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Preparation and Characterization of AgNp/PVDF Composite Ultrafiltration Membrane

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ABSTRACT

In this study, polymeric ultrafiltration (UF) membranes were prepared by phase inversion method to obtain both antibacterial and organic antifouling properties. The membranes were cast from a solution of polyvinylidene fluoride (PVDF) and formative silver (Ag) nanoparticles were successfully immobilized on a polymer. This was done using a solvent N, N-dimethylformamide (DMF) which is a solvent for the PVDF polymer meanwhile it is a reducing agent for silver ion. The effect of silver nanoparticles additives on the performance of polymeric ultrafiltration membrane was verified. Chemical composition and morphology of the surfaces of the membranes were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The antibacterial property of modified membrane and the influence of silver nanoparticles on pure water flux of composite membrane at 0.2 Mpa were also verified. The experimental results obtained concluded that the composite membrane properties have been improved by the integration of Ag nanoparticles. The grafted membrane with silver nanoparticles has shown a clear ability to inhibit the growth of E. coli, Pseudomonas Aeruginosa, and Bacillus Cereus. While the clean PVDF membrane (without any additives) did not show any effect of preventing the growth of these species of bacteria referred to above. The pure water flux, porosity and the mean pore size of composite membrane can reach 261.8 L/m^2 h, 85.4%, and 0.0206 µm, respectively, and it was much more than that of pure PVDF membrane.

Keywords: Ag nanoparticles: PVDF membrane; antifouling and antibacterial.

تحضير وتوصيف غشاء فائق الدقة مركب من الفضة النانوية ومادة بولي فينلدين فلورايد

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باحث علمي
وزارة العلوم والتكنولوجيا

الخلاصة

في هذه الدراسة، تم تحضير غشاء بوليمرى فائق الدقة، باستخدام عملية الأنعكاس الطوري للحصول على خواص مضادة للانسداد العضوي والبكتيري على حد سواء، حيث تم تشكيل الغشاء من محلول تم فيه تثبيت جزيئات الفضة النانوية المشكلة بنجاح على البوليمر بولي– فينلدين- فلورايد (PVDF)، باستخدام المذيب (DMF) كعامل مختزل لأيون الفضة ومذيب للبوليمر بنفس

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الوقت. تم التحقق من تأثير أضافة جزيئات الفضة النانوية على أداء غشاء PVDF فائق الدقة. حيث تم توصيف التراكيب الكيميائية للسطح وتراكيب الشكل للسطح باستخدام جهاز مطياف الاشعة تحت الحمراء والمجهر الألكتروني الماسح. كذلك تم التحقق من قابلية الغشاء المضادة للنمو البكتيري وتأثير أضافة جزيئات الفضة النانوية على جريان للماء النقي خلال الغشاء المركب عند ضغط 0.2MPa. النتائج التجريبية أشارت بأن إضافة جزيئات الفضة النانوية قد حسنت مواصفات الغشاء المركب. حيث أظهر غشاء ال PVDF المطعم بالفضة النانوية قدرة تثبيط هامة نحو بكتريا أي كولاي و سيدومونس و السلاسل العصوية (باسيلس سيريس) بينما لم يظهر غشاء ال PVDF النظيف (بدون أي إضافات) أي تأثير منع نحو نمو أي من انواع البكتريا المشار اليها أعلاه. جريان الماء الصافي عبر الغشاء المركب والمسامية ومتوسط حجم المسام يمكن ان يصل الى 261.8 $L/(m^2h)$ و 85.4% و 0.0206 µm على التوالي، وهو كان أكثر بكثير من الغشاء غير المطعم بالفضة النانوية./

الكلمات المفتاحة: جزيئات الفضة النانوية، غشاء بولي– فينلدين- فلورايد، الانسداد العضوي والبكتيري

1. INTRODUCTION

Phase inversion process is considered one of the methods for preparation of membranes. This method has been used widely as a method for the manufacture of asymmetric polymeric membranes, **Zheny, et al., 2006**, **Zhang, et al., 2006**. Most microfiltration and ultrafiltration polymeric membranes which are used to filter liquids have been prepared using the phase inversion process via dipping precipitation, **Akthakul, et al., 2002**. This technique is a process that leads to the preparation of semi-permeable membranes by immersing a thin layer of the polymer solution into a non-solvent bath. Sometimes the precipitation process is recognized as a demixing (liquid-liquid). The structures of membranes formed in this way are very complex and depend on the solution of casting formation and coagulation bath, **Young,** and **Chen, 1995**. PVDF is a material that can form asymmetric membranes; this material can produce membranes with high permeability, high surface porosity, and good pore structure. PVDF membranes show outstanding antioxidation activities, strong hydrolytic and thermal, resistant to corrosion by most chemicals and organic compounds and good mechanical and film-forming properties. PVDF membranes can be used in UF processes through various modifications, **Yan, et al., 2006**. However, there is still room for improvement to increase the performance of the PVDF membranes. Improvements to the PVDF membranes can be made through physical blending, chemical grafting, and surface modifications, **Rahimpour, et al., 2009 and Panu,** and **Tai-Shung, 2009**. Generally, several alternative methods have been used to increase the performance of PVDF membranes, such as the addition of inorganic fillers to increase the permeability and enhance the mechanical properties of the membrane and to improve control of the membrane surface properties, **Rahimpour,** and **Madaeni, 2007**. Many efforts have been devoted to preparing the nanoparticles–PVDF composite membranes by using a phase inversion method. This method included a small proportion of the nanoparticles, which is an effective way to improve the membrane performance. A lot of efforts have been devoted to applying the phase inversion technique to prepare modified composite membranes of nanoparticles / PVDF. In this method a small percentage of nanoparticles is used, which is sufficient to improve the performance of the membranes. Currently, nanomaterials that have been incorporated into the manufacture of polymeric membranes are such as ZrO_2, **Bottino, et al., 2002**, Al_2O_3, **Yan, et al., 2006**, Fe_3O_4, **Jian, et al., 2006**, SiO_2, **Tripathi, et al., 2010**, TiO_2, **Silvia, et al., 2017**. Many researchers and previous studies have reported that the addition of nanomaterials has improved the performance of polymeric membranes such as permeability, hydrophilicity, and mechanical strength, **Damodar, et al., 2009, Pang, et al., 2011,** and **Yalei, et al., 2014**. Surface membrane modification with silver nanoparticles (AgNp) may also be reduced membrane bio-fouling, there are several previous research studies on the properties of silver nanoparticles against bacterial growth, **Gogoi, et al., 2006**, where the silver nanoparticles could attach at the cell membrane surface and inhibits the respiration process, **Holt and Bard, 2005**, consequently, it can block or damage vital metabolic processes. Nanoparticles can also implement through the cell, and react with deoxyribonucleic acid (DNA), take possession of functional groups (succinate, proline and glutamine, amine and phosphate), **Rai, et al., 2009**. In addition, it was shown that Ag^+ ions prohibit DNA replication by binding to the molecules, hence resulting in bacterial death. **Feng, et al., 2000**. This is what has been mentioned in a number of previous studies, including the researcher. **Zhang, et al., 2012** prepared hollow fibers membrane of PAN loaded with silver-containing (0.5 wt% of silver nitrate) by modification of wet spinning using a dry jet technique. The membrane surface has been found free of the growth of bacteria such as E. coli and Staphylococcus aureus when adding 1% wt% of the silver nanoparticles (these ratios are specific to research and not general) when forming the membrane. According to previous studies, there are very few studies about the use of phase inversion process to develop ultrafiltration membranes incorporated with nano-silver particles formed in "situ". Herein, the "new in this research" the anti-bacterial properties and permeability are addressed together by manufactured PVDF modified ultrafiltration membranes enhanced with in situ formed Ag nanoparticles and combined with a phase inversion process for the preparation of modified membrane.

2. MATERIALS AND METHOD

2.1 Materials

Poly (vinylidene fluoride) (PVDF; FR904) powder was received from (Shanghai Fluorine Chemical Industry Co. Ltd, China) and used after it has been dried for 24 hours at 100 °C. Analytical grade Silver nitrate ($AgNO_3$), solvent (DMF; >99%, reagent) and polyvinylpyrrolidone (PVP; K-30) were purchased from Sigma Aldrich.

2.2 Modified membrane preparation

The flat sheet PVDF/AgNp membrane was prepared by phase inversion process, **Rahimpour, et al., 2009**. The casting solution was prepared at 45–55 °C for dissolution of PVP/PVDF in DMF with a concentration of the polymer at 23% (w/w). PVDF (15 wt. %) and Polyvinylpyrrolidone (PVP) with a concentration of 4 wt% was used as pore former, the casting solution was dissolved in DMF in a 250 ml flask, The solution is then placed in a water bath and heated to a temperature of 50 °C, with stirring rate of 300 rpm using a magnetic stirrer up to obtain a homogeneous mixture. In another flask, in order to minimize Ag reduction, a certain amount of silver nitrate ($AgNO_3$) is dissolved in a certain amount of solvent DMF at room temperature, The solution $AgNO_3$/DMF mix well using ultrasonic then added to solution of PVP/PVDF with continued stirring the mixture at 50 °C for a period of not less than 7 hours. The composition of the casting solution and the content of $AgNO_3$ particles in the membranes are detailed in **Table 1**. Gradually, the colorless polymer solution was changed from pale yellow to dark brown; this is clear evidence that the casting solution PVDF/AgNp contains a dispersion of n-Ag (silver nanoparticles) through the membrane matrix, **Xin, et al., 2013**. The modified Ag/PVDF-UF membranes were appointed as PVDF-N, where N identified to the silver concentration, Table 1.

The homogeneous casting solution was preserved stagnant in the dark place for at least 24 h to let the air bubbles out to prevent defects in the membrane. Afterward, some polymer solution was cast on a clean glass plate and dispersed using a homemade casting knife with 100 µm thickness. After 15 s evaporation time of the casting solution, the glass is submerged in a bath of deionized water at room temperature to induce phase inversion process. To remove the solvent remaining in the membrane formed, the membrane is rinsed completely using deionized water. Then, the membrane prepared was stored at room temperature in ultrapure water containing 1 wt % formaldehyde to prevent bacteria growth.

2.3 Modified membrane characterization

Characterization of Ag/PVDF-UF membranes is important since it allows insight into the relation between membrane chemistry, structure and transport properties. The most commonly used method of characterization to evaluate membrane performance is measuring the permeate flux decline during filtration. This measurement gives a general indication of the performance of a specific membrane. However, membrane surface characteristics, structure, and their role in the filtration process and solute transport cannot be fully understood with only flux data. Therefore, other parameters have been measured using characterization techniques in an attempt to diagnose and predict membrane performance.

The morphology of prepared membranes was observed on the top and bottom surfaces by a scanning electron microscope (SEM, VEGA3 - TESCAN, Czechoslovakia) after being sprayed with gold. The porosity of membrane ε (%) is specified as the volume of the pores divided by the total volume of the porous membrane. It could generally be set by the gravimetric method, determining the liquid weight (pure water here) contained in the membrane pores, **Zhang, et al., 2006** and **Yalei, et al., 2014**.

$$\varepsilon = \frac{(w_{wet} - w_{dry})/\rho_w}{(w_{wet} - w_{dry})/\rho_w + w_{dry}/\rho_p} * 100\% \qquad (1)$$

Where:

w_{wet} the weight of the wet membrane (g).
w_{dry} the weight of the dry membrane (g).
ρ_w the pure water density (0.998 g/cm^3).
ρ_p the polymer density (as the inorganic content in the membrane matrix was small and ρ_p was approximate to ρ_{PVDF}, viz 1.765 g/cm^3).

Mean pore radius rm (μm) can be calculated by filtration velocity method. Using equthe ation of Guerout–Elford–Ferry, **Xu, et al., 2009**:

$$rm = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta t Q}{\varepsilon \times A \times \Delta p}} \qquad (2)$$

Where Δp is the differential operational pressure (0.2MPa), Q is the amount of permeated pure water per unit time (m^3/s), η is water viscosity (8.9×10^{-4} Pa s), t is the membrane thickness (m) and A is the effective area of the membrane (m^2).The water permeation of the membranes was measured in a dead-end filtration cell (effective filtration membrane area of 14.6 cm^2), was purchased from (STERLITECH HP4750, **Fig. 1**). In order to get a steady flux, the modified membranes were pre-pressured at 0.25 Mpa, after that by recording the volume of permeation water every 5 min the flux (J) was measured at a pressure of 0.2Mpa.

2.4 Antibacterial properties investigation

Halo test was used to investigate the antibacterial property of PVDF/AgNp membrane. The "gram-negative" bacteria Escherichia coli (E-coli) were used as test microorganisms by using plate smearing method. Furthermore, the antibacterial property of the modified membrane was confirmed toward the growth of (Pseudomonas Aeruginosa and "gram-positive" bacteria Bacillus Cereus) by using the swabbing technique. The E-coli was inoculating on the culture media and then E-coli has been activated and spread at the sold nutrient agar **HiMedia, ISO 900, WHO GMP** which poured in Petri dish, as a mat shape using a stick by Lab of biotechnology. The PVDF/AgNp membrane was cut into a square-shaped coupon of 1cm by 1cm. The smooth surface of PVDF/AgNp membrane was placed on the inoculated agar plate, where the bacteria were cultured and incubated at a temperature of 37ºC for a period of 48 hours. Experiments have been conducted within a bacteria-free environment. Inhibition zone formed after the passage of 24 hours, which shows that the anti-bacterial growth membrane property, where it was depicted by a digital camera.

2.5 Evaluation of silver leaching

The releasing behavior of Ag from the silver-loaded membranes was investigated in the filtration process. High-purity water was filtered through the certain area of PVDF/Ag membrane at room temperature. To achieve this assay dead-end cell (STERLITECH HP4750) has been used. Operating conditions were 0.2 Mpa for 8 h. The samples of permeate water were collected after an hour and then after four hours and eight hours. Finally, the samples that have been collected were analyzed to measure the concentration of silver in each sample. Using an atomic absorption spectrophotometer (AA-7000: Shimadzu, Japan).

3. RESULTS AND DISCUSSION

3.1 Characterization of modified membrane

The effects of PVP on the PVDF membrane as well the effect of a collection of both PVP and AgNp on the PVDF membranes were investigated by SEM images as depicted in **Fig. 2**. The size of AgNp in the casting solution was about 20 to 30 nm measured using (ZetaPALS, Brookhaven Instruments Corporation, USA**), Fig. 3**. The prepared membranes showed typical asymmetric morphology with pores linked by sponge walls and perfectly developed macro voids at the bottom. It can be seen from **Fig. 2** that there is a spherical structure with the presence of small pores between the globes that have appeared in the pure PVDF image. This Figure shows that the Ag nanoparticles have been taken a place in the sponge membrane pores. There was also no distinct difference on the top surface between the PVDF/PVP blend membrane and the composite membrane PVDF/PVP/Ag which displayed the flat and a smooth surface. The porosity (ε) of modified membrane increased with adding the AgNp as shown in **Table 2**, the cause is due to the phase-inversion process kinetics, instantaneous immersed of membrane matrix in ultrapure water will accelerate the shrinkage of the organic phase and leads to a macro void structure, **Yang, et al., 2009**. Adding Ag nanoparticles with casting solutions reduces the interaction between solvent and polymer molecules that lead to an acceleration in the exchange of non-solvent and solvent during the separation phase, and then, the macro voids formed at the bottom of the composite membranes.

3.2 Composite membrane anti-bacterial growth characteristics

The results shown in **Fig. 4** indicated that the composite membrane showed a clear inhibition capacity against E-coli. While PVDF membrane without adding AgNp did not show any inhibition of coliform bacteria growth, this is evident through the growth of bacteria around the edge of the membrane (PVDF-0). On the other hand, clear halo areas were seen surrounding the samples of

PVDF/AgNp spot and well (drops taken from the membrane matrix) and the PVDF/AgNp membrane. These indicated that antibacterial effectiveness was at most caused by the Ag nanoparticles and not because of the presence of the PVDF polymer. In addition, the antibacterial property of PVDF/AgNp membrane was furthermore confirmed toward the growth of (Pseudomonas Aeruginosa and Bacillus Cereus) by using the swabbing technique as shown in **Fig 5**. Whereas these types of bacteria did not grow on the compound membrane while the growth of these species of bacteria on the membrane without additions was obvious.

3.3 Analysis of Ag leaching

The amount of released Ag^+ from PVDF/AgNp ultrafiltration membranes during filtration was analyzed by Atomic Absorption Spectrophotometer (AA-7000: Shimadzu, Japan) and is presented in **Fig 6**.The silver released progressively from the PVDF/AgNp-mixed matrix nanocomposite and the concentration of silver in filtered water across the membrane decreases whenever continued water filter together with the increase of time.

From the above, it can be assumed that the releasing of Ag during filtration was mainly from the membrane surface, it can also be said that Ag^+ was the main cause of the membrane resistance against bacterial growth, **Zhang, et al., 2012**. Further, a test of bacterial growth and silver releasing analysis from the surface of the membrane should be balanced for the optimal situation when preparing membranes. Referring to the specification for drinking water of the World Health Organization (WHO), the Ag threshold is limited to 100 ppb **World Health Organization, 2004**. From the above, it can be concluded that the PVDF/AgNp composite UF membranes are a suitable choice for the purpose of water purification, provided that silver released after the filtration process be less or within the permissible limits according to international standards

3.4 Flux and rejection of composite membrane (PVDF/AgNp)

The effect of adding AgNp to the membrane on the flux of permeate during the filtration process experiments was investigated. These experiments were proceeding. **Fig. 7** illustrated the permeate flux of the PVDF/AgNp composite UF membrane during the first 12 hours of testing silver leaching from the membrane surface. **Table 2** shows the flux of permeate of the ultrafiltration composite membrane (PVDF/PVP/Ag)) at the pressure of 0.2 Mpa and pure PVDF membrane. A minimum value of 87.5 L/m2 h of ultrapure water is given for PVDF-0 and an upper value of 261.8 L/m2 h presented for PVDF-1.5, (these results showed in **Fig. 7**, is consistency with the flat sheet performance reported in the literature by, **Xin, et al., 2013**. And it is in agreement with the polyvinylidene fluoride (PVDF) membranes with a typical flux of 130 GFD (Gallons per square foot of membrane per day) which is equal 221 LMH (liter per square meter of membrane per hour) at 0.2MPa were purchased from STERLITCH (GE Osmonics PVDF, YMJXSP3001, USA). As explained above, confirming that the hydrophilicity of the composite membrane surfaces highly effectiveness by the addition of AgNp. The hydrophilicity of membrane has a significant impact on increasing the permeability of the membrane where it will enhance the attraction of water molecules into the membrane matrix and thereby increase the flux. In addition to the above, the content of silver nanoparticles added to the membrane matrix must be within the optimum limits, where any increase occur that can lead to clogged pores of the membrane and thus reduce the permeability and increase the rejection rate. As shown in **Table 2**, mean pore radius increased by adding the AgNp, this may be due to the rapid exchange between the solvent and non-solvent, and this happens through the phase inversion process and thus leads to enlarging the size of the pores of the membrane.

3.5 Analysis of Fourier transforms infrared (FTIR)

The chemical composition of the membranes prepared was examined using the infrared device using (Shimadzu ir-prestige-21). The Fourier transforms infrared spectra of the PVDF-0 membrane (a), and PVDF-1.5 (b), were depicted in **Fig. 8 (a)** and **(b)**. The chemical structure of PVDF-0 membrane was exhibited in **Fig.8 (a)**. The bands located at 3022.45 cm^{-1} and 2980.02 cm^{-1} corresponding to the CH2 symmetric and asymmetric vibration of PVDF. Where it was at the peak absorption at 1400.32 cm^{-1} was attributed to CH2 wagging vibration. The peak at 1180.44 cm^{-1} was related to a C-C band of PVDF, **Madaeni, et al., 2011**. The CF stretching vibration and C–C–C asymmetrical stretching vibration of PVDF were observed at peaks 873.75 cm^{-1} and 862.18 cm^{-1} (Kumar et al. 2009). The chemical structure of modified PVDF/AgNp membrane PVDF-1.5 was displayed in **Fig. 8(b)**. With regard to the pure PVDF membrane has emerged peaks characteristic absorption and retained by the membrane composite, **Fig. 8(b)**. For example, the peaks at 3016.67cm^{-1} and 2978.09 cm^{-1} represented CH2 symmetric and asymmetric vibration was displayed. The peak at 1402.25 cm^{-1} was related to the CH2 wagging vibration of PVDF. In **Fig. 8(b)** for the PVDF membrane was also observed the peak at 839.03 cm^{-1} corresponded to C–F Stretch vibration. Nevertheless, there were some differences between **Fig. 8 (a)** and **(b)**. With the deposition of AgNP, the intense absorption peak at 1662.64 cm^{-1} was observed in the spectrum **Fig. 8 (b)** of the PVDF /AgNP membrane, which might be due to the presence of AgNP, suggesting the formation of AgNP on the modified membrane. Peek at 1662.64 cm^{-1} could not be found in **Fig. 8 (a)**, **Menglong, et al., 2017**.

4. CONCLUSIONS

Modified composite membrane Poly (vinylidene fluoride) (PVDF) incorporation with silver nanoparticles for ultrafiltration was successfully prepared by phase inversion process. The size of AgNp formed within a UF membrane was about 20-30 nm. Variations of surface morphology, performances and antibacterial of PVDF ultrafiltration membranes were verified. All experimental results have proved that the prepared composite membrane properties improved when adding of n-Ag due to the hydrophilicity. The permeability of the composite membranes was improved by adding Ag nanoparticles when the content of Ag^{+} was 1.5 wt %, the ultrapure water flux was increased from 87.5 L/m^{2} h of pure PVDF membrane to 261.8L/m^{2} h of the composite membrane. Modified membrane (PVDF/AgNp) mean pore size and porosity were 280 nm and 85.4% respectively. By using the halo zone test swabbing technique the antibacterial features of the membrane comprising AgNp were measured. An apparent antibacterial property of the modified UF membrane (PVDF/AgNp) against E. coli, Pseudomonas Aeruginosa, and Bacillus Cereus was confirmed by these methods. Reference to the above it can be concluded that the UF composite membrane that has been prepared is very useful in preventing or reducing organic and biological fouling when using the membrane in water treatment and wastewater treatment. Fouling is inevitable; But despite that, reducing the pollution of water treatment membrane making operations more economical, high productivity, and longer operational life and thus less energy consumption.

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Table 1. The compositions of casting solution used in this study (mass %).

	PVDF-0	PVDF-1.5
PVDF(%)	15	15
DMF(%)	81	79.5
PVP(%)	4	4
$AgNO_3$(%)	-	2.36

Table 2. Different performance parameters for PVDF/AgNp membranes.

	ε (%)	Flux (L/m^2h)/	Mean pore radius rm (μm)
PVDF-0	80.5	87.5	0.0126
PVDF-1.5	85.4	261.8	0.0206

Figure 1. Photograph of the dead-end filtration cell (STERLITECH HP4750).

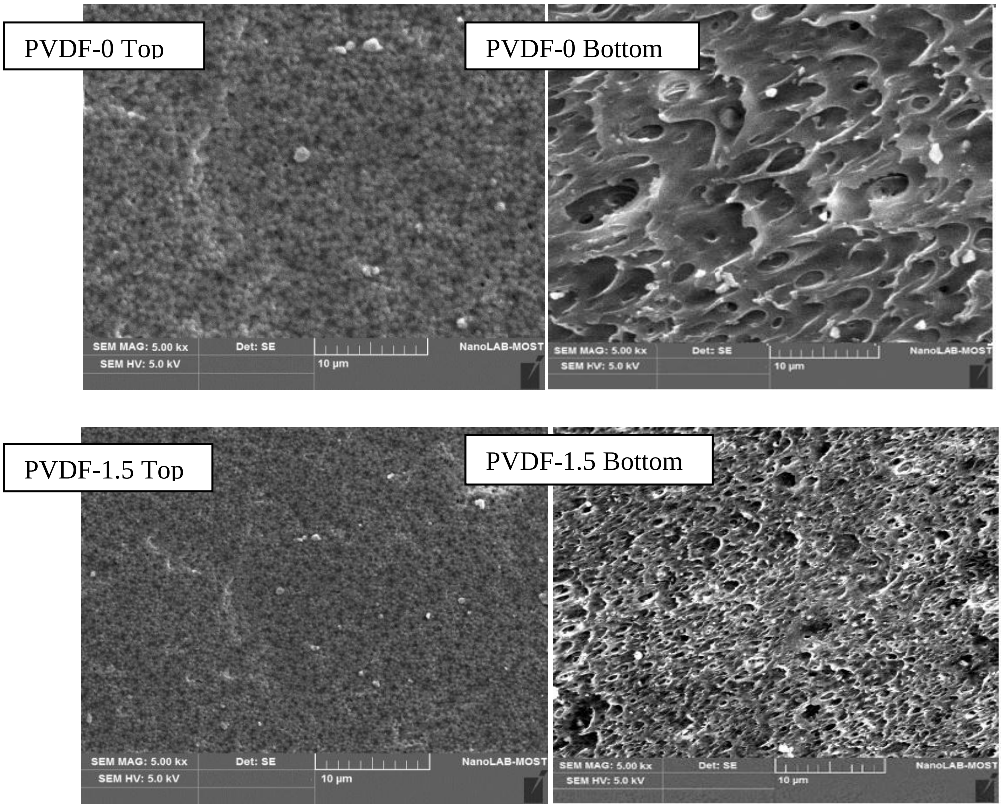

Figure 2. SEM images of the Top surface and Bottom surface morphology: PVDF-0 and PVDF-1.5.

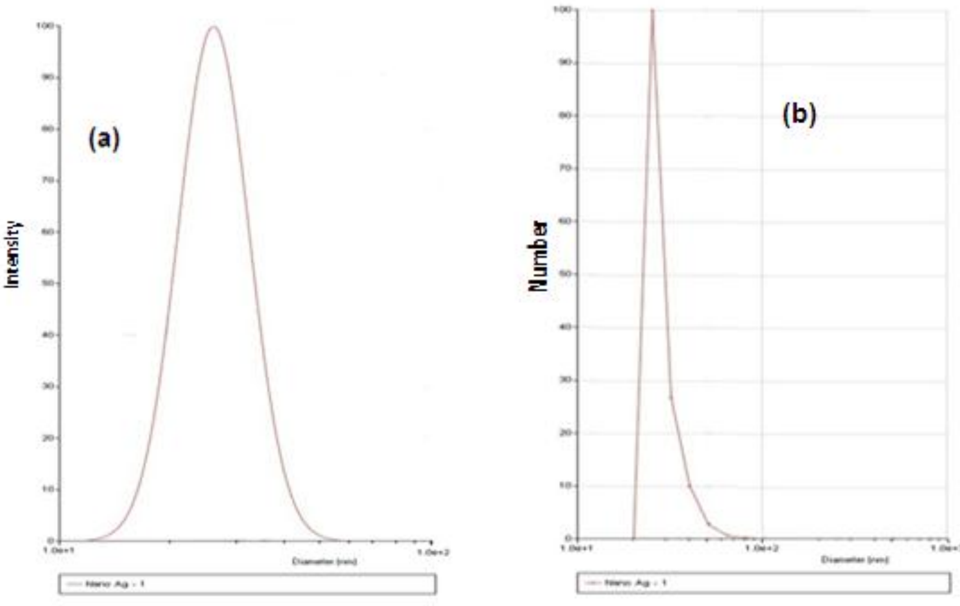

Figure 3. The size of the AgNp (a) Intensity with Ag nanoparticle diameter (b) Number of Ag nanoparticle with the diameter.

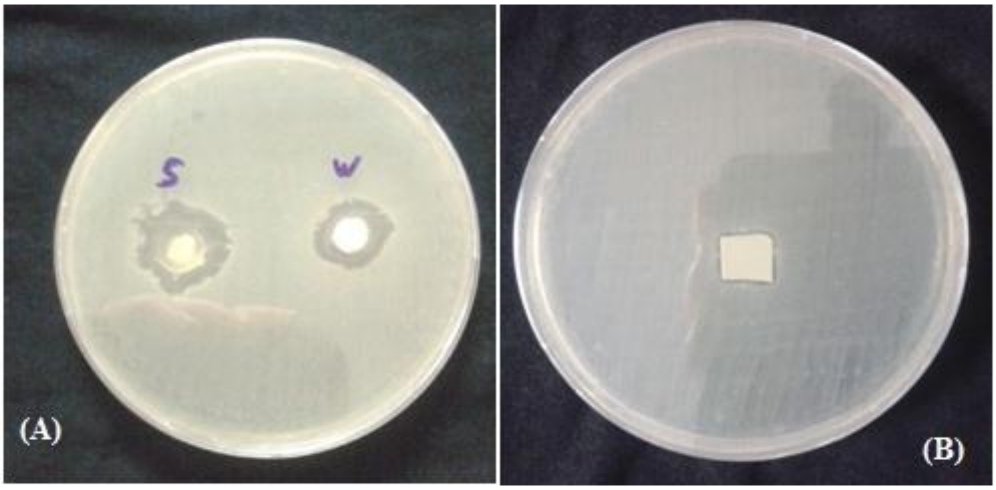

Figure 4. Results of antibacterial activity test(inhibition of *E-coli*) using (A) PVDF/AgNp spot and well (B) PVDF/AgNp membrane, with 15 % PVDF and 1.5% Ag.

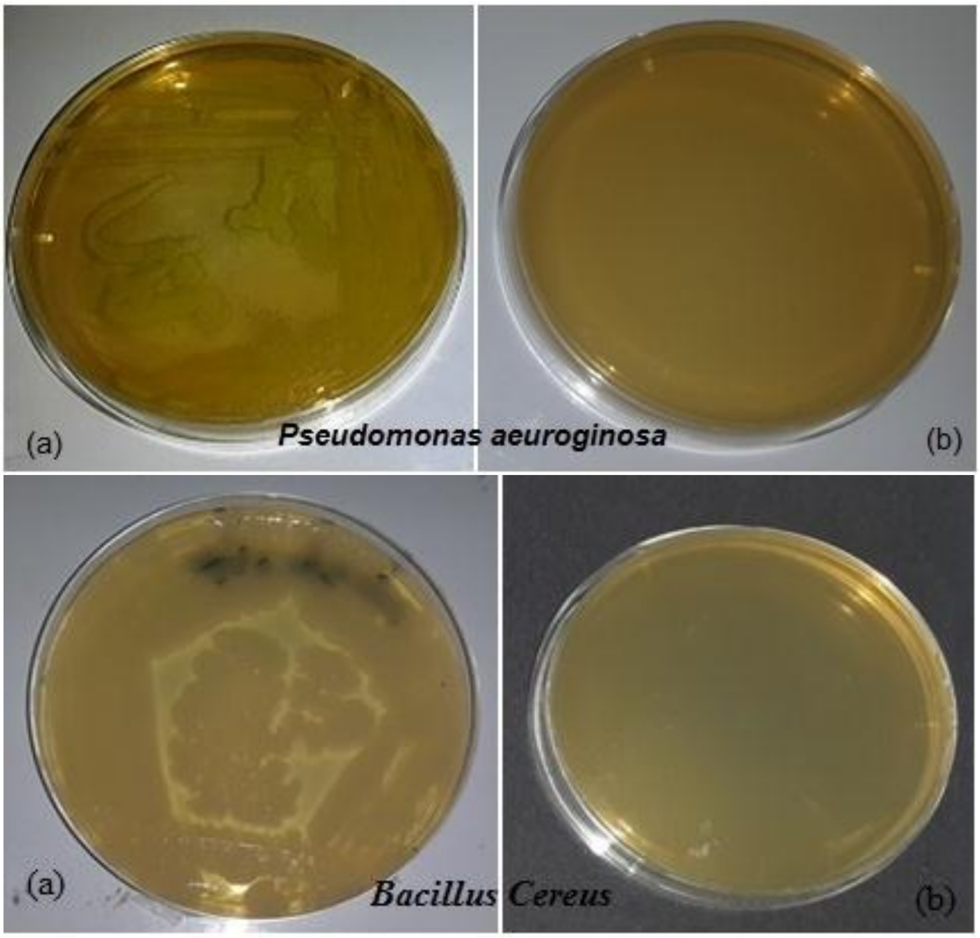

Figure 5. Results of antibacterial activity against (*Pseudomonas Aeruginosa* and *Bacillus Cereus*) test of PVDF/AgNg membrane using swabbing technique

with 15 % PVDF and (A) 0% Ag, (B) 1.5% Ag.

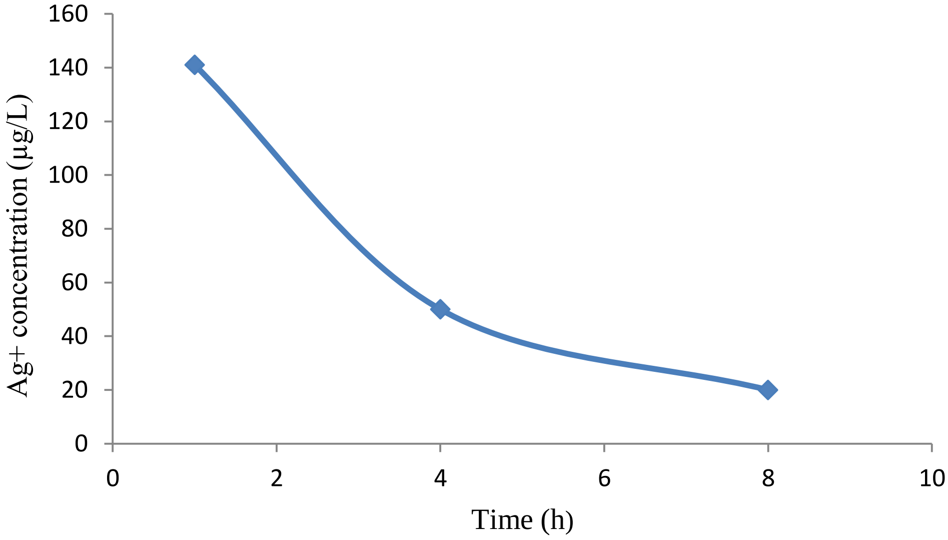

Figure 6. The concentration of leaching Ag in the permeate flux filtrated by the PVDF/AgNp membrane.

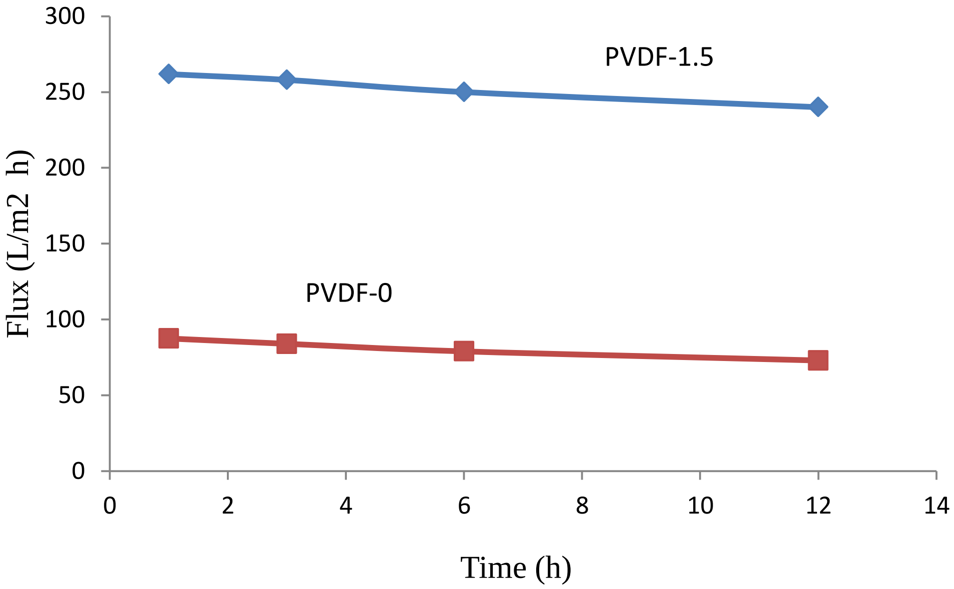

Figure 7. Flux change of pristine PVDF and PVDF/AgNp membrane.

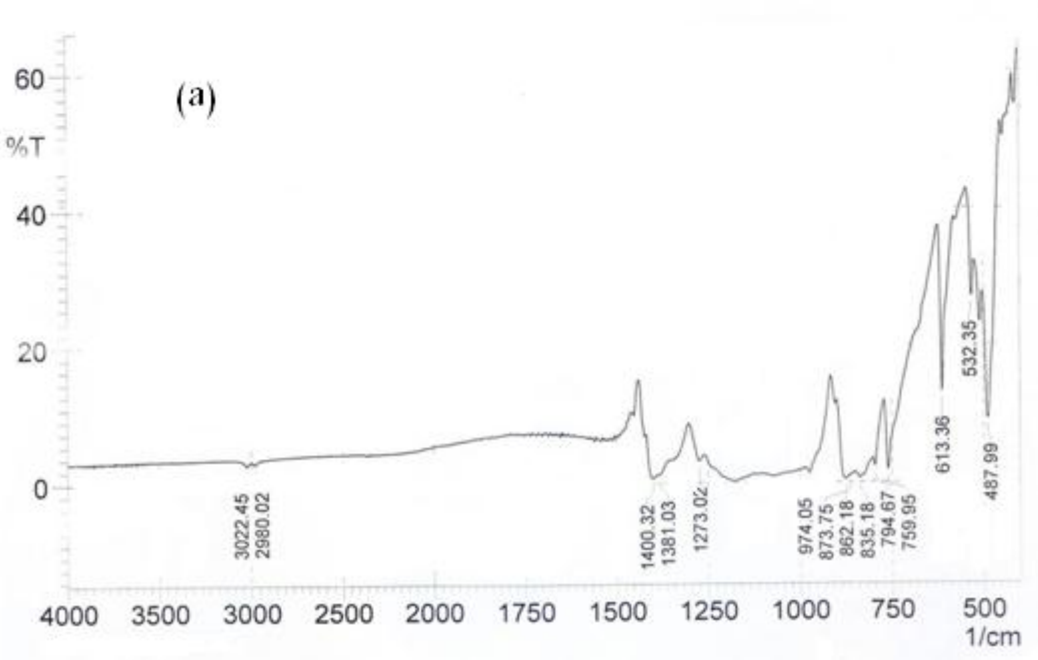

Figure 8 (a). FTIR spectrum: Pure PVDF membranes (PVDF-0).

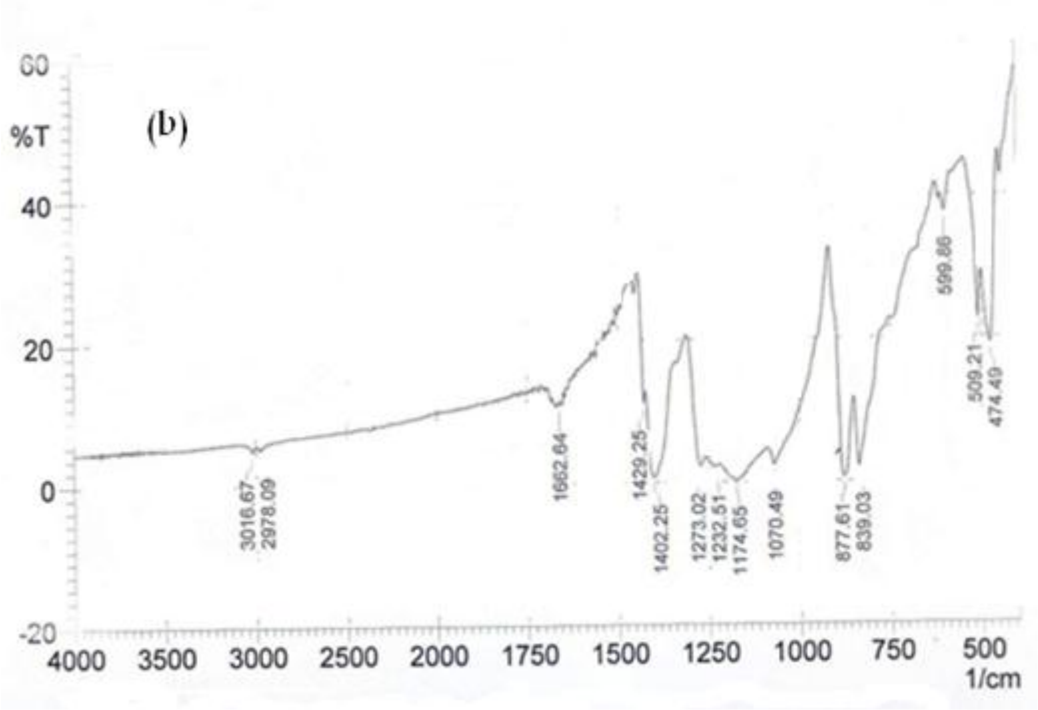

Figure 8 (b). FTIR spectrum: Composite membrane (PVDF-1.5).