An official publication of the International Society for Energy, Environment and Sustainability (ISEES)

Journal of Energy and Environmental Sustainability

Journal homepage : www.jees.in

Wastewater Treatment Containing Oil Using Polyvinylidene Fluoride (PVDF) Ultrafiltration Membrane Modified with Functionalized SiO_2 Nanoparticles

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ARTICLE INFO

Received : 01 February 2019
Revised : 24 March 2019
Accepted : 27 April 2019

Keywords:
Wastewater Treatment, Oil in water Emulsion, Polymer Membrane, Polyvinyl dine Fluoride, Removal Percentage

ABSTRACT

Polyvinylidene fluoride (PVDF) ultrafiltration membrane was fabricated by phase inversion method for the treatment of wastewater containing oil. In order to achieve less fouling and high rejection, modification of PVDF membrane had been done by blending of hydrophilic Poly(ethylene glycol) methyl ether methacrylate functionalized-SiO_2 nanoparticles. Successful functionalization of SiO_2 nanoparticles was done by measuring weight percentage of elements present using energy dispersive X-ray spectroscopy (EDX) and particle size analyzer. The morphology of the plain and modified membranes was evaluated using field emission scanning electron microscope (FESEM). The contact angle (CA) was investigated for evaluation of hydrophilicity of the membranes. The hydrophilicity result reveals that the antifouling property of modified membrane was higher compare to plain membrane. Plain PVDF membrane showed less oil rejection of about 69% whereas functionalized nanoparticles helped to improve the oil rejection to the maximum value of 89%. Thus the PVDF/Polyethylene glycol 6000/ functionalised-nanoparticles membrane is desirable in the treatment of wastewater containing oil.

1. Introduction

Every year huge amount of oil containing wastewater is generated by petrochemical, food, pharmaceutical and metallurgical industries which results poor environmental pollution and trouble in resource utilization. Conventional oily wastewater treatment methods namely gravity separation and skimming, air flotation, coagulation, de-emulsification and flocculation have the inherent drawbacks such as low efficiency, high operating cost, corrosion and recontamination problems [Honga et al., 2003] that then lead to ineffective removal of emulsified oil droplets (size: micron and sub-micron) [Hussein et al., 1993]. Moreover, emulsified oily wastewater by the addition of surfactants is extremely hard to remediate because of the efforts required to crack down the interfacial films created between oil and water [Zhou et al., 2009; Canizares et al., 2007]. In consideration of these limitations in conventional treatment methods, numerous kinds of polymeric membrane separation processes such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been recently utilized for oil-water treatment [Peterson, 1993; Freeman and Pinnau, 2004]. On account of its appropriate pore sizes (2–50 nm) and the ability of separating emulsified oil droplets without any de-emulsification processes, UF has been established as an capable method in the treatment of oil-water emulsions [Vedavyasan, 2007; Yang et al., 2012]. However, fouling is a severe problem intrinsic in UF membranes due to hydrophobic nature of polymer. Fouling caused by either deposition of oil on the membrane surface or inside of membrane pores that that ends up in a substantial flux loss [Hilal et al., 2005]. The membrane properties such as pore structure, surface characteristics, as well as process and operating conditions are the factors which affects the membrane fouling. Hydrophilic rich moieties like inorganic nanoparticles, organic solvents, macromolecules and amphiphilic copolymers have been set up to impart antifouling property by means of membrane modification. Saraswathi et al. synthesized polydopamine coated PVDF ultrafiltration membranes for BSA and humic acid separation from aqueous stream. They obtained that the fouling resistance experiments with BSA and HA indicate an increasing fouling resistance trend in the modified membranes, as their rejection and recovery ratios are higher than that of neat membrane [Saraswathi et al., 2017]. Huang et al. prepared the PVDF/SiO_2 hybrid ultrafiltration membranes by sol–gel method for the concentration of fennel oil in herbal water extract. The hybrid membranes exhibited excellent permeability and rejection rate as well as antifouling properties compared with PVDF membrane [Huang et al., 2015]. Mericq et al. conducted their study to obtain low fouling membranes. TiO_2 nanoparticles were entrapped in PVDF membranes prepared by the NIPS wet-process. Membrane structure, hydrophilic properties and permeability were improved in comparison with PVDF neat membrane when increasing TiO_2 concentration up to an optimum concentration of 25% wt. For TiO_2 content beyond 25% wt, TiO_2 particles agglomeration prevents the improvement of hydrophilic properties and permeability [Mericq et al.,

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2015]. Ngang et al. prepared polyvinylidene fluoride/silica-poly (N-isopropylacrylamide) (PVDF/SiO_2-PNIPAM) mixed matrix membranes using diffusion induced phase separation techniques via direct blending method. They had observed the flux recovery ratio of 69.91% through oil emulsion separation using cross-flow ultrafiltration and the PVDF/SiO_2-PNIPAM membrane showed higher alternated thermal cleaning ratios (N=2.04) especially at higher SiO_2-PNIPAM particle concentrations compared with pristine PVDF membrane [Ngang et al., 2017]. Shen et al. prepared antifouling hybrid PVDF membrane with poly(N-acryloylmorpholine)-grafted ZrO_2 (ZrO_2-g-PACMO) nanoparticles and they observed that modified membranes showed lower adsorption of protein than unmodified PVDF membrane [Shen et al., 2017]. Lin and Rutledge used electrospun fiber membranes for the treatment of oil in water emulsion stabilized by different types of surfactants. The membrane was shown to have high oil rejection (92.7%), sufficient to meet EPA's regulatory limit, when separating emulsions stabilized by anionic surfactant in cross-flow filtration, while maintaining a steady flux of 44.3 l/m^2h [Lin and Rutledge, 2018]. Yan et al. synthesized PVDF ultrafiltration membrane for Al_2O_3 particles. The permeation flux increase of the modified membrane was attributed to increases in the surface hydrophilicity and the efficient filtration area due to the addition of hydrophilic inorganic nano sized Al_2O_3 particles [Yan et al., 2006]. Zheng et al. described on the fabrication of PVDF/ZrO_2 hybrid membranes and observed that both the hydrophilicity and antifouling property was stronger than those of plain PVDF membrane [Zheng et al., 2011]. Pang et al. also found the similar experimental results in their study [Pang et al., 2014]. Although some significant achievements have been gained, there is an extreme requirement to defeat some drawbacks such as agglomeration. The agglomeration of the nanoparticles always makes it the uneven distribution in the membrane matrix, leading to the decreased strength of antifouling property of the membranes [Yin and Zhou, 2015].

In this work PVDF membrane modification using Poly(ethylene glycol) methyl ether methacrylate functionalized-SiO_2 nanoparticles have been reported. The functionalized nanoparticles were characterized by EDX and particle size analyzer. The plain and modified membranes were characterized by SEM, EDX pure water flux and water contact angle. Afterwards the ultrafiltration study was conducted using oil in water emulsion to represent as an industrial model pollutant. Finally, the separation performance of plain and modified membrane for oil in water emulsion was evaluated in terms of percentage removal of oil in water emulsion and fouling parameters.

2. Experimental

2.1. Materials and methods

PVDF pellets, PEGMA and N,N-Dimethylacetamide (DMAc) were purchased from M/s. Sigma Aldrich, India. Poly ethylene glycol (PEG) was purchased from M/s, Loba chemicals, India. Silicon oxide (SiO_2) nanoparticles were supplied by Otto Chemie Private Limited, India. All chemicals were used as received without further purification. Initially, the Poly(ethylene glycol) methyl ether methacrylate functionalized-SiO_2 nanoparticles were synthesized via radical polymerization of SiO_2 nanoparticles and PEGMA in methanol using A-A-azo-iso-butyronitrile (AIBN) as initiator. Modified nanoparticles were characterized for particle size distribution by particle size analyzer (Malvern Mastersize 2000, Model, MAL1083109) and successful functionalization of nanoparticles by energy dispersive X-ray spectroscopy (EDX) analysis. After that the optimize concentration of functionalized nanoparticles (0.5 wt%) was used to modify the PVDF membrane. Plain PVDF membranes was synthesized with 15 wt% of PVDF pellets with 5 wt% of pore forming agent without nanoparticles on dissolving into DMAc solvent and subsequent fabrication by phase inversion method. The optimized modified membrane was synthesized by 15 wt% of PVDF pellets with 5 wt% of pore forming agent and 0.5 wt% of functionalized nanoparticles on dissolving into DMAc solvent. The synthesis steps for membrane fabrication by phase inversion method are shown in Fig. 1.

2.2. Membrane characterization

Membrane hydrophilicity was analysed by measuring contact angle made by water drop on the membrane surface (Sinha and Purkait, 2013). Plain and modified membrane were analysed for top surface morphology by SEM (LEO 1430VP, UK) and existence of modified nanoparticles in the membrane by EDX.

In order to evaluate membrane performance oil in water emulsion (100ppm) as feed was used in dead end batch filtration setup. The schematic of batch filtration cell used in this study is shown in Fig. 2.

The turbidity of the oil in water emulsion feed and permeate were

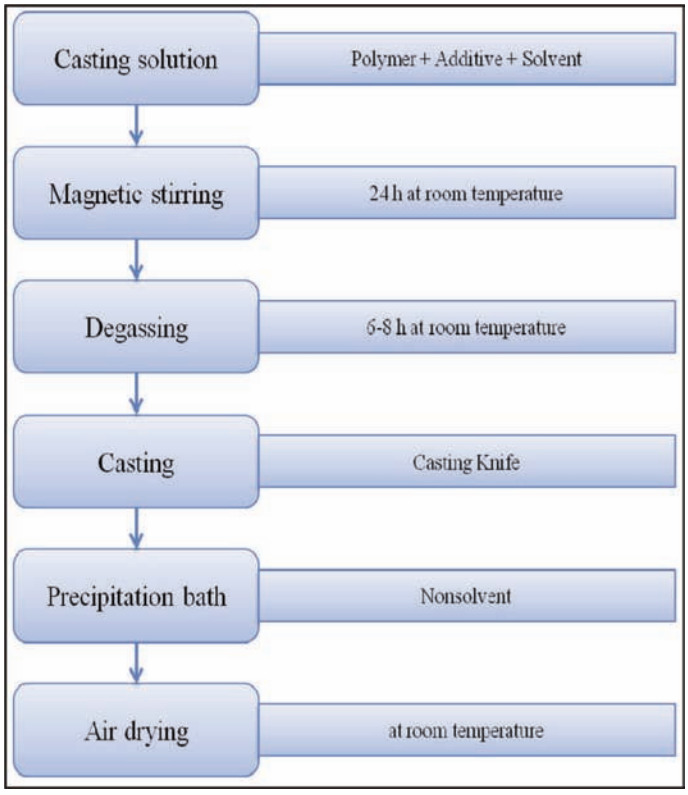

Fig. 1 Steps for membrane fabrication by phase inversion method.

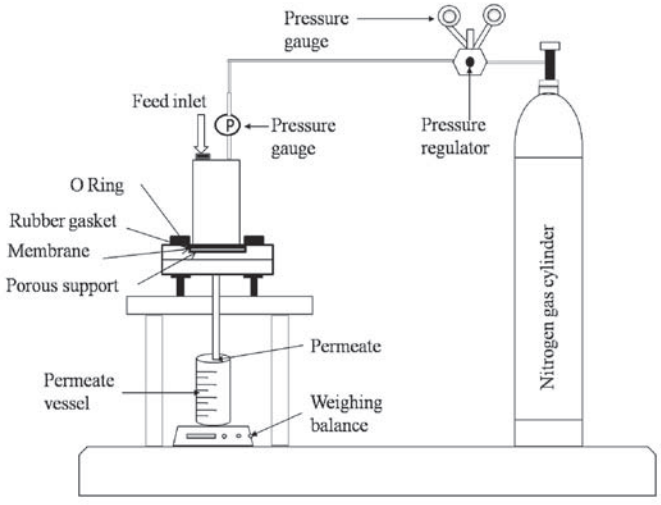

Fig. 2 The schematic diagram of batch filtration cell.

determined using a portable nephlometer turbidity meter (Model: 2100Q, Hach) and the feed turbidity was 259 NTU. The removal percentage of o/ w emulsion was calculated using feed and permeates concentration with the help of UV–vis spectroscopy at wavelength of 202 nm in oil in water emulsion ultrafiltration study.

Ultrafiltration experiment was conducted in batch filtration setup of 350 mL capacity and effective filtration area of the membrane was 50 mm. Nitrogen gas was used to pressurize the system. Pure water flux, oil in water emulsion flux and removal percentage (% R) of oil in water emulsion was determined by following equations [Shen et al., 2017]:

$$J = \frac{V}{A\Delta T} \quad (1)$$

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where *J, V, A* and ΔT represents pure water flux (L/m² h), volume of permeating liquid (L), effective surface area of membrane (m²), permeation time (h), respectively. *Cf* and *Cp* represents the concentrations of feed and permeate (mg/L), respectively.

From ultrafiltration experiments, some ratios such as irreversible fouling (F_{ir}), reversible fouling (F_r), total fouling (F_t) and selection parameter (*Sp*) were determined by following equations:

$$F_{ir}(\%) = \left(\frac{J_1 - J_2}{J_1}\right) \times 100 \quad (3)$$

$$F_r(\%) = \left(\frac{J_2 - J_o}{J_1}\right) \times 100 \quad (4)$$

$$F_t(\%) = \left(\frac{J_1 - J_o}{J_1}\right) \times 100 \quad (5)$$

Where J_f, J_{pw1} and J_{pw2} indicates feed flux, pure water flux before and after oil in water emulsion ultrafiltration.

In addition, the flux recovery ratio ($Flux_{RR}$) and flux decline ($Flux_D$) were determined using the value of pure water flux at steady state before and after cleaning of membrane using the following equations:

$$Flux_{RR} = \frac{J_{pw2}}{J_{pw1}} \quad (6)$$

$$Flux_D = \left(1 - \frac{J_{pw2}}{J_{pw1}}\right) \quad (7)$$

The selection parameter (S_p) (L/m² h) was also determined to compare the performance of different membranes using the following expression:

$$S_P = \frac{J_{pw2}R}{Flux_D} \quad (8)$$

3. Result and Discussion

3.1. Particle size and EDX analysis

To ensure the nano size range of plain nanoparticles and functionalized nanoparticles, the particle size analysis on volume (%) basis had been done using particle size analyzer. Fig. 3. shows the particle size distribution of plain and functionalized nanoparticles. It was observed that the size of functionalized nanoparticles was slightly larger compare to the size of plain nanoparticles as a result of functionalization with hydrophilic polymer compound. However, size of functionalized nanoparticles was in the nanometre range. From the particle size analysis, it was concluded that the size of nanoparticles remains in nano size range after functionalization with hydrophilic polymer chains which makes it suitable for blending in casting solution. Apart from particle size analysis, the EDX analysis of plain and functionalized nanoparticles was conducted in order to determine the elemental composition as well as to confirm the successful functionalization of nanoparticles. The EDX analysis of the nanoparticles was conducted and results are shown in Fig. 4. In plain nanoparticles spectra, only Si and O element peaks were observed. Whereas, functionalized nanoparticles spectra shows the presence of one extra peak of C element (41.2 wt%) along with peaks of Si (12.3 wt%) and O (46.5 wt%) elements. The difference between the spectras of plain and functionalized nanoparticles clearly confirms the successful functionalization of SiO_2 nanoparticles by hydrophilic polymer chains.

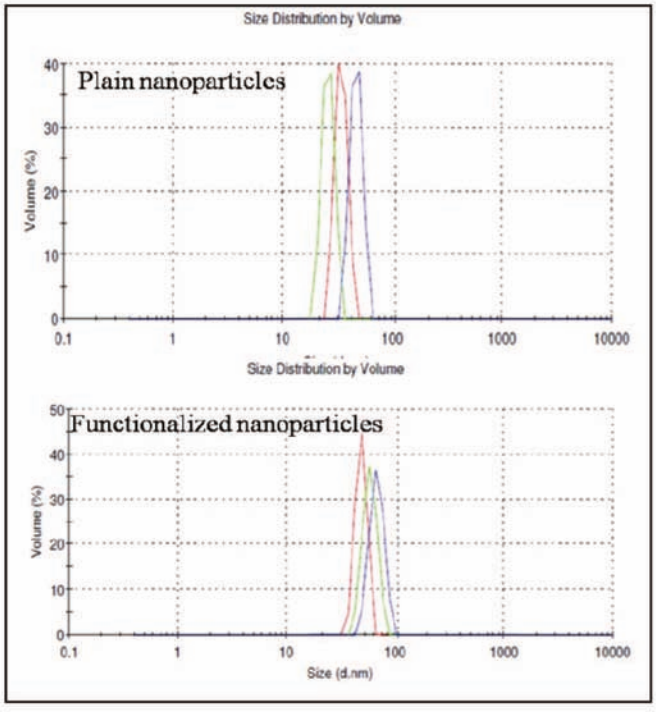

Fig. 3 Particle size analysis for plain and functionalized nanoparticles.

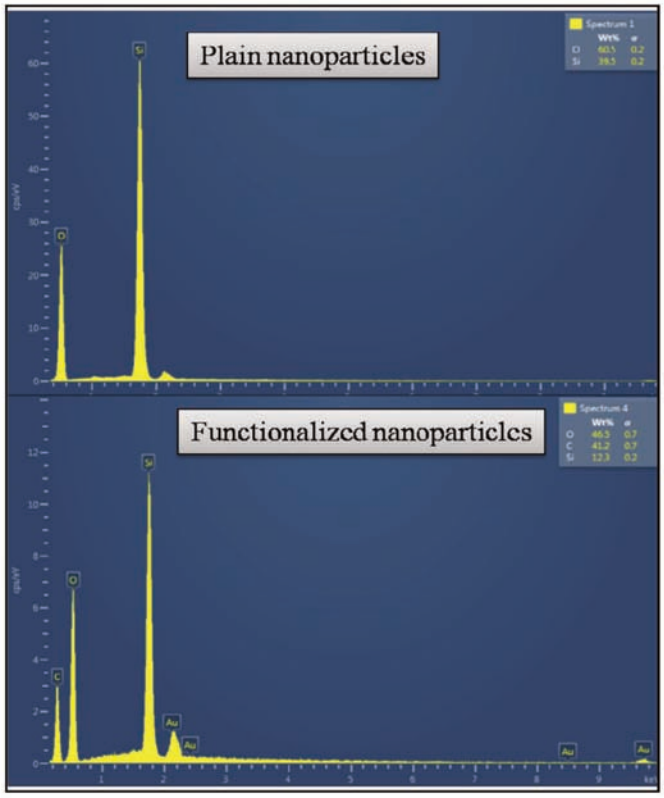

Fig. 4 EDX Images for plain and functionalized nanoparticles.

3.2. Hydrophilicity and morphology of the membrane

The hydrophilicity of the plain and modified membrane was assessed by measuring water contact angle made by water drop on the surface of membrane. The plain PVDF membrane has the highest water contact angle of 68.7°, showing poor hydrophilicity and it decreased around 55° (for modified membrane) with addition of functionalized nanoparticles in the membrane. Lower water contact angle higher the hydrophilicity and vice versa. The modified membrane has higher hydrophilicity compare to plain membrane which also indicates the improved fouling resistance property of the modified membrane. These results showing that blending of functionalized nanoparticles into the casting solution for modification of PVDF membrane were capable to significantly improve the membrane surface hydrophilicity.

In order to see the effect of functionalized nanoparticles on the microstructure of the fabricated PVDF membranes, SEM micrographs of top surface was obtained. The top surface SEM images showed that the blending of nanoparticles have power to affects the membrane formation mechanism and final structure of the membranes. Fig. 5 shows the top surface images of plain and modified membranes. From Fig. 5 it was observed that the surface of plain membrane was smooth with less pore density whereas the modified membrane with addition of functionalized nanoparticles, the pore density of the modified membranes was increased. From SEM results, it is expected that the permeability of the membrane will increase with increase in pore density. This observation was also found by other researchers in their studies [Wang et al., 2012; Yin and Zhou, 2015] and may be acceptable by the following reasons: (1) incorporation of hydrophilic nanoparticles additive increases the thermodynamic instability of the casting solution results formation of big

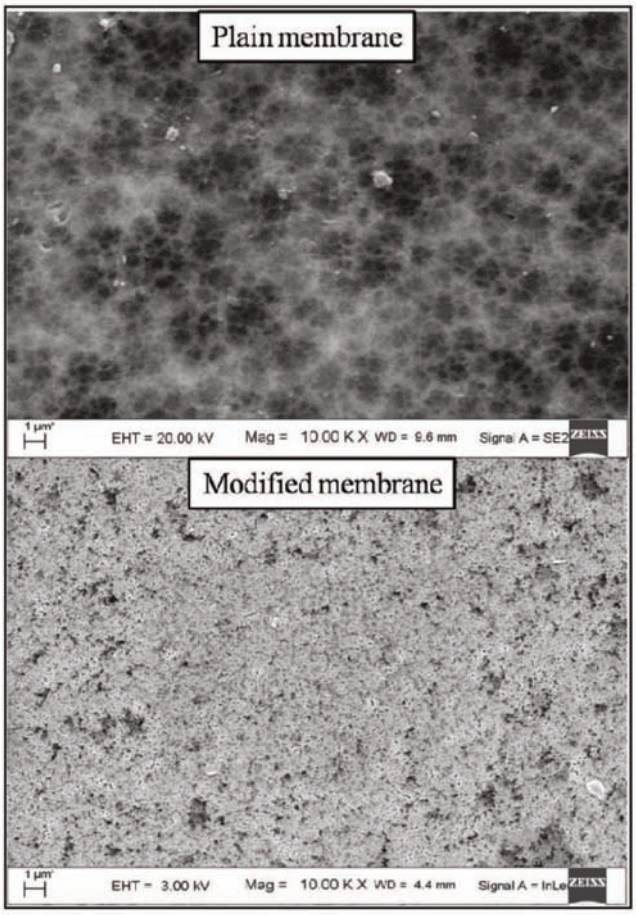

Fig. 5 SEM Images of plain and modified membrane.

surface pore size and high porosity [Vatanpour et al., 2012]; (2) during formation of membrane film, polymer precipitated eagerly and hydrophilic nanoparticles additive migrated spontaneously on the membrane surface in order to decrease interfacial energy. Simultaneously, some quantity of hydrophilic nanoparticles can leach out from the membrane film and then act as a pore forming agent resulting to highly porous nature of membrane with large pore size [Zhao et al., 2011]; (3) viscosity of the casting solution increases with addition of hydrophilic nanoparticles concentration, which results delayed demixing of solvent and nonsolvent as well as restrict the formation of large pore size [Liu et al., 2011].

The EDX images of plain and modified membrane are shown in Fig. 6 to determine the inorganic elements composition of plain and modified membrane. The EDX results of plain membrane indicated the 0.0 wt% of Si element, which confirms the non-existence of functionalized nanoparticles in the plain membrane. Whereas, modified membrane spectra shows the 0.7 wt% of Si element from nanoparticles which confirm the existence of functionalized nanoparticles in modified PVDF membrane. The F (51.2 wt%) and C (47.9 wt%) element peaks are present due presence of C and F in PVDF polymer.

3.3. Membrane performance analysis

After the hydrophilicity, elemental composition and morphological characterization of fabricated membranes, both membranes were analysed for their performance in terms of pure water flux and percentage removal of foulant present in the wastewater using batch filtration setup. The effective membrane surface area of 50 mm is required for permeation study. The performance study was conducted through a cycle ultrafiltration using pure water-oil in water emulation-pure water. First pure water flux (j_1) was measured for 1 h after that oil in water emulsion (j_0) passes through the membrane for another 1 h. Then membrane was cleaned with fresh water and further pure water (j_2) was measured for next 1 h. The synthetic wastewater of oil in water emulsion (100 ppm concentration) was prepared using Indian crude oil (density: 911.2 kg/m^3) without any treatment. Crude oil was used as oil phase in deionised water and concentration in water was kept at the desired value (100 ppm). Mixture of crude oil and water was sonicated by using probe sonicator (Model: VCX 500, Ultrasonic Processor 500 W, 20 Khz) for 6–8 h at 30 °C to prepare the oil in water emulsion. The average oil droplets size of oil in water emulsion was 311.5 nm with a volume average which was determined using particle size analyzer (Malvern Mastersize 2000, Model, MAL1083109). The pH of the oil in water emulsion prepared for this study was 7.03. After permeation of oil in water emulsion through modified membrane, the photograph of oil in water emulsion (feed) and permeate is shown inset of Fig. 7. Fig. 7 clearly indicates the difference between oil

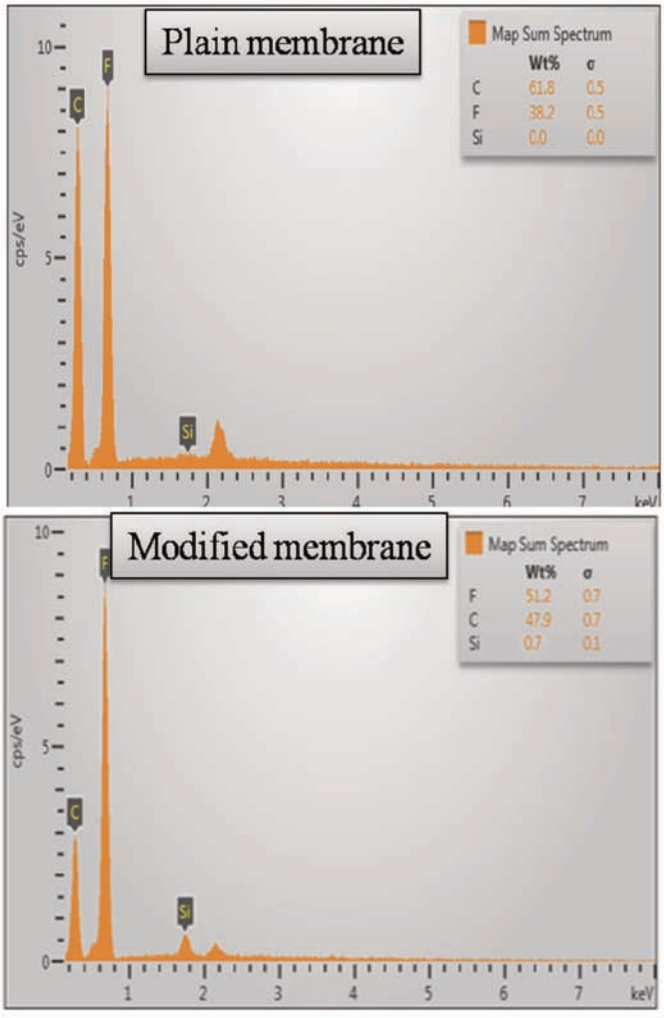

Fig. 6 EDX Images for plain and modified membranes.

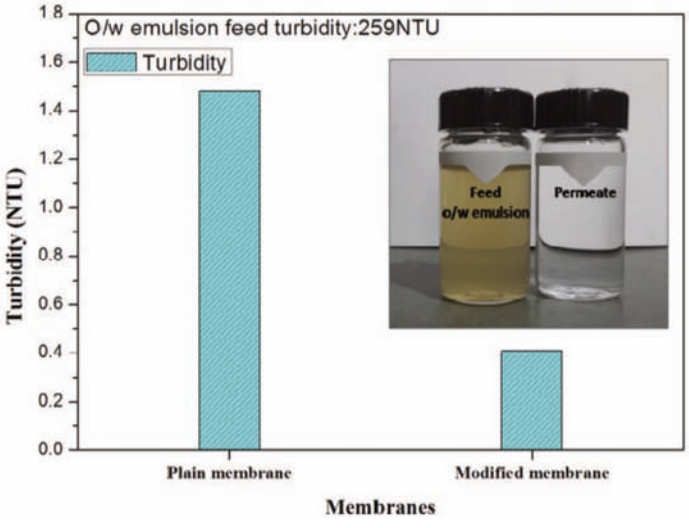

Fig. 7 Turbidity values of permeate through plain and modified membrane; (inset: image of feed and permeate)

in water emulsion feed (turbid water, yellowish-brown) and permeates (more clear water) on visual comparison. The turbidity of the oil in water emulsion was 259 NTU, after permeation this value decreased upto 1.4 NTU and 0.4 NTU through plain and modified membranes, respectively. A drastic change in turbidity was observed from feed to permeate. From the turbidity result, it can be concluded that the plain and modified membranes were capable for treatment of oil in water emulsion water in terms of turbidity as well as concentration. The feed flux was also measured using batch filtration setup. As shown in Fig. 8, The feed flux through the modified membrane is 4.5 times of the feed flux of plain membrane flux with oil in water emulsion feeds. This may be due to higher pore percent or pore density of modified membrane compare to the plain membrane which were determined in our previous work [Saini et al., 2018]. The high pore density leads to the increase in flux. The results of oil in water emulsion ultrafiltration study are reported in Table 1.

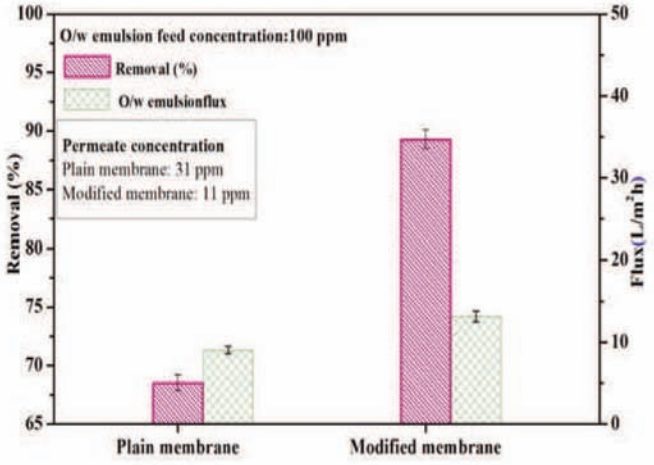

Fig. 8 Oil in water emulsion flux and removal percentage through plain and modified membrane

Table 1. Fouling study data in oil in water emulsion ultrafiltration.

Parameters	Membranes	
	Plain	Modified
J_1 (L/m² h)	19.19	70.24
J_o (L/m² h)	9.03	40.23
J_2 (L/m² h)	10.12	58.98
F_t	0.53	0.43
F_{ir}	0.47	0.16
F_r	0.06	0.27
$Flux_{RR}$	0.53	0.84
$Flux_D$	0.47	0.16
S_p (L/m²h)	14.65	320.22

From table 1, initial and final pure water flux were observed grater in modified membrane compare to plain membrane. These results represent the increase in permeability of the modified membrane compare to plain membrane. The fouling ratios were also determined using equation 3, 4 and 5. The total fouling was 0.43 in modified membrane, whereas this value was 0.53 in plain membrane. The decrease in total fouling indicates the enhancement in flux and rejection percentage of foulant. The ratio of irreversible fouling decreased from 0.47 for lain membrane to 0.16 for modified membrane. The irreversible fouling is generated due to adsorption/deposition of foulant inside the pore or pore blocking. The decrease in irreversible fouling shows that the decrease in adsorption or deposition of irreversible foulant inside the pore of the membranes. The value of reversible fouling ratio was increased from 0.06 for plain membrane to 0.26 for modified membrane. This represents the conversion of irreversible foulant to the reversible foulant. The $Flux_{RR}$ was calculated as ratio of j_2 to the . The $Flux_{RR}$ was increased from 0.53 (for plain membrane) to 0.84 (for modified membrane) in oil in water emulsion ultrafiltration process. This indicated the pure water flux recovery after the permeation of feed. The value of $Flux_D$ decreased from 0.47 (for plain membrane) to 0.16 (for modified membrane). The significant increment of rejection percentage of oil in water emulsion was observed from plain to modified membrane. For plain to modified membrane, the rejection percentage of oil in water emulsion was increased from 69% to 89% due enhancement in hydrophilicity as well as antifouling property of the modified membrane. Therefore, retention property of modified membrane against oil in water emulsion ultrafiltration was higher than plain membrane due to high surface hydrophilicity and smaller pore size of the membrane. Thewas also investigated to compare the overall performance of all fabricated membranes. The selection parameter of the plain and modified membrane was 14.65 L/m²h and 320.22 L/m²h, respectively. This value provides the criteria for the selection of membrane in terms of flux and retention property against foulant.

4. Conclusion

Functionalized nanoparticles were successfully synthesized and blended in Polyvinylidene Fluoride (PVDF) membrane and were able to modify the hydrophilicity and performance of the membrane for oil in water emulsion removal from wastewater. Hydrophilicity and performance of PVDF membrane were found to enhance with functionalized nanoparticles. For plain to modified membrane, the rejection percentages of bovin serum albumin and oil in water emulsion were increased from 69% to 89%. In summary, functionalized nanoparticles were found to be an effective hydrophilic additive to improve the performance of ultrafiltration PVDF membrane. PVDF/Poly ethylene glycol 6000/ functionalized nanoparticles membrane showed enhanced hydrophilicity, antifouling property, and oil in water emulsion flux compared to plain PVDF membrane.

Acknowledgement

This work is financially supported by grant from Pandit Deendayal Petroleum Univesity, Gandhinagar under student research program with Project No.- ORSP/R&D/SRP/2016/TPBS.

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