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# Carbon based Nanofillers Embedded Fouling Resistant Polyvinyl Chloride Nanocomposite Membranes for Oil-water Separation

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ABSTRACT

Herein, we discussed the development of polyvinyl chloride (PVC) based nanocomposite ultrafiltration (UF) membrane by embedment of nanofillers such as carbon black (CB), graphitized carbon black (GCB) or mesoporous carbon, multiwalled carbon-nanotube (MWCNT), carboxylated multiwalled carbon-nanotube (CMWCNT) with increased permeate flux and fouling resistance. Ultrafiltration membranes were prepared using casting solution of PVC in N, N-dimethylacetamide (DMAc) solvent with polyethylene glycol with average MW 600Da (PEG-600) as additives with and without nanofillers. Membranes prepared were characterized in terms of pure water permeability, separation of single uncharged solutes like polyethylene oxide (PEO), water contact angle and tensile strength. Membranes were tested with synthetic oily waste water (1000 ppm oil-water emulsion) followed by pure water flux recovery after cleaning by flow reversal flushing using deionized water. The product flux was observed to increase by ~35.5%, ~11.4% & ~44.4% in PVC-GCB, PVC-MWCNT and PVC-CMWCNT membranes respectively than the pure PVC membranes. The flux recovery on cleaning of fouled membranes is ~56% in pure PVC membrane, whereas it is ~72%, ~74% & ~80% for PVC-GCB, PVC-MWCNT and PVC-CMWCNT membranes respectively. Incorporation of the carbon based nanofillers in pure polymer matrixes not only enhances the water permeability with marginal decrease of the separation performances but also it increases mechanical strength and the fouling resistance of the membranes. The carbon fillers-based PVC nanocomposite membranes are found promising candidates for cleaning oily wastewater.

**Keywords:** Ultrafiltration, polyvinyl chloride, carbon black, carbon nanotube, oil-water separation

# I. INTRODUCTION

Ultrafiltration (UF) is a well-established pressure driven membrane process used for water treatment to separate macromolecules, colloids, microorganisms etc [1]. Separation of oil from oil-water mixture is one such application area where membrane-based treatment processes are employed successfully over conventional separation techniques used such as coagulation, flocculation, photocatalysis, ultrasonic separation, air floatation, chemical de-emulsification, advanced oxidation process. The conventional methods have disadvantages like higher energy consumption, lower efficiencies, generation of secondary contaminants, large space requirement etc. [2, 3]. As an alternate method, ultrafiltration and microfiltration membranes are used nowadays for emulsified oil/water separation due to the high separation efficiency, easy control and scale-up and it is an energy efficient with simple operational process [4]. Membranes with desired chemical, thermal and mechanical stability combined with excellent fouling resistant properties are used for ultrafiltration process in wide spread separation applications. UF membranes are prepared from both hydrophilic and hydrophobic polymers such as polysulfone, polyethersulfone, polyacrylonitrile, polyvinylidene fluoride, polypropylene, polyvinyl chloride etc. Among others, polyvinyl chloride (PVC) membranes got extensive attention due to its advantages of low cost, resistant to chemicals like many alcohols, fats, oils, common corroding agents including inorganic acids, alkalis and salts with decent mechanical properties. However, pure PVC membranes are readily prone to membrane fouling upon long-term operation and have lower flux [5]. Numerous strategies have been adopted to increase fouling resistance of pure polymeric membranes such as, surface modification through surface coupling of suitable polymers/biomolecule or additive segregation to form a polymer brush layer, blending of hydrophilic polymer with hydrophobic polymer etc [6, 7]. Later, mixed-matrix membranes consisting of PVC polymer and inorganic nanoparticles like titanium dioxide ($TiO_2$), iron oxide ($Fe_2O_3$), zinc oxide (ZnO) have been developed to achieve enhancement of the membrane performances along with the better fouling resistance properties [8-10]. Being carbon-based nanomaterials, carbon blacks (CBs) and Carbon Nanotubes (CNTs) as fillers have advantages of compatibility with commonly used organic membrane polymers than any of the inorganic nanomaterials with respect to fabrication of homogeneous nanocomposite membrane. In this study, the PVC based nanocomposite UF membrane were developed by embedment of carbon black (CB), graphitized carbon black (GCB) or mesoporous carbon, multiwalled carbon-nanotube (MWCNT), carboxylated multiwalled carbon-nanotube (CMWCNT) with the aim of increase in permeate flux and fouling resistance.

# II. EXPERIMENTAL

Membranes are prepared by casting the polymer casting solution prepared by dissolving 16% (w/w) PVC (Avg. Mw=43000Da; Avg. Mn=22000Da) beads & 5% (w/w) polyethylene glycol with average MW 600Da in 79%(w/w) N, N-dimethyl formamide solvent. For nanocomposite membranes, 0.8%(w/w) of the nanomaterials [carbon black nanopowder, graphitized carbon black (<500 nm particle size (DLS), >99.95% trace metals basis), multiwalled carbon-nanotube (>95% carbon basis, O.D. × L 10-40 nm × 0.5-1.5 mm) and carboxylated multiwalled carbon-nanotube (>8% carboxylic acid functionalized, avg. diam.× L 9.5 nm × 1.5 μm,)] were dispersed in DMF first and then PVC & PEG-600 was added into the nanofiller dispersed solvent. The suspension was then agitated until complete polymer dissolution to form homogeneous casting solution. For membrane preparation, the casting solution was spread over a nonwoven fabric support using doctor knife edge under a steady casting shear followed by immersion in a gelling bath containing DI water. Finally, the membranes were washed several times with DI water to remove excess solvent and stored in water at ~5-7°C water. Water contact angle on membrane surface was determined using the sessile drop method on a standard drop shape analysis system (DSA100, KRu¨SS GmbH, Germany). The ultimate tensile strength of the membranes was measured using a mechanical testing instrument (Instron 5540 Series Single Column Testing Systems; Instron, Norwood, Massachusetts, USA).

The performance of the UF membranes was evaluated using a cross-flow filtration device operated at recirculation mode at 2.0 bar pressure. The oil-water feed was prepared by mixing 1000 mg/L liquid oil and 5 mg/L sodium dodecyl sulfate at 2500rpm for 24hours. The separation of oil was determined by measuring total organic carbon (TOC) & turbidity of feed and permeate samples for all the membranes. After 3-4 hrs of operation, DI water is used as a feed to determine the reversibility of fouling by flow reversal flushing. Fouling studies are carried out at constant initial flux (50 $L.m^2.h^{-1}$) for proper comparison of fouling tendency on change in membrane material.

## III. RESULTS & DISCUSSIONS

The amount of nanoparticle loading was optimized through several experiments to get the optimum membrane performance in terms of solute rejection properties and it was found that the optimum concentration for CB & GCB is 0.8% whereas it is 0.5% for MWCNT & CMWCNT. PVC based ultrafiltration membranes prepared with and without nanofillers were characterized in terms of pure water permeability (PWP), rejection of neutral uncharged solutes (PEO-300kDa), water contact angle and mechanical strength data. The results are given in Table 1. Nanocomposite membranes become more hydrophilic upon incorporation of nanomaterials onto PVC membranes. Carboxylated-MWCNT is found more effective to increase the hydrophilicity than that of other carbon based nanofillers. The ultimate tensile strength (UTS) i.e., the strength of all the nanocomposite membranes is more than the pure polymeric PVC membrane. The increase of strength of the nanocomposite membranes are also indications of proper compatibility of carbon-based nanomaterials with the PVC polymer. The PWP through the membrane in UF permeation experiment follows the order: PVC-CB < blank-PVC < PVC-MWCNT < PVC-GCB < PVC-cMWCNT with almost similar solute rejection properties. This indicates that all the membranes have almost same pore sizes. Being a non-porous material, carbon black (CB) can block some of the pores in the PVC-CB membranes resulting lowering of product flux marginally whereas the flux is more for porous nanomaterials-based nanocomposite PVC membranes. The performance of the membranes was evaluated for separation of oil from 1000ppm oil-water emulsion in terms of the turbidity removal efficiency at 2.0 bar pressure and the result is given in Table 2. The permeate flux pattern follows the same trend with PWP and with <98% turbidity removal efficiency.

TABLE 1: MEMBRANE PERFORMANCE & CHARACTERIZATION DATA OF UF MEMBRANES

| Memb. | Conc. of filler (%) | Ultrafiltration membrane performance (Pressure:2bar) | | Water contact angle (deg.) | Tensile Strength (MPa) |
|---|---|---|---|---|---|
| | | Pure water Permeabi-lity (LMH) | PEO-300kDa rejection (%) | | |
| PVC | Nil | 54.3±3.5 | 86.5±0.5 | 82.0±0.5 | 4.2±0.4 |
| PVC-CB | 0.8 | 52.7±4.1 | 88.2±0.5 | 78.2±0.8 | 6.3±0.7 |
| PVC-GCB | 0.8 | 73.6±5.6 | 84.7±0.4 | 77.0±0.7 | 5.7±0.8 |

| | | | | | |
|---|---|---|---|---|---|
| PVC-MWCNT | 0.5 | 60.5±2.9 | 85.2±0.7 | 74.2±0.9 | 5.8±1.0 |
| PVC-CMWCNT | 0.5 | 78.4±4.2 | 84.7±0.6 | 70.7±0.8 | 6.3±0.9 |

TABLE 2 : TURBIDITY REMOVAL EFFICIENCY OF MEMBRANES

| Membrane | Turbidity removal efficiency (%) |
|---|---|
| PVC | 98.2±0.5 |
| PVC-CB | 99.0±0.4 |
| PVC-GCB | 98.1±0.6 |
| PVC-MWCNT | 98.5±0.8 |
| PVC-CMWCNT | 98.4±0.5 |

For fouling studies of the membranes, the DI water stabilized flux is taken as $J_0$ at time zero and then oil-water emulsion was taken as feed and the water flux at time t is denoted as Jw. The plot of normalized flux ($J_w/J_0$) as a function of time is given in Fig. 1. The product flux decreases with time for all the membranes as expected due to the formation of oily film over the membrane surface, but nanocomposite membranes exhibit relatively lower flux decline. As nanocomposite membrane surfaces are more hydrophilic, it resists oil-film deposition in greater extent. After this oil-water filtration till 3 hrs. (180mins.), all the membranes were washed with DI water by reversing the feed flow direction and then tested again in UF set up to determine flux recovery. The results of flux recovery experiments are given in Fig. 2. The flux recovery in pure polymeric PVC membrane is much less (~56%) than the PVC-CB (~69%), PVC-GCB (~72%), PVC-MWCNT (~74%) and PVC-cMWCNT (~80%) membranes which indicates that the oil-film adhesion tendency on hydrophobic pure polymeric membrane is much more than the relatively hydrophilic nanocomposite membranes.

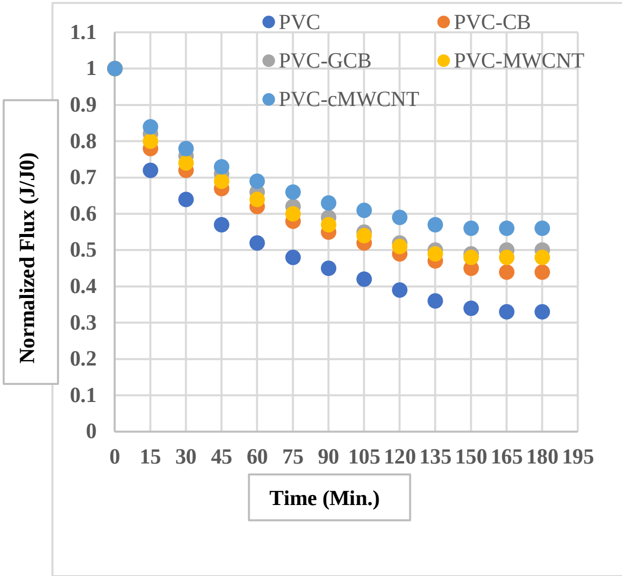


Figure 1 : Flux versus time of UF membranes during oil-water filtration

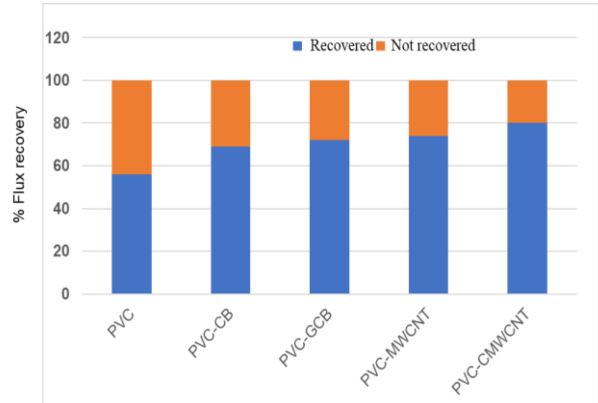


Figure 2 : Flux recovery on washing by flow reversal of UF membranes after oil-water separation

## IV. CONCLUSIONS

It can be concluded that the carbon-based nanomaterials such as carbon black, graphitized carbon black or mesoporous carbon, multiwalled carbon-nanotube, carboxylated multiwalled carbon-nanotube are potential nanomaterials for enhancement of product permeation rate with better mechanical strength of the PVC based nanocomposite ultrafiltration membranes for cleaning oily wastewater. Carboxylated-MWCNT is found more effective nanomaterials not only to increase the hydrophilicity of the membrane but offers ~45% more water flux than the pure PVC membranes for oil-water separation. Nanocomposite membranes were found more fouling resistant than the pure polymer membranes with excellent turbidity removal and higher flux recovery.

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