 180 min to allow equilibrium to be reached. Then the CMS@CS-F was separated using an external magnet and washed with deionized water several times. The CMS@CS-F was then added to 500 ml 0.1 M Na₂EDTA, stirring for 50 min. The CMS@CS-F was magnetically separated and thoroughly washed with deionized water. Then it was fully dried by freeze-drying at −30 °C before being reused in the same procedure.

3. Results and discussion

3.1. Structure and magnetism

The morphology of CMS@CS and CMS@CS-F microspheres is very similar to the naked eye. Both are light black balls. But their compressive strength is different. CMS@CS has larger strength. 6 CMS@CS microspheres can support 2 Kg weight, while the same number of the CMS@CS-F particles can only support 0.8 Kg weight. The method for the compressive strength comparison is described in support information section 2. Although the surface of CMS@CS and CMS@CS-F looks smooth by the naked eye, they are not smooth under SEM, as shown in figures 3(a), (e), and S3 in support information. Many bulges are observed on the surface of both samples due to the presence of CMS particles under the surface. This indicates that the distribution of CM particles S in CS is uniform. Both the two kinds of microspheres are about 110–240 μm in diameter. The appearance of CMS@CS and CMS@CS-F is very similar, but their internal structure is different. Figure 1(b) shows the sectional view of CMS@CS microsphere. It is found that it is a hollow sphere with a thick and solid wall. The distribution of the CMS particles in the wall is clear. By contrast, the CMS@CS-F microsphere is a solid sphere, and the inside structure is very loose. As shown in figures 3(c), (d), the microsphere has a lot of micro- or nano-pore structures.

The porous structure of CMS@CS-F was further verified by BET nitrogen adsorption. As shown in table 2 and figure 4(S), the specific surface area of raw coal fly ash, CMS particles, CMS@CS, and CMS@CS-F microspheres are tested as 4.85, 6.17, 0.85, and 81.49 m² g⁻¹, respectively. The specific surface area of CMS@CS is even lower than that of the CMS particles for its solid wall structure. The CMS@CS-F has a 96 times larger specific surface area than that of CMS@CS. It also has a large micropore surface and micropore volume, 14.06 m² g⁻¹ and 0.0093 cm³ g⁻¹, respectively. The large specific surface area and high micropore ratio of CMS@CS-F is

Table 2. Surface properties of coal fly ash, CMS particles, CMS@CS, and CMS@CS-F.

| Samples            | CFA     | CMS particles | CMS@CS | CMS@CS-F |
|--------------------|---------|---------------|--------|----------|
| Specific surface area (m² g⁻¹) | 4.85    | 6.17          | 0.85   | 81.49    |
| Micropores surface (t-plot; m² g⁻¹) | 1.88    | 1.94          | /      | 14.06    |
| Micropores volume (t-plot; cm³ g⁻¹) | 0.0004  | 0.0006        | /      | 0.0093   |
conducive to the adsorption of heavy metal ions. Due to the hollow spherical structure and porous structure, CMS@CS and CMS@CS-F have an approximate density of 1.45–1.65 g cm$^{-3}$. A similar density with water would improve the suspendability of CMS@CS-F in water. The element distribution in the CMS@CS-F was investigated by the EDS mapping. As shown in figures 3(e)–(h), Fe, and Si, the main elements of CMS are evenly distributed in the microspheres and well match each other. This means the CMS particles are well incorporated and evenly distributed in the microspheres. Since CMS has little C element, the C element surrounding the CMS particles should belong to chitosan.

Figure 4 shows the XRD patterns of CMS, CMS@CS, and CMS@CS-F. CMS has a complex composition. Thus magnetite, hematite, mullite, and quartz could be found in the CMS spectrum. Since the iron oxide, e.g., spinel Fe$_3$O$_4$, is the dominant component, the CMS particles have strong magnetism. The spectrum of CMS@CS and CMS@CS-F consists of almost all the diffraction peaks of CMS, but the intensity decreases. Interestingly, an additional weak and broad peak presents at 2$\theta$ = 20° around. This peak could be assigned to chitosan [4, 7, 24]. This peak in the CMS@CS-F spectrum is weaker than that in the CMS@CS spectrum, indicating the lower density and crystallinity of chitosan. This is in consistent with the BET result.

The mass percentage of CMS in the CMS@CS and CMS@CS-F was determined by TG. As shown in figure 5(a), CMS shows little significant weight loss at 0 °C–600 °C. The mass loss of CMS@CS and CMS@CS-F at 54 °C–300 °C and 300 °C–550 °C corresponds to the dehydration and the CS decomposition process, respectively [25–27]. The residual mass tends to be constant after 550 °C. Considering CS and another organic component has been burned out, the mass percentage of CMS in CMS@CS and CMS@CS-F should be 33.6%.
and 32.4% around, respectively. This is further proved by the magnetic investigation. As shown in figure 5(b), the magnetism of CMS@CS and CMS@CS-F is measured as 10.17 emu g⁻¹ and 10.04 emu g⁻¹, respectively, which is near the 1/3 of that of the CMS particles (31.12 emu g⁻¹). Yet, the magnetism is strong enough for effective magnetic separation. As illustrated in the inset of figure 5(b), the microspheres could be separated easily by a permanent magnet.

The chemical structures of the CMS, CMS@CS, and CMS@CS-F were characterized by FTIR. As shown in figure 6, the major absorption peaks at 3460 cm⁻¹ and 1635 cm⁻¹ around are attributed to O-H bond stretching of adsorbed water. The peaks at 585, 470, and 1100 cm⁻¹ belong to Fe-O, Si-O, and Si-O-Si bond, respectively [28–30]. The small peaks at 1376 and 2369 cm⁻¹ could be assigned to the bond between other ions and O atom. All these peaks of CMS present in the CMS@CS and CMS@CS-F spectra, but the intensity decreases. Three new peaks are found in the CMS@CS spectrum. The peaks at 2854 and 2926 cm⁻¹ are attributed to aliphatic hydrocarbon (C–H) stretching vibrations [31], and the peak at 896 cm⁻¹ corresponds to the β-anomer N-bond stretching bond [28, 32]. These peaks well proved the presence of chitosan molecular. The CMS@CS-F spectrum contained two extra small peaks at 1427 and 1127 cm⁻¹, which could be assigned to N-C=S and C=S stretching vibrations, respectively [28, 33]. This strongly indicates the presence of xanthate groups bonded to CS.

3.2. Cu(II) adsorption

Figure 7(a) shows the Cu(II) adsorption of CMS particles, CMS@CS, and CMS@CS-F at pH = 5.1. The Cu(II) adsorption of CMS particles, CMS@CS, and CMS@CS-F are 1.14, 6.25, and 22.41 mg g⁻¹, respectively. The Cu(II) adsorption is the highest, 3.59 times of that of CMS@CS. As shown in the CMS@CS-F curve, the Cu(II) adsorption increases sharply at the beginning, and then slows down gradually until it reaches the adsorption
equilibrium at 160 min. The Cu(II) adsorption exceeds 20 mg g$^{-1}$ within the first 90 min, which is shorter than most of the previously reported CS adsorbents \[6, 13, 14, 16, 28, 30, 33–42\]. This suggests the CMS@CS-F could be used as a fast and efficient Cu(II) adsorbent. The Cu(II) adsorption is significantly affected by the solution pH. As shown in figure 7(b), the adsorption of all the three samples is very low at pH $= 3$, but increases fast with the increasing of pH till pH $= 5.1$. Then the adsorption keeps a slow increase until pH $= 7$. Since the precipitation effect of Cu(II) ion is significant when pH $> 5.5$, the highest adsorption of CMS@CS-F should be at pH $= 5.1$ around, 22.41 mg g$^{-1}$.

### 3.3. Recycling of the adsorbent

The efficiency and application will be highly improved if the adsorbent could be recycled and reused. Five consecutive adsorption–desorption cycles were performed to test the reusability of CMS@CS-F. As shown in figure 8, the adsorption capacity decreased slightly after each cycle, owing to the incomplete desorption of Cu(II). The adsorption capacity remained over 82% of the original value after five cycles.

### 3.4. Adsorption mechanism

To study the P adsorption mechanism of the CMS@CS and CMS@CS-F, pseudo-first- and pseudo-second-order kinetic models were employed to fit the time-dependent experimental data \[43\] (support information section 3). The fitting parameters have been calculated and are listed in table 3. The fitting curves of the two kinetics models are shown in figure 9. By the pseudo-second-order model fitting, the correlation coefficient (R$^2$) of CMS@CS and CMS@CS-F is 0.997 and 0.992, respectively. While the R$^2$ values are 0.911 and 0.893, respectively, by the pseudo-first-order fitting. This suggests the Cu(II) adsorption should be better described by the pseudo-second-order model, belong to chemical adsorption.

The Cu(II) adsorption of CMS@CS-F is stronger than that of CMS@CS may be related to two factors. One is the much larger specific surface area, which enhanced the physical adsorption, the number of adsorption sites, and chemical groups. The other is the surface modification. The surface of CMS@CS-F has more functional groups such as amino, hydroxy, and sulfuric groups owing to the xanthation. These chemical groups have a strong chemical affinity for Cu(II), thus could adsorb more Cu(II) ions. The overall adsorption mechanism could be described as a two-step procedure, as shown in figure 10. Firstly, Cu(II) ions were adsorbed onto the surface of CMS@CS-F by physical adsorption. Under the weak acidic condition, the hydroxy groups on the chitosan surface were ionized and negatively charged. Thus the positively charged Cu(II) ions tended to be

![Figure 8. Cu(II) adsorption performance of the regenerated CMS@CS-F.](image-url)

### Table 3. Kinetic fitting parameters of Cu(II) adsorption on CMS@CS and CMS@CS-F.

| Adsorbent | $Q_{exp}$ (mg g$^{-1}$) | $q_e$ (mg g$^{-1}$) | $K_1$ (min$^{-1}$) | $R^2$ | $Q_e$ (mg g$^{-1}$) | $K_2$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ |
|-----------|------------------------|---------------------|-------------------|-------|---------------------|--------------------------------|-------|
| CMS@CS    | 6.25                   | 3.29                | 0.0237            | 0.891 | 6.81                | 0.0051                         | 0.992 |
| CMS@CS-F  | 22.41                  | 14.81               | 0.0156            | 0.935 | 22.57               | 0.0065                         | 0.997 |
adsorbed by electrostatic attraction. The Cu ions quickly reached the adsorption-desorption equilibrium and formed a high Cu(II) concentration area at the solid-liquid interface. Secondly, Cu(II) ions chemically bonded with the functional groups on the modified CS surface. The amino group supplies a lone pair of electrons to the empty atomic orbital of a Cu(II) ion, forming an amino-metal chelate complex [28, 35]. The dithiocarbamate group (a soft base) also has a strong affinity for Cu(II) ions (a soft acid) according to the hard and soft acid and base theory. Due to the high concentration of the functional chemical groups, CMS@CS-F adsorbed more Cu(II) ions.

4. Conclusions

In summary, a simple extrusion-dripping method was developed to prepare CMS@CS and CMS@CS-F magnetic adsorbents. The highest Cu(II) adsorption of CMS@CS-F is tested as 22.41 mg g\(^{-1}\) at pH = 5.1. The CMS@CS-F has a density of 1.45–1.65 g cm\(^{-3}\), which can improve the suspend ability in the water. The CMS@CS-F adsorbents could be magnetically separated effectively and reused for several times after appropriate treatment. The Cu(II) adsorption mechanism could be explained as a two-step procedure, electrostatic attraction followed by chemical adsorption.

CMS is obtained from industrial waste, and CS is the richest natural polymer. Thus CMS@CS-F is a cheap, green, and well-sourced. In addition, the extrusion-dripping method could be used in industrial production after an appropriate improvement. Therefore, the CMS@CS-F adsorbent should have a promising future in industrial applications.
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Data availability statement

Some or all data, models, or codes that support the findings of this study are available from the corresponding author upon reasonable request.

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