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Fabrication of Immobilized Eggshell/TiO_2 Photocatalytic Composite-based Membrane

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Abstract

The immobilized photocatalyst in the photocatalytic membrane has been proved as one of the advanced oxidation processes (AOPs) that greatly promote the photocatalytic degradation of pollutants. To increase the photocatalytic process, the adsorption capacity should be enhanced by integrating the adsorbent with photocatalytic material to produce a composite. Eggshell as a green recycle waste was used as an adsorbent integrated with titanium dioxide (TiO_2) to produce eggshell/ TiO_2 composite. In this study, different ratios (10:0, 9:1, 8:2, 7:3, 6:4, 5:5) of eggshell/TiO_2 composite were prepared with immobilization in a flat sheet membrane. The formulation of the dope solution was achieved with 10wt% of polyvinylidene fluoride (PVDF), 2wt% of eggshell/TiO_2 composite, and 88wt% of dimethylacetamide (DMAc). The distribution of TiO_2 nanoparticles was proven by SEM images and could be actively functioned as a photocatalyst. The structure of the membranes characterized by the lengths were elongated by the length of their finger-like voids was significantly affected by the TiO_2 nanoparticles. Based on the findings, it can be concluded that immobilized eggshell/ TiO_2 composite photocatalyst inside membrane fabrication could enhance the flux permeation due to the development of a finger-like structure.

1. Introduction

Dyes, regarded as highly hazardous organic substances for the environment, are one of the most important types of pollutants [1]. Because the dyes have a synthetic origin and a complicated molecular structure, they are more stable and difficult to decompose once they have gotten into the water. Dye molecules are made up of two main components: chromophores, which are responsible for producing color, and auxochromes, which can not only complement the chromophore but also make the molecule soluble in water and increase its affinity for tissue [2]. However, some of the treatment processes are unable to reduce the dye contaminants thus discharging awfully into the water bodies and harming the aquatic life. Hence, it shows the importance of efficient dye treatment to ensure all the toxic dyes are purified before being released into the river.

The dyeing process involves a lot of water, and not all places practice effective ways of treating the water before it is discharged back into the environment making it a huge pollutant around the world. Some chemicals found in synthetic dyes are sulfur, naphthol, nitrates, acetic acid, soaps, and heavy metals such as copper, arsenic, lead, cadmium, and other chemicals. They are very toxic and have a high negative impact on wastewater quality

[3]. Numerous research and treatment process was provided for the removal of a dye such as Methylene Blue (MB) in physical treatment using adsorption and filtration, and biological treatment. AOPs are proven to be one of the best methods to achieve dye degradation and it is also non-toxic [4].

There has been an increase in the use of AOPs for textile wastewater treatment due to their advantages over traditional methods. The use of a TiO_2 photocatalyst on the asymmetric membrane surface and pores provides simultaneous pollutant retention and photodegradation, allowing for long-term device operation without fouling, the practical lack of concentrated retentate, and cost-effective clean water generation [5]. AOPs are distinguished by the formation of hydroxyl radicals (OH) and attack selectivity, which is a valuable property of an oxidant. Ozone (O_3), hydrogen peroxide (H_2O_2), TiO_2, and ultraviolet (UV) radiation are widely used to speed up the generation of hydroxyl radicals. When photocatalysis is present in an aqueous solution, it allows for the entire breakdown of most organic compounds, which is preceded by numerous processes that produce hydroxyl radicals, which aid in the oxidation of organic contaminants into non-toxic end products like water (H_2O) and carbon dioxide (CO_2) [4].

Chicken eggshells are a type of municipal organic waste that can be used as a soil conditioner, food additive, calcium supplement, agricultural fertilizer, and adsorbent, among other things. Calcium carbonate (94%), organic matter (4%), and other minerals are the major components of eggshells. The calcination process has been proven for the conversion of calcium carbonate ($CaCO_3$) to calcium oxide (CaO), which increases its adsorption properties. As a result, eggshell waste could be converted into useful adsorbents using this method. Many writers have advocated using eggshells as adsorbents to remove pollutants such as cyanide, dye (malachite green), methylene blue, carbon dioxide, hydrogen sulfide, acid mine drainage, and heavy metals [6]. Thus, this major organic waste has the potential to be recycled as an adsorbent in this study.

It is very interesting to investigate the integration of eggshell as an adsorbent with TiO_2 as functions as a photocatalyst to produce eggshell/ TiO_2 composite and then embedded into a flat sheet membrane. Membrane fabrication methods such as dip-coating method and chemical grafting method to prepare hybrid thin-film composite (TFC) membrane [7] and N-TiO_2/graphene oxide grafted membrane [8][9], respectively. In this study, the flat sheet membrane was prepared using the casting method.

2. Materials and Methods

2.1 Materials

In this study, Polyvinylidene fluoride (PVDF), Solef MW6012 grade in powder form, Emory laboratory reagents) was chosen polymer, in the making of the base for full name (IPC) membrane. TiO_2 was used in nano-sized powder. The eggshell powder was used as an adsorbent and integrated with TiO_2. N, N-Dimethylacetamide (DMAc, AR Grade from Vchem) was used as a solvent to dissolve and mix PVDF, TiO_2 and eggshell.

2.2 Preparation of Eggshell/TiO_2 Composite

Eggshell powder and TiO_2 were weighed as the ratio stated in Table 1. Next, each of the eggshell/TiO_2 ratio powders was transferred inside their crucible. Then, the mixed composite was calcined for 1 hour at 450°C in a furnace. After that, the composite was sieved once the calcined eggshell/TiO_2 had cooled to ambient temperature. Each sieved composite ratio was labeled and kept in a petri dish. The weight of each mixed eggshell/TiO_2 composite was recorded before and after the calcination process to provide the data regarding weight loss in percentage as described in (1).

$$W(\%) = \frac{W_i - W_f}{W} \times 100 \qquad (1)$$

Where W_i is the initial weight of eggshell/TiO_2 composite before calcined and W_f is the final weight of the calcined composite.

Table 1 *Ratio of the eggshell/TiO_2 and dope solution composition*

Membrane identification code	Eggshell/TiO_2 ratio	Dope composition		
		PVDF (wt.%)	Eggshell/TiO_2 (wt.%)	DMAc (wt.%)
IPC-0.0	0:10	10	2	88
IPC-0.5	5:5	10	2	88
IPC-0.7	7:3	10	2	88

IPC-0.8	8:2	10	2	88
IPC-0.9	9:1	10	2	88
IPC-1.0	10:0	10	2	88

2.3 Preparation of Flat-sheet Membrane

Dope solutions are prepared before mixing them with PVDF powder to produce a casting solution. PVDF powder was first heated in an oven at 50°C for 1 hour to remove any moisture. To make the dope solution, eggshell/TiO_2, and DMAc were mixed in a Scott bottle for 2 hours at 200rpm with an overhead stirrer, relative to their desired amount following Table 1. PVDF powder was added gradually after the mixture had been well mixed to avoid clumps of PVDF powder forming. To ensure that the dope solution is thoroughly combined, it is left for another 2 hours.

According to Dzinun et al., 2020, they were prepared the dope solution by combining 3 wt.% TiO_2 nanoparticles and 82 wt.% DMAc, then 15 wt.% PVDF powder was gradually added to make the casting solution [10]. However, in this study 50ml of DMAc was added to reduce the viscosity of the dope solution, 50ml of DMAc solution was added. As a result, a new casting solution formula was developed, as shown in Table 1. Immersion in an ultrasonic bath for 1 hour is required to eliminate bubbles created by operating the overhead stirrer to make casting solutions.

To control the membrane thickness, the side of a 20cm × 20cm glass plate was taped with two layers of cloth tape during the membrane casting process. The glass plate surface was cleaned to ensure that it was free of dust and moisture. On the top section of the glass plate, the casting solution was poured as directed. The casting solution was then spread uniformly across the plate using a glass rod. The glass plate containing the casted solution was quickly placed in a water bath for two hours. Solvent non-solvent exchange will occur at this period, removing surplus solvent from the casted solution and resulting in a flat-sheet membrane.

Following that, a 1-hour post-treatment bath in a 50:50 wt.% water: ethanol solution was used. This post-treatment procedure was carried out to control if any pores in the membranes had formed. According to [10], the membrane was then immersed in a 100% ethanol bath for 1 hour to promote wettability and pore collapse. Finally, the membranes were dried for one day at ambient temperature without being exposed to direct sunshine. After then, the membranes were labeled based on their relative eggshell/ TiO_2 ratio.

3. Results and Discussion

3.1 Preparation of Eggshell/TiO_2 Composite

Based on the observation, the color of eggshell powder change into peach and the TiO_2 nanocomposite is white. The eggshell/TiO_2 composite was successfully synthesized as photocatalytic powder as shown in Fig. 1. Both substances were mixed with the presence of ethanol. The composite also successfully undergoes a pyrolysis process also called calcination to remove any volatile compound and produce C-O bond at 450°C in a furnace.

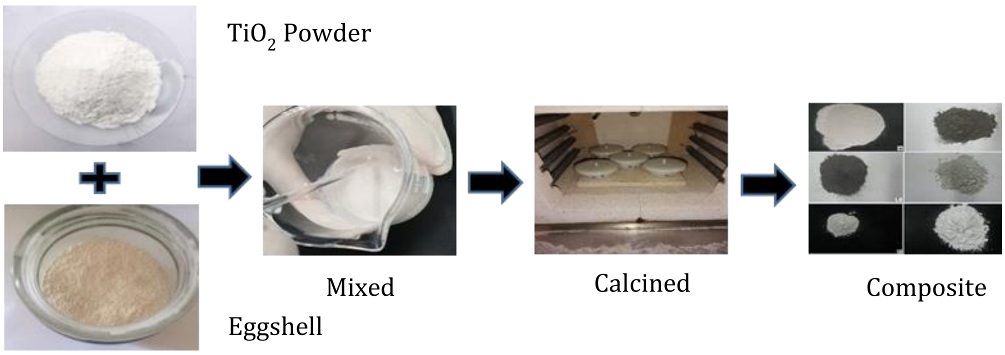


Fig. 1 *Preparation of eggshell/TiO_2 composite for each ratio*

Table 2 *Weight loss of the eggshell/TiO_2 composite after calcined*

Eggshell/TiO_2 Ratio	Initial weight (g)	Final weight (g)	Weight Loss (%)
10:0	10.05	9.91	1.39
9:1	10.03	9.93	0.99
8:2	10.03	9.95	0.79
7:3	10.06	9.76	2.98
5:5	10.01	9.97	0.39

As listed in Table 2, the weight loss was calculated from 0.39 up to 2.98%. During this process, the complete combustion of the composite with the air turned the color of the composite darker. The color of each ratio also varies as the ratio of the eggshell increases, the darker the color of the eggshell/TiO_2 composite after the calcination process as clearly shown in Fig. 1. These composites were expected to be immobilized inside the flat sheet membrane and used in dye treatment.

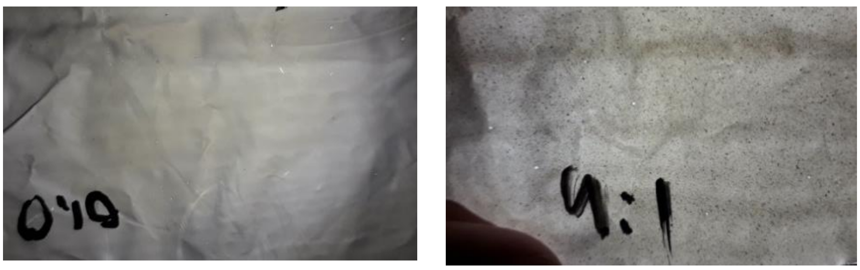
The noticeable changes in the composite color are affected by different ratios of eggshell powder after the calcination process calculated in percentage. $CaCO_3$ is one of the major elements in eggshell powder. During the calcination process, $CaCO_3$ will turn to CaO based on (2) when heat is applied. The successfully calcined eggshell powder can act as an absorbent due to the existence of the CaO element. CaO can be used as a heterogeneous catalyst. Thus, CaO capability used as an absorbent in removing heavy metals in synthetic and real wastewater has been proved. The change of color from light grey to dark grey through the calcination process of $CaCO_3$ and TiO_2 is due to high temperature during the calcination process. Regarding the reduction of mass for each composite ratio, it is because CO_2 has been released during the calcination process thus showing some changes in composite mass.

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

3.2 Preparation of Eggshell/TiO_2 Flat-sheet Membrane

After the casting solutions for each eggshell/TiO_2 ratio were produced inside the Scott bottle, the observation for each casting solution was made and resulted in a change of viscosity and color as the ratio of eggshell/TiO_2 powder increased for the eggshell powder (0:10, 5:5, 7:3, 8:2, 9:1, 10:0). The more eggshell powder in the eggshell/TiO_2 ratio, the higher viscosity of casting solutions. Other than that, each color of casting solutions also changed darker as the eggshell powder ratio increased as shown in Fig. 2.

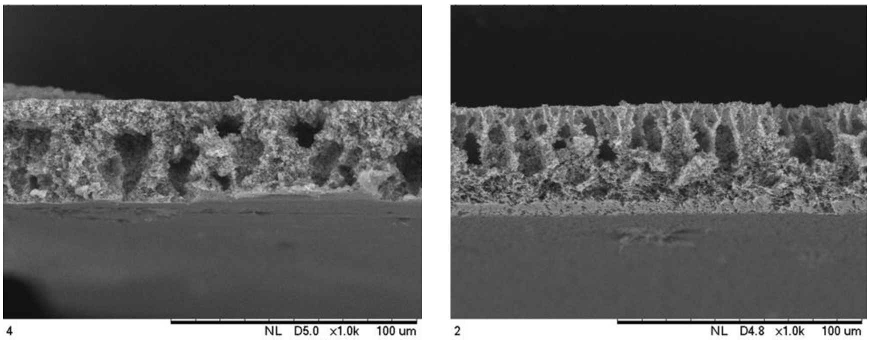
Thus, the eggshell powder ratio also affects the surface roughness of a membrane and exhibits differences in color. After the membrane was successfully synthesized, observation was made and provided that the surface of the membrane part facing the glass plate was rougher than the surface cast by the glass rod. This observation and the same results were also noticed on any other eggshell/TiO_2 membrane ratio. However, the membrane surface for ratio 0:10 which only contained TiO_2 nanoparticles was smooth on both sides. Based on this observation result, the surface roughness of the membrane is affected by the viscosity of casting solutions due to the amount of colloidal particle size.



(a) (b)

Fig. 2 *Immobilized eggshell/TiO_2 photocatalytic composite-based membrane for ratio (a) 0:10; (b) 9:1*

Fig. 3 shows SEM images of the flat sheet membrane with different loading of composite photocatalysts. The addition of eggshell in composite photocatalysts does not affect the morphology of the membrane but the TiO_2 addition into the membrane matrixes has significant effects on their pore sizes and morphologies as previously discussed by Dzinun et al., (2015) [11]. As proven in Fig. 3(b), the finger-like structure was developed due to the addition of TiO_2 nanoparticles where the solvent/non-solvent exchange rate during the phase inversion process. By comparing to Fig. 3(a), no finger-like structure appears due to no addition of TiO_2 inside the dope solution.



(a) **(b)**

Fig. 3 *SEM images cross section flat sheet membrane for ratio (a) 0:10; (b) 9:1*

4. Conclusion

To summarize, the eggshell/TiO_2 photocatalyst composite was successfully synthesized. It was also able to immobilize it in casting solutions, resulting in the creation of an eggshell/TiO_2 flat-sheet membrane. The difficulty of stirring the casting solutions has also been addressed with a new formulation for casting solutions. The addition of composite photocatalysts has influenced the morphology of the membrane surface and consequently increases the flux permeation.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Haikal Hafiy Abdul Kadir, Ungku Nor Akmal Ungku Mohd Abdullah, Zarul Haziq Muhammad, Hazlini Dzinun;* ***data collection:*** *Haikal Hafiy Abdul Kadir, Ungku Nor Akmal Ungku Mohd Abdullah, Zarul Haziq Muhammad, Hazlini Dzinun;* ***analysis and interpretation of results:*** *Haikal Hafiy Abdul Kadir, Ungku Nor Akmal Ungku Mohd Abdullah, Zarul Haziq Muhammad, Hazlini Dzinun;* ***draft manuscript preparation:*** *Haikal Hafiy Abdul Kadir, Ungku Nor Akmal Ungku Mohd Abdullah, Zarul Haziq Muhammad, Hazlini Dzinun. All authors reviewed the results and approved the final version of the manuscript.*

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