RECENT ADVANCES IN POLYMER NANOCOMPOSITE MEMBRANES FOR WATER TREATMENT

Abstract

Polymeric membranes are an emerging field in recent years and it has drawn the attention of researchers, owing to the scarcity of drinking water as well as the utility of membranes in different fields rather than water purification. Here, we present an overview of the current - advancements and strategies which have been used to augment the separation mechanisms in polymeric membranes including membrane fouling, permeability, stability, etc. For this purpose, the new trend in membranes is the incorporation of nanomaterials into the polymeric matrices which shows superior properties compared to the virgin polymeric membrane. Various nanomaterials and different approaches have been put forward which shows immense promise in the separation technologies, especially for water treatment processes. This chapter represents a detailed view of the current progress of polymeric nanocomposite membranes for the treatment and purification of water. Though several nanocomposite membranes have been reported till now, here the main focus is on how nanomaterials help in reducing membrane fouling as well as how they help to enhance the permeability of the membrane.

Keywords: Polymeric membranes, Nanocomposites, Membrane fouling, Permeability

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I. INTRODUCTION

Recent growth in population exerts immense pressure o the clear water supply. Considering the massive problem, membrane filtration is considered the most feasible technology to overcome the challenges related to water scarcity and other water-related issues. In the year 2010, Shannon et al. published in their report that membrane filtration needs minimum energy input such as chemical or thermal, and during the procedure, it does not harvest any harmful side products.[1] Besides this, the important factor is that membrane filtration is effective for the selective removal of different types of contaminants by adjusting the structures and pore sizes of the membranes.[2,3] For these membranes to work properly a driving force is required and here for the separation of the contaminants through the membrane the most important driving force is pressure. Hence, depending upon the pore size, structure, and operating mechanisms these pressure-driven membranes can be categorized as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Among all, microfiltration is used to separate suspended solids, bacteria, yeasts, and fungi, whereas, ultrafiltration is used to remove viruses, various macromolecules, and colloids. Nanofiltration primarily targets the removal of heavy metals, and dissolved organic matters, on the other hand, the purpose of reverse osmosis is water reuse, desalination, and production of ultrapure water.[3,4] On the other hand, in the case of polymeric membranes, the pore sizes can be controlled and the properties of these membranes can be adjusted by modifying different factors such as the selection of monomers and their concentrations, the casting conditions, and the selection of additives. However, apart from all the advantages polymeric membranes also have several drawbacks. In addition to this, fouling is a major issue related to membrane separation. In this regard, chemical cleaning (at high temperature) can be one option to eliminate that biofouling. Chlorine treatment is very common here, but chlorine is highly active and it can react with some polymeric membranes. Therefore the such type of chlorine wash is not appropriate for these types of polymeric membranes.[5] Nowadays researchers have focused on developing new-type of membranes, where the nanoparticles have been embedded into polymeric membranes to overcome their flaws by getting the advantages of nanoparticles. Depending on the structure of the membrane and the position of nanoparticles, various nanocomposite membranes can be fabricated such as conventional mix-matrix nanocomposite membrane, thin-film nanocomposite membranes, and surface-located nanocomposites.[2,3]. This chapter aims to provide an idea of the development of nanocomposite membrane, their antifouling activity, and permeability.

1. **Membrane fouling:** The main objective of a membrane is to separate various foulants such as biomolecules, different particles, etc from water to obtain safe and pure water. These foulants can be of different types such as colloidal fouling, organic fouling, crystalline fouling, and biofouling. During this separation process, those foulants deposited to the membrane surface or sometimes get adhered into the internal structures of the membrane. Consequently, the membrane pores become narrow, and even sometimes get blocked and that causes the reduction in flux. Nowadays the main focus is biofouling, where the microorganisms get attached to the hydrophobic, nonpolar membranes. Essentially, this type of nonpolar, hydrophobic membrane is favorable for the attachment of these bio-foulants. Therefore, a wide number of nanoparticles have been embedded into polymeric membranes to investigate their efficiency to reduce fouling and thereby increase water flux. Fundamentally, the incorporation of

nanoparticles into polymers causes some changes in the characteristics of the membranes, which helps to reduce membrane fouling.

In surface-modified carbon nanotubes (CNTs) and graphene oxide (GO), the reactive oxygens can influence direct contact with the microorganisms.[6] Lee et al. significantly modified the surfaces of CNTs to improve their hydrophilicity by acid treatment.[7,8] As a result, oxygen-containing groups grow on the CNT surface, which helped the modified CNTs to behave as negatively charged particles, and intensify their hydrophilicity. Zhang et al. showed that polyamide/polysulfone thin-film nanocomposite membrane with 0.2% (m/v) modified CNTs depicted a lower water contact angle rather than the pure polymeric membrane.[9] Another research work using polyethersulfone/CNT membrane showed excellent confrontation towards protein fouling.[10] It was seen there that with the increasing amount of CNTs, the amount of fouling of bovine serum albumin decreased, owing to the enhanced hydrophilic nature of the nanocomposite membrane. But the recovery rate was higher in the case of nanocomposite membranes compared to pure polymeric membranes. Generally, the functional groups which can enhance the hydrophilicity of CNTs include carboxyl functional group, amine group, and polyethylene glycol.[11] Various reports are suggesting that various functionalization on the CNT surface may lead to the declination in the antifouling activity of those nanocomposite membranes.

Another nanomaterial that has been incorporated into membranes is Graphene oxide. Hu et al. encountered that graphene oxide (GO) and reduced graphene oxide (RGO) decline the activity of E. coli bacteria.[12] Perreault et al. also reported that polyamide membrane containing GO can effectively inhibit the growth of E. coli bacteria.[13] Thereafter, various reports are there projecting that different functionalization on GO was further explored to improve the performance of the GO nanocomposite membranes. In another article, Choi et al. presented a reverse osmotic membrane, which they formed by deposition of GO multilayers on the surface of polyamide thin-film composite via layer-by-layer assembly of oppositely charged GO nanosheets.[14] They observed that the membrane was highly stable and they also measured the average roughness with 10 alternative layers of GO and found that roughness was reduced by 53.8% as compared to the pure membrane.

There is a wide application of metal-based nanoparticles in polymeric membranes. Koseoglu-Imer et al. synthesized a polysulfone membrane loaded with silver (Ag) nanoparticles and the membrane depicted excellent hydrophilicity and lower roughness. They also reported a reduction in the water contact angle with silver nanoparticle loading compared to the pure membrane.[15] Wang et al. fabricated polyethylene/titanium oxide (TiO_2) nanocomposite membrane and observed greater antifouling activity for this membrane than.[16] Likewise, TiO_2, Zinc oxide (ZnO_2) nanoparticles were also investigated in polymeric membranes due to their antimicrobial activity. On the other hand, Hong and He observed that polyvinylidene fluoride (PVDF) membrane loaded with ZnO_2 nanoparticles exhibited enhanced self-cleaning properties.[17] They also varied the wt% of ZnO_2 from 0.5 and 1.5 to 3.0 wt%, which improves the decolonization efficiency which accredited to the production of reactive oxygen species.[18]

2. **Permeability:** Permeability of a membrane is referred to its ability to pass through the membrane. while separating the targeted particles from the rest of the fluid. The high

selectivity of a membrane requires small and uniform pores.[19] Generally, in most of the membranes, it could be seen that they have a trade-of association between permeability and selectivity. Therefore, in the case of synthetic membranes, the key features which are helpful to overcome the trade-off between permeability and selectivity, include small and uniform pores, a thin active layer, and interaction between target particles and the membranes.[20] In this regard, microfiltration and ultrafiltration membranes can reject only 20 to 50% of organic matter while nanofiltration and reverse osmosis membranes, can block ~90% of organic matter. In a few reports, we got the necessary information that higher valence ions generally have a better rejection rate owing to the effective electrostatic repulsion in charged membranes.[21]

Yang et al. observed that CNTs into a polystyrene membrane, the fluid flow rate was enhanced 4-5 times compared to the original polystyrene membrane.[22] It was also proved theoretically, that the strong hydrophobic interactions of CNTs with polymeric materials enable the nanocomposite membranes to achieve superior rejection of natural and hydrophobic organic components.[7,8] Qiu et al. suggested that bulky as well as hydrated salt ions can be excluded by the innermost tubes of CNTs.[23] Not only that they obstructed through steric effects by introducing different functional groups on CNTs. There are different types of functional groups, if it is a charged ion, then the same charged ions will be repelled, whereas oppositely charged ions will be attracted. Recently, there are several reports showing improvements in the relationship between selectivity and permeability by adding CNTs to membranes. As shown by Zhang et al. the permeation fluxes were enhanced as the content of modified CNTs increased in the polymeric membranes.[9] Not only the hallow channels of CNTs but also the aggregated nature of CNTs can form interconnected networks in addition to the previously present pores, which can lead to enhanced flux. The appropriate functionalization of CNTs can result in better performance. Lee et al showed the proper examples in their reports, where they checked that the excellent increment in the water flux is due to the synergistic effect of the membrane porosity and the hydrophilicity.[7,8]

GO containing nanocomposite membranes is another type that exhibits higher permeability; however, the reason for this enhanced permeability is not fully explained yet. In one report it was seen that the larger lateral size of GO nanosheets can lengthen the 2D hydrophobic channels. Consequently, it results in a higher speed of the water at the end of the channels.[24]

In the case of permeability metallic nanoparticles also plays a major role. For example, 70 nm sized silver (Ag) nanoparticles were added to the polysulfone membrane, which resulted in a lowering of water flux while the addition of 30 nm sized Ag nanoparticles (0.5 wt%) caused to 186.7% increment in water flux (Mollahosseini et al. 2012.[25] The relatively inferior performance of larger-sized (70 nm) Ag nanoparticles might be due to blockage of pores. But smaller nanoparticles (30 nm) tuned the membrane surface smoother and reduced pore size. Kusworo et al. showed that the UV-irradiated polyethersulfone/ZnO_2 nanocomposite membrane has a molecular weight cut-off (MWCO) of 5275 Da, which was 13.7% higher than a similar nanocomposite membrane without the UV radiation.[26] Among all the metal-oxide nanoparticles, the nanoparticles of zirconium oxide are more stable chemically, and therefore under harsh conditions also they are the most suitable for membrane filtration. Maximus et al. in their report showed that polyethersulfone/zirconium oxide nanocomposite membrane had excellent water permeability (20 times higher) than pure polymeric membrane.[27]

II. CONCLUSION

In a nutshell, the nanocomposite membranes exhibit superior properties and higher performances as compared to their respective pure polymeric membranes. The different properties of nanoparticles such as their size, shape, composition, and surface properties also the type of polymers have strong impressions on the outcome/performance of the nanocomposite membranes. The optimal concentration of nanoparticles and membrane materials also plays an important role in the performance of nanocomposite membranes. Sometimes higher concentration of nanoparticles does not enhance their performance. Therefore, understanding the exact combinations of nanoparticles and polymeric matrices is always required to achieve the optimal outcome of the membranes through comprehensive experimental evaluations. This chapter intends to offer inspiration for further progress in the water treatment and desalination area engaging polymeric nanocomposite membranes.

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