

## **Preparation and Application of SPPEES-TiO<sub>2</sub> Composite Micro-porous UF Membrane for Refinery Effluent Treatment**

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### **Abstract**

In the present work composite UF membrane for refinery effluent treatment was prepared using sulfonated Poly (1, 4-phenylene ether ether sulfone) (SPPEES) and TiO<sub>2</sub> nano-sized particles by phase inversion method. The sulfonation of PPEES was done to improve its chemical and thermal stability. The PVP was added in the blending solution as a pore forming agent. The sulfonation of PPEES also improves the hydrophilicity of the membrane. The addition of nanosized TiO<sub>2</sub> particles also increases the hydrophilicity of the prepared membrane and improves its antifouling property. The surface morphology was studied using SEM. The mechanical strength and water contact angle of the membrane was studied before application of membrane for refinery effluent treatment. The refinery effluent was collected from IOCL refinery Panipat, and was used to test treatment efficiency of the prepared membrane. The result of water flux and permeate flux was shown at constant velocity and transmembrane pressure of 3m/s and 0.3MPa respectively. The experimental results obtained in the present work shows the permeate flux decline of 35% after 75 minutes. The permeate water obtain was having almost 95% removal of TDS and 50% removal of organic contaminants. The possible use of SPPEES-TiO<sub>2</sub> membrane for refinery effluent treatment was discussed.

**Keywords:** SPPEES-TiO<sub>2</sub> membrane; refinery effluent; permeate flux.

## 1. Introduction

Working towards the development of technology having high separation efficiency using less energy and considering the cost of process the membrane separation technology was found to be preferable one [1-3]. Based on the literature study it was concluded that the recent work was continue to develop different blends of polymer at different composition. Some studies are based on the development of polymeric composite materials which were found better in performances and can be develop easily. To obtain high permeate flux an asymmetric membrane was reported to be good [4]. There are more advantages while using membrane technologies for separation of industrial effluents at lower cost [5]. There are several ways to reduce fouling of membranes as reported by the researchers like modification of surface, pre treatment of feed, increasing hydrophilicity of the membrane, using back wash system and optimising the process condition [6]. Poly (1, 4-phenylene ethe-ether-sulfone) is a kind of polymer hardly used in membrane synthesis till last decades because of its hydrophobic characteristics. It was also studied from the literature that it is easy to form a dense membrane for gas separation using modification in PPEES [7]. The SPPEES was used as a base material to form a microporous ultrafiltration membrane, with PVP and inorganic material ( $\text{TiO}_2$  nano sized particle). The addition of PVP was for pore formation and inorganic material ( $\text{TiO}_2$  nano sized particle) was to increase the hydrophilicity and reduce the fouling of membranes [6, 7]. Also the some literatures studies shows that the main function of additives was to conquer the formation of macro voids, increase pore formation and improve pore interconnectivity [8-10]. For this improvement the ceramic materials are found to be more suitable. The different nanosized particles used to prepare composite membranes have differences in improving membranes. [11]. We have investigated the performance of SPPEES material for ultrafiltration membrane synthesis. The different membranes are casted of which one containing 5 weight % PVP (pore former) and 2 weight %  $\text{TiO}_2$  nano sized particle was reported. The prepared membrane was found to hydrophilic low fouling composite membrane useful for ultrafiltration process for oily waste water treatment. The permeate flux obtained and the fouling time has been calculated. The present study reports the surface morphology of the SPPEES material and effect of addition of  $\text{TiO}_2$  nano sized particle in the formation of membrane.  $\text{TiO}_2$  nano sized particle was used as an antifouling material and PVP for pore forming agent. The surface morphological study was done using SEM. The permeate flux against time were recorded.

## 2. Material and Characterization

### 2.1 Materials

Poly (1, 4-phenylene ethe-ether-sulfone) was procured from sigma Aldrich as a membrane polymer. 1-methyl-2-pyrrolidone (NMP), polyvinyl pyrrolidone (PVP, with  $M_w = 40,000$  g/mol), Titanium oxide nano-sized particles ( $\text{TiO}_2$ , particle) were used. Isopropyl alcohol and distilled water were used as non-solvent.

### 2.2 Preparation of SPPEES membrane modified with and TiO<sub>2</sub> nano-sized particles

The flat sheet membrane was prepared by phase inversion method. Sulfonation of PPEES was done in the laboratory using sulphuric acid. The blend of sulfonated polymer and ceramic material was prepared using NMP as a solvent. Small amount of PVP (5% weight % of solution) used as a pore forming agent was added in the casting solution. The solution was sonicated for 3 hr in a sonicator. For homogeneous mixing of solution stirring was done at 800 rpm for 15 hr at room temperature. The homogeneous polymer composite solution was then kept in a store at room temperature for 24 hr to remove air bubbles. The composition used was (SPPEES) (13 wt. %), PVP (5 wt. %), TiO<sub>2</sub> (2 wt. %) and NMP (80 wt. %). The membrane was casted using a membrane casting applicator on a glass plate. This was immediately moved to the non- solvent bath (distilled water) for 1 hr, then to isopropyl alcohol for another hour for complete removal of water. The prepared membrane was dried in an oven by placing on filter paper for 24 hr at 50<sup>0</sup>C. Other two membranes are prepared in the similar way changing the composition of polymer and TiO<sub>2</sub> as (SPPEES) (14 wt. %), TiO<sub>2</sub> (1 wt. %), and (SPPEES) (15 wt. %), TiO<sub>2</sub> (0 wt. %), the composition of rest was same.

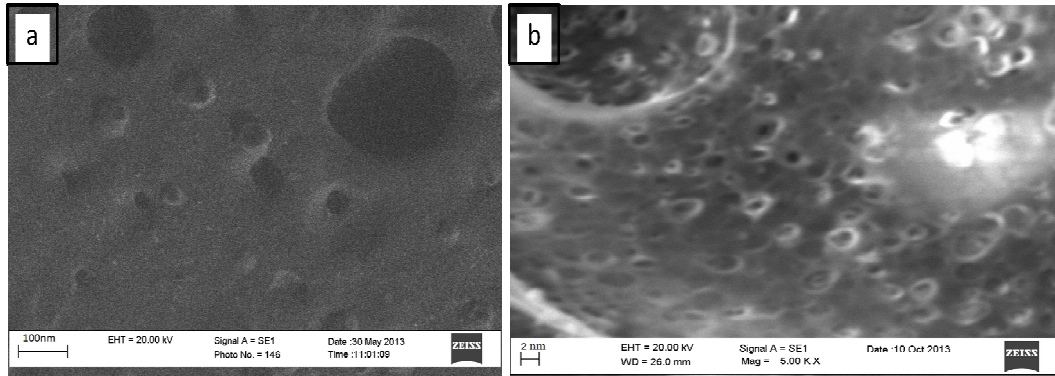
### 2.3 Characterisation of membranes

**Table 1:** Contact angles and Mechanical properties of SPPEES-TiO<sub>2</sub> membranes with different TiO<sub>2</sub> concentration.

Membrane no.	TiO <sub>2</sub> concentration (wt %)	Contact angle □ (°)	Tensile strength (N)
S1	0	94	08.346
S2	1.0	83	09.4521
S3	2.0	77	10.7986

#### 2.3.2. Morphological studies

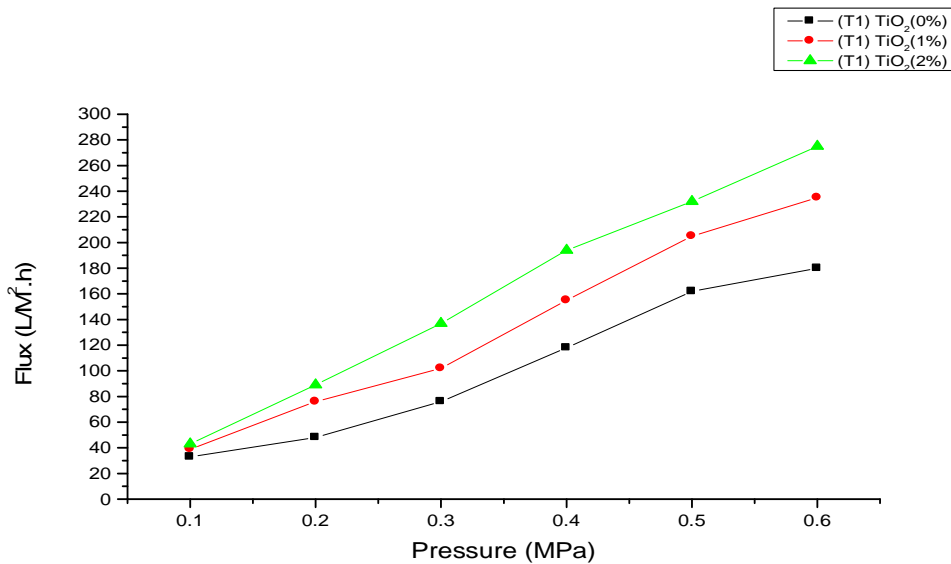
Figure 1 shows the SEM images of surface of the membrane. The surface morphology of the prepared membrane having 2 % TiO<sub>2</sub> nano-sized particles shows the formation of large macro voids in the sub layer. These shows that the particles are uniformly distributed on the membrane surface. The surface of the membrane is composed of a micro-porous structure with number of pores. It was found on the surface that both interconnected holes and their networks are formed. The TiO<sub>2</sub> nano-particles are also found nearby and outside the pores the forming a nano level roughness on membrane surfaces.



**Fig. 1:** Cross-section and surface images of SPPEES/ TiO<sub>2</sub> membranes a) surface image Of 0 wt % TiO<sub>2</sub>. b) Surface image Of 2wt % TiO<sub>2</sub>

### 3. Results

#### 3.1. Water flux of membranes



**Fig. 2:** Water flux of membranes.

#### 3.2. Performance and antifouling properties of membranes

Figure 2 shows the effect of addition of TiO<sub>2</sub> nano-particles in the membrane on pure water flux. The pure water flux of membranes increases as the concentration of TiO<sub>2</sub> nano-particles in the casting solution increases up to 2 % beyond this the trend changes and no improvement in water flux was obtained. The decline in pure water flux of SPPEES membrane compare to TiO<sub>2</sub> modified membranes is due to the higher hydrophilicity and higher ratio surface areas. The result shows that the antifouling property of the TiO<sub>2</sub> modified membrane was improved. It was also found that the antifouling property of the membrane can be enhanced by adding TiO<sub>2</sub> concentration up to 2 %, further addition of TiO<sub>2</sub> concentration will not affect the flux decline.

For refinery effluent treatment transmembrane pressure (TMP) was 3 bars, oil content of the feed was 78 ppm, feed velocity was maintained at 3m/s. Fig.3 Shows that the permeation flux of the membrane declines as the time increases up to a certain period after that it follows a steady value. Permeate flux was recorded at interval of 5 min. The flux obtained after 75 min shows 35 % decline in flux values, the improvement in fouling time shows the increase in hydrophilicity.

### 3.3. Permeate flux of membranes

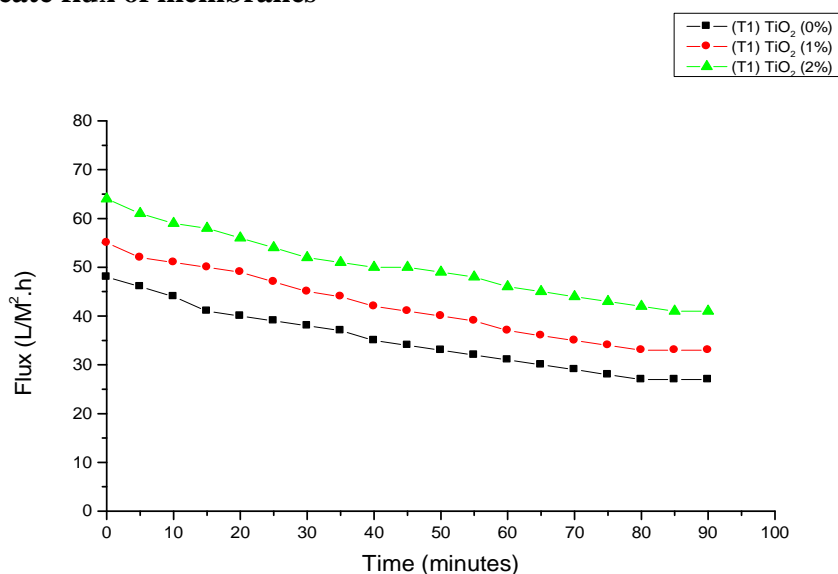


Fig. 3: Permeate flux of membranes.

## 4. Conclusion

SPPEES/PVP membrane with improve anti-fouling property has been prepared by addition of TiO<sub>2</sub> nano-particles in the casting solution. The membrane is casted using phase inversion method. The SEM studies show the pore formation and the presence of TiO<sub>2</sub> nano-particles on the surface of membrane. The contact angle value indicates the increment in surface hydrophilicity of the TiO<sub>2</sub> modified membrane. There is more than 25 % improvement in tensile strength and elongation at break values of modified membrane. The flux values obtained and anti-fouling properties of TiO<sub>2</sub> modified membrane has found improved. The prepared UF membrane efficiently removes almost (95 %) suspended solids and more than 50 % removal of organic compound. There exist a constant removal of all impurities related TURBIDITY, TSS, Oil and Grease and TOC.

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