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Adsorptive removal of copper ions with highly porous chitosan/cellulose acetate blend hollow fiber membranes

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Abstract

In this study, highly porous adsorptive hollow fiber membranes were directly prepared from chitosan (CS) and cellulose acetate (CA) blend solutions and were examined for copper ion removal from aqueous solutions in a batch adsorption mode. Four types of hollow fiber membranes were spun from two CS/CA blends (with a CS/CA/forming acid ratio of 3/12/85 or 2/18/80) in two types of coagulants (water or 3 wt.% NaOH solution). All the CS/CA blend hollow fiber membranes displayed sponge-like and macrovoids-free structures, with specific surface areas in the range of 12.2–15.2 m^2/g, porosities of 70.4–79.7%, and pore sizes of 0.05–0.2 μm, depending on the CS/CA ratios and the type of coagulants used. Adsorption experiments showed that the CS/CA blend hollow fiber membranes had good adsorption capacity (up to 35.3–48.2 mg/g), fast adsorption rates and short adsorption equilibrium times (less than 20–70 min) for copper ions, and can work effectively at low copper ion concentrations (<6.5 mg/L) to reduce the residual level to as low as 0.1–0.6 mg/L in the solution. X-ray photoelectron spectroscopic (XPS) study confirmed that the adsorption of copper ions on the CS/CA blend hollow fiber membranes was mainly attributed to the formation of surface complexes with the nitrogen atoms of CS in the hollow fiber membranes, hence higher CS contents in the blend hollow fiber membranes rendering the membranes more adsorptive to copper ions. It was found that the copper ions adsorbed on the hollow fiber membranes can be effectively desorbed in an EDTA solution (up to 99% desorption efficiency) and the hollow fiber membranes can be reused almost without loss of the adsorption capacity for copper ions.

Keywords: Adsorptive membrane; Chitosan/cellulose acetate blend hollow fiber; Copper removal; Adsorption kinetics and mechanisms; Desorption

1. Introduction

Heavy metal contamination of various water resources is of great concern because of the toxic effect to the human beings and other animals and plants in the environment [1]. Membrane separation, particularly reverse osmosis (RO), has been used to remove heavy metal ions from various industrial effluents [2]. Although the RO membranes may be effective in the removal of heavy metal ions, the process has a very small water flux and also consumes a significant amount of energy, attributed to the small pore size of the membranes ($\sim 10^{-4}$ to 10^{-3} μm) and the high process pressure applied to drive the water flow. Membranes with larger pores, such as microfiltration (MF, $\sim 10^{-1}$ to 10^{1} μm) and ultrafiltration (UF, $\sim 10^{-2}$–10^{-1} μm) membranes, can provide greater water fluxes, but the conventional MF and UF membranes usually do not have the capability to retain metal ions ($\sim 10^{-4}$ μm) because the pore sizes of these membranes are too large and the surfaces of the membranes are inert.

In recent years, adsorptive MF or UF membranes have emerged as an attractive means to remove heavy metal ions from aqueous solutions [3]. Such adsorptive MF or UF membranes have reactive functional groups on the surfaces, including –COOH, $-SO_3H$, and $-NH_2$ groups, that can bond with heavy metal ions through surface complexation or ion exchange mechanisms. Hence, heavy metal ions can be removed from aqueous

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solutions when the metal ions in the solutions are in contact with the surfaces of the membranes, even though the pore sizes of the membranes may be much larger than the dimensions of the metal ions. In comparison with the conventional MF, UF and RO membranes, the adsorptive MF or UF membranes provide the advantages of high retaining efficiency for metal ions, together with the benefits of low energy consumption and high permeate flux. With the application of such adsorptive membranes, the function of the membrane process can be expanded from filtration separation only (for particle removal) to filtration plus adsorption separation together (for particles and heavy metal removal).

Separation of heavy metal ions with adsorptive membranes can also have advantages over that with adsorptive beads, although both separation methods use the same separation mechanism (ion exchange or surface complexation, for example). The separation rate of adsorptive membranes can be much faster than that of adsorptive beads because the metal ions to be removed can be brought to the external and internal binding sites by convective flow in the adsorptive membrane systems, rather than by slow external or internal diffusions in the adsorptive bead systems [4].

Although adsorptive membranes have great potentials for the removal of heavy metal ions from aqueous solutions, commercially available adsorptive membranes have so far been rather limited. Most commercial membranes are made from relatively inert polymers, such as polysulfone, polyvinylidene difluoride, polypropylene, polyethylene, and nylon, etc., and these polymers are lack of reactive functional groups on their backbones. The current methods to prepare adsorptive membranes have therefore been mainly through surface modification of these inert membranes. For example, radiation-induced graft copolymerization method has often been used to prepare adsorptive membranes (from hydrophobic membranes) by introducing reactive monomers (such as acrylic acid, acrylonitrile, acrylamide, or those containing the epoxy-group, i.e., glycidyl methacrylate, divinylbenzene, etc.) onto the membrane surfaces [5–14]. Other examples include chemical attachment of various dyes to the more hydrophilic membranes made from polymers such as polyvinylalcohol, polyvinylbutyral, poly(2-hydroxyethyl methacrylate) and so on [15–17] or expensive polyamino acids to cellulose and cellulose acetate membranes [18,19]. Although the modified membranes become adsorptive or have high adsorption capacities for heavy metal ions, the polymeric base membranes are often deteriorated due to the harsh physical or chemical treatment for surface modification, or the functional chemicals used to modify the membrane surfaces are too costly to be used for practical applications in heavy metal removal. The surface modification method has also made it difficult to retain the pore sizes or porous structures of the original base membranes, often resulting in significant reduction in the permeate flux of the membranes [20,21].

A new development in recent years for heavy metal removal is to use chitosan (CS) as the adsorptive material. CS is a natural biopolymer with a high content of the amine ($-NH_2$) functional group and is inexpensive and abundant, widely available from seafood-processing wastes [1,22–25]. CS has been found to have high binding capacities, normally greater than 1 mM metal/g CS, for many heavy metal ions, including Cd, Hg, Pb, Cu, etc., and the capacities have been reported to be even greater than polyaminostyrene, the constituent of expensive ion exchange resins [26]. The good performance of chitosan in adsorbing heavy metal ions has been attributed to the capability of the amine group of chitosan to form surface complexes with many heavy metal ions in aqueous solutions [1,22,23]. However, most of the early studies used chitosan material in the form of powders, flaks, or gel beads that are either difficult to be reused for practical application or have slow adsorption kinetics. There has been considerable research interest to prepare chitosan membranes (flat or preferably in hollow fiber form for high packing density) for adsorptive separation purpose, including removal of heavy metal ions [27–30], but the scope of preparing pure chitosan membranes has been largely limited due to the poor mechanical strength and chemical stability of chitosan. To improve the mechanical strength, chitosan has often been coated on supports such as flat membranes [29,31] to make composite chitosan membranes. The coating method has however encountered some problems in such as easy detachment of the coated chitosan film or incomplete and nonuniform coverage of the support membranes. More recently, blending chitosan with other polymers has been found to be an effective way to overcome the shortcomings of chitosan [1,25,32–35], because blending, especially at the microscopic level through chemical interactions, can provide chitosan with the desired mechanical strength and chemical stability.

In our laboratory, effort has been made to fabricate adsorptive hollow fiber membranes directly from biopolymers, particularly chitosan, without the need for further surface modifications of the base membranes [30,36]. Chitosan/cellulose acetate (CS/CA) blend hollow fiber membranes with adsorptive performances were prepared by wet-spinning a CS and CA blend solution into a non-solvent (or coagulant). CA in the blend hollow fiber membranes acts as matrix support and CS provides the functional groups (i.e., $-NH_2$ in this case) for metal ion adsorption. Preliminary studies have also indicated that the CS/CA blend hollow fiber membranes can be made highly porous with pore sizes in the micrometer or nanometer ranges and with large specific surface areas [36]. In this study, we examined the adsorptive hollow fiber membranes prepared from two different CS and CA ratios in the blend solutions and with two different types of coagulants or non-solvents in the spinning process, and investigated the adsorption behaviors and performance of the hollow fiber membranes for copper ion removal, especially under low copper ion concentrations. The choice of using copper ions as the model heavy metal species in the study was based on a consideration that a large quantity of copper ion effluent has been generated in the electrical and semiconductor industry, such as wafer fabrication, in Singapore, with low to moderate copper ion concentrations in the effluent that is often difficult for further effective treatment by conventional technologies.