# FABRICATION OF CHITOSAN NANOFIBERS MEMBRANE AND ITS TREATMENT

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## ABSTRACT

Chitosan (biopolymer) nanofibers were fabricated *via* electrospinning by varying solution concentration (4, 6 and 8 wt % (w/v)), applied voltage (18 and 22 kV), flow rate ( 0.4 ml/h and 0.8 ml/h ), needle diameter ( 0.2 mm and 0.8 mm) and distance between needle tip and collector (100 and 140 mm). The electrospun nanofibers with beads were observed for 4 wt% chitosan in trifluoroacetic acid (TFA), where as scanning electron microscope (FE-SEM) showed improved physical texture, decrease in the number and size of microspheres and beads when applied voltage was increased to 22 kV, and beads free nanofibers were obtained when the concentration of solution was changed from 4 to 6 wt%. The optimized conditions (i.e., 6 wt%, 22 kV, 0.4 mL/h, 0.8 mm and 100 mm) were used to produce nanofibers membranes. The membranes were then functionalized by glutaraldehyde (($C_5H_8O_2$) GTA vapors). The chemical structure of the nanofiber membranes after functionalization was studied by using Fourier transform infrared (FT-IR).

## 1. INTRODUCTION

Nanofibers membranes produced from natural polymers have received more attention due to their ease of fabrication and the ability to control their compositional, structural and functional properties. The key advantage of producing nanofibers is positioned in their small diameters, large surface area to volume ratio, high porosity and superior mechanical performance [1]. A number of processing techniques such as drawing [2], template synthesis [3, 4], phase separation [5], self-assembly [6, 7], electrospinning [8, 9], etc. have been used to prepare polymer nanofibers in recent years. However, electrospinning was found an efficient fabrication technique as compared to the above mentioned processes because it is cost effective, utilize simple equipment, produces dry fibers, creates fibers with diameters in the range of nanometer(nm) to micrometer (µm), have very high specific surface area [10, 11] and superior mechanical properties[12] In addition to the above mentioned advantages, electrospinning seem to be the only process that can be developed for mass production of continuous nanofibers from a variety of polymers [11]. Electrospinning was first patented by Formhals in 1934 [13] and started to be used into nanotechnology and materials science since 1980s, and more recently has attracted increasing attention. In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field and an electric charge is induced on the liquid surface due to this electric field. When the electric field applied reaches a critical value, the repulsive electrical forces overcome the surface tension forces. Eventually, a charged jet of the solution is ejected from the tip of the Taylor cone and an unstable and a rapid whipping of the jet occurs in the space between the capillary tip and collector, which leads to evaporation of the solvent, leaving a polymer [14, 15]. The typical set up of electrospinning apparatus is shown in Fig. 1. Basically, an electrospinning system consists of four basic components: a high voltage supply, a syringe pump, a syringe with a metal needle and a collector (that can be electrically grounded)

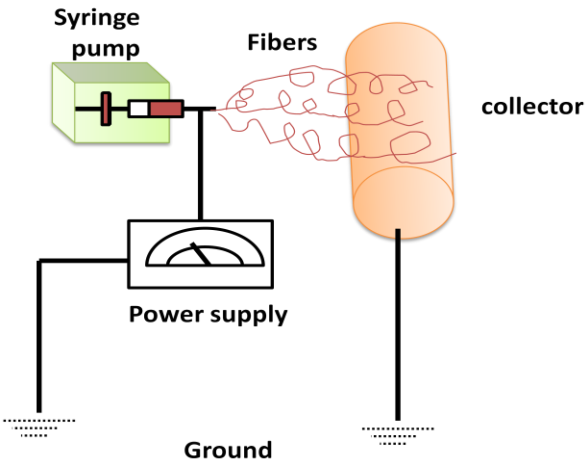

Fig.1. Schematic representation of the electrospinning setup used in this study (NANO-1A)

## 2. MATERIALS AND METHODS

Medium molecular weight chitosan powder and Trifluoroacetic acid (($CF_3COOH$) TFA) were purchased from Sigma-Aldrich and Alfa Aesar. 4 and 6 wt% chitosan solutions were prepared by dissolving chitosan in TFA in a sonicator bath (Branson Model 2510) at 55 $^oC$ for 90 minutes. For electrospinning the solutions were added to 5 mL plastic syringe of 10 mm diameter with stainless steel needles of 0.2 and 0.8 mm diameters. The basic electrospinning setup NANO-1A, Japan was used in this study. The syringe was placed in syringe pump and the needle was connected with high voltage supply, which cloud generated high voltage of up to 30 kV. In this study, the applied voltages were 18 kV and 22 kV, the flow rates were 0.4 mL/h and 0.8 mL/h and the distances between needle tip and collector were 100 mm and 140 mm. After electrospinning the nanofibers mats were removed from the aluminum foil (rolled on the rotating drum), dried in the vacuum oven at 60 oC and stored in the desiccator for further characterizations. The field emission-scanning electron microscopy (FE-SEM) micrographs of the Pt-coated electrospun chitosan nanofibers were taken using a Hitachi S-570 FE-SEM. The functionalization reaction of chitosan nanofibers membrane was carried out by placing the membranes on a porous ceramic shelf and 25% glutaraldehyde (($C_5H_8O_2$) GTA vapors) aqueous solution were purchased from Loba Chemie in a dish at the bottom of the sealed desiccators at room temperature for 48 h. After the reaction, the membrane samples were dried in a vacuum oven at 60 °C and -0.1 MPa for 24 h and stored for characterization.

## 3. RESULT AND DISCUSSTION

Fig.2 Shows the FE-SEM micrographs for 4 and 6 % at various applied voltages, distance between needle and collector, flow rates and needle diameters. In case of 4wt%, the FE-SEM micrographs showed partially electrospun nanofibers with beads and microspheres Fig. a. and decrease in the number and size of the beads Fig.b. The presence of microspheres might be attributed to the low polymer concentration, When the polymer concentration is low, microspheres appears in electrospun nanofibers and the process become electrospraying when the concentration become low enough [16], whereas ,the decrease in the number and size of beads and microspheres Fig. a-b with increase in the voltage from 18 kV to 22 kV might be referred to the surface tension of polymer solutions; higher voltage overcame the surface tension of the polymer solution and initiated jet formation [17, 18]. Bead free electrospun nanofibers were obtained Fig.c. when the solution concentration was increased to 6 w% and the other parameters were 0.4 ml/h, 140mm, 0.8 mm and 18kV. Increase in the polymer concentration has increased the viscosity of the solution to a critical value, therefore, eliminating the beads completely [19].

The average diameters of nanofibers were, however, decreased from 170.38 nm (Fig.2c & Fig. 3a) to 129.7 nm (Fig.2d. & Fig.3b), when the applied voltage and flow rate were increased to 22 kV and 0.8 ml/h, and the distance between needle tip and collector was decreased to 100 mm while keeping the needle diameter 0.8 mm. The decrease in the average diameter of the nanofibers might be due to the larger electrostatic stretching force, which resulted in the jet acceleration and stretching in the electric field, thereby favoring thinner fiber formation [19]. At 8 w%, solution concentration, no electrospinning was observed as the solution was very viscous (semi-solid), which resulted in the drying of the drop at the needle tip [20].

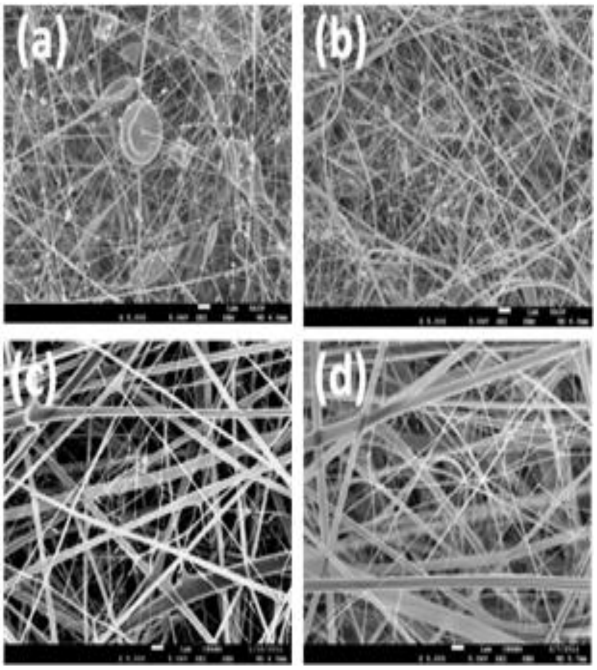

Fig.2. FE-SEM micrographs of the electrospun nanofibers; (a) 4 wt%, flow rate = 0.4 mL/h, distance = 140 mm, needle diameter 0.2 mm, applied voltage = 18 kV, (b) 4 wt%, flow rate = 0.4 mL/h, distance = 140 mm, needle diameter = 0.2 mm, applied voltage = 22 kV , (c) 6 wt%, flow rate = 0.4 mL/h, distance = 140 mm, needle diameter 0.8 mm, applied voltage = 18 kV, (d) 6 wt%, flow rate = 0.8 mL/h, distance = 100 mm, needle diameter = 0.8 mm, applied voltage = 22 kV

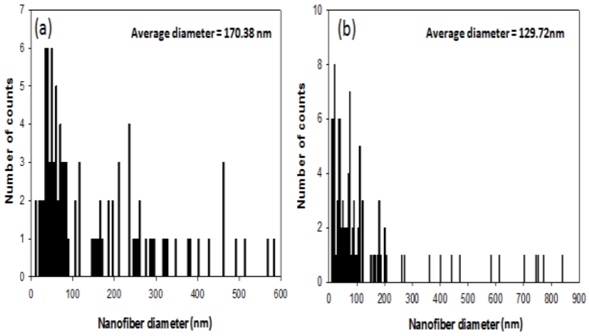

Fig.3. Diameter distributions of chitosan nanofibers at concentration 6 w% and needle diameter 0.8 mm (a) flow rate 0.4 mL/h, needle tip to collector

distance 140 mm, , and applied voltage 18 kV (b) flow rate 0.8 mL/h, needle tip to collector distance 100 mm, , and applied voltage 22 kV.

### 3.1 Preparation and Functionalization of the Nanofibers Membrane

Fig.4. shows the successful preparation of the bead free nanofibers membrane at optimal conditions (e.g. concentration of solution 6 w%, applied electrical potential 22 kV, flow rate 0.4 mL/h, needle diameter 0.8 mm and needle to collector distance 100 mm). FE-SEM micrographs of functionalized nanofibers membrane without any serious cracks or degradation are shown in. Fig.5.

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Fig.4. Digital images for chitosan nanofiber membrane

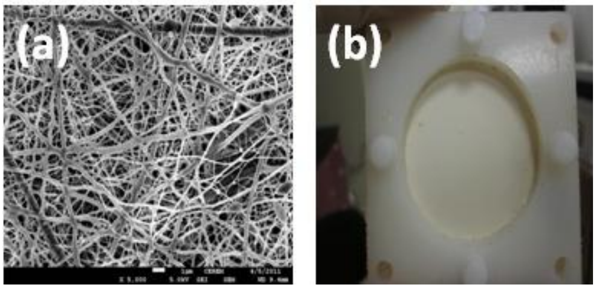

Fig.5. (a) FE-SEM micrograph of the surface of the chitosan nanofibers membranes after functionalization and (b) Digital images of the functionalized nanofibers membrane

### 3.2 Characterization of the Nanofibers Membrane

Fig.6. Shows the FT-IR spectra of as spun nanofibers and functionalized nanofibers membranes. FTIR spectra of as spun nanofibers showed typical scissor vibration of the amine (-NH$_2$) at 1630 cm$^{-1}$ and carbonyl group (C=O) stretching of the N-acetyl and trifluoroacetate (CF$_3$COO$^-$) ions (at 1680 cm$^{-1}$) and a band for ammonium ion at 1538 cm$^{-1}$ [21]. In the functionalized nanofibers membrane, the shoulder scissor vibration of the amine at 1630 cm$^{-1}$ decreased and the intensity of the C=O stretching at 1680 cm$^{-1}$ (primarily assigned to N-acetyl) is increased [22]. This increase in intensity might be due to the overlapping of C=O and C=N (imine) stretching bands. Imine formation (aldol type of reaction) between free amino and aldehyde group of glutaraldehyde has been reported in the literature [10].

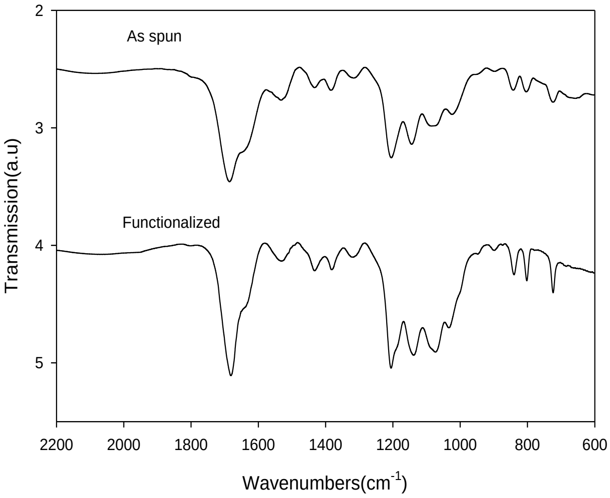

Fig. 6. FTIR spectra of the as spun nanofibers and functionalized nanofibers membrane

## 4. CONCLUSION

The electrospinning conditions were optimized and the nanofibers membrane was successfully prepared. The nanofibers membrane was functionalized and stabilized in aqueous medium. The combination of electrospinning and functionalization is a recent approach and is expected to have more potential applications as compared to as spun nanofibers and microfibers. Thanks to the more efficient technology for membrane preparation. With the ability to mass-produce nanofibers, electrospinning technique may well be one of the most significant nanotechnologies of this century.

## 5. ACKNOWLEDGEMENTS

Financial support from the KACST through NPST, King Saud University, Saudi Arabia, under the grant 09-NANO869-02 is greatly acknowledged.

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