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# Fabrication and Performance of Blended Titanium Dioxide Nanoparticles Enhanced Cellulose Acetate Forward Osmosis Membrane

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## Abstract:

A Blended Nano-composite Cellulose Acetate (CA) membrane incorporated with titanium dioxide ($TiO_2$) nanoparticles along with control CA polymeric membrane was prepared by phase inversion method to evaluate the performance of Forward Osmosis (FO) membrane system. $TiO_2$ nanoparticles were added into the CA matrix to improve the desalination performance of the CA membrane and enhancing hydrophilicity and stability. The membranes were fabricated by casting of CA/$TiO_2$ with PVP as a pore former on a polyester woven mesh. The performance of the FO membrane was tested using 1M NaCl as the draw solution (DS) and Deionised (DI) water as the feed solution (FS) in FO mode. The water flux obtained by CA polymeric membrane was 14.5 LMH, while it was 26.6 LMH, 30.5 LMH, and 21.71 LMH for blended nano-composite CA membrane at $TiO_2$ concentrations of 0.5 wt%, 1 wt% and 1.5 wt%, respectively. The blended nano-composite membrane prepared using CA substrate embedded with 1 wt% exhibited the most promising results by showing high water permeability. The enhanced hydrophilicity and favourable structure formed are the main factors resulting in high water flux of nano-composite substrate. Although, increase in $TiO_2$ nanoparticles from 0.5 wt% to 1.5 wt% resulted in low water permeability. Based on the results obtained in this work, it can be concluded that adding an appropriate amount of $TiO_2$ nanoparticles into CA substrate could potentially improve the performance of CA polymeric membrane and improve the membrane permeability, mechanical strength and stability.

***Keywords*** — **Forward Osmosis, Titanium Dioxide Nanoparticles, Water Flux, Cellulose Acetate Polymer,Phase Inversion Method.**

## I. INTRODUCTION

Global water crisis and clean water shortage have become a serious challenge faced by humanity today due to rapid population growth and economic development [1, 2]. In addition, the situation has been exacerbated by the disposal and released of hazardous pollutants, leading to contamination of water resources. All these incidents have led to water scarcity crises in various regions of the world. The consequences of water pollution and overexploitation of water resources are increasingly critical and putting lives and livelihoods at risk and reducing socio-economic growth in many countries [3]. Addressing these problems requires innovative technologies that provide energy-efficient and cost-effective solutions to recover potable water from unconventional water sources such as seawater, brackish groundwater and wastewater [4]. Membrane technology has become one of the major technologies used in various water and wastewater treatment processes due to its efficient removal of contaminants from water bodies. For instance, reverse osmosis (RO) has been widely used to extract clean water from seawater. Whilst RO is efficient at removing almost all impurities and contaminants in the water, its use in producing clean water poses several challenges. The operation of RO requires high hydraulic pressure, which increases the energy consumption and fouling of the Membrane [5].

Engineered osmosis process has received much attention as the alternative technology with no/low external energy consumption, in comparison to hydraulic pressure-driven membrane separation processes. Forward osmosis (FO) involves the use of a semi-permeable membrane to establish preferential movement of solvent molecules from a solution of low osmotic pressure (feed solution) into another solution with higher osmotic pressure (draw solution). Due to the difference in chemical potential energy between the two solutions, spontaneous permeation of solvent across the membrane is favoured in nature. Therefore, the energy consumption of FO process itself is very low as compared to other membrane processes [6]. Therefore, FO process benefits from its relatively low energy consumption, high rejection to feed contaminants and low membrane fouling propensity. These merits enable FO process to be widely applied in desalination, water purification, and power generation [7]. As such, it has been proposed to couple FO with other hydraulic pressure-driven or thermal driven membrane processes to produce potable water with reduced overall energy consumption and lower membrane fouling potential [6].

As of late, FO has stood out as competitive membrane technology for wastewater treatment with several advantages over the present membrane technologies. These advantages comprise low power consumption, less fouling, and applicability for a varied range of feed solutions. In spite of the advantages of the FO process, the membrane suffers from several drawbacks, for instance, concentration polarization (CP), reverse solute flux (RSF), and low permeability. Also, fouling materials accumulation on the membrane surface, especially in the treatment of complex feed solutions or when the pre-treatment process is insufficient to provide a high-quality feed solution to the FO process [8]. One of the possible solutions for these problems is to use nanotechnology to boost the performance of the FO membrane performance. Also, nanoparticle helps to beat the issues of low water permeability, low mechanical strength, and fouling propensity. Application of nanomaterial improves permeability and lowers the occurrence of concentration polymerization (CP) [9]. Phase inversion method is used for fabrication of polymer nano-composite membranes in either hollow fibre or flat sheet configurations by dispersing nano-materials in polymer solution prior to Phase Inversion process. In blended nano-composite membrane, nano-particles along with polymer are dispersed in casting solution prior to membrane casting. Nano-composite membranes obtained in this way are known as nano-particles entrapped membranes or nano-particles blend membranes [10].Cellulose Acetate (CA) polymer has been extensively used to fabricate RO membranes with an asymmetric structure through the phase inversion process.

## II. EXPERMENTAL ANALYSIS

### *A. Materials and chemicals*

Cellulose acetate (Extra pure) Assay (acetyly group) 29-45% (CAS NO. 9004-35-7) was purchased from Lobachemiepvt. Ltd. Polyvinyl pyrrolidone k-25 (Povidone, PVP) (c6h9no) M.W:-10000 (CAS no. 9003-39-8) and N-Methyl-2-pyrrolidone (N-Methyl pyrrolidone, 1- Methyl-2-pyrrolidone) MW: 99.13 (CAS no. 872-50-4) was supplied by central drug house (p) Ltd were used for TFC substrate synthesis. Sodium chloride (NaCl) MW: 58.44 (CAS no. 7647-14-5) obtained from Thermo Fisher Scientific India pvt. Ltd. was used for salt solution preparation for FO tests. Commercial Titanium oxide ($TiO_2$) was used as nano-filler to prepare nano-composite substrate. Polyester Woven mesh was supplied by local vendor near New Delhi, India.

### *B. Polymer solution preparation and CA membrane fabrication*

To prepare the dope solution of 20ml, PVP was first added into NMP and stirred for 10 min. It was followed by adding nanoparticle $TiO_2$ into the solvent. CA was then added into the mixture under vigorous stirring. Then the casting solution was kept under continuous stirring at 200 rpm for 8 h until the solution became completely homogenous. The solution was then stored at room temperature for 1 day to deaerate.

The fabrication involved in this work was conducted via a phase inversion process. Then a polyester woven mesh was placed on the surface of

a clean horizontal glass plate carefully to avoid wrinkles. Specifically, the polymer solution was spread evenly on the polyester woven mesh using a casting knife at a gate height of 100 µm. The polyester woven mesh was embedded in the solution automatically due to capillarity. After evaporation for a few seconds, the whole composite was immediately immersed into a coagulation bath containing DI water at various temperatures to initiate phase separation. The resultant membrane was peeled off gently from the glass plate and was rinsed with flowing tap water overnight to remove the residual solvent. The fabricated membranes were stored in DI water prior to use.

Table 1 Composition of titanium dioxide ($TiO_2$) modified CA membrane casting solution

| Wt % of $TiO_2$ | $TiO_2$ (gm) | CA (gm) | PVP (gm) | NMP (ml) |
|---|---|---|---|---|
| 0.5% | 0.1 | 3 | 0.1 | 16.8 |
| 1% | 0.2 | 3 | 0.1 | 16.7 |
| 1.5% | 0.3 | 3 | 0.1 | 16.6 |

### *C. FO membrane performance test*

The experiments were conducted using a specially designed cross-flow membrane cell which has a symmetric channel on each side of the membrane. The effective area of the cell used for FO membrane is 17× 13.5 cm. A schematic diagram of the laboratory scale unit used in this study Fig. 1.3, the draw and feed solutions flowed on the draw side and the feed side, respectively, both of which were controlled independently by a DC magnetic pump and the flow-rates were measured with a flow-meter. Logging software was used to monitor the weight changes of the draw solution due to the water flux across the membrane, from which the water flux was calculated. Electrical conductivity and feed concentration were also monitored continuously for every 30 minutes. FO unit was operated by recycling the feed and draw solutions, the water flux will decrease significantly with time as the draw and feed solution will be diluted and concentrated with time, respectively. 1 M NaCl aqueous solution as a DS, while DI water was used as the FS. Water flux was calculated by measuring the weight increase of the draw solution over a certain period after the water flux had stabilized for half an hour. The rate at which the volume increases (determined from the weight change) divided by the membrane area yields the water flux ($J_w$, L/ ($m^2$·hr)).

$$J_w = \frac{\Delta V}{\Delta t \times S}$$

Where, ΔV (L) is the permeation water collected over a predetermined time Δt (hr) in the FO process; Sis the effective membrane surface area ($m^2$).

## III. RESULTS AND DISCUSSION

### *D. Performance of the CA and commercial FO membrane*

The water flux and Electrical Conductivity (EC) of commercial CA membrane and fabricated control CA membrane was evaluated using pilot scale FO membrane unit and presented in Table 2. The experiments were carried out using DI water as FS and 1 M NaCl as DS. As can be seen, the fabricated CA membrane exhibited higher water flux 14.5 LMH than that of commercial membrane 9.45 LMH. Overall, the performance of fabricated CA membrane is better than commercial membrane

Table 2. Water flux and EC result of commercial and fabricated control CA membranes

| Membrane | Draw conductivity (mS/cm) | | | Feed conductivity (µs/cm) | | | Water flux (LMH) |
|---|---|---|---|---|---|---|---|
| | Initial | Final (after 3 hr run) | Decrease (%) | Initial | Final (after 3 hr run) | Increase (%) | |
| Commercial | 79.3 | 49.8 | 37.2 | 110 | 138.5 | 20.57 | 9.45 |
| Cellulose Acetate | 75.2 | 28.2 | 62.5 | 110.6 | 200.4 | 44.81 | 14.5 |

Electrical conductivity was checked before the starting of the membrane test, which was almost equal for both CA and commercial FO membrane. Figure 1 and 2 shows the change in electrical conductivity from starting and end of the experiments, showing the dilution of draw solution as its conductivity decreases. It can be seen that the fabricated TFC CA membrane the lab performed

much more effective than the commercial membrane.

Li et.al (2015) fabricated a Polyethylene terephthalate mesh (PET) enhanced CA membranes via phase inversion process. The performance of the optimal FO membrane was tested using 0.2M NaCl as the feed solution and 1.5M glucose as the draw solution. The membrane displayed a water flux of 3.47 LMH [11]. Sahebi et.al (2018) fabricated a robust thin film composite membrane reinforced on woven mesh backing fabric support and achieved a water flux of 8.1 LMH using 0.5M NaCl as a draw solution and DI water as feed solution. As can be seen, water fluxes of these membranes are lower than the results obtained in this study.

Hydrophilic CA or CTA membrane materials have been widely used in water purification and desalination membrane processes. However, one problem for CA membrane is its relatively poor toughness and roughness. Since the traditional cellulose ester-based membranes have inherent advantages in low fouling propensity, good chlorine resistance, and low cost some other molecularly designed novel cellulose ester based FO membranes have been developed.

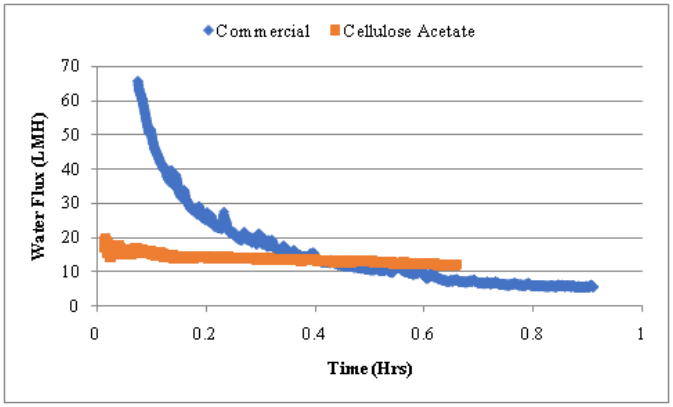


Figure 1Water fluxes of commercial TFC and TFC CA membranes

### *E. Performance of the $TiO_2$ blended polymeric membrane*

The effect of using nanoparticles on CA membrane with respect to water flux was evaluated using pilot scale FO setup and the results are presented in Table 3. The water fluxes of CA membranes made of nano-composite substrates were in the range of 15- 25 LMH. These values were higher than that of CA membrane**.**

Table 3 Water flux and EC result of $TiO_2$ modified TFN CA membrane

| Membrane | Draw conductivity (mS/cm) | | | Feed conductivity (µs/cm) | | | Water flux (LMH) |
|---|---|---|---|---|---|---|---|
| | Initial | Final (after 3 hr run) | Decrease (%) | Initial | Final (after 3 hr run) | Increase (%) | |
| CA + $TiO_2$ (0.5%) | 94.3 | 30.2 | 67.97 | 79 | 935 | 92.6 | 26.6 |
| CA + $TiO_2$ (1%) | 84.4 | 20.26 | 75.9 | 80 | 421 | 80.39 | 30.5 |
| CA + $TiO_2$ (1.5%) | 85.2 | 21.4 | 74.9 | 82.3 | 134.8 | 41.5 | 21.71 |

This significant improvement could be due to the improved substrate hydrophilicity owing to the addition of $TiO_2$. But increasing the concentration of $TiO_2$ (1.5 wt%) also inversely affected the water flux with respect to membrane with $TiO_2$ concentrations 0.5 wt% and 1 wt% as the water flux decreased to 21.71 LMH as shown in Table 3. The decrease of membrane flux at higher $TiO_2$ concentrations could be due to the increased $TiO_2$ density incorporated on the membrane surface, thus increasing the mass resistance through the membrane. Jing Guo et.al incorporated $TiO_2$ nanoparticles in PES membrane with different concentrations. At lowest dosage of $TiO_2$ nanoparticles (0.1 wt %), membrane porosity was similar to that of the bare PES membrane. This may be attributed to the well-dispersity of the $TiO_2$ nanoparticles without forming their aggregate within membrane pore matrix. Highest dosage of $TiO_2$ nanoparticles (2.0 wt %), however, decreased membrane porosity by 6% due to aggregation of the $TiO_2$ nanoparticles within the membrane.Titanium dioxide nanomaterial ($TiO_2$) emerged as an outstanding material for the fabrication of nano-composites membranes due to their photo catalytic and hydrophilic nature for the degradation of organic pollutants in waste water treatment.

Emadzadeh et.al (2014) had the almost similar result while using $TiO_2$ as a nanoparticle in

Polysulfone membrane. The TFN membrane prepared using Polysulfone substrate embedded with 0.5 wt% $TiO_2$ nanoparticles exhibited the most promising results by showing high water permeability and low reverse solute flux. Although further increase in $TiO_2$ nanoparticles loading to 0.75 and 1 wt% could result in higher water permeability, their FO performances were compromised by a significant increase in reverse solute flux. The results illustrated that the porosity and hydrophilicity obviously improved after the modification, which led to a considerable remission of the ICP [12].

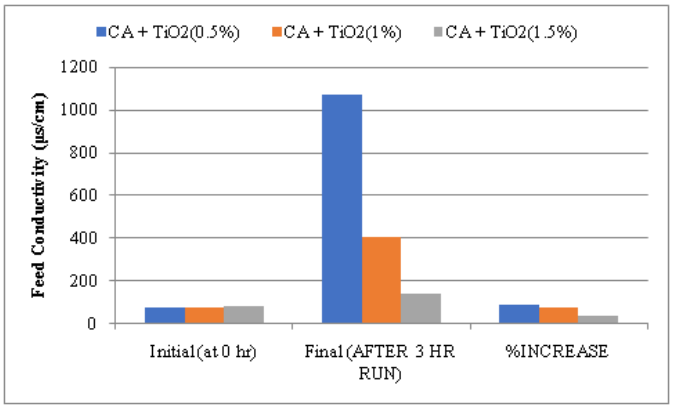


Figure 1 Changes EC of FS in TFN membrane

## IV. CONCLUSIONS

Titanium dioxide nano-fibers were successfully synthesized and incorporated into CA to give nano-composite membranes. The increase in membrane hydrophilicity due to $TiO_2$ resulted in significant improvement in water flux. The addition of nano-materials in the CA-based substrate has potential to increase the hydrophilicity of top and bottom substrate surface as well as its surface roughness. In terms of water flux, $TiO_2$ (1%) exhibited the highest water flux of 30.5 LMH followed by $TiO_2$ (0.5%) 26.6 LMH meanwhile $TiO_2$ (1.5%) showed only 21.71 LMH. Among the $TiO_2$ modified CA membranes prepared in this work, $TiO_2$ (1%) membrane was found to be the best performing FO membrane for water desalination process owing to its high water permeability. In the present study, FO membrane prepared by blending $TiO_2$ nanoparticles in a support layer, showed good permeability and thermal stability.

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