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Application of Nanometer Aluminum Magnesium Hydroxide in PVDF Membrane Modification

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Abstract

In this article, we adopted the phase inversion process to prepare nanometer aluminum magnesium hydroxide/PVDF hybrid membrane, studied the influences of nanometer materials on pure water flux, retention, pore diameter, porosity, microstructure, mechanical property and adsorption property for membranes, researched the influences of different AMH contents on membrane property, and analyzed element contents of membrane transect through x-radial energy dispersive analysis (EDS). Comparing with PVDF membrane without nanometer materials, the results indicated that the addition of nanometer materials obviously enhanced the pure water flux, retention, microstructure, mechanical property and adsorption property for membranes, and didn't largely influence the pore diameter and porosity for membranes. The analysis of SEM indicated that the addition of nanometer materials could obviously change the microstructure of membrane.

Keywords: Nanometer aluminum magnesium hydroxide, Polyvinylidene fluoride (PVDF), Property modification, Hybrid membrane

PVDF is a sort of macromolecule material with good property, and it possesses good chemical stability, heat stability and tenacity, so the research of PVDF membrane is extensively emphasized by domestic and foreign research institutions, and it is successfully applied in many domains such as chemical industry, electron, textile, food and biochemistry (O. Shina K H, 1996, p.137-145, Degen, 1998, Yang, 1997, p.75-86, Degen, 1995). With continual development of PVDF membrane application, different applied situations require different requirements for its property, so we need to modify its property in use process. In recent years, the modification method which introduces few hydrophilic inorganic nanometer particles into hydrophobic polymer system arouses human large interests, especially for the introduction of Organo-mineral technology since 1990s, and this technology introduces ceramic powders into polymer system, and adopts translation technology to prepare composite membrane, which could effectively combine the heat-resistant, chemical stability of ceramic with flexibility and low cost of polymer and fully enhance the pore diameter and pollution-resistant of membrane (Doyen, 1996, P.247-258 & Genne, 1996, P.343-350).

Because nanometer materials possess many properties such as small grain size, large surface area and high surface activity, so we introduce them into the polymer system to modify its property, which make obtained material possess special excellent properties than original materials (Doyen, 1996, P.247-258, Genne, 1996, P.343-350, Li, 2004, P.709-712 & Qu, 2006).

The nanometer materials in the experiment are homemade nanometer aluminum magnesium hydroxides which are hydrophilic materials, and they possesses the layered structure similar with brucite, and because part of Mg^{2+} is isomorphously replaced by Al^{3+} and brings permanent positive charges, and adsorbs Cl- and OH- to keep the electric neutrality, so they are a sort of charged materials. There are many researches about the adsorption property of nanometer aluminum magnesium hydroxide (E. Klumpp, 2004, P.111-116, Ramesh, 2005, P.45-51 & Wei, 2005, P.31-33).

In this article, we select nanometer aluminum magnesium hydroxide to modify the property of PVDF micro-porous filtered membrane, and utilize dry/wet phase translation method to prepare nanometer aluminum magnesium hydroxide/ PVDF hybrid micro-porous filtered membrane. We studied the influence of the introduction of nanometer materials on flux of pure water, retention, pore diameter, porosity, mechanical property, adsorption, and micro structure for membrane, fully utilize the characters of nanometer materials to perfect the property of PVDF membrane, endows its charged property to enhance its function, and studied the influence of the introduction of different nanometer materials on the property of membrane.

1. Experiment

1.1 Reagents

PVDF: Shanghai 3F New Materials Co., Ltd, FR904.

N,N-Dimethylacetamide (DMAc): analytical reagent, Tianjin Hongyan Chemical Reagent Factory.

Polyvinyl pyrrolidone (PVP): analytical reagent, BASF import to load separately, K-30.

Nanometer aluminum magnesium hydroxide: homemade.

Bovine serum albumin (BSA): molecular weight 67000, Tianjin Lianxing Biological Technology Co., Ltd.

Titan Yellow: molecular weight 695, Purchase and Supply Center of Chemical Reagents of Shanghai.

1.2 Preparation of membrane

Add nanometer aluminum magnesium hydroxide into solvent DMAc, and after ultrasonic separation, add PVDF and additive PVP, control certain water bathing temperature, obtain the casting solution after mixing of beater, defoaming quietly, scrape membrane on clean glass board with homemade drawknife under certain liquid membrane thickness, pre-vaporize certain time, and immerge concretion bathing of pure water to form membrane, and the finished membrane piece is immerged in the pure water to defoam solvent and additive, waited to test. Note the made hybrid membrane as sample A, and adopt same membrane making method and technical condition to prepare the PVDF membrane without nanometer materials, and note it as sample B.

The additive of nanometer aluminum magnesium hydroxide selected in the experiment is PVDF which quality molecular weight is 2%, and the molecular formula is $Mg_{2.04}Al(OH)_{6.48}Cl_{0.60}$, and the average size of crystal grain is 15.1nm, and the ζ electric position is about 42mV, and it has strong positive electricity (Ma, 2007, P.193-195).

1.3 Analysis and testing

Test the pure eater flux of micro-pore filtered membrane by homemade equipment, and the testing conditions are room temperature, 0.1MPa and pure water, and measure the BSA retention of 400ppm and the 10μg/ml Titan Yellow removal rate by ultraviolet-visible spectrophotometer (UV-1700 series made by Shimadu Corp), and the adopt Coulter-porometer Ⅱ to measure the pore diameter of membrane (Zheng, 1999, P.31-33). The porosity is computed by following formula.

$$porosity = \frac{(W_{wet} - W_{dry}) / \rho_{water}}{(W_{wet} - W_{drt}) / \rho_{water} + W_{dry} / \rho_{PVDF}} \qquad (1)$$

In the formula (1), W_{wet} is the wet weight of membrane (the unit is g), W_{dry} is the dry weight of membrane (the unit is g), ρ_{water} is the density of water (the unit is g/cm^3), ρ_{PVDF} is the density of PVDF material (the unit is g/cm^3) which density is 1.77g/cm^3 in the experiment.

Represent the micro-structure of membrane by scanning electron microscope (SHIMADZU SS-550), test the mechanical property of sample on the mechanical tester of Instron 5865 (Super Duper Multi National Conglomerates R Us. Corporation), adopt Nicolet308 infrared spectrum meter (Thermo Electron Corporation) to represent the infrared property of membrane, and analyze the transect element of membrane by SEM/EDS (JEOL, JSM-6700F).

2. Results and discussions

2.1 Infrared spectral analysis

Utilize infrared spectral analysis to judge the hybrid character, and judge whether pure physical mixing or chemical function exists though comparing infrared spectrums of hybrid membrane and PVDF membrane (seen in Figure 1). In the FT-IR spectrum of PVDF membrane, the position near 1404cm^{-1} is the distortion libration apex of CF_2 in PVDF, and the position near 1180cm^{-1} is the flexing libration apex of CF_2 in PVDF, the positon near 1640cm^{-1} is the adsorption apex of carbonyl group because PVP is not dissolved completely and few PVP leaving in the sample induces the occurance of disturbtion apex. PVDF membrane presents half crystablline phase state, and it is composed by non-crystal state, α phase and β phase, and the positions near 880cm^{-1} and 840cm^{-1} are character apexes without amorphous state, and the postions near 763cm^{-1} and 613cm^{-1} are weak α phase libration apex, and the postion near 1280cm^{-1} has weak β phase libration apex (Huang, 2003, P.45-48). Comparing with the spectrum of PVDF membrane, the infraed spectrums of nanometer aluminum magnesium hydroxide/PVDF hybrid membrane have not new adsorption apex, which indicates that the there is no new chemical bond in the hybrid membrane, i.e. it is pure physical mixing.

2.2 Influence of nanometer materials on membrane microstructure

Figure 2 and Figure 3 respectively are SEM photos of nanometer aluminum magnesium hydroxide/PVDF hybrid membrane and PVDF membrane, and it is obvious that the transects of PVDF membrane and hybrid membrane are asymmetric structure, and above surface of PVDF membrane is the dense function layer, and the lower surface is obvious figure pore structure, but the transect structure of hybrid membrane changes obviously, and its transect structure is the micro-network pore structure close to two layers, and this structure foams because the existence of nanometer particles enhance the mass transfer resistance of nonsolvent in solvent and gelatin bathing in the casting solution, and baffle the mass transfer speed to some extent, and in the process that the micro-pores form in the separation when casting solution enters into the gelatin bathing, the internal stress could be eliminated and the hybrid membrane could foam finally. This structure could enhance the mechanical property of membrane, and the above surface has obvious white points comparing with PVDF membrane, and we think they are atoms of nanometer aluminum magnesium hydroxide on the membrane surface which could perfect the property of membrane. Next, the introduction of nanometer materials reduces the cortex thickness little and changes the sub-cortex structure of membrane, which could enhance the pure eater flux of membrane to some extents.

2.3 Influence of nanometer materials on membrane separation

Table 1 is the property index of nanometer aluminum magnesium hydroxide/PVDF hybrid membrane and PVDF membrane. From table 1, we can see that for the hybrid membrane obtained from the introduction of nanometer particles in casting solution, its separation property could be enhanced obviously. Comparing with common membrane, the pure water flux of hybrid membrane could be enhanced from 971.04 $L \cdot m^{-2}h^{-1}$ to 1344.40 $L \cdot m^{-2}h^{-1}$, and the porosity could be enhanced little, and the average pore diameter of hybrid membrane reduce, and the retention of BSA is enhanced from 57.79% to 78.01%. The property of hybrid membrane is excellent because the nanometer particles in the casting solution eliminate the stress produced when the pure waters in solution and solidification bathing exchange to foam micro-pore, which could effectively avoid the occurrence of big pores and limitation, and the nanometer aluminum magnesium hydroxide has good hydrophilicity, which could improve the hydrophilicity of membrane and enhance the dense pressure of membrane, so the hybrid membrane puts up large pure water flux, small average pore diameter and high retention.

2.4 Influence of nanometer materials on membrane mechanical property and adsorption property

From Table 2, we can see that the mechanical property of hybrid membrane could be enhanced obviously, and the breaking stress could be enhanced from 0.95MPa to 1.30MPa, and the breaking strain basically changes little. The reasons for the enhancement of mechanical property of hybrid membrane are that the accession of nanometer material eliminates the internal stress produced when the membrane pore foams and effectively avoid the productions of big pores and limitations and the accession of nanometer materials changes the pore structure of membrane. The adsorption property could be presented by the removal experiment of Titan Yellow with 2 negative charges in the molecule, and from the data in Table 2, the removal rate of hybrid membrane to Titan Yellow is two times than PVDF membrane. Because the molecular weight of Titan Yellow is 695, so the removal basically depends on the adsorption property of membrane. The nanometer aluminum magnesium hydroxide in the hybrid membrane has obvious positive electricity, big proportion surface area and pore capacity, and it has obvious adsorption property to Titan Yellow with negative electricity, so the removal rate of hybrid membrane to Titan Yellow could be obviously enhanced.

2.5 Influence of different AMH contents on membrane structure and properties

Implement property testing to the membrane formed by the casting solutions with different AMH contents and the obtained curves are seen in Figure 4 to Figure 7. The results show that with the increase of nanometer particle contents, the water flux of membrane increases, the increasing speed is quick, the porosity of membrane changes little, the pore diameter gradually declines, the retention and removal rate of membrane increase, and the breaking stress and breaking strain first reduce and then go to stable. Because of the increase of AMH accession, the viscidity of casting solution will increase, which will baffle the exchange speed of solution and non-solution, and AMH is rigid particle, and its accession will increase the pressured density, so the flux of membrane will increase and the mechanical property of membrane will be enhanced, but with the increase of accession, the membrane will become crisp, so the breaking elongation rate reduces. The increase of nanometer material accession could enhance the adsorption property of membrane and the removal rate of Titan Yellow.

2.6 EDS element analysis

EDS is a sort of measure to analyze the composing of surface election for material. In the experiment, we analyze the element composing of hybrid membrane transect through EDS. Because of the deficiency of analysis measure and the convenience of analysis, we adopt EDS to analyze the transect of hybrid membrane (the removal ratio is 68.2%) which content of nanometer aluminum magnesium hydroxide in PVDF is 8% to judge the composing content of transect element for hybrid membrane. The analysis results are seen in Figure 6 and Figure 7, and from Figures, we can see that nanometer aluminum magnesium hydroxide presents uneven distribution on the transfect of membrane and the nanometer content near the surface of membrane are more. From the EDS element content analysis, we can see that the content of total nanometer material of membrane transect approaches the theoretical appending quantity, and it indirectly indicates the distribution of nanometer materials is basically even in the casting solution, but the re-uniting phenomena occurs in the local areas of transect, which may be induced by that the increasing probability of collision in the membrane foaming process with the increase of nanometer material accession.

3. Conclusions

Comparing with general PVDF membrane, nanometer aluminum magnesium hydroxide/ PVDF hybrid micro-porous filter membrane prepared through phase translation method possesses following characters.

(1) The pore structure changes obviously, and this sort of pore structure is more propitious to enhance the mechanical property of the membrane.

(2) The flux of pure water and the retention to BSA are enhanced notably, and the pore diameter and porosity change little.

(3) The mechanical property of membrane is enhanced obviously, and the removal rate to Titan Yellow is 2 times than PVDF membrane.

(4) The increase of AMH content could obviously enhance the flux of pure water and removal rate for the membrane.

(5) EDS analysis indicated that nanometer aluminum magnesium hydroxide distributed unevenly in the membrane, and was contained more in cortex and near cortex, but it distributed evenly in the total membrane.

Thus it can be seen that the introduction of nanometer particles could perfect membrane property, enhance the function of membrane, prepare the charged membrane with special separation function and develop the application of PVDF membrane in water treatment and other domains.

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Table 1. Separation property comparison of nanometer aluminum magnesium hydroxide hybrid membrane and PVDF membrane

Sample	Flux of pure water ($L \cdot m^{-2}h^{-1}$)	Retention (%)	Maximum Pore Diameter (μm)	AveragePore Diameter (μm)	Porosity (%)
A	1344.40	78.01	0.230	0.197	88.45
B	971.04	57.79	0.244	0.213	87.03

Table 2. Mechanical property and adsorption property comparison of nanometer aluminum magnesium hydroxide hybrid membrane and PVDF membrane

Sample	Breaking stress (MPa)	Breaking strain (%)	Yang's simulation (MPa)	Removal rate (%)
A	1.30	65.18	22.96736	41.67
B	0.95	64.45	18.91604	20.18

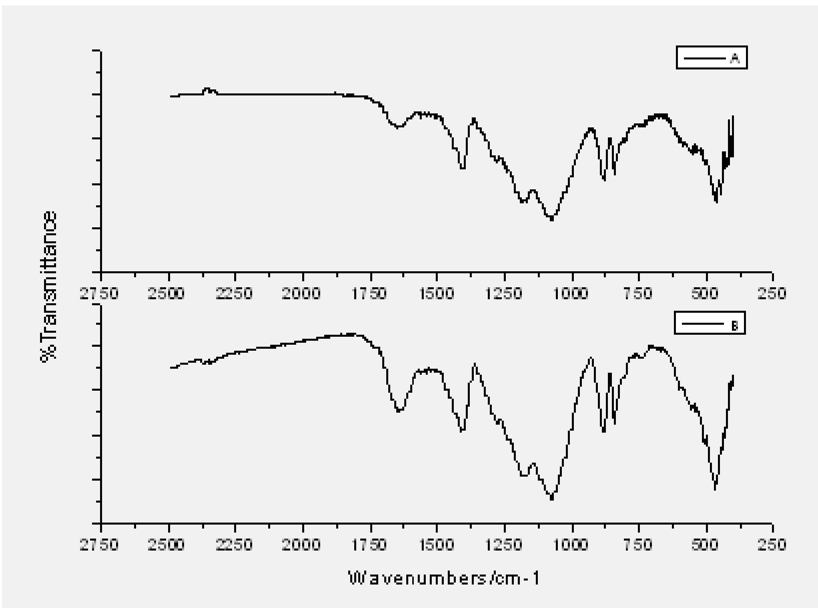


Figure 1. Infrared Spectrogram of Nanometer Aluminum Magnesium Hydroxide Hybrid Membrane and PVDF Membrane

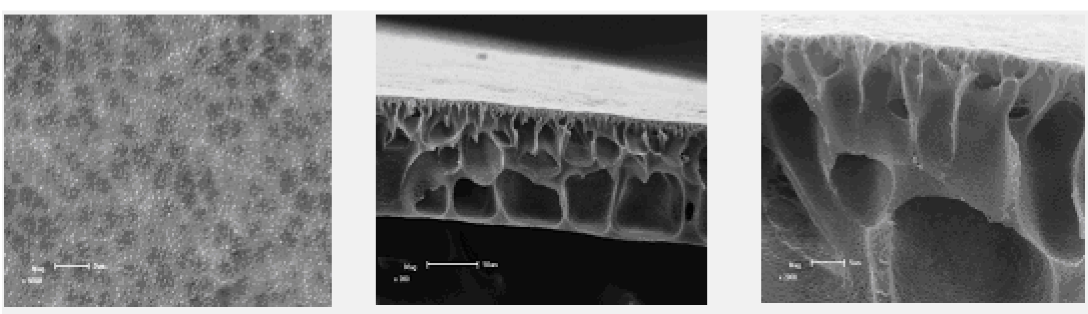


Figure 2. Surface and Transect SEM Photos of Nanometer Aluminum Magnesium Hydroxide Hybrid Membrane

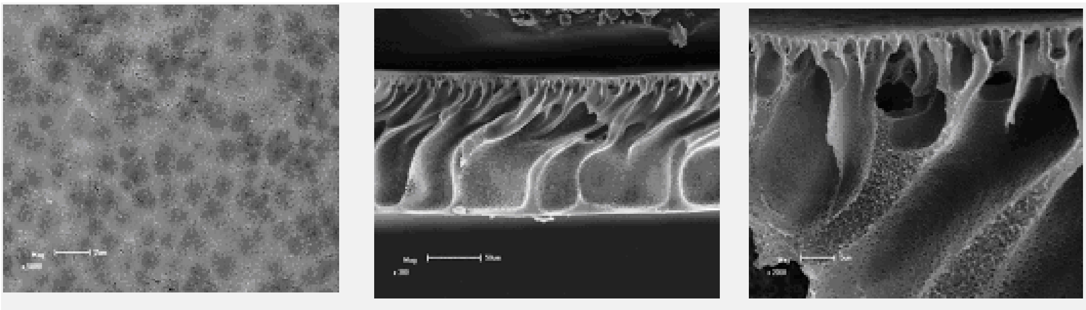


Figure 3. Surface and Transect SEM Photos of PVDF Membrane

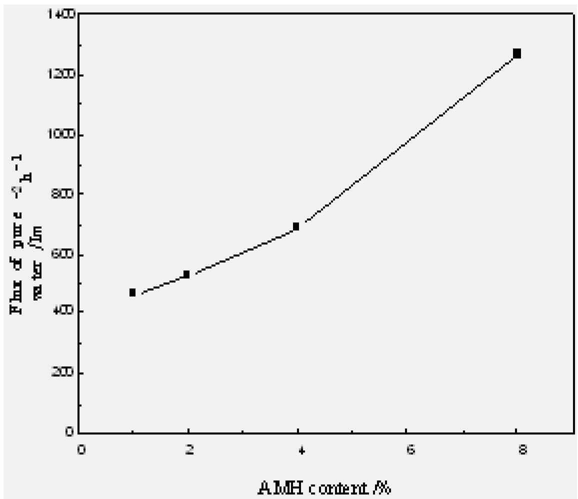


Figure 4. Influence of Different AMH Contents on Membrane Flux

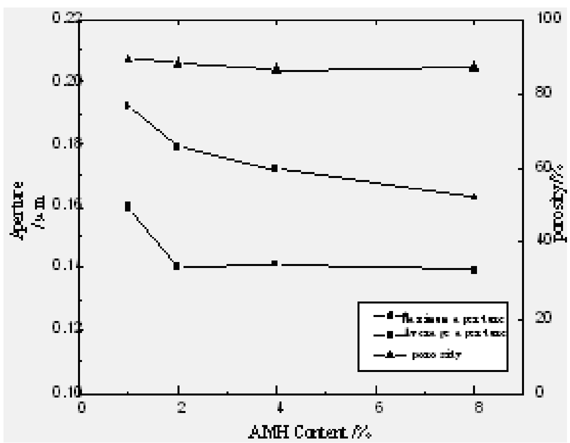


Figure 5. Influence of Different AMH Contents on Membrane Pore Diameter and Porosity

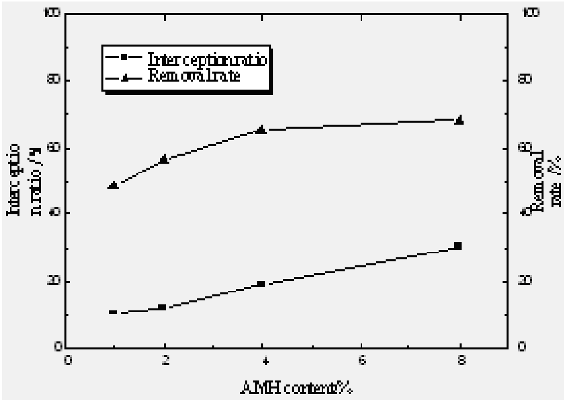


Figure 6. Influence of Different AMH Contents on Membrane Retention and Removal Rate

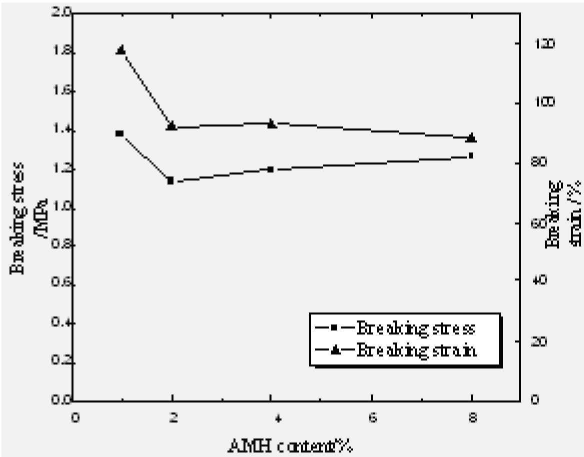
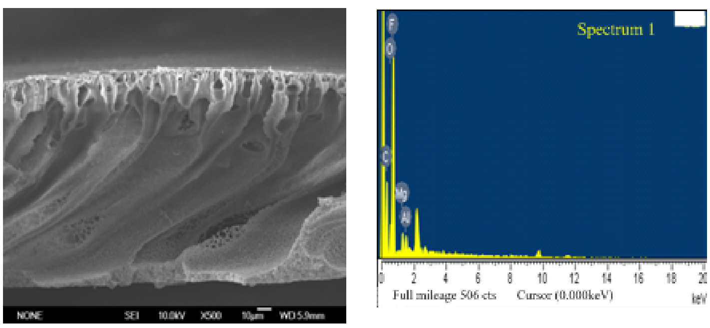


Figure 7. Influence of Different AMH Contents on Membrane Extension Property



Element	Weight proportion	Atom proportion
C	32.30	42.71
O	9.15	9.09
F	54.97	45.95
Mg	2.30	1.50
Al	1.28	0.75
Total	100.00	

Figure 8. Transect SEM/EDS Analysis of Nanometer Aluminum Magnesium Hydroxide/ PVDF Hybrid Membrane

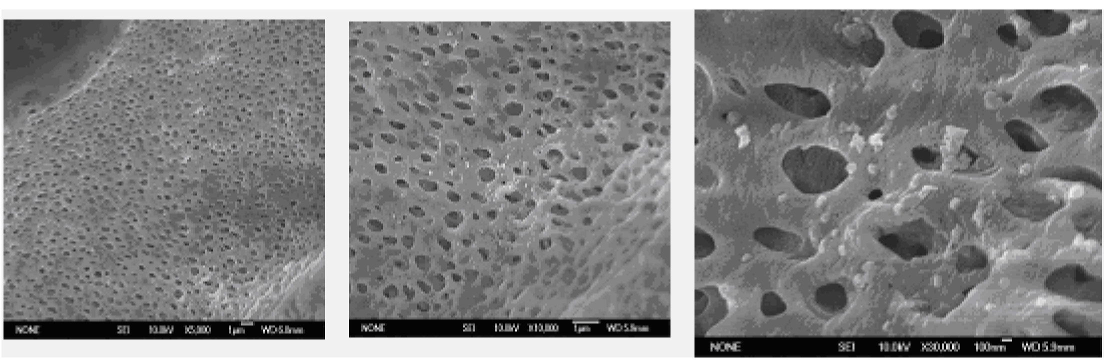


Figure 9. Local Transect SEM Magnified Image of Nanometer Aluminum Magnesium Hydroxide/ PVDF Hybrid Membrane