

Fabrication of highly porous PMMA electrospun fibers and their application in the removal of phenol and iodine

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Abstract Highly porous polymethyl methacrylate (PMMA) fibers were fabricated via an electrospinning technique using a binary solvent system (8:2 dichloromethane:dimethylformamide) and controlled humidity. The electrospinning process was carried out in a closed hood under humid conditions (varying the humidity from 15 to 70 %). The effects of the concentration, electrospinning parameters, and humidity on the morphology of the PMMA fibers were assessed by field emission scanning electron microscopy (FE-SEM). The surface area, porosity, and mean interfiber pore size of membranes made from the fibers were measured with the Brunauer–Emmett–Teller (BET) method, and the diameter of the fibers was measured using an image analyzer. Nonporous and porous electrospun PMMA fibers exhibited concentration-dependent variations in their morphologies. No effect of the electrospinning parameters, such as the voltage and flow rate, was observed. The porosity of the PMMA fibers increased when the humidity was changed from 15 to 70 %. The porous PMMA fibers had a large surface area (139.0 m²/g) and a small interfiber pore size (34.8 Å), along with an average fiber diameter of 2 μm. The capacities of the porous and nonporous fibrous membranes to adsorb iodine and phenol were tested. The large surface areas of the membranes led to excellent adsorption capacity of the porous PMMA fiber membrane (iodine: 203 mg/g; phenol: 3.73 mg/g), in contrast to the adsorption capacities of the nonporous PMMA fiber membrane (iodine: 117 mg/g; phenol: 1.8 mg/g). A facile, easily accessible approach for fabricating porous fiber membranes is

presented in this work, and it is believed that the product may find potential application—as a possible substitute for conventional material—in the removal of organic and inorganic pollutants from water.

Keywords PMMA · Controlled humidity · Porous fibers · Adsorption

Introduction

The electrospinning process is one of the most discussed and frequently used processes in the modern research world. Fibrous materials with unique properties such as an ultrafine diameter (in the range of a few nanometers (nm) to several hundred nanometers (μm)), a high surface area per unit mass, good porosity, gas permeability, and a small interfiber pore size can be conveniently prepared using the electrospinning process [1–3]. Nonwoven electrospun nanofiber membranes are particularly useful for applications in bioengineering (such as enzymatic catalysis based membrane bioreactors, protein purification, and enhancing the immobilization and adhesion of biomacromolecules or cells) and in environmental engineering (such as in the removal of metal ions, dyes, and microbes from aqueous liquids and the removal of airborne particles from the air) [4, 5]. Depending on the electrospinning parameters and the materials used, polymeric fibers can be used to fulfill certain criteria for specific applications. In environmental applications, the as-spun fibers act like filter paper and adsorb toxic materials from water. The already excellent absorbing capacity of polymeric fibers can further be enhanced by exposing the internal area of the fibers to absorbing species. One way to achieve this goal is to produce porous polymeric fibers.

Porous polymeric fibers with excellent physical strength and enhanced adsorption capacities are in great demand for a wide range of applications in the fields of adsorption,

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ultrafiltration, and ion-exchange resins, and as carriers for catalysts and reagents [6–8]. Porous fibers have fulfilled many needs in the above areas due to their intrinsically high surface area, small interfiber pores, and engineering versatility [7]. Phase separation based on the evaporation of solvents is the main mechanism behind the formation of porous fibers [9–11]. When a more volatile solvent is used in the electrospinning process, solvent-rich regions begin to form. The solvent-rich regions are transformed into pores as soon as the solvents are evaporated [11, 12]. A second method of producing porous fibers relies on the spinning of two different polymers blended together. One of the polymers is removed after fiber formation by dissolution in a solvent in which the other polymer is insoluble [13]. Xia et al. showed that highly porous fibers membranes can be obtained by selective dissolution (in the case of polymer fibers) or calcination (in the case of composite fibers) using a coaxial spinneret with miscible solvents and immiscible polymers [14, 15]. A third method of producing fibers is to control the humidity during electrospinning. The characteristics of the fibers during electrospinning depend on the solution properties, such as the viscosity, surface tension, conductivity, boiling point, and dielectric constant [16]. The morphology of the electrospun fibers also depends on the electrospinning parameters, such as the concentration, spinning distance, voltage, needle diameter, flow rate, as well as ambient parameters, especially the humidity [17], which can be adjusted to produce porous fibers. For example, at low humidity, the probability that the electrospinning jet will come into contact with water molecules is low [18]. On the other hand, at high humidity, water vapor easily condenses into droplets (a similar phenomenon can also be observed during cloudy conditions, rain, mist, and especially in foggy conditions, when water droplets reach a certain size due to condensation and tend to settle on particulate matter present in the atmosphere). The relatively large size of the water droplets allows them to make proper contact with the jet and attach to the surfaces of the fibers, resulting in the formation of circular pores/voids on the fiber surfaces. The size of the circular pores in the fibers increases with increasing humidity until they eventually coalesce to form large, nonuniform-shaped structures. The depth of the pores also increases with increasing humidity. However, above a certain humidity, the depth and number of pores become so large that the fibers lose their uniform porosity [19].

Water pollution has emerged as a major concern recently, mainly due to rapid industrialization. Most industries, apart from those producing primary products, also produce organic and inorganic by-products [17] (e.g., benzene, naphthalene, anthracene, cyanide, ammonia, phenols, cresols, iodine, and some metal ions) that are not needed. These by-products are usually in liquid/solution form, and the appropriate mechanisms to discard them are often not in place, so they are

thrown away as waste into nearby rivers or ponds, where they cause waterborne diseases not only in humans but also in animal hosts. Therefore, it is essential to remove all of these pollutants in order to obtain high-quality water for use by humans and to provide a clean environment. Various techniques have been reported for the removal of pollutants from water. Among them, filtration, sedimentation, ion exchange, and adsorption are the most commonly used techniques [20, 21]. Organic pollutants such as benzene and phenol, and some inorganic pollutants such as metal ions and iodine, can easily be removed with adsorption methods [22, 23].

A literature review revealed that a number of biological adsorbents have been investigated for the removal of industrial waste from water. These include activated carbon, maize cob, wood, coal, nutshell, and rice hull [24, 25]. It is known that activated carbon is a versatile adsorbent because of its sufficient surface area, pore volume, and high degree of surface reactivity, and it has reasonable adsorption capacities [26] for decolorants in aqueous solutions. Adsorption is enhanced because of the presence of mesopores together with micropores in the activated carbon. There are some commercially available active carbons, but these are expensive [22–28]. Therefore, porous fibers may be a good substitute for activated carbon, and could be used in filter media to remove toxic chemicals from water wastes using the adsorption method.

In this paper, we report our findings on the preparation of highly porous PMMA fibers via electrospinning using a binary solvent system (DCM/DMF) and controlled humidity. During electrospinning, all of the spinning parameters were kept constant and only moisture was varied (from 15–70 %). Porous fibers were generated by evaporating the solvent and water from the fibers. Finally, the adsorption capacities of porous fiber membranes (and nonporous membranes, for comparison) for iodine and phenol in water waste were measured.

Materials and methods

Materials

PMMA (350K), DMF, DCM, phenol, iodine, sodium thiosulfate, and starch were purchased from Sigma–Aldrich (St. Louis, MO, USA). Distilled water was used to prepare the synthetic adsorbate solutions. All chemicals were of analytical reagent grade and were used without further purification.

Solution preparation and electrospinning setup

PMMA was dissolved (to various concentrations in the range 12–21 wt%) in a binary solvent system (8:2 DCM:DMF), and the solution was stirred overnight at room temperature until complete dissolution. The prepared solution was then subjected to electrospinning. The electrospinning experiments

were performed at room temperature, and the apparatus for the electrospinning was assembled based on a study done by Lee et al. [26]. The PMMA solution was placed into a 10-ml glass syringe fitted with a needle with an inner diameter of 0.4 mm. The voltage was 15 kV, 18 kV, or 20 kV, and the flow rate was 0.5, 1, or 2.0 mL/h. The electrospinning chamber (Fig. 1) contained a humidifier, a heater, and a digital humidity indicator. Prior to electrospinning the solution, water vapors were generated until a target humidity value was achieved (as displayed by the digital humidity indicator). A clamp connected to a high-voltage power supply that could supply voltages from 1 kV to 50 kV was connected to the needle tip. A piece of aluminum foil was placed 17 cm from the needle tip. The polymer jets generated from the needle when the high voltage was applied were collected at the rotating drum as a fiber membrane. Finally, the fiber membranes were dried overnight at 40 °C to remove the solvent.

Characterization

The viscosity of each PMMA solution in a binary solvent mixture was measured with a viscometer (DV-II Pro, Brookfield, Middleboro, MA, USA) at room temperature using spindle number 6 at 100 rpm. The morphologies of the prepared electrospun nonporous and porous fibers were examined using FE-SEM (S-4300, Hitachi, Tokyo, Japan). The porosity and mean interfiber pore size of the porous and nonporous PMMA fibers were measured with a Brunauer–Emmett–Teller (BET) surface area analyzer (Nova 2000 and Autosorb-1-c, Quantachrome, Boynton Beach, FL, USA). The average diameter of the electrospun fibers was measured with an image analyzer Image J software.

Adsorption studies of phenol and iodine

The adsorption studies of phenol and iodine were carried out at 25 °C using the batch technique. A calculated amount of the adsorbent (fiber mesh, 1 mg) and 25 mL of synthetic

phenol or iodine solution were separately added to a 100-mL conical flask and closed with a stopper. The flask was placed in a shaking bath for 1 h. After shaking, the sample solution was centrifuged for 5 min to remove any undesired particles. Ten milliliters of the supernatant were removed and the concentration was determined. The concentration of phenol was determined with a spectrophotometer at 269 nm (UV; model 160D, Shimadzu, Kyoto, Japan), while the concentration of iodine was determined by titration with a sodium thiosulfate solution. The amount adsorbed was calculated as follows:

$$q = \frac{(C_o - C_f)V}{M},$$

where q is the amount adsorbed (mg/g); C_o is the initial concentration; C_f is the final concentration (mg/L), V is the volume of the solution (L), and M is the amount of adsorbent (g) used.

Results and discussion

Preparation of electrospun PMMA fibers

Figure 2 shows the variation in the viscosity as the concentration of the PMMA was increased. Increasing the PMMA concentration led to an exponential increase in the viscosity. At 18 wt%, however, the increase was abrupt, which may have had an impact on the morphology of the electrospun PMMA fibers [29]. The SEM micrographs of the electrospun fibers from the PMMA solutions with different concentrations (ranging from 12 to 21 wt%) are shown in Fig. 3. When the concentration was below 15 wt%, beaded fibers were generated by electrospinning. Uniform and continuous fibers were obtained when the concentration was above 18 wt%. The formation of bead-free fibers could be attributed to the increase in the viscosity of the solution. The solution viscosity increased as the polymer concentration increased up to a critical value, at which point the beads vanished completely [30–32]. The viscosity showed no effect on the average diameter of the fiber, which was calculated to be 2 μm. Therefore, in this study, a solution concentration of 21 wt% of PMMA was used in the preparation of the porous fiber membranes under different humidity conditions.

Preparation of porous fibers under controlled humidity

Figure 4 is a schematic showing the formation of the porous PMMA fibers using the electrospinning technique. During the electrospinning of the PMMA solution (using the binary solvent containing DCM and DMF), stretching of the polymer solution occurs due to the electrostatic interaction of the

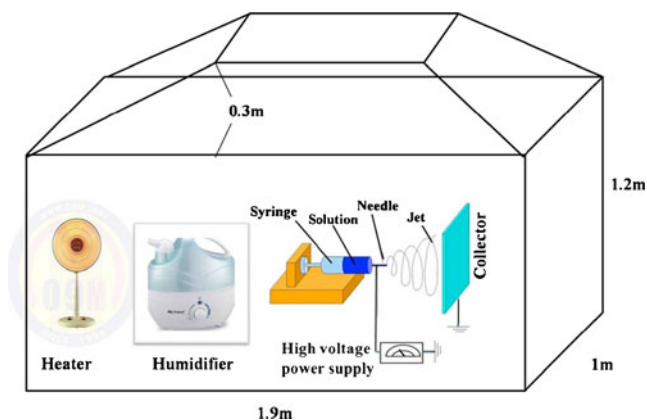


Fig. 1 Schematic of the electrospinning chamber used in this study

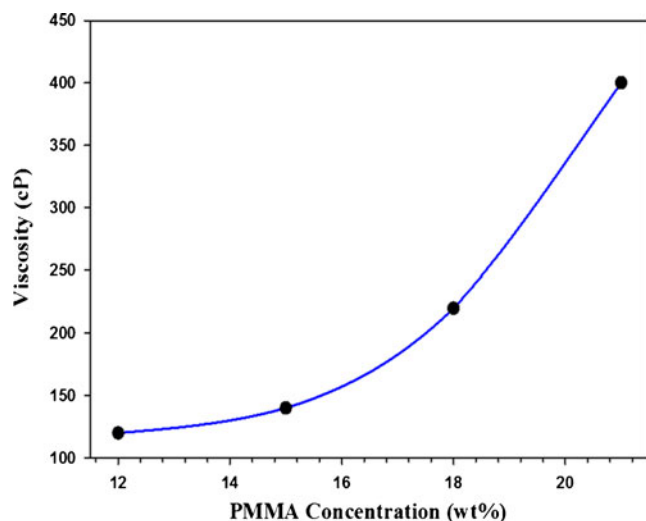


Fig. 2 Relationship between the PMMA concentration in a mixed solvent of dichloromethane and dimethylformamide (8:2) and the solution viscosity

charges when the high voltage is applied. Due to the stretching of the PMMA polymer solution, fiber formation starts from the Taylor cone, which is formed at the tip of the needle, and the fibers are collected at the rotating drum. During the process of fiber formation, the more volatile solvent (DCM) starts to evaporate earlier than the less volatile solvent (DMF). With the evaporation of the DCM (while the fibers are flying towards the collector; Fig. 4a), the temperature inside the hood decreases due to the cooling effect caused by the evaporation of DCM. This phenomenon can also be observed during perspiration. The decrease in the temperature in the hood leads to the condensation of water vapor, as also observed during cloudy conditions or in fog. Due to condensation, the water vapor present in the hood forms water droplets that become enlarge and settle on the fibers. Since water is miscible with

DMF, they mix well with each other on both the inner and outer surfaces of the fibers. Complete evaporation of the solvents and the water from the fibers results in the formation of porous electrospun PMMA fibers.

Effect of the humidity level on the formation of porous fibers

Figure 5 shows the effect of varying the humidity from 15 to 70 % on the degree of porosity while keeping all other electrospinning parameters constant (DCM/DMF, 8/2; PMMA concentration, 21 wt%; needle to collector distance, 17 cm; applied voltage, 18 kV, and flow rate, 2.0 mL/h). At a humidity level of <25 %, the fibers were smooth and no pores formed (Fig. 5a). When the humidity was increased from 26 % to 40 %, there were some morphological changes in the fibers due to the formation of pores. The pores were uniform but relatively small in number and were randomly distributed (Fig. 5b). As the humidity was further increased from 40 to 55 %, the size of the pores remained the same but the numbers of pores increased and were randomly distributed (Fig. 5c). The most remarkable morphological change was noticed when the electrospinning was carried out at humidities ranging from 56 to 70%; small spaces between two adjacent pores in the fibers were observed. Moreover, the number of pores was also high (Fig. 5d) compared to the other samples (Fig. 5b and c). From Fig. 5d, it is evident that as the humidity was increased from 25 to 70 %, the number of pores increased and they were uniformly distributed, which is in agreement with the formation of porous fibers under controlled humidity, as discussed above. Figures 5e and f show cross-sectional images of the nonporous and porous electrospun PMMA fibers obtained at 25 % (Fig. 5e)

Fig. 3a–d SEM images of the electrospun PMMA fibers obtained at polymer concentrations of **a** 12, **b** 15, **c** 18, and **d** 21 wt% and at a humidity of 25 %

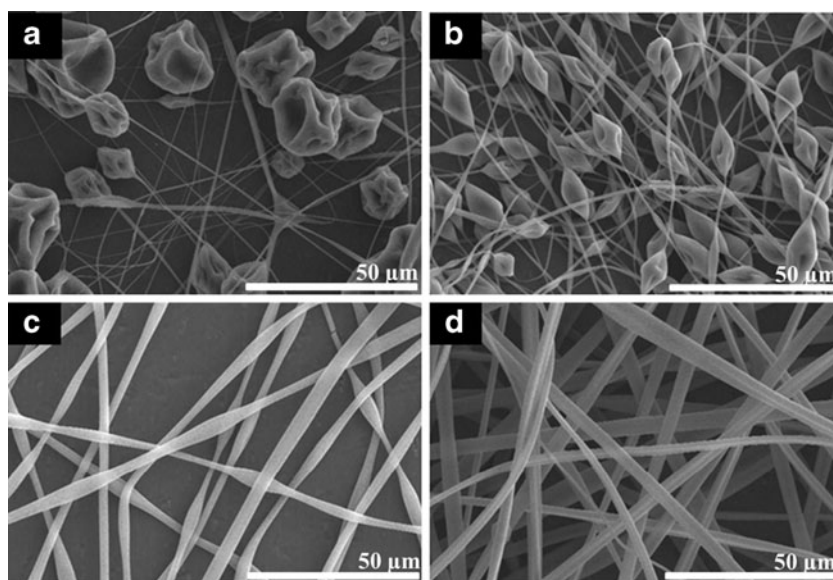
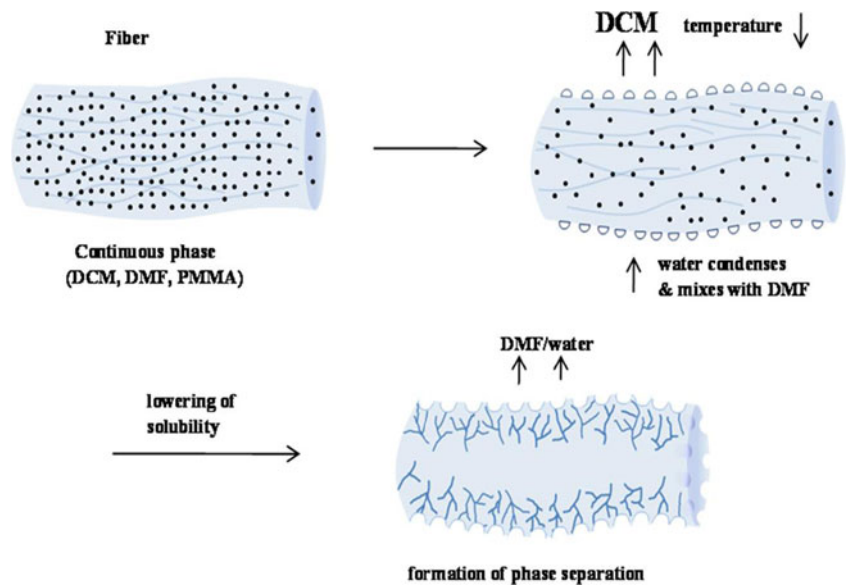


Fig. 4 A schematic diagram showing the formation of pores during electrospinning

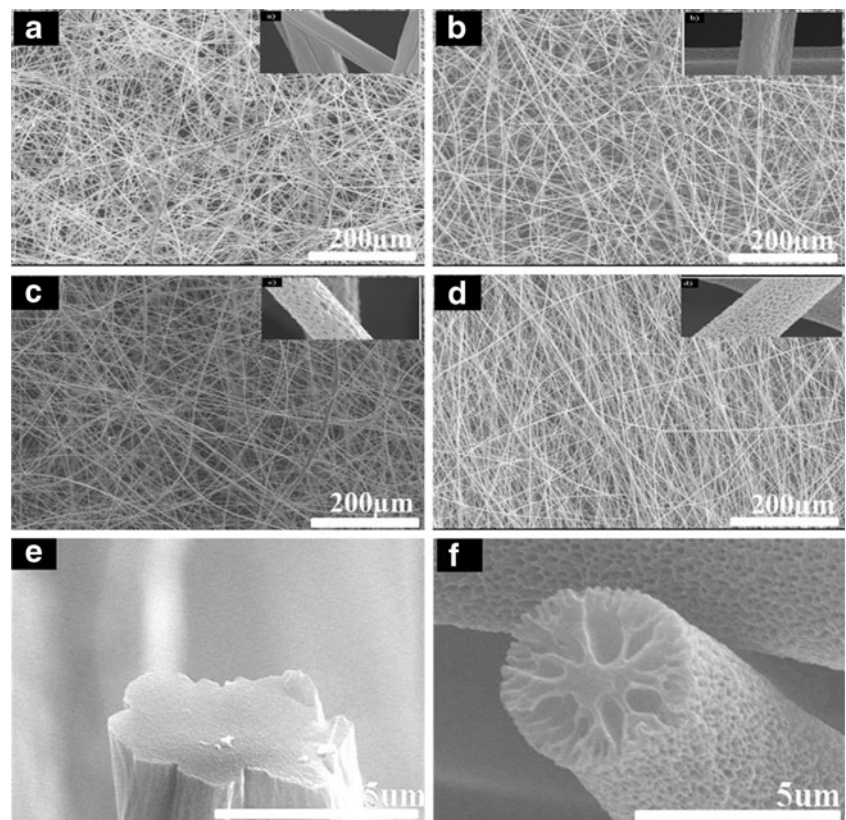


and 70 % (Fig. 5f) humidity, respectively. The cross-sectional morphology further supports the above statement that the maximum number of pores formed when the humidity was between 56 and 70 %. At this humidity level (56–70 %), pores on both the outer and inner surfaces (Fig. 5d and f) were observed [33, 34]. The average pore size was around 35 Å, and the pore structure was similar to that of activated carbon [35, 36], with a huge surface area of 139.0 m²/g.

Surface area and porosity

Figures 6a and b show the mean interfiber pore sizes of the porous and nonporous fiber membranes, respectively. The interfiber pore size of the porous fiber membrane (35 Å) was slightly smaller than that of the nonporous fiber membrane (38 Å). However, the surface area of the porous fiber membrane (139 m²/g) was significantly larger than that of the nonporous fiber membrane (20.4 m²/g; Table 1). The

Fig. 5a–f FE-SEM images of the electrospun PMMA fibers obtained under different humidity conditions: **a** 15–25 %, **b** 26–40 %, **c** 41–55 %, **d** 56–70 %. **e** Cross-section of a nonporous fiber, and **f** cross-section of a porous fiber



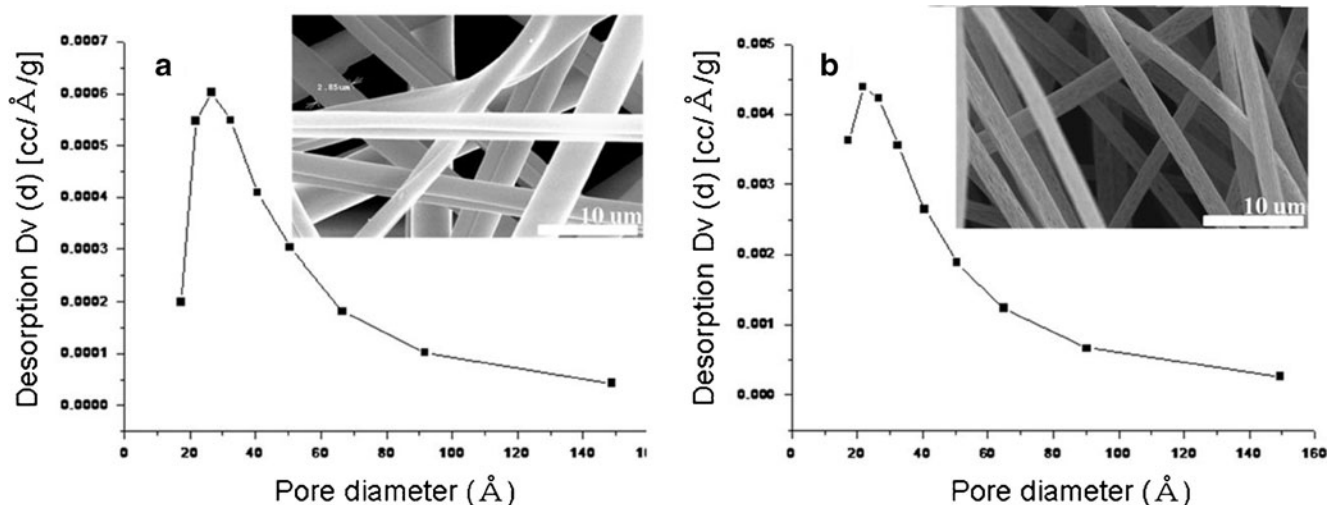


Fig. 6a–b The interfiber pore diameters for **a** the nonporous PMMA fiber membrane and **b** the porous fiber membrane

increase in the surface area of the porous fiber membrane may be due to the formation of pores on the outer as well as the inner walls of the PMMA fibers (Fig. 6a and b) [36].

Adsorption of iodine and phenol

The amounts of phenol and iodine adsorbed from synthetic water waste by nonporous and porous PMMA fiber membranes are presented in Table 1. The amount of iodine adsorbed by the porous PMMA fiber membrane prepared at 70 % humidity was significantly higher (203 mg/g) than that adsorbed by the nonporous PMMA fiber membrane prepared at 25 % humidity (117 mg/g). The increase in the adsorption capability of the porous electrospun PMMA fiber membrane can be attributed to its large surface area ($139 \text{ m}^2/\text{g}$) as well as to its inter- and intrafiber porosity [36]. Its large surface area attracts stray adsorbate molecules, while the small interfiber pore size entraps them in the second phase through capillary action. A similar trend for adsorption was observed for the phenol: the adsorption capacity of the porous electrospun PMMA fiber membrane (3.7 mg/g) was higher than that of the nonporous electrospun PMMA fibers membrane (1.8 mg/g). Phenol adsorption was low compared to iodine. This may be due to the decreased entrapping of phenol molecules by the small-sized pores. The above results confirm that the porous electrospun PMMA fiber membrane has enhanced adsorption capabilities compared to the nonporous electrospun PMMA fiber membrane.

Conclusion

Nonporous and porous electrospun PMMA fiber membranes were prepared by controlling the humidity during the electrospinning of a PMMA polymer solution. At a humidity of <25 % and when the other spinning parameters were kept constant (voltage, 18 kV; distance of the tip to the collector, 17 cm; polymer concentration, 21 wt%; flow rate, 2.0 mL/h), bead-free, smooth fibers were obtained. However, the pore density of the PMMA fibers increased as the humidity increased from 25 % to 70 %. The porous PMMA fiber membrane obtained at 70 % humidity was highly porous, had a large surface area ($139 \text{ m}^2/\text{g}$), and showed no change in average diameter. The porous PMMA fibers exhibited enhanced adsorption capacities for iodine (203 mg/g) and phenol (3.7 mg/g) compared to the nonporous PMMA fibers (adsorption capacity for iodine 117 mg/g and phenol 1.8 mg/g). The availability of the raw materials used, the simplicity of the method used to prepare the porous electrospun PMMA fibers, and its excellent adsorption capability make PMMA fiber membrane a competitive material along with activated carbon for use in the removal of contaminants from water waste. This study provides a road map for viable future projects aiming at the production of porous electrospun PMMA fibers on a commercial scale for use as water filters that purify water by removing the contaminants present in it.

Table 1 Characteristics and adsorption capacities of the porous and nonporous PMMA fiber membranes

Sample	Surface area (m^2/g)	Pore diameter (\AA)	Adsorption	
			Phenol Q (mg/g)	Iodine Q (mg/g)
Nonporous PMMA fibers ^a	20.4	38	1.8 ± 0.1	117 ± 3
Porous PMMA fibers ^b	139.0	35	3.7 ± 0.1	203 ± 4

^aPrepared at 25 % humidity

^bPrepared at 70 % humidity

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