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Preparation and characterization of carboxyl multi-walled carbon nanotubes/calcium alginate composite hydrogel nano-filtration membrane

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ABSTRACT

Carboxyl multi-walled carbon nanotubes/calcium alginate (CMWCNT/CA) composite hydrogel nano-filtration membrane was prepared using polyethylene glycol 400 as the pore-forming agent. The membrane was characterized by SEM, TEM and FT-IR. And the strength, anti-fouling property and dye rejection were investigated. Results showed that the CMWCNT/CA membrane had a high tensile strength up to 1.83 MPa. The flux of bovine serum albumin (BSA) solution was 96.87% of the pure water flux (*PWF*), indicating that the membrane exhibited good anti-fouling property. Even after the saturated adsorption, the rejection for Congo red still reached 98.62%.

1. Introduction

Nano-filtration membrane separation technology has been used to remove heavy metal ions, nanoparticles and dye molecules from wastewater [1–3]. However, the interactions between the relatively hydrophobic membrane and organic compounds in water result in the generation of irreversible fouling, which reduces the reliability of membrane filtration equipment and seriously limits its further development [4]. Much effort has been exerted to membrane modification by coating a hydrophilic polymer layer such as polyvinyl alcohol and chitosan to improve the anti-fouling property [5–6]. However, these methods are complex and cost much, and they often produce chemical pollutants.

Sodium alginate (SA) is a natural anionic polysaccharide and can be cross-linked by calcium ions to form calcium alginate (CA) hydrogel [7]. The CA hydrogel can mitigate membrane fouling. However, the pure CA hydrogel has lower strength. Some inorganic particles are usually mixed to improve the mechanical strength of CA hydrogel [8–9]. Carbon nanotubes have attracted wide attention due to their unique structures and mechanical properties. The composites of carbon nanotube doped alginate have good mechanical strength and can be used to remove heavy metal ions, dye and natural organic virus in wastewater as adsorbent [10–12]. So the composite CA hydrogel was often used as encapsulation or microspheres [13–14]. However, no study of carbon nanotubes/calcium alginate hydrogel filtration membrane has ever been reported.

In this paper, carboxyl multi-walled carbon nanotubes/calcium alginate (CMWCNT/CA) hydrogel nano-filtration membrane was prepared through Ca^{2+} cross-linking using polyethylene glycol 400 (PEG400) as pore-forming agent. The strength, anti-fouling property and dye rejection of the CMWCNT/CA membrane were systematically investigated.

2. Experimental

2.1. Materials

Sodium alginate (SA), polyethylene glycol 400 (PEG400) and calcium chloride anhydrous ($CaCl_2$) were purchased from

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Shanghai Sinopharm Chemical Reagent Co., Ltd. Carboxyl multi-walled carbon nanotubes (CMWCNT) were purchased from Nanjing XFNANO Materials Technology Co., Ltd. Bovine serum albumin (BSA, MW 67 kDa) was purchased from Lanji of Shanghai Science and Technology Development Company. Congo red was purchased from Tianjin Umbrella Science & Technology Co. Ltd.

2.2. Preparation of CMWCNT/CA hydrogel filtration membrane

A homogenously mixed solution was obtained by dispersing various contents of CMWCNT, 2.5 wt% SA and 2.5 wt% PEG400 in deionized water. The proportion of CMWCNT in SA was 0 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 3 wt% and 5 wt%. Then the stringy mixture was outspread on a flat glass by a glass rod enlaced with brass wire (the diameter of the brass wire was 0.3 mm). The flat glass with the stringy mixture was immediately immersed in 2.5 wt% $CaCl_2$ aqueous solution for cross-linking 12 h. Finally, the CMWCNT/CA composite filtration membrane was obtained after being eluted for 48 h in water to remove PEG400.

2.3. Characterization

Digital camera and scanning electron microscope (SEM, HITACHI, Japan) were used to observe the morphology of CMWCNT/CA filtration membrane.

Transmission electron microscope (TEM, FEI Tecnai G2 F30) was carried out to survey the dispersion of CMWCNT in CMWCNT/CA filtration membrane.

Fourier transform infrared (FT-IR, TENSOR37, German) spectroscopy was used to analyze the internal molecular structure of the CMWCNT, SA, CA and CMWCNT/CA membranes.

The wet samples were cut into the 10 mm × 5 mm rectangle. The strength of wet samples was determined at ambient temperature at a stretching rate of 10 mm/min using a tensile testing machine (LLY-06F, China).

2.4. Filtration property test

A membrane evaluation device was used to measure the flux and rejection rate of the CMWCNT/CA filtration membrane. First, 0.5 g/L BSA and 0.1 g/L Congo red aqueous solutions were prepared. The concentrations of BSA or Congo red solution in feed and permeate solutions were measured by a UV spectrophotometer. The flux (J, L/m^2 h) and the rejection (R, %) were calculated by following equations [15]:

$$J = V/(A*t), \quad (1)$$

$$R = \left(1 - C_p/C_f\right) \times 100\%, \quad (2)$$

where V is the permeate volume (L), A is the membrane area (m^2), t is the time (h), C_p and C_f are the BSA or dye concentrations of the permeate and feed, respectively.

The pure water flux (*PWF*) of the CMWCNT/CA filtration membrane was determined at 0.1 MPa and denoted as J_{w1} (L/m^2 h). Then, the feed solution was switched to BSA solution for 30 min, and the flux of BSA solution was denoted as J_{B1}. Afterward, the feed solution alternation process was repeated for four times. The anti-fouling property of the membrane was determined by calculating the flux recovery rate (*FRR*) using the following equation:

$$FRR_i\,(\%) = J_{wi}/J_{w1} \times 100\%, \quad (3)$$

where J_{wi} is the *PWF* of i time.

3. Results and discussion

3.1. Characterization of CMWCNT/CA filtration membrane

Fig. 1 presents the digital photograph, SEM and TEM of CMWCNT/CA filtration membrane. The color of the filtration membranes became black and the transparency of the membranes decreased with increase of CMWCNT content. The thickness of the CMWCNT/CA filtration membrane was 0.116 mm and the addition of CMWCNT led to a reduction in thickness of 15.9%. The surface of CMWCNT/CA filtration membrane became rough compared with the CA membrane and some grooves appeared on the surface of the CMWCNT/CA filtration membrane (Fig. 1(c)). After the removal of PEG400, the CMWCNT/CA filtration membrane exhibited some micropores. These pores reduced the transparency of the filtration membrane and increased its surface roughness. The addition of CMWCNT affected the cross-linking structure of calcium alginate hydrogel (shown in Fig. 2(a)). Fig. 1(d) shows that CMWCNT was uniformly dispersed in the hydrogel, the inner and the outer diameter of CMWCNT was approximately 5.16 nm and 10.87 nm, respectively.

Fig. 2(a) shows the FT-IR spectra of CMWCNT, SA, CA and CMWCNT/CA filtration membrane. The strong bands at 1614 and 1411 cm^{-1} were assigned to the antisymmetric and symmetric stretching vibration of the salified carboxyl group (COO^-), respectively. The band of stretching vibration of –OH in CA was shifted to lower wave numbers (3128 cm^{-1}), and the miscellaneous peak appeared at 3626 cm^{-1}. This showed that the SA was cross-linked by $CaCl_2$ solution [16]. Compared with CA, the characteristic peak of CMWCNT/CA at 3626 cm^{-1} moved to the lower band at 3427 cm^{-1}, indicating that the –COOH of CMWCNT and the –COOH of SA were cross-linked synchronously with calcium ions. Fig. 2(b) shows the strength of CMWCNT/CA membrane. The tensile strength of the CMWCNT/CA membranes was higher than the CA membrane. When the CMWCNT content in SA was 1 wt%, the maximal tensile strength was reached with a value of 1.83 MPa. This was due to the Ca^{2+} cross-linking synchronously with the $-COO^-$ of CMWCNT and the $-COO^-$ of SA in CMWCNT/CA membrane. The formation of hybrid structure (see Fig.2(a)) increased the cross-linking density and improved the strength of the CMWCNT/CA membrane.

3.2. Filtration properties of the CMWCNT/CA filtration membrane

Fig. 3 shows the fluxes of pure water and BSA solution and the water flux recovery of CMWCNT/CA nano-filtration membrane. The fluxes slightly decreased with time, and reached stable values after 70 min. The flux of BSA solution was approximately 96.87% of the *PWF*. When the feed solution was changed from pure water to BSA solution, the flux reduced slightly. After repeated for four times, the flux recovery rate still maintained 90.35% of the *PWF* without any washing operation, indicating that the CMWCNT/CA filtration membrane exhibited excellent protein anti-fouling property.

Fig. 4 shows the flux and rejection for Congo red of the membrane after saturated adsorption and original membrane. The stable flux and rejection for Congo red (Mw=696.68) aqueous solution of original CA membrane were 18.03 L/m^2 h and 98.1%, while the stable flux and rejection for Congo red of CMWCNT/CA filtration membrane were 19.56 L/m^2 h and 99.19%. The formation of hybrid structure made the CMWCNT/CA membrane thinner, and denser than the CA membrane. The decreased thickness of the CMWCNT/CA filtration membrane resulted in the increase of the flux. The stable rejection of saturated adsorption membrane was slightly decreased and still reached 98.62%, indicating that the separation of dyes was mainly due to the membrane rejection