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High flux electrospun nanofiberous membrane: Preparation by statistical approach, characterization, and microfiltration assessment

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ABSTRACT

Preparation, characterization and evaluation of new generation of micro-filters based on polyacrylonitrile electrospun nanofiberous membrane (ENM) were thoroughly investigated. First, quantitative relationships between average diameter, bead area density of nano-fibers and certain electrospinning parameters, *i.e.*, concentration, voltage, spinning distance, and feed rate, were established by empirical modeling based on a central composite design. The analysis revealed that concentration, voltage and distance are the significant parameters. Also, adequacy checking indicated the appropriateness of fit for the models. Afterwards, bead-free ENMs with diameter of 100–500 nm were prepared and characterized in terms of porosity, pore size and mechanical properties. The results indicate that as the nano-fiber diameter increases from 100 nm to 500 nm, porosity decreases from 74% to 61%, pore radius increases from 0.48 μm to 1.40 μm and tensile properties slightly decrease. Moreover, pure water flux increased with increasing nano-fiber diameter and membrane compaction was observed with increasing applied pressure for each membrane. Finally, ENM with fiber diameter of 100 nm showed the highest rejection rate of 99% and steady permeate flux of 118 l/m^{2}h using TiO_2 micro-particles suspension. Such finding demonstrates that ENMs with proper fiber diameter and morphology are excellent choices for high flux microfiltration applications.

1. Introduction

Due to the increasing global population and a rising concern over environmental pollution, water purification has to be made more efficient. The membrane filtration processes, *i.e.*, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are some of the most economical and practical water treatment technologies. Among these, MF is the lowest energy consuming process, which is applicable to pretreatment of wastewater and removal of bacteria, algae or protozoans from contaminated water by passing them through a porous membrane with pore sizes from 0.1 μm to 10 μm [1]. The most important objective in the preparation of micro-filters for particle, contaminant removal is improving the filtration efficiency in a way that both permeation rate and particle rejection rate for MF applications increase. Conventional polymeric membranes fabricated by the phase inversion technique have their inherent drawbacks, *e.g.* low-flux and high-fouling performance. The low-flux performance of these membranes is due to their low porosity. Also, the high-fouling performance is chiefly due to the asymmetric pore size distribution and having small pores on the surface [2].

Electrospinning is a well-known process for making continuous sub-micron to nanosize fibers in nonwoven mat form. In the process, polymer solution coming out of the tip of a needle connected to a syringe is deformed into a conical shape, *i.e.*, Taylor cone, due to the influence of the electrostatic field. A thin electrified jet is ejected from the Taylor cone when the applied voltage passes a required value at which electrostatic forces overcome surface tension. As the charged jet flies through the air, the solvent evaporates while the polymer fiber is stretched, elongated, whipped and finally deposited on the grounded collector as a random electrospun nanofiberous mat. Recently, electrospun nanofiberous membranes (ENMs) have been gaining considerable attention in filtration applications [1,3–8]. It is because these new types of membranes have several remarkable functional characteristics such as lower basis weight, larger effective surface area (up to 40 m^2/g depending on the fiber diameter), higher porosity (of the order of ≥ 80%) and lower production cost with continuously interconnected pores in comparison to conventional ones [5]. Due to these unique features, ENMs can overcome some limitations of conventional polymeric membranes. The high porosity may increase permeability and the interconnected pores may resist fouling more efficiently [6]. In addition, the production cost of ENMs is estimated to be 20 €/m^2 which is much lower than the 50 €/m^2 production cost for conventional membranes [9].

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Nomenclature

Y	predicted response
X_i	independent parameter
X_j	independent parameter
β_0	constant term
β_i	linear regression coefficients
β_{ii}	quadratic regression coefficients
β_{ij}	interactive regression coefficients
ε	Porosity
ρ	density of the ENMs (g cm^{-3})
ρ_0	density of PAN bulk polymer (g cm^{-3})
r_p	mean pore radius (nm)
J	permeation flux (l/m^2 h)
Q	permeated volume (l)
A	effective area of the membrane (m^2)
Δt	the permeation time (h)
C_P	TiO_2 concentration in permeate
C_F	TiO_2 concentration in feed
C_b	critical minimum concentration (wt%)
F_{cr}	Fisher's F value
D	overall desirability function
μ	viscosity of water (Pa s)
τ	tortuosity
ΔP	pressure difference across membrane (bar)
Δx	thickness of membrane (μm)

ENMs structure is highly correlated with the diameter and morphology of nano-fibers [1]. For example, the relationship between the porosity and mean pore size of ENMs and average nano-fiber diameter has been addressed by a number of studies [10–13]. In addition, nano-fiber morphology and diameter are tunable by varying solution, processing and ambient parameters. Solution parameters include concentration, viscosity, molecular weight, conductivity and surface tension. Process parameters include applied voltage, tip to collector distance (spinning distance), feed rate, type of collector, and diameter of needle. Finally, ambient parameters encompass humidity and surrounding temperature. However, previous studies have shown that solution concentration, applied voltage, spinning distance and feed rate are among the most important parameters [1,14]. Hence, by appropriate manipulation of these parameters, ENMs of desired characteristics can be obtained.

In the present study, in order to optimize and predict the morphology and average fiber diameter (AFD) of polyacrylonitrile (PAN) ENMs, the effects of four most influential electrospinning parameters including solution concentration, applied voltage, spinning distance and feed rate are investigated through response surface methodology (RSM). After preparation of ENMs with desired morphology and AFD, an emphasis is placed on the relationships between AFD and the structural parameters of ENMs, *i.e.*, porosity, mean pore size and mechanical properties. Furthermore, the MF performance of the ENMs in terms of pure water flux and particle rejection rate is thoroughly investigated in order to evaluate the capability of the membranes as micro-filters.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, with average molecular weight of 100,000 g/mol) was purchased from Polyacryl Co. (Iran). *N-N*, dimethylformamide (DMF) was used as PAN solvent and obtained from Merck Co. (Germany). The non-woven polyethylene terephthalate (PET) substrate was obtained from Sanko Co. (Japan). Moreover, TiO_2 micro-particles were purchased from Degussa (Japan).

2.2. Preparation of nanofiberous membranes

Polymer solutions with different concentrations ranged from 4 to 18 wt% were prepared by dissolving PAN powder in DMF and stirring for 16–24 h at 60 °C until homogeneous solutions were achieved. Electrospinning was conducted in an electrospinning unit (ES1000, Fanavaran nano-meghyas Co., Iran). The machine consisted of a high voltage DC power supply which is able to generate positive DC power up to 35 kV, a grounded rotating drum collector and a digitally adjusted syringe pump. The rotating drum was covered with PET nonwoven substrate and the rotating speed was fixed at 300 rpm. A 20 gauge blunt needle (0.6 mm inner diameter) was used as the spinneret and the spinneret speed was fixed at 10 mm/s. At surroundings temperature of 30 °C and relative humidity of 40%, PAN/DMF solutions were electrospun directly onto the PET nonwoven substrate.

2.3. Fiber morphology and measurements

The morphology of electrospun PAN fibers was observed by scanning electron microscopy (SEM) from Philips Co. (Holland) after being gold-coated. The AFD and bead area density (BAD) of the ENMs were determined from the SEM images using the ImageJ software [15]. For AFD measurements, four images with 2 μm magnification from different areas of each mat were used and atleast 100 different segments were randomly measured. For BAD measurement, the total surface area covered by beads was measured with the ImageJ software using SEM images with 20 μm magnification. Finally, total area of images divided by bead area resulted in the BAD of the mat.

2.4. Experimental design

Various methods in RSM such as Central Composite Design (CCD) [16,17], Box Behnken experimental design [18,19] and two-level full factorial design [20] have been used by researchers so as to predict the ultimate response(s). CCD allows the calculation of linear and quadratic effects, as well as interactions for any pair of selected parameters with the best possible precision at minimum number of experiments. This method involves three steps: conducting the designed experimental runs, assessing the coefficients and discarding insignificant terms in a mathematical model, and validating the model by predicting the response(s). If k parameters are investigated, this design consists of 2^k factorial points, coded as $\pm$ 1 notation; $2k$ axial, *i.e.*, star points that are located at a specified distance α from the center in each direction on each axis defined by the coded parameter levels; and specified replicate runs at the center point. Replicate runs at the center point give information about the existence of curvature, as well as allow an independent estimation of error to be obtained. Also, the estimation of the pure quadratic properties of the model can be carried out by the star points.

In order to establish a quantitative relationship between AFD and BAD with spinning parameters, the influence of four vital parameters including solution concentration, applied voltage, spinning distance, and feed rate were investigated. The experimental parameters, their levels, and their codes are given in Table 1. The ranges of the parameters were chosen to be wide enough but not too wide as it reduces the prospect of a good regression fit of the response surfaces to the actual responses [21–23]. A quadratic polynomial (Eq. (1)) was used to describe the effect of parameters in terms of linear, quadratic, and interactive terms.

$$Y = \beta_0 + \Sigma\beta_i X_i + \Sigma\beta_i X_i^2 + \Sigma\Sigma\beta_{ij} X_i X_j \quad (1)$$

where Y is predicted response value; X_i and X_j are independent parameters; β_0 is a constant term, *i.e.*, the average value of the response