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Removal of Dyes and Cd²⁺ in Water by Kaolin/Calcium Alginate Filtration Membrane

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Abstract: Kaolin/calcium alginate (kaolin/CaAlg) free-standing membranes were prepared by adding different amounts of Kaolin into the sodium alginate (NaAlg) casting solution and crosslinked by Ca²⁺ using urea as porogen agent. The morphology of the kaolin/CaAlg filtration membrane was characterized by scanning electron microscope (SEM). Then the kaolin/CaAlg membrane was used for the removal of dyes and Cd²⁺. The kaolin significantly improved the mechanical behavior and flux of the kaolin/CaAlg membrane. The flux reached 17.53 L/m²·h at 0.1 MPa and when the content of Kaolin in NaAlg was 70 wt.%. The filtration of BSA solution and oil-water emulsion indicated that the kaolin/CaAlg composite filtration membrane exhibited good anti-fouling properties. The rejection of Brilliant Blue G250, Congo red, and methylene blue by the kaolin/CaAlg filtration membrane was 100%, 95.22%, and 62.86%, respectively. The removal rate of Cd²⁺ reached 99.69%, with a flux of 17.06 L/m²·h at 0.1 MPa.

Keywords: Kaolin; CaAlg hydrogel; filtration membrane; anti-fouling; dyes Cd²⁺ removal

1. Introduction

The rapid development of urbanization and industrialization has led to a wide range of water pollution [1], so how to deal with the water pollution has quickly and effectively become an important issue in environmental protection. Heavy metal ions in water bodies are harmful to the ecological damage and human health. Cadmium (II) is a non-essential element of the human body. It is often present in the form of a compound in nature and generally does not affect human health. However, when the environment is contaminated with cadmium, cadmium can enter the human body through the food chain and be enriched in the liver and kidneys, causing chronic poisoning [2]. Even if the contact time is short, symptoms such as vomiting, abdominal pain, gastrointestinal cramps, diarrhea, and even death may occur [3]. Cadmium (II) is one of ten chemicals that major public health concern considered by the World Health Organization [4]. Several recent studies have shown that pollution in Africa, South America, etc., is rising, and similar challenges exist in other parts of the world [5–7].

Many dyes are widely utilized in textile industry, paint industry and the dye pollution is also an important reason for water pollution. The dyes can contaminate bodies of water, modify the ecosystem and affect biological cycles. Like cadmium (II), dyes can also cause severe damage to human health and the environment, such as the dysfunction of the liver, kidneys, brain, and central nervous system [8].

Therefore, sustainable and environmentally friendly methods must be developed to remove dyes and Cd^{2+} in water [9–11].

Membrane separation has become an energy efficient new separation technology due to its easy operation, low energy consumption, and no secondary pollution [12,13]. Currently, membrane separation technology has been greatly developed in the treatment of waste water. However, due to the hydrophobic nature of most polymer separation membranes and the low surface energy, there are still significant challenges, such as the severe membrane fouling [14,15]. Much effort has been exerted to modify the membrane, including blending [16,17] surface coating [18] and surface grafting [19,20].

Alginic acid is abundantly obtained as a marine biological resource, being especially produced by brown-algae seaweed, and alginate has been widely used in food industry [21], pharmaceutical and tissue engineering [22–24]. Our previous effort has focused on the preparation of a free-standing calcium alginate (CaAlg) filtration membrane using polyethylene glycol (PEG) as porogen agent [25]. The anti-fouling property, protein rejection rate and flux of the CaAlg filtration membranes were investigated on different conditions. Simple process, low cost, and without producing organic waste water were all the advantages of the CaAlg filtration membrane. The CaAlg filtration membrane has a promising application prospect in the field of oil-water separation, protein separation and microorganism filtration, where the traditional polymer membranes are easily contaminated. However, the poor strength restricted the application of the CaAlg filtration membrane.

Clay minerals are hydrous alumino-silicates with a layered crystalline structure which can accommodate polar organic compounds between their layers to form a variety of intercalated compounds [26]. Therefore, introduction of clay minerals to membrane matrix may increase its strength and stiffness properties. Mineral powders are hydrated layered alumino-silicate with reactive -OH groups on the surface. The interaction of mineral powders, reactive site of natural polymers, and monomers resulted in a composite membrane [27]. Kaolin is dispersed easily in water even at high concentration, forming a stable suspension [28].

In this study, kaolin/CaAlg composite membranes were prepared by adding different amounts of Kaolin to the NaAlg solution using urea as porogen agent. The main novelty of the work lies in the introduction of kaolin in CaAlg filtration membrane in order to improve the mechanical behavior and the flux of the CaAlg membrane. The kaolin/CaAlg filtration membrane was used to remove Cd^{2+} and dyes synchronously.

2. Materials and Methods

2.1. Materials

Sodium alginate (NaAlg) and calcium chloride (CaCl_2) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Kaolin and urea granules were provided by Tianjin Guangfu Technology Development Co., Ltd. (Tianjin, China). Brilliant Blue G250 ($M_W = 854.02$ Da), Congo Red ($M_W = 696.68$ Da), and methylene orange ($M_W = 332.40$ Da) were obtained from Tianjin North Tianyi Chemical Reagent Factory (Tianjin, China). All the reagents used in the study were of AR grade. Bovine serum albumin (BSA, $M_W = 67$ kDa) as purchased from Lanji of Shanghai Science and Technology Development Company (Shanghai, China). $\text{Cd}(\text{NO}_3)_2$ was obtained from Tianjin First Chemical Reagent Company (Tianjin, China). 0# diesel was purchased from the local market. Tween 80 was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). All of the chemicals were used as received without any further purification.

2.2. Preparation of Kaolin/CaAlg Membrane

In a beaker 0.6185 g urea was dissolved in 20 mL deionized water under magnetic stirring, and different contents of kaolin powder were added at room temperature. The kaolin powder was homogeneously mixed using ultrasound bath to assistant the uniform distribution of kaolin powder, after that, 0.5128 g NaAlg was added into the mixture to obtain a uniform casting solution after

standing for degassing. Various amounts of Kaolin were added to the casting solution and the effect of kaolin was studied in concentrations of 0, 10, 30, 50, 70, and 100 wt.% of NaAlg, respectively.

To prepare the kaolin/CaAlg membrane, 6 g of casting solution was spread onto a flat glass plate and unrolled uniformly by a glass rod twining copper wire at both ends of the glass rod at room temperature. The diameter of the copper wire was 0.5 mm. After that, the plate was immersed in a 2.5 wt.% CaCl₂ water solution for crosslinking 12 h to obtain a calcium alginate (CaAlg) hydrogel membrane containing kaolin particles. Finally, the membrane was washed with warm water to remove urea and stored in 1.0 wt.% CaCl₂ solution before any treatment or testing.

2.3. Characterizations

Granulometric analysis of Kaolin powder in water was performed using a laser scanner particle size analyser (Mastersizer 2000, English Malvern Instruments Co., Ltd., Worcestershire, UK).

The CaAlg membrane prepared with 2.5 wt.% NaAlg and 2.5 wt.% urea was used for the characterization of scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan). The kaolin/CaAlg membrane prepared with 2.5 wt.% NaAlg, 70 wt.% kaolin in NaAlg and 2.5 wt.% urea was used for the SEM characterization. All the samples were dried at 25 °C. The morphology of CaAlg membrane and kaolin/CaAlg membrane were observed at a field emitting-scanning electron microscopy (FE-SEM, S-4800, Hitachi, Tokyo, Japan) with an accelerating voltage of 5 kV after sputter-coating with gold under vacuum.

2.4. Mechanical Behaviors of the Kaolin/CaAlg Membrane

The mechanical behaviors of the kaolin/CaAlg membranes prepared with different kaolin contents were carried out on an LLY-06F tensile testing machine (Laizhou Electronic Instrument Co., Ltd., Laizhou, Shandong, China) with the stretching speed of 10 mm/min. The wet membranes were prepared with 5 mm wide and 20 mm long. The samples were prepared with 2.5 wt.% NaAlg and 2.5 wt.% urea.

2.5. Evaluation of Anti-Fouling Properties of the Kaolin/CaAlg Membranes

A membrane evaluation device from Tianjin Motimo Membrane Technology Co., Ltd. (Tianjin, China) was used to measure the flux and rejection rate of the kaolin/CaAlg filtration membrane [25]. Crossflow filtration of the solution containing emulsified oil and BSA solution was employed to evaluate the anti-fouling performance of the kaolin/CaAlg filtration membrane.

For the oil-fouling experiment, an oil/water emulsion was prepared by blending 0# diesel/Tween 80 (9:1, *w:w*) with deionized water (total organic concentration: 100 ppm). The concentration of oil/water emulsion in permeated and retentated solutions was analyzed by a total organic carbon analyzer (TOC-V CPH, SHIMADZU, Kyoto, Japan).

For the protein-fouling experiment, 0.5 g/L BSA aqueous solution was prepared as the feed solution and the concentrations in feed and permeate solutions were measured with a UV spectrophotometer (TU-1901, Beijing General Instrument Co., Ltd., Beijing, China) [29]. The rejection rate (*R*) of oil/water emulsion and BSA was calculated as follows:

$$R = (1 - C_p/C_f) \times 100\% \quad (1)$$

where C_p is the permeate concentration and C_f is the feed concentration.

The flux (J , L/m²·h) of pure water, oil/water emulsion or BSA solution was defined as Equation (2):

$$J = V/(A \times t) \quad (2)$$

where V is the permeate volume (L), A is the membrane area (m²), and t is the time (h).

2.6. Dyes Removal of Kaolin/CaAlg Membrane

Dyes rejection values of kaolin/CaAlg membrane were calculated by measuring the dyes concentrations in the feed and in permeate according to the literature [25,30]. In this paper, Brilliant Blue G250 ($M_W = 854.02$), Congo Red ($M_W = 696.68$), and methylene orange ($M_W = 332.40$) were used and the concentration of each dye feed solution was 100 ppm. The CaAlg membrane prepared with 2.5 wt.% NaAlg and the kaolin/CaAlg membrane prepared with 2.5 wt.% NaAlg, 70 wt.% kaolin in NaAlg were used for the dyes removal experiment. The concentrations of dyes in feed and permeate solutions were measured with a UV spectrophotometer and the removal rate (R) of dyes was calculated using Equation (1).

2.7. Cd^{2+} Removal of Kaolin/CaAlg Membrane

An aqueous solution containing 10 mg/L Cd^{2+} was used as the feed solution to investigate the removal rate of Cd^{2+} . The tests were carried out at 25 °C and the operating pressure was 0.1 MPa. The Cd^{2+} concentration was tested using an ICP-OES analyzer (Varian 715-ES, Palo Alto, CA, USA), and the removal rate (R) was calculated using Equation (1).

3. Results and Discussions

3.1. Granulometric Analysis of Kaolin Powders in Water

The granulometric analysis of kaolin powder in water was presented in Figure 1. Granulometric analysis of the kaolin showed quite homogeneous particle-size distribution. Approximately 95% (in volume) of kaolin particles are smaller than 26 μm and have a volume average diameter of 14.85 μm . From the granulometric viewpoint, this narrow particle size distribution is excellent for hydrogel [31].

Figure 1. Granulometric analysis of kaolin powders.

3.2. Morphology of CaAlg Filtration Membrane

Figure 2 shows the surface digital photos and SEM images of the CaAlg (a,c) and kaolin/CaAlg filtration membrane (b,d) with 2.5 wt.% urea as the pore-forming agent. The kaolin content is 70% of NaAlg in the kaolin/CaAlg composite membrane. Both of the CaAlg and kaolin/CaAlg membrane show good film-forming properties. As can be seen from Figure 2a,b, the thickness of CaAlg and kaolin/CaAlg membrane was 0.234 and 0.235 mm, respectively. The CaAlg membrane was transparent, while the kaolin/CaAlg membrane became opaque due to the addition of kaolin. From the SEM images in Figure 2c,d, it was found that the surface of CaAlg film was smooth, while that of kaolin/CaAlg film was rough. The kaolin was dispersed in the CaAlg membrane matrix and remained integral.

Figure 2. The surface digital photos and SEM images of CaAlg membrane (a,b) and kaolin/CaAlg composite membranes (c,d) (kaolin content: 70 wt.%; pore-forming agent urea: 2.5 wt.%).

3.3. Effect of Kaolin Content on the Mechanical Properties of Kaolin/CaAlg Membranes

Figure 3 shows the mechanical properties of the kaolin/CaAlg membranes prepared with different Kaolin contents. Compared to the pure CaAlg membrane, the composite membrane had better mechanical properties. The stress the kaolin/CaAlg membranes initially increased and then decreased with the increase of kaolin content. When the content of kaolin in NaAlg was 70%, the stress of kaolin/CaAlg membrane reached 963.95 KPa, which was three times of the stress of CaAlg membrane (316.85 KPa). However, when the content of kaolin in NaAlg reached 100%, the stress of kaolin/CaAlg membrane decreased because of the aggregation and non-uniform dispersion of kaolin. The literature indicates that the interaction between kaolin particles and CaAlg hydrogel may be the result of a combination of hydrogen bonding and electrostatic forces, which increases the strength of kaolin mixed with CaAlg hydrogel [32,33].

Figure 3. Mechanical properties of composite membrane prepared with different kaolin content.

3.4. Pure Water Flux of Kaolin/CaAlg Membranes Prepared with Different Kaolin Contents

Figure 4 shows the pure water flux (PWF) of kaolin/CaAlg membranes prepared with different Kaolin contents under different pressure. For the CaAlg membrane (Kaolin/NaAlg = 0 wt.%), when the pressure was from 0.22 to 0.3 MPa, the flux tended to become stable with the increase of pressure. The decrease of the flux can be explained by the compression of membrane pores. At low operating pressure, the deformation of the hydrogel membrane was small, and the connective pores were maintained adequately. Hence, the flux of the membrane increased with the increase of operating pressure. When the pressure was above 0.22 MPa, the connective pores collapsed, but the trans-membranous pressure changed slightly, so the flux reached a constant value [25].

For the kaolin/CaAlg membrane, the water flux increased with the increase of kaolin content. When the content of kaolin in NaAlg was 70 wt.%, the flux reached 17.53 L/m²·h at 0.1 MPa, while the flux of CaAlg membrane was only 9.48 L/m²·h. The flux of CaAlg membrane was lower than the previous paper because the thickness of the CaAlg membrane in this paper was thicker [25]. As mentioned in the previous section, the incorporation of kaolin significantly improved the strength of the CaAlg filtration membrane, keeping the structure of connective pores in compression states. Thus, kaolin can not only improve the mechanical properties of the membrane, but also increase the flux of the kaolin/CaAlg membrane.

Considering the mechanical properties and the pure water flux of the membrane, the kaolin/CaAlg membrane with 70 wt.% kaolin content was selected for the subsequent experiments.

Figure 4. Pure water flux (PWF) of kaolin/CaAlg membranes prepared with different kaolin contents under different pressures.

3.5. Anti-Fouling Properties of the Kaolin/CaAlg Filtration Membrane

Figure 5 shows the alternating filtration flux of kaolin/CaAlg filtration membrane between pure water and BSA solution at 0.1 MPa. The initial pure water flux (J_{W0}) of the membrane reached 17.04 L/m²·h. After the feed solution was switched to BSA solution, the flux was measured. The feed solution was then changed back to pure water again after the membrane was rinsed for 30 min with 1% CaCl₂ solution, and the first recovered water flux (J_{W1}) was recorded. The first-round flux recovery rate ($FRR_1 = J_{W1}/J_{W0}$) was 97.73%. After three consecutive BSA filtrations, the FRR still reached 92.74%, indicating that the kaolin/CaAlg filtration membrane exhibited excellent anti-fouling properties for BSA.

Figure 6 shows the pure water flux (PWF), oil-water emulsion flux and rejection of oil-water emulsion of the kaolin/CaAlg membrane. The flux slightly reduced when the feed solution change from pure water to oil-water emulsion, and the flux reached stable values at 17.30 and 14.95 L/m²·h for pure water and oil-water emulsion, respectively. The stable flux of oil-water emulsion was 86.4% of the PWF, indicating that the kaolin/CaAlg composite filtration membrane exhibited good anti-fouling properties for oil-water emulsion. The rejection rate of oil-water emulsion reached 99.65% but not 100% because some Tween 80 ($M_W = 428.6$) penetrated through the kaolin/CaAlg filtration membrane.

Figure 5. The alternating filtration flux between water and BSA solution of kaolin/CaAlg membrane.

Figure 6. The PWF, oil–water emulsion flux and rejection of oil–water emulsion of the kaolin/CaAlg membrane. The digital photos of feed solution (right) and permeate solution (left).

3.6. Dyes Removal of Kaolin/CaAlg Filtration Membrane

To confirm the potential of the kaolin/CaAlg as a nano-filtration membrane, the filtration of dyes solutions was investigated at 0.1 MPa. As shown in Figure 7, the kaolin/CaAlg membrane exhibited almost 100% rejection for Brilliant Blue G250 ($M_W = 854.02$ Da), and fairly high rejection (95.22%) for Congo red ($M_W = 696.68$ Da). For the dyes with a relatively small molecular weight, the membrane showed part of rejection, which was 62.86% for ethyl orange ($M_W = 332.4$ Da). The rejection of Brilliant Blue G250, Congo red, and methylene blue by CaAlg membrane was 100%, 99.5% and 80.56%, respectively [25]. The addition of kaolin improved the flux of the kaolin/CaAlg membrane, but some dye molecules may permeate through the pore size of kaolin because of the larger particle size of kaolin. Figure 7D–F shows the bottles of Brilliant Blue G250, Congo red, and methylene blue. The feed solution is on the left and the permeate solution is on the right). The Brilliant Blue G250 and Congo red after filtered by kaolin/CaAlg membrane had almost no color. The methyl orange solution is much lighter after filtering.

It has been proved that the separation of dyes by the CaAlg membrane was due to the membrane rejection instead of adsorption. In fact, the adsorption capacity of the three above dyes by the kaolin/CaAlg membrane was relatively low. The adsorption of dyes on the membrane had little effect on the stable filtration performance [25]. Thus, the dye's removal by the CaAlg membrane was due to the membrane rejection instead of adsorption. The kaolin/CaAlg self-standing membrane could be an efficient loose nano-filtration membrane for separating organic dyes molecules or contaminants with the molecular weight over 690 Da.

It is shown in Figure 7 that the flux of dye solution was similar to that of pure water, and the flux did not decrease with time, which indicates that the membrane was resistant to dye pollution.

The simple preparation method, good anti-pollution performance, and high removal rate of dyes make the kaolin/CaAlg membranes have good application prospects in wastewater treatment.

Figure 7. The flux and rejection of dyes solution by the kaolin/CaAlg membrane. The digital photos of feed solution (right) and permeate solution (left). (A) Brilliant Blue G250 ($M_W = 854.02$ Da), (B) Congo Red ($M_W = 696.68$ Da), (C) Methylene orange ($M_W = 332.40$ Da), (D) Right: Brilliant Blue G250; Left: permeate solution, (E) Right: Congo Red; Left: permeate solution, (F) Right: Methylene orange; Left: permeate solution.

3.7. Removal of Cd^{2+} Ion by Kaolin/CaAlg Filtration Membrane

Figure 8 shows the effect of NaAlg concentration on the flux and removal rate of Cd^{2+} by kaolin/CaAlg filtration membrane. When the NaAlg concentration increased from 1.5 wt.% to 3.5 wt.%, the flux of the membrane decreased from 19.40 to 15.78 L/m²·h. In our previous work, the effects of preparation conditions of CaAlg membrane and operating conditions on the removal of Cd^{2+} were researched. The removal mechanism of the Cd^{2+} by CaAlg filtration membrane was investigated [9]. Just like the literature, the removal rate of Cd^{2+} increased with the increasing of NaAlg concentration, and when the NaAlg concentration was 2.5 wt.%, the removal rate of Cd^{2+} by kaolin/CaAlg filtration membrane reached 99.69%, with a flux of 17.06 L/m²·h at 0.1 MPa. Both the flux and the Cd^{2+} removal rate of the kaolin/CaAlg membrane were higher than the CaAlg membrane because the kaolin can not only prove the flux of the membrane but also can adsorb more Cd^{2+} during the filtration process.

Figure 9 shows the effect of kaolin content on the flux and removal rate of Cd^{2+} . When the kaolin in NaAlg increased from 0 to 70 wt.%, the flux and the removal rate of Cd^{2+} both increased. The flux and the Cd^{2+} removal rate of the kaolin/CaAlg membrane was 16.53 L/m²·h and 99.67% when the kaolin in NaAlg was 70 wt.%. More kaolin (100%) may lead to the permeation of Cd^{2+} from the pore size of kaolin particles like dyes in filtration process. Anyway, the removal rate of Cd^{2+} by filtration was much higher than the adsorption process of CaAlg.

Figure 8. The effect of NaAlg concentration on the flux and removal rate of Cd²⁺.

Figure 9. The effect of kaolin content on the flux and removal rate of Cd²⁺.

4. Conclusions

Free-standing kaolin/CaAlg membranes were prepared by adding kaolin into the NaAlg casting solution and crosslinked by Ca²⁺ using urea as porogen agent. The kaolin with a volume average diameter of 14.85 μm was dispersed in the CaAlg membrane matrix and remained integral. Kaolin significantly improved the mechanical behavior and when the content of kaolin in NaAlg was 70%, the stress of the kaolin/CaAlg membrane reached 963.95 KPa, which was three times that of the stress of the CaAlg membrane (316.85 KPa). The flux of the kaolin/CaAlg reached 17.53 L/m²·h, much higher than the flux of the CaAlg membrane (9.48 L/m²·h). The first-round flux recovery rate reached 97.73% after rinsing with 1 wt% CaCl₂ solution for 30 min, indicating that the kaolin/CaAlg membrane exhibited good anti-fouling properties. The kaolin/CaAlg membrane exhibited almost 100% rejection for Brilliant Blue G250 ($M_W = 854.02$ Da), and fairly high rejection (95.22%) for Congo red ($M_W = 696.68$ Da). The removal rate of Cd²⁺ by the kaolin/CaAlg filtration membrane reached 99.69%. The simple preparation method, good anti-pollution performance, and high removal rate of dyes and cadmium ions show that the kaolin/CaAlg membrane has good application prospects in wastewater treatment.

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