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Filtration and adsorption properties of porous calcium alginate membrane for methylene blue removal from water

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HIGHLIGHTS

- Porous calcium alginate membrane was prepared by a freeze drying method.
- Filtration studies show that removal percentage reaches 84.6%.
- The maximum adsorption capacity of the porous membrane can reach 3506.4 mg/g.
- The adsorption process was characterized by kinetics and isotherm analysis.

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ABSTRACT

Porous sodium alginate membrane was first prepared by vacuum freeze-dry method, then, sodium ions were substituted by calcium ions through cross-linking reaction to obtain the porous calcium alginate membrane via natural drying. The filtration and the adsorption properties of methylene blue on the porous calcium alginate membrane were studied through investigating the experimental parameters such as the pH, contact time, temperature and dosage. The data of the adsorption equilibrium were described by the Langmuir and Freundlich isotherms. The pseudo-first order, pseudo-second order, and intra-particle diffusion equation were used to evaluate the kinetic data. Thermodynamic analysis indicated that the adsorption of methylene blue on to the porous calcium alginate membrane was an exothermic reaction.

1. Introduction

The increasing dye contamination is a worrying environmental problem because of its toxic effect to human being as well as the fauna and flora. Dyes are colored and organic compounds. They are widely used in textile, leather, paper-making, food additives, cosmetic and other industries [1]. Most dyes have complex aromatic structures which are stable and non-degradable under light or heat, even in presence of oxidizing agents [2]. Long-term intake of water containing excessive dyes may be mutagenic and carcinogenic, in more serious, cause direct severe damage to the liver, digestive system and the central nervous system of human beings [3].

Therefore, it is necessary to purify the effluent which contains dyes to meet the emission before the wastewater is discharged into the environment. Various techniques, including flocculation-coagulation [4], precipitation [5], photocatalytic degradation [6], biological oxidation [7], ion exchange [8], adsorption [9] and membrane filtration [10], have been investigated and applied into the purification process. Membrane filtration blocks passage of contaminants through physical obstruction, chemical adsorption, or a combination of both processes and can remove far more contaminants than any other purification method [11,12]. Adsorption takes an important role in membrane filtration process. So it is significant theoretically and practically to seek for the adsorbents with high efficiency and large adsorption capacity.

Currently, a wide range of adsorbent materials have been used to adsorb dyes from aqueous solutions, such as activated carbon [13], zeolite [14,15], natural polymeric materials [16,17], agricultural wastes [18], silicate [19] and clay [20]. Alginates, which are extracted from brown algal species and built up of α-L-guluronic

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acid and β-D-mannuronic acid, have been widely applied to water treatment due to their biocompatibility, nontoxicity, high viscosity and low-cost relatively compared to other polymeric materials [21]. However, the systematic studies of the filtration and adsorption properties of porous calcium alginate membrane for dye removal have not been reported up to now.

The aim of this work is to adopt a vacuum freeze-drying method to prepare porous calcium alginate membrane with 3D network structure. The filtration properties of the membrane for methylene blue (MB) removal were investigated by varying the experimental parameters which affect the porous structure of the membrane such as the weight ratio of sodium alginate to deionized water and the concentration of calcium chloride. The adsorption properties were also studied by changing the influencing parameters such as initial solution concentration, solution pH, temperature, contact time and adsorbent dosage.

2. Materials and methods

2.1. Materials

Sodium alginate was provided by Shanghai Aibi Chemistry Preparation Co., Ltd. Calcium chloride (analytical grade) was purchased from Tianjin Basf Chemical Co., Ltd. The MB was obtained from Tianjin Red Cliff Chemical Reagent Factory in China. All other chemicals were used without any further purification. Deionized water was used for the preparation of all the required solution.

2.2. Preparation of calcium alginate membrane

Sodium alginate was put into deionized water and stirred by a magnetic stirrer until it was dissolved completely. The weight ratios of sodium alginate to deionized water were 1–5%. The solutions were set for 12 h to remove the air bubble. They were frozen in a Haier refrigerator (Haier BCD-215KAW, Qingdao, China) for 12 h. Subsequently, they were dried in a vacuum freeze drying machine (FD-1–50, Boyikang Laboratory Apparatus Co., Ltd, Beijing, China). Then, the membranes were soaked into 0.5 M aqueous solution of calcium chloride for 12 h to prepare calcium alginate membranes. The membranes were washed several times with deionized water to remove the residual calcium chloride and dried under natural conditions. In order to investigate the effect of the concentration of calcium chloride on the filtration property of the membrane, the different concentrations of calcium chloride (0.1–0.9 M) solutions were used to cross-link with fixed weight ratio (2 wt.%) of sodium alginate.

2.3. Characterization of the adsorbents

The surface morphological structures of the calcium alginate membrane were characterized by scanning electron microscopy (SEM, JSM 6700F, JEOL Ltd., USA).

2.4. Characterization of the filtration properties of the membrane

The membrane was cut into a wafer with appropriate size and put into a mold, then, a certain amount of the dye solution was pressed into the filterable mold with an injector and passed through the membrane. The concentration of the filtrate was detected by a UV–visible spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd., Beijing).

2.5. Batch adsorption experiments

MB was dissolved in deionized water to get 1000 mg/L stock solution. A fixed adsorbent (10 mg) of calcium alginate membrane was added into 20 mL of MB solution with initial concentration from 300 to 1000 mg/L. Then the solution was shaken in a temperature-controlled water bath shaker (SHZ-82A) to reach equilibrium on dye adsorption at room temperature.

The equilibrium concentration of the dye in the solution was determined using UV–visible spectrophotometer. The adsorbed amount at equilibrium, q_e (mg/g) was calculated by:

$$q_e = \left(\frac{c_0 - c_e}{W}\right) \times V \tag{1}$$

where c_0 and c_e are the initial and equilibrium concentration (mg/L) of MB solution, respectively; V is the volume of working solution (L) and W is the weight (g) of adsorbent used.

The effect of adsorbent dosages on the adsorption of MB was determined by adding different quantity of the adsorbent dosages (2–40 mg) into 20 mL of solution with MB concentration of 300 mg/L.

The effect of pH was studied by carrying out the adsorption process at the pH values ranged between 3.3 and 10.1. The influence of contact time was studied by contacting 0.3 g of adsorbent with 600 mL MB of definite concentration of the adsorbate (250 mg/L and 300 mg/L of MB). The concentration of the adsorbate was determined at predetermined interval time; the adsorption capacity at time t, q_t (mg/g) was calculated by:

$$q_t = \left(\frac{c_0 - c_t}{W}\right) \times V \tag{2}$$

where c_t (mg/L) is the liquid-phase concentration of MB at time t. The above experiments were done at room temperature (293 K). The effect of temperature was examined by adding 10 mg of adsorbents into 20 mL of different MB concentrations solutions (300–1000 mg/L) and shaken at 288 K, 298 K and 308 K.

3. Results and discussion

3.1. Characterization of the membrane

Fig. 1a shows that the sodium alginate membrane frozen in the refrigerator has a smooth surface. After dried by a vacuum freeze drying method, the ice in the membrane was sublimed to form a loose sodium alginate membrane (Fig. 1b). The loose membrane was immersed into the solution of calcium chloride, the sodium alginate membrane will take place cross-linking interaction with Ca^{2+}. It makes the calcium ions connect to the α-L-guluronic acid blocks between α-L-guluronic acid and β-D-mannuronic acid chains to form calcium alginate membrane.

Fig. 2 shows SEM images of the calcium alginate membranes. It can be seen that the freeze-dried calcium alginate membranes have the porous structure. The membrane has the impact porous structure at the weight ratio of sodium alginate to deionized water at 1% (Fig. 2a). With increasing the weight ratio of sodium alginate to deionized water from 2% to 5%, the porous structure of the membrane becomes more and more developed. The holes that connecting through each other also become significantly increased (Fig. 2b–e). Freeze drying method is an effective way to form porous structure based on sublimation. During the drying process, only the ice in the sodium alginate membrane is sublimated and the pores are left to form a porous sponge-like structure. The porous structure is more favorable for enhancing adsorption rate and adsorption capacity by providing more accessible and active sites directly and by allowing faster ion diffusion.