**Investigating the effect of TiO2 nanoparticles on the performance of Nanocomposite Membranes from PAN for Produced Water Treatment**

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**Highlights**

* PAN nanofiltration membranes developed for effective produced water treatment.
* The effect of inclusion of TiO2 nanoparticles was examined by RSM.
* Membranes with improved separation efficiency were obtained for treating oily wastewater.

**1. Introduction**

Many governments have regulated discharge limit concentrations in order to at least alleviate the destructive impacts of contaminants on the environment. Several stand-alone or integrated systems are currently in operation for produced water treatment. Among these common systems, membrane filtration offers indisputable advantages while maintaining the high process efficiency. These have attracted researchers to utilize different kinds of membranes for the produced water treatment.

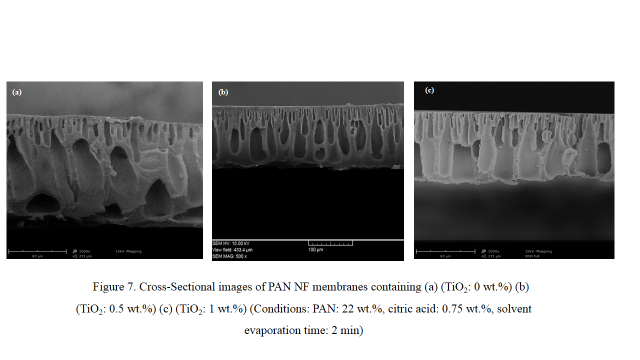
**2. Methods**

Dope solutions containing prescribed amounts of polymer (22 wt.%), organic and inorganic additives were prepared by moderately dissolving PAN, TiO2 and citric acid in DMF. Dope solutions were cast onto the nonwoven polyester substrates using a knife casting at 70˚C. After a distinct time spans of solvent evaporation, nascent films were submerged in coagulation bath containing pure water with different temperatures. Membranes were characterized by various methods.

**3. Results and discussion**

Figure 1 shows the cross-section morphology of NF membranes with TiO2 variation. All membranes were asymmetric having both macrovoid and sponge-like structures. It was found that increasing the TiO2 concentration in the dope solution, the porosity of NF membranes was increased from 45.74% to 63.28%. Moreover, both mean macrovoid size and area fraction of macrovoids increased from 29.06 to 51.60 µm and from 0.28 to 0.34 respectively. Also, an increment in TiO2 concentration led to a decrease in contact angle of NF membranes. It is worth mentioning that the reduction of membrane contact angles is not only attributed to the presence of TiO2, but also the surface roughness of the membrane plays an important role in determining the terminal contact angle values. It was also clear that owning to the agglomeration of nanoparticles on the surface of membrane, number and height of the surface curvatures was increased as the TiO2 content of the dope solution was increased. As stated by Cassie-Baxter theory, the surface hydrophilicity of a pristine hydrophilic surface intensifies when it gets rougher. Therefore, the final contact angle values of NF membranes are determined by the superimposition of surface roughness and modification effects. The emerged changes in the membrane structure might be related to the hydrophilicity enhancement of membrane surface due to the presence of TiO2 nanoparticles which led to the instantaneous demixing process.

Based on the results, the PWF was enhanced from 108.8 to 131.5 (lit.m-2.h-1) through TiO2 addition to dope solution up to 1wt.%. This might be demonstrated by the reduction in the surface contact angles of NF membranes. Despite the positive effect of TiO2 addition on membrane flux, the intensity of PWF variations diminishes at high TiO2 concentrations. The observation could be explained due to the fact that nanoparticles tend to agglomerate on the surface of the membrane, considering their hydrophilic nature. High concentrations of TiO2 in the dope solution, reduces the distance between nanoparticles due to the presence of different forces (i.e.: hydration, bridge, Van der Waals) which provides the chance for them to agglomerate and reduce their surface energy. Also, increasing the TiO2 concentration resulted in an increment in CaSO4 rejection and elevated the rejection from 73.5% to 83%. Considerable changes in the membrane salt rejection could be conceived by the aggregation of nanoparticles on the surface of the membrane. Higher contents of TiO2, increase the viscosity of the polymeric film which delays the demixing process and provides the opportunity for the nanoparticles to form aggregates on the membrane surface to plug the surface pores and reduce the effective membrane mean pore size.



**Figure 1.** Cross-Sectional images of PAN NF membranes containing (a) (TiO2: 0 wt.%) (b) (TiO2: 0.5 wt.%) (c) (TiO2: 1 wt.%) (Conditions: PAN: 22 wt.%, citric acid: 0.75 wt.%, solvent evaporation time: 2 min)

**4. Conclusions**

The effect of several fabrication and design parameters including the concentration of TiO2, on the PWF of PAN NF membranes was assessed. RSM technique was employed to explore the effect of the selected variables on the performance and characteristics of PAN NF membranes. Zeta potential and surface hydrophilicity of NF membrane were also intensified. As the TiO2 nanoparticles were added to the dope solution, the area fraction and the membrane porosity were increased. Considering the effect of TiO2 on the membrane performance, both the PWF and the salt rejection of membranes were promoted via the enhancement of membranes hydrophilicity and nanoparticles agglomeration on the surface of membranes.

**References**

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