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An Investigation Effects Of Electrospinning Parameters: Process Optimization By Application Of Response Surface Methodology

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Abstract. Effects of material and process parameters on the electrospun polyacrylonitrile fibers were experimentally investigated. Response surface methodology (RSM) was utilized to design the experiments at the setting of solution concentration, voltage and the collector distance. It also imparted the evaluation of the significance of each parameter on pore size, contact angle, modulus young and clean water permeability. Effect of applied voltage in micron-scale fiber diameter was observed to be almost negligible when solution concentration and collector distance were high. However, all three factors were found statistically significant in the production of nano-scale fibers. The response surface predictions revealed the parameter interactions for the resultant fiber diameter, and showed that there is negative correlation between the mean diameter and coefficient of variation for the fiber diameters were in agreement with the experimental results. Response surfaces were constructed to identify the processing window suitable for producing nanoscale fibers. A sub-domain of the parameter space consisting of the solution concentration, applied voltage and collector distance, was suggested for the potential nano scale fiber production.

1. Introduction

The market for carbon fibers is dominated by fibers made from polyacrylonitrile (PAN) due to their combination of good mechanical properties (high-strength, low-density composite materials and high break strength (particularly tensile strength, and reasonable cost). The high strength and modulus of carbon fibers make them useful in the reinforcement of polymers, metals, carbons, and ceramics, despite the fibers' brittle nature [1]. Carbon fibers prepared from PAN precursor fibers by conventional techniques have a minimum diameter between 5-7μm. The bulk of production cost incurred during carbon fibers production is due to long heating times required to stabilize and carbonize the precursor fiber, in addition to engineering costs to maintain tension on fibers during stabilization.

In this experiment-oriented work, PAN polymer solution was electrospun to produce nano-scale fibers, and emphasis was given to the effect of polymer solution concentration, applied voltage, and the collector distance. Their effects were investigated within the context of response surface methodology (RSM) that incorporates design of experiments (DOE) and linear regression. This approach enables experimental investigation of the individual factors and the interactions of the factors (variables or parameters) simultaneously. A surrogate model that is a response surface approximation was constructed. Such an empirical model allows the evaluation of significance of the parameters based on experimental results and provides prediction capability for the process domain of targeted in response [2].

The objective of this study was to investigate the electrospinning process parameters (screen distance, polymer concentration and voltage) and interactive effects on the PAN nanofiber membrane pore size, contact angle, young modulus and clean water permeability.. Another aim was to predict the optimum of the parameters electrospinning where targeted PAN nanofiber can be achieved.

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1.1 Response surface methodology

RSM is derived from mathematical and statistical technique. It can be used for studying the effect of several factors at different level and their influence on each other. RSM has 4 major steps, which are experimental design, model fitting, model validation and condition optimization [3].

1. Identification of variables ξ_1, ξ_2, ξ_3…..for response η.
2. Calculating of corresponding coded variables (x_1, x_2, x_3…..) by using the following equation.

$$x_1 = \frac{\xi_i - [\xi_{Ai} + \xi_{Bi}]/2}{[\xi_{Ai} - \xi_{Bi}]/2} \quad (1)$$

where ξ_{Ai} and ξ_{Bi} refer to the high and low levels of the variables ξ_i, respectively.

3. Determination of the empirical model by multiple regression analysis to generate theoretical responses (ŷ). The second-order model is widely used in RSM. The general equation for response η of the second-order model is given by:

$$H = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \Sigma \sum_{i<j=1}^{k} \beta_{ij} x_i x_j \quad (2)$$

where k is the number of factors, x_i are the coded variables for responsesand β are coefficients.

4. Calculation of the coefficients β to fit the experimental data as close as possible.

2. Experimental

2.1 Materials and dope preparation

Polyacrylonitrile (PAN) powder of 150 000 molecular weight, N, N-dimethylformamide (DMF) and acrylamide (AM) were obtained from Aldrich Chemical and were used without further purification. Dope solutions were prepared by dispersing predetermined amount of silica nanoparticles (1 wt.% to PAN) into 15, 16, 17.5, 19 and 20 wt.% PAN solution in DMF. The mixture was mechanically stirred for at least 24 h at 60 °C in order to obtain homogeneous silica dispersed PAN solutions. The viscosity of the solutions of was determined by using Brookfield Dial Viscometer.

2.2 Electrospinning

The experimental set-up used for the preparation of nanofibers mat consisted of apparatus such as power supply, a collecting drum and a reservoir. A 100 mL reservoir was used to hold the electrospinning solution. The PAN solution prepared in section 2.1 was pumped at a constant rate of 2 mL/h with the help of a metering pump through a stainless steel needle of inner diameter 0.8 mm. A drum of 15 cm diameter connected to a variable speed motor, was used to collect the nanofibers. A high DC voltage was applied to the needle with the help of high voltage regulated DC power supply (Model ES 30P-5W, Gamma High Voltage Research, Ormond Beach, FL, USA). The collecting drum was ground so as to generate the desirable electric field strength between the tip of the spinneret and the collector surface. The nanofibrous mat was carefully removed from the collector, and the residual solvent associated with nanofiber mat was removed by keeping the mat in an oven for at least 2 days at 40 °C. The dried electrospun mats were stored in desiccators.

3. Characterizations nanofibers membrane

3.1 Pore size

The pore size of the PAN nanofiber membrane was determined using the bubble-point method. It is based on the measurement of pressure necessary to blow air through a liquid-filled membrane. In order to determine membrane surface porosity, membranes were immersed in distilled water for 4 hours at 25 °C. Membrane in wet state was weighed in an electronic balance after carefully wiping the surface with a clean tissue. This wet membrane was dried in an oven at 50–60 °C for 24 h. Then, membrane was weighed again in dry state.

3.2. Tensile test

Tensile test of PAN fibers was performed using tensile tester machine (LRx2.5 KN LLYOD Instrument with a load cell of 1 N, accordance with ASTM D 3379 (25 mm gauge length are used for each PAN fibers) [4]. The tensile specimen was prepared by fixing the filament on a paper holder with an instant cyanoacrylate adhesive [5], while its gauge length, L was 25 mm and crosshead speed was 5 mm/min [6]. The tensile test, σ, gives a load, P as a function of extension, d_f is the function of diameter of fiber. Tensile stress was calculated as follow: $\sigma = P/(\pi d_f^2/4)$.

3.3.Clean water permeability

Clean water permeability (CWP) with used the water permeation system represents the maximum flux achievable dependent on the state of the membrane. It can be determined by measuring the flux at different trans membrane pressures (TMP). The slope of the resulting curve is considered as the CWP [7]. The CWP test was performed at 25 °C.

4. Results

4.1. Model fitting and statistic analysis

The second-order polynomial regression model containing 4 backward and 4 quadratic was employed by using RSM. All models was found to be significant with R^2 higher than 0.80. The R^2 for these response variables was higher than 0.80, indicating that the regression models explaining the reaction is acceptable. Lack of fit was insignificant, it means that thismodel accurately represents data in the experimental region.

4.2. Response surface methodology approach for optimization of factors

Based on the RSM approach (Table 1), the runs were conducted in CCD model-designed experiments to visualize the effects of independent factors on the response and the results along with the experimental conditions. According to the sequential model sum of squares, the model was selected based on the highest-order polynomials where the additional terms were significant.

Table 1. RSM procedure to optimize the process parameters for the electrospinning process

Std	Run	Block	Factor 1 Distance (cm)	Factor 2 Pol. Conct (wt.%)	Factor 3 Voltage (Volt)	Response 1 Pore size (micron)	Response 3 Young modulus (Pascal)	Response 4 CWP ($L/m^2hr.bar$)
1	14	Block 1	6.00	16.00	15.00	0.3	789	1878
2	18	Block 1	15.00	16.00	15.00	0.24	800	1900
3	7	Block 1	6.00	19.00	15.00	0.2	870	1989
4	4	Block 1	15.00	19.00	15.00	0.23	896	1993
5	2	Block 1	6.00	16.00	25.00	0.16	1036	2036
6	6	Block 1	15.00	16.00	25.00	0.12	977	2003
7	13	Block 1	6.00	19.00	25.00	0.3	1020	2010
8	9	Block 1	15.00	19.00	25.00	0.12	1076	2001
9	8	Block 1	2.93	17.50	20.00	0.3	977	2010
10	11	Block 1	18.07	17.50	20.00	0.15	937	2011
11	15	Block 1	10.50	14.98	20.00	0.26	973	1958
12	1	Block 1	10.50	14.98	20.00	0.3	986	1988
13	10	Block 1	10.50	17.50	11.59	0.16	776	1988
14	3	Block 1	10.50	17.50	28.41	0.17	1005	2009
15	12	Block 1	10.50	17.50	20.00	0.16	935	2012
16	5	Block 1	10.50	17.50	20.00	0.16	978	1997
17	17	Block 1	10.50	17.50	20.00	0.23	950	1998
18	16	Block 1	10.50	17.50	20.00	0.24	958	1956

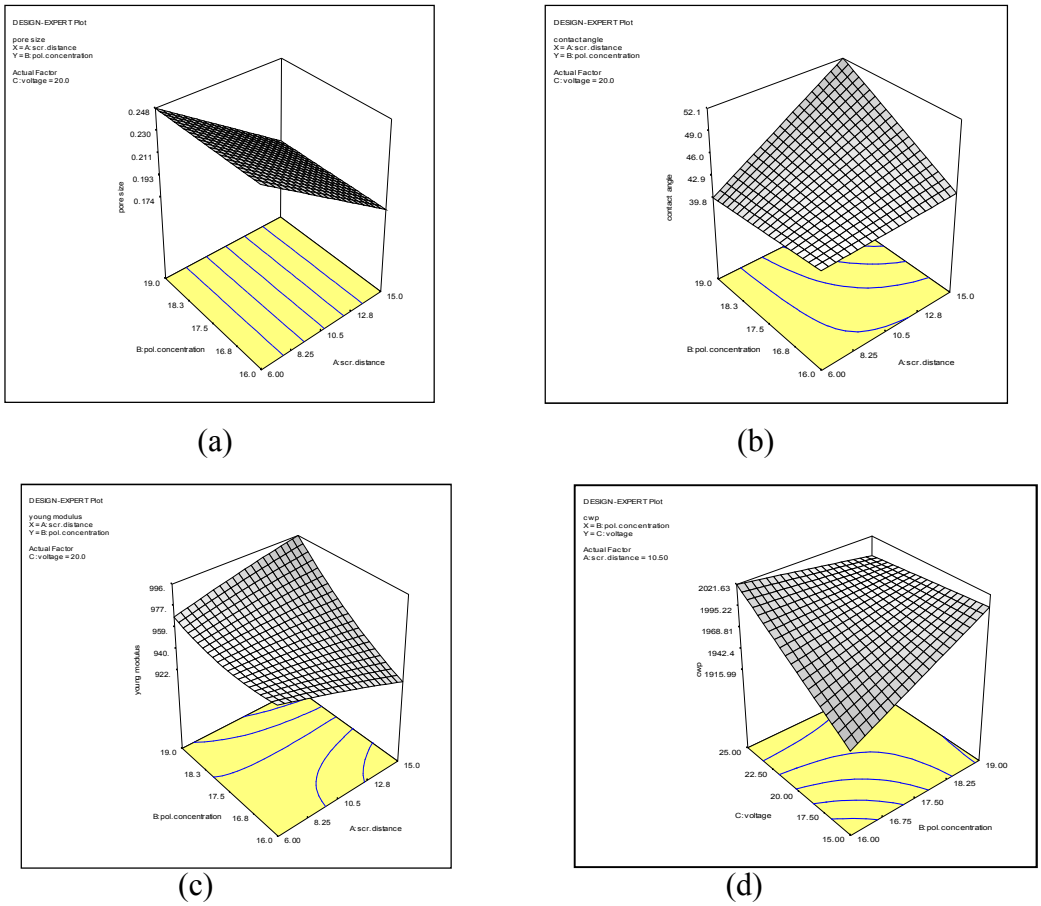

Fig. 1. 3D-contour plots

Fig. 1 (a) Interaction effect between polymer concentration and screen distance demonstrated a remarkable decreased of pore size when screen distance increased. Using increase of screen distance ranging from 6 to 15 cm, the pore size of membrane decreased significantly; while similar trend was observed with the increase of polymer concentration. The enhancement brought by decreasing pore size appears to be slightly greater at higher screen distance of 15 cm. In addition, the change of pore size was also analyzed as a function of all process parameters studied. It should be noted that the pore size was affected most strongly by increase of screen distance, resulting in the best membrane morphology.

Fig. 1 (b) demonstrated a remarkable increase in contact angle as polymer concentration increased from 16 wt.% to 19 wt.% and screen distance increased from 8.00 cm to 15 cm. The drastically contact angle value was achived using highest value of both factors of 19 wt.% and 15 cm, respectively. The highest contact angle value was 52.1^{o}, which indicated the hydrophilicity of electrospun nanofiber membrane. It is worth to note that the hydrophilicity was the important response forapplying in water treatment.

The Young's modulus values (Fig. 1 (c)) were found maximum at approximately maximum coded level factor (1). It is worth to note that the change of polymer concentration did not affect significantly on young modulus value. On the other hand, the increase of screen distance increased the Young's modulus, especially at higher polymer concentration (17.5 wt.% to 19 wt.%). This indicated that the greater polymer concentration led to a higher Young's modulus. Meanwhile, at lower polymer concentration, the Young's modulus values were slightly increased

Fig. 1 (d) shows contour plots in the case of response of clean water permeability (CWP). At higher voltage of 25 kV, decrease of polymer concentration resulted approximately maximum value of CWP. On the other hand, lower voltage brought about a drastic increase of CWP with polymer concentration. At higher polymer concentration of 19 wt.%, the resulted CWP values were in

ranging of 1995.22 to 2021.63 L/m^2 h bar as voltage changed from 15 kV to 25 kV. The response indicates that changes in CWP are more responsive to voltage at the lower polymer concentration. The responses indicated that nanofibers can be produced in a range of process conditions. Figure 4 (d) also shows that nanofibers of high CWP can be theoretically produced at high concentrations ranging from 18.25 wt.% to 19 wt.% and at a broad range of voltage in ranging from 15 kV to 25 kV. Meanwhile, the best value of CWP (20121.63 L/m^2 h bar) was achieved by the highest voltage and lowest polymer concentration of 25 kV and 16 wt.%, respectively. However, this result follows the direction obtained from contour plots suggesting that the lower concentration gives lower fiber diameter.

5. Conclusions

A full factorial design and central composite design of response surface methodology can be used to determine the significant variables and optimum condition for submerged ultrafiltration of refinery wastewater with respect to flux and COD removal. Experimental results showed that a submerged ultrafiltration process using modified membranes has a great potential for refinery produced wastewater treatment. The quartic equation developed in this study shows the presence of a high correlation between observed and predicated values.

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