



Study of Porogens in Polymer-0D Nanomaterial Composite membrane

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Available online at: www.isca.in

Received 7th May 2014, revised 23rd May 2014, accepted 4th June 2014

Abstract

Polymer nano particle composite membrane has drastically increases the efficiency in purification process. In view of its practical applicability it leaves a platform for the researcher to synthesize, characterize and study of pore size of 0D-nanomaterial composite membrane. Metal nanoparticles of different size are introduced into a polymer solution and dispersed by continuous stirring. The polymer nanometal particle membrane is isolated by removing the solvent. The samples were structurally characterized by SEM analysis, Porosimetry by mercury intrusion and measurements of weight by immersion, for ion exchange capacity, morphology, and performance.

Keyword: Polymer-Ag, nanomaterial, composite membrane, antifouling PVDF.

Introduction

In water purification process, membrane technology is significantly increase its importance in the industry as well as in the society. All the microscopic impurities, colloids, bacteria and bio impurities are separated from water to make fit for drinking by the help of membrane technology. Membrane technology plays a vital role in purification of municipality water supply as well as in desalination process^{1,2}. Polymeric membrane has been established its position in the purification market after development of RO system by Loeb and Sourirajan^{3,4}. Polymeric membrane in water treatment has huge potential because of its excellent physicochemical properties and good membrane-forming capacity. The inherent hydrophobic surface of polymeric membranes adsorbs or blocks organic foulants (pathogens, polysaccharides, protein etc.) from contaminated water which decreases membrane utility efficiency. Filtration capacity and its potential, rigidity hardness depends on its surface phenomenon along with structural morphology⁵⁻⁸. Hydrophilic modification on the surface of polymeric membranes enhances the capacity of fouling resistance in water treatment⁹. A lot of effort in pore morphology is being carried out in membrane chemistry. Polymer nanometal composite membranes have already been applied in the water filtration technique to discuss the issues like mechanical strength, fouling capacity, permeability and selectivity.

In the new technology era the polymer-nanometal composite membrane technology bring modern opportunity to develop advanced water filtration membranes to get high purity of water production and exact impurity separation, leaving with high purity of water. Of course the selectivity and properties of nanomaterials were studied by initiating the step from fabrication process. Inorganic nanoparticles (ZnO, TiO₂, SiO₂,

and MgO etc), metal nano particle (Ag, Au, etc) may increase the pore size in the polymer-nanometal composite membrane.

Methodology

Synthesis of Polymer -0D Nanomaterial Composite Membrane. Ag -nanoparticles synthesis is mostly based on the colloidal route. A solution of polymer is coated on a substrate and metal precursor is incorporated to it. The metalnanoparticles are then embedded by heat treatment. The organic PVDF matrix and metal nano Ag particles are mixed together in solution with definite concentration and pH¹⁰. By solution blending method it is easy to fabricate polymer nanometal particle composite membrane. Polymer PVDF matrix in a solvent to form a homogeneous solution with specified concentration to that Ag metal nanoparticles are added in to the solution drop by drop with constant stirring. The polymer nano metal particles composite membrane is cast by removing solvent. The permeability, strength, and pore size may varied by adding amount of Ag-nano particle with specified concentration. Due to the presence of heterogeneous nuclei (Ag-nanoparticle) the possibilities of formation of the crystal like PVDF spherulitic is discouraged in the slowly cooling process. It is found that, it improve its capacity of filtration of these nanometerial composite membrane because of its porosity and mechanical strength. Selected concentration of Ag-nanoparticles during the synthesis of polymer Ag nano material composite membrane effectively enhances membrane permeation, tensile strength, and biofouling capacity. Two partially hydrolyzed molecules can link together by a condensation reaction leading to form polymeric gel¹¹. Generally metal salt, soluble in water, are taken as the starting material Gelatin is introduced by dehydration of the solution. When the pH of the solution increases, the repulsive force between particles reduces, leading to spontaneous coagulation.

Nanomaterials and Porogens: Nanomaterials are not enough hydrophilic to originate with specific dimension of pores in liquid phase separation method¹². The existence of polyethylene glycol in polymer matrix solution as foreign substance for pore initiator, smaller Ag nano nanoparticles (10nm) could increase the separation of impurities efficiency. It is because of crystallization changes in polymer matrix and nanomaterial composite solution reduces the mean pore size on surface of membrane. To avoid hydrophobicity of nanoparticles, some composite (PES/Ag) has been synthesized nano ultra filtration membranes in the presence of polyvinylpyrrolidone (pvp K40). After the mechanical and chemical modification of Ag nanoparticles¹³. Size of pores could be controlled in the polymer nano composite membrane. The higher impurities separation ratio and presence of least undesirable contain in the filtrate part possible with small amount of Ag nanomaterial loading in composite membrane. Yan et al. prepared polyvinylidene fluoride (PVDF) ultra filtration membrane along with Al_2O_3 nanoparticles in the presence of hex disodium phosphate as the dispersant and PVP as the porogen^{14,15}. When Al_2O_3 is added, it has no influence in controlling the pore size /dimension in the polymer nano composite membrane but increase its hydrophilicity character of membrane which enhance the removing impurities capacity of the membrane. The presence of $FeCl_2$ or $FeCl_3$ and $CaCl_2$ as the porogens, along with metal nanoparticles could changes the characteristics like, viscosity, thermal stability and mutual diffusion.

Discussion

Silver nano particles with (1-10nm) dimension were interacted with poly vinylidene fluoride matrix results high impurity recovery ratio, increase its hydrophilicity, thermal stability, viscosity. Controlling of pore size is enhanced in presence of nano materials in the polymer membrane. Different pore size are obtained in the Ag nano material composite membrane which are corroborated by pore size distribution count per micro meter. The longer mailing time reflect the homogeneous distribution of pore in Ag-nanocomposite membrane. Average size of 0.012-0.01 micro meter has been observed in Ag doped layer in polymeric membrane. Membrane permeation and antibacterial tests were carried out to characterize the antifouling performance of PVDF membrane. This biological testing indicates that the water is totally clean and it does not have any micro-organism. That might be because of the photo thermal effect of nanocomposites which raise the temperature and cause bacteria death or because of silver nanoparticles which has super antiseptic and anti bacterial activity.

Pores with average size 0.22-0.34 micro meter are found in PVDF –Ag nano composite membrane respectively. Introduction of 50 vol. % of porogenic agent caused an apparent porosity of 39 and 33% vol in the PVDF and Ag nano composite membrane.

Table-1
Filtration process based on Porosity dimension

Pore dimension	Molecular weight	Process	Filtration	Impurities
>10		Classic filter		
>0.1micro. m	>5000kDa	Micro filtration	<2 bar	Larger bacteria, Yeast
100-2nm	5-5000KDa	Ultra filtration	1-10 bar	Bacteria, macromolecules, proteins, larger viruses.
2-1 nm	0.1-5KDa	Nano filtration	3-20 bar	Viruses, 2-valent ions
<1nm	<100Da	Reverse osmosis	10-80 bar	Salts, small organic molecules

Table-2
Comparison porosity supported with nanocomposite

	PVDF supported on Ag nano composite	Porous PVDF membrane 2 h milling	Porous PVDF membrane 20 min. of milling	Ag nano non supported composite
Total porosity%	58.78	62.76	61.88	49
Apparent porosity%	33.23	41.21	37.29	21.67
Apparent density	2.26	2.25	2.22	3.98
Closed pores%	31.89	29.9	30.01	31.11

Conclusion

Flux recovery ratio (FRR) increased about 40% after the presence of silver nano particles on the PVDF membrane surface, elucidating the anti organic fouling performance of PVDF membrane was elevated by silver nano particles. Anti bacterial test confirmed that PVDF membrane showed superior anti-biofouling activity because of Ag nanoparticle.

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