Fabrication of solid alginate particles containing functionalized MWCNTs using a microfluidic technique

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Abstract. A series of solid alginate particles containing different amounts of functionalized multi-walled carbon nanotubes (MWCNTs) have been successfully prepared by microfluidic technique. The influence of MWCNTs doping on the surface morphology, structure and properties of calcium alginate (CA) particles has been investigated using SEM, FTIR, XRD, TGA and UV-Vis spectra. SEM indicates that the obtained hybrid particles are of good morphological characteristics, and its color changes from yellow to black which proves MWCNTs is successfully dispersed in CA particles. Moreover, the particles surface changes rough from smooth after MWCNTs doping. FTIR results verify the interactions between functional groups of CA and MWCNTs. Besides, the incorporation of MWCNTs to CA particles can efficiently enhance the thermal stability of CA particles at high temperatures, which is ascribed to the better thermal stability of MWCNTs as well as the interactions between MWCNTs and CA particles. The removal efficiency of CA particles doped with a lower percentage of MWCNTs (0.06 wt. %) for methylene blue is 96.38%, which is much higher than that of pure CA particles (61.21%).

1. Introduction

Sodium Alginate (SA), a linear polysaccharide, is naturally occurring polymer composed of α-guluronate and β-mannuronate residues. Its solutions can be transformed into a hydrogel on addition of metallic divalent cations such as Ca²⁺. Moreover calcium alginate (CA) hydrogel particles can be used as good adsorbents for removal of different metal cation or organic pollutes due to the presence of carboxyl and hydroxyl groups along its chains [1-2]. However, some prepared CA particles still have some drawbacks, such as low adsorption capacity or poor thermal stability [2-3], which make them difficult to be further used in environmental pollution management.

To solve problems above mentioned, alginate particles have been blended with some especial filler to improve its adsorption capacity. Sun et al [4] reported that the GO/CA composite particles had higher adsorption capacities for acridine orange than those without GO. Hassan et al [5] proposed the use of activated carbon/CA hybrid particles for the removal of arsenic from aqueous solutions. The results indicated that the adsorption capacity of composite particles has higher adsorption capacity for arsenic comparing with pure CA particles or activated carbon. Besides these, other studies [6-7] also reported the enhancement of the adsorption capacity of CA particles for Pb (II) or methylene blue could be achieved by adding some magnetic materials such as glycine-Fe₃O₃ or Cyanex 272.
Carbon nanotubes (CNTs) is a more promising nano-filler for polymers compared to above-mentioned filler. It has been reported that incorporating of nanotubes into some adsorbents can effectively improve their ability to capture dyes or metal ions from aqueous phase [8-9], which can be attributed to nanotubes’ large specific surface area, exceptional hollow and layered structures. Our previously studies also proved that CNT impregnation is a good method to enhance adsorption capacity of chitosan hydrogel particles [10]. However, to the best of our knowledge, the detailed study on the effect of CNTs doping on the morphology and structure of CA particles has hardly been reported. Moreover, no study about the thermal stability of CNTs/CA has been reported. On the other hand, functionalized microspheres consisting of various organic or inorganic materials can be prepared using a microfluidics technology [11-12], but the fabrication of solid alginate particles containing functionalized MWCNTs by the microfluidic technique has not received much attention.

In this study, a series of solid alginate particles containing different amounts of functionalized multi-walled carbon nanotubes (MWCNTs) are fabricated by microfluidic technique. The hybrid particles are characterized by means of SEM, FTIR, XRD, TGA and UV-Vis spectra. The effect of MWCNTs doping on the structure and properties of CA particles is discussed in detail. The possible influence mechanism is also investigated.

2. Experimental

2.1. Materials and device
Sodium alginate (SA) and methylene blue (MB) are obtained from Sigma Aldrich (USA). MWCNTs (diameter: 10–30 nm, length: 5–15 μm) are purchased from Beijing Nachen Nanotech Co.Ltd and MWCNTs are further acid-treated by the previously established methods [10]. The acid-MWCNTs can be dispersed into sodium alginate solution and no precipitation is observed in the solution after several weeks. All other agents are of analytical grade. Deionized (DI) water is used in all experiments. The microfluidic device used in this study is supplied by Beijing CapitalBio Corporation.

2.2. Preparation of particles
Fig. 1 shows the schematic for the production of particles. 1.5 g SA are added into 100mL DI water in a beaker to obtain SA solution and then stirred for 12 h at 60 °C. A certain amount of acid treated-MWCNTs are added to the SA solution in an ultrasonic bath and loaded into a single out-put syringe as the disperse phase, and peanut oil is loaded into a double output syringe as the continuous phase. Then the disperse phase and continuous phase are simultaneously injected into the microfluidic chip through Teflon tubes by using Syringe pumps (WHP01 Model, Baoding Longer, and CHI). A water-in-oil (w/o) emulsion is formed at the cross-junction by using two continuous peanut oil streams to shear the SA and MWCNTs-SA solution. The droplets are dripped into a stirring calcium chloride solution through the other Teflon tube. The water-soluble droplets are transformed into water-insoluble MWCNTs-calcium alginate particles (Marked M-CA particles) in the condition of calcium chloride. Finally, the obtained MWCNTs-CA particles are washed with deionized water several times to remove residual calcium chloride from particle surface and then air-dried for 24 h, followed by drying at 55 °C for 12 h. In comparison, the pure CA particles are also prepared according to the above procedure. (Marked CA particles).
2.3. Measurements

The molecular structure analyses of all the samples are carried out with FTIR (Nicolet 5700, USA) with the wavenumbers recorded from 400 to 4000 cm\(^{-1}\) at a 1 cm\(^{-1}\) resolution. Sample structures are analyzed by XRD (D8 Advance, GER) with Cu K\(_{\alpha1}\) radiation. The surface morphology of the dried particles is measured by SEM (FEI Sirion 200, NLD). TGA is performed on a TG/DTA thermal system (Model HCT-2, CHI) with a heating rate of 5 \(\degree\)C min\(^{-1}\) over the temperature range of 0\(\sim\)950 \(\degree\)C under air atmosphere.

Batch adsorption experiments are conducted according to the following procedure. 100 mg of hydrogel particles are added into erlenmeyer flask containing 25 mL of MB solution (initial concentration 200 mg/L, initial pH 8.0). After shaken at 30 \(\degree\)C overnight to establish the adsorption-desorption equilibrium, and the dye solution was separated from the adsorbent by centrifugation at 4000 rpm for 30 min. The concentrations of MB in filtrate are determined by a double beam UV-Visible spectrophotometer (Model TU-1901, CHI) at 666 nm with a linear regression equation (\(y = 0.1043x - 0.0133, R^2 = 0.9998\)), which is obtained by plotting a calibration curve for dye over a range of concentrations. All experiments are conducted in triplicate.

The removal percentage \((R\ %)\) of MB by hydrogel particles at the equilibrium can be calculated using Eq (1).

\[
R(\%) = \frac{C_0 - C_e}{C_0} \times 100\%
\]  

Where \(C_0\) (mg/L) and \(C_e\) (mg/L) are the liquid phase concentration of MB at initial and equilibrium, respectively.
3. Results and discussion

3.1. Morphology

The surface morphology of CA and M-CA particles are shown in Figure 1. Macroscopically, the particles obtained are all spherical in shape, and the addition of MWCNTs does not alter the macroscopic surface morphology of the particles. However, one noticeable characteristic of the particles is its yellow to black color (Inset in Fig 2), which confirms MWCNTs is successfully dispersed in CA particles.

The microscopic surface morphology of particles was observed by SEM. The CA particles have a tight and smooth surface (Fig. 2a) with some concave structures spotted on the surface of particles, which might be caused by partly collapsing the polymeric gel network during drying [13]. The surface of M-CA particles is, however, highly rough although the spherical shape is maintained (Fig. 2b). Another noticeable characteristic of M-CA particle surface is very homogeneous and has not any concave structures. These obvious surface morphological changes might be due to the homogeneous dispersion and supportive role of MWCNTs in CA particles.

![Figure 2. The surface micrographs of CA and M-CA particles](image)

(a) CA particles, (b) M (0.06 wt %) -CA particles

3.2. FT-IR analysis

Fig. 3 shows the FTIR spectrum of CA, MWCNTs and MWCNTs/CA in the region of 4000 to 400 cm\(^{-1}\). The FTIR spectra of CA particles shows the characteristic peaks at 3415, 1612, 1430, 1087 and 1033 cm\(^{-1}\), which are due to the stretching of O-H, -COO (asymmetric), -COO (symmetric) and C-O-C, respectively (Fig. 3a). In the FTIR spectrum of acid-MWCNTs, the principal absorption peaks appearing at 3434 cm\(^{-1}\) for -OH stretching, 1630cm\(^{-1}\) for C=C skeleton vibrations, 1710 and 1590cm\(^{-1}\) for -COO stretching in the -COOH groups reveal the -COOH functionalization of MWCNTs (Fig. 3b). Incorporating functionalized MWCNTs into CA particles causes an obvious shift to lower wavenumber and a decrease in intensity of -OH stretching peaks of CA particles (Fig. 3c). This indicates that an intermolecular hydrogen bonding is formed between CA and functionalized MWCNTs. And the formation of hydrogen bonding can possibly occur between the carboxyl groups on the MWCNTs and hydroxyl groups of CA. Moreover, it can also be seen that the intensity of the band representing -COO (1597 and 1417 cm\(^{-1}\)) stretching of carboxyl groups becomes weaker and has a noticeably red shifting when CA particles doped with MWCNTs. It is possible to explain that the negative charge of the carboxyl group in the alginate has some electrostatic interaction with the positive charge of MWCNTs.
Figure 3. The FTIR spectra of (a) the CS particles, (b) acid-MWCNTs and (c) the M (0.1 wt %)-CS composite particles.
3.3. XRD analysis
Molecular interaction of CA and MWCNTs in hybrid particles is also investigated using XRD. CA gel particles only has a broad diffraction (0 0 1) peak around 10.4 (Fig 4a), indicating the defective crystals and a low crystallinity of CA particles [14]. The pure MWCNTs shows a sharp peak centered on 2θ value of 25.6 corresponding to the (0 0 2) planes of MWCNTs (Fig 4b). The composite particles (Fig 4c) present the characteristic peaks of both MWCNTs and CA without any additional new bands, which represent the absence of covalent interactions between the phases. Moreover, the crystallization behavior of the CA particles is not changed.

![Figure 4. X-ray diffraction patterns of (a) the CA, (a) acid -MWCNTs and (c) M (0.06 wt %) -CA particles](image)

3.4. Thermal stability
Thermal stability of different hydrogel particles (Fig. 5) are analyzed by the TGA test. The TGA thermogram of pure CA particles shows four distinct stages at 80-125 °C, 220-480 °C, 510-750 °C and 750-790 °C, corresponding to the loss of residual water, the destruction of glycosidic bonds, the oxidation of the intermediate carbonaceous char material, and the partial decomposition of calcium carbonate, respectively. Similar TGA data were previously reported [15]. The TGA curve of M-CA particles is almost the same as that of pure CA particles between 50-250°C. However, when the temperature is higher than 250°C, the TGA curve of M-CA particles becomes slightly different from that of pure CA particles. The TGA curve of M-CA particles shows that the residue weight is increased by adding MWCNTs. The residue weight of M-CA particles at 840°C is about 20.38%, higher than that of pure CA particles (12.45%), which indicate that the existence of MWCNTs in the composite particles can enhance the thermal stability of CA particle at high temperatures. This is ascribed to the better thermal stability of MWCNTs [16] as well as the special interactions, such as inter-molecular hydrogen-bonding interaction and the electrostatic interaction between MWCNTs and CA lattices, which limit the motivation of CA.
3.5. MB removal efficiency

As shown in Fig. 6, the MB removal efficiency of hydrogel particles increased with an increase in the concentration of MWCNTs. The CA particles doped with 0.06 wt% MWCNTs have higher removal efficiency (96.38%) than that of pure CS particles (61.21%). The good MB removal efficiency of composite particles suggested the strong affinity of M-CA particles towards dye molecules, which is likely to be due to the following reasons. On one hand, as a nano-filler, MWCNTs has good adsorption capacity for dyes because their large specific surface area, hollow and layered nanosized structures [17-18]. Moreover, the abundant oxygen-containing functional groups on surfaces of functionalized MWCNTs also can provide numerous chemical adsorption sites to increase the adsorption capacity of particles. On the other hand, as shown in SEM, the addition of MWCNTs into CA particles made the surface of M-CA particles much larger wrinkles. The presence of these wrinkles indicates that there is a large exposed surface area of hybrid particles, which may be convenient for the dye molecules to penetrate into the polymeric network of the composites, leading to the increase in the absorption capacity of MB to a certain extent.

Figure 5. TGA thermograms of (a) pure CA and (b) M (0.06 wt%) -CA particles
Figure 6. Effect of the MWCNTs concentration on adsorption capacity of particles for MB Adsorption experiments: dye concentration: 200mg/L; sample dose: 0.1g/25.00mL; natural pH 8.0; temperature: 30℃; equilibrium time: 3 hour.

4. Conclusions
In summary, functionalized MWCNTs/CA hybrid particles have been successfully prepared using a microfluidic technique. The results suggest that MWCNTs doping has a significant influence on the morphologies, thermal stability and MB removal efficiency of CA particles. The obtained hybrid particles are of good morphological characteristics, and the color change from yellow to black proves MWCNTs is successfully dispersed in CA particles. The incorporation of MWCNTs to CA particles can efficiently enhance the thermal stability of CA particles at 840°C, which is ascribed to the better thermal stability of MWCNTs as well as some special interactions between MWCNTs and CA particles. The removal efficiency of CA particles doped with a lower percentage of MWCNTs (0.06 wt %) for methylene blue is 96.38 %, higher than that of pure CA particles (61.21 %). Therefore, we consider that the MWCNTs/CA hybrid particles prepared by microfluidic technique might be used as a promising, effective adsorbent for the removal organic dye from wastewater.

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