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ORIGINAL PAPER

Influence of Titanium Dioxide Particles on the Filtration of 1,4-Dioxane and Antibacterial Properties of Electrospun Cellulose Acetate and Polyvinylidene Fluoride Nanofibrous Membranes

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Abstract

This article reports the fabrication, characterization, and evaluation of electrospun nanofibrous membranes consisting of poly (vinylidene fluoride) (PVDF) and cellulose acetate (CA) infused with varying concentrations of titanium dioxide (1 wt%, 3 wt%, 5 wt% and 7 wt%) on the removal of toxic organic contaminant 1,4-dioxane. The formation of nanofibrous membranes and the present distribution of titanium dioxide particles were ascertained using scanning electron microscopy (SEM). The PVDF/CA electrospun membranes were assessed for intermolecular interactions using Fourier transform infrared spectroscopy (FTIR) and antibacterial property. The membranes were tested for suitability in the filtration of 1,4-dioxane ($C_4H_8O_2$) through the Buchner filtration test. It could be seen that the filtration efficiency of the membranes improved up to 55% upon the addition of TiO_2. This revealed that the filtration efficiency of the membranes enhanced by increasing the contents of TiO_2. Furthermore, the membranes with TiO_2 also exhibited better antibacterial activity against the pathogens viz., *Escherichia coli*, *Pseudomonas aeruginosa Bacillus licheniformis*, and *Staphyllococcus aureus*.

Keywords Polymer membranes · Poly(vinylidene fluoride) · Cellulose acetate (CA) · Titanium dioxide (TiO_2) · 1,4-dioxane

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Introduction

There are a mounting demand and scarcity of clean water due to rapid urbanization, an increase in population, and disruptive climate change all around the globe [1]. A World Health Organization (WHO) report says that nearly 2 in 10 people around the globe do not have access to harmless drinking water. Because of unhealthy water and hygiene conditions, around 4000 children die every day [2]. The ground and surface water are getting more vulnerable day by day due to the contaminant of toxic chemicals from industries. 1,4-Dioxane, a heterocyclic ether, is among toxic organic contaminants of concern that has been released from various industries. 1,4-Dioxane has been majorly utilized as a stabilizer for chlorinated solvents, applied for degreasing purposes. It was also found as an ethoxylated by-product detected in wastewater from chemical, textile, and personal care product industries [3]. Intensive use and improper disposal of wastes from these industries are the major causes of the contamination of the compound in the environments. Once released, 1,4-dioxane can widespread in surface water or groundwater since the molecule of 1,4-dioxane is stable, high-water soluble, and resistant to adsorption by soil particles. 1,4-Dioxane is a public and ecological health concern due to its toxic and carcinogenic effects. 1,4-Dioxane can affect the liver and kidney [4]. Moreover, it is listed in Class B2 carcinogen based on classification by the International Agency for Research on Cancer (IARC) [5]. To prevent the adverse effect due to the exposure of 1,4-dioxane, effective remedial technology must be applied to remove 1,4-dioxane. While standard water treatment technologies such as air stripping and carbon adsorption were proven as an ineffective approach to remove 1,4-dioxane from water, bioremediation and advanced oxidation technology are among effective methods for 1,4-dioxane remediation [3, 6]. Biodegradation was proven as an effective method for remediation of 1,4-dioxane [7, 8]. However, its performance depends on many complicated factors, including the effects of co-contaminants, such as heavy metals, organic ligands, and chlorinated solvents. Many researches revealed the possibility of utilizing unconventional oxidation processes for redressal of 1,4-dioxane, but these technologies require intensive consumption of chemicals and energy and probably produce toxic by-products [9–11]. Alternatively, membrane technologies are considered as a viable physical technique for water treatment [2]. It is a promising technology for point-of-use and industrial applications with lower-chemical sludge effluent. However, filtration through low-pressure membranes such as microfiltration and ultrafiltration are ineffective to eliminate 1,4-dioxane from water [12]. Improvement of membrane property for low-pressure filtration is, thus, essential for better treatment of 1,4-dioxane. It is well known that the membranes possess lower chemical sludge effluent and excellent filtration efficiency [13].

Electrospinning is a fascinating and straightforward technique to fabricate nanofibrous membranes for filtration systems [14]. The main advantage of this technique is that high porous membranes can be fabricated, which enables their potential use in liquid filtration applications such as the membrane distillation [15]. Electrospun nanofibrous membranes are used in different applications in the treatment of wastewater, water remediation, and recovery of surfactants in industrial cleaning etc. [16]. Plastics have a significant role in the biomedical, pharmaceutical, and aid industries, and also in the high filtration industry. Most of the membranes to date are made of plastic materials since they offer a variety of structures and properties [17]. Synthetic polymers such as polysulfone (PS), polyethersulfone (PES), polyacrylonitrile (PAN), and polyurethane (PU) etc. are commonly used as membrane materials due to their high-water flux, solute rejection, and better functional properties such as mechanical and thermal stability [18]. Many researchers have attempted in the fabrication of electrospun membranes with different polymers and fillers or additives for potential use in filtration applications. Electrospun PAN membranes incorporated with polyamidoamine (PAMAM) as a dopant exhibited excellent filtration of anionic dyes such as direct red 80 and 23 with a high adsorption retention rate [19]. Similarly, electrospun PU membranes infused with in-situ generated silver nanoparticles showed better filtration of organic dyes and carcinogenic ions form the water [20]. In another research, electrospun cellulose acetate (CA)/nylon blends were found to be effective in aerosol filtration [21]. Homaeigohar et al. [22] studied the effect of heat treatment on the filtration performance on electrospun PES nanofibrous membranes and found that the heat treatment improved the mechanical strength without considerable change in fiber diameter and pore size; however, both treated and untreated membranes had the same filtration efficiency. PVDF is one of the most commonly used fluoropolymers in water filtration. It was found in a study that the anti-fouling ability of the PVDF membranes can be improved by the infusion of graphene oxide (GO) [1, 23, 24]. Similarly, in another study, it was found that the PVDF nanofiber membranes produced safe drinking water from saline water by air-gap membrane distillation [25]. Zhang et al. [26] examined the distillation efficiency of polytetrafluoroethylene (PTFE) and PVDF based membranes and reported that the PTFE membranes produced higher flux, salt rejection, and mass transfer coefficients compared to the PVDF membranes. Inclusion of chemically stable and high fouling resistant ceramic particles such as aluminum dioxide (Al_2O_3), titanium dioxide (TiO_2), zirconium oxide

(ZrO_2), and zinc oxide (ZnO) in the polymeric membranes can increase their effectiveness [27]. Among these, due to its multifunctional characteristics, titanium dioxide is used in applications such as ground and wastewater remediation. Furthermore, TiO_2 offers photocatalytic ability and super hydrophilicity, which decreases undesirable adsorption of organic and biological species to the membrane surface [28–30]. It was also described that TiO_2 plays an essential part in the degradation of 1,4-dioxane via dark catalytic oxidation and photooxidation [9, 31]. The blending of TiO_2 into the membrane is, thus, an alternative approach to improve membrane efficiency for the elimination of 1,4-dioxane in water.

This investigation aims in the fabrication of PVDF/CA electrospun nanofibrous membranes with varying loadings of TiO_2 (1wt%, 3wt%, 5wt% and 7wt%) and to study the influence of varying concentration of the TiO_2 particles on the efficiency of the PVDF/CA membranes on 1,4-dioxane removal.

Materials and Methods

Chemicals

Cellulose acetate (Mw: 264.23 g/mol), PVDF (Mw: 64.03 g/mol), acetone, hydrochloric acid, and dimethylacetamide (DMAc) were all acquired from Sigma Aldrich (Saint Louis, MO).

Membrane Preparation

The PVDF/CA nanofibrous membranes were fabricated by electrospinning a solution comprising of 17 wt% of PVDF and 3 wt% of CA with various loadings (1, 3, 5, and 7 wt%) of TiO_2. For comparison, PVDF/CA solution without TiO_2 particles was fabricated. Acetone and DMAc in the ratio of 2:3 was used as the solvents for making the PVDF/CA/TiO_2 solutions. The solution containing PVDF/CA and different concentrations of TiO_2 was stirred at 50 °C for around 2–3 h prior to electrospinning for the proper dispersion of TiO_2 particles. The blend solution was then electrospun at a rate of 1 mL/h with an applied voltage of 10 kV. The membranes were preserved in a desiccator before testing.

Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the PVDF/CA electrospun nanofibrous membranes with varying loadings of TiO_2 were recorded in a Shimadzu IR Tracer machine in reflection mode. The spectra were recorded in the 4000−500 cm^{-1} range with 32 scans and at a resolution of 4 cm^{-1}.

Scanning Electron Microscopy (SEM)

A scanning electron microscope (Quanta FEI 450) was used to inspect the distribution and the morphology of the TiO_2 particles in the electrospun PVDF/CA nanofibrous membranes. All the samples were sputter-coated before the SEM characterization.

Thermogravimetric Analysis (TGA)

The thermal stability of the PVDF/CA nanofibrous membranes with varying loadings of TiO_2 particles was measured using a TGA/DSC 3^+ thermogravimetric analyzer (Mettler Toledo). The test was conducted under a N_2 atmosphere in the temperature range of 30–700 °C with a heating rate of 10 °C/min.

Antibacterial Test

The antibacterial property of the membranes was evaluated by the disc diffusion procedure [32]. Gram-negative bacterial strains, including *E.coli* MTCC 1652 and *P.aeruginosa* MTCC 2453, and gram-positive bacterial strains, including *B.licheniformis* MTCC 73,537 *S.aureus* MTCC 96, were used in this study. Membranes with a 5 mm radius were kept in an inoculated medium (LB agar medium autoclaved at 120 °C for 15 LPS) and incubated at 37 °C for about 48 h. The antimicrobial property was found by the inhibition of the pathogens through the clear zones.

Filtration Test

The efficiency of the nanofibrous membrane on the removal of 1,4-dioxane was evaluated in this investigation. Four-layer membranes having a different concentration of titanium dioxide were cut into circles with a radius of 3.5 cm. The membranes were placed in the Buchner funnel and conditioned with Deionized water (DI) water before the filtration test. For evaluating the efficiency of the membrane, 50 mL of 100 mg/L 1,4-dioxane was loaded into the Buchner funnel and vacuum-suctioned at a flow rate of 0.15 L/min. The filtrate samples were collected and preserved with hydrochloric acid (pH less than 1) before the analysis of 1,4-dioxane.

Analysis of 1,4-Dioxane

A gas chromatograph was used to examine the concentration of 1,4-dioxane in the original samples and filtrates. Briefly, the aqueous samples (2 µL) were injected into an Agilent 6890 gas chromatograph equipped with FID and Agilent

J&W DB-5 column (30.0 m × 0.25 mm × 0.25 µm) (Agilent Technologies, Westlake Village, CA) under splitless mode. The temperatures of the inlet and detector were set at 220 and 250 °C, respectively. The oven was programed at 75 °C for 4 min. The resolution of the 1,4-dioxane peak was detected at a retaining time of 2.25 min. 1,4-Dioxane concentration in samples was estimated based on the calibration curve constructed from injecting 1,4-dioxane standards prepared by concentrating pure 1,4-dioxane in DI water.

Results and Discussion

FTIR Analysis

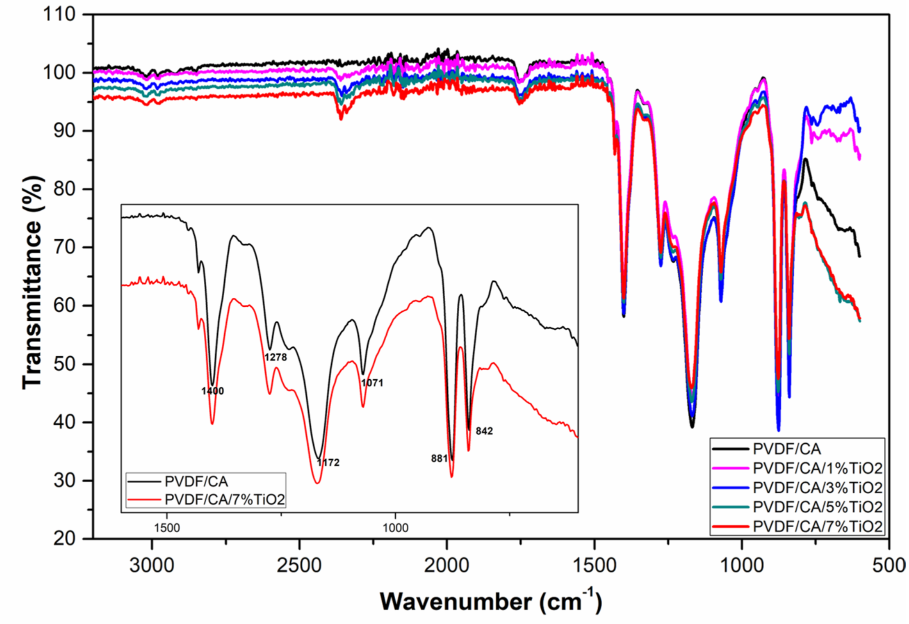
The IR spectra of the PVDF/CA nanofibrous membranes are infused with varying loadings of TiO_2 particles (1wt%, 3wt%, 5wt%, and 7wt%) is presented in Fig. 1. The small peak at 3021 cm^{-1} is related to the hydroxyl group stretching of CA [24]. The peaks at 881 and 842 cm^{-1} agree to the amorphous phase of PVDF, and the intense peak at 1172 cm^{-1} could be ascribed to the symmetrical stretching vibration of the crystalline phases [33, 34]. From this, it is clear that PVDF is in both semi-crystalline and amorphous phases. Further, the band at 1400 cm^{-1} was attributed to the deformation vibration stretching of CF_2 [35–37]. The absorption peak corresponding to 673 cm^{-1} could be allotted to the symmetric deformation vibration of the Ti–O–Ti group [33, 34]. It can be noted that this characteristic group is absent in the nanofibrous membranes without TiO_2 particles.

The peak at 1742 cm^{-1} matches to the symmetrical stretching of the carbonyl group [33]. Hence, it is evident that the bands of PVDF/CA and TiO_2 particles were identified from the IR spectra of the PVDF/CA/TiO_2 nanofibrous membranes. The enhancement in the interfacial interaction could be ascribed to the formation of hydrogen bonding by the C–F bond of PVDF and hydroxyl/carbonyl groups of CA.

Microscopic Analysis

The SEM micrographs of the PVDF/CA nanofibrous membranes with varying concentrations (1wt%, 3wt%, 5wt%, and 7wt%) of TiO_2 particles are represented in Fig. 2. Figure 2a illustrates the control membrane (PVDF/CA) without the infusion of TiO_2 particles. It is evident from the SEM micrographs that the electrospinning process was successfully able to produce electrospun PVDF/CA nanofibrous membranes with a homogeneous distribution of TiO_2 particles. This could be credited to the choice of appropriate solution constraints such as suitable solvents for the polymer, solution concentration, solution conductivity, and the processing conditions such as applied voltage, flow rate, needle diameter, distance from the needle to the collector, etc. [38, 39]. It can also be observed that there was an increase in the particle density along with the fiber as the TiO_2 concentration increased. The homogeneous distribution of TiO_2 particles could be ascribed to the ultrasonic process employed during the TiO_2 dispersion in acetone and DMAc. The distribution of the TiO_2 particles is highlighted in yellow circles in Fig. 2b–e.

Fig. 1 FTIR spectra of PVDF/CA nanofibrous membranes with varying loadings (1wt%, 3wt%, 5wt%, and 7 wt%) of TiO_2 particles



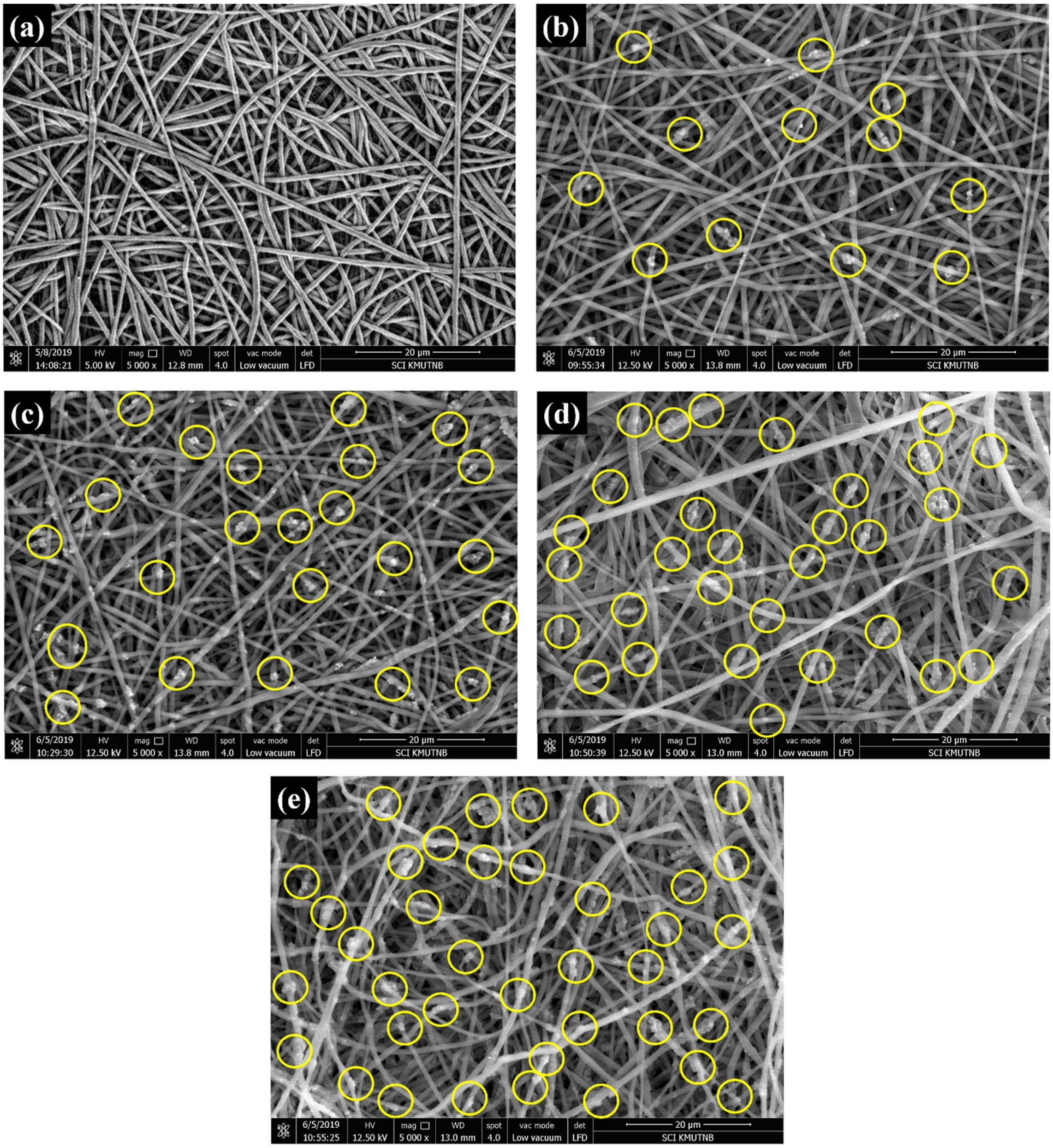


Fig. 2 SEM images of PVDF/CA nanofibrous membranes with varying loadings of TiO_2 particles **a** control; **b** 1wt% TiO_2; **c** 3wt% TiO_2; **d** 5wt% TiO_2 and **e** 7 wt% TiO_2. *Yellow circle indicated the TiO Particle distribution

Thermogravimetric Analysis

The primary and derivative thermograms of the TiO_2 filler and the PVDF/CA nanofibrous membranes with varying loadings of TiO_2 particles (1wt%, 3wt%, 5wt%, and 7wt%) are presented in Fig. 3. It could be witnessed for the thermograms of TiO_2 fillers that it is very stable throughout the temperature till 700 °C and did not get decomposed. The thermal degradation of the PVDF/CA nanofibrous membranes with varying loadings (1wt%, 3wt%, 5wt%, and 7 wt%) of TiO_2 particles took place in two stages. The first stage could be noticed at around 350 °C, which represents the thermal degradation of cellulose acetate chains [33]. The second step starts at around 410 °C, which signifies the carbonization of the degraded products to ash. The thermograms shown in Fig. 3 indicate that the addition of TiO_2 particles decreased the thermal stability of membranes where the onset temperatures reduced with the incorporation of TiO_2 particles. Further, the increase in the TiO_2 particles reduced the decomposition temperatures and increased the residual mass. Since the TiO_2 is very stable and no decomposition took place below 700 °C (as evidenced from the

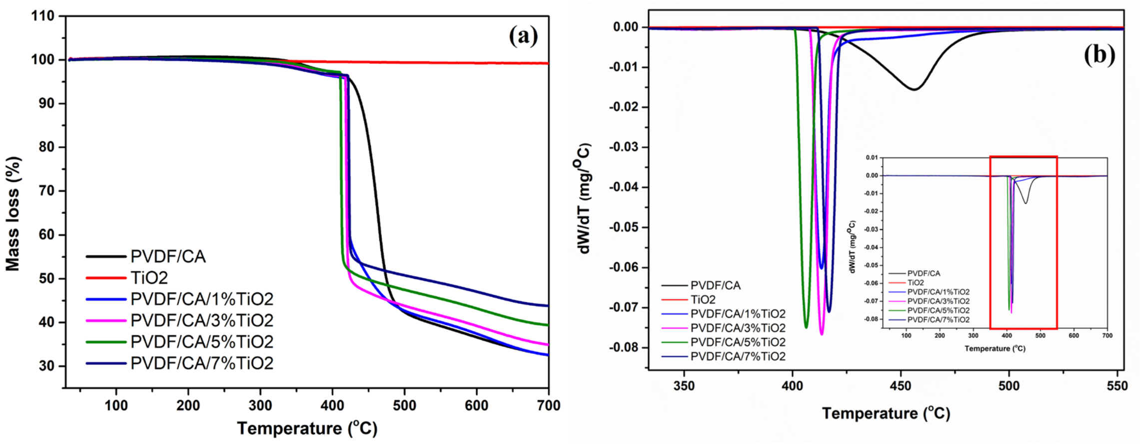


Fig. 3 Primary thermograms (**a**) and Derivative thermograms (**b**) of TiO_2 filler, PVDF/CA nanofibrous membranes with varying loadings (1wt%, 3wt%, 5wt%, and 7 wt%) of TiO_2 particles

TGA curves), the probable reason for the reduced thermal stability might be the presence of metal oxide-catalyzed oxidative decomposition pathways in the membranes, which is attributed to the catalytic effect of TiO_2 in the decomposition of PVDF and CA. The reason for higher residual mass could be attributed to the introduction of unsaturation in PVDF backbone, which is difficult to decompose completely, and further, the catalytic effect of TiO_2 might have also influenced this factor resulting in a higher amount of residual mass. Furthermore, the reaction between the chelating ligands of titanium ion and the production of fluoride during backbone homolysis in the PVDF decomposition could also result in new products that are hard to decompose [40, 41]. However, the nanofibrous membranes were stable until a temperature of around 350 °C.

Antimicrobial Properties

The antibacterial activity of the PVDF/CA nanofibrous membranes with varying loadings (1wt%, 3wt%, 5wt% and 7 wt%) of TiO_2 particles was found against gram-negative bacterium *E.coli* (MTCC 1652), and *P.aeruginosa* (MTCC 2453) and gram-positive bacterium *S.aureus* (MTCC 73537) and *B.licheniformis* (MTCC 96) by disc diffusion technique and their corresponding inhibition zones are presented in Fig. 4. It is to be noted that when the membranes are subjected to the filtration of foreign particles, chances of biofilm formation due to the adhesion of bacteria and their consequent growth on the membrane surface is very high. This can affect the efficiency of the membrane. Hence the efficiency of the membranes depends on the addition of antibacterial fillers. Figure 4 revealed that PVDF/CA nanofibrous membranes without TiO_2 particle had no inhibitory effect on gram-positive and gram-negative bacterial strains. However, the amendment of TiO_2 in the PVDF/CA nanofibrous membranes exhibited excellent antibacterial activity against all tested bacteria.

Furthermore, the diameters of the clear zone varied as the amount of TiO_2 in the membrane was increased. For instance, the inhibitory zone diameter against *E.coli* increased with an increase in TiO_2 particles in the membranes. Similarly, the zone diameters also increased for increased TiO_2 particles for other tested bacteria. The inhibition zone diameters for different membranes and the bacteria are presented in Table 1.

This is in agreement with the fact that TiO_2 possesses cell wall opacifying agents (bleaching), which leads to better antimicrobial properties. Further, its high surface area to volume ratio can attach to the bacterial cell membranes and penetrate the cytoplasm. The antibacterial effect of TiO_2 particles can be explained through different possible mechanisms. It may be attributed to the generation of reactive oxygen species during the photocatalytic process in the presence of either ultraviolet (UV) or visible light. The existence of reactive oxygen species, known as strong oxidizing agents, causes the oxidation of bacterial cells' components, which includes the intracellular protein, membrane, and DNA [42]. Further, the ability of TiO_2 particles to activate free hydroxyl radicals also extends its antibacterial effects. The mechanism of the antibacterial activity is illustrated in Fig. 5. Here, the mechanism of TiO_2 particles involving in the release of positively charged ions to the response medium linked to (negative charges) of the proteins on the cytoplasmic membrane led to the capture of the cell wall and increased permeability, which deforms the construction of the cellular components such as the DNA and cellular enzymes. The impairment on the cell wall leads to the agitation of different cellular progressions, which then leads to the leak of cytoplasm, lastly bacterial inactivation, and decease [43, 44]. This finding coincided with the previous study revealing the long-term

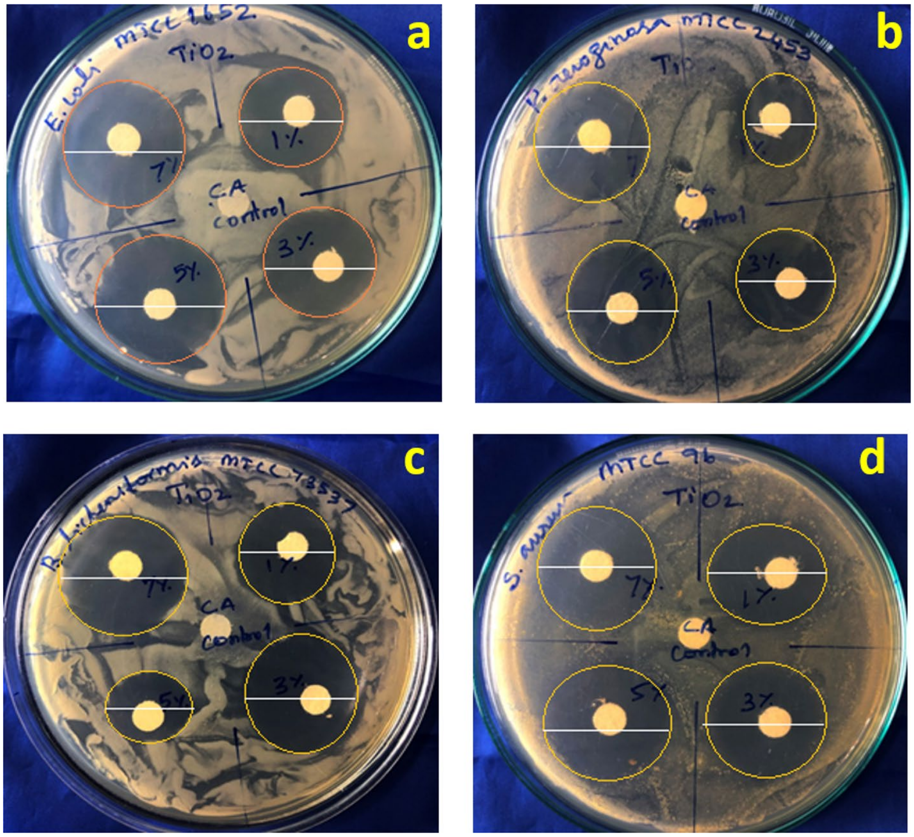


Fig. 4 Antibacterial inhibition zones of **a** *E.coli*; **b** *P.aeroginosa*; **c** *B.licheniformis* and **d** *S. aureus* of PVDF/CA nanofibrous membranes with varying loadings (1wt%, 3wt%, 5wt% and 7 wt%) of TiO_2 particles

Table 1 Antibacterial inhibition zone diameters of control and PVDF/CA nanofibrous membranes with varying loadings (1wt%, 3wt%, 5wt%, and 7 wt%) of TiO_2 particles

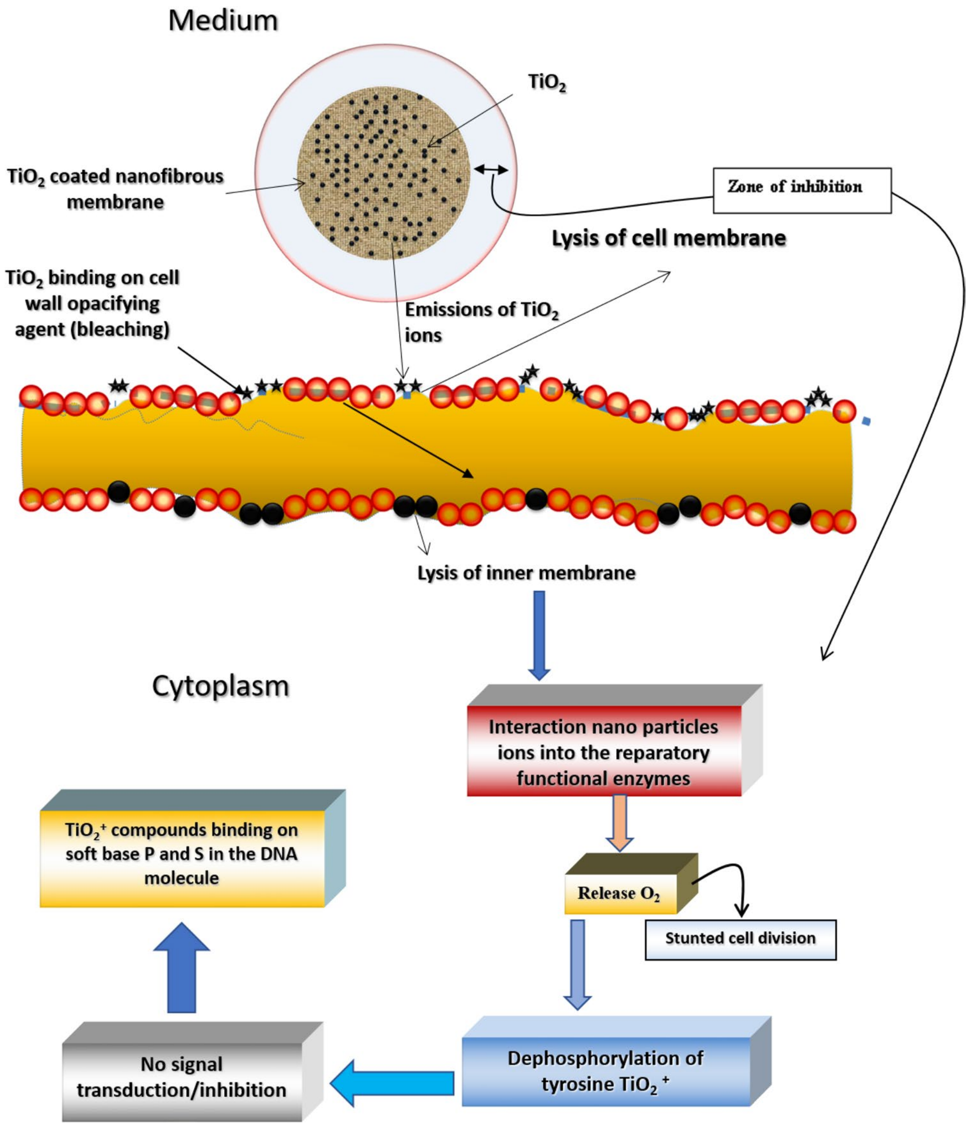
Control and TiO_2 infused membranes	Inhibition zone diameters (cm)			
	Gram-negative bacteria		Gram-positive bacteria	
	E.coli	*P.aeroginosa*	*B.licheniformis*	*S.aureus*
Control	No inhibition	No inhibition	No inhibition	No inhibition
1 wt% TiO_2	1.62	1.09	1.45	1.86
3 wt% TiO_2	1.71	1.57	1.71	1.88
5 wt% TiO_2	2.02	1.71	1.38	1.95
7 wt% TiO_2	1.83	1.83	1.95	1.78

antibacterial property of TiO_2 amended composite [45]. Besides the ability of the membrane to inactivate bacteria, the addition of TiO_2 into the membrane may reduce biofouling and operating costs for membrane cleaning infiltration systems

Filtration Test

Figure 6 demonstrates the efficacy of membranes with various amounts of titanium dioxide on the removal of 1,4-dioxane in water. While PVDF/CA nanofibrous membrane without the TiO_2 amendment was ineffective to remove 1,4-dioxane, the addition of TiO_2 could enhance the efficiency of the membrane on 1,4-dioxane elimination. The 1,4-Dioxane removal efficiency was highest (55.14 ± 1.04% removal) when 5% TiO_2 was added into the nanofibrous membrane. This suggests that the addition of TiO_2 into the membrane could improve removal efficiency. It is possible that TiO_2 in the membrane probably involved in 1,4-dioxane degradation through either advanced electrochemical oxidation or photooxidation [9, 31]. The addition of TiO_2 may be an applicable approach for improving low-pressure membranes (such as nano filter or ultrafilter), which were ineffective in rejecting 1,4-dioxane in water.

Fig. 5 Mechanism of antibacterial activity of PVDF/CA nanofibrous membranes with varying loadings (1wt%, 3wt%, 5wt%, and 7 wt%) of TiO_2 particles



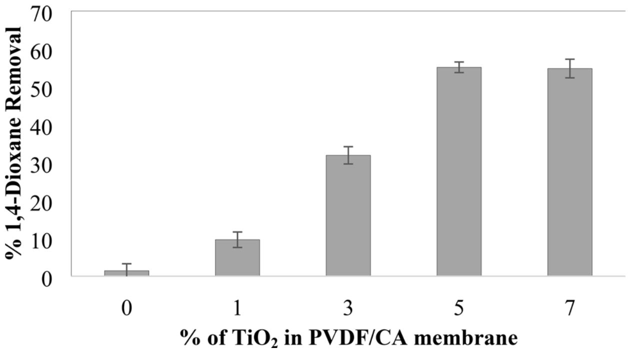


Fig. 6 1,4-Dioxane removal efficiency of membranes with various amounts of TiO_2

Conclusions

The PVDF/CA nanofibrous membranes were successfully electrospun with different concentrations of TiO_2, which could be ascertained from the SEM micrographs. Furthermore, an increase in the particle density along the fiber could be observed as the TiO_2 concentration increased. The thermograms of the nanofibrous membranes showed that they possessed increased thermal stability with an increase in the TiO_2 concentrations. The nanofibrous membranes exhibited excellent antibacterial activity against gram-negative bacterium *E.coli* (MTCC 1652) and *P.aeruginosa* (MTCC 2453) and gram-positive bacterium *S.aureus* (MTCC 73537) and *B.licheniformis* (MTCC 96). The addition of TiO_2 also enhanced the efficiency of the membrane on 1,4-dioxane removal. It could be noted that the membrane with 5wt% TiO_2 showed the maximum elimination of 1,4-Dioxane

(55.14 ± 1.04% removal). Hence, these PVDF/CA nanofibrous membranes amended with TiO_2 particles having better thermal, antibacterial, and filtration properties could be used as a potential filtration membrane.

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Compliance with Ethical Standards

Conflict of interest The authors declares that they have no conflict of interest.

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