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POLYVINYL ALCOHOL/POLYVINYL CHLORIDE (PVA/PVC) HOLLOW FIBER COMPOSITE NANOFILTRATION MEMBRANES FOR WATER TREATMENT

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ABSTRACT

Two different polyvinyl alcohol/polyvinyl chloride (PVA/PVC) hollow fiber composite nanofiltration membranes were prepared after PVC hollow fiber membranes were coated using dip-coating method with PVA aqueous solution, which was composed of PVA, fatty alcohol polyoxyethylene ether (AEO_9), and water [PVA/AEO_9/water (4:0.5:95.5) wt%]. Effect of two different PVC hollow fiber immersion times in coating solution were studied. Cross-section, internal and external surfaces of the PVC hollow fibers and PVA/PVC composite nanofiltration membranes structures were characterized by scanning electron microscopy (SEM), pure water permeation flux and solutes rejection. It was found that, the coating layer thickness on the outer surface of the 19 wt% PVC hollow fiber was thin and about (6µm), while the coating solution penetrates through the outer edge of the PVC hollow fiber and it looks like sponge-like structure with increase of the dip-coating time from 20 to 30 sec. Besides, the pure water permeation flux decreases and solutes rejection increases with an increase of the coating time from 20 to 30 sec for the two PVA/PVC composite nanofiltration membranes.

Molecular weight cut-off (MWCO) of the PVA/PVC composite nanofiltration membranes were in the range of NF (i.e. 200-3000 Mw).

Keywords: Hollow fiber composite membrane; Nanofiltration; Polyvinyl Chloride; Polyvinyl Alcohol**;** Morphology; Separation performance.

INTRODUCTION

The development of nanofiltration technology in separation processes is being widely studied because of its advantages, such as low operation pressure, high flux, high retention of multivalent anion salts and organic molecules above 300 MW. Therefore, it has given rise to worldwide interest [1].

Most nanofiltration (NF) membranes developed to date are composite membranes, with a selective layer on top of the micro-porous substrate. The choice of membrane materials depends on both chemical and physical compatibility of the selective layer with the substrate, which in turn determines the stability and performance of the resulting composite membranes. Several researchers studied different methods for

The preparation of composite NF membranes, for example, vapor deposition, plasma initiated polymerization, photo initiated polymerization, the dip coating method, electron beam irradiation, atom transfer radical polymerization, resin-filled chelating, in situ amines cross-linking, and vacuum coating process [2-10].

Several studies were done on the preparation of the composite NF membrane by coating methods, for example, Nela [11] has studied the preparation and characterization of composite nanofiltration membranes consisting of poly (acrylonitrile) (PAN) ultrafiltration support membrane and polydimethylsiloxane (PDMS) as the selective top layer. Influence of the coating solution concentration upon the membrane performance and the contact time of the membrane with coating solution in dip-coating method were investigated. Tao He [12] studied the preparation and characterization of nanofiltration membrane based on coating of a sulfonated poly (ether ether keton) (SPEEK) layer on top of a polyethersulfone or polysulfone support for ion separation and removal. It was found that the rejection can be improved by an increase in the coating thickness, polymer concentration in the coating solution and the pore size of support membrane. Besides, N, O-carboxymethyl chitosan (NOCC) composite nanofiltration membranes has been prepared using coating and cross-linking method by Miao et al. [13].

Iraq suffers from lack of water in addition to the high salinity in the rivers of Tigris and Euphrates and among the proposals and recommendations for solving this problem is to build systems for water desalination. This leads to the challenge of the fabrication of the hollow fiber nanofiltration membranes for the purpose of the water desalination of Iraqi rivers. In this effort, polyvinyl alcohol/polyvinyl chloride (PVA/PVC) hollow fiber composite nanofiltration membranes were prepared after PVC hollow fiber membranes were coated using dip-coating method with PVA aqueous solution, which were composed of PVA, fatty alcohol polyoxyethylene ether (AEO_9), and water. PVA/PVC composite nanofiltration membranes structures were characterized by scanning electron microscopy (SEM). In the present study, nanofiltration tests were conducted using different solutes of different molecular weights, polyethylene glycol, PEG; and Na_2SO_4.

Materials

Poly vinyl Alcohol PVA (75,000-79,000 Da) in powder form and Fatty alcohol polyoxyethylene ether (AEO_9) were obtained from Sigma–Aldrich Chemical Company, used as coating materials. The hollow fiber membrane was poly (vinyl chloride) used as supported membrane. PVC hollow fiber membranes were prepared in laboratory in previous work and all specifications were summarized in Table 1 [14]. Na_2SO_4 and polyethylene glycol (PEG 600Mw) were used as solutes and obtained from Chem.-supply, S. Australia and Searle Company, England, respectively.

Table 1 *Characteristics of the PVC hollow fiber membranes prepared in previous work [14].*

Membrane type	**I.D. (mm)**	**O.D. (mm)**	**Thickness (mm)**	**Porosity (ε%)**	**Mean pore size (μm)**
PVC 17%	0.680	0.830	0.075	55.81	0.12
PVC 19%	0.720	0.955	0.117	55.60	0.15

Preparation of the PVA/PVC composite NF membranes and post-treatment

For the preparation of the coating solution, PVA/water/AEO_9 (4:95.5:0.5) (concentrations in wt.%) solutions were prepared as follow: PVA was dissolved in water at 90°C with agitation to become PVA aqueous solution. After cooling the PVA aqueous solution to room temperature, AEO9 was mixed with the PVA solution, which was supposed to decrease the solution interfacial tension with PVC hollow fiber surface until the coating solution became homogeneous. Finally, PVC hollow fiber membranes were coated by dip-coating method, where the hollow fibers were immersed in the coating solution for 20 and 30 seconds. The PVA-coated PVC hollow fiber composite membranes were then dried at room temperature. The final PVA/PVC hollow fiber composite nanofiltration membranes were obtained after heat treatment in an oven at 70 ºC for two hours.

SEM observations

The membrane's morphology was observed by using scanning electron microscope (Cambridge Stereoscan 360). Fibers cross sections were prepared by freeze fracturing the samples in liquid nitrogen, to produce a clean brittle fracture. The internal and external surfaces were also observed.

Measurements of permeation flux and solute rejection

Three pieces of hollow fibers were sealed into stainless steel tube with two stainless steel tees to make the lab-scale modules with 20 cm effective length and 0.5 cm inner diameter. These modules were left overnight for curing before testing in terms of permeation flux and solute rejection. Each module was immersed in distilled water for 24 hours, and run in the test system for one and half hours before any sample collection.

Fig. (1) shows a schematic diagram of solute–water separation unit. At a transmembrane pressure 1 bar and feed solution temperature 25 ºC, all experiments were performed in hollow fiber modules. Three modules were prepared for each hollow fiber sample. Pure water permeation fluxes (PWP), were obtained as follows:

$$J_w = \frac{Q_w}{\Delta P\, A_s} \qquad (4)$$

where J_w is the permeation flux of membrane (l/(m^2.h.bar)), Q_w is the volumetric flow rate (l/h), ΔP is the transmembrane pressure drop (bar), and A_s is the membrane surface area (m^2). Na_2SO_4 and PEG 600Da with 1000 ppm were used for the measurement of solute rejection of each hollow fiber module, respectively. The membrane rejection R (%) is defined as:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (5)$$

where C_f and C_p are the solute concentration in feed and permeate solution respectively. The concentration of Na_2SO_4 was determined based on conductivity meter (Model DDS-307). While the concentration of PEG 600Mw in feed and permeate streams were determined by using Dragendorff reagent. 5 ml of PEG solution were kept in 10 ml volumetric flask and mixed with 3 ml of 0.05 M HCl, then 1 ml of Dragendorff reagent was added and the volume of the mixture was completed with 0.05 M HCl. After at least 15 minutes, the solution concentration was measured based on its absorbency with UV-spectrophotometer (Cary-Australia) at 510 nm [15].

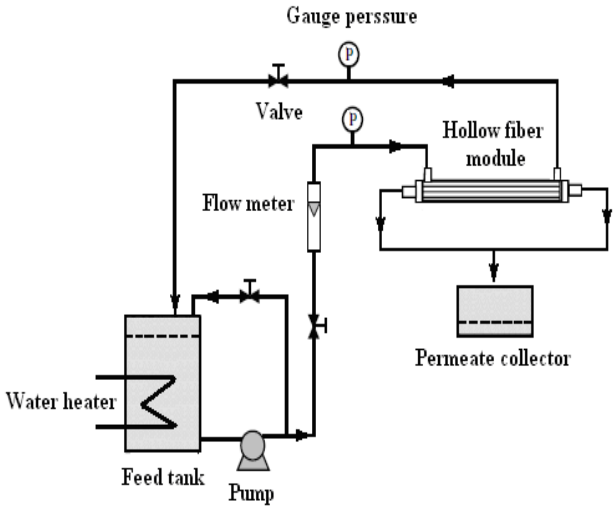

Fig. 1 *Schematic diagram of the NF experimental set-up.*

RESALUTS AND DISCUSSION

PVA/PVC hollow fiber composite NF membranes have been prepared by deposition of PVA selective layer on PVC hollow fiber membranes using dip-coating method. Polyvinyl alcohol (PVA) is one of the strong hydrophilic materials that is suitable for the separation of aqueous mixture [16]. Two different PVC hollow fiber membranes were prepared in previous work used as a supported membrane for the preparation of NF composite membrane and the characteristics of the PVC hollow fiber membranes are summarized in Table 1 [14]. Figures 2-5 show the SEM cross-section and external surfaces images for the two hollow fiber membranes prepared from 19 and 17 wt% PVC before and after coating, respectively. It can be seen that two small finger-like structure layers are situated at both edges of the hollow fiber and the layer has large macrovoids in the shape of finger-like structure and there is a sponge-like structure situated between the large macrovoids structure and the outer finger-like in Figure 2A. Figure 2B shows the effect of 20 seconds dip-coating time of the PVC membrane in PVA / AEO_9 / water (4:0.5:95.5) (concentrations in wt.%) solution on the outer surface of the membrane. It can be seen that the coating layer thickness on the outer hollow fiber surface was thin and about (6µm), while the coating solution penetrates through the outer edge of the PVC hollow fiber and it looks like sponge-like structure with increase of the dip-coating time to 30 seconds as shown in Figure 2C. Yangishita et al. [5], observed that the composite membranes after coating by 1 wt% poly(amic acid)tri-ethylamine salt (PAA salt) methanol solution did not show finger-like structure because the coating solution penetrated into the supporting membrane, and filled up in the finger-like structure. In Figure 3, the porous external surface was changed to dense and rough surface (no pores) after coating with 20 and 30 sec.

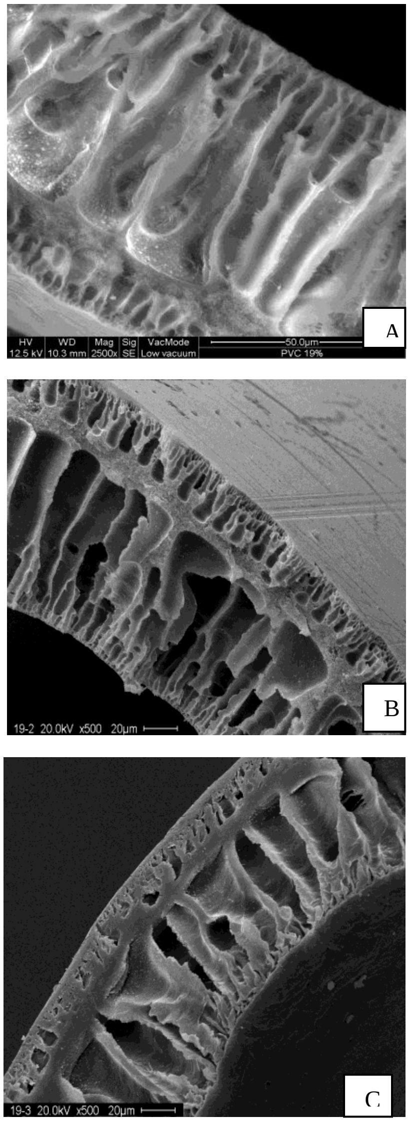

Figure 2 SEM cross-section images for the hollow fiber membranes prepared from 19 wt% PVC**,** (A) without coating, (B) coating time is 20 sec (C) coating time is 30 sec.

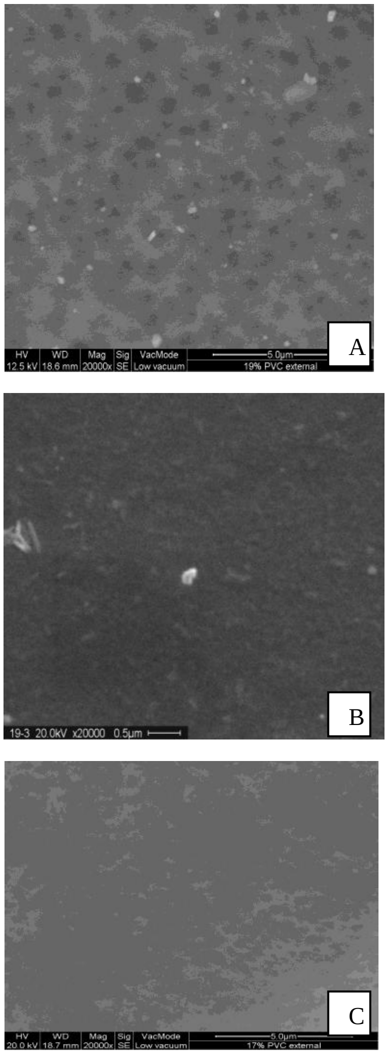

Figure 3 SEM external surface images for the hollow fiber membranes prepared from 19 wt% PVC**,** (A) without coating, (B) Coating time is 20 sec (C) coating time is 30 sec**.**

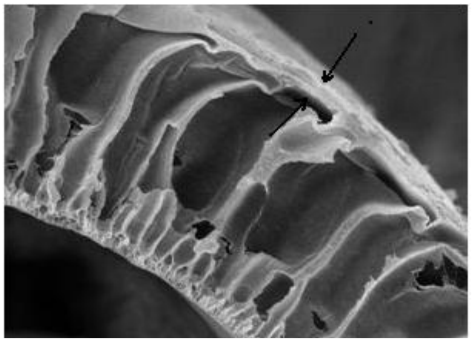

Figure 4 SEM cross-section image of the hollow fiber membrane prepared from 17 wt% PVC with 20 seconds coating time.

From the cross-section SEM images of the hollow fiber membrane prepared from 17 wt% PVC and after dip-coating with PVA/water/AEO_9 (4**:**95.5**:**0.5) (concentrations in wt.%) solution it can be seen that there is a distinct coating layer over porous support layer without pore intrusion as shown in Figures 4. This might be explained as the external skin layer having small pore size which is sealed by coating solution; consequently, the thickness of skin layer has been increased. In agreement, Jansen et al. [17], has explained that the average pore size, and thus the molecular weight cut-off of the membranes was sufficiently small to avoid penetration of the polymer molecules in the pores, so that

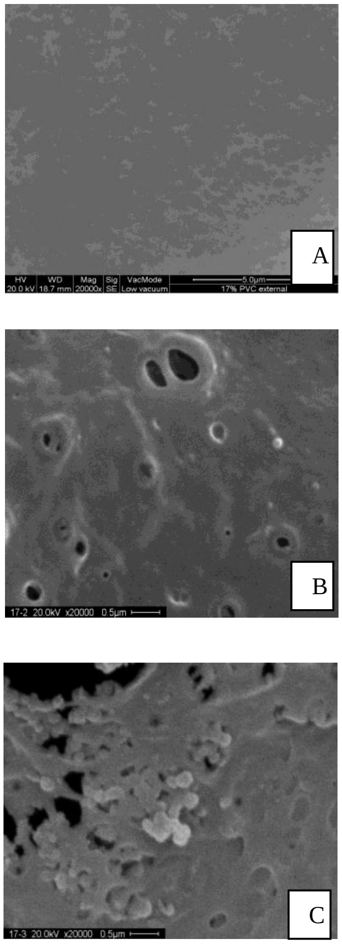

Figure 5 SEM external surface images for the hollow fiber membranes prepared from 17 wt% PVC**,** (A) without coating, (B) coating time is 20 sec (C) coating time is 30 sec**.**

only a thin film of the polymer is formed on the support surface. The increasing of skin layer thickness has more influence on decreasing permeate flow and in the same time will ameliorate the retention function of the membrane. On the other hand, there are no distinct surface pores indicating that pore size has been largely decreased as shown in Figure 5. The surface defects shown in Figure 5B and 5C probably due to the shrinkage of the film during the evaporation of the last traces of the solvent from the film, this phenomenon which is also observed in membranes prepared by Jansen et al. [17].

Table 2 shows effect of coating time on the PVA/PVC composite hollow fiber nanofiltration membranes performance.

It can be observed that the permeation flux of all hollow fiber nanofiltration membranes have largely decreased compared with those bare fibers. Moreover, the permeation flux decrease and solutes rejection increased with an increase of coating time. For hollow fiber NF membrane prepared from 17% PVC, the permeation flux has declined by 61% with 20 seconds coating time compare to bare fiber and further decreased when coating time is increased to 30 seconds. On the other hand, the PEG 600Da rejection significantly increased with coating time. These results imply that the coating layer thickness increased with coating time. Nela [11] found that the thickness of top layer was increased with increasing of the contact time with coating solution.

Table 2 PVA / PVC composite hollow fibre nanofiltration membranes performance

Membrane type	**Coating time (sec)**	**PWP[1] before coating**	**PWP[1] after coating**	**Na_2SO_4 Rejection (R %)**	**PEG600 Rejection (R %)**
PVC 17%	**20**	**66.5**	**25.3**	**6.42**	**1**
PVC 17%	**30**	**66.5**	**8.2**	**Nm***	**60.3**
PVC 19%	**20**	**129**	**9.0**	**10.5**	**13**
PVC 19%	**30**	**129**	**5.9**	**6.5**	**49**

***: Not measured.**
1: Pure water permeability in $Lm^{-2}.hr^{-1}.bar^{-1}$

In the case of hollow fiber NF membranes prepared from 19% PVC, the permeation flux decreased by 93-95% compared to that obtained from uncoated hollow fibers, while the solutes rejection increased when the coating time was increased from 20 to 30 seconds. From Figure 2 the finger-like structure beneath the outer skin layer was filled up with coating solution, thus there was much reduction in permeation flux and this is attributed to the higher resistance through the support membrane. According to the results mentioned above, hollow fiber NF composite membranes have a good NF characteristic membrane with permeation flux in the range of NF membranes (i.e. 5-15 $l.m^{-2}.hr^{-1}.bar^{-1}$), and 60% solute rejection for PEG 600Mw suggests that MWCO would be in the range of NF (i.e. 200-3000 Da).

CONCLUSIONS

PVA/PVC hollow fiber composite membranes were prepared for aqueous nanofiltration separation systems, using dip-coating method. The effects of coating time on the structural morphology and performance of the resulted membranes were studied. The structure and performance of the membranes were characterized by Scanning electron microscope (SEM), permeation flux and solutes rejection. It was found that the permeation flux of the prepared NF composite membranes highly decreased with coating time on the base membranes with increase of the solute rejection. Besides, the coating layer thickness on the outer hollow fiber surface was thin and about (6μm), while the coated solution penetrates through the outer edge of the PVC hollow fiber and it looks like sponge-like structure with increasing dip-coating time to 30 seconds. The molecular weight cut-off of the prepared hollow fiber NF composite membranes was 1000 Da.

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الخلاصة

تم تحضير نوعين من اغشية الالياف المجوفة والنانوية المكونة من PVA/PVC بواسطة طريقة الاكساء بالتغطيس في محلول PVA المائي المكون من بولي فنيل الكحول PVA ، الماء و Fatty Alcohol (AEO_9) Polyoxyethylene Ether وبنسب وزنية مئوية(0.5, 95.5, 4) على التوالي.
تم دراسة تاثير وقتين مختلفين لزمن اكساء اغشية الالياف المجوفة على التركيب الداخلي والخارجي لاغشية الياف PVA/PVC المركبة والنانوية باستخدام جهاز المجهر الالكتروني الماسح (SEM) وايضا على اداء الاغشية في فصل المذابات وانتاج الماء النقي. وجد ان سمك طبقة الاكساء للالياف المحضرة من19% PVC كان رقيقا وبسمك 6µm بينما يدخل محلول الاكساء خلال السطح الخارجي ويسد التراكيب الاصبعية الشكل عندما يزداد زمن الاكساء من 20-30 ثانية. بالاضافة الى ذلك، تقل نفاذية الماء النقي ويزداد فصل المذابات بزيادة زمن الاكساء من 20-30 ثانية لكلا نوعي الالياف المجوفة النانوية. ان الوزن الجزيئي للمذابات المفصولة(MWCO) لاغشية الياف PVA/PVC المجوفة النانوية كان ضمن مدى اغشية الفصل النانوية (200- 3000 Da).