Journal of the Taiwan Institute of Chemical Engineers 000 (2015) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Performance improvements in structural characteristics of chitosan-based nanofibrous composite membrane for using in liquid filtration

Mohsen Askari[a], Babak Rezaei[a], Ahmad Mousavi Shoushtari[a,*], Majid Abdouss[b]

[a] *Department of Textile Engineering, AmirKabir University of Technology, Tehran 15875-4413, Iran*
[b] *Chemical Department, Amirkabir University of Technology, Tehran, Iran*

ARTICLE INFO

Article history:
Received 28 January 2015
Revised 28 April 2015
Accepted 3 May 2015
Available online xxx

Keywords:
Chitosan
Nanofibers
Structural characteristics
Plasma
Performance

ABSTRACT

The chitosan-based electrospun nanofibrous composite membrane (ENCM) was fabricated based on electrospinning of a high performance chitosan (CS) /Poly vinyl alcohol (PVA) mat on a polyethylene terephthalate (PET) non-woven. Structural stability (*i.e.* water resistance and chemical resistance against acidic and basic solutions) of the nanofibrous layer was improved and confirmed by FT-IR, SEM, degree of stability and solubility tests. Also, performance improvement of the ENCMs through assessment of structural uniformity and interfacial stability of the nanofibrous layer onto the substrate was deduced. Plasma pre-treatment of the substrate and area–weight optimization was adopted to provide interfacial stability and structural uniformity of the nanofibrous layer, respectively. High-values of filtration characteristics (flux, permeability and anti-fouling) along with significant breakthrough volumes for solutions of Cu(II) and Ni(II) ions in dynamic adsorption studies suggest that the innovative structural characteristics of the improved ENCMs are capable of developing as a highly efficient filtration.

1. Introduction

In recent decades, there is a growing demand for high quality water due to the increasing world population, rising standard of living, further load on traditional water sources and spread of human activities [1,2]. Membranes are especially appealing structures for filtration processes thanks to their compactness, high throughput, energy-efficiency and low-cost operation [3]. As one of the most ongoing topics, a tremendous amount of worldwide research works are being allocated for boosting the membrane performance in terms of filtration efficiency along with chemical resistance, flux rate, anti-fouling property, *etc.* [4–6]. Many different types of membranes have been put into service for decontamination of liquid media, but low adsorption capacity and slow adsorption rate have restricted their progression [3].

The unique characteristics of the nanostructures have made them a topic of great interest for scientists and engineers [7], which opened a panoramic window for promotion of the membrane structures. Nanofibrous membranes as a medium enjoying unique surface architecture, lower fouling, acceptable selectivity, high surface porosity, high permeability, lower base weight, continuous interconnected pores with adjustable sizes and low production cost [8,9] can be fabricated through the electrospinning technique. The simplicity of the electrospinning and diversity of suitable materials make it a promising candidate for the membrane manufacturing process.

Chitosan (CS) as a well-accepted polymer for liquid filtration is an excellent cationic adsorbent with high adsorption capacity for contaminants [10,11]. Despite chitosan is being produced in a variety of structures with excellent properties [12], its operation as a practical adsorbent still faces some problems such as complication of reusing, slow adsorption kinetics [13], small specific surface areas [14] *etc.*, and it seems that chitosan in the form of electrospun nanofibrous membranes (ENMs) can cope with some of these difficulties [15,16].

A high performance CS/(PVA)polyvinyl alcohol electrospun nanofibrous mat was described in our previous work [17]. The prepared mat was mostly comprised of CS (80%) with desirable morphology (bead-free and uniform diameter) of superfine fiber (mean diameter of 104 ± 18 mm). It is obvious that such a unique structure can be a favorable nominee for achievement of a highly efficient liquid filtration based on the sorption mechanism. In fact, high chitosan content and the least possible fiber diameter are supposed to enhance the membrane performance by the way of increasing the accessibility of the sorption sites to adsorbates. Furthermore, the high permeate flux, which is affected by the structural and morphological properties of the membrane [3], is expected to be provided by the convenient

* Corresponding author. Tel.: 98 21 64542638.
E-mail addresses: babakrezaei@aut.ac.ir (B. Rezaei), amousavi1958@gmail.com, amousavi@aut.ac.ir (A. Mousavi Shoushtari).

http://dx.doi.org/10.1016/j.jtice.2015.05.007
1876-1070/

morphology so that a high-value of permeate flux will be obtained [2,18]. Though practical development of this structure is still dealing with hindrances, preparing a filter media with an effective and stable structure may escalate the filtration performance and open new windows for industrial progress of the chitosan-containing membrane.

CS and PVA have a hydrophilic nature in which the former will swell in water and will be soluble in the acidic media [19] and the latter will dissolve in water. Therefore, structural stabilizing is required for the CS/PVA nanofibrous layer to render them stable in aqueous solutions [20].

While the nanofibers can most often be coated on an extremely permeable microfiber structure such as nonwoven substrate to form a readily manageable composite structure [21,22], creating a stable interface between the substrate and nanofibrous layers for obviating delamination between them and supplying satisfactory durability against flexion and abrasion is one of the major concerns in preparation of electrospun nanofibrous composite membranes (ENCMs) [23,24]. Accordingly, the membrane performance may be influenced by the interface stability of the layers. Post-heat treatment of the ENCMs is the more widely adopted strategy to yield interface stability [21], but in order to prevent the risk of dimensional shrinkage owing to entropic relaxation of stretched polymer chains [25], the temperature should be controlled carefully below the glass transition temperature of the electrospun polymer [21]. Moreover, reduction in the membrane functioning will occur through probable damage of the nanofibers structure. The mentioned drawbacks are restrictions of the post-heat treatment method. In contrast, the plasma as an environmentally friendly treatment, has been widely utilized to modify the surface properties of textile materials. Comparing with traditional methods plasma treatment is only able to modify the outermost layer of the surface, while the bulk properties will be kept untouched [26]. Seemingly, pre-treatment of the substrate by the plasma technique can be a preferable approach to enhance the integration of the composite membrane. A broad class of plasma source that operates with high voltage power from low frequency AC is called dielectric barrier discharge (DBD) which is the most commonly applied technology in order to achieve an easily up-scalable, non-thermal plasma for thermo-sensitive materials and is a uniform one [27].

As well, our preliminary experiments in the present study revealed that successful formation of a chitosan nanofiber uniform layer is also a considerable issue. Although increasing electrospinning time results in increasing the adsorption sites (capacity and rate of adsorption), it may also gradually lead to a non-uniform layer which directly has an effect on filtration efficiency. Besides, the electrospinning time in fabrication of the nanofibrous membrane is very pivotal, for it is mostly associated with material cost [8]. Hence, an optimum balance should be established to increase the area-weight and avoid non-uniform structural formation.

As a result, deep investigation of the chitosan-based ENCM preparation can yield helpful information in performance enhancement of the filter media. In the current work, the preparation of chitosan-based ENCM was followed by three strategies on its structural characteristics: (i) Attempt to achieve structural stability for the nanofibrous layer in aqueous solutions, (ii) using the plasma treatment for promoting the stable interface between the substrate and nanofibrous layer and (iii) obtaining a uniform nanofibrous layer. Flux, permeability and anti-fouling properties were measured to assess the ENCM characteristics and a dynamic process of copper and nickel ions adsorption was performed to evaluate adsorption capabilities.

2. Experimental

2.1. Materials

CS (Mw = 190–310 kDa, degree of deacetylation >75%), was purchased from Sigma-Aldrich. Poly vinyl alcohol, (PVA) (Mw = 72 kDa, degree of hydrolysis 97%), Poly ethylene glycol (PEG, Mw = 6000 g/mol), Glutaraldehyde (GA) (25% solution in water), acetic acid, hydrochloric acid (HCl), sodium hydroxide (NaOH), analytical grade of $Cu(NO_3)_2{\bullet}3H_2O$,and $Ni(NO_3)_2{\bullet}6H_2O$ were obtained from Merck. All experiments were conducted with distilled water. Thermal bond nonwoven polyester (100 g/m^2) was purchased from Laeisaz Company (Iran). All compounds and materials were used as received. Stock solutions of Cu(II) and Ni(II) were prepared (1000 mg/L) and diluted with distilled water to get determined concentration. The pH was adjusted using HCL or NaOH.

2.2. Experimental set-up

A self-assembled dynamic filtration set up as a column-flow system (Fig. 1) was employed to evaluate filtration characteristics and

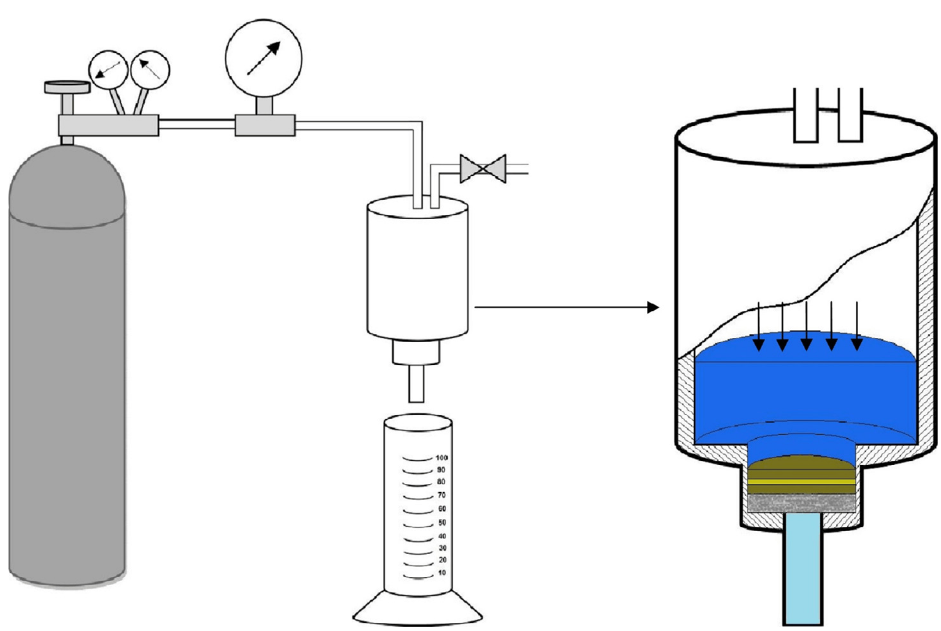

Fig. 1. Schematic diagram of the column-flow system and a cross section of the utilized dead-end filtration cell.

Please cite this article as: M. Askari et al., Performance improvements in structural characteristics of chitosan-based nanofibrous composite membrane for using in liquid filtration, Journal of the Taiwan Institute of Chemical Engineers (2015), http://dx.doi.org/10.1016/j.jtice.2015.05.007