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TITANIA NANOPARTICLES DOPED ELECTROSPUN MEMBRANES

Electrospun membranes exhibit very promising properties, such as high surface area, high surface area-to-pore volume ratio, high pore interconnectivity, and uniform pore distribution. Nanoparticles are a promising alternative for improving the properties of the electrospun membranes. Titania nanoparticles, which are stable, resistant, and non-toxic, have various applications including water treatment, sensors, food additive and cosmetics. Due to the high hydrophilicity of titania nanoparticles, membrane fouling is reduced in titania nanoparticles doped membranes. Titania nanoparticle doped polyacrylonitrile (PAN) nanocomposite electrospun membranes were prepared by electrospinning method in this work. Compared to bare PAN electrospun membranes 0.05% titania nanoparticles doped electrospun membranes have thinner nanofibers, higher hydrophilicity and almost 2 times lower bovine serum albumin adsorption, which shows lower fouling tendency.

Keywords: Electrospinning; titania nanoparticles; polyacrylonitrile; electrospun membranes; fouling

1. Introduction

One dimensional nanocomposite fibers are used in sensors, membrane filtration, biomedical applications, energy production, etc. due to their improved electrical, optical and chemical properties [1-7]. There are various methods to produce nanofibers, including drawing, templates, phase separation, self-assembly, and electrospinning [8]. Among them, electrospinning is the most practical, economical, and fast [9,10]. Electrospinning has attracted attention since its discovery in 1934. Nanofibers prepared by electrospinning has many remarkable features such as small diameter (50 nm-10 mm), high aspect ratio (length-to-diameter ratio), large specific surface area (ratio of surface area to volume), diversity in composition, unique physicochemical properties, flexibility in chemical / physical surface functionalization [5,11,12]. Nanomaterial addition can enhance the properties of electrospun nanofibers like electrical conductivity, mechanical properties, antibacterial properties, etc. [13]. There are many studies about preparing nanomaterials doped electrospun nanofibers to be used in energy generation and storage, water treatment and environmental remediation, healthcare and biomedical engineering [14].

Electrospun membranes have very promising properties such as high surface area, a high surface area-to-pore volume ratio, high pore interconnectivity, and uniform pore distribution. Due to these properties, electrospun membranes are gaining a wide attention to be used in separation processes [15]. One limitation of the electrospun membranes is pore size [16] which ranges from 10 nm to 100 μm [17]. Membranes with smaller pore size cannot be produced by electrospinning. In addition, electrospun membranes might act as adsorbents with an interpenetrating porous structure [18]. There are many recent researches in functionalizing electrospun nanofibers to improve their applicability in different areas [19]. Nanoparticles are a promising alternative for improving the properties of the electrospun nanofibers. Properties like uniform pore size, narrow pore size distribution, hydrophilicity, mechanical strength, and stability can be enhanced by nanoparticle addition in the nanofiber structure [19]. Even though nanoparticle leaching might be possible in nanoparticles doped polymeric materials, it can be prevented by chemical bonding with novel immobilizing strategies [20]. In addition, nanoparticles might possess higher risk of toxicity than the corresponding bulk. The potential hazards of the metal nanoparticles to humans are not fully elucidated yet [21].

Titania nanoparticles are stable, resistant, and non-toxic. Hence, they have various applications, including water treatment, sensors, food additive and cosmetics [22-24]. Due to the high hydrophilicity of titania nanoparticles, membrane fouling

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is reduced in titania nanoparticles doped membranes [25]. The objective of this work is to synthesize titania nanoparticles doped polyacrylonitrile (PAN) nanocomposite electrospun membranes by electrospinning with lower fouling tendency. Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) were employed for characterizing the nanocomposite electrospun membranes. The major obstacle to the application of membranes is fouling, which is mostly caused by adsorption of proteins [26] or protein-like substances [27]. Bovine serum albumin, mostly used macromolecule in membrane filtration tests [28], was chosen as a model protein in this study and bovine serum albumin adsorption of nanocomposite electrospun membranes was determined.

2. Materials and methods

Titania nanoparticles (with a diameter of less than 25 nm) and anhydrous N, N-dimethyl formamide (DMF, 99.8%) were purchased from Sigma (USA), and PAN (with a molecular weight of 150,000) from Polysciences Inc. (USA).

The dope solution for the nanofiber synthesis was prepared as follows: Initially, titania nanoparticles were ultrasonicated in DMF, then PAN was dissolved. Afterwards, the solution was ultrasonicated to remove air bubbles. All nanofibers were synthesized by using the electrospinning instrument (NE100, Inovenco Co. Ltd., Turkey) represented in Fig. 1.

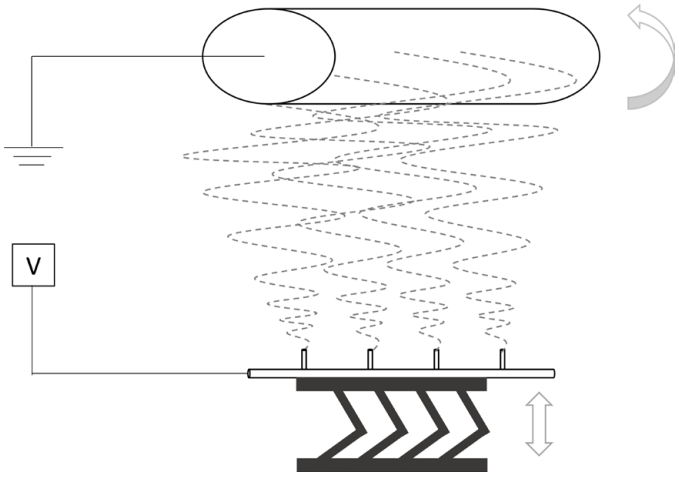

Fig. 1. Schematic representation of electrospinning instrument

Electric field was generated between the nozzle system and a rotating collection drum. There were 4 nozzles with an inner diameter of 700 μm each. The rotation speed of the collection drum was 350 rpm. A syringe pump was used for pumping the dope solution. Nanofibers were collected on a non-woven fabric. Initially, voltage applied, distance between the nozzle system and the collection drum, and the feed rate of the dope solutions were optimized for all solutions. Then these values (TABLE 1) were used for nanocomposite electrospun membrane synthesis.

TABLE 1

Electrospinning characteristics

Membrane Name	$nTiO_2$ Ratio (%)	Voltage (kV)	Feed Rate (mL/h)	Distance (cm)
P/T-0	0	35	6	16
P/T-0.05	0.05	34	12	16
P/T-0.10	0.10	34	12	16
P/T-0.20	0.20	34	10	16

A viscosimeter (Vibro, And, Japan) was used to measure the viscosities of the polymer solutions. SEM (Quanta FEG 250; FEI, USA) and FTIR (Spectrum Two, Perkin Elmer) were used to determine the surface morphologies and the structure of the nanocomposite electrospun membranes, respectively. Average fiber diameters were reported by averaging the diameters of the 20 nanofibers from each of 20 different SEM images for each membrane.

The structures of the electrospun membranes were examined by FTIR (Spectrum Two, PerkinElmer, USA), and their surface hydrophilicity was determined using a contact angle goniometer (Theta Lite, Attension, Sweden). It is calculated by averaging at least seven contact angle values measured for each membrane.

For the adsorption tests, membranes were cut into small pieces and immersed into 1 g/L BSA solution, prepared using a 10 mM phosphate buffer solution at pH 7, at room temperature for 4 h. Afterwards, the coupons were ultrasonicated in DI water for 2 min. The amount of the adsorbed BSA was directly measured using a UV-vis spectrometer (UV-VIS Spectrophotometer Shimadzu, Japan) at 280 nm. Calibration curve of BSA at concentrations ranging from 0.020 g/L to 1.0 g/L was used for BSA quantification. The linear calibration equation of the data was $y = 0.0006x - 0.0068$ ($R^2 = 0.9998$). The average of at least two measurements was reported.

3. Results and discussion

Viscosities of the polymer solutions of the electrospun membranes are given in TABLE 2. As shown in the table titania nanoparticles addition increased the viscosity of the polymer solution. The increase in the viscosity in the polymer solution improved the dispersion of the nanoparticles in the polymer solution.

TABLE 2

Viscosities of the polymer solutions

Membrane Name	Viscosity (Pa.s)	Temperature (°C)
P/T-0	3.25	21.0
P/T-0.05	4.09	20.3
P/T-0.10	3.70	20.1
P/T-0.20	3.65	20.2

SEM images of the electrospun membranes are given in Fig. 2. SEM images show that no beads were formed in any of the

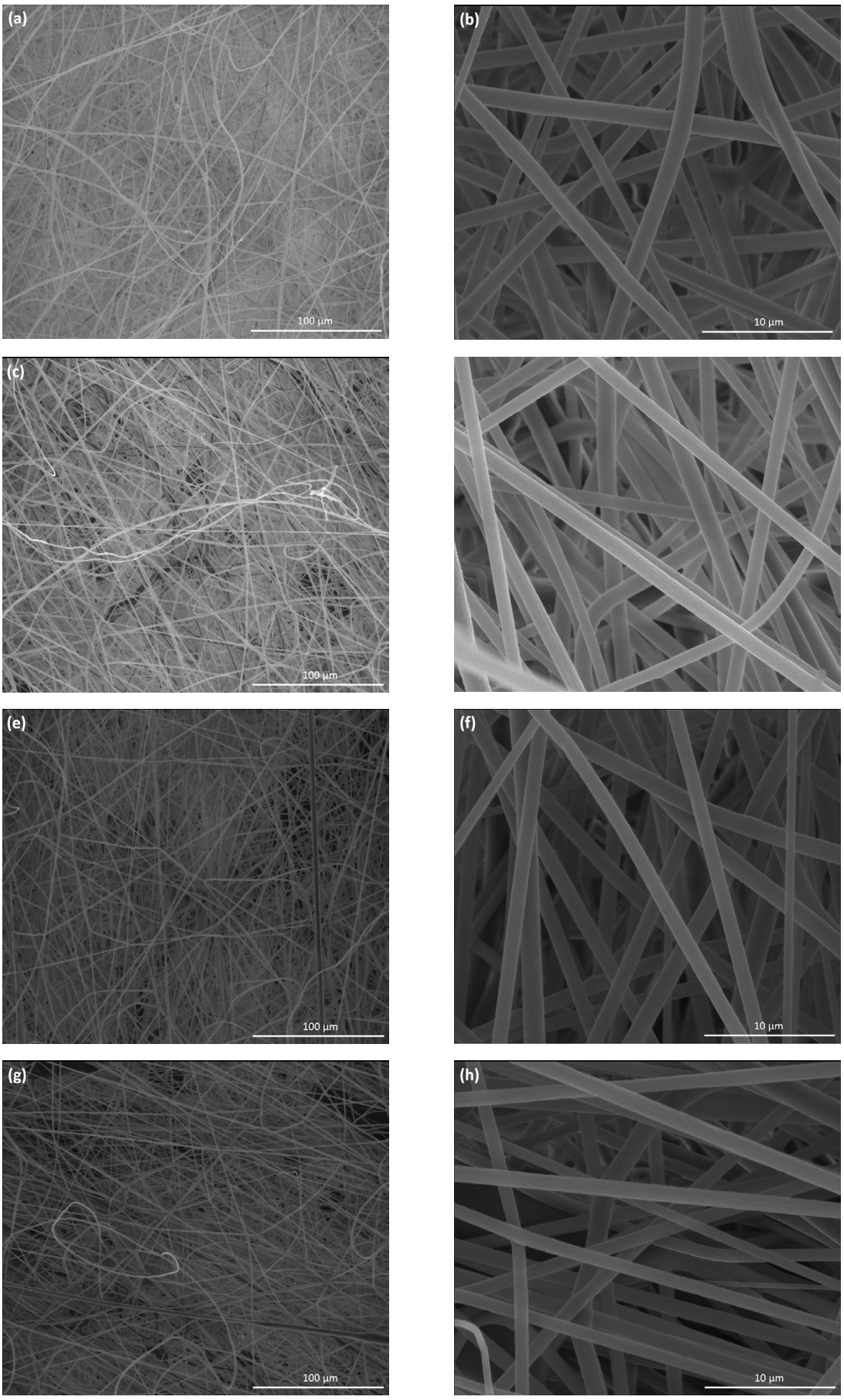

Fig. 2. SEM images of electrospun membranes at different magnifications; (a) P/T-0 at 1000× magnification, (b) P/T-0 at 10000× magnification, (c) P/T-0.05 at 1000× magnification, (d) P/T-0.05 at 10000× magnification, (e) P/T-0.1 at 1000× magnification, (f) P/T-0.1 at 10000× magnification, (g) P/T-0.2 at 1000× magnification, (h) P/T-0.2 at 10000× magnification

electrospun membranes. The balance between the electrostatic repulsion, surface tension, and viscoelastic forces determines the quality of the fibers in the electrospinning process. Increase in viscosity of the polymer solution results in suppression of the surface tension due to the electrostatic repulsion and viscoelastic forces. Bead free and smooth fibers were formed by the dominating viscoelastic forces [9].

The average of the nanofiber diameters determined is shown in Fig. 3. Reported nanofiber diameters of the electrospun membranes are the average of the 20 nanofibers from 20 different SEM images for each membrane. Addition of 0.05% titania nanoparticles in the polymer solution reduced the nanofiber diameter. However, further increase in the titania nanoparticles amount resulted in increased nanofiber diameter.

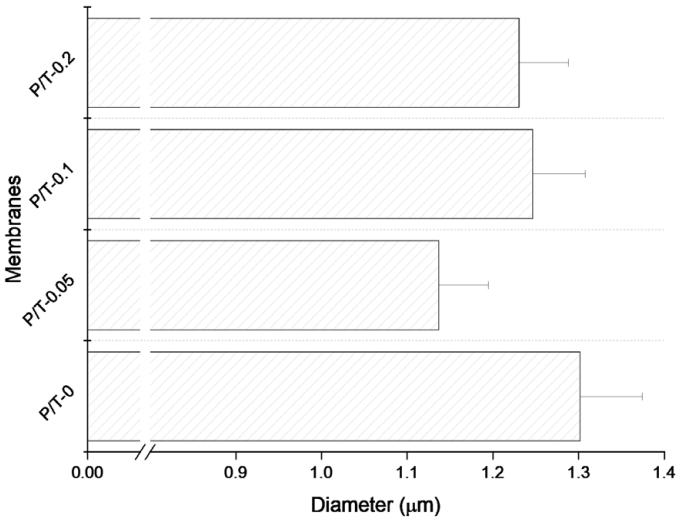

Fig. 3. Fiber thicknesses of the electrospun membranes

FTIR spectra recorded in the spectral range of 4000-400 cm^{-1} of the electrospun membranes are given in Fig. 4. The peak around 2250 cm^{-1} corresponds to C≡N stretching vibration [29], around 1260 cm^{-1} corresponds to weak ether peak (C–O–C) of PAN [30]. Compared to the bare PAN electrospun membrane, (P/T-0) two new peaks were observed in titania nanoparticles doped PAN electrospun membranes (P/T-0.05, P/T-0.1, P/T-0.2) around 874 cm^{-1} and 972 cm^{-1} corresponding to Ti–O–Ti vibrations [29,31], which confirmed the presence of titania nanoparticles into the nanofiber matrix.

Hydrophilicity of the membranes was evaluated by determining contact angles (Fig. 5). Lower contact angle shows higher hydrophilicity and higher contact angle shows higher hydrophobicity. Addition of titania nanoparticles increased the hydrophilicity of the electrospun membranes. Moreover, increasing the titania nanoparticles amount in the fiber composition increased the hydrophilicity of the electrospun membranes. The increased hydrophilicity of the membrane can not only increase the water permeability but also reduce the fouling by reducing protein adsorption [32].

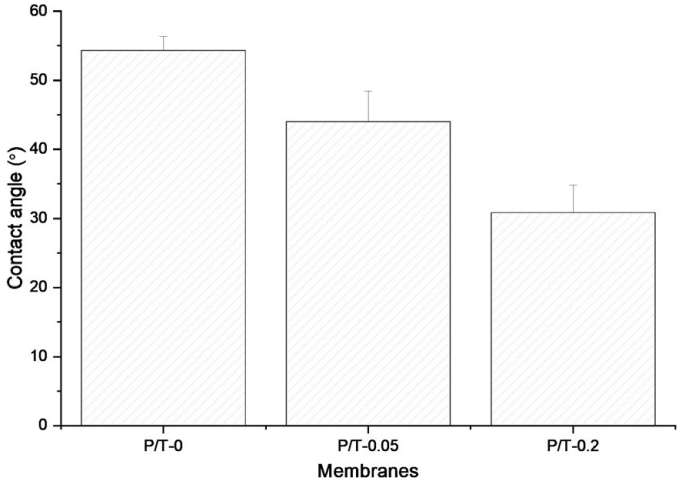

Fig. 5. Contact angles of the electrospun membranes

BSA was chosen as a model protein for determining the adsorption resistances of the electrospun membranes. BSA adsorption on electrospun membranes is shown in Fig. 6. Ad-

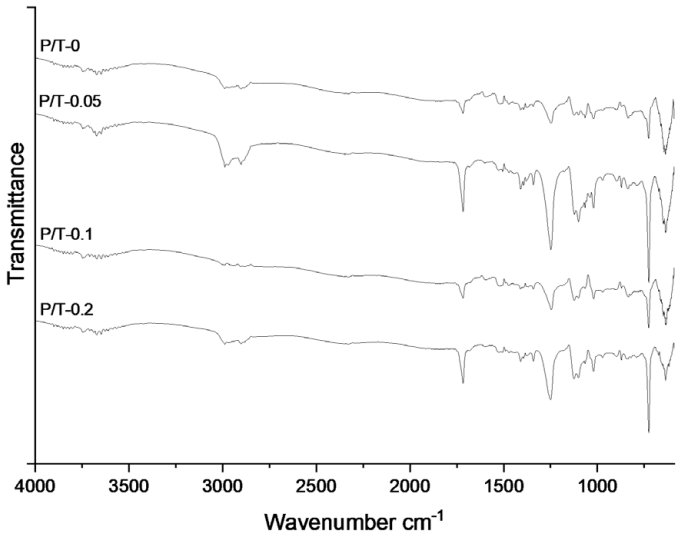

Fig. 4. FTIR spectra of electrospun membranes

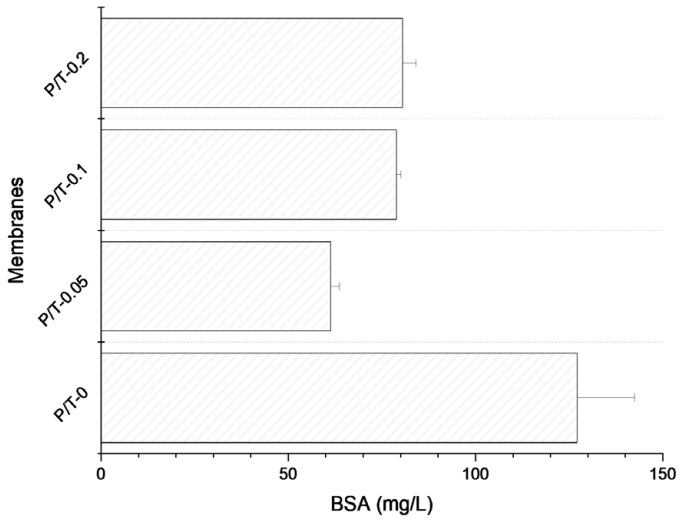

Fig. 6. BSA adsorption on electrospun membranes

dition of titania nanoparticles in the structure of the nanofibers of the electrospun membranes reduced the BSA adsorption almost 2 times compared to the bare membranes at neutral pH. This indicates the potential usage of titania nanoparticles for alleviating the fouling. Al-Ani et al. [33] showed a prolonged membrane lifetime during long-term applications of titania nanoparticles doped membranes. Similarly, titania nanoparticles doped electrospun membranes prepared in this study might be used for a long time applications with reduced fouling.

4. Conclusions

The preparation and fouling behavior of titania nanoparticles doped PAN electrospun membranes were investigated, with several conclusions subsequently drawn. These conclusions include the following.

- Titania nanoparticles doped PAN electrospun membranes were successfully synthesized by the electrospinning method. New peak formations in FTIR analysis confirmed that titania nanoparticles successfully blended into the nanofiber structure.
- Nanofibers of the titania nanoparticles doped PAN electrospun membranes are thinner than the bare membranes.
- Titania nanoparticles doped PAN electrospun membranes are more hydrophilic than the bare membranes.
- BSA adsorption on titania nanoparticles doped PAN electrospun membranes are almost 2 times lower than the bare membranes, indicating potential usage of titania nanoparticles for alleviating the fouling.
- Titania nanoparticles doped PAN electrospun membranes can be an alternative to surface water filtration with their reduced adsorptive fouling tendency. However, additional studies, including filtration tests with complex water matrix and composition of the feed water effects on the fouling behavior of the membranes, will need to be performed in the future.

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REFERENCES

[1] L. Wang, Y. Yu, P.C. Chen, D.W. Zhang, C.H. Chen, Electrospinning synthesis of C/Fe3O4 composite nanofibers and their application for high performance lithium-ion batteries. J. Power Sources **183**, 717-723 (2008).

[2] J.J. Wang, L.X. Dai, Q. Gao, P.F. Wu, X.B. Wang, Electrospun nanofibers of polyferrocenylsilanes with different substituents at silicon. Eur. Polym. J. **44**, 602-607 (2008).

[3] J. Wu, J.L. Coffer, Strongly emissive erbium-doped tin oxide nanofibers derived from sol gel/electrospinning methods. J. Phys. Chem. C **111**, 16088-16091 (2007).

[4] G.C.R. Jian H. Yu, Electrospinning, in: Encyclopedia of Polymer Science and Technology. John Wiley & Sons, Inc, (2007).

[5] D. Li, Y.N. Xia, Electrospinning of nanofibers: Reinventing the wheel? Adv. Mater. **16**, 1151-1170 (2004).

[6] S. Agarwal, J.H. Wendorff, A. Greiner, Use of electrospinning technique for biomedical applications. Polymer **49**, 5603-5621 (2008).

[7] W.X. Zhang, Y.Z. Wang, C.F. Sun, Characterization on oxidative stabilization of polyacrylonitrile nanofibers prepared by electrospinning. J. Polym. Res. **14**, 467-474 (2007).

[8] S. Ramakrishna, An introduction to electrospinning and nanofibers. World Scientific, Hackensack, NJ, 2005.

[9] D. Zhang, A.B. Karki, D. Rutman, D.R. Young, A. Wang, D. Cocke, T.H. Ho, Z.H. Guo, Electrospun polyacrylonitrile nanocomposite fibers reinforced with Fe3O4 nanoparticles: Fabrication and property analysis. Polymer **50**, 4189-4198 (2009).

[10] L. Ghadiri, A. Bozorg, A. Shakeri, Electrospun polyamide thin film composite forward osmosis membrane: Influencing factors affecting structural parameter. Membr. Water. Treat. **10**, 417-429 (2019).

[11] R. Chen, S.Z. Zhao, G.Y. Han, J.H. Dong, Fabrication of the silver/polypyrrole/polyacrylonitrile composite nanofibrous mats. Mater. Lett. **2**, 4031-4034 (2008).

[12] M.M. Demir, I. Yilgor, E. Yilgor, B. Erman, Electrospinning of polyurethane fibers. Polymer **43**, 3303-3309 (2002).

[13] F. Fadil, N.D.N. Affandi, M.I. Misnon, N.N. Bonnia, A.M. Harun, M.K. Alam, Review on Electrospun Nanofiber-Applied Products. Polymers-Basel, **13** (2021).

[14] Kenry, C.T. Lim, Nanofiber technology: current status and emerging developments. Prog. Polym. Sci. **70**, 1-17 (2017).

[15] F.E. Ahmed, B.S. Lalia, R. Hashaikeh, A review on electrospinning for membrane fabrication: Challenges and applications, Desalination **356**, 15-30 (2015).

[16] A. Nadaf, A. Gupta, N. Hasan, Fauziya, S. Ahmad, P. Kesharwani, F.J. Ahmad, Recent update on electrospinning and electrospun nanofibers: current trends and their applications. Rsc. Adv. **12**, 23808-23828 (2022).

[17] S. Aghayari, The Porosity of Nanofiber Layers. In: M.M.M. Elnashar, S. Karakuş (Eds.) Biocomposites – Recent Advances, (2023).

[18] N.A.A.M. Amin, M.A. Mokhter, N. Salamun, M.F. Mohamad, W.M.A.W. Mahmood, Anti-fouling electrospun organic and inorganic nanofiber membranes for wastewater treatment. South African Journal of Chemical Engineering **44**, 302-317 (2023).

[19] S.S. Ray, S.S. Chen, N.C. Nguyen, H.T. Nguyen, Electrospinning: A Versatile Fabrication Technique for Nanofibrous Membranes for Use in Desalination. Micro & Nano Technol. 247-273 (2019).

[20] S.H. Park, Y.S. Ko, S.J. Park, J.S. Lee, J. Cho, K.Y. Baek, I.T. Kim, K. Woo, J.H. Lee, Immobilization of silver nanoparticle-decorated

silica particles on polyamide thin film composite membranes for antibacterial properties. J. Membrane Sci. **499**, 80-91 (2016).

[21] N.D. Zhang, G.Y. Xiong, Z.J. Liu, Toxicity of metal-based nanoparticles: Challenges in the nano era. Front Bioeng Biotech 10 (2022).

[22] F. Mehrpouya, H. Tavanai, M. Morshed, M. Ghiaci, The formation of titanium dioxide crystallite nanoparticles during activation of PAN nanofibers containing titanium isopropoxide. J. Nanopart Res. **14** (2012).

[23] M. Alzamani, A. Shokuhfar, E. Eghdam, S. Mastali, Influence of catalyst on structural and morphological properties of TiO2 nanostructured films prepared by sol-gel on glass. Prog. Nat. Sci.-Mater. **23**, 77-84 (2013).

[24] F. Mohamadi, N. Parvin, Preparation and characterization of TiO2 membrane on porous 316 L stainless steel substrate with high mechanical strength. Membr. Water Treat. **6**, 251-262 (2015).

[25] Y.C. Su, C.P. Huang, J.R. Pan, W.P. Hsieh, M.C. Chu, Fouling Mitigation by TiO2 Composite Membrane in Membrane Bioreactors. J. Environ. Eng.-Asce. **138**, 344-350 (2012).

[26] T.W. Xu, R.Q. Fu, L.F. Yan, A new insight into the adsorption of bovine serum albumin onto porous polyethylene membrane by zeta potential measurements, FTIR analyses, and AFM observations. J. Colloid. Interf. Sci. **262**, 342-350 (2003).

[27] A.R. Shaikh, H. Karkhanechi, T. Yoshioka, H. Matsuyama, H. Takaba, D.M. Wang, Adsorption of Bovine Serum Albumin on Poly(vinylidene fluoride) Surfaces in the Presence of Ions: A Molecular Dynamics Simulation. J. Phys. Chem. B **122**, 1919-1928 (2018).

[28] P. Le-Clech, Protein Fouling Mechanisms. In: E. Drioli, L. Giorno (Eds.) Encyclopedia of Membranes, Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 1-2 (2015).

[29] E. Bahmani, H.S. Zonouzi, S. Koushkbaghi, F.K. Hafshejani, A.F. Chimeh, M. Irani, Electrospun polyacrylonitrile/cellulose acetate/MIL-125/TiO(2)composite nanofibers as an efficient photocatalyst and anticancer drug delivery system. Cellulose **27** 10029-10045 (2020).

[30] S. Hartati, A. Zulfi, P.Y.D. Maulida, A. Yudhowijoyo, M. Dioktyanto, K.E. Saputro, A. Noviyanto, N.T. Rochman, Synthesis of Electrospun PAN/TiO2/Ag Nanofibers Membrane As Potential Air Filtration Media with Photocatalytic Activity. Acs Omega **7**, 10516-10525 (2022).

[31] A.G. Koozekonan, M.R.M. Esmaeilpour, S. Kalantary, A. Karimi, K. Azam, V.A. Moshiran, F. Golbabaei, Fabrication and characterization of PAN/CNT, PAN/TiO2, and PAN/CNT/TiO(2)nanofibers for UV protection properties. J. Text. I **112**, 946-954 (2021).

[32] E. Celik, L. Liu, H. Choi, Protein fouling behavior of carbon nanotube/polyethersulfone composite membranes during water filtration. Water Research **45**, 5287-5294 (2011).

[33] F.H. Al-Ani, Q.F. Alsalhy, R.S. Raheem, K.T. Rashid, A. Figoli, Experimental Investigation of the Effect of Implanting TiO2-NPs on PVC for Long-Term UF Membrane Performance to Treat Refinery Wastewater. Membranes-Basel, **10** (2020).