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Electrospun silver/poly (vinyl alcohol) nanocomposite membrane: A model for the study, design and characterization of antibiofouling and high performance water purification membranes

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Abstract : Electrospinning has attracted a great deal of interest because of its simplicity, low cost, ability to produce nanofibres with exceptional properties such as high porosity and surface to volume ratio and scaling up capability for commercial production. Membrane biofouling is a major challenge encountered in membrane filtration processes, and it is a key factor in determining their practical application in water treatment technology. We have synthesized silver/PVA nanocomposite fibremates at different $AgNO_3$ loadings of 1mM, 2.5mM and 5mM. The Ag/PVA nanocomposite membrane was characterized by UV- Visible spectroscopy for absorption characteristics of silver nanoparticles in the polymer matrix, powder X-ray diffraction (XRD) for structural analysis, Scanning electron microscopy (SEM) for fibre morphology and Attenuated total reflection infrared (ATR-IR) spectroscopy for chemical structure of the nanocomposite membrane. ATR-FTIR spectroscopy was also used to characterize the biofouling layer in order to provide information about its chemical nature. To enhance nanofibre integrity and mechanical properties the Ag/PVA nanocomposite fibres were deposited on polyethylene terephthalate (PET) microfibrous nonwoven sub layer and heat treated at 85 °C. The resultant membrane showed excellent structural stability and a remarkable antimicrobial activity at low nanosilver loading.

Key words: Electrospinning, Nanofibres, Biofouling, Antimicrobial activity.

Introduction

Membrane processes such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, can be used to remove a diverse range of pollutants during water and waste water treatment. However, membrane biofouling is an aspect which is difficult to control and substantial economic resources have been devoted to the development of effective biofouling monitoring and control strategies[1].

Nanotechnology affords a wide range of nanomaterials that enable applications, to a wide range of existing water treatment processes. For example electrospinning is a top to down approach to prepare continuous fibers with diameters ranging from tens of nanometers to several micrometers[2]. Owing to the small diameter, extremely long length, high surface area and complex pore structures, electrospun fibers have being attracted extensive research interests for their applications in many fields, such as tissue engineering, drug delivery and wound healing, as well as energy and environmental engineering[2,3,4]. The relatively large specific surface area and high porosity make electrospun nanofibres to attract substantial attention in developing water filtration membranes. Nanoparticles with antimicrobial properties such as silver and copper nanoparticles have been doped in polymer films by different chemical and physical methods[5].

Rubber composite fibers containing silver nanoparticles (Ag NP) with high morphological stability have been synthesised through the electrospinning technique and the nanocomposite mate demonstrated strong antimicrobial activity[6]. The detailed mechanism(s) of antimicrobial activity of silver nanoparticles remains to be fully understood. However, it has been demonstrated that silver nanoparticles cause structural changes and damage to bacterial membranes resulting in cell death. The particular studies propose that sulphur containing proteins in membranes or inside cells and phosphate containing elements such as DNA, are likely to be preferentially binding sites of silver nanoparticles[7]. Other researchers suggest that silver nanomaterials appear to wield bacteriocidal activity predominantly through increasing membrane permeability, loss of the proton motive force, inducing de-energization of the cells and efflux of phosphate, leakage of cellular content, and disruption DNA replication[7, 8]. Silver nanoparticle stability is controlled by particle size, shape, and capping agents as well as solution pH, ionic strength, specific ions and ligands, and organic macromolecules, all of which influence silver nanoparticle stability and bioavailability[8]. The broad-spectrum antimicrobial properties of silver embolden its use in many industrial and consumer products. With the rapid development of nanotechnology, silver nanoparticles have found many applications so much that it has become an engineered nanomaterial of interest[7, 8].

In this paper we explore the use a nanosilver doped electrospun nanofibre membrane for the design of membranes which are resistant to biofouling. Antimicrobial studies against a wide range of microbes present in sea water and a gram negative bacterium, *Escherichia coli* were carried out. ATR-FTIR studies were used to make a qualitative analysis of components of microbial secretions involved in the biofouling process.

Experimental

Materials

Poly(vinyl alcohol) (M_w = 125 000), N,N- Dimethylformamide (DMF), Tetrahydrofuran (THF), Polyvinyl pyrrolidone (PVP) (M_w = 40 000) was supplied by Sigma – Aldrich (India) and $AgNO_3$ granules by Sisco Research laboratories (India). All reagents were analytical grade and used without further purification.

Preparation of Ag NP/PVA electrospun nanocomposite membrane

Solution preparation was done according to a slightly modified previous study[9, 10]. PVA solutions of 5, 10 and 15 wt% were prepared by dissolving corresponding masses of PVA granules in deionized water for the optimization of the electrospinning process parameters. The solutions were heated at 60°C under magnetic stirring for 1.5 hours followed by cooling to room temperature. Silver nanoparticles were synthesized according to previously used modified methods [10,11]. The Ag/PVA solution was then prepared by mixing nano silver solution and PVA in a ratio of 1:2 and magnetically stirred for 2 hours. Table 1.0 shows the parameters which were used for optimisation of the electrospinning parameters using ESPIN NANO.

Table 1.0 Electrospinning parameters of Ag NP/ PVA solution

Ag NP/PVA Solution (wt%)	Syringe Type (ml)	Voltage (kV)	Distance (H) between syringe tip & Collector	Flow rate (ml/hr)	Drum speed (rpm)
5	2	21	15	0.6	1000.00
10	2	23	15	0.6	1000.00
15	2	25	15	0.9	1000.00

The 15 wt% Ag NP/PVA nanofibres were finally deposited on a polyethylene terephthalate (PET) microfibrous nonwoven sub layer and subjected to heat treatment at 85 °C for 2 hours.

Characterization

The absorption properties of the colloidal silver nanoparticle solution was characterized using UV-VIS the Labinda UV 3000^+ UV-Visible Spectrophotometer, structural analysis was done using X'pert Powder XRD System and chemical structures were determined using Alpha-T FT-IR Spectrometer in ATR mode. The fibre morphology of the nanocomposite sample was characterized by (SEM) (LEO 1530FEGSEM) Scanning Electron Microscope.

Antimicrobial activity tests of Ag NP/PVA nanocomposite membrane

The antimicrobial activity of Ag NP/PVA nanocomposite fiber mate at different $AgNO_3$ loading were tested against Gram negative *Escherichia coli*. The agar plates containing test samples and the control, nanofiber mate without Ag NPs were incubated at 37°C for a period of 24 hours. Further tests were done by emersing heat treated Ag/PVA nanocomposite fibre in sea water along with PVA nanofibre mate as control. Both nanofibre mates had equal dimensions of 10 cm length and 5 cm in width and were immersed in 250ml of sea water obtained from Mariana beach, Tamil Nadu, India for a period of 14 days. The sea water had the following mean parameters, Chemical Oxygen Demand (COD) of 980 mg/L and Biological Oxygen Demand (BOD) of 630 mg/L.

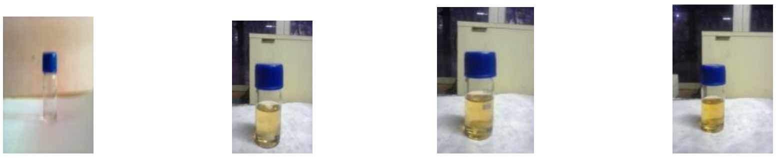
Results and Discussion

Visual Observations- Formation of Ag NPs

The rapid colour change of the reaction mixture from colourless to yellow was indicative of silver nanoparticles formation. DMF was used as a reducing agent and PVP as a capping agent. Silver nanoparticle formation occurs according to the following reaction:

$$HCONMe_2 + 2Ag^+ + H_2O \longrightarrow 2Ag^0 + Me_2NCOOH + 2H^+$$

Colour change was a result of the excitation of surface plasma resonance vibrations in the metal nanoparticles [11]. Figure 1 shows the observed colour changes during the progress of the reaction.



a) b) c) d)

Figure 1. Colour change of $AgNO_3$/DMF/PVP solution after a) 0 min b) 5 min c) 10 min and d) 30 min.

Electrospun nanofibre mates

Figure 2 shows images of electrospun nanofibre mates obtained during the electrospining process. The PET containing hybrid membrane c) was heat treated to improve membrane compactness, mechanical properties, chemical stability and reduce intra-membrane layer delamination[11,12]. The 15 wt% solution gave continuous fibres during the electrospinning process whilst the 5 and 10 wt% were forming discontious nanofibres.

a) PVA nanofibre nonwoven sub layer **b) AgNP/PVA nanofibre** **c) Heat treated AgNP/PVA on PET microfibrous**

Figure 2. Electrospun nanofibre mates

Characterization

UV- Visible Absorption spectrum

Figure 3 shows the absorption spectrum of Ag NP colloidal solution with an absorption peak at 428 nm.

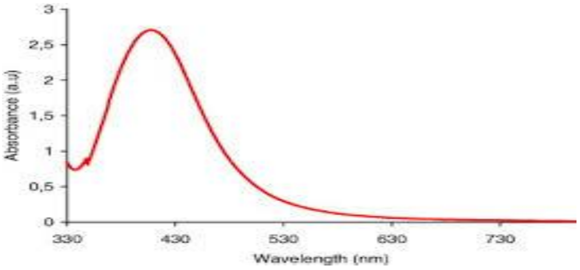


Figure 3. UV absorption spectrum of Ag NPs containing 1wt% $AgNO_3$

The position of the peak did not change and remained at approximately 428 nm when the reaction time was up to 150 min. The observed absorption peak is indicative of Ag NP formation[12].

XRD features

The X-ray diffraction pattern of the silver nanoparticles is shown in figure 4. A number of strong Bragg reflections can be seen which correspond to the (111), (200), (220) (311) and (222) reflections of fcc silver. All the reflections correspond to pure silver metal with face centered cubic symmetry. The high intense peak for fcc materials is generally (1 1 1) reflection, which is observed in the sample[13].

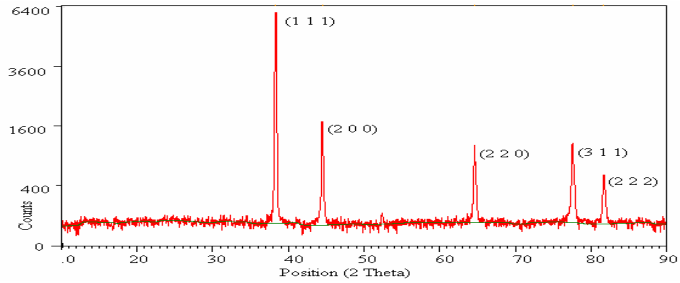


Figure 4. Powder XRD pattern of Ag

The average size of the Ag nanoparticles estimated from the Debye–Scherrer formula was found to be 38 nm.

SEM Analysis

Scanning electron microscopy (SEM), was utilized to study the fibre morphology. Figure 5 shows the SEM image of nanocomposite fibres collected using a $AgNO_3$ solution loading of 1mM. The fibers have an average diameter calculated using image J software of 170 ± 3.0 nm.

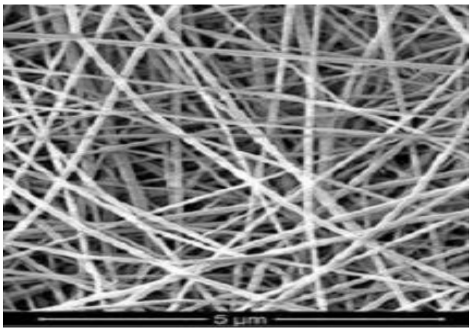


Figure 5. SEM micrograph of Ag/PVA composite fibers

ATR-FTIR and Antimicrobial tests

ATR- FTIR can be used to examine polymer surfaces creating a spectrum which represents the molecular fingerprint of the sample[14,15]. ATR-IR was used to study the chemical structure of PVA nanofibre membrane and Ag/PVA nanofibre membrane after the electrospinning process. The same procedure was also used to analyse the same fibres after immersion in sea water.

Figure 6 shows the spectrum of PVA nanofibre membrane, Ag NP/PVA. The ATR-FTIR spectrum of PVA and AgNP/PVA (PVA1 from the graph) were the same and it was concluded that there was no formation of new bond between the silver nanoparticles and PVA. The peak at 3262.73 cm^{-1} is characteristic of O-H stretching and intermolecular and intramolecular hydrogen bonds and at 1637.43 cm^{-1} is due to C-O stretching because of residual acetyl content present in the PVA matrix.

New peaks at 1554.14, 1409.40, 1272.55, 949.60 cm^{-1} were observed when electrospun PVA nanofibre membrane (PVA2) was immersed in sea water for 14 days. ATR-FTIR helps to make a qualitative analysis of the possible composition of the biofouling layer. Sea water contains a lot of microbes such bacteria whose activity can significantly lead to biofouling of the membrane. The new peaks are due to microbial secretions on the surface of the membrane during the initial phases of the biofouling process. The secretions are mainly composed of proteins, carbohydrates and nucleic acids, collectively known as extracellular polymeric substances (EPS)[16,17,18,19]. The peak at 1554.14 cm^{-1} is due to N-H bending which can be associated with proteinaceous components of the EPS. The peak at 1452.66 cm^{-1} is due to C-H stretching. The C-H bonds are present in protein, carbohydrate and nucleic acids which make up the EPS. The peak at 1272.55 cm^{-1} is due to C-N stretching in aromatic amines. The C-N bond is present in the aromatic rings of nucleic acids and can be associated with nucleic acids present in the EPS. The last significant peak at 949.60 cm^{-1} is due to O-H bends present in carboxylic acids. Carboxylic acids are present in the protein components of the EPS.

Examination of the Ag/PVA sample (PVA3) spectrum corresponding to the membrane which was also immersed in sea water for the same period of time as PVA nanofibre membrane (PVA2) showed no change in absorption spectrum when compared with Ag/PVA (PVA1) which was analysed just after synthesis. This result shows that there was no microbial activity at the surface of PVA nanofibres doped with silver nanoparticles. Secretion of the EPS components was significantly inhibited by the presents of silver nanoparticles.

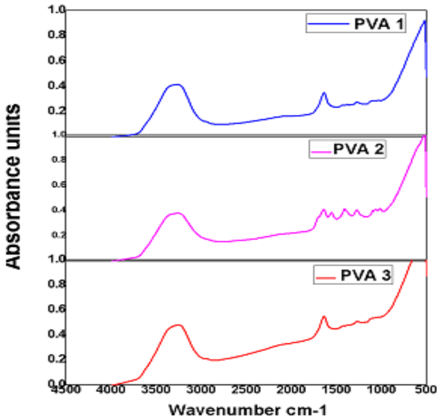


Figure 6 ATR-FTIR Spectrum PVA and AgNP/PVA membranes

Another antimiocrobial test result showed that *E.coli* colonies failed to grow in agar plates containg PVA nanofibres impregnated with silver nanoparticles. This result further supports the efficacy of Ag NPs' reamarkable antimicrobial properties.

Conclusions

Biofouling denotes a multifaceted mechanism where microbes attach to the surface of water purification membranes leading to the formation of a biofilm layer compromising the efficiency of the treatment processes. Effective design of these membranes by incorporating nanomaterials with excellent antimicrobial properties such as silver nanoparticles can significantly reduce challenges associated with biofouling, resulting in high performance water purification membranes. The benefit can be realised for example in the maintenance of the operational membrane flux because of the absence of a low permeability biofilm on the membrane surface and a constant differential pressure and feed pressure needed to maintain the same production rate.

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