# Separation of oil/water emulsion for wastewater treatment: Review

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**Abstract**

In this review study on nanocomposite membrane to remove oil molecules from oil-water emulsion is reported. Alumunium oxide (HAO) nanoparticles which proves best anifouling ultrafiltration membrane, was used on polyslfone (PSf) based membrane for removing oil from oil-water mixture. Polysulfone is widely used for fabrication of membranes. Its main drawback is that it leads to poor membrane performance since it is hydrophobic in nature. So PSF membrane can be functionalised by adding $SiO_2$ or Alumunium oxide or MWCNT's. Study was performed after adding different wt% of nanomaterials. Membrane was characterised using SEM, FTIR, contact angle, tensile strength and TGA analysis. Stabilisation of F-MWCNT's in membrane matrix was studied from FTIR result. Membrane defect free surface was analysed through SEM. At different wt% of F-MWCNT's permeate flux was obtained and highest permeate flux was observed at 0.5 wt% F-MWCNTs. Result showed that oil rejection decreased with pressure.

**Keywords:** Agglomeration, Casting, nanocomposite, oil rejection, permeate flux, transmembrane pressure, ultrasonication.

## 1. Introduction

Waste water streams from different industrial unit contains toxic chemicals, heavy metals, microorganisms, biological substances, microplastics, oil and viruses. United Nation Educational, Scientific and Cultural organisation reported that more that 80% of the wastewater is released in open water channels without proper treatment[1]. Wastewater treatment is not properly adopted in industry due to high operational cost, installation cost and large space area requirement. Some countries have taken initiative for water pollution control and water saving. For example China has focussed on water resource conservation and protection by enforcing water pollution control plan. Industries are forced to design waste water treatment plant to separate pollutant from water and reuse it [5]. Oily wastewater is carcinogenic and mutagenic to human health. Oily wastewater discharge without proper treatment reduce sunlight penetration in water and disturbs the aquatic ecosystem. Technological advancement in wastewater treatment has been achieved by multidisciplinery approach and advancement in nanomaterial. The review is expected to benefit research and industry for oily wastewater treatment system and lead their effort in proper direction for better output of treatment.

## 2. Materials and method

As per the research paper published by Javad, Majid[6] separation process of oil-water emulsion using Psf/Pebax/F-MWCNT Polysulfone (PSf) was used to prepare porous substrate. N-methylpyrrolidone (NMP), isobutanol and deionised water was purchased. Functionalised MWCNTs of diameter < 30 nm, length 5–15μm and purity> 95% was used. Tween-20 as emulsifier agent and Corn oil was used. For F-Psf/$SiO_2$ nanocomposite membrane polysulfone, N-dimethylacetamide, silicon dioxide (nanopowder, 5–15 nm), mesitylene (Tween 80) was purchased[6]. In PsF/HAO nanocomposite membrane n-methyl-2-pyrrolidone, aluminum oxide (HAO) nanoparticles was utilised .

## 3. Membrane preparation

There are different membrane preparation techniques available. Solution casting and solvent evaporation technique was used in preparation of composite membranes of pebax on PSf substrate by scientist Ahmad, Majid and Ooi. Phase inversion method was done from 12% (w/v) solution of polymer in NMP solvent. Film was casted and immersed in water bath for 24 h. Bubble free solution of polymer at 90°C was casted on PSf substrate. Solvent was evaporated at 60°C for 10 min to obtain PSf/pebax composite membrane. Finally F-MWCNTs was dispersed and 30 min sonication done to prepare nanocomposite membrane. In functionalised PsF/$SiO_2$ nanocomosite membrane PSf dried at 50°C. Liquid induced phase inversion method was used for PSf/$SiO_2$ composite membrane. $SiO_2$ nanoparticles were dissolved and sonicated for 10 min. Casting solution was cast in polyester fabric with nominal thickness using casting machine.

**4. Emulsion preparation**

Wastewater can be collected from industry or emulsion can also be prepared. For preparation of emulsion blender was used and mixing was continued for 5 min at high speed with corn oil, Tween-20 and distilled water.

**5. Membrane characterisation**

Reasearch papers suggests different suitable method for characterisation. Few methods were suggested by scientist Gohari and Lou which was published in the year 2015. PSf/HAO membrane was produced by phase inversion technique. HAO nanoparticle was added to it and ultrasonication was done to provide homogeneous dispersion. Membrane was fabricated by casting the solution on flat plate to form a film. Further this flat sheet was stored in DI water for 3days and finally it was dried. Various analysis was carried out with FTIR, SEM, TGA, Mechanical Strength test and water contact angle. Surface morphology of fabricated membrane was observed and reported by them in research paper.

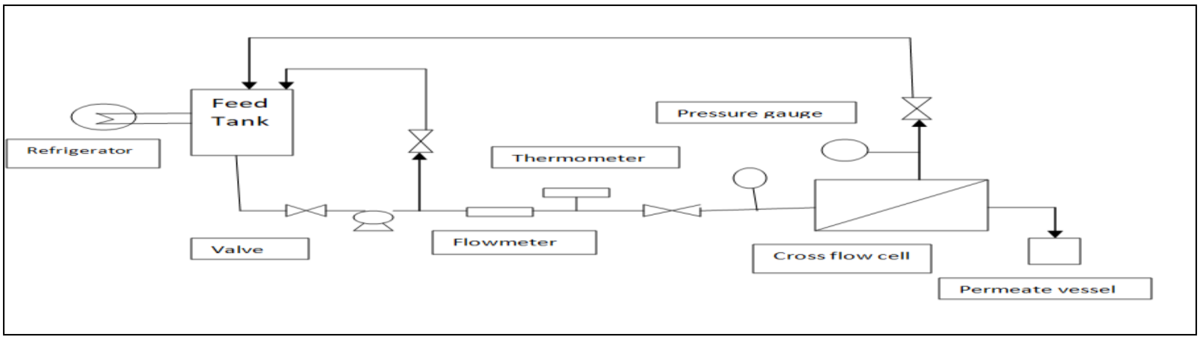


Fig 1.Nanofiltration setup

5.1. Fourier Transform Infrared spectroscopy (FTIR)

Research paper that was published in the year 2016, presence of functional group in F-MWCNTs was studied with FTIR technique.

5.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is used to analyse surface and cross section of membrane. Sample of this fabricated membrane was frozen in liquid nitrogen and fractured. Then gold was sputtered and viewed under microscope.

5.3. Thermogravimetric analysis (TGA)

In TGA-50 Shimadzu TGA was carried out for PSf/pebax membrane and PSf/pebax/F-MWCNTs nanocomposite membrane. Sample was heated in room temperature to 850°C at a heating rate of 10° C/min.

5.4. Mechanical strength test

Tensile strength is analysed with help of universal testing machine (ZWICK-Z250, Germany). Deformation speed of 5 mm/min at room temperature applied and average tensile strength was reported.

5.5. Water contact angle test

Measuring instrument (OCA15plus, Dataphysics, Germany) was used to measure static contact angle. With use of this instrument membrane hydrophilicity contact angle was measured between water and membrane surface and finally reported.

**6. Nanofiltration experiments**

Scientist Javad and Majid designed a cross flow system that is shown in fig 1. Permeate flux, permeate sample is collected after 1 h operation. Stainless steel cell has effective membrane area of 9.62 $cm^2$. Permeate flux was calculated using equation:

$J = \frac{V}{A.t}$ where V(l) is the volume of permeate, $A(m^2)$ is effective membrane surface area and t (h) is the permeate collection time. Concentration was analysed using ultraviolet spectrophotometer at a wavelength of 243.4 nm.

Oil rejection efficiency was calculated by following equation :

$$R(\%) = [1 - \frac{\%\ oil\ in\ permeate}{\%\ oil\ in\ feed}] \times 100$$

**7. Analysis of membrane fouling**

After filtration membrane was washed with distilled water and then immersed in distilled water for 20 min. Flux recovery ratio was calculated using following equation:

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FRR = $\frac{Jw2}{Jw1} \times 100$

where JW1 (L /m$^2$ h) is pure water flux before filtration of O/W emulsion and water flux of cleaned membrane is JW2 (L/m$^2$ h). Generally, higher FRR implies better antifouling property of the nanofiltration membrane.

**8. Observations:**

8.1. Characterisation of F-MWCNTs:

**Fig. 2.** The FTIR spectra of (A) Raw MWCNTs and (B) Functionalized MWCNTs

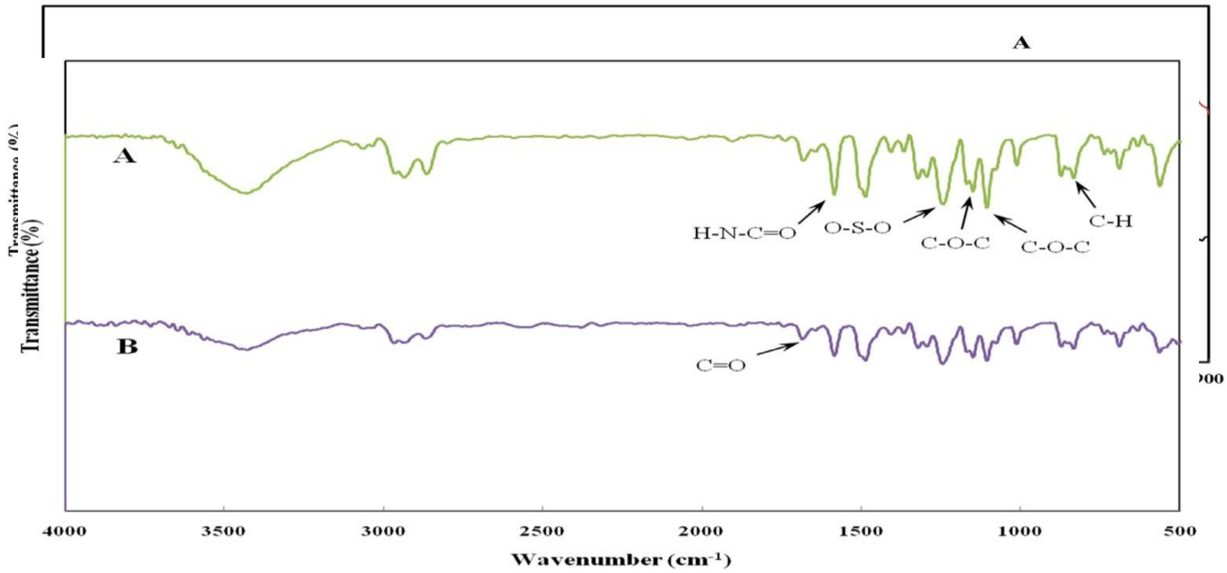



**Fig. 3.** The FT-IR spectra of (A) PSf/Pebax and (B) PSf/Pebax/F-MWCNT membranes

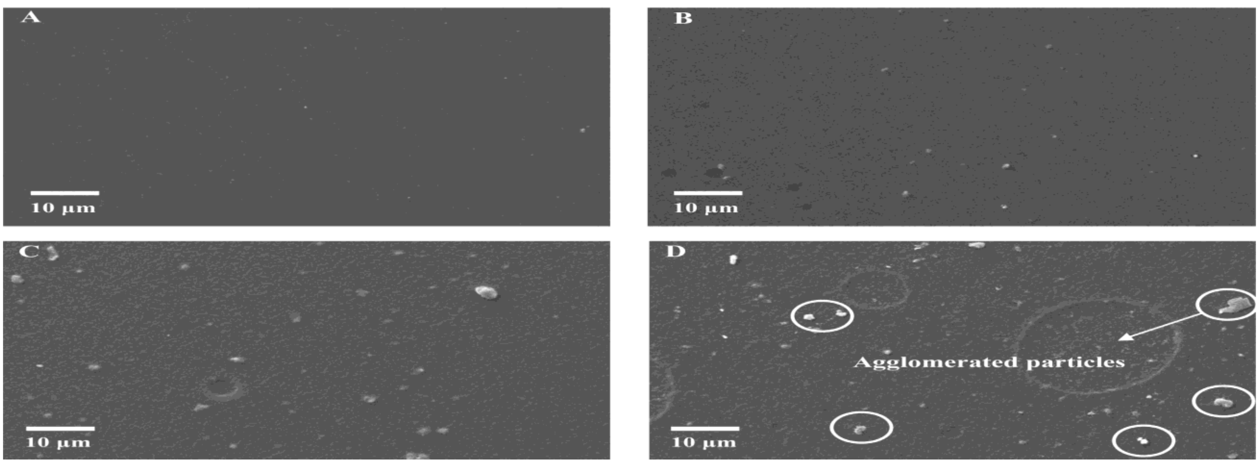
FTIR was used to identify introduced functional group on the surface of modified MWCNT. Research paper of oil/water emulsion separation published in 2016 reported FTIR spectra. It was observed from FTIR spectrum of Fig. 3, the new peaks emerges at 1021, 1258 and 1715 cm$^{-1}$ after the functionalization of MWCNTs corresponds to C–O, $OSO_3H$ and O–H and C=O bonds, respectively. The band at 1580 cm$^{-1}$ is likely due to conjugation of C=O with C=C bonds or interaction between localized C=C bonds and carboxylic acids. This confirms the attachment of the functional groups onto the MWCNTs [6].

8.2. Water contact angle:

| Membrane | Contact angle (°) |
|---|---|
| PSf/Pebax | 55.1 (+/-) 0.63 |
| PSf/Pebax/0.5% F-MWCNT | 50.6 (+/-) 0.44 |
| PSf/Pebax/1% F-MWCNT | 45.3 (+/-) 0.96 |
| PSf/ pebax/2% F-MWCNT | 42.5 (+/-) 0.28 |

8.3. Scanning Electron Microscope (SEM)

**Fig. 4.** Surface SEM images of PSf/pebax nanocomposite membranes prepared with different F-



MWCNTs loading: (A) 0.0 wt%, (B) 0.5 wt%, (C) 1 wt% and (D) 2 wt%

SEM image was also observed by scientist Javad and Majid and reported in research paper. Surface SEM image is shown in fig 4. PSf/Pebax membrane was free of F-MWCNT particles and increasing the loading of F-MWCNTs increases number of light spots. Some bright spot on the surface of membrane containing CNTs can be seen from SEM image. SEM image of membrane containing 4 wt% CNTs indicated agglomeration of MWCNTs. PSf support provides porosity and good strength.

**9. Oil/water nanofiltration experiments**

9.1. Transmembrane pressure effect on permeate flux

Transmembrane effect was also studied by scientist Javad and Majid. Fig 5 and 6 shows the variation of permeate flux at TMP from 10 to 20 bar for PSf/Pebax nanocomposite membrane with different F-MWCNTs loading. It can be concluded that the increase of permeate flux under lower TMP was greater than that under higher TMP. The rate of increase of permeate flux was reduced when TMP was greater than 15 bar. When TMP increases both solvent and solute pass rapidly through the membrane but molecules accumulate both on temperature surface and in membrane pore which causes membrane fouling.

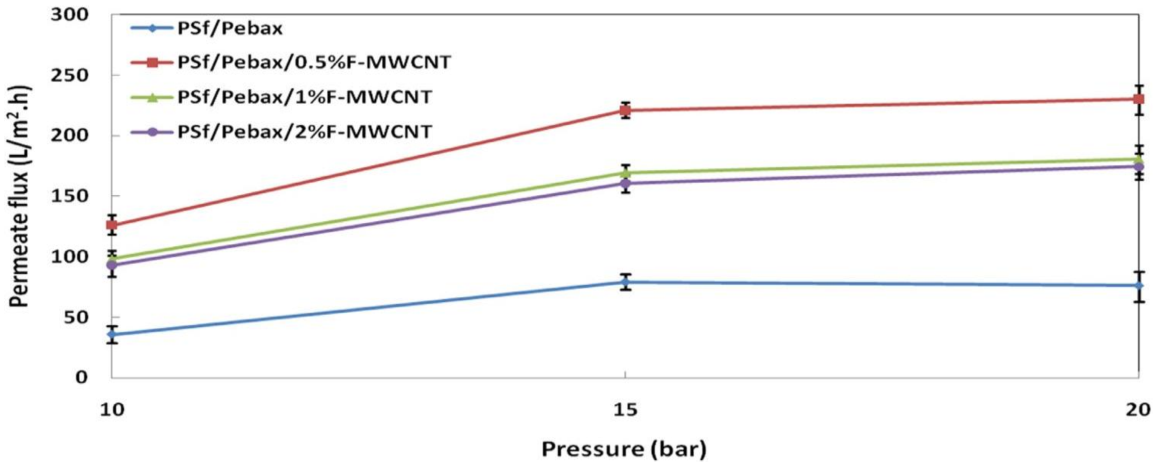



Fig5.Flux of PSf/Pebax nanocomposite membranes prepared with different contents of F-MWCNTs [6]

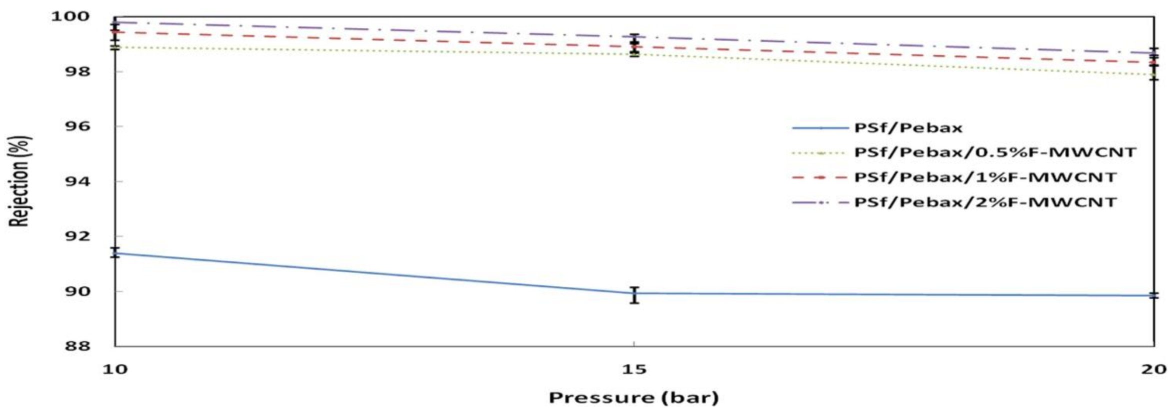



Fig6. Effect of TMP on oil rejection of PSf/Pebax nanocomposite membranes prepared with different contents of F-MWCNTs

9.2. Effect of F-MWCNTs on permeate flux

Different Scientists also published about the important factor that control permeate flux. Hydrophilicity and porosity are the most important factors that control permeate flux. F-MWCNT to PSf/Pebax membrane increases permeate flux upto 0.5 wt% of F-MWCNT but flux decreases on further increasing the loading of F-MWCNT. When loading of F-MWCNT increases beyond 0.5 wt% viscosity of casting solution increases.

9.3. Effect of TMP on oil rejection

It was observed in research paper published in 2016 that Rejection is more at lower pressure range but at higher pressure, rejection shows decreasing trend. Higher pressure drop across the membrane enhances coalescence of oil droplet by increasing convection and due to this some oil droplet pass through the membrane pore along with the permeate.

9.4. Effect of F-MWCNTs on oil rejection

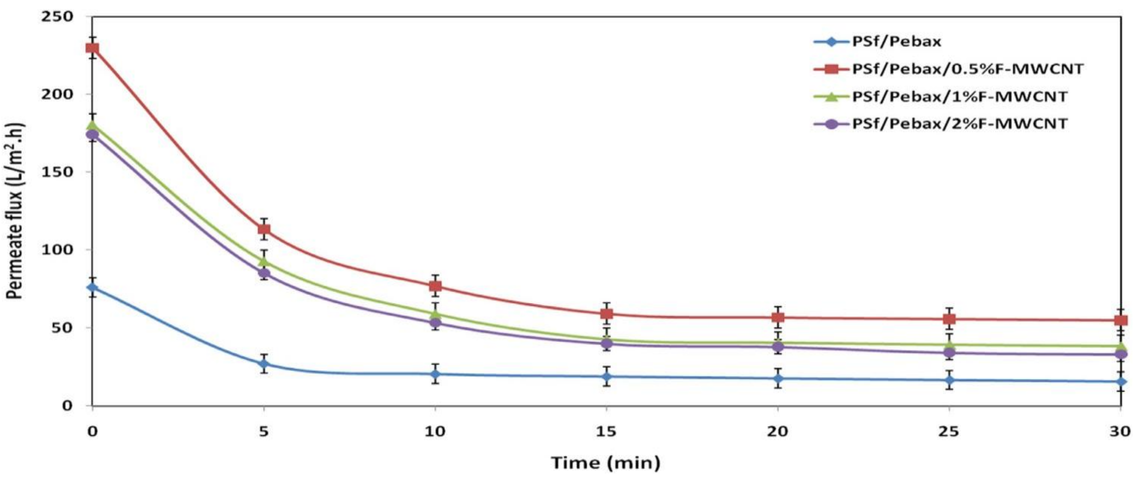
It was reported by scientist Javad and Majid in research paper publised in 2016 that addition of F-MWCNT into pebax improves oil rejection. It was observed that oil rejection at TMP of 10 bar for PSf/Pebax membrane is 91.40% and for PSf/Pebax/2%F-MWCNT membrane is 99.79%, which is about 8% higher [6].

**10. Antifouling and recycling properties of the membranes**

10.1. Flux decline

It was observed that permeate flux varied in two stages , first one was a sharp decay and next was pseudo-steady stage. At the beginning of filtration, flux reduces very quickly due to rapid membrane blocking and fouling. The reduction rate in permeate flux becomes slow after 15 mins and thus approaches pseudo-steady values.

Fig7. Flux declines of the prepared nanocomposite membranes at TMP of 20 bar



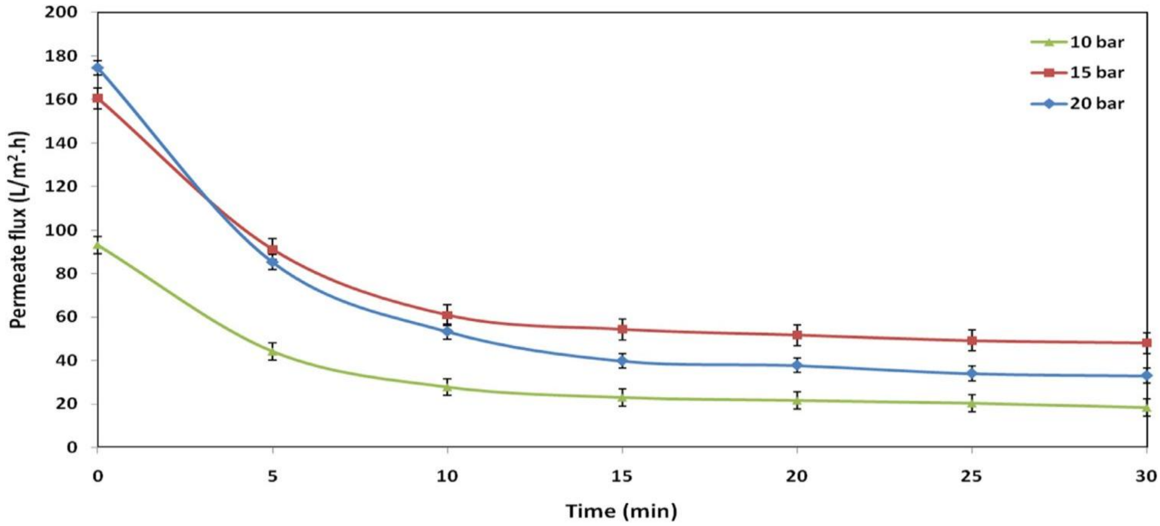




Fig 8.Flux decline of PSf/pebax/2%F-MWCNT membrane at various TMP.

**11. Conclusion**

Scientist Javad and Majid concluded that PSf/Pebax composite membrane was successfully prepared and characterised. Further it was modified by adding different proportions of F-MWCNT. Resultant behaviour was observed with 0.5,1 and 2 wt % F-MWCNT. Characterization was done with help of FTIR, SEM. Contact angle decreased on increasing the loading of F-MWCNT. Tensile strength was also increased by addition of F-MWCNT. Addition of F-MWCNT enhances the thermal stability of membrane. 0.5wt % F-MWCNT content increases permeate flux and further increasing of loading caused decrease of permeate flux. Rejection of oil/water emulsion is higher at low pressure but decreases gradually on increasing the pressure. Research paper published by Gohari and Lao stated that the addition of HAO inorganic nanofillers led to significant enhancement of membrane hydrophilicity . PSf/HAO containing the highest quantity of HAO showed a maximum of 67% of flux recovery confirming its excellent antifouling behavior.Thus it can be concluded compared to plane polymeric membrane that PSF/HAO blended membrane can be adopted to purify oily wastewater. Thus fabrication of nanocomposite membrane is a successful approach in separation of oil from oil/water emulsion. This method can prove to be a beneficial solution for industrial waste water treatment.

References

1. Y.S. Li, L. Yan, C.B. Xiang, L.J. Hong, Treatment of oily wastewater by organic– inorganic composite tubular ultrafiltration (UF) membranes, Desalination 196 (2006) 76–83.
2. W. Chen, Y. Su, L. Zheng, L. Wang, Z. Jiang, The improved oil/water separation performance of cellulose acetate-graft-polyacrylonitrile membranes, J. Membr. Sci. 337 (2009) 98–105.
3. L. Li, L. Dinga, Z. Tua, Y. Wanb, D. Claussea, J.-L. Lanoiselléa, Recovery of linseed oil dispersed within an oil-in-water emulsion using hydrophilic membrane by rotating disk filtration system, J. Membr. Sci. 342 (2009) 70–79.
4. Li B, Zhang J, Gao Z, Wei Q. Semitransparent superoleophobic coatings with low sliding angles for hot liquids based on silica nanotubes. J Mater Chem A 2016;4:953–60.
5. Zhang J, Seeger S. Polyester materials with superwetting silicone nanofilaments for oil/water separation and selective oil absorption. Adv Funct Mater 2011;21:4699–704.
6. Javad Saadati, Majid Pakizeh, Separation of oil/water emulsion using PSf/pebax/F-MWCNT nanocomposite membrane, 2016.