

RESEARCH ARTICLE

# Development of Silica-Eggshell Ceramic Membranes for Dye Removal via Forward Osmosis

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Abstract Water is an essential resource for life on earth and human development. Unfortunately, many hazardous and persistent chemicals, such as polycyclic aromatic hydrocarbons in dyestuff effluent, can degrade ecosystems and threaten the survival of numerous species. For example, Malaysia faces challenges related to air and water pollution, waste management, and health effects caused by textile industrial activities. Therefore, the purpose of this study is to synthesize and characterize a hollow fibre ceramic membrane made of silica-eggshell to remove dye from the solution through forward osmosis. The membranes were fabricated using a phase inversion method. The results from the characterization and filtration processes of the silica-eggshell membranes with different ratios were compared. The ATR-FTIR results indicated the presence of silica and calcium carbonate in the membranes, confirming the completion of the fabrication. The FESEM results also showed that the 1:2 (silica: eggshell) ratio membrane had more active sites compared to the 1:1 (silica: eggshell) ratio membrane. From the forward osmosis results, it was observed that the membrane with a higher eggshell content (1:2 ratio) efficiently filtered the dye, achieving a 65.33% dye removal efficiency with 30 ppm Remazol Brilliant Blue R dye, compared to the 1:1 (silica: eggshell) membrane. The membrane with a 1:2 silica-to-eggshell ratio also showed an increasing trend in dye removal efficiency when reused in the forward osmosis system for approximately 10 minutes. In conclusion, domestic waste, such as eggshells, can be used to fabricate membranes and effectively remove RBBR dye from the solution. Furthermore, eggshells are a natural material, and incorporating them into membrane fabrication reduces the dependence on synthetic or harmful substances, thereby minimizing the environmental impact of the membrane production process.

**Keywords**: Ceramic membrane, eggshell, hollow fibre, dye, forward osmosis.

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# Introduction

Membrane technology is used in many industries, including chemical, beverage, food, metallurgy, and water treatment for both homes and businesses [28]. It separates components of liquids or gases through mechanical methods, using a membrane to filter out unwanted elements while allowing the desired substances to pass through. This study focuses specifically on the forward osmosis system among various membrane techniques.

The forward osmosis method uses a thick hydrophilic, semi-permeable membrane to separate two water solutions with different osmotic pressures: the feed solution and the osmotic agent solution. The difference in osmotic pressure drives the process. Unlike other membrane methods, forward osmosis works without external pressure [21]. According to [23], forward osmosis concentrates the feed stream while diluting the osmotic agent. [12] highlights that an ideal membrane should have high porosity,



strong hydrophilicity to reduce contamination, and thin thickness to increase flow. Additionally, an effective draw solute with high osmotic pressure and easy separation is crucial.

A "membrane" is a thin layer or sheet that separates two different phases of fluid, gas, or vapour. It can be in a liquid, gel, or solid-state and acts as a molecular sieve to separate tiny particles and molecules. Membranes are made of fine mesh or microscopic pores [28]. One example is the hollow fibre ceramic membrane, which allows full product flow while retaining cells [29]. Hollow fibre membranes have several advantages, such as low transport resistance, high packing density, low cost, and a self-supporting structure [24]. Ceramic membranes are mainly classified as porous or dense. Porous ceramic membranes are often used for water purification, while dense membranes are used for processes like atomic, ionic, and molecular diffusion [13][16].

In comparison to polymeric membranes, ceramic ones are easier to modify in terms of pore size and exhibit greater chemical, thermal, and mechanical stability. Therefore, ceramic membranes are superior to polymeric ones in terms of performance. Asymmetrical three-layer structures are common in ceramic membranes [14]. The ceramic membrane schematic diagram is illustrated in Figure 1 [19]. The intermediate layers act as a link between the two and gradually reduce the pore size, while the support layer is often in charge of providing mechanical strength. The selective layer, which is on top of a membrane, is where the separation happens. Figure 1 shows that the support's holes grow smaller as one moves through the membrane and reaches the top layer, where the medium containing the substances to be separated comes into touch with the tiniest pores. Nevertheless, the utilisation of large-scale applications is still limited because of the substantial expenses associated with it [4]. Therefore, there is a current push to find ways to create ceramic membranes using low-cost natural materials. Zirconia, alumina, titania, and silica are the primary components that are utilised in the manufacturing process of ceramic membranes.

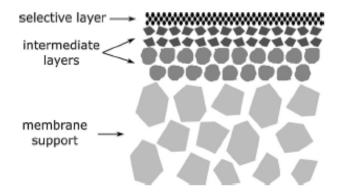


Figure 1. Schematic diagram of the ceramic membrane [19]

[27] stated that instead of using harmful mineral fertilisers, the biowaste products may be used as a greener option. One practical way to preserve nutrients while using waste things is to use organic waste materials as a source of nutrients. There has been a long-standing undervaluing of eggshell (ES) use due to its reputation as a waste product. However, due to its intriguing structure, it possesses peculiar properties that are currently the focus of a lot of research [6]. The four basic components of an egg, according to anatomy and physiology, are the egg shell, the albumen, the vitellus, and the egg white. According to the [20], organic matter makes up 4% of eggshells, followed by calcium phosphate at 1%, magnesium carbonate at 1%, and calcium carbonate at 94%. It is possible to speed up the adsorption process on an eggshell surface since the microparticles are all around the same size. Adsorbents can minimise wastewater pollution because their surface area is directly related to their active surface area, which allows polluted solutions to penetrate the material [8].

Polluting the environment means putting harmful chemicals into the Earth's living things and changing the way it normally works. Chemical compounds are considered pollutants when they accumulate in harmful amounts or when they hurt the environment [29]. Many different compounds are released into wastewater daily as a result of water usage by industry, farms, and the general population. According to [18], Most of the textile industry's emissions (about 80% of all emissions) end up in waterways without being cleaned. This is what hurts the environment the most. Dysentery, typhoid, and diarrhoea are just a few of the waterborne diseases that can be caused by viruses, bacteria, and intestinal parasites found in contaminated water [10].



Fluorescent dyes, including Remazol Brilliant Blue R (RBBR), are a concern in Malaysia and many other countries. Introducing these dyes into water reduces sunlight penetration, increases oxygen demand (BOD and COD), disrupts photosynthesis, and harms plant growth [3]. Fluorescent dyes absorb and emit light in large amounts, which makes them useful in industries like printing, leather, paper, and textiles. RBBR, a reactive dye, contains polycyclic aromatic hydrocarbons (PAHs) with condensed aromatic rings [7]. According to [26] and [2], RBBR is a persistent pollutant that poses health risks, such as skin and eye irritation, and can lead to serious health issues like cancer, allergies, heart disease, and genetic damage.

This research aims to synthesize and characterize ceramic membranes derived from eggshells as an affordable material. Additionally, the study will assess the efficiency of hollow fibre ceramic membranes in removing dye from solution through forward osmosis by comparing the removal percentages of RBBR dye at two different silica: eggshell ratios. This comparison will demonstrate how the performance of the membranes is influenced by the amount of eggshell added. Moreover, silica will play a supporting role in enhancing the membrane's properties, thanks to its excellent characteristics and relative abundance and cost-effectiveness. Silica is chemically and thermally stable, and it provides a large surface area, making it useful for filtration, catalysis, and separation.

# **Materials and Methods**

Utilising waste eggshells, silica sand powder with a purity of 99.99% and a particle size of 20 nm by Xinglu Chemical, polyethersulfone (PES) by Solvay as the binder, Polyethyleneglycol 30-dipolyhydroxystearate (Arlacel) by Corda as the dispersant, and N-Methyl-2-Pyrrolidone (NMP) by Sigma Aldrich as the solvent, ceramic membranes were manufactured. A kitchen in Arked Meranti, UTM Skudai, was the source of the eggshells that were recovered. The eggshells were rinsed many times with deionized water and dried overnight at temperatures below 65°C. Once the eggshells were completely dried, they were ground into a fine powder using a powder grinder machine. The powder was sieved using a mechanical siever (400µm) and then placed in a sealed container for future usage.

For the characterization part, several analyses were done to determine and ensure the composition, and mechanical and chemical properties of the hollow fibre ceramic membrane. Perkin Elmer Model 1600 Infrared-Attenuated Total Reflection was used to determine the kind of functional group present in eggshell powder, and silica-eggshell hollow fibre ceramic membrane. The wavelength of the infrared spectrum that will be utilised to identify the membrane material and its functional group has been adjusted at (650 cm<sup>-1</sup> – 4000 cm<sup>-1</sup>). Using Field Emission Scanning Electron Microscopy (FESEM), the morphology and pore size distribution of a silica-eggshell hollow fibre ceramic membrane were measured. Hitachi model SU8020 was the model used for morphology analysis. Surface charge and wettability of the tubular membrane also had been investigated by measuring Zeta potential and contact angle, respectively and the model used was a goniometer contact angle (OCA Dataphysics). Mercury Intrusion Porosimetry (MIP) was used to analyse the pore size of the membranes and the model used was AutoPore V.

# **Membranes Preparation**

The phase inversion approach had been used to create a silica-eggshell hollow fibre ceramic membrane. Modifications were made to [1] to obtain the synthesis process. The process began by crushing the eggshells into a powder. Next, the eggshell powder was combined with silica powder in proportions of 1:4, 1:2 and 1:1 (silica: eggshell) until a homogeneous mixture was achieved. In the meantime, NMP and Arlacel had been thoroughly dissolved and homogenised with gentle stirring. The next step was to grind the mixture using a ball mill set at 192 rpm for 48 hours after adding eggshells and silica to the solution. The PES was then been added, and the suspension was ball-milled for a further 48 hours to achieve homogeneity. To prevent faults in the tubular membrane construction, air bubbles were eliminated from the mixture by a 30-minute degassing procedure at room temperature under vacuum conditions with a mild mixture. All percentages of weight are listed in Table 1.

Table 1. Composition for preparation of dope suspension

Name of sample	Ratio of silica- eggshell	Ceramic- PES ratio	PES (wt%)	NMP (wt%)	Arlacel (wt%)	Silica sand (wt%)
Α	1:1	4:1	9.00	40.00	1	50.00
В	1:2	4:1	9.00	40.00	1	50.00
С	1:4	4:1	9.00	40.00	1	50.00



The blend was placed into syringes made of stainless steel and then forced through a spinneret that had an outer diameter of 2.8 mm and an inner diameter of 0.5 mm after it had been degassed. Using the specified parameters, the spinning operation was carried out at ambient temperature detailed in Table 2. It was necessary to immerse the extruded precursors of hollow fibres in water for a whole day to complete the phase-inversion process. The fibre precursors were then been sliced and air-dried at room temperature after being washed with water. Sintering takes place in a tubular furnace at high temperatures, with the temperature rising from room temperature to 600 °C at a rate of 2 °C per minute. The hollow fibre passed through this process. The temperature had been maintained at 600 °C for two hours to guarantee the removal of the polymer binder. The temperature was then been maintained for 6 hours at 1000 °C with a heating rate of 5 °C/min. At a rate of 5 °C per minute, the temperature had been brought back to room temperature.

Table 2. Spinning parameters of silica sand hollow fibre ceramic membranes

Spinning Parameter	Condition
Bore fluid extrusion rate	10 ml/min
Suspension extrusion rate	9 ml/min
Air gap	5 cm
Internal coagulant (bore fluid)	Distilled water
External coagulant	Tap water

### **Filtration Studies**

The first step was to prepare the dye solution which is Remazol Brilliant Blue R. After that, to determine the dye removal efficiency, a forward osmosis system was used. By dissolving 0.5 g of RBBR dye in 500 mL of deionized water, an RBBR dye stock solution of 1000 ppm was been created. Next, by diluting the original stock solution into a 50 mL beaker containing deionized water, 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm, 30 ppm and 35 ppm solutions were been obtained. The UV-Vis range of Remazol Brilliant Blue R covers wavelengths from approximately 500 to 700 nanometers (nm). NaCl was used as a salt solution and it was prepared by the same method as the preparation of dye solution. The UV-Vis range of NaCl solution covers wavelengths from approximately 190 to 400 nanometers (nm). A calibration graph of RBBR dye solution and NaCl solution was prepared in the concentrations of 5 to 35 ppm and 5000 to 35000 ppm, respectively. Each standard was analysed by using UV-Vis.

For the filtration part, the process was performed using a forward osmosis filtration system at the Advanced Membrane Technologies Research Centre (AMTEC). 30 ppm of an RBBR dye solution was added to the filtration feed vessel in this experiment, while a higher total dissolved salinity (TDS) solution which was 30000 ppm NaCl flowed in the draw tank. The hollow fibre membrane had separated two solutions with different concentrations. This experiment was conducted at room temperature using an osmotic pressure system. Contaminants stayed in the feed stream when water molecules moved from the feed solution into the draw solution due to osmotic pressure, which was generated by the concentration difference between the two sides. Then, to constantly remove water from the feed stream, the diluted draw solution was cycled back to the forward osmosis phase. The filtered water had been transferred into the draw tank that has a digital weight balance. Therefore, the volume of solution in the draw tank had increased as it now has more filtered water in it. Then, the solution in the feed tank and draw tank were analysed using UV-Vis analysis. The efficacy of filtration of the tubular membrane was determined using Equation (1) [23]. According to the equation, R% was the dye removal efficiency, C was the final concentration of the draw (ppm) and C<sub>0</sub> was the initial concentration of the draw (ppm).

$$R\% = (C_0 - C) / C_0 \times 100\%$$
 (1)

# **Results and Discussion**

This study focuses on determining the removal effectiveness (R%) of fluorescent dye from a polluted solution utilising a hollow fibre ceramic membrane composed of eggshells and silica in varying proportions. This part addresses in depth the membrane's characteristics and its ability to remove fluorescent dye through the forward osmosis method.

### **Fabrication of Hollow Fibre Ceramic Membrane**

The fabrication of hollow fibre ceramic membrane for a ratio of 1:1, 1:2 and 1:4 (silica: eggshell) has been successfully fabricated. Additionally, each of these membranes had undergone the sintering



procedure to remove the polymer contained in the membranes. Membranes A (1:1, silica: eggshell) and B (1:2, silica: eggshell) maintained the shape and longevity of hollow fibres, respectively. In contrast, membrane C (1:4, silica: eggshell) was exceedingly brittle and transformed into a powdery state upon contact. Therefore, only membranes A and B will be utilised in the continuation of this undertaking. Figure 2 shows the form of a hollow fibre ceramic membrane before and after sintering.

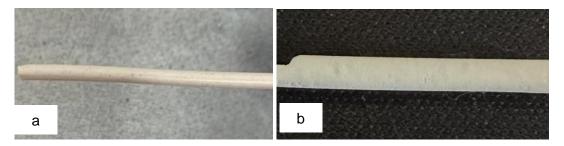


Figure 2. Hollow fibre ceramic membrane (a) before and (b) after sintering

### **Fourier Transform Infrared**

The characterization of eggshell powder has been done using FTIR-ATR analysis. The result of the FTIR spectrum of normal eggshell powder has shown a C-N peak at 1083.06 cm<sup>-1</sup> and a C=O peak at 1652.47 cm<sup>-1</sup>. The broad peak is at 1399.01 cm<sup>-1</sup> due to the CH<sub>2</sub> functional group. Other than that, the N-H group at 3366.55 cm<sup>-1</sup> and the C=N group at 2327.39 cm<sup>-1</sup>. There is also a presence of CaCO<sub>3</sub> at 711.87 cm<sup>-1</sup> and 872.78 cm<sup>-1</sup> associated with the in-plane deformation and out-plane deformation modes. Figure 3 shows the spectrum of the eggshell.

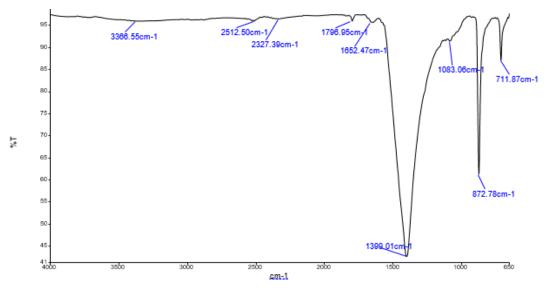


Figure 3. IR spectra of eggshell

Hollow fibre ceramic membrane have been made by using Teledyne ISCO D-Series Pump Controller and Cole-Parmer Syringe Pump. The spectrum for membrane A had the CaCO<sub>3</sub> peaks at 899.04 cm<sup>-1</sup> and 716.30 cm<sup>-1</sup> which indicate the out-of-plane and in-plane bending, respectively. According to [17], the region between 930 and 730 cm<sup>-1</sup> had the best correlation coefficient which was 0.995 in determining the presence of CaCO<sub>3</sub>. The peaks at 1066.68 cm<sup>-1</sup>, 936.70 cm<sup>-1</sup> and 796.30 cm<sup>-1</sup> referred to Si-O-Si asymmetric stretching, Si-OH stretching and Si-O-Si symmetric stretching vibrations, respectively. [15] had stated that three prominent peaks of silica were to occur around 1100 cm<sup>-1</sup>, 960 cm<sup>-1</sup> and 798 cm<sup>-1</sup>, respectively. Figure 4 shows the spectrum of hollow fibre ceramic membrane for membrane A (1:1, silica: eggshell) and membrane B (1:2, silica: eggshell).

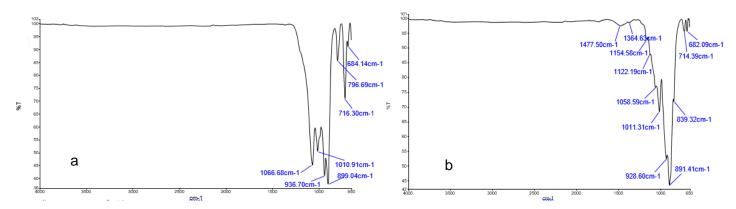


Figure 4. IR spectra for hollow fibre ceramic membrane before filtration for (a) membrane A and (b) membrane B, respectively

The characterization of membrane B (1:2, silica: eggshell) shows IR spectra peaks at 891.41 cm<sup>-1</sup> and 714.39 cm<sup>-1</sup> which indicate the presence of CaCO<sub>3</sub> out-of-plane and in-plane bending, respectively. Furthermore, the presence of Si-O-Si asymmetric stretching, Si-OH stretching, and Si-O-Si symmetric stretching vibrations can be seen at peaks 1058.59 cm<sup>-1</sup>, 928.60 cm<sup>-1</sup> and 839.32 cm<sup>-1</sup>, respectively.

After the forward osmosis process, the membranes were then characterized to investigate the mechanism of RRBR dye removal (trapped) on the surface or at the pores of the membrane as proof of successful filtration. From the data, it can be seen that the peaks at 1070.70 cm<sup>-1</sup> (a) and 1075.36 cm<sup>-1</sup> (b) in Figure 5 belong to S=O stretching which are from RBBR dye functional groups. Other than that, the presence of N-H stretching can be seen at peak 3495.24 cm<sup>-1</sup>(b) even though it is a weak stretching. Furthermore, no peaks for membrane A and also no presence of the OH- group for both membranes. This can be explained due to the membranes that had been exposed to the heat at 120°C for 10 minutes, to remove the membranes from the module that holds it in the permeation system.

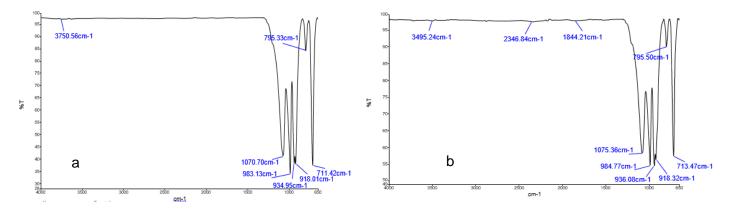


Figure 5. IR spectra for hollow fibre ceramic membrane after filtration for (a) membrane A and (b) membrane B, respectively

### **Water Contact Angle**

Water contact angle measurements were done on hollow fibre ceramic membranes with 1:1 and 1:2 ratios of silica and eggshell. This water contact angle measurement was performed to determine the membrane's wettability by using a goniometer contact angle (OCA Dataphysics). As soon as the water droplet was discharged from the needle of the water contact angle device for both membranes, it entered the membrane spontaneously. Theoretically, all of the membranes must display significant hydrophilicity by showing an angle of less than 90° between the water droplet and the surface of the membrane. In terms of wettability, there will be no substantial changes between the two membranes since their qualities allow water to readily permeate both membranes. However, both of the membranes were not able to give any result regarding the angle measurement. This can be seen in Figure 6 where the water droplet had entered the membrane without any trace. This situation has been recorded for both of the membranes. Therefore, no angle measurement had been done. Nonetheless, these membranes can be classified as hydrophilic membranes.



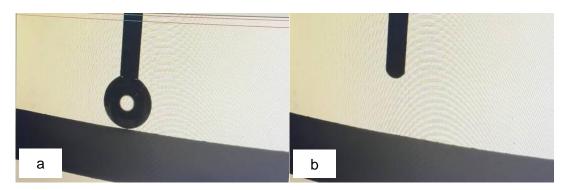


Figure 6. The surface of the membrane (a) before and (b) after the water droplet is discharged

# **Field Emission Scanning Electron Microscopy**

FESEM analysis was done to provide the structure and morphology of the membranes. Figure 7, clearly shows that the 1:2 ratio membrane has a rougher surface than the 1:1 ratio membrane. The pore size for the 1:2 ratio membrane is about 0.7µm while the 1:1 ratio membrane has 1.5µm for the pore size. The particle sizes are larger and the pore channels are narrower for a 1:2 ratio membrane compared to a 1:1 ratio membrane. This means that the 1:2 ratio membrane has more active sites for adsorption compared to the 1:1 ratio membrane because eggshell particles dominate the surface of the former. According to [30], electrospun nanofiber membranes with smaller pore sizes and a more uniform pore size distribution lead to improved filtration performance. [9] also stated that a narrow pore size enhances filtration by efficiently separating sub-micrometer-sized droplets, even when multiple layers are used. Therefore, a 1:2 ratio membrane will have a greater capability for RBBR dye removal than a 1:1 ratio membrane.

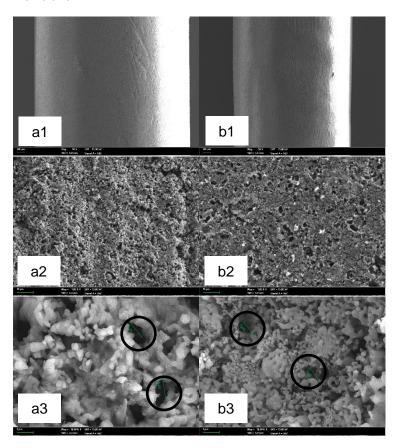


Figure 7. FESEM images for (a) 1:1 ratio membrane and (b) 1:2 ratio membrane. (1) 50 X magnification, (2) 1.00K X magnification and (3) 10.00K X magnification



# **Mercury Intrusion Porosimetry**

The foundation of Mercury Intrusion Porosimetry (MIP) is the ability to apply controlled pressure to push mercury into a material's pores. The size of the holes determines the pressure needed to force mercury into them. One of the benefits of MIP is that it can characterise both closed and linked pores, and it can analyse pore sizes ranging from nanometers to hundreds of micrometres. Table 3 shows the result of pore diameter and porosity. Based on the table, membrane B has a lower pore diameter than membrane A. However B has a higher porosity percentage than membrane A. This means that there are more interconnected spaces through which water molecules can pass in membrane B while having more capacity to hold contaminants (dye) compared to membrane A.

According to [21], the membrane pore size is a key factor influencing dye removal. Their studies showed that as the pore size decreases, the membrane's ability to retain the sulfonate azo dye (MO) molecule and prevent it from passing through improves, leading to increased treatment efficiency. Additionally, [5] demonstrated that incorporating cellulose nanocrystals into a polyamide membrane (CNC-TFC-M6) enhanced the membrane's properties, such as reducing pore size and imparting a negative charge. As a result, the modified membrane performed better than the control polyamide membrane in terms of dye removal.

Table 3. Data of pore diameter and porosity

Membranes	Pore diameter (nm)	Porosity (%)
A (1:1)	374.12	0.78
B (1:2)	92.67	5.42

### **Forward Osmosis Result**

The forward osmosis was done on a couple of sets of concentrations of Remazol Brilliant Blue R dye solutions (as a solution to be treated-feed) and NaCl solutions (as draw solution) for each ratio membrane. Table 4 shows the condition for the membranes to be run by a forward osmosis system. The time for each run was set at 2 minutes. To find and test the capability for each membrane, the experiment needs to be run 2 times for both membranes where each run with different concentrations of dye and NaCl solutions. The result reported from this permeate system was calculated and identified using UV-Vis spectroscopy. Figure 8 and Table 5 show the results for the efficiency of each membrane.

Table 4. Sets of conditions for the membranes

No. of run	Label	Initial feed concentration (ppm)	Feed flow rate (I/hour)	Initial draw concentration (ppm)	Draw flow rate (I/hour)
1	A1 (1:1 ratio membrane)	10	94	10000	94
2	A2 (1:1 ratio membrane)	30	94	30000	94
3	B1 (1:2 ratio membrane)	10	94	10000	94
4	B2 (1:2 ratio membrane)	30	94	30000	94

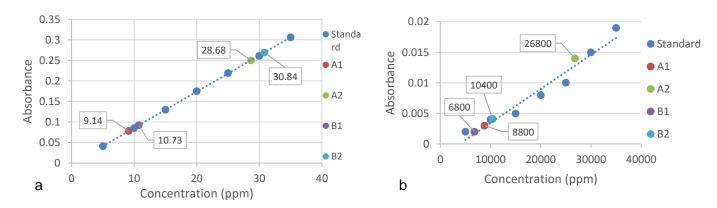


Figure 8. Graph of concentration against absorption for (a) RBBR dye solution and (b) NaCl solution, respectively



Table 5. Forward osmosis results for each membrane

Label	Final feed concentration (ppm)	Final draw concentration (ppm)	Concentration loss due to permeate (ppm)	Efficiency of dye removal (%)
A1 (1:1 ratio membrane)	9.14	8800	1200	12.00
A2 (1:1 ratio membrane)	28.68	26800	3200	11.00
B1 (1:2 ratio membrane)	10.73	6800	3200	32.00
B2 (1:2 ratio membrane)	30.84	10400	19600	65.00

Based on the result reported, membrane A has the lowest dye removal efficiency compared to the membrane B. On the lowest concentration of RBBR dye, membrane A has a slightly higher percentage of dye removal which was 12% compared to the highest concentration of RBBR dye which was 11% only. Membrane B has a higher value of dye removal efficiency on 30 ppm of RBBR dye which was 65% compared to the 10 ppm of RBBR dye which was 32%. Even on the low concentration of RBBR dye, membrane B has a higher value on the efficiency of dye removal compared to membrane A on both concentrations of RBBR dye. Therefore, the membrane with a higher content of eggshells can give better performance of dye removal compared to the membrane that has a similar ratio of silica and eggshells.

Furthermore, membrane B has undergone another run. As it is the most promising membrane to remove dye in this project, the forward osmosis system was run for about 10 minutes with intervals of 2 minutes. The concentrations for RBBR dye and NaCl solution were prepared at 30 ppm and 30000 ppm, respectively. Figure 9 shows the result of dye removal efficiency for membrane B.

Based on the data from both graphs, the trend for membrane B on dye removal efficiency is increasing. It shows a positive result despite the first 2 minutes which the percentage is slightly lower compared to the first run of the test. It also proves that this membrane has a good consistency in trapping dye from entering the draw tank. The reason for this reusability test is to assess whether the silica-eggshell membrane can be reused effectively and as a consecutive occurrence on this forward osmosis system. As a result, this may also help in reducing the development costs of the membrane and time-saving.

In addition, the ionic properties of both the dye and the membrane play a critical role in dye removal. The fabricated ceramic membrane is neutral in charge, while the RBBR dye is anionic. As a result, the dye removal percentage is relatively low because no electrostatic repulsion occurs. In contrast, the study from [11] showed that the cationic imidazole derivative membrane (IL-NH2) achieved a higher percentage of Safranin O dye removal compared to the pristine membrane. This is because the cationic imidazolium ring on the IL-NH2 membrane surface effectively repels cationic dyes through electrostatic interactions.

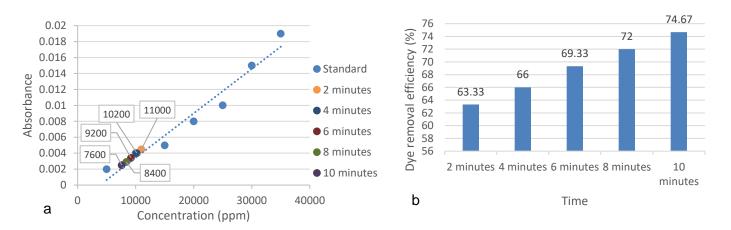


Figure 9. Graph of (a) concentration against absorbance and (b) dye removal efficiency (%) for membrane B, respectively



# Conclusions

In summary, the first objective in fabricating the ceramic membrane made up of eggshells and silica as its main materials was successfully done. From the characterization of the membrane using ATR-FTIR, water contact angle measurement and other analyses, it has been confirmed that the membrane contains carbonate and silica, and has high hydrophilic properties and porosity. It has been demonstrated that the forward osmosis process by using a 1:2 ratio of silica: eggshell hollow fibre membrane can give the highest and best removal efficiency of RBBR dye for the concentration of 30 ppm of RBBR dye solution when compared to the 1:1 ratio. The efficiency of removing RBBR dye increases by increasing the content of eggshells. Other than that, the membrane also provides positive feedback when undergoing a reusability test. 1:2 ratio of silica: eggshell has an increasing percentage of dye removal efficiency when tested for 10 minutes under the condition of 30 ppm of RBBR dye and 30000 ppm of NaCl solution. Furthermore, eggshell-based ceramic membranes are biodegradable under specific conditions, unlike some synthetic materials. As a result, if the membrane degrades or is disposed of, its environmental impact would be lower compared to non-biodegradable alternatives. Forward osmosis utilises osmotic pressure, whereas reverse osmosis utilises hydraulic pressure. This indicates that forward osmosis uses less energy than reverse osmosis to transport water. In this project, the permeation system (forward osmosis) that has been used is not capable of recovering the permeate itself from the draw tank. To overcome this, a modification or replacement of a better permeation system that comes with a draw recovery system needs to be used. This is to make sure that clean water can be recovered from the dye. In addition, a further study should be done by comparing it with other materials that have high filtration capability such as activated carbon. A comparison study between the membrane fully fabricated by eggshell and the seashell itself also can be done. This is to measure which domestic waste has higher filtration capacity.

# **Conflicts of Interest**

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

# **Acknowledgement**

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# References

- [1] Alftessi, S. A., Othman, M. H. D., Adam, M. R., Farag, T. M., Ismail, A. F., Rahman, M. A., *et al.* (2021). Novel silica sand hollow fibre ceramic membrane for oily wastewater treatment. *Journal of Environmental Chemical Engineering*, *9*(1), 104975.
- [2] Antecka, K., Zdarta, J., Siwińska-Stefańska, K., Sztuk, G., Jankowska, E., Oleskowicz-Popiel, P., & Jesionowski, T. (2018). Synergistic degradation of dye wastewaters using binary or ternary oxide systems with immobilized laccase. *Catalysts*, 8(9), 402.
- [3] Ardila-Leal, L. D., Poutou-Piñales, R. A., Pedroza-Rodríguez, A. M., & Quevedo-Hidalgo, B. E. (2021). A brief history of colour, the environmental impact of synthetic dyes and removal by using laccases. *Molecules*, 26(13), 3813.
- [4] Asif, M. B., & Zhang, Z. (2021). Ceramic membrane technology for water and wastewater treatment: A critical review of performance, full-scale applications, membrane fouling and prospects. *Chemical Engineering Journal*, 418, 129481.
- [5] Bai, L., Liu, Y., Ding, A., Ren, N., Li, G., & Liang, H. (2019). Fabrication and characterization of thin-film composite (TFC) nanofiltration membranes incorporated with cellulose nanocrystals (CNCs) for enhanced desalination performance and dye removal. *Chemical Engineering Journal*.
- [6] Baláž, M. (2014). Eggshell membrane biomaterial as a platform for applications in materials science. Acta Biomaterialia, 10(9), 3827–3843.
- [7] de Sousa Krueger, M. D., Carolina Volkmann, A., & Thaise Rainert, K. (2019). Removal of textile dye Remazol Brilliant Blue Reactive (RBBR) using fibers of *Citrullus lanatus* (watermelon) and *Cocos nucifera* (green coconut) as adsorbent material. *Revista Eletrônica em Gestão, Educação e Tecnologia Ambiental, 23.*
- [8] Fadhil, D. H., Al-Hussin, A., & Yousif, E. (2019). Removal of methylene blue dye from water using ecofriendly waste product (eggshell) as an adsorbent and using the optimum adsorption conditions with real water sample



- from Tigris river. Al-Nahrain Journal of Science, 22(1), 9-14.
- [9] Feng, C., Ji, Z., & Qiangqiang, Q. (2018). Effect of pore size and layers on filtration performance of coalescing filters with different wettabilities. Separation and Purification Technology, 201, 71–78.
- [10] Gambhir, R. S., Kapoor, V., Nirola, A., Sohi, R., & Bansal, V. (2012). Water pollution: Impact of pollutants and new promising techniques in purification process. *Journal of Human Ecology*, *37*(2), 103–109.
- [11] Guo, J., Yang, Q., Meng, Q., Lau, C., & Ge, Q. (2021). Membrane surface functionalization with imidazole derivatives to benefit dye removal and fouling resistance in forward osmosis. ACS Applied Materials & Interfaces.
- [12] Hilal, N., Ismail, A. F., & Wright, C. (Eds.). (2015). Membrane fabrication. CRC Press.
- [13] Hubadillah, S. K., Othman, M. H. D., Matsuura, T., Ismail, A. F., Rahman, M. A., Harun, Z., *et al.* (2018). Fabrications and applications of low cost ceramic membrane from kaolin: A comprehensive review. *Ceramics International*, *44*(5), 4538–4560.
- [14] Issaoui, M., & Limousy, L. (2019). Low-cost ceramic membranes: Synthesis, classifications, and applications. Comptes Rendus Chimie, 22(2–3), 175–187.
- [15] Karu, E., Magaji, B., Moh'd, A., & Shehu, A. (2024). Synthesis and spectroscopic analysis of Illite clay-silica nanocomposite. *Dutse Journal of Pure and Applied Sciences, 10,* 173–180.
- [16] Kozhukharov, V., Machkova, M., & Brashkova, N. (1999). Dense ceramic membranes: A review of the state of the art. Boletín-Sociedad Española de Cerámica y Vidrio, 38, 5–14.
- [17] Legodi, M. A., de Waal, D., Potgieter, J. H., & Potgieter, S. S. (2001). Rapid determination of CaCO<sub>3</sub> in mixtures utilizing FT–IR spectroscopy. *Minerals Engineering*, 14(9), 1107–1111.
- [18] Lellis, B., Fávaro-Polonio, C. Z., Pamphile, J. A., & Polonio, J. C. (2019). Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnology Research and Innovation*, 3(2), 275–290.
- [19] Mestre, S., Gozalbo, A., Lorente-Ayza, M. M., & Sánchez, E. (2019). Low-cost ceramic membranes: A research opportunity for industrial application. *Journal of the European Ceramic Society*, 39(12), 3392–3407.
- [20] Mittal, A., Teotia, M., Soni, R. K., & Mittal, J. (2016). Applications of egg shell and egg shell membrane as adsorbents: A review. *Journal of Molecular Liquids*, 223, 376–387.
- [21] Mondal, S., Field, R. W., & Wu, J. J. (2017). Novel approach for sizing forward osmosis membrane systems. *Journal of Membrane Science, 541*, 321–328.
- [22] Morsi, R., Corticelli, F., Morandi, V., Gentili, D., Cavallini, M., Figoli, A., Russo, F., Galiano, F., Aluigi, A., & Ventura, B. (2023). Influence of the fabrication conditions on the physical properties and water treatment efficiency of cellulose acetate porous membranes. *Water*.
- [23] Nandi, B. K., & Patel, S. (2017). Effects of operational parameters on the removal of brilliant green dye from aqueous solutions by electrocoagulation. *Arabian Journal of Chemistry*, 10, S2961–S2968.
- [24] Pian, C., Shen, J., Liu, G., Liu, Z., & Jin, W. (2016). Ceramic hollow fiber-supported PDMS composite membranes for oxygen enrichment from air. Asia-Pacific Journal of Chemical Engineering, 11(3), 460–466.
- [25] Rastogi, N. K., & Nayak, C. A. (2011). Membranes for forward osmosis in industrial applications. In Advanced membrane science and technology for sustainable energy and environmental applications (pp. 680–717). Woodhead Publishing.
- [26] Reghioua, A., Barkat, D., Jawad, A. H., Abdulhameed, A. S., Rangabhashiyam, S., Khan, M. R., & ALOthman, Z. A. (2021). Magnetic chitosan-glutaraldehyde/zinc oxide/Fe<sub>3</sub>O<sub>4</sub> nanocomposite: Optimization and adsorptive mechanism of Remazol Brilliant Blue R dye removal. *Journal of Polymers and the Environment*, 29(12), 3932–3947.
- [27] Saeid, A., & Chojnacka, K. (2019). Fertilizers: Need for new strategies. In Organic farming (pp. 91–116). Woodhead Publishing.
- [28] Saleh, T. A., & Gupta, V. K. (2016). Nanomaterial and polymer membranes: Synthesis, characterization, and applications. Elsevier.
- [29] Suzuki, T., Hidaka, T., Kumagai, Y., & Yamamoto, M. (2020). Environmental pollutants and the immune response. *Nature Immunology*, *21*(12), 1486–1495.
- [30] Wang, R., Liu, Y., Li, B., Li, B., Hsiao, B., & Chu, B. (2012). Electrospun nanofibrous membranes for high flux microfiltration. *Journal of Membrane Science*, 392, 167–174.
- [31] Wang, S. B., Godfrey, S., Radoniqi, F., Lin, H., & Coffman, J. (2019). Larger pore size hollow fiber membranes as a solution to the product retention issue in filtration-based perfusion bioreactors. *Biotechnology Journal*, 14(2), 1800137.