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# Performance of combined PTFE hydrophilic and hydrophobic membrane during laundry/detergent wastewater treatment by air gap membrane distillation (AGMD): an experimental study

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## ABSTRACT

Membrane distillation (MD) is making a rapid progress in desalination and wastewater treatment research. Though MD produces lower distillate yield compared with other membrane processes, its ability to be used with varieties of renewable and waste energy source coupled to produce ultrapure water makes it a competitive choice. One of the major drawbacks of MD is the fouling and pore wetting of the membrane surface, and therefore modifications to membrane surface characteristics and combining MD with other techniques are necessary for successful rejection of all sorts of organic, inorganic and biological contaminants, except few. One of them is household wastewater containing common laundry detergent sodium dodecylbenzenesulfonate. Although it has been reported that alkaline surfactant causes pore wetting in hydrophobic membranes, but the extent of damage and the severe drop in permeate quality has not been reported. In this work, the preliminary experiments have been carried out with standard laundry wastewater and it has been observed that commercially available hydrophobic polytetrafluroethylene membrane permits all the constituents of the feed water in presence of small amount of laundry detergent. Complete pore wetting of the membrane makes it reach very high permeate flux (40 L/m$^2$ h) and the distillate quality is near to the feed water (>2,400 μS/cm). A simple technique was developed to prevent pore wetting, by combining hydrophilic and hydrophobic membrane without using any interfacial-bonding agent or crosslinking agent. This simple technique successfully produced pure distillate from feed water containing detergent with a conductivity of 12–20 μS/cm.

*Keywords:* Membrane distillation (MD); Air gap membrane distillation (AGMD); Hydrophilic-hydrophobic membrane; Membrane pore wetting; Laundry/detergent wastewater treatment

## 1. Introduction

Membrane distillation (MD) has proven to be a promising technology in the recent times due to its many advantages over other water treatment methods. Especially in the field of desalination and wastewater reuse, MD has been able to draw significant attention as it is least affected by feed concentration and can continue operation with low-level energy. Furthermore, the ability to incorporate several green and alternative energy sources makes the process more feasible compared with energy-intensive desalination processes such as reverse osmosis, multistage flash distillation and multieffect distillation [1].

MD is a thermally driven separation process, where the thermal energy creates vapor pressure difference between the two sides of a hydrophobic membrane. Only vapor molecules travel through the hydrophobic membrane and

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condense on the other side, becoming pure distillate. The microporous hydrophobic membrane prevents the aqueous solution to transfer through the pores, except if the pressure is higher than the liquid entry pressure or if the pore is wetted via surfactant. The temperature difference between the two sides of the membrane is sustained by flowing hot feed over the membrane's hydrophobic side while maintaining coolant arrangement on the other side of the membrane.

Over the past decades, MD has been successfully applied for different varieties of wastewater research ranging from highly saline brine to radioactive wastewater [2,3]. However, such as all the membrane processes, MD also suffers from fouling and scaling. Fouling causes a separate layer to form in the membrane surface, which can be porous or nonporous. Depending on the fouling condition, it can reduce permeate flux by adding temperature and concentration polarization or by pore clogging which imposes mass transfer resistance. But, the worst case is pore wetting where the permeate becomes contaminated. There are various degrees of pore wetting mainly surface wetting, partial wetting and full wetting. In case of producing potable water, the distillate quality is of high concern and thus complete (full) pore wetting should be considered as the biggest threat for pure distillate production.

Laundry water is among the few wastewaters which causes this pore wetting in hydrophobic membranes whose main constituent is detergent. This grey water constitutes about 50%–80% of the total household wastewater [4]. In order to achieve a small-scale portable household water treatment facility, treatment of this laundry water is essential. Current means of treating laundry water require several steps that include filtration step (pretreatment) and disinfection step (posttreatment) and other types of treatment are normally chemical treatment. However, these technologies can't treat the wastewater to drinkable quality. Using nanofiltration membranes lead to satisfactory grey water, which can be reused as the feed for the washing machine [5]. However, the produced water quality is still not suitable for drinking. MD also has not shown much potential in treatment of grey water as the surfactants present in detergent decreases the surface tension of water and the liquid-membrane contact angle, both of which reduce the entry pressure through the membrane. Thus, the membrane loses its hydrophobicity and the permeate becomes contaminated. As our first endeavour, experiments were conducted to observe the severity of the membrane damage by common household laundry water on commercially available hydrophobic membranes. It was observed that within minutes, all of the constituents of feed water penetrated through the membrane and complete pore wetting took place. This shows that commercially available hydrophobic PTFE membranes alone can't be used to even partially decontaminate this wastewater, rather a suitable pretreatment or modification of the commercially available membrane should be carried out prior to attempting household water treatment by MD.

Xu et al. [6] first mentioned pore wetting by detergents, citrus juice and whole milk. Two other studies found that humic acid can also cause pore penetration [7,8] to a moderate extent. Several techniques were discovered to prevent this wetting by depositing a separate hydrogel coating to the membrane surface and thus preventing these surfactants to come in contact with the membrane pores while letting the water permeate through since the coatings are hydrophilic. However, coating a hydrophobic membrane is a tedious process involving several chemicals. Also, the crosslinking agent and interfacial-bonding agent become a key factor as the adhesion strength between the coating and the membrane is low. Moreover, the coating may wash away if used for a long time or if the feed flow rate is high.

The objective of this paper is to show the severity of pore wetting for hydrophobic PTFE membranes when commercial detergents are used in the feed water and a simple but effective remedy to mitigate this problem. A simpler technique of adding a separate hydrophilic membrane on top of the hydrophobic membrane was attempted in this work and it was possible to avoid the pore wetting while using the water containing detergent.

## 2. Experimental setup and method

### 2.1. Air gap membrane distillation method

The vapour transferring through the membrane is cooled by different methods to get the pure distillate. Depending on this cooling method, MD can be classified to direct contact membrane distillation, air gap membrane distillation (AGMD), sweep gas membrane distillation and vacuum membrane distillation. In AGMD instead of directly letting the permeate vapor mix with the cold solution, an air gap is used to separate them. The permeate vapour is cooled by the coolant plate which is in direct contact with the circulating cold solution. Fig. 1 shows how AGMD works. AGMD has some advantages over other MD techniques such as high thermal efficiency and incorporation of internal heat

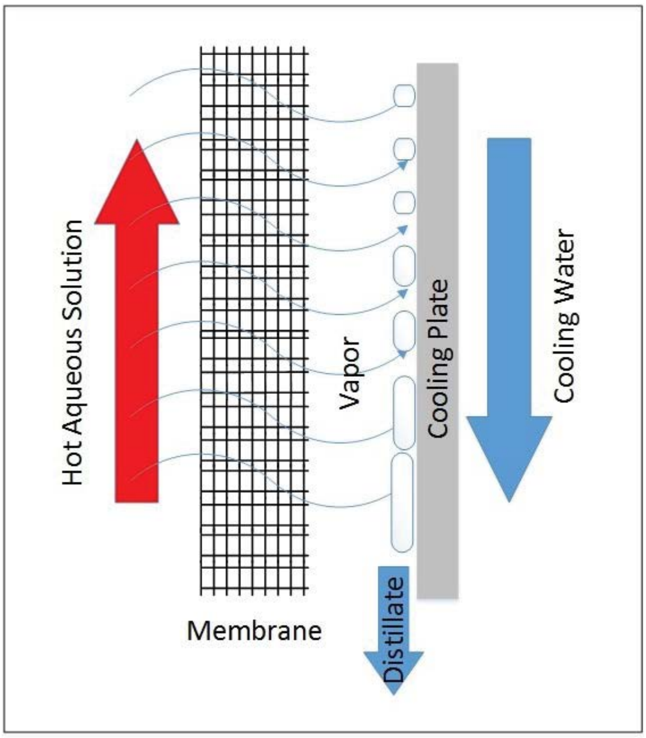

Fig. 1. Working principle of AGMD.

recovery. In our study, AGMD was mainly selected because of its ability to keep the cold solution and the distillate separate.

### 2.2. Membrane properties

The membranes used in this experiment were hydrophobic Fluoropore® polytetrafluroethylene (PTFE) membrane (bonded to a high-density polyethylene support) and hydrophilic Omnipore® PTFE membrane both from Merck Millipore Ltd., Selangor. The membrane properties are listed in Table 1.

According to the supplier (Merck Sdn Bhd, Selangor), this hydrophobic Fluoropore PTFE membrane filter features broad chemical compatibility with acids, bases and solvents [9] while the hydrophilic Omnipore PTFE membrane is capable of treating. The Omnipore membrane is hydrophilic PTFE compatible with virtually all solvents, acids and alkaline solutions [10].

### 2.3. Module design and process

The designed module was made out of grade 'A' polycarbonate sheets having a thickness of 5 mm and the hot and cold chamber had these dimensions 162.4 × 162.4 × 106.6 mm. It consisted of six parts: (1) hot solution chamber, (2) membrane, (3) membrane ramp, (4) air gap frame with hole on the bottom surface to collect distillate, (5) coolant plate and (6) cold solution chamber, as seen in Fig. 2. The air gap thickness was 11 mm. The schematic diagram of the setup is shown in Fig. 3. The feed side was heated from 40°C to 50°C and the cold side was varied from 15°C to 20°C by two water recirculators with a flow rate of 2 L/min on both sides. The distillate is collected by a metered flask at the bottom of the module. Feed solution was prepared by mixing detergent with tap water and the concentration of detergent was 2.61 g/L for the solo hydrophobic membrane and 1.18 g/L for the combined membrane experiment. After connecting all equipment and pouring feed and coolant to recirculators, the power was turned on and the hot feed and the coolant chambers were filled by respective fluids with food colour (red) added to the feed side. The purpose of the colour was to detect any leakage in the system immediately. With presence of any leakage, the distillate's colour would also start to show the tint of red, otherwise, it would remain clear distilled water. The system was duly insulated. To test the permeate water quality, an electrical conductivity meter having 1 μS/cm resolution was used. Scanning electron microscope (SEM) was used to observe the membrane surface quality after use. Module performance parameter, permeate flux $J$ (L/m$^2$ h) was evaluated using Eq. (1) as follows:

$$J = \frac{V}{A \times t} \tag{1}$$

where $V$ is the volume of the permeate collected (L), $A$ (m$^2$) area of the membrane used and $t$ is the time of collection of distillate (h).

Table 1
Properties of membranes used

| Wettability | Hydrophobic-Fluoropore® | Hydrophilic-Omnipore® |
|---|---|---|
| Max operating temperature (°C) | 130 | 130 |
| Pore size (μm) | 0.45 | 0.45 |
| Porosity | 0.85 | 0.80 |
| Filter thickness (μm) | 150 | 65 |
| Filter diameter (mm) | 142 | 142 |

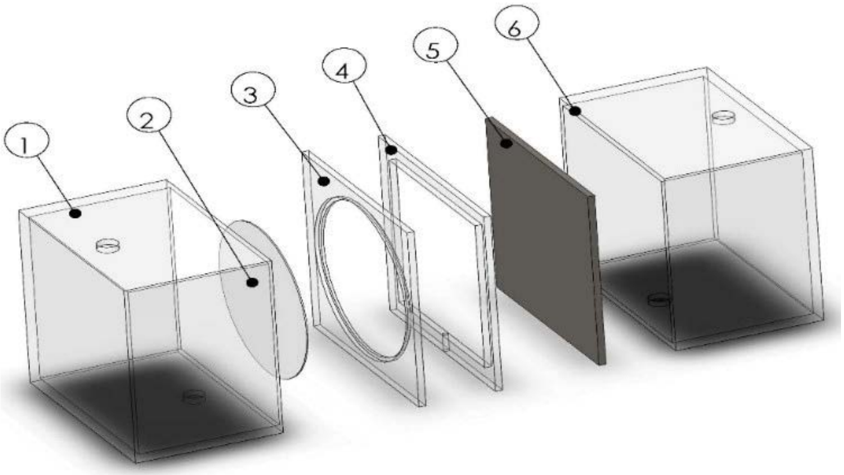

Fig. 2. Membrane setup for the MD module.

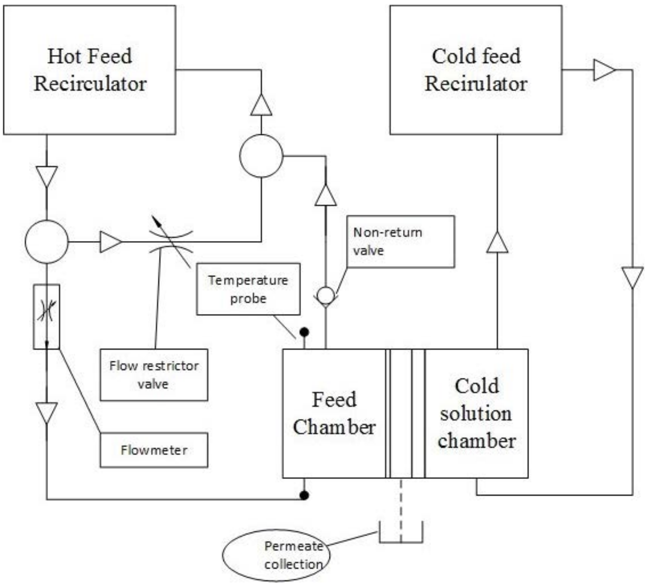

Fig. 3. Schematic of the AGMD module.

### 2.4. Module consisting both hydrophilic and hydrophobic membrane

Same module design was used where two membranes were glued on top of another. Only the perimeter region was glued and no other interfacial bonding agent or crosslinking agent was used between them. The first membrane facing the feed solution was hydrophilic and the following membrane was hydrophobic. The flow pressure inside the feed chamber was high enough to hold the two membranes together without any gap between them. The rest of the apparatus and procedure remained the same.

## 3. Results and discussion

### 3.1. Performance of hydrophobic membrane

The module was first run by a fresh membrane having 40°C feed side temperature and 15°C cold side temperature. After adding detergent with concentration of 2.61 g/L, within minutes, the permeate had shown tint of the food colour meaning the pores have been wetted and the membrane had started to lose its hydrophobicity. The permeate flux was recorded 27 L/m$^2$ h and the permeate quality rose from 785 to 2,473 µS/cm within 4 min. Whereas previous experiments for desalination with the same module produced 13 L/m$^2$ h (highest) permeate flux with a highest conductivity meter reading of 12 µS/cm.

In the next stage, a different module with same characteristics was used to reconfirm the result. The PTFE membrane used successfully separated NaCl salt from feed water in a previous experiment. While performing the distillation of water added with laundry detergent, this module also exhibited full membrane wetting. The permeate flux had increased from 15.16 to 40 L/m$^2$ h when feed side temperature was increased by 10°C. Initially, the conductivity meter test showed about 1,790 µS/cm permeate quality and then it rose to 2,400 µS/cm after 10 min.

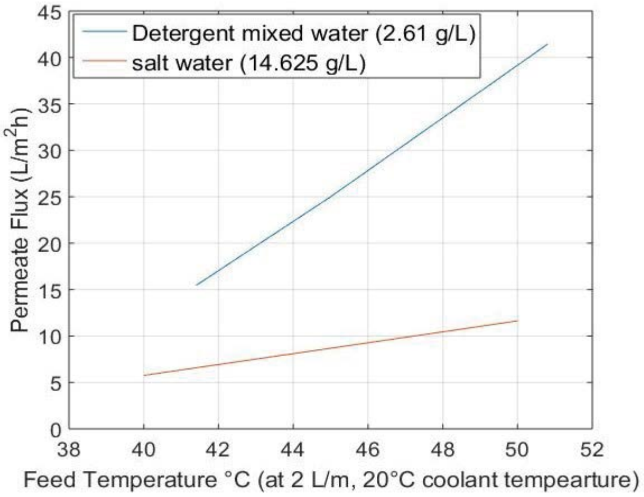

Fig. 4. Comparison of permeate flux between detergent mixed water and salt water.

Fig. 4 shows the comparison of permeate flux between detergent mixed water and salt water. Due to the significant pore wetting, the permeate flux of detergent mixed water is several times higher than salt water with a steeper trend in permeate production. Figs. 5 and 6 show the membrane surface when it was in process for 20 min and when the second pretested membrane was kept in process for 3 h, respectively. The amount of fouling with respect to time can be seen in these figures. It should be noted that the centre portion of the membrane surface underwent major fouling as it was closest to the cold plate (the membrane used to bulge towards the cold plate due to the feed pressure).

Figs. 7–9 show the SEM images taken from the pretested membrane surface. At highest magnification (Fig. 7) detergent crystals can be seen to clog and wet the membrane pores. On further zooming out we can see the entire surface is covered with theses crystals (Fig. 8). Finally, a magnification of

Fig. 5. Image of the fresh unused membrane after 20 min with detergent water.

Fig. 6. Image of the pretested membrane after 3 h with detergent water.

25× shows the relative scale of deposition on the membrane surface only in about 3 h (Fig. 9).

### *3.2. Performance of combined hydrophilic and hydrophobic membrane*

To prevent membrane wetting, the same experiment was carried out, but this time, a hydrophilic membrane was glued on top of the hydrophobic membrane. The combined membrane was first tested with tap water to get the normal permeate flux data. As expected, the permeate flux was lower than that produced by the single hydrophobic membrane because of an additional mass transfer resistance. After adding detergent to the feed solution having concentration of 1.18 g/L, the permeate quality was checked for several hours. Pure distillate was obtained during the operation having 12–20 μS/cm distillate quality. It should be noted that although the permeate was pure, but the aroma of detergent was still present in the distillate. The combined membranes continued to produce pure distillate for about 2 h and after that the quality started to deteriorate and finally the

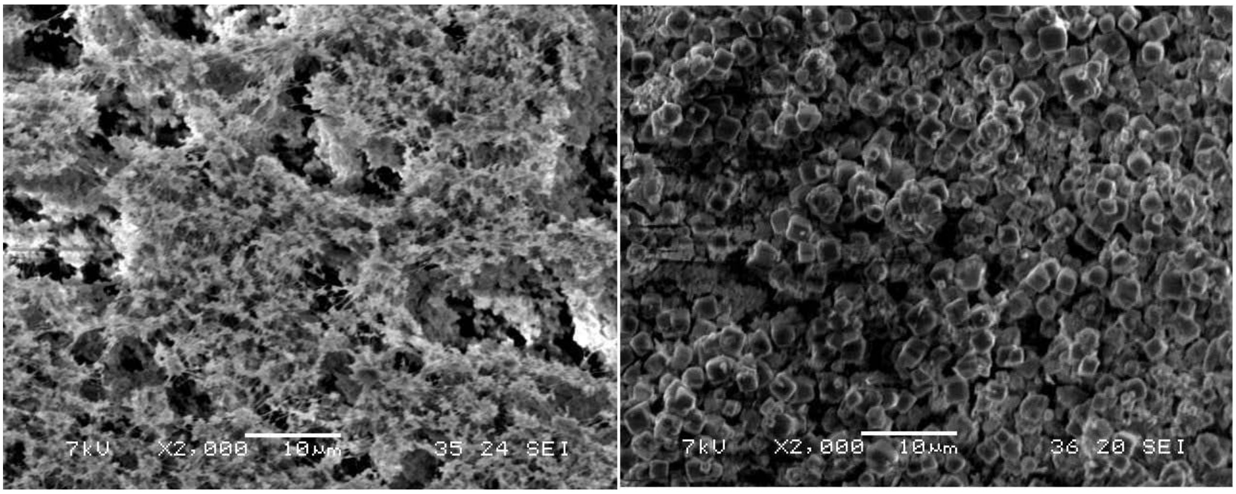

Fig. 7. Fresh membrane surface (left), detergent crystal clogging the membrane pores (right) at 2,000× magnification.

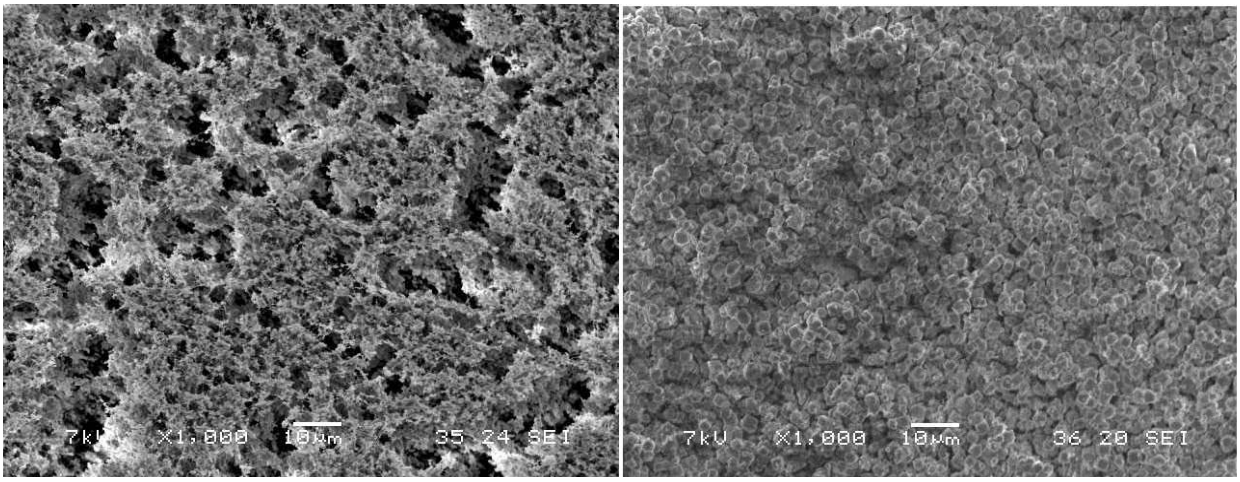

Fig. 8. Fresh membrane surface (left), detergent crystal covering the entire membrane surface (right) at 1,000× magnification.

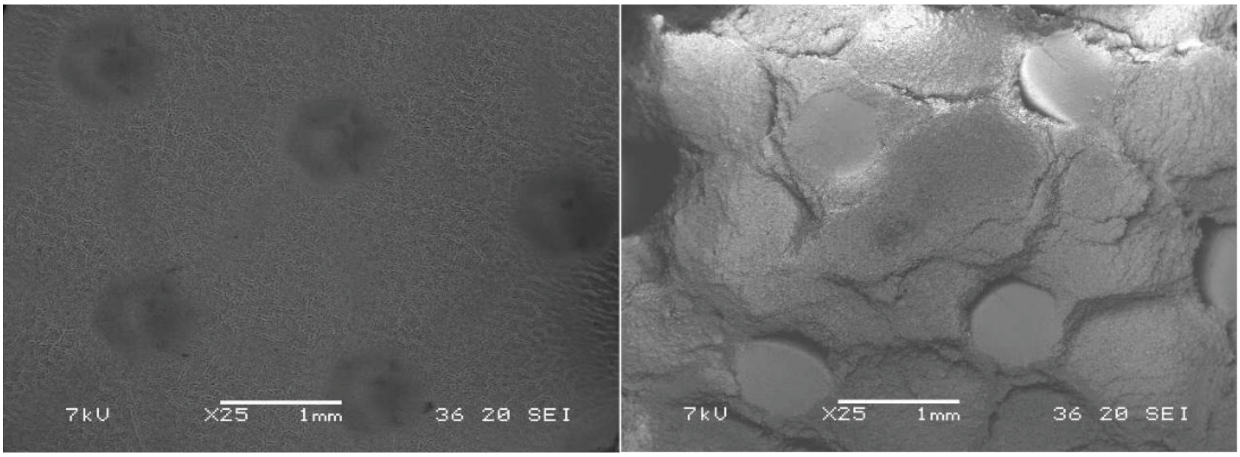

Fig. 9. Fresh membrane surface (left), detergent crystal covering the entire membrane surface (right) at 25× magnification.

same fouling images were visible on the membrane surface. Fig. 10 shows the comparison of permeate flux between different types of feed solution for the combined membrane. Minimum permeate flux recorded for the combined membrane was 2.5 L/m$^2$ h while at the same concentration. Xu et al.'s coated membrane produced 1.5 L/m$^2$ h permeate flux.

### 3.3. Discussion

Although it was known that highly surface active agents such as detergent causes membrane wetting but the extent of damage and the rapid wet out was not investigated before. Initial experiments carried out on both virgin and nonvirgin hydrophobic membranes show that detergent causes membrane wet out almost instantly and thus these surfactants should be removed beforehand by a suitable pretreatment method before using these membranes in conventional desalination. The reason behind this wet out can be explained by the amphiphilic nature of detergent. The hydrophobic portion of detergent forms van der walls bond with the hydrophobic membrane surface and at the same time the hydrophilic portion of detergent bonds with water molecules through hydrogen bonding. Thus their combined effect reduces the hydrophobicity of the membrane and causes the membrane wet out to occur [11]. In simple terms, detergent and other strong surface active agents increase the adhesive force of the solution with the pore wall of the membrane and decrease the cohesive force of the solution and thus wet out occurs.

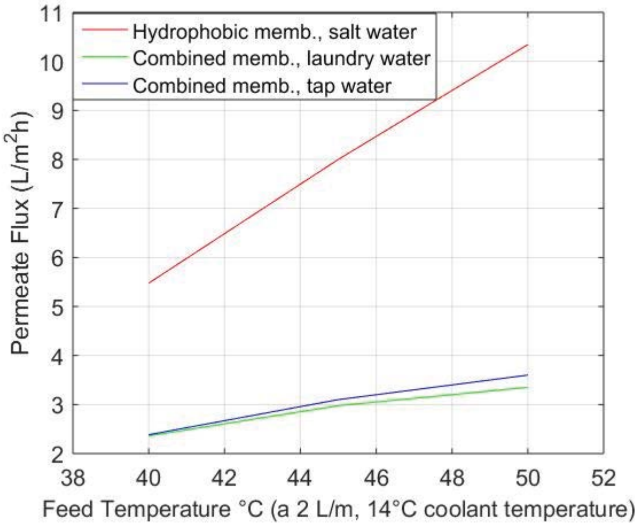

Fig. 10. Comparison of permeate flux between hydrophobic membrane alone and combined membrane with detergent mixed water.

From the combined membrane experiment it was seen that the membranes can hold out against this wet out for a certain period of time because the hydrophilic membrane rejects the major hydrophobic group from the laundry wastewater, thus the performance of the combined membrane is heavily dependent on the hydrophilic membrane's rejection capabilities. Further experiments should be carried out by combining hydrophobic membrane with different hydrophilic membranes available to get the best results and also to determine effect of temperature and concentration on the duration of successful treatment.

## 4. Conclusion

In this work, an attempt was made to apply MD for laundry wastewater treatment to produce freshwater. Previous studies indicated surface modification of the hydrophobic membrane, whereas in this case, a simple attachment of hydrophilic membrane over the hydrophobic membrane has shown successful distillation of soap water. Though the duration of successful treatment of laundry water was shorter compared with that of [6] (22–24 h), but still the result is significant as it shows the effectiveness of combining commercial membranes instead of going through complex coating procedures. Furthermore, the coated membranes had very small surface area (10.2 cm$^2$) which may be the reason to their high longevity as smaller surface area produces low flux and therefore it takes surfactant more time to be adsorbed into the membrane. By choosing the optimum hydrophilic membrane material containing greater water absorption capability and improved resistance against surface active agents the performance of combined membrane can be further increased to the point that MD can be effectively used to treat all kinds of grey waters.

## Acknowledgements

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