POLY (VINYLIDENE FLUORIDE)/TIO$_2$-CNT NANOCOMPOSITE ULTRAFILTRATION MEMBRANES FOR WASTEWATER TREATMENT

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Abstract
Nowadays incorporation of nano-materials into polymers becoming a focus research area in membrane separation and purification technology. The fabricated nano-composite polymers offers an increased hydrophilicity and photo-catalytic benefits. However, the main advantages of each type of the nano-materials are limited. In this study ultra-filtration polymer nano-composite membranes were prepared using TiO_2 and CNT. Our recent work aims to examine the effect of TiO_2 and CNT on filtration properties of PVDF membrane. The contact angle of the neat membrane was78º, which could be lowered in case of the modified membranes of PVDF-TiO_2 and PVDF-TiO_2-CNT to 57.9 º and 64.63 º respectively. This implies that TiO_2 and CNT made the PVDF membrane hydrophilic due to their functional groups. It was found that the modification reduces the filtration resistance and enhances the flux. The water flux (L/m^2h) for neat PVDF membrane, PVDF-TiO_2 and TiO_2-CNT- PVDF was 67.22, 82.94 and 81.07 respectively. Neat PVDF membrane shows higher filtration resistance than TiO_2-PVDF and TiO_2-CNT-PVDF membrane. The irreversible foaling for neat PVDF was higher than the modified membranes. Regeneration of the fouled modified membranes by UV irradiation was possible.BSA and COD rejection was promising. The neat PVDF membrane rejects 99.84% BSA and 99.83% COD. The modified PVDF-TiO_2 also rejects 97.58% BSA and 99.74% COD while PVDF-TiO_2–CNT showed a rejection of 97.46% BSA and 97.05% COD. Relatively better regeneration of the fouled membrane was observed in the presence of CNT. The reasons for this phenomenon could be due to the reduction in recombination of electrons/holes and enhancement of photo-catalytic activity of TiO_2 by CNT as it sinks electrons/ holes. These results may offer significant new findings which are useful to development of modified membrane.

Keywords: nano-material, polymer, photo-catalytic nano-composite membranes, hydropholicity

1. Introduction

Nowadays, membrane separation technology has attracted interest due to the ease of operation and integration with other processes, reliable contaminant removal without production of any harmful by-products and low cost[1].Ultrafiltration (UF) membranes have received considerable attention because of the efficient rejection of bacteria, colloidal matter, protein, suspended particles, organic compounds, and better purification and concentration of food and paper products in industrial separation processes[2].

Among the polymeric materials, polyvinylidene fluoride (PVDF) is used widely in UF because of its superior properties such as high mechanical strength, excellent chemical resistance and better thermal stability[3].However hydrophobic nature and low surface energy of PVDF membranes leads it to be fouled easily by natural organic matter (NOM), protein and oily wastewater, results a decline in flux and negatively impact production efficiency by reducing the longevity of a membrane and increasing the energy costs [4].An increase in membrane hydrophilicity seems to be a promising strategy to overcome membrane fouling. Recently, antifouling and self-cleaning membrane fabrication that has maximum permeate and long membrane life time is a focus research area in membrane separation and purification technology [5].

Titanium dioxide (TiO_2) nanoparticle is considered to be superior over other due to its excellent physical and chemical properties, availability, high photocatalytic activity, desirable hydrophilic and potential antifouling properties[6]. However the photocatalytic activity of TiO_2 is restricted by the recombination of the photogenerated electron-hole pairs [7].

Carbon nanotubes (CNTs) have attracted a considerable attention due to outstanding properties, such as unique mechanical (stiffness and flexibility), large specific surface area, high thermal and electrical conductivities [8]. They offer a large surface area support for TiO_2 particles due to the unique texture/morphology and adsorption capacity of CNTs. It also serves as an electron scavenger and significantly hinder the recombination of electrons and holes [8]. However, these photocatalysts have been conducted in the form of powders. In this paper, the preparation of $TiO_2$and CNT-TiO2 -PVDF composite membrane with various ratios by phase inversion is reported.

2. Experimental design

2.1 Preparation of modified PVDF membrane and filtration

Ultra-filtration membranes (17.5 wt% (polymer + NPs)and 82.5wt% (solvent)) were prepared with a phase-inversion process.. The fabricated membranes were cut into the desired cross-sectional area corresponding to the ultra-filtration (UF) dead-end cell experiments. The membrane filtration experiments were using1g/L bovine serum albumin (BSA) [9].

2.2.Analytical methods

Membrane contact angle. The water contact angle of the prepared membrane was measured manually by the sessile drop method (Data physics Contact Angle System OCA15Pro, Germany). Standard potassium-dichromate oxidation method was the technique used to determine COD in our experiment.BSA concentrations in feed and permeate solutions were measured using a spectrometer(Hitachi Co., U-2000, Japan) at a 280 nm. Water and permeate fluxes of the neat and modified membranes were compared, organic content (COD: chemical oxygen demand), and protein rejection were investigated. Fouling resistance parameters including total fouling resistance (Rt), reversible fouling resistance (Rr) and irreversible fouling resistance (Rir) were calculated to study the fouling of the membranes process in detail through the resistances-in-series model [10].

3. Results and discussion

Water contact angle measurements

Contact angles were measured to study the surface hydrophilicity of the PVDF membrane, and the contact angles formed by distilled water on the surface of pristine and modified PVDF membrane were calculated using mean of six sample points..The contact angles of the neat PVDF, PVDF-TiO_2 and PVDF-CNT were72.23º, 57.9 º and 64.63º respectively. This implies that TiO_2 and CNT made the PVDF membrane very hydrophilic due to their functional groups.

A similar study by Hossein et al. [11] indicated hydrophilicity improvement of neat PVDF membrane by nanoparticles.

Filtration of BSA solution

In order to check the fouling mitigation ability of modified membranes protein (BSA) solutions were filtered and filtration resistances were calculated through the use of Eqs. (4)–(7). The membrane resistance (*RM*), irreversible resistances (*Rirrev*), reversible resistances (*Rrev*) and total resistances (*RT*) are presented in Figure 1. Pristine membrane shows the highest filtration resistance. It was found that the modification significantly decrease the membrane resistance.

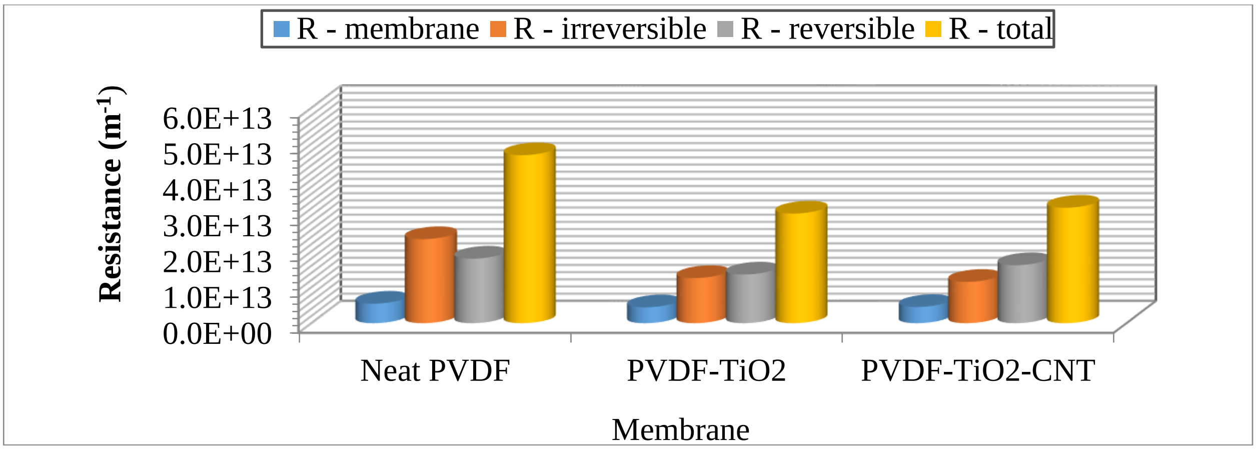

Figure 1. Filtration resistances by pristine and modified membranes

Unlike the neat membrane, reversible fouling of modified membranes were more than irreversible fouling, this can be explained by low contact angle. Our results are in accordance with the earlier observations [12].

Rejection

The BSA and COD rejections of the pristine and modified membranes are illustrated in Fig. 5. The neat PVDF membrane rejects about 98.88% BSA and 99.83% COD. The modified PVDF-TiO_2 also rejects 97.58% BSA and 99.74% COD while PVDF-TiO_2–CNT showed a rejection of 97.46% BSA and 97.05% COD. It was found that the modified membranes shows almost similar BSA and COD rejection as neat PVDF membrane this could be due to the formation of larger pores by nanoparticles [5].

Regeneration of BSA fouled membrane

Regeneration of fouled modified membranes can be achieved by 3 hours UV radiation (λ_{max} = 360 nm) light exposure. The extent of flux restoration for PVDF-TiO_2 a bit lower than PVDF-TiO_2-CNT. The reasons for this phenomenon could be due to the reduction in recombination of electrons/ holes and enhancement of photo-catalytic activity of TiO_2 by CNT as it sinks electrons/ holes [8].

4. Conclusion

This work investigates the effects of TiO_2-CNT incorporated PVDF polymeric membranes on the rejection of a model protein, bovine serum albumin (BSA) solution. Pristine PVDF and TiO_2-CNT- PVDF and TiO_2-PVDF membrane are fabricated by phase inversion method. Phase inversion is a simple and economical strategy method used to fabricate membranes. The membrane modification produced hydrophilic membrane surface, as was proven by contact angle measurements on pristine and modified PVDF membranes. TiO_2-CNT- PVDF and TiO_2-PVDF membrane revealed a better water flux than the neat PVDF membrane. Neat PVDF membrane shows higher filtration resistance than TiO_2-CNT- PVDF and TiO_2-PVDF membrane. The irreversible foaling is higher for neat PVDF than the modified membranes. Regeneration of the fouled modified membranes by UV irradiation is possible. However 3 hours UV exposure is not enough to achieve the original flux which requires further investigation. A little more flux restoration is observed for TiO_2-CNT- PVDF than TiO_2-PVDF membrane. The reasons for this phenomenon could be due to the reduction in recombination of electrons/ holes and enhancement of photo-catalytic activity of TiO_2 by CNT as it sinks electrons/ holes.

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