Carbohydrate Polymers 140 (2016) 299–307

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Chemical filtration of Cr (VI) with electrospun chitosan nanofiber membranes

Lei Li[a,b,c], Yanxiang Li[a,b], Chuanfang Yang[a,b,*]

[a] National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form
27 November 2015
Accepted 24 December 2015
Available online 29 December 2015

Keywords:
Electrospun chitosan nanofiber membrane
Chemical filtration
Chromium (VI) adsorption
Breakthrough curves
Model fitting

ABSTRACT

Chitosan nanofibers (average diameter of 75 nm) were electrospun on polyester (PET) scrim to form composite nanofiber membranes with controlled pore size. The membranes were then stacked as a membrane bed for chemical filtration of Cr (VI) of 1–5 mg/L. The performance of the bed with respect to loading capacity at breakthrough, bed saturation and utilization efficiency were carefully investigated. The results showed that while these three parameters were dependent on pH, flow rate, flow distribution and packed pattern of the membrane, the latter two were less affected by feed Cr (VI) concentration and bed length. The maximum bed loading capacity for 1 mg/L Cr (VI) filtration at breakthrough was found to be 16.5 mg-chromium/g-chitosan, higher than the static adsorption capacity of 11.0 mg-chromium/g-chitosan using nanofiber mats, indicating the membranes' better potential for dynamic adsorption. The minimum bed length required to avoid breakthrough was determined to be three layers of stacked membranes with nanofiber deposition density of 1 g/m^2 by applying bed depth service time (BDST) model.

1. Introduction

Electrospinning is a simple and versatile method for preparing nanofibers in the form of either a loose web, or a dense membrane, depending on the fiber's deposition density (Ahmed, Lalia, & Hashaikeh, 2015; Bhardwaj & Kundu, 2010; Doshi & Reneker, 1995; Reneker & Yarin, 2008; Rutledge & Fridrikh, 2007; Teo & Ramakrishna, 2006). Electrospun nanofibrous membranes exhibit extraordinary properties, such as small fiber diameter, large surface area and high porosity, as well as easy pore size tailorability. These properties make such membranes more attractive than common nonwovens or even casted membranes for a wide variety of mechanical filtration and chemical filtration—a filtration process involving interface reaction between the porous material surface and the target solute (Aliabadi, Irani, Ismaeili, Piri, & Parnian, 2013; Deng et al., 2011; Li, Li, Cao, & Yang, 2015; Ma, Hsiao, & Chu, 2013; Niu et al., 2013). Adsorptive filtration is one of the examples. Adsorptive electrospun nanofiber membranes have drawn considerable interest in adsorption applications (Aliabadi et al., 2013; Hardick, Dods, Stevens, & Bracewell, 2013; Li, Li, et al., 2015; Yoon, Hsiao, & Chu, 2008) because they offer high flow rate and fast mass transfer advantages of microporous membranes for filtration. Another advantage of using the randomly deposited fiber membrane is the creation of impeded flow that results in reduced channeling (Suen & Etzel, 1992).

However, in many of the studies, electrospun nanofibrous membranes were simply used for static adsorption. In these cases, electrospinning processes were allowed to last for relatively long time till the randomly deposited fibers formed a mat. Such multilayered nanofibers normally overlap tightly and form very small internal pores, which unavoidably sacrifices some intended surface area and causes slow liquid infiltration that work against effective adsorption, leading to disappointing adsorption capacity. This problem, as also observed in our past work using electrospun-tailored chitosan nanofibers (Li, Li, et al., 2015), could be addressed in three ways. The first one is to use a faster yield spinning technique such as the recently reported force spinning (Sarkar et al., 2010; Yang, 2012), which allows for large quantities of nanofiber production in short times to form a fluffy and porous "spun cotton candy" structure. However, this kind of structure is believed to provide only the benefits of more effective static adsorption because of easier accessibility of most of the small fibers by the solute to be captured. In addition, the structure also depends on

* Corresponding author at: National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.
E-mail addresses: lileilyq@outlook.com (L. Li), yxli@ipe.ac.cn (Y. Li), cfyang@ipe.ac.cn (C. Yang).

http://dx.doi.org/10.1016/j.carbpol.2015.12.067
0144-8617/

the nature of the polymers to be spun. For chitosan, a hydrophilic polymer with abundant functional groups that tend to enforce a dense 2D nanofibrous structure by itself, force spinning may not generate the open 3D structure highly desired. The second way is to produce thinner and loosely packed chitosan nanofiber mats by electrospinning, which will adversely lead to high cost and low productivity of nanofiber production. The third way is to fabricate a dense, non-self-supportive nanofiber membrane on a strong substrate with tunable pore size and porosity, and use the membrane by allowing water to flow through it for chemical filtration of the heavy metals targeted. In its essence, the membrane now acts as an affinity membrane, and by pressure-driven flow, most of the adsorption sites can be accessed by the solute to enhance adsorption.

Affinity membranes have rapid mass transfer rate because of the small pore size and the non-existence of internal pores such as adsorption resins typically used for a fixed bed column. There are only a few studies illustrating the use of electrospun nanofibrous membranes in dynamic filtration processes to remove heavy metals. Horzum prepared electrospun chitosan nanofiber mats and filled them into a micro-column to test the filtration performance for Fe (III), Cu (II), Ag (I) and Cd (II) ions (Horzum, Boyaci, Eroglu, Shahwan, & Demir, 2010). The result showed that the affinity of the nanofibers toward Fe (III) and Ag (I) was different from that observed in static sorption, while similar behavior was found for Cu (II) and Cd (II). Desai fabricated electrospun chitosan/PEO nanofibers on spunbond polypropylene for Cr (VI) adsorption (Desai et al., 2009). He found that the dynamic metal binding capacity for ten consecutive flow passes using as little as 0.5 gsm (gram per square meter) of un-cross-linked nanofibers was up to 35 mg-chromium/g-chitosan. However, the capacity achieved was mainly due to recirculation of the solution through the medium that made the mass transfer approximated to that in static adsorption.

Single-pass flow dynamic adsorption of heavy metals is preferred because it offers sustainable process control, high throughput and flexibility for both small and large-scale applications. Cr (VI) is a toxic metal that must be removed from water as per regulation, and the effectiveness of electrospun chitosan nanofibers for its removal has been confirmed earlier (Li, Li, et al., 2015). The objective of this work is to study the chemical filtration behavior of chitosan nanofiber membranes with respect to their interaction with Cr (VI), similar goal was discussed in Mahadevaiah's work for a fixed bed column (Mahadevaiah, Venkataramani, & Prakash, 2008). To this end, first, chitosan nanofiber membranes with different nanofiber deposition density on spunbond PET scrim were fabricated by electrospinning. The as-prepared membranes were then cross-linked with glutaraldehyde to minimize their solubility and swelling in acidic water. Second, a single-pass flow was applied to challenge the membranes stacked in layers as a membrane bed for dynamic adsorption of Cr (VI) in small concentrations. The effect of feed concentration, membrane thickness, pH, flow rate, and membrane packing pattern on the adsorption was investigated in detail. The performance criteria of the nanofiber membranes including loading capacity, bed saturation and bed capacity utilization efficiency were also determined.

2. Experimental

2.1. Materials and chemicals

Chitosan powders (Mw = 300 kDa, degree of de-acetylation (DDA) 90%, 80 meshes) were purchased from Golden-Shell Pharmaceutical Co., Ltd., China. Acetic acid was purchased from Beijing Chemical Works, China. The spunbond PET scrim with basis weight of 25.5 g/m^2 was obtained from Fiberweb, Inc. All other chemicals were analytical grade and used without purification.

2.2. Electrospinning and cross-linking process

An electrospinning solution containing 5 wt% chitosan was prepared by dissolving chitosan in 90 wt% acetic acid solution (Li, Li, et al., 2015). The apparatus used for electrospinning was purchased from Ucalery Co., China. The solution was ejected from the syringes using a feed rate of 0.1 mm/min, an applied voltage of 23 kV, and a tip-to-collector distance of 6.8 cm. The fibers 75 nm in diameter were collected on the spunbond PET substrate continuously. Composite membranes with different nanofiber basis weight were obtained by controlling the electrospinning time. After electrospinning, the composite membranes were placed in a vacuum oven at 60 °C for 24 h to remove the remaining solvent. They were then transferred to a desiccator containing 20 mL glutaraldehyde liquid for cross-linking by glutaraldehyde vapor at room temperature for 12 h. The cross-linked nanofiber membranes were dried in a vacuum oven at 60 °C for 12 h to remove the remaining cross-linker.

2.3. Dynamic adsorption experiments

The set-up for filtration experiments is shown in Fig. S1 in Supplementary Material file. It is composed of a peristaltic pump, a pressure gauge and a cylindrical membrane holder. The effective diameter of the holder is 34.7 mm. Membrane discs 47 mm in diameter were layered together to form a stacked membrane bed as shown in Fig. 1. The bed was then placed in the holder and sealed. Water containing Cr (VI) was pumped through the membrane just once for continuous adsorption. The feed concentration of Cr (VI) was controlled at 1–5 mg/L. pH of the solutions was adjusted using diluted H_2SO_4 and NaOH. Flow rate was 1–3 ml/min. Effluent samples were collected at different times for Cr (VI) concentration measurement.

The amount of Cr (VI) adsorbed on the membrane was determined by comparing the difference of feed and effluent concentrations of Cr (VI). The ratio of the effluent concentration and feed concentration was plotted against time to obtain the breakthrough curves. The adsorption capacity of the membrane was determined using the following equation:

$$q = \frac{\int_0^t (C_0 - C_t) Q dt}{m} \quad (1)$$

where q is the amount of adsorbed Cr (VI) onto unit mass of the nanofibers (mg/g); C_0 and C_t (mg/L) are the feed concentration and the effluent concentration at time t, respectively; Q is the flow rate (ml/min) and m the amount of adsorbent (g) used.

In this work, breakthrough and saturation points of the membrane bed are defined as the time elapsed for the effluent concentration to reach 10% and 80% of the feed concentration. The bed utilization efficiency ε, which represents the percentage of saturation bed capacity used, is defined by the following equation:

$$\varepsilon = \frac{q_{tb}}{q_{ts}} = \frac{\int_0^{tb} (C_0 - C_t) Q dt}{\int_0^{ts} (C_0 - C_t) Q dt} \times 100\% \quad (2)$$

where q_{tb} and q_{ts} are the amounts of adsorbed Cr (VI) onto unit mass of the membrane at breakthrough time and saturation time (mg/g). For an ideal membrane bed, the bed utilization efficiency should be close to 100%, and the breakthrough curve is typically a step function. The non-ideal situation always gives a breakthrough curve with a profile of changing slope, which is commonly encountered in practice. Nonetheless, higher bed efficiency is always desired