Preparation and Characterization of Poly (Vinylidene Fluoride)/MCM-41 Nano-Composite Flat Sheet Membrane for Water Purification

Dr. Abdulkhaleq Kamal Mahmood,

Middle Technical University, Head of Water Resource Department, Kut Technical Institute.

Asst. Lecturer Nabil KadhimTaieh

Middle Technical University ,Technical Engineering college, Materials Engineering Department.

Mobile No: +9647801035785.

Abstract:-

In this research, an effort has been done to enhance the Poly vinylidene fluoride (PVDF) membrane by addition of mobile composition of materials (MCM-41) nanoparticles prepared by chemical reaction for water purification. The membranes were prepared by wet phase inversion method, using N, N-dimethylformamide (DMF) as solvent and different percentage weight of MCM-41 nanoparticles (0.0, 0.01, 0.02, 0.04, 0.06, 0.1). The membranes structure and properties were characterized by scanning electron microscopic (SEM) and atomic force microscopic (AFM). The investigation of the effect of addition of MCM-41 nanoparticles to the polymer mixture shows no change in the morphology while an increase of the hydrophicity and porosity occurs, which lead to an increase about 19.2 % of water flux at optimal concentration (0.04wt% of MCM-41) at pressure 4 bars and temperature 23±1^{0}C. Mechanical properties of the PVDF membranes containing 0.04 wt. % of MCM-41 shows an increase in tensile stress about 18% relative to membrane without nanomaterial's.

Key words:- **poly vinylidene fluoride, membrane, MCM-41 water, purification.**

1. Introduction

In recent year, Membrane are used increasingly for water purification for removal of particulates, microorganisms, bacteria, heavy metals , and natural organic and inorganic material, which can influence the color, tastes, and odors to water and may be form disinfection byproducts by their reaction with disinfectants.

Microfiltration (MF) and ultrafiltration (UF) membranes are fabricated of different types of materials, such as cellulose acetate, poly vinylidene fluoride, poly acrylonitrile, polypropylene, poly sulfone, poly ether sulfone. These materials have different properties related to their strength, flexibility, degree of hydropholicity, and surface charge.

Now a days, poly vinylidene fluoride (PVDF) has been used more than other materials for membranes such as poly sulfone (PS), poly ether sulfone (PES) and polyimide (PI) in industrial application such as distillation and membrane contract, due to their easy dissolve in most organic solvent and their excellent thermal stability [1].

Although polypropylene (PP) and polytetrafluroethylene (PTFE) are more hydrophilic than PVDF but their application are limited due to their complexity in solvent selection.

Porous PVDF membranes can be syntheses via thermally induced phase inversion method or wet phase inversion methods. The latter is a simple immersion precipitation process and more applicable in industrial use. [2]

Table 1.1 shows some of published papers of PVDF membrane from 2008 to 2013.

Table 1.1 Some of published papers of PVDF membrane from 2008 to 2013.

Researcher	Type of polymer	Solvent type	The geometry	Year
Zhao Liang et al.[3]	PVDF	Acetyl tri butyl citrate (ATBA)	Flat sheet, Hollow fiber	2013
Ji et al. [4]	PVDF	DBP, di(2-ethylhexyl) phthalate(DEHP)	Flat sheet	2008
Li et al. [5]	PVDF	DBP	Flat sheet	2008
Lu et al. [6]	PVDF	DBP, DOP	Flat sheet	2009
Lin et al.[7]	PVDF	DPC	Flat sheet	2009
Tang et al.[8]	PVDF	DPK,1,2-propylene glycol (PG)	Flat sheet	2010
Ma et al.[9]	VPDF/poly methyl methacrylate (PMMA)	Methyl salicylate (MS), benzophenone (BP)	Flat sheet	2011
Rajabzadeh et al. [10]	PVDF	Diethyl phthalate (DEP)	Hollow fiber	2102

Recently, one of the attractive methods used by the researchers in synthesis of polymeric membranes is addition of inorganic nanomaterial. Inorganic nanomaterial that have been integrated into PVDF membranes comprise TiO_2 [11], Al_2O_3 [12], ZrO_2 [13], and SiO_2 [14].

Inorganic nanoparticles has been added to PVDF membrane to improve their properties such as fouling resistance, hydrophlicity, tensile stress, mass transfer, and selectivity.

The objectives of the present study is preparation of PVDF ultrafiltration membrane by wet phase inversion method, and investigation the effect of addition of MCM-41 nanoparticles to the polymer mixture on the morphology, hydrophicity, pore size, pore distribution, mechanical properties and water permeability for membrane used for water purification.

2. Experimental work

2.1 Materials

Poly (vinylidene fluoride) $(C_2H_2F_2)x$-, Sigma-Aldrich, laboratory chemicals. Appearance form: pellets, color: white, relative density 1.78 g/mL at 25 °C dissolved in N,N dimethylformamide (DMF, 99.8%, Aldrich) used as solvent for the fabrication of the membrane. A modified MCM-41 nanomaterial was produced by chemical reactions [15] , and used as additives. Deionized (DI) water produced by Millipore DI system from local market (18.2 MΩ.cm) was used for solution preparation and filtration study. Kerosene was purchased from local market for porosity determination. Chemicals used are ACS reagents.

2.2 Preparation of PVDF membrane

Poly (vinyldene fluoride) membrane was prepared using the phase inversion casting method. 15 gm of PVDF were heated in oven at 150 ^{0}C for 5 hours to degassed, and then dissolved in 85 gm of N, N-dimethylformamide (DMF) for the 15.0 wt. % concentration.

The mixture was stirred at 500 rpm with 50 C^0 for 24 hours. The function of stirrer is to ensure a good mixing between polymer (PVDF) and solvent (N-N DMF) to obtain a homogeneous solution. The thermometer measured the temperature during the mixing process and to reduce the amount of bubbles in the solution the casting solution was kept in dark. A knife of stainless steel was used for membrane casting. The thickness of polymer casting taken approximately 200 µm. The glass plate was moved and soaked in water its temperature (23 ± 1.0 ^{0}C) to remove residual solvents. The membrane was then washed with DI water (18.2 MΩ. cm) and stored in DI water at 4 ^{0}C. For PVDF membrane containing different ratio of MCM-41, predetermined amounts of MCM-41

(0 – 0.1 wt. %) were added to the PVDF casting solution. Six samples were prepared (0.0, 0.01, 0.02, 0.04, 0.06 and 0.1wt. %) to study the optimal tensile strength and membrane performance. Membranes marked as 0.04 wt. % MCM-41 refer to membranes prepared in a casting solution in which the content of the MCM-41with respect to (PVDF +N-N DMF) was 0.04 wt. MCM-41 was sonicated for 1hr in casting solution before addition of the polymer to the solution. Table 2.1 shows the physical properties of MCM-41 nanomaterial which previously prepared by chemical reaction [15].

Table 2.1 Physical properties of synthesis MCM-41[15]

sample	a_0 (nm)	S_{BET} (m^2/gm)	V_{meso} (cm^3/gm)	d_p (nm)	W_t (nm)
MCM-41	4.03	958	0.67	3.13	0.9

Where a_0 is the distance between two successive pores, S_{BET} is surface area, V_{meso} is volume of mesopore, d_p is diameter of pore, and W_t is the thickness of pore wall.

2.3 Characterization of PVDF Membranes

The membrane cross section and morphology were characterized by SEM. (SEM Model: TESCAN-VEGA/USA).

The membranes samples were coated with gold to increase their electric conductivity before showing with SEM.

The surface morphology of the fabricated membranes is analyzed by the AFM device (Spm Ntegra NT-MOT) from (Ministry of Science and Technology-Baghdad-Iraq). The surface morphology is explained by the mean roughness's, the root mean roughness and mean differences between highest and lowest point.

2.4 Porosity

Five samples of each type of PVDF membrane were used to find the porosity. The samples were firstly weighed dry, then the samples are soaked in kerosene for 48 h. the wet weigh also measured and the porosity of each sample was calculated according to the following correlation:

$$\varepsilon = \frac{(m_w - m_d)/\rho_w}{(m_w - m_d)/\rho_w + m_d/\rho_p} \times 100\% \quad (2\text{-}1)$$

Where m_w and m_d are the weights of the wet and dry membranes, respectively, and ρ_w and ρ_p are the kerosene and polymer densities, respectively. Finally the average values for each type are reported.

2.5 Measurement of Pore Size Distribution and Mean Pore Size

The mean pore size distribution and pore size of different types of PVDF/ MCM-41 membranes were determined by MEGA program used with AFM techniques in laboratory. (Ministry of Science and Technology-Baghdad- Iraq).

2.6 Water uptake and Contact Angle Measurement

The water uptake of the PVDF ultrafiltration membrane containing different ratio of MCM-41 were determined by the gravimetric method.

Five samples of each type of membrane (10 *10 mm) were weighed dry and then soaked in DI water for 24 h, and weighed again after removing the excess water on the surface. The water uptake was calculated according to the following correlation:

$$U = [(W_W - W_d) / W_d] * 100 \quad (2\text{-}2)$$

Where W_w is the wetted weight, W_d is the dried weight of the samples and U is the water uptake ratio.

Five samples of each type of PVDF are also used with distilled water to measure the average contact angle. Multiple droplets can be deposited in various locations on the sample to determine heterogeneity.

The instrument (CAM 110, Germany) was used to measure the contact angle (Membrane Laboratory, Chemical Engineering Department /University of Technology).

2.7 Water permeability

The experiments were carried out at room temp. (23 ± 1^0C). Cross flow filtration system was used to conduct the test. A 47 mm diameter (effective surface area 12.56 cm^2) membrane coupon was tested and three specimens for each composition. Initially each membrane sample was pressurized at 6 bars for I hour, and then the pressure was lowered to the operating pressure of (0.5-4) bars. A mechanical pump controlled by pressure regulators used to pressurized the membrane module and then the pressure was lowered to the operating pressure (0.5-4 bars). The cumulative pure water flux was weighted by an electronic balance and then the pure water flux was calculated according to

J=V/A*T (3-3)

Where J is the permeable flux (L/m^2*h) , V is the volume of permeate(liter), A is the effective membrane surface area(m^2) and T is the time(hour) .

2.8 Mechanical Properties

The mechanical test were conducted at room temperature ($23\pm1C^0$) using a tensile testing machine (Instorn model 4500, canton, MA) with an extension rate of 50mm/minute. Tests were conducted according to ASTMD638-10. Five samples of each types of PVDF membrane were tested for tensile strength, percentage of elongation, and elastic modulus. Specimens with dimension 63.5mm in length and 3.3 mm in width were used.

3. Results and Discussion

3.1. Membrane Morphology of MCM-41/PVDF Membranes

The morphology of the PVDF membrane is affected greatly by the concentration of polymer, quenching temperature and Nano particles as additive. The morphologies of membrane fabricated no.1 (0 % wt. MCM-41) and membrane no.4 (0 % wt. MCM-41) shows In fig. 3-1, the surface structure of the 0 % MCM-41 (membrane no. 1) has high roughness. In addition, It can be seen that the outer surface of flat sheet membrane synthesis from concentration 0.04%.wt modified MCM-41 nanoparticles have smooth surface morphologies and high porosity compared with membrane no.1.

With an increase in the concentration of modified MCM-41in cast solution the exchange of the solvent system was increased through the phase separated polymer solution, which increases the porosity in the polymer phase. The cross-section of membrane structure of PVDF/MCM-41 nanocomposite membrane form nos. 1 and 4 cast solutions are shown in fig. 3-2. From this figure the PVDF/MCM-41 membranes have the similar structure.

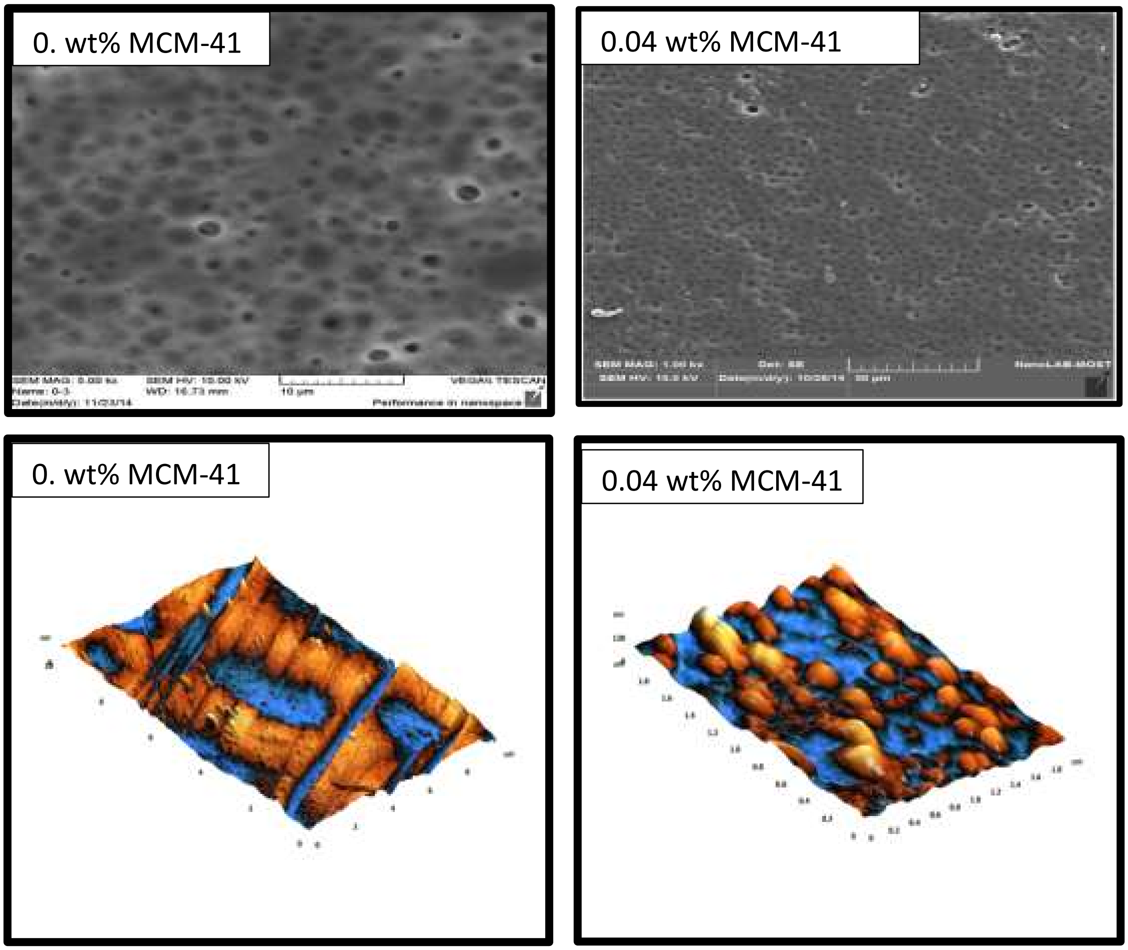

Fig 3-1. SEM and AFM Images of MCM-41/ PVDF Flat sheet Membrane.

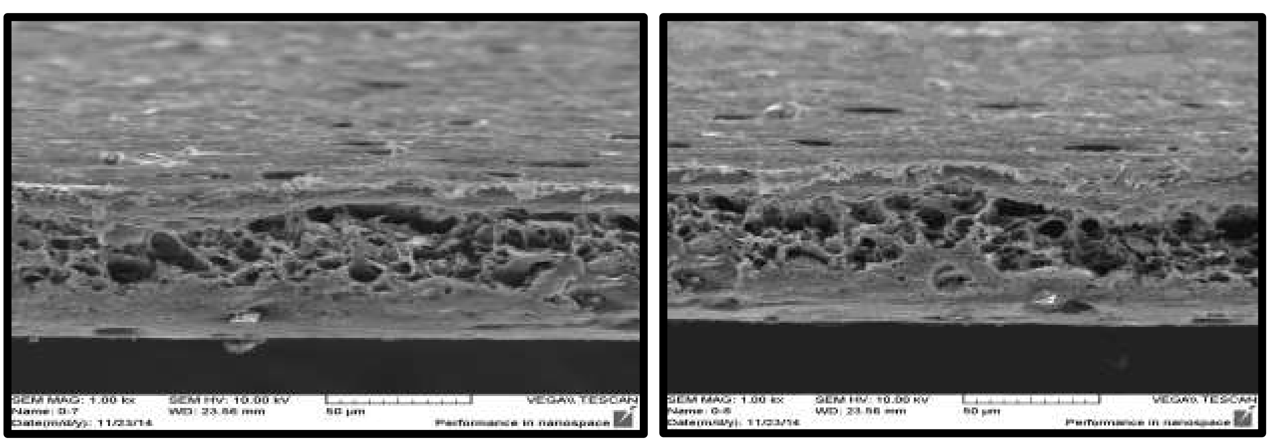

Fig 3-2. Cross-section structures of MCM-41/ PVDF Flat sheet Membrane(SEM).

3.2. Pore size, porosity, water uptake and contact angle

Pore size, porosity, water uptake and contact angle are critical for performance data analysis and in choosing the perfect flat sheet membrane for nanocomposite membrane preparation.

Table 3-1 shows mean pore size and porosity of membranes fabricated of different ratio of MCM-41 nanoparticles . As MCM-41 concentration increased in cast solution, porosity and water uptake also increased till 0.04 wt.% then they are decreased.

Furthermore, from table 3-1, membrane no. 1(0.0 wt.% MCM-41), membrane no. 2 (0.01 wt.% MCM-41), membrane no. 3 (0.02 wt.% MCM-41), membrane no. 4 (0.04 wt.% MCM-41), and membrane no. 5 (0.06 wt.% MCM-41) it can be noticed that the addition of MCM-41 nanoparticles cannot affect any change in membrane mean pore size, meanwhile increasing porosity. Nanoparticles in a polymer matrix can obstruct its chain packing, which increases the free void in the polymer phase.

Table 3-1 Show the PVDF membrane with different percent of added MCM-41 nanomaterial with their mean pore size and porosity.

No.	Percent of MCM-41 in PVDF membrane	Mean pore size(μm)*10^{-1}	Porosity (%)
1	0.0	0.125	0.69
2	0.01	0.116	0.72
3	0.02	0.127	0.76
4	0.04	0.123	0.79
5	0.06	0.132	0.70
6	0.1	0.122	0.71

Table 3-2 Water uptake and contact angle of PVDF membrane fabricated with different ratio of MCM-41 nanomaterial.

No.	Percent of MCM-41 in PVDF membrane	Water up take %	Contact angle degree
1	0.0	12	87
2	0.01	16	79
3	0.02	25	73
4	0.04	32	66
5	0.06	35	74
6	0.1	28	77

3.3 Mechanical Properties

The impacts of MCM-41nanoparticles on mechanical properties of flat sheet membranes are shown in table 3-3. Indicate that with increasing content of MCM-41 nanoparticles, tensile strength and elongation ratio of the membranes significantly increased at first, increasing tensile strength and elongation due to decreases the motion of polymer molecules, which leading to increase the resistance of a material to plastic deformation [19]. In addition, Tensile strength and elongation ratio of membranes decreased slightly at 0.06 % MCM-41, due to accumulation and segregation of MCM-41in polymer matrix. However, the mechanical property of filled membranes is much better than that of pure PVDF membrane.

Table 3-3 Mechanical properties of the polyvinyldene fluoride membrane with and without mcm-41

No.	Specimen	Tensile stress MPa	Elongation %
1	PVDF 0 wt.% MCM-41	1.98±0.8	6.66±1.38
2	PVDF+ 0.01wt.% MCM-41	2.11±0.6	6.12±1.28
3	PVDF + 0.02wt.% MCM-41	2.22±0.95	6.10±0.65
4	PVDF + 0.04wt.% MCM-41	2.33±0.55	6.94±1.12
5	PVDF + 0.06 wt.% MCM-41	2.15 ±0.70	6.94±1.24
6	PVDF+ 0.1wt.%MCM-41	2.05±0.65	6.90±1.15

3.4. Pure water flux (Water permeability)

The pure water permeation test show that an increases of water flux from 545 to 650L/ m^{2}h, which represent 19.2% by addition of 0.04wt. % modified MCM-41 nanoparticles. Mostly, adding of nanoparticles in a polymer matrix can obstruct its chain packing, which increases the free void in the polymer phase. In addition, voids at the polymer-particle interface or between particles in particle aggregates result in an increase in total porosity [19].

Increased total porosity cause increases in water permeability and in this way lead to pure water flux to be larger in MCM-41 nanocomposites membrane than in pure polymer. Good dispersion of particles in the polymer matrix enhances the specific surface area and pore volume of particles in membranes. Since modified MCM-41 is a hydrophilic material was used an additive for the preparation of PVDF flat sheet membranes, results of membrane no. 1 (0.0 wt.% MCM-41, the flux = 545 (L/m^2.h)) and membrane no. 4 (0.04 wt.%MCM-41, the flux = 650 (L/m^2.h)) are consistent with what have been predicted.

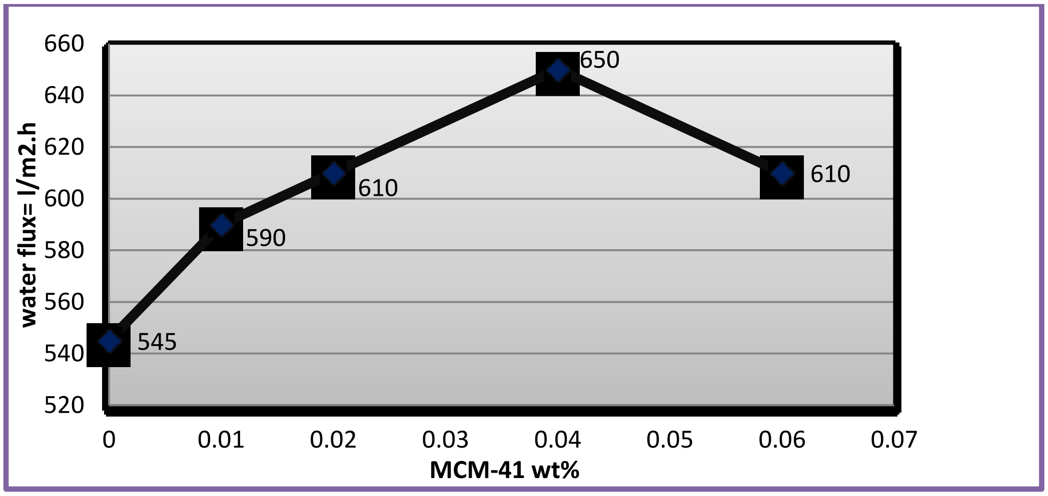

Fig 3-3. Water flux of PVDF membranes containing different ratio of MCM-41 at pressure 4 bar and temp. 23±1^{0}C.

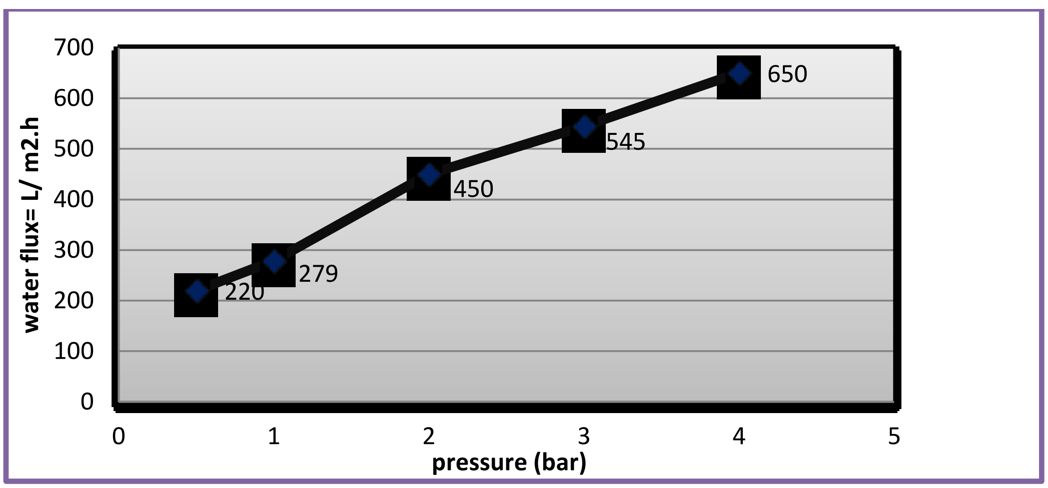

Fig 3-4. Water flux of PVDV membrane containing 0.04wt% of MCM-41 nanomaterial's at different pressure and at temp.23±1^{0}C.

4. Conclusion

The results showed that the addition of MCM-41 nanoparticles not affected the morphology of the PVDF membrane, even though an increase of hydrophilicity representing by increasing porosity, roughness, and contact angles occurs due to addition of MCM-41 nanomaterial. The pores structures and the negative charge of nanomaterial lead to an increase of permeability about 19.2% at optimal amount of 0.04%wt. MCM-41 nanomaterial also provide an improvement in tensile strength to PVDF membrane about 22%, this was observed even at low concentration of 0.04%wt.

Acknowledgment

The author wish to acknowledge the Nano Center Research (University of Technology) / Bagdad and Iraqi Ministry of Science and Technology.

References

1- **A.** F. Liu Hashim, Y.T. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of PVDF membranes, J.Membr.Sci.375 (2011)1–27.

2- A. Bottino, G. Capannelli, A. Comite, Novel porous poly (vinylidene fluoride) membranes for membrane distillation, Desalination 183 (1–3) (2005) 375–382.

3- Zhao Liang Cui, Naser Tavajohi, Suk Young Lee, poly (vinylidene fluoride) membrane preparation with an environmental diluent via thermally induced phase separation, J of Membrane Science444(2013) 223-236.

4- G. Ji, L. Zhu, B. Zhu, C. Zhang, Y. Xu, Effect of diluents on crystallization of poly (vinylidene fluoride) and phase separated structure in a ternary system via thermally induced phase separation, Chin.J.Polym.Sci.26 (2008)291–298.

5- X. Li, Y. Wang, X. Lu, C. Xiao, Morphology changes of poly vinylidene fluoride membrane under different phase separation mechanisms, J.Membr.Sci.320 (2008)477–482.

6- X. Lu, X. Li, Preparation of poly vinylidene fluoride membrane via a thermally induced phase separation using a mixed diluent, J.Appl.Polym.Sci.114 (2009) 1213–1219.

7- Y. Lin, Y. Tang, H. Ma, J. Yang, Y. Tian, W. Ma, X. Wang, Formation of a bi continuous structure membrane of poly vinylidene fluoride in diphenyl carbonate diluent via thermally induced phase separation, J. Appl. Polym. Sci. 114(2009)1523–1528.

8- Y. Tang, Y. Lin, W. Ma, Y. Tian, J. Yang, X. Wang, Preparation of microporous PVDF membrane via TIPS method using binary diluent of DPK and PG,J. Appl. Polym. Sci.118 (2010)3518–3523.

9- W. Ma, S. Chen, J. Zhang, X. Wang, Kinetics of thermally induced phase separation in the PVDF blend/methyl salicylate system and its effect on membrane structures, J. Macromol. Sci. Part B: Phys.50 (2011)1–15.

10- Rajabzadeh. Liang, Y. Ohmukai, T. Maruyama, H. Matsuyama, Effect of additives on the morphology and properties of poly(vinylidene fluoride) blend hollow fiber membrane prepared by the thermally induced phase separation method, J.Member.Sci.423(2012)189–194.

11- X. Cao, J. Ma, X. Shi, Z. Ren, Effect of TiO2 nanoparticle size on the performance of PVDF membrane, Applied Surface Science 253 (4) (2006) 2003– 2010.

12- L. Yan, Y.S. Li, C.B. Xiang, Preparation of poly (vinylidene fluoride) (pvdf) ultrafiltration membrane modified by nano-sized alumina (Al2O3) and its antifouling research, Polymer 46 (18) (2005) 7701–7706.

13- A. Bottino, G. Capannelli, A. Comite, Preparation and characterization of novel porousPVDF-ZrO2 composite membranes, Desalination 146 (1–3) (2002) 35–40.

14- L.Y. Yu, Z.L. Xu, H.M. Shen, H. Yang, Preparation and characterization of PVDF SiO_2 composite hollow fiber UF membrane by sol–gel method, Journal of Membrane Science 337 (1–2) (2009) 257–265.

15- Abdulkhaleq K. Mahmood "Fabrication of Nanocomposite membrane containing nanomaterial's for water purification" Ph. D thesis, University of Technology, Building and Construction Engineering Department, 2015.

16- L. Yan, S. Hong, M.L. Li, Y.S. Li, Application of the Al_2O_3-PVDF nanocomposite tubular ultrafiltration (UF) membrane for oily wastewater treatment and its antifouling research, Separation and Purification Technology 66 (2) (2009) 347–352.

17- J. H. Li, Y.Y. Xu, L. P. Zhu, J. H. Wang, C. H .Du, Fabrication and characterization of a novel TiO2 nanoparticle self-assembly membrane with improved fouling resistance, Journal of Membrane Science 326 (2) (2009) 659–666.

18- N.A. Hashim, F. Liu, K. Li, A simplified method for preparation of hydrophilic PVDF membranes from an amphiphilic graft copolymer, Journal of Membrane Science 345 (1–2) (2009) 134–141.

19- Momeni. M and Pakizeh. M Preparation characterization and GA Permeation Study of PSf / MgO Nano composite Membrane, Brazilian Journal of Chemical Engineering, Vol. 30, No. 03, pp. 589 - 597

تحضير وتوصيف غشاء المتراكب النانوي بولي فينيليدين/ (ام سي ام- 41) لغرض تنقية المياه

د. عبد الخالق كمال محمود

م.م. نبيل كاظم

الخلاصة :-

في هذا البحث تم العمل لتحسين خصائص غشاء بولي فنيليدين فلورايد باضافة المادة النانووية (ام سي ام- 41) والمعدة بواسطة التفاعل الكيمياوي لغرض تنقية المياه. تم تحضير الغشاء بطريقة انقلاب الطور الرطب مستعملا مادة داي مثيل فورماميد كمذيب مع نسب وزنية مئوية مختلفة من المادة النانووية ام سي ام -41 (0.0 ,0.01 , 0.02 , 0.04 , 0.06 , 0.1) من وزن المزيج. تم تشخيص وفحص الاغشية بواسطة المجهر الماسح الالكتروني ومجهر القوة النووية. اظهرت نتائج الدراسة عدم تأثر التركيب الداخلي للأغشية بالمواد النانووية المضافة في حين ادى الى زيادة النفاذية وامتصاص الماء للغشاء مما زاد من كفاءة الغشاء لنفاذية الماء بنسبة 19.2 ٪ عند القيمة المثلى للمادة النانووية المضافة عند 0.04 ٪ وعند ضغط 4 بار ودرجة حرارة 23± 1 م. اظهرت دراسة الخواص الميكانيكية لغشاء بولي فنيليدين فلورايد الحاوية على المادة النانووية ام سي ام -41 وبنسبة 0.04 ٪ من الوزن المزيج زيادة في جهد الشد بمقدار 18٪ مقارنة بالاغشية غير الحاوية على هذه المواد.