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PREPARATION OF ANTIBACTERIAL UF MEMBRANE FOR WASTEWATER TREATMENT USING COMPOSED OF POLYSULFIDE COMBINED WITH ZnO/Ag NANOMATERIALS

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Abstract: In this work, innovative composite flat sheet polymeric membrane, made of polysulfide (PSF) combined with nanoparticles (AgNp) and nano zinc oxide (ZnONp), which have been prepared for wastewater treatment using phase inversion. The structural properties for PSF/ZnO/Ag composite UF membrane were then characterized using scanning electron microscopy (SEM), EDX analysis, and surface roughness measurement using atomic force microscopy (AFM). The mean roughness and the root mean square of this membrane are much less valuable than the polysulfide membrane without nonmaterials. On the other hand, it has been found that the pure water flux was increased from a low of 250 L/m^2h for the pristine membrane to a high of 410 L/m^2h for the composite membrane and the rejection rate using water containing sodium chloride was increased from 50% to 70% for the polysulfide membrane with nonmaterial's than the polysulfide membrane without nonmaterial's using the same saline solution. In addition, the membrane efficiency was studied as an antifouling due to bacterial contamination using pure bacterial colonies of Staphylococcus Aureus, and Escherichia coli. Practical experiments have shown that this combination of Zinc oxide and silver nanoparticles combined with polysulfide can be the best choice for having double characteristics of anti-bacterial and bacteriological pollution to improve membrane for wastewater treatment.
Key words: Antibacterial, Nano materials, UF membrane, Waste water.

1. INTRODUCTION

Contamination of drinking water and the subsequent outbreak of waterborne diseases are the leading cause of death in many developing nations. Therefore, virus removal during water treatment has received more attention due to the epidemiological significance of these pathogens [1-3]. Traditional water/wastewater treatment technologies remain ineffective for providing adequate safe water due to the increasing demand for water coupled with stringent health guidelines and emerging contaminants. In order to ensure safe drinking water for all, some membranes such as reverse osmosis forward osmosis, membrane distillation, and capacitive deionization could be promising in the desalination of both sea and brackish water. But, other conventional water treatment technologies such as physical (boiling, distillation, filtration, sedimentation, microfiltration, nanofiltration, ultrafiltration, sludge storage, and removal, coagulation and flocculation); chemical degradation (ozone, chlorine, chloramines, ultraviolet, H_2O_2 oxidation, solar water disinfection or photocatalytic degradation, supercritical water oxidation, sonochemical degradation); and biological (microbial water sludge treatment) have failed because of their dependence on influent water qualities [4, 5]. Membrane fouling especially biofouling remains one of the most challenging issues in Membrane separation processes which hinder wider applications of UF in wastewater treatment system [6, 7]. Membrane fouling can be defined as the undesirable deposition of retained particles, colloids, macromolecules, salts, etc. at the membrane surface or at the pore wall inside the pores [8]. Therefore, many efforts have been made to develop anti-fouling strategies. From the viewpoint of fouling components, the fouling can be classified into three major categories: biofouling, organic fouling, and inorganic fouling [9].

Today, in the area of water purification, nanotechnology offers the possibility of efficient removal of pollutants and germs. Research is underway to use advance nanotechnology in water purification for safe drinking. Nanotechnology, the deliberate manipulation of matter at size scales of less than 100nm, holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales, because of their high reactivity due to the large surface to volume ratio [10]. Nanoparticles are expected to play a crucial role in water purification [11]. Also, nanoparticles, nanomembrane, and nanopowder used for detection and removal of chemical and biological substances include metals, nutrients, cyanide, organics, algae viruses, bacteria, parasites, and antibiotics.

Membrane fouling can be defined as the undesirable deposition of retained particles, colloids, macromolecules, salts, etc. at the membrane surface or at the pore wall inside the pores [8]. From the viewpoint of fouling components, the fouling can be classified into three major categories: biofouling, organic fouling, and inorganic fouling [9]. Among them, biofouling is the most complicated one which seriously hampers the application of membrane processes. Biofouling results from the accumulation of assimilable organics, biofilm formation and regrowth of microorganisms on the membrane surface [12]. To reduce biofouling, and functional membranes containing antibacterial materials have attracted tremendous interest. Silver is one of the most widely studied biocides because of its excellent biocidal properties [13]. Silver nanoparticles have been successfully introduced into various membrane materials such as polysulfone [14], polyethersulfone [15], polyvinylidene fluoride [16], polyamide [17] and chitosan [18]. The addition of silver nanoparticles into the poly membranes improved the membrane performance in terms of their flux and fouling resistance, attributing to an increase of hydrophilicity or change in membrane morphology.

On the other hand, Photocatalysis, using nanostructures of metal oxide semiconductors like zinc oxide, titania, etc., can be an attractive way of water purification as it is capable of removing chemical as well as biological contaminants [19]. Especially, zinc oxide nanoparticle materials were used in many applications in our life [20]. Also, ZnONPs are common constituents in many consumer products such as sunscreen, cosmetics, paints, and coatings, etc., because of their excellent UV absorption and reflective properties [21]. Currently, there is no evidence to suggest that humans are adversely affected by ZnONPs through their use in consumer products. However, ZnONPs are known to partially dissolve in water, hence ZnONPs containing products are likely to release both dissolved zinc and ZnONPs into the environment which is likely to persist and bioaccumulate. Ecotoxicological literature has reported the adverse effect of ZnONPs on bacteria and other microbes, algae and plants, invertebrates, and vertebrates [22].

Recently, a major advantage of the use of antimicrobial nanomaterial like silver (Ag), zinc oxide, etc. in water purification is the prospect of developing point-of-use systems [23]. The concept of decentralized water treatment systems is being considered due to deterioration of water quality in old distribution networks and the ever-increasing transportation costs. The importance of membranes in drinking water and waste water treatment systems is gaining importance [24]. Now a day, a rare of studies to manufacture new type of Ag/ZnO with PSF/ PVA composite membrane was exhibited excellent anti-bacterial activity. The main objective of this study is to fabricate and characterize properties of the Ag/ZnO with PSF/ PVA mixed matrix membranes. Furthermore, we studied the effect of silver release on the filtration performance of the nanocomposite membranes. The antibacterial and antifouling performances were evaluated by the disk diffusion method, activated sludge immersion test as well as bacterial suspension filtration experiment.

2. EXPERIMENTAL

2.1 Materials

Polysulfone (PSF) was purchased from (Sigma-Aldrich, MO, molecular weight = 35,000) and Poly (vinyl alcohol) PVA (Sigma- Aldrich, molecular weight = 13,000–23,000, 87–89% hydrolyzed). These polymers were blended together For the purpose of formation of dissolution with the solvent 1-methyl-2-pyrrolidone (NMP) supplied from (Sigma-Aldrich), Sodium chloride (NaCl). Also, (Ag) nanoparticles 40 nm and zinc oxide (ZnO) nanoparticles supplied by Sigma-Aldrich were used after treated by using thermal evaporation method at 800ºC to modify ZnO nanoparticles as received.

2.2 Preparation of composite membranes

Pure PSF and modified composite PSF-Nano Ag/ZnO membranes were prepared with the phase-inversion method, which was used for preparing another type of membranes in the literature [1, 2]. Casting solutions were prepared by dissolving of Polysulfone (PSF) in the solvent NMP at a water bath at (75-80)ºC with a continuous stirring rate of 500rpm. Ag/ZnO nanoparticles were mixed with a sensible amount of solvent by an ultrasonic device for half an hour. After that PVA and blending of Ag/ZnO nanoparticles were added slowly to the solution with continuous stirring for 7h to create the best dispersion of nanoparticles in the solution. The casting solution was then kept in a conical flask in the dark for at least 24h at room temperature for degassing (release the air bubbles) to prevent defects in the membrane. Afterward, a suitable amount of the casting solution was poured onto a 35cm×20cm clean glass plate and dispersed with a casting knife. The thickness of the membranes was set to 200µm. After 15s evaporation time of the casting solution on the glass plate to the air, the glass plate was immediately immersed in a (23–25)ºC ultrapure water coagulation bath at room temperature for the phase-inversion process remainder.The formed membranes were separated from the glass plate and rinsed with distilled water for at least 30min. Then, the membranes were stored in distilled water containing 1 wt % formaldehyde for the purpose of maintaining the membrane by preventing the growth of bacteria under ambient conditions. The PSF (17 wt % of the solution) was dissolved in NMP (83 wt % of the solution) to formation Polymer dopes. The modified membrane was cast by using the PSF-Nano Ag/ZnO-mixed matrix materials and it was prepared by the solution dispersion blending by added nano-ZnO particles (0.2 wt %) nano-Ag particles (0.5 wt %) to the PSF and NMP solution.

2.3 Membrane performance

The performance of prepared membranes was studied by measuring the pure water flux and an aqueous solution of NaCl permeability and rejection. The 100 ppm NaCl solution with pH=7±0.2 was used as feed solution. All the Permeation testing were conducted using a laboratory-scale dead-end system (Sterlitech HP4750: Sterlitech Corporation, WA) at a temperature of (25±1)°C and pressure of 6bars, after compaction at a pressure of 7bars. The dead-end filtration cell had an effective membrane area of 14.6cm^2. The membrane was fixed between two stainless steel parts and also was sealed with an O-ring. A magnetic stirrer was also located under the membrane cell to stir feed in order to decrease the effect of concentration polarization on the flux, the permeate sample collection was started after 10min. The flux (*Jw*) was calculated using equation (1) as the following, [25]:

$$J_w = \frac{V}{A \times t} \qquad (1)$$

where J_w is the pure water flux (L/m^{2}h), A is the membrane surface area (m^2), V is the permeated water volume (L) and t is the time (h).

2.4 Salt rejection

Solute rejection, through the pure PSF and PSF-Nano Ag/ZnO nano-composite modified membrane, was evaluated using 1000rpm NaCl aqueous solution at (5-6)bars. The active membrane area was 14.6cm^2. Rejection was calculated by measuring permeate and feed concentrations of aqueous solution of metal ions through. The membrane solute rejection (R) was calculated using equation (2) as the following, [25]:

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (2)$$

Where C_p (mg/ml) and C_f (mg/ml) are the NaCl concentrations in permeate and feed respectively.

2.5 Membrane characterization

The Ag/ZnO with PSF/ PVA mixed matrix membranes were subsequently characterized by various tools: the outer surface and cross sectional morphology of membranes was examined by scanning electron microscopy (SEM), model JOEL JSM-6460LV. The presence of silver and ZnO on the membrane surfaces was investigated by means of a using energy dispersive X-ray spectrometer (EDX). Also, the samples of the membrane preparation were frozen fractured in liquid nitrogen and sputtered with gold. The SEM micrographs of dried membrane samples were taken at certain magnifications. The surfaces of membranes were scanned in a scan size of 5μm by atomic force microscopy (AFM) to determine the roughness of membranes. The surface roughness parameters which are expressed in terms of the mean roughness (Sa) and the root mean square roughness (Sq) were calculated from AFM images.

2.6 Inhibition zone test

Inhibition zone experiment was used to show the antibacterial capability of prepared membranes. A pristine membrane as a control sample and The Ag/ZnO with PSF/ PVA mixed matrix membrane containing a different concentration of each a silver and ZnO nanoparticles were cut into 5mm diameter disk shape pieces. The antibacterial property of modified membrane was investigated by the halo test. The gram-negative (*E-coli*) and gram-positive (*Staphylococcus aureus*) were used as test microorganisms. *E-coli* & *Staphylococcus aureus* were inoculated on the prepared media by plate smearing method (HiMedia, ISO 900, WHO GMP). The inhibition zone formed after 24h served as an indicator for the antibacterial property and was recorded by a digital camera.

3. RESULTS AND DISCUSSION

3.1 Morphologies of membranes

It is revealed from SEM and AFM studies Figure 1 that the pure PSF/PVA membrane and the nano Ag/ZnO with PSF/PVA composite membrane have similar flat smooth surfaces without obvious aggregation on membrane surfaces.

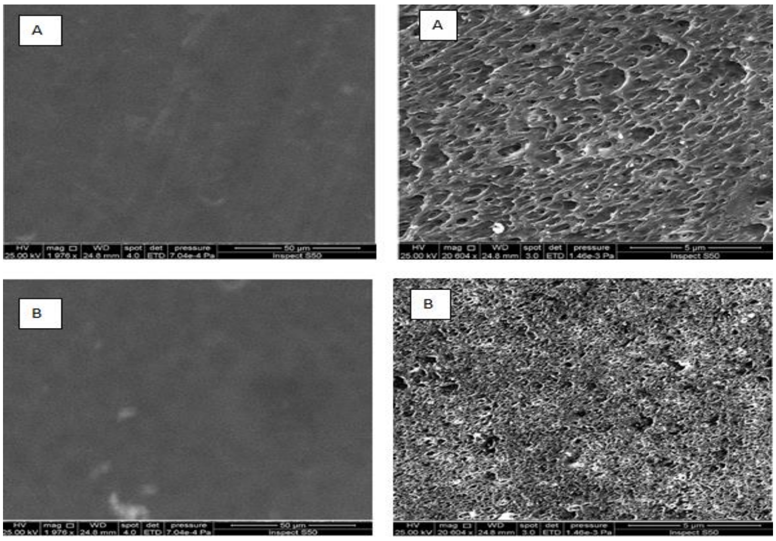


Fig. 1. SEM images (A) the pure PSF/ PVE membranes (B) nano Ag/ZnO with PSF/ PVA composite membranes

The PSF/Ag/ZnO mixed matrix membranes had sponge-like morphology with uniform, well-interconnecting pores, and smooth surface. The membrane with this morphology exhibits small flow resistance leading to higher flux values. Moreover, an increment in the flux for the modified membrane could be due to the combined effects of porosity, a change in pore structure, and the increase in the segmental gap between the PSF and ZnO nanoparticles. While EDX analysis Figure 2 was used to check up the elemental compositions found on each of the nanomaterials.

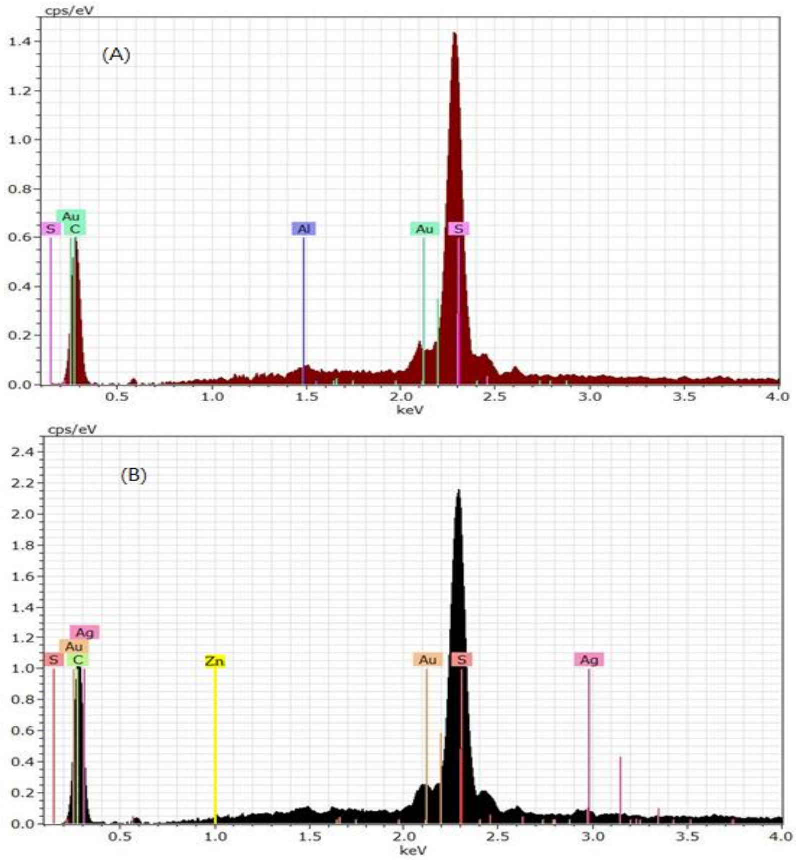


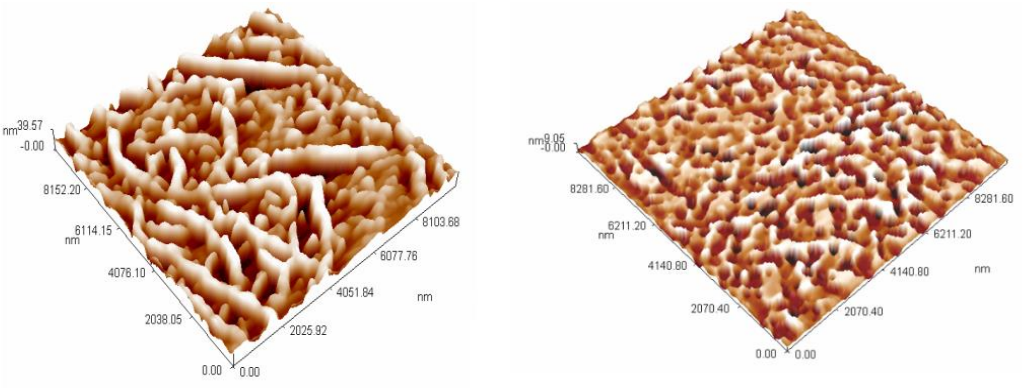
Fig. 2. EDX spectra of: (A) the pure PSF/ PVE membranes;
(B) nano Ag/ZnO with PSF/ PVA composite membrane

The mean roughness (Sa) of the membrane surface was also found for polysulfone (PSF) which incorporated with nanomaterials, as well as the root mean squareness (Sq) of this membrane is much less valuable than the polysulfone membrane that is not incorporated with nanomaterials as shown in Table 1.

Table 1. Surface roughness rate and square root rate of surface roughness of processed membranes.

Membrane	**Sa**	**Sq**
PSF	10.1 nm	11.7 nm
PSF-Ag/Zno	4.5 nm	6.1 nm

This result corresponds to the shape of the smooth surface that was seen using the AFM (Figure 3) and that the reason for the appearance of the smoother surface is due to changes in the viscosity of the casting solution.



A **B**

Fig. 3. AFM images of the surface of polysulfide membranes: (A) before the addition of nanomaterials (B) after the addition of nanomaterials

3.2 Membranes filtration

For the above reasons described in subsection 3.1, nanomaterials exhibit a small resistance to flow, leading to higher permeability of the membrane, in other word, best flow values. Figure 4 and Figure 5 shows the results of the flow rate produced through the membrane during the transfer of pure water and water containing NaCl respectively via the enhanced membrane PSF-Nano Ag/ZnO, compare with the membrane without additives (PSF). Furthermore, the results showed that the rejection rate for the polysulfone membrane that was not incorporated with nanomaterials was 50% when the saline solution was used (1000ppm NaCl aqueous solution) while the rejection rate was 70% for the for the polysulfone membrane that was incorporated with nanomaterials using the same solution, as shown in Figure 6. ZnO nanoparticles added to the membrane improved hydrophilicity, thus improving performance. The improved hydrophilicity of nanocomposite membrane would enhance the fouling resistance of the membranes.

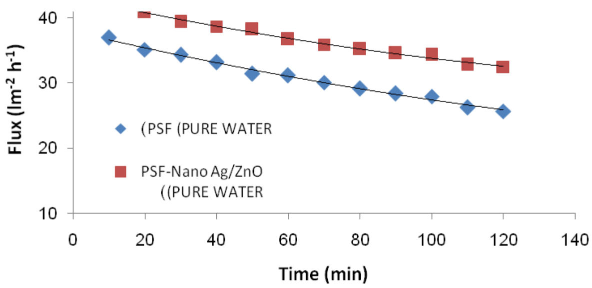


Fig. 4. Flux for NaCl aqueous solution of pristine PSF and (PSF-Nano Ag/ZnO) composite flat sheet membrane

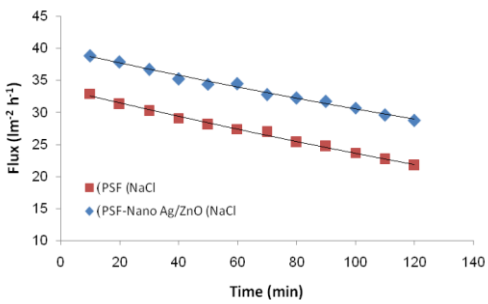


Fig. 5. Flux for pure water of pristine PSF and (PSF Nano Ag/ZnO) composite flat sheet membrane

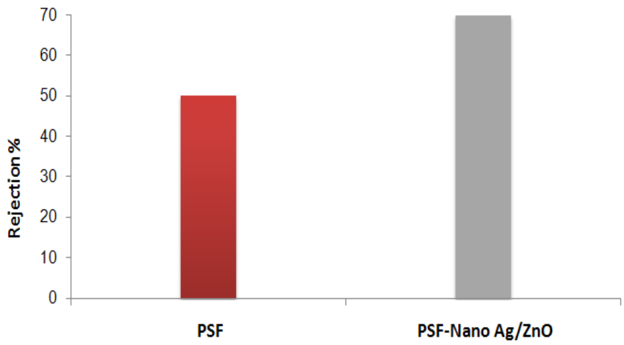


Fig. 6. The NaCl rejection of pure PSF and (PSF-Nano Ag/ZnO) composite flat sheet membrane

3.3 Composite membrane anti-bacterial growth characteristics

According to several previous comprehensive studies on the anti-bacterial properties of nanoparticles for both silver and zinc oxide these nanoparticles can stick to the cell membrane and inhibit the breathing process, thus it can impede or disrupt vital metabolic processes. Nanoparticles can also penetrate the cell and interact with proteins or DNA. In addition, Ag + ions have been shown to disrupt DNA functions, which are considered as computer programs and the cell is the computer and DNA is the program. The program is the one which gives instructions to the computer and tells the computer how to behave and how to function when disabled and host DNA leads to the death of bacteria. The results showed in Figure 7 that the improved membrane had a clear inhibitory ability towards the growth of E-Coli and Staphylococcus where clear halo regions were observed on a sample of the enhanced membrane while the pure PSF membrane (without any additions) showed no inhibitory effect.

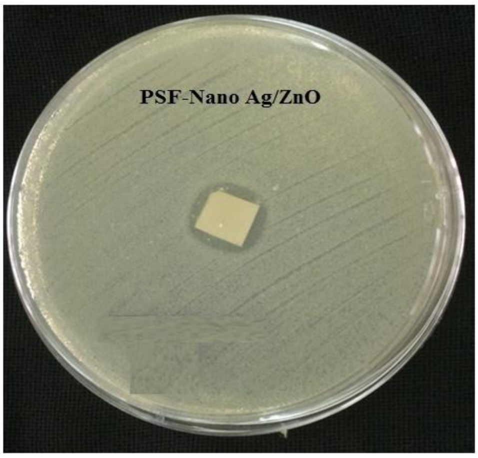


Fig. 7. Inhibition area of the bacteria used to examine the viability of the membranes as antibacterial

4. CONCLUSIONS

The results showed that the increase in the flow rate was due to several factors combined, including the change in pore structure and porosity and the increase in the size of the sub-layers in the PSF polymer contact with Ag/ZnO nanoparticles. On the other hand, the improved membranes proved a good possibility of rejecting the salts by using a solution of sodium chloride at 1000rpm (higher than the membranes without additions). This improvement is mainly due to the incorporation of nanoparticles, which have anti-bacterial properties, increase membrane viability to hydrophilic and thus improve anti-fouling properties, which reduce the adsorption of organic pollutants into a structure the membrane. The other cause can be due to the dense and porous surface caused by the cohesion and good interaction between silver nanotubes and zinc oxide (Ag/ZnO) with PSF membranes. Thus, nanoparticles led to the construction of a membrane structure with a tightly filled surface with the construction of a squishy structure with a very thin surface layer, which is often not visible. This explains the high rates of rejection of dissolved salts. The PSF/ZnO/Ag membrane was evaluated using an inhibition zone experiment to demonstrate antibacterial capacity by manufactured membranes.

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