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Photocatalytic performance of TiO_2/Eggshell composite for wastewater treatment

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ABSTRACT

The utilization of eggshells as a primary source for developing value-added materials has received significant attention recently due to its ability as an excellent adsorbent and support. This study used the solid-state dispersion method to prepare composite photocatalyst TiO_2/eggshells of different ratios. TiO_2 and eggshell photocatalysts were also used as control samples. Scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), and X-ray diffraction (XRD) analyses were used to characterize the samples. Finally, the efficiency of the composite photocatalyst was evaluated in the suspension system using methylene blue (MB) solution as the target pollutant. Among three different ratios, TiO_2/eggshell (1:9) is the optimum ratio that achieved the highest adsorption and 56.41% photocatalytic degradation of MB solution. Besides, pure eggshells exhibited relatively high adsorption but did not show any significance in photocatalytic degradation. It proves that the ability of eggshell as an adsorbent is very high even though it only acted as support to the TiO_2 in the TiO_2/eggshell composite photocatalyst. The increased surface area of the TiO_2/eggshell composite photocatalyst could enhance MB solution adsorption and photocatalytic degradation, thereby increasing its effectiveness. Overall, it can be concluded that eggshell has excellent potential as support for photocatalyst and as an environmentally friendly catalyst.

1. Introduction

An egg is an essential food widely consumed worldwide for domestic and industrial purposes. As a result, egg-processing industries generate a significant amount of their waste product, eggshells, and this residue is disposed of as waste in landfills, becoming an organic pollution source. Natural, porous bioceramic eggshells contain 96% calcium carbonate, with the remaining 1% being magnesium carbonate and calcium phosphate, proteins and water. Eggshells are an excellent source of calcium carbonate has piqued the interest of researchers, who have extracted natural eggshell calcium for food fortification and the production of nutritional supplements, lactose-free milk, and milk tablets [1].

Some papers have reviewed the uses of eggshell waste as a catalyst for specific applications such as metal matrix composites [2–3], biodiesel production [3–5], bioactive compounds in anaerobic fermentation [6], and wastewater treatment [7]. Besides, hydroxyapatite from avian eggshells can be used in medical [8] and dental therapy [9–10]. Eggshell can also be used to create nanocomposites with other metals by preparing it using a variety of techniques, such as reducing and stabilising it with Cacumen platycladi extract in an aqueous solution [11].

Effective removal of reactive dyes by adsorption using eggshell has been carried out previously by Li et al. [12]. By combining eggshell membrane (ESM) obtained from a local supermarket with titanium dioxide nanoparticles, the self-assembly method created a low-cost and efficient composite photocatalyst material. In their research, ESM was carefully stripped and washed before being modified with polyethyleneimine (PEI) and TiO_2 to form TiO_2–PEI–ESM. When exposed to simulated sunlight via a xenon lamp, the TiO_2–PEI–ESM composite photocatalyst demonstrated superior adsorption and photocatalytic dye degradation capabilities [12].

Another study by Chen et al. proved that eggshell is more suitable to be used as a support of nanoparticles photocatalyst compared to clamshell and $CaCO_3$ powder. They demonstrated that

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the composite photocatalytic activity's adsorption capacity and photocatalyst were enhanced at a TiO_2 content of 30%, below 500 °C, and that 50-minute heat treatment was enhanced, significantly increasing the efficiency of Acid Red B removal [13].

Sree et al. synthesized natural calcium from eggshells and converted it to calcium oxide (CaO) nanoparticles by calcination [14]. They revealed that the CaO prepared has strong stability as a catalyst in methylene blue and toluidine blue degradation even after seven cycles. Besides, eggshell membranes have been successfully developed for lead removal from wastewater [15]. The bond strength between TiO_2 and eggshell powder is high [16]. Calcium hydroxide $Ca(OH)_2$ derived from waste eggshells has a high carbonation efficiency and thus effectively removes cadmium and lead from wastewater [17].

The surface analysis of eggshell and ESM shows that these porous materials can be effective adsorbents. Guru and Dash assert that the microporous structure is a promising adsorbent material for the removal of a variety of environmental pollutants, including textile dyes and heavy and harmful inorganic ions. Thus, using eggshells and ESM as adsorbents has two benefits: removing hazardous chemicals and reducing landfill loads is less expensive. Eggshell waste materials have been widely utilised in biomedical research, composite and nanomaterial synthesis, catalysis, and organic synthesis [18].

Today, various advanced oxidation processes (AOPs) for textile wastewater treatment have been increasingly applied because of their advantages compared to conventional methods. AOPs are characterized by radical hydroxyl production, which assists in oxidizing organic pollutants into nontoxic end-products such as water and carbon dioxide [19]. Heterogeneous photocatalysis has emerged as an essential part of greener technology in textile wastewater treatment as it obeys the application of AOP where it uses environmentally friendly oxidants.

The use of eggshell, a natural protein-membrane composed of protein with highly crosslinked fibres, could potentially be an excellent support to photocatalyst due to its porous structure and large surface area from the fibrous network [12]. By utilizing the ability and properties of eggshell, TiO_2/eggshell composite photocatalyst was prepared by solid-state dispersion (SSD) method. The effectiveness of TiO_2/eggshell as photocatalyst in suspension system was investigated by using methylene blue as a model pollutant.

2. Experimental

2.1. Materials

This study used chicken eggshell powder with 75 µm particle sizes and ethanol (QRëC, 95% denatured) without purification. Titanium dioxide, TiO_2 (Sigma-Aldrich, 21 nm, 95% purity) was used as the photocatalyst in the methylene blue (MB) photocatalytic degradation experiments.

2.2. Synthesis of TiO_2/eggshell composite photocatalyst

The TiO_2/eggshell composite photocatalyst was prepared using the solid-state dispersion (SSD) method in the ratios of 1:9, 2:8, and 3:7 described by Nikazar et al. On a 10 g basis, the composite photocatalyst was ready and compared to 100 % TiO_2 and eggshell [20].

First, using an agate pestle and mortar and ethanol as a solvent, 10% TiO2 was mixed with 90% eggshell powder. The samples were then evaporated in an oven at 35 °C overnight. The samples were calcined in the furnace at 450 °C for 60 min. Finally, the samples were crushed into powder and then sieved to get the fine powder. The same steps were repeated to prepare TiO_2/eggshell composite photocatalyst in the ratios of 2:8 and 3:7.

2.3. Characterization of composite photocatalyst

The structural morphology, element identification, and crystallinity of the TiO_2/eggshell composite photocatalyst were investigated using scanning electron microscopy (SEM, HITACHI TM3000), energy-dispersive X-ray (EDX Bruker, QUANTAX 70), and X-ray diffraction (XRD, Bruker D2 PHASER).

2.4. Photocatalytic suspension test

The experiment setup was prepared as shown in Fig. 1. Two grams of TiO_2/eggshell composite photocatalyst was added to an MB solution of 4 ppm. The suspension was first stirred without a UV lamp using a magnetic stirrer for 30 min for adsorption equilibrium. After taking the sample for adsorption, the UV lamp and the stirrer were turned on for photocatalytic activity testing. The experiment was conducted for 100 min, and at each 25 min interval, 1 mL sample from the MB solution was taken and centrifuged at 1000 rpm for 20 min. The samples were analyzed by a UV–vis spectrophotometer (HITACHI U-3900H).

The absorbance data obtained from the UV–vis spectrophotometer was converted to concentration (ppm) using the calibration curve's linear equation. The percentage of MB degradation was calculated using the equation below:

$$\%MBdegradation = \frac{C_i - C}{C_i} \times 100\% \quad (1)$$

where C_i is the initial concentration and C is the retained concentration of MB solution. Using the following equation, the photocatalytic rate constant was calculated.:

$$\ln\frac{C_o}{C} = k_{app}t \quad (2)$$

where k_{app} is the apparent rate constant (min^{-1}) and C_o is the initial concentration of MB (mg/L) [21].

3. Result and discussion

3.1. Morphology and physiochemical properties of TiO_2/eggshell composite photocatalyst

Fig. 2 depicts the XRD diffraction patterns of various photocatalysts. The prominent TiO2 peak observed at 2θ = 25.4° is attributed to anatase phase TiO_2 reflections. The constituent of eggshell is

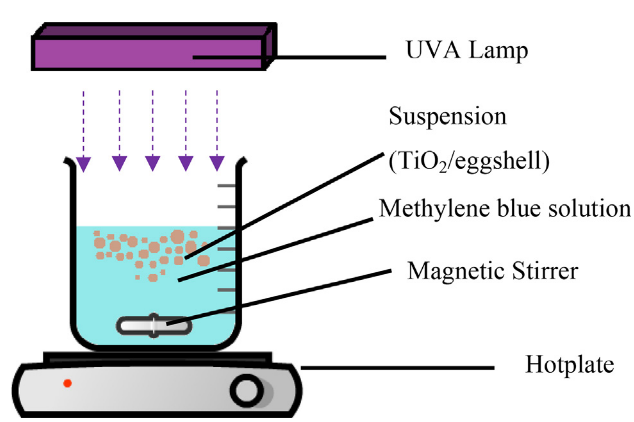

Fig. 1. Schematic diagram of the suspension system for MB photocatalytic activity testing.

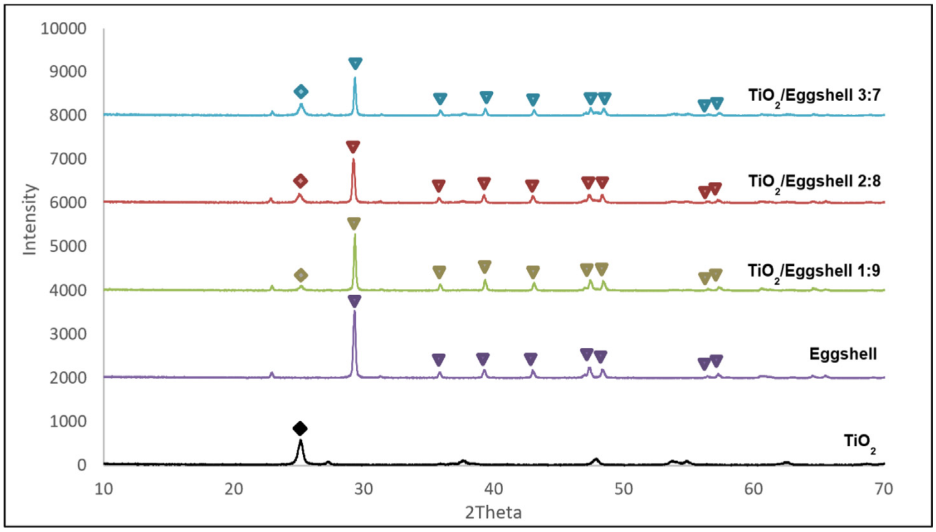

Fig. 2. XRD patterns of eggshells, TiO_2, TiO_2/eggshell (1:9), TiO_2/eggshell (2:8), and TiO_2/eggshell (3:7).

mainly $CaCO_3$, where the highest diffraction peak exists at 2θ = 29.5°. A comparable outcome has been reported by [22]. The peaks 2θ = 36°, 39°, 43.2°, 47.8°, 48.8°, 56.5°, and 57.6° correspond to the eggshell phases as shown in Fig. 2. The main peak of eggshell and TiO2 remained constant regardless of temperature, indicating that the eggshell's frame structure remained intact after TiO_2 loading. As clearly shown in Fig. 2, the intensity of TiO_2 increased as the amount of TiO_2 loading increased.

The morphological structures of TiO_2, eggshells, and TiO_2/eggshells of different ratios were examined by SEM as shown in Fig. 3. TiO_2 appeared as fine particles (Fig. 3a), whereas the eggshell is more prominent due to the micro-sized particles and exhibits irregular shape and size (Fig. 3b).

The distribution of TiO_2 on the surface of the eggshell is depicted in Fig. 3c–3e, where the fine particles of TiO_2 are dispersed across the surface of the eggshell. As depicted in Fig. 3c, the distribution of eggshell particles is more clearly observed compared to TiO_2 nanoparticles in the SEM images due to the high loading of eggshells. In contrast to Fig. 3d and 3e, the increasing TiO_2 nanoparticle loading caused it to cover the eggshell particles. However, it has been established that the TiO_2 and eggshell particles bonded together and formed a composite photocatalyst fol-

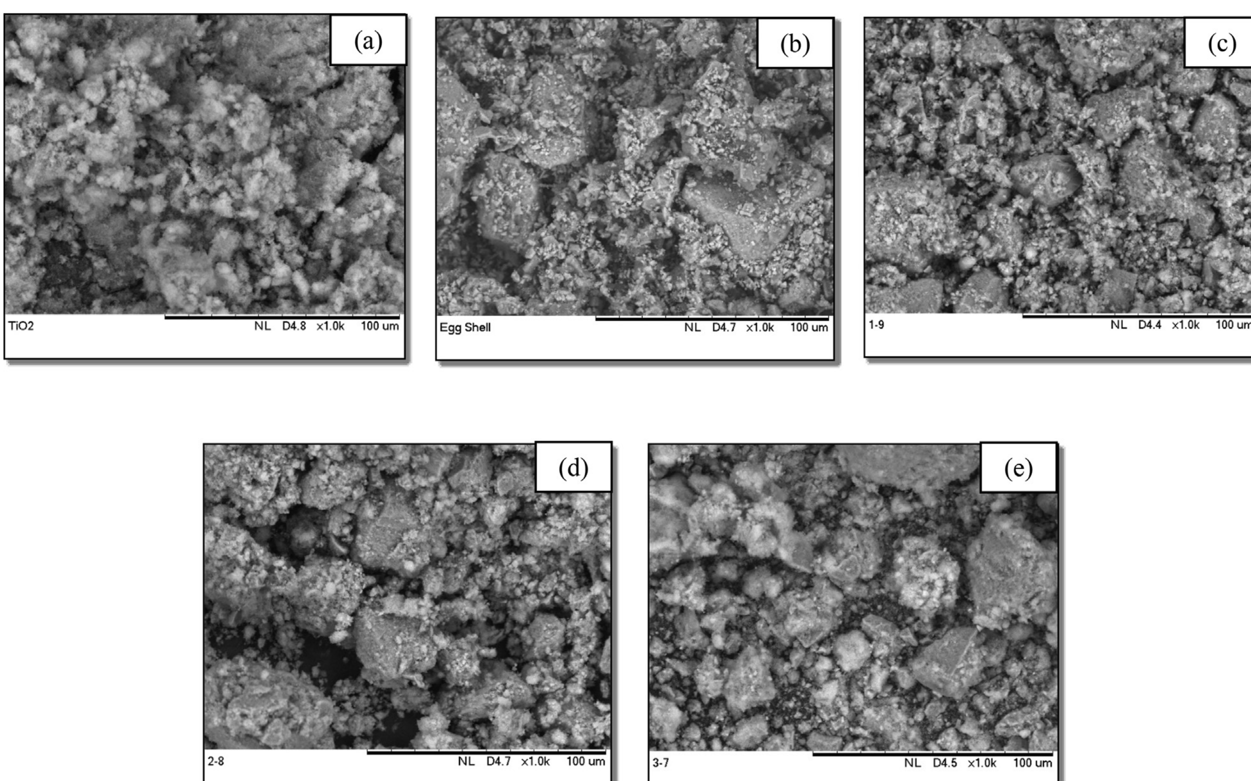

Fig. 3. SEM images of (a) TiO_2, (b) eggshells, (c) TiO_2/eggshell (1:9), (d) TiO_2/eggshell (2:8), and (e) TiO_2/eggshell (3:7) with 5 k of magnification.

lowing the calcination process. The SEM results for the photocatalyst are consistent with the XRD results, indicating that there was no significant change in the structure.

Fig. 4 shows the distribution of the elements on the composites using SEM–EDX where the dispersion of TiO_2 covering the surface of the eggshell and all the elements of $CaCO_3$ and TiO_2 were detected. This proves that the TiO_2/eggshell composite photocatalyst was successfully formed through SSD method.

3.2. Photocatalytic activity of methylene blue solution

When the photocatalytic degradation of MB was carried out under UV illumination for 100 min, the photocatalytic efficiency of the TiO_2/eggshell composite photocatalyst was determined. The results are shown in Fig. 6. When the eggshell was used as an adsorbent, there was no photocatalytic degradation of the MB solution, which was as expected (Fig. 6a). By comparison of three different ratios (3:7, 2:8, and 1:9), TiO_2/eggshell (1:9) exhibited the highest adsorption and achieved 56.40% of MB photocatalytic degradation compared to others. In comparison to the 2:8 and 3:7 ratios, the high proportion (90%) of eggshell in the composite photocatalyst may have accelerated the adsorption process and thus the photocatalytic activity of MB. It is interesting to note that by increasing loading of eggshell for 2:8 and 3:7 ratios, the photocatalytic activity of MB was reduced may be due to the threshold level was achieved at 1:9 ratio. Therefore, the excess loading of eggshell was not significant for the adsorption process. It can be concluded that the TiO_2/eggshell composites present an individual behaviour as adsorbent and photocatalyst in the suspension.

Surprisingly, only 10% TiO_2 nanoparticles in TiO_2/eggshell composites were found to be capable of accelerating MB photocatalytic degradation when compared to other composites, except for those containing 100% TiO_2 nanoparticles. According to Zhang et al. [23], TiO_2 typically performs well in photocatalytic degradation because of the photogenerated electrons and holes that migrate rapidly from TiO_2 to the reactant. Furthermore, eggshells can aid in the improvement of the activity of TiO_2 by absorbing both TiO_2 and the reactant on the surface of the TiO_2 particle. The internal surface area of the eggshell accounts for most of its total surface area, and only the external surface area can be used for adsorption purposes. It appears that this statement is supported by the fact that, during the photocatalytic experiment, a decrease in the colour intensity of

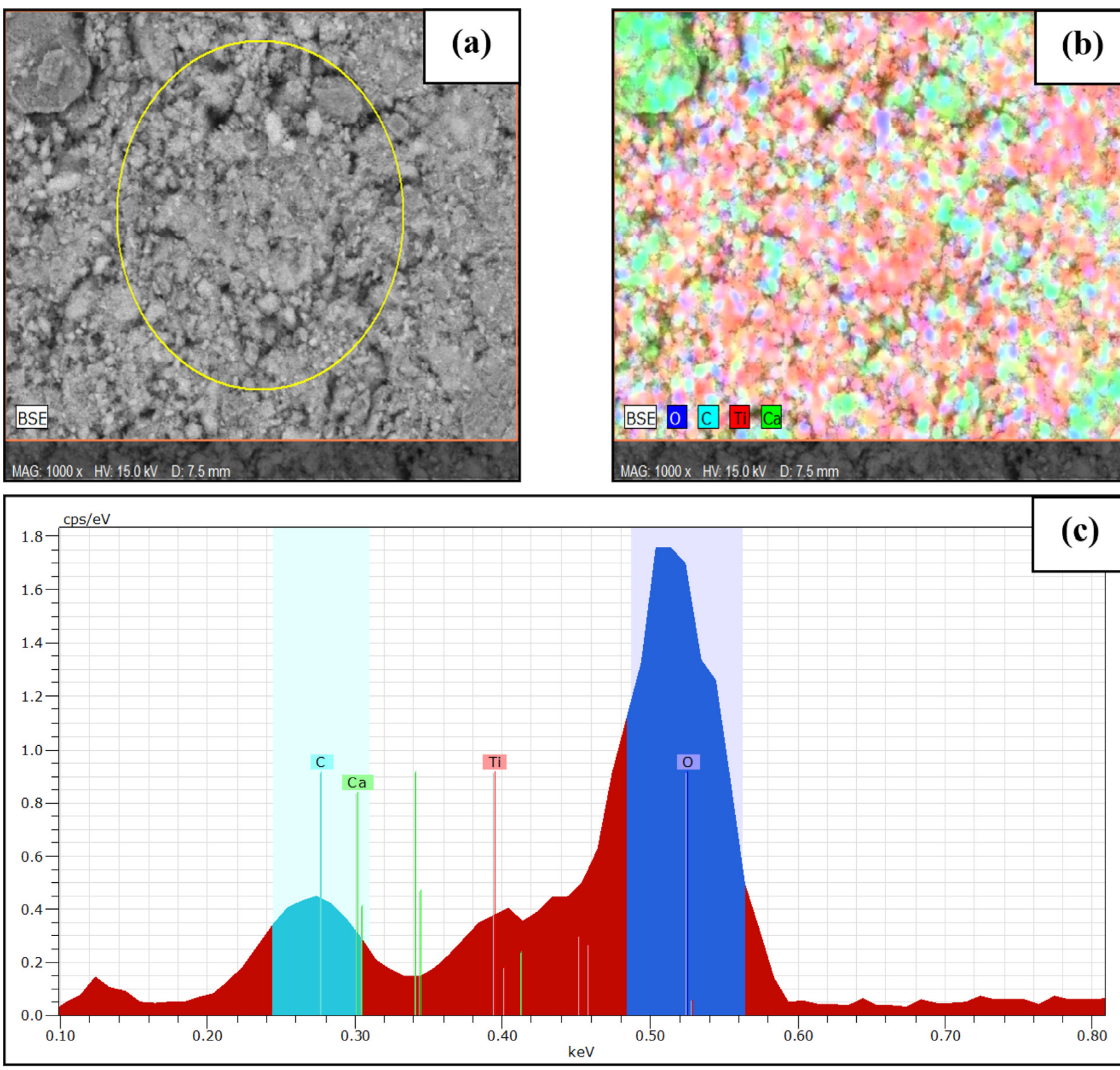

Fig. 4. (a) SEM images, (b) EDX mapping, and (c) percentage element of TiO_2/eggshell (3:7).

MB from a dark navy blue to a light blue was observed under dark conditions from 0 to 130 min, as shown in Fig. 5.

As shown in Fig. 6, 100% TiO_2 demonstrated the highest rate of MB photocatalytic degradation, followed by TiO_2/eggshell at a 1:9 ratio, with 0.0129 and 0.0092 min1 for 100% TiO_2 and 1:9 for TiO_2/eggshell, respectively. A possible explanation for the obtained results is the nanoscale particle size of the TiO_2 photocatalyst, which results in a large surface area due to its nanoscale particle size. While this is happening, the eggshell particle size that was used is in the micro size range. It is worth noting, however, that the efficiency of the TiO_2/eggshell composite would have been improved if the eggshell particle had been nanosized instead of micro-sized.

3.3. Comparison of results with previous research

A comparison of eggshell integrated with other materials (Table 1) shows that the TiO_2/eggshell composites are the most efficient for MB degradation due to the synergistic effect between eggshell and TiO_2 nanoparticles. Compared to Singh et al. [24], their research focuses on the effectiveness of TiO_2 synthesized via the solvothermal method instead of eggshell. They used eggshells as the support, and the eggshell was not integrated with TiO_2. They also did not evaluate the performance of MB degradation by using 100% eggshell as a control.

Besides, the uses of eggshell supported on ZnO–CuO can be questionable, in which Congo red (CR) percentage removal was insignificant by using eggshell as photocatalyst for photocatalytic process in the presence of visible light. The eggshell does not contain the element that acts as a catalyst to be activated under visible light irradiation. In addition, based on Khairol's result, eggshells did not significantly impact when added as support on ZnO–CuO [25].

Many researchers [22,26,27,28] have proven that eggshell has a good performance as an adsorbent, especially in dye removal. Most researchers used synthetic pollutants as model pollutants. Until now, only Foroutan and his research group [24] have tested eggshells using real wastewater. They claimed that eggshell nanoparticles have a high potential to be applied as an adsorbent in the field. Hence, it can be concluded that researchers can deeply explore recyclable wastes like eggshells to improve the efficiency of the treatments further and simultaneously reduce waste

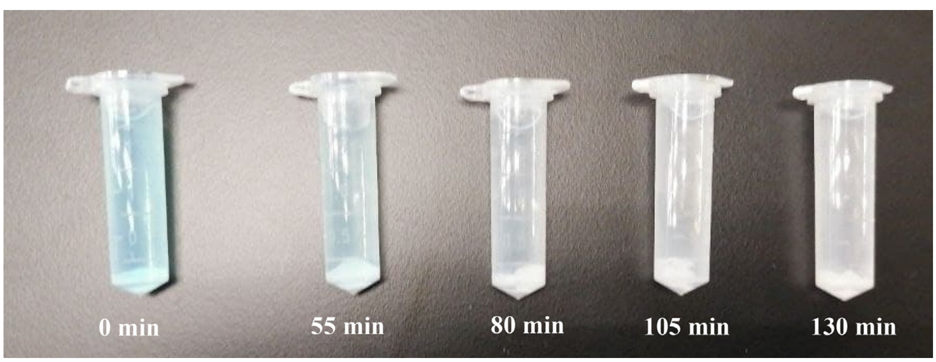

Fig. 5. Reduction color intensity of MB during photocatalytic experiment.

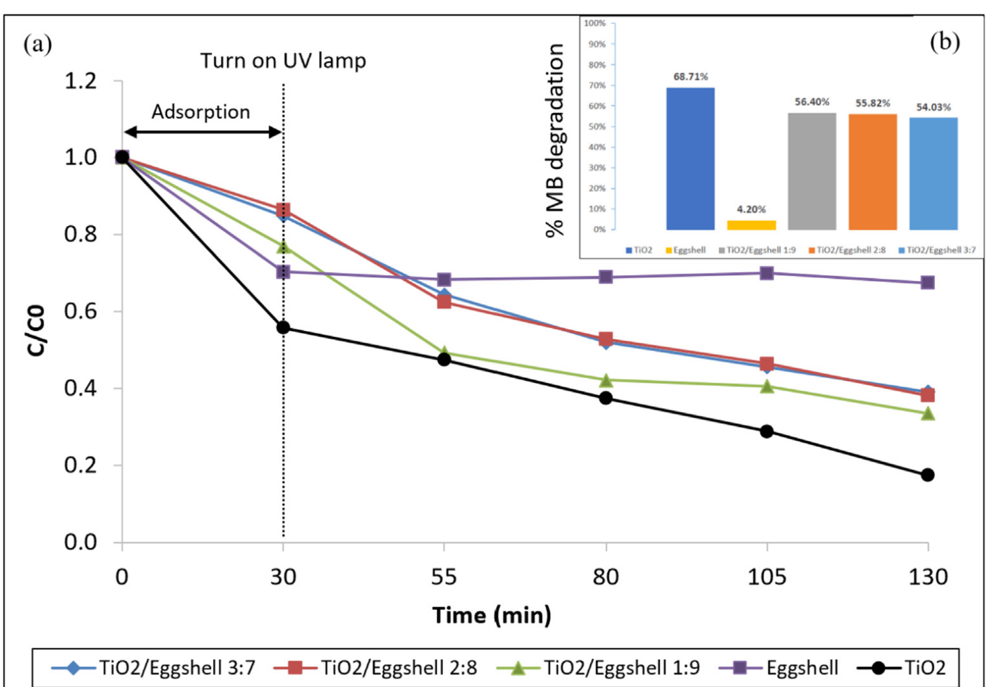

Fig. 6. (a) Normalized degradation behavior of MB using different types of photocatalyst and (b) MB percentage degradation.

Table 1
Comparison of eggshell performances integrated with other materials for different types of pollutant.

Pollutant	Catalyst	Process	Period of reaction time	Result	References
Hg(II) and methyl violet from aqueous solutions and real wastewaters	A nanoscale sorbent produced from eggshell wastes	Adsorption	50 min	The maximum sorption capacities of Hg(II) and MV using eggshell nanoparticles were 116.27 and 123.45 mg/g, respectively. After using the nanoadsorbent for seven cycles, only 10% of its efficiency was reduced.	[26]
4-Nitrophenol	Cu/eggshell, Fe_3O_4/eggshell, and Cu/Fe_3O_4/eggshell	Adsorption	100 s	K values were 1.74, 0.84, and 0.72 min^{-1} for Cu/eggshell, Fe_3O_4/eggshell, and Cu/Fe_3O_4/eggshell nanocomposites, respectively.	[22]
4-Nitrophenol	CuO/eggshell using a green root extract of pomegranate dried peel as a novel adsorbent nanocatalyst	Adsorption	25 min	CuO/eggshell efficiently removed the aromatic compounds of the crude oil sample and was also employed to reduce 4-nitrophenol to 4-aminophenol.	[27]
4-Nitrophenol	Eggshell/Ag binary nanocomposite by using *Cacumen platycladi* extract as reducing and stabilizing agents in aqueous solution at room temperature	Catalytic degradation	5 min or less	Nanocomposite exhibited dual functional properties as catalytic degrader and bactericidal growth inhibitor. The binary nanocomposite degraded 4-NP at room temperature completely and can be recycled up to five cycles while still working efficiently.	[11]
Congo red dye	ZnO, CuO, and ZnO–CuO/ES	Photocatalysis using fluorescent lamp as light source	4 h	By using ZnO–CuO as a catalyst, the CR percentage removal was the highest compared to others.	[25]
Congo red	CuO–ZnO (CZ) nanocomposites using a bio-templated method from biowaste-eggshell membranes (ESM), CuO–ESM, ZnO–ESM, and CZ–ESM nanopowder	Adsorption	12 min	CZ–ESM showed the highest adsorption due to synergistic interaction between Zn^{2+} and Cu^{2+}. CZ–ESM nanocomposites are expected to play essential roles in environmental remediation and water disinfection by combining excellent adsorption and catalysis with solid antibacterial activities.	[28]
Methylene blue	TiO_2 nanocrystal supported on ground nanoeggshell (ES) waste with ratios TS-ES (0.5 g:0.25 g), TS-ES (0.5 g:0.5 g), and TS-ES (0.5 g:1 g)	Photocatalysis using solar irradiation as light source	5 h	K values were 0.00797 min^{-1} for 100% TiO_2 and 0.01346 min^{-1} for TS–ES (0.5 g:0.25 g)	[24]
Methylene blue	TiO_2/eggshell (TiO_2/ES) composite via solid state dispersion method. TiO_2/ES prepared in different ratios 9:1, 8:2, and 7:3. Control: 100% TiO_2 and ES	Photocatalysis using UVA lamp as light source	130 min	The optimum performance of the adsorption and the photocatalytic process was shown by the ratio 9:1 TiO_2/eggshell composite, which gave the highest MB degradation compared to other ratios, which was 56.40% within 100 min under UV radiation.	This work

production. It could be the following revolutionary wastewater treatment method and thus can help sustain the environment's health.

4. Conclusion

TiO_2/eggshell composite photocatalyst was successfully prepared by the solid-state dispersion (SSD) method with different ratios. The adsorption and photocatalytic activity were investigated using a suspension system and methylene blue as model pollutants. The TiO_2/eggshell composite consisted of 10 wt% TiO_2 and 90 wt% eggshell exhibited higher MB degradation within 100 min under UV irradiation in suspension condition than composites of other ratios. As a composite photocatalyst, eggshell has a high potential for adsorption, even though it is micro-sized. Specifically, nanosized eggshells could be more effective. As a result of their high adsorption capacity, eggshells can be used as a valuable material for removing reactive dyes.

CRediT authorship contribution statement

Hazlini Dzinun: Investigation, Writing-original draft preparation, Conceptualization, Validation. **Nur Hafizah Abd Khalid:** Conceptualization. **Nur Hanis Hayati Hairom:** Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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