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Removal of Remazol Brilliant Blue R Dye from Water Using Eggshell Mixed Matrix Membrane through Filtration and Adsorption

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ABSTRACT

Water pollution causes flora and fauna to be destroyed and this process might be irreversible as well as lead to other bad consequences, especially towards human beings. Due to the inefficiencies of the dyeing process, it is estimated that up to 200,000 tonnes of dyes are released into wastewater annually by the textile industry. This research aimed to fabricate the mixed matrix membranes made up of eggshells that were combined with silica (SiO_2) for dye removal of Remazol Brilliant Blue R (RBBR). Poly ether sulfone (PES) and N-methyl-pyrolidone (NMP) will be added in the formulation as a binder and solvent, respectively. The results from the characterisation and filtration process of the ceramic membrane with different ratios of eggshells and silica for removing Remazol Brilliant Blue R (RBBR) dye were compared. The ATR-FTIR showed a strong existence of carbonate minerals and silica proving its functional group and properties of having good capacity in filtration. The water contact angle measurement of the 4:1 ratio of eggshell: silica gave a low contact angle value which is 2.16° while the contact angle for a 1:1 ratio membrane is 1.99°, thus, the synthesis of the membrane was successful. From the filtration process, it was discovered that the 4:1 ratio of eggshell: silica was able to remove the 50 ppm blue dye with a removal efficiency of 81.39% compared to the 1:1 ratio with a removal efficiency of 76.17%. The adsorption capacity or the amount of dye adsorbed onto hollow fibre membrane and flat sheet membrane were found to be 1.423mg/g with an adsorption percentage of 71.15% and 1.616mg/g with an adsorption percentage of 80.80% respectively. To sum up, eggshells are a practical way to remove RBBR dye from a solution and a potential raw material for membrane manufacturing.

Keywords: Eggshell, mixed matrix membrane, filtration, adsorption, dye

1.0 INTRODUCTION

Dyes are utilized in a various of industries, including paint, coatings, automotive, textiles, food, and many more. One of the "ingredients" used by businesses like cosmetics, textile painting, and printing is dye [1]. Synthetic dye was commonly used in the industrial sector, particularly in the textile industry. Because of their chemical structure stability, synthetic dyes are more difficult to remove than natural dyes [2]. According to [3], the chemical structure and intended use of a dye determine its classification. The chromophores, a collection of atoms, are the ones responsible for the dye's colour. These chromophore-containing centres house a range of functional groups, including azo, anthraquinone, methine, nitro, aril methane, and

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carbonyl. As an example, Remazol Brilliant Blue R (RBBR) is widely used in fabric industries such are nylon, silk and wood to provide a wide range of colourfast and bright hues. It is reported that RBBR is classified as a carcinogenic, recalcitrant pollutant, toxic, and it is very harmful to aquatic and vegetative lives [4].

To preserve aquatic life in bodies of water, there is a current emphasis on finding affordable ways to clean wastewater discharged by textile companies. Therefore, the approaches may be biochemical, physio-chemical, or a mix of the two; either way, they might provide textile industry wastewater treatment solutions that effectively remove contaminants. [5] stated that when compared to other physical and chemical methods, biological methods are the most cost-effective option. However, its application is frequently limited due to technical constraints. According to [6], biological treatment requires a large amount of land and has limitations due to its sensitivity to daily changes and the toxicity of some chemicals. It also has less flexibility in terms of design and operation.

Filtration is a physicochemical and commonly used unit operation for a variety of purposes such as separation, clarification, and concentration. Dialysis, electro-dialysis, pervaporation, microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are all forms of filtration that rely on differences in concentration or electrical charge. For industrial applications dealing with big volumes of materials to be filtered, pressure-driven filtration is a frequent choice. Microfiltration (MF) is used, for example, to separate microorganisms such as bacteria. Ultrafiltration (UF) is employed for the separation of tiny particles, including proteins and viruses while nano-filtration (NF) is used for even smaller particles such as sugar molecules or insecticides. Salt ions, the smallest species, can be removed by reverse osmosis (RO). [7] stated that membrane-based pre-treatment such as microfiltration, ultrafiltration, as well as nanofiltration, give better water quality compared to the conventional pre-treatment method that involves coagulation or medium filtration and variations.

Other than that, adsorption also is effective as well as an effective and economical method for decolourisation of water. One of the adsorbents that is useful is eggshell waste. The majority of an egg's composition is calcium carbonate (approximately 94.03% of the total), with a small amount of calcite and calcareous minerals [8]. Eggshells are believed to be a magnificent biosorbent due to the amino acids included in their cellulose structure. Moreover, several trials have been made to utilise eggshells as an adsorbent, given that substantial quantities of waste eggshells are generated in various regions globally and subsequently end up in landfills annually. For example, the study of the use of eggshells for arsenic removal [9] and [10] studied the removal of methylene blue dye from water using eggshells as an adsorbent. Other studies also show eggshell adsorption mechanism follows the isotherm model of Langmuir, with a high specific surface area contributing to its high cadmium removal efficiency [11].

Eggshell has the potential to speed up the adsorption process on its surface due to the relatively uniform micro sizes of its particles. Because the surface area is closely correlated with the active surface area, wastewater pollution is decreased and contaminated solution can reach the adsorbent surface. The porosity nature of the eggshell membrane, as well as its fibril structure, are responsible for its excellent adsorption characteristics. The eggshell membrane is a translucent, delicate layer that adheres to the eggshell and becomes apparent when the boiled egg is peeled. The amorphous natural biomaterial of an egg gives stable intricate lattice and insoluble fibers. The membranes are usually light pink with double-layered membranes that are composed of protein fibre. Typically, the eggshell is composed of ceramic materials that are arranged in a three-layered structure. This structure includes a spongy (calcareous) layer, an interior lamellar (or mammillary) layer, and the epidermis on the outer surface [12]. It has been stated that the by-product eggshell's chemical substances (by weight) are composed of 94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate, and 4% organic matter [13].

The glassy structure of polyethersulfone (PES) makes it a versatile polymer with several uses in membrane technology, including gas separation, operability, stability, cheap cost, and good heat resistance [14]. PES a has high asymmetric pore structure and is well known as a polymeric material which is used in microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and gas separation due to its unique properties such as exceptional thermal, mechanical, hydrolytic properties in both environments hot and wet [15]. It is also known to have a wide distribution of pore sizes, which makes the separation of soluble materials difficult, and the fractions have limited applications [16].

N-methyl-pyrrolidone (NMP) is a highly water-attracting aprotic organic solvent composed of a 5-membered lactam. This solvent exhibits a moderate amine odour, is extremely polar, and can withstand high temperatures, with a boiling point of up to 202 °C. It is also non-toxic. It is used as a solvent in the petrochemical and plastics industries, taking advantage of its non-volatility and ability to dissolve a wide range of materials [17]. Based on [18], polyimide membranes fabricated by using the NMP solvent where led to a 157% rise in CO_2/CH_4 ideal selectivity as much as compared to the one fabricated using the dichloromethane (DCM) solvent. NMP enhances hydrogen bonding in polymer hydroxide (OH^-) segments, leading to the observed outcome. It reduces the formation of macrovoids [19].

This research aims to synthesise, and characterise mixed matrix membrane derived from eggshells as a low-cost material and determine the efficiency of flat sheet mixed matrix membrane to remove dye from the solution through filtration by comparing percentages of removal of RBBR dye between two different ratio of eggshell: silica. This is to prove how well the performance of the membranes will depend on the amount of eggshells being added. The membrane produced also was used for studying and comparing the adsorption performance between hollow fibre mixed matrix membrane and flat sheet mixed matrix membrane. The data obtained will be investigated whether it follows Langmuir isotherm or Freundlich isotherm.

2.0 METHODS

2.1 Materials

Analytical-grade chemicals and reagents were utilised without further purification for all experiments and analyses. The mixed matrix membrane was prepared to remove RBBR dye from water solution using waste eggshells, silica sand powder with a particle size of 1.6 µm and a purity of 99.5%, Polyethersulfone (PES) as the binder, Polyethyleneglycol 30-dipolyhydroxystearate (Arlacel) as dispersant, and N-Methyl-2-Pyrrolidone (NMP) as the solvent. Eggshell waste has been collected from Arked Meranti, UTM. The recovered eggshells were repeatedly cleaned in deionised water and then allowed to air dry. The eggshells were dried in a vacuum oven at 105ºC for 30 minutes. The dry product was grounded and sieved by using the eggshell grinder machine. Finally, the product was kept in a sealed container. By using the phase inversion and sintering method from [20], the fabrication of the Silica-Eggshell tubular ceramic membrane will be done. This method was chosen to ensure the strength of the production of thin-walled silica hollow fibre. The eggshell powder that was ground will be mixed with silica powder with different ratios (1:1) 50%:50% and (4:1) with 80%: 20% ratio respectively and mixed homogeneously.

2.2 Fabrication of Hollow Fibre Mixed Matrix Membrane

Arlacel was weighed and solubilised in NMP. Then, silica-eggshell mixture will be added to the solution and will be ball-milled for 48 hours at 192 rpm. PES will then be added and continue to ball-mill for another 48 hours to produce a homogenous mixture. All weight percentages are stated in Table 1. Any air bubbles present in the suspension were eliminated by gently combining them under vacuum conditions at ambient temperature for 30 minutes.

Hollow fibre membranes were made by pouring the mixture into stainless steel syringe and then forcing them out via a tube-in-orifice spinneret (internal diameter = 0.5 mm, exterior diameter = 2.8 mm). Table 2 shows the spinning settings that were used to complete the procedure at room temperature. The mixture will flow from syringe into the coagulant bath.

This phase-inversion process was completed by immersing the extruded hollow fibre precursors in tap water for 24 hours. Then, the fibre precursors were rinsed with water, sliced, and dried at ambient temperature.

2.3 Fabrication of Flat Sheet Mixed Matrix Membrane

Previous steps from the fabrication of hollow fibre membrane were repeated for both ratios of 1:1 and 4:1 (eggshell: silica) without spinning and phase inversion extrusion step. The dope was poured and flattened onto a flat glass plate. Then, the plate will be immersed in a water bath for 24 hours. After that, the ceramic flat sheet membrane was cut into 2 cm x 2 cm size.

Table 1 Composition for preparation of dope suspension

Solution Code	Ratio of eggshell-silica	PES (wt%)	NMP (wt%)	Dispersant (wt%)	Silica sand (wt%)
SEPN50	1:1	6.00	43.00	1	50.00
SEPN80	4:1	6.00	43.00	1	50.00

Table 2 Spinning parameters of hollow fibre membranes

Spinning Parameter	**Condition**
Bore fluid extrusion rate (ml/min)	10
Suspension extrusion rate (ml/min)	6
Air gap (cm)	5
Internal coagulant (bore fluid)	Distilled water
External coagulant	Tap water

2.4 Characterization of Hollow Fibre and Flat Sheet Membranes

The structures and properties of the eggshell-silica membrane have been characterized by various methods. IR spectrum used to determine the membrane materials and their functional group present was set at (650 cm-1 – 4000 cm-1). Perkin Elmer Model 1600 Infrared-Attenuated Total Reflection was used to characterize silica-eggshell membrane. Morphology and pore size distribution of silica-eggshell flat sheet of membrane was measured using Field Emission Scanning Electron Microscopy (FESEM). Hitachi model SU8020 field emission scanning electron microscopy was used to determine the small topography of silica-eggshell membrane. Prior to the FESEM examination, the sample was lightly coated with either gold or gold palladium. The wettability of the membrane also was analyzed using a goniometer contact angle (OCA Dataphysics). A syringe was used to dispense a drop of distilled water (approximately 1.0 µL) onto the membrane. Through the intermolecular interaction of liquid and solid, the water was spread evenly on the membrane. Then, the wettability of the membrane was measured by the computer linked to the instrument. This process was repeated by dispensing water on three different membrane surfaces to collect average measurements to minimize the error.

2.5 Filtration and Sorption Testing

Five standard solutions of Remazol Brilliant Blue R Anthraquinone dye (RBBR) have been prepared as 10, 20, 30, 40, and 50 ppm. 1.0 g of RBBR dye was dissolved in 1000 ml of deionised water to create the stock solutions. The UV-Vis spectrophotometer was used to find the maximum wavelength of RBBR with a 50 ppm standard solution. The solutions were stored in a dark location for use in subsequent experiments.

The filtration process was performed using a microfiltration system in the Advanced Membrane Technology Research Centre (AMTEC) located at Universiti Teknologi Malaysia, Malaysia (Figure 1). The experiment was done in a laboratory scale test. This test was focused on comparing the performance of flat sheet mixed matrix membranes between a 4:1 ratio of eggshell: silica and a 1:1 ratio of eggshell: silica to remove RBBR dye. In this experiment, a concentration of 50 ppm of RBBR dye solution was poured into the filtration feed tank. This experiment will be done in total recirculation mode at room temperature. The permeate was collected for UV-Vis analysis.

Figure 1 Diagram for the membrane filtration at AMTEC, UTM

For the adsorption studies, the flat sheet and hollow fibre membranes were ground to a fine powder by using a grinder machine. Then, five conical flasks were used for 0.1 gram of flat sheet membrane powder and another five conical flasks were used for 0.1 gram of hollow fibre membrane powder, which has been added to each flask. Each flask was filled with a 10 ml amount of the 50 ppm standard solution. They were shaken by using an orbital shaker with 180 rpm within 25 minutes (Figure 2 (a)). Afterwards, each solution was centrifuged for five minutes at 3000 RPM, and its absorbance at 664 nm was measured using UV-VIS analysis (Figure 2 (b)). The adsorption of RBBR solution by eggshell was described using Langmuir and Freundlich isotherms. When it comes to adsorption to solution material in an aqueous solution, the Langmuir adsorption isotherm is the most frequently utilised. According to the [21] study on eggshell-derived hydroxyapatite is an excellent low-cost adsorbent for Ni^{2+} removal from contaminated waters, the Langmuir isotherm model was best fitted for adsorption study compared to the Freundlich isotherm. This isotherm is predicated on the theory of single-layer adsorption on an equally structured adsorbent. The Freundlich isotherm is an empirical equation that states the relationship between the surfaces of heterogeneous adsorbents. For this sorption testing, it was focused on comparing performance between hollow fibre membrane and flat sheet membrane.

(a) (b)

Figure 2 Diagram of adsorption experiment; (a) solutions were shaken by using an orbital shaker and (b) solutions were centrifuged after adsorption.

3.0 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The result of the FTIR spectrum of normal eggshell powder is shown in Figure 3. From the spectrum, it shows that the C-N peak is at 1083 cm^{-1} and the C-O peak is at 1644.41 cm^{-1}. The broad peak at 1401.03 cm^{-1} existed due to the CH_2 functional group. C-H stretch at 2921.22 cm^{-1}, N-H group at 3285.98 cm^{-1}, and C=N group at 2165.57 cm^{-1}. There is also a presence of $CaCO_3$ at 711.56 cm^{-1} and 872.74 cm^{-1}.

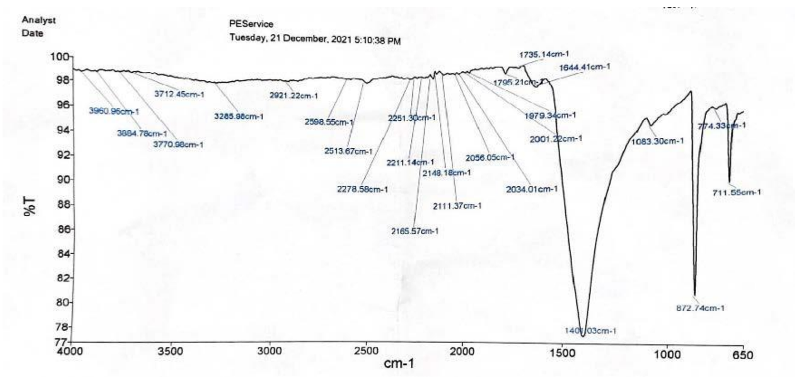


Figure 3 FTIR spectra of eggshell powder

The hollow fibre membrane was made by using a Teledyne ISCO D-Series Pump Controller and Cole-Parmer Syringe Pump. It was crushed by using a mortar pestle afterwards in order to obtain the final product in powder form. The FTIR spectrum of hollow fibre membrane is shown in Figure 4. It can be seen from the spectrum that shows a C-H peak at 2979.48 cm^{-1}, a peak at 1425.53 cm^{-1} which corresponds to the Si-CH_3 [22] and C-H stretching at the peak of 1746.61 cm^{-1}. The sharpest peak presented and observed at 1094.36 cm^{-1} indicated the Si-O-Si peak where it is in the range of 1021-1200 cm^{-1}. Meanwhile, the peak at 815.13 cm^{-1} is attributed to the presence of vibration of Si-C [23].

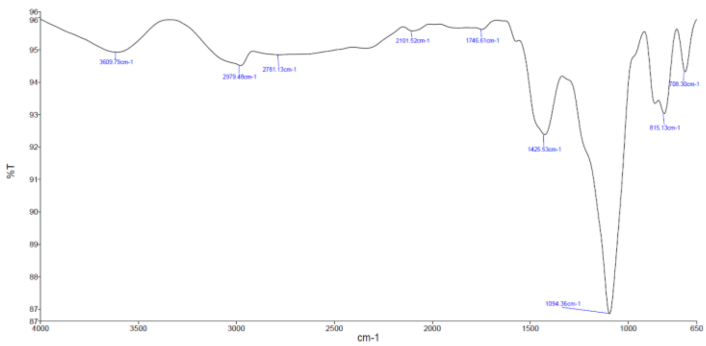


Figure 4 FTIR spectra for hollow fibre mixed matrix membrane

The flat sheet method was chosen to compare its efficiency compared to hollow fibre in terms of dope size and bubble-free. This research also study is either its simple procedure could produce an excellent adsorbent rather than a more complex procedure of hollow fibre membrane. The FTIR spectrum obtained for flat sheet membrane is approximately similar to hollow fibre membrane (Figure 5). It can be seen from the spectrum that peaks at (4:1) 1417.67cm^{-1} and (1:1) 1468.80 cm^{-1} correspond to the Si-CH_3 [22]. The sharpest peaks presented and observed at (4:1) 1093.40 cm^{-1} and (1:1) 1086.78 cm^{-1} indicated the Si-O-Si peak where it is the range of 1021-1200 cm^{-1}. Meanwhile, the peaks at (4:1) 867.85 cm^{-1} and (1:1) 808.42 cm^{-1} are attributed to the presence of vibration of Si-C [23].

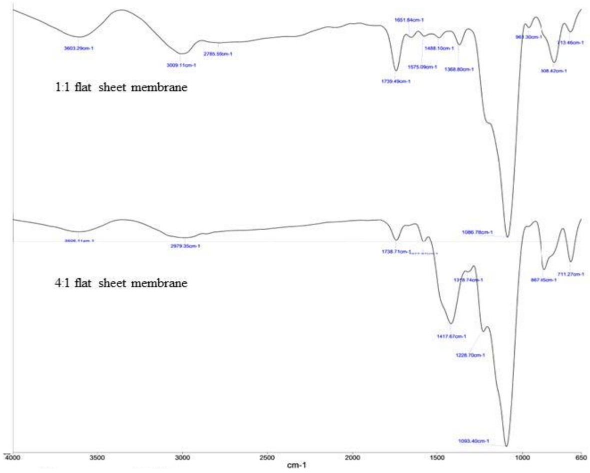


Figure 5 FTIR spectra for flat sheet membrane with 1:1 and 4:1 ratio of eggshell: silica

Upon completion of the filtering procedure, the membranes were further assessed to confirm the presence of RBBR dye either on the surface or within the pores of the membrane, therefore confirming the effective filtration. Based on the data, it is proven that the RBBR dye did attach to the membrane as it can be observed at peaks 3291.85 cm^{-1} (1:1) and 3294.17 cm^{-1} (4:1) in Figure 6. Those peaks are attributed to N-H and O-H stretching while 1637.21 cm^{-1} (1:1), and 1636.80 cm^{-1} (4:1) owing to the formation of C=C, C=O and C-N from the RBBR. The peak at 3291.85 cm^{-1} (1:1) and 3294.17 cm^{-1} might be attributed to the -OH which comes from the aqueous RBBR solution that has been used for the filtration process. Since the membranes are very hydrophilic, it can be related to this appearance of -OH peak where the water molecules were trapped on the membrane pores.

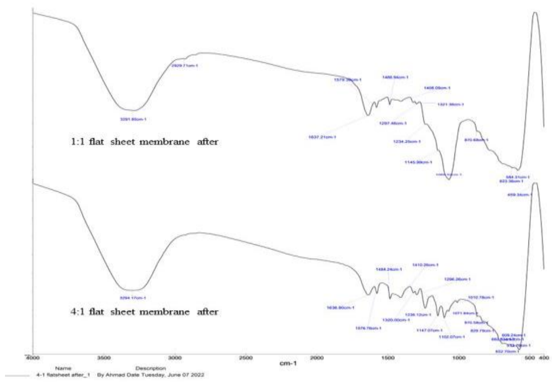


Figure 6 FTIR spectra for flat sheet membrane with 1:1 and 4:1 ratio of eggshell: silica after filtration

3.2 Water Contact Angle Measurement

Measurements of the water contact angle were also done for flat sheet membranes with an eggshell: silica ratio of 1:1 and 4:1. The results of both membranes as reported by the water contact angle measurement equipment are displayed in Figure 7 and Table 3.

(a) (b)

Figure 7 Contact angle images for (a) 1:1 flat sheet membrane and (b) 4:1 flat sheet

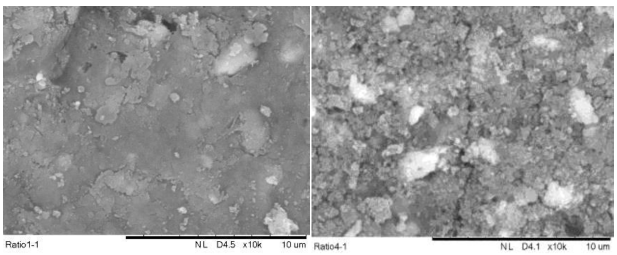
Table 3 Composition for preparation of dope suspension

Membrane	Contact angle (º)		
	left	**right**	**Average**
1:1 ratio	2.16	2.16	2.16
4:1 ratio	1.99	1.99	1.99

The purpose of measuring the water contact angle was to determine how wettable each membrane was. Upon dispensation from the needle of the water contact angle instrument, the water droplet penetrates the membrane for both membranes. This means that both membranes exhibit high hydrophilic characteristics. There were no significant differences between both membranes in terms of wettability due to its properties which let the water penetrate both membranes rapidly.

3.3 Scanning Electron Microscopy (SEM)

The membranes' structure and morphology were determined through SEM analysis. Figure 8(a) shows the SEM analysis for a 1:1 ratio membrane. From the figure, the morphology can be translated as a rough surface with a lot of active sites for the membrane’s surface to adsorb particles. Figure 8(b) shows the SEM analysis for the 4:1 ratio membrane. From Figure 8, it is clear that a 4:1 ratio membrane has a rougher surface due to the eggshell particles that dominate the surface compared to a 1:1 ratio membrane providing a more active site for adsorption to occur during filtration. So, a 4:1 ratio membrane should give better RBBR dye-removing capacity when compared to a 1:1 ratio membrane.



(a) (b)

Figure 8 SEM images for (a) 1:1 flat sheet membrane and (b) 4:1 flat sheet membrane

3.4 Filtration Performance

The filtration was done on a concentration of 50 ppm of dye solution with a filtration system provided in AMTEC, UTM. The dye removal efficiency was identified and calculated using UV-VIS spectroscopy. The R^2 determined from the graph was 0.9975. The result of the filtration experiment was reported in Figure 9. The 4:1 ratio of eggshell: silica flat sheet membrane shows performance with 81.39% of dye removed while 1:1 ratio with 76.17% dye removal for 50 ppm concentration of dye solution. The calculation was done using the Equation (1).

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

Where C_o and C are the initial and final concentrations of dye (mg/L), respectively. 4:1 ratio gave better filtration capacity with 5.22% higher than the 1:1 ratio. From the results obtained, the membrane with higher eggshell content gives better performance in removing RBBR dye compared to the membrane that has a similar proportion of eggshell and silica. This demonstrates that eggshells are a practical and plausible raw material for membrane production and RBBR dye removal from solutions. Another study such as [24] also proved that the modified eggshell-graphene oxide membrane can filter methylene blue up to 33.53% and reduce its concentration from 4.91 mg/L to 3.53 mg/L.

3.5 Adsorption performance

The results of the adsorption experiment via UV-Vis were reported in Figure 10. The trend explains that as the concentration increased, the absorbance obtained also increased. Flat sheet membrane showed a better absorption from hollow fibre membrane. It shows stable increasing absorbance where it started at 0.435 and 0.438 at 10 ppm and 20 ppm respectively. The value of absorbance was recorded as much as 0.916 at 30 ppm and 1.297 at 40 ppm. The highest absorbance was recorded at 50 ppm with a value of 1.7. The graph of absorbance for both membranes is plotted as shown in Figure 11.

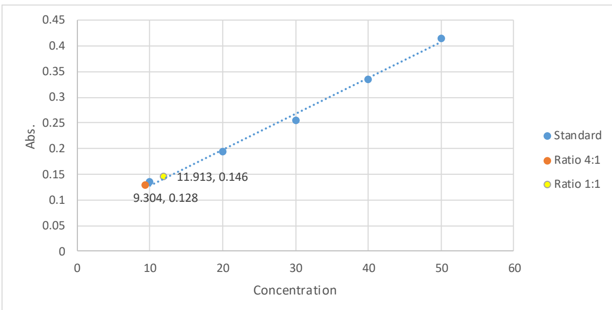
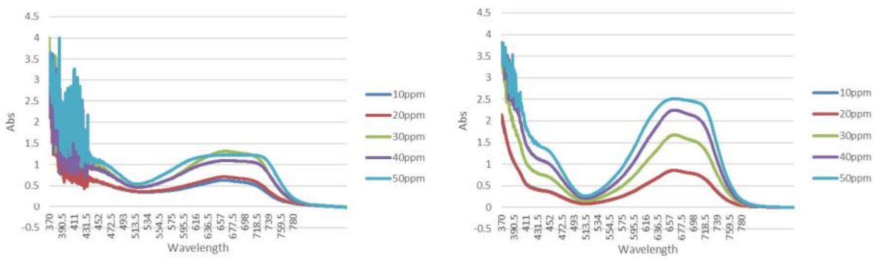
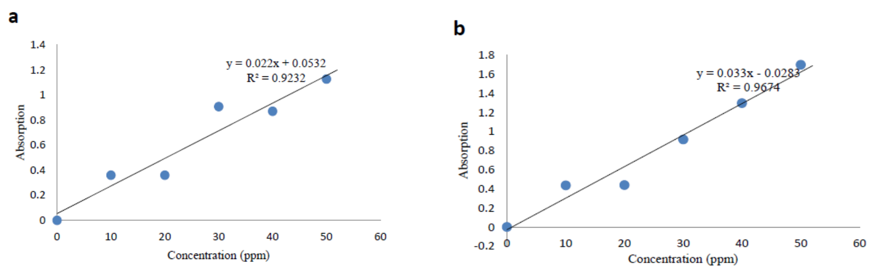


Figure 9 Removal efficiency of RBBR dye



(a) (b)

Figure 10 UV-Vis graphs for (a) hollow fibre membranes and (b) flat sheet membranes



(a) (b)

Figure 11 Graph of absorbance vs concentration for (a) hollow fibre membrane and (b) flat

3.6 Isotherm Calculation

By using Beer-Lambert Law Equation (2) and Equation (3), at 664 cm^{-1} with a concentration of 50 ppm, it resulted in as much as 1.423 mg/g of dye adsorbed onto the hollow fibre membrane and 1.616 mg/g for flat sheet membrane. The percentage of dye removal efficiency in hollow fibre membrane and flat sheet membrane were calculated.

$$A = \varepsilon cl \quad (2)$$

Where c is the molar concentration (M), l is the optical path length (cm), and A is the absorbance. The molar absorption coefficient (M^{-1} cm^{-1}) may be found on the graph.

$$qt = (C_o - C_t)V/m \quad (3)$$

Where qt represents the quantity of dye adsorbed onto the hollow fibre membrane and flat sheet membrane at time t, C_o represents the initial dye concentration (mg/L), C_t represents the concentration of dye at any time t, V represents the volume of the solution (L), and m represents the mass of the adsorbents, which are the hollow fibre membrane and flat sheet membrane.

3.6.1 Langmuir Isotherm

By using the linearised form of Langmuir from equation (4) and also Equation (5), R^2 values can be obtained by plotting the graph C_e/q_e versus C_e (Figure 12).

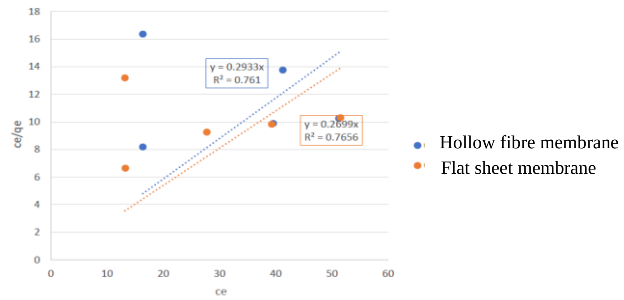


Figure 12 Graph C_e/q_e versus C_e for Langmuir Isotherm

Hollow fibre membrane recorded R^2 = 0.761 and flat sheet membrane recorded R^2 = 0.7656. This isotherm explains the mechanism of chemisorption where there could be no interaction between the adsorbed molecules and it is associated with mono-molecular layer adsorption. This result varies from [11] studies where the eggshell's adsorption mechanism follows the isotherm model of Langmuir due to homogeneous adsorption while this project unlikely to favour Langmuir (heterogeneous adsorption).

$$C_e/q_e = 1/k_L(q_m) + C_e/q_m \quad (4)$$

$$Ce = \text{absorbance/molar extinction coefficient} \quad (5)$$

Where C_e represent the equilibrium concentration of dye in solution (mg/L), q_e denotes the quantity of dye adsorbed per gram of adsorbent (mg/g), q_m represents the theoretical saturation capacity of monolayer adsorption (mg/g), and k_L represents the Langmuir constant (L/mg) obtained by plotting C_e versus $C_e q_e$.

3.6.2 Freundlich Isotherm

By using the linearised form of Freundlich from equation 6, R^2 values can be obtained by plotting the graph ln q_e versus ln C_e (Figure 13). Hollow fibre membrane recorded $R^2 = 0.8406$ and flat sheet membrane recorded $R^2 = 0.9996$. This isotherm explains the physisorption phenomenon where this study shows the interaction between adsorbed molecules can occur due to a multi-layered process.

$$\ln q_e = \ln K_f + (1/n) \ln C_e \quad (6)$$

Where Kf represents the Freundlich constant. Flat sheet membrane favoured Freundlich isotherm the most because its R^2 approaching 1. It explains that flat sheet membranes favoured multilayer adsorption on a heterogeneous site, where it assumes the surface rates of adsorption and desorption are not equal with zero at equilibrium conditions [25]. [26] studied also showed that the surface morphology of eggshells is porous and consists of irregular particles of various sizes has led to the adsorption of heavy metals in surfaces of eggshells obeyed the Freundlich isotherm. It also displayed multilayer adsorption. Thus, this project has a similar outcome as the [25] and [26] studies. The adsorption of heterogeneous RBBR dye on the surface of eggshell membranes has led to the Freundlich isotherm.

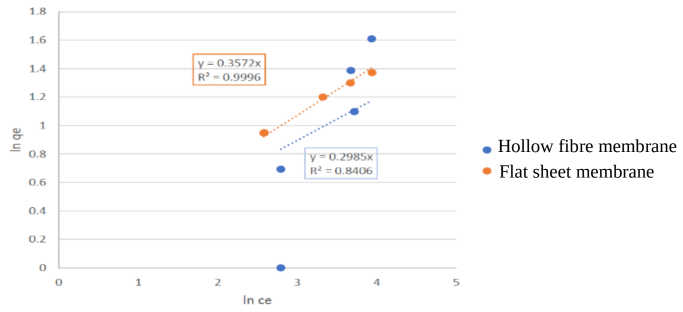


Figure 13 Graph ln qe versus ln Ce for Freundlich Isotherm

4.0 CONCLUSION

In conclusion, the initial objective of fabricating the mixed matrix membrane, which is composed of eggshells and silica as its primary components, was effectively accomplished. This membrane can be used in removing RBBR dye. It has been shown that the filtration process can achieve the highest and most effective removal of RBBR dye at a concentration of 50 ppm when using a 4:1 ratio of eggshell: silica flat sheet membrane, as opposed to a 1:1 ratio, which results in 80.38% and 75.16%, respectively. The removal efficacy of RBBR dye is enhanced with higher eggshell content. It has also been proved that the adsorption process by hollow fibre membrane and flat sheet membrane followed Freundlich isotherm by calculating and plotting the graph. The R^2 value that has been recorded from the linearized form of Langmuir is 0.761 for hollow fibre membrane and 0.7656 for flat sheet membrane. Meanwhile, the R^2 value that has been obtained from the linearized form of Freundlich is 0.8406 for hollow fibre membrane and 0.9996 for flat sheet membrane. Hence, the flat sheet membrane is more effective in the removal of Remazol Brilliant

Blue R Anthraquinone dye (RBBR) than the hollow fibre membrane based on the calculation of the percentage of dye adsorption. It was proven that the membrane consists of carbonate and silica, has good hydrophilic characteristics and porosity, and is a superb adsorbent based on the characterisation of the membrane using ATR-FTIR, water contact angle measurement, scanning electron microscopy, and UV-Vis.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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