Chapter

Mollusk Shell Waste as Composite Photocatalyst for Methylene Blue Removal

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Abstract

Mollusk shell is abundant in particular areas and frequently deposited in landfills, contributing to environmental pollution. However, mollusk shell waste has been proven as an absorbent that has a high possibility of acting as a photocatalyst when integrated with metal support in composite form due to the synergistic effect. Therefore, in this study, mussel and cockle shells as agricultural wastes were selected to be innovated as support for photocatalysts. The solid-state dispersion (SSD) method was used to prepare a composite photocatalyst where mussel and cockle were integrated with titanium dioxide (TiO_2) nanoparticles at a ratio of 9:1. In total, 100% of mussel and cockle were used as control samples. The prepared composite photocatalyst was evaluated with methylene blue (MB) removal in the suspension system. The result reveals that mussel/TiO_2 and cockle/TiO_2 composite photocatalyst show 25.92 and 24.08% for MB removal within 2 hours. It is due to the prepared composite photocatalyst particle sizes, where mussel/TiO_2 and cockle/TiO_2 were 259 and 268 nm, respectively. It is interesting to note that the prepared composite photocatalyst particle size should be in nanosize, where it can enhance the photocatalytic performance. Overall, agricultural waste should be utilized to ensure a clean environment for future generations.

Keywords: mollusk shell waste, composite photocatalyst, methylene blue removal

1. Introduction

Industrial development is a significant contributor to a country's financial status, including using dyes to produce an eye-catching product that meets the consumers' demand [1]. Estimated that 10–15% of dyes used in textile processing were lost in the wastewater. Coincidentally, methylene blue (MB), a sulfur-containing heterocyclic aromatic dye, is mostly applied in textiles industries for dyeing cotton, silk, and wool [2, 3].

In addition, other applications in chemistry, biology, and medical science also use this basic cation dye in the treatment of methemoglobinemia and cyanide poisoning [4].

Biological and chemical precipitation is the standard dye removal treatment [5] while several conventional wastewater treatment methods have also been tested for the same purpose. Coagulation or flocculation, ozonation, chemical oxidation, and electrochemical treatment reported by Subki et al., [6], novel technology, such as membrane filtration and bio-sorption [7]. Among all of the possible techniques, the photocatalysis process has proven to be the most favorable technology in textile wastewater treatment, where the most organic matter can be oxidized to water, carbon dioxide, and simple inorganics materials using light radiation and selected catalysts [8].

Due to the expensive production of chemical photocatalyst compounds, utilizing waste materials as adsorbents integrated with metal oxides to form composite photocatalysts has become the main focus of researchers nowadays in maintaining the sustainability of both the treatment and the environment. Mollusk shells catch attention as a potential derived catalyst in dye removal due to the high content of calcium carbonate ($CaCO_3$) in raw material to produce calcium oxide (CaO) as the most promising heterogeneous alkali catalyst obtained *via* the calcination process [9]. As the most heavily traded bivalve ample mollusk shell, cockle shells have been recorded to have a high percentage of CaO contained in the natural compound of the shell, which is 99.17% of $CaCO_3$ before calcined [10] while mussel shells came in the second place with 98.37% of $CaCO_3$ [11].

In order to get the small microstrain of CaO from $CaCO_3$ through the calcination process, Sari et al., [12] investigated the effect of calcination temperature on the crystallization of CaO from green mussel shells. They found out that the calcined CaO at 950°C obtained a small microstrain compared to the samples calcined at other temperatures. Besides, CaO calcined at 950°C exhibited the largest crystallite size, meaning it had high crystallinity and a shortened amorphous phase. The CaO calcined at 950°C showed a small microstrain compared to the other samples, meaning the crystal defects in the sample were small.

The particle sizes of composite photocatalysts are also one of the factors for enhanced photocatalytic performances. Based on previous researchers, they used various methods for synthesizing mollusk shells with various particle sizes produced. Among cockles, scallops, oysters, pyramidella, green mussels, razor clams, golden apple snails, and snail shells, the highest CaO is produced from cockle and green mussel shells [11]. Commonly, the synthesized waste shell involves the same steps, which are cleaning, drying, crushing, grinding, sieving, and calcination process. Mostly, the particle sizes of CaO are produced in micro-size as prepared by Buasri with his group research starting 2013 [11] until 2015 [13] with various types of shells. Interesting to note that Gbadeyan et al., [14] was successfully synthesized snail waste shells in nanosized *via* dry and wet ball milling methods.

The ratio of adsorbent with metal oxides to form a composite photocatalyst needs to be considered in order to get the highest removal of pollutants. Dzinun et al. [15] found that the optimum ratio for the highest adsorption and MB photocatalytic degradation was achieved by using a (1/9) ratio of TiO_2/eggshell. Therefore, in this study, 9:1 ratio of mollusk shell with TiO_2 was investigated. In total 100% of mollusk and cockle shell was used as the control sample with indicated ratios of 10:0. The composite photocatalyst was prepared by solid-state dispersion (SSD) method for MB removal in the suspension system.

2. Experimental

2.1 Materials

This study used the raw mussel and cockle shell waste then synthesized into powder form. TiO_2 (Sigma-Aldrich, 21 nm, 95% purity) was used and integrated with prepared powder of mussel and cockle shell to be a composite photocatalyst. Ethanol (95%) was used from QRëc.

2.2 Synthesis of cockle and mussel shell in powder form

Wasted mussel and cockle shells were washed and brushed several times with tap water to remove any foreign matter and impurities present. The cleaned shells were dried until no moisture was left then proceeded to crush into smaller sizes. Dry-milled both shells for 45 minutes at 500 rpm in batch mode. Then, the crushed shells were sieved to a particle size of ≤75 μm using Cooper's TG-0411/0412 Sieve Shaker for an average of 10 minutes. The powdered cockle shells then were mixed with 50 mL of ethanol in a 250 mL stainless steel jar and were wet-milled at 500 rpm for 4 hours equivalent to 240 minutes in a clockwise direction. The same condition was set for powdered mussel shells except for the volume of ethanol used is 30 mL. Dry and wet milling processes were operated in a planetary ball mill (Pritsch Pulverisette 6) to gain nanosize powder [14]. Both shells were purified *via* the decantation method four times every 20 minutes before filtration. Then, the fine particles were dried in a drying oven at 40°C for 3 days corresponding to 72 hours. After cockle and mussel shells dried, the samples were calculated in a muffle furnace (Protherm-Furnaces) of 950°C with a heating rate of 10°C/min for a whole 4 hours. The obtained CaO powder was cooled before being stored in a sealed zipper bag.

2.3 Synthesis of composite photocatalyst

The composite photocatalyst of mussel shell/TiO_2 and cockle shell/TiO_2 was prepared using the solid-state dispersion (SSD) method. There were two different samples of mussel shell/TiO_2 and cockle shell/TiO_2 with a ratio of 9:1 with a 10 g basis and also two control samples consisting of 100% of mussel shell and cockle shell. The samples were evaporated for 24 hours in a 35°C oven. Finally, the samples were calcined in a muffled furnace for 5 hours at 450°C.

2.4 Characterization of composite photocatalyst

The functional group was characterized using Fourier Transform Infrared (Agilent Cary 630 FT-IR). UV–Vis Spectrophotometer (HITACHI U-3900H) was used for the determination of photocatalytic degradation performance. The structural morphology of composite photocatalyst was investigated using scanning electron microscopy (SEM, HITACHI TM3)00).

2.5 Methylene blue removal testing

The setup of MB removal testing was prepared as in the previous study [15]. 10 mg/L of MB solution was prepared in a 200 mL beaker. 0.8 g of the composite

photocatalyst was added into a beaker. 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 150 min and for each 10 min interval, the aliquot samples were taken and centrifuged at 6000 rpm [16] for 5 minutes to measure the concentration of MB with a UV–Vis spectrophotometer at 665 nm as the maximum absorbance [17]. The samples were analyzed by a UV–Vis spectrophotometer.

The calibration curve is a method for determining the sample concentration that must be completed before the photocatalytic suspension test. The absorbance value of each sample from each experiment run was determined using a UV–Vis spectrophotometer. The sample absorption value can be translated into concentration using the linear equation obtained from the calibration curve (ppm). After normalizing the measurement, the removal of MB can be computed using the formula:

$$MB\,removal\% = \frac{(C_o - C_t)}{C_o} \times 100\% \quad (1)$$

where R is the removal efficiency of MB in percentage, C_o (mg/L) as initiate al concentration of dye solution, and C_t (mg/L) as the concentration of dye solution at equilibrium [18].

3. Results and discussion

3.1 Morphology and physiochemical properties of composite photocatalyst

Figure 1 shows the synthesizing of cockle and mussel shells into powder form. Raw waste shells were crushed into smaller sizes that are allowable for the milling process, where $CaCO_3$ powder was obtained, as shown in **Figure 1a** and **b**, respectively. After 4 hours of calcination at 950°C, the composite powder converted into CaO powder as shown in **Figure 1c**, and was used as an adsorbent for MB removal. The difference in color shows each shell has its appearance throughout the whole process. An investigation of mass reduction on both samples after calcination was performed, and

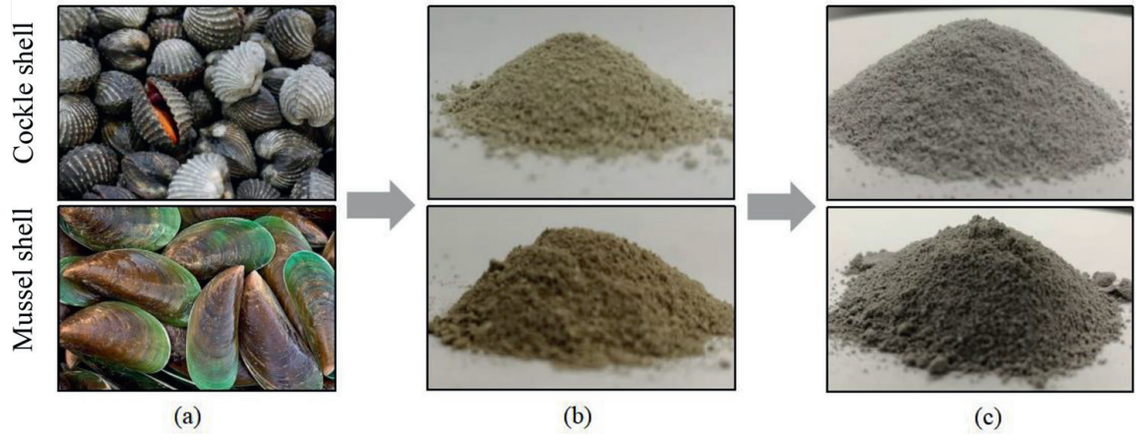


Figure 1.
(a) Raw waste shells, (b) powder shells before, and (c) after the calcination process to produce CaO.

it was discovered that the mass for CCS reduced to 5.56 g from 10.06 g, while CMS depleted from 10.08 to 5.12 g, both shells proved to lose half of its mass after conversion of CaO. A similar finding was observed in a study of $MgCO_3$ conversion to MgO, the mass loss was 50% approximately at a calcination temperature equal to or higher than 700°C, independent of the duration [19].

FT-IR analysis was performed on both shells to identify the composite formed before and after calcination as shown in **Figure 2**. Uncalcined cockle shell as proved in **Figure 2a** has a peak of C-O bond at 1438 cm^{-1} wavelength that comes in a group with a few bands at 1088, 861, and 714 cm^{-1} representing carbonate ion, CO_3^{2-} with aragonite microstructure [20] indicating the $CaCO_3$ presence before calcination. This result slightly corresponds to Ref. [21] with sharp bands found around 1450, 1080, 858, and 712 cm^{-1}.

Situated at the peak of 939 and 1438 cm^{-1} in the calcined cockle shell band (**Figure 2b**), the C-O bonds seem to lose their former strength as the

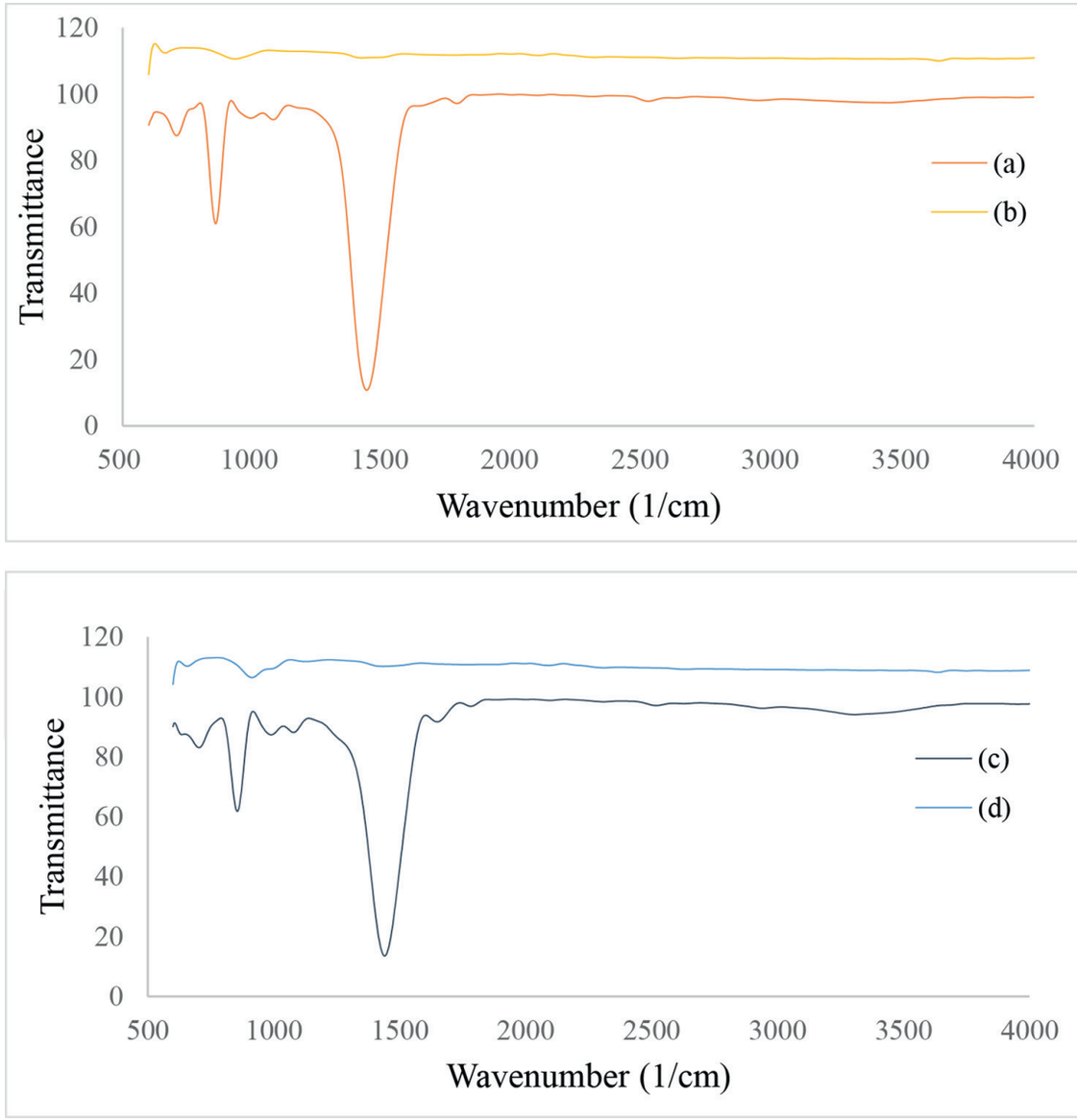


Figure 2.
FT-IR spectrum of (a) uncalcined and (b) calcined cockle shell, (c) uncalcined, and (d) calcined mussel shell.

CO_3^{2-} presence is gradually lost in the calcination process, which causes the shifting in the mentioned peak. This discovery occurred due to dissipation in the reduced mass of the functional group associated with CO_3^{2-} ion [22]. The same theory applied to uncalcined mussel shells concerning that both shells are one of the few types of mollusk shells.

As for the uncalcined mussel shell, as shown in **Figure 2c**, the C-O bonds were observed at 1442, 1077, 853, and 711 cm^{-1} peaks except there is a slight difference in the intensity of these peaks compared to **Figure 2a**, which have a stronger intensity of C-O content. The calcined cockle shell lost its C-O functional group, where the peak intensity of 924 and 1449 cm^{-1} is weakening (**Figure 2d**). According to Sari et al., [12], the functional group of CaO was formed starting at a temperature of 750°C, which is agreeable with this study as the CaO bond was formed at 656 cm^{-1} still in the range of 667.32 cm^{-1} from their characterization results.

The morphological structures of a mussel shell, mussel/TiO_2, cockle shell, and cockle/TiO_2 composite photocatalyst were examined by SEM as shown in **Figure 3**. TiO_2 appeared as fine particles (**Figure 3c** and **d**), whereas the cockle and mussel shell is more prominent due to the micro-sized particles and exhibits irregular shape and size (**Figure 3a** and **b**). The particle sizes of mussel and cockle shells were bigger than mussel/TiO_2 and cockle/TiO_2 composite photocatalysts due to the integration of TiO_2 in nanoparticles size. Besides, it has been established that the TiO_2 and mollusk shell particles bonded together and formed a composite photocatalyst following the calcination process.

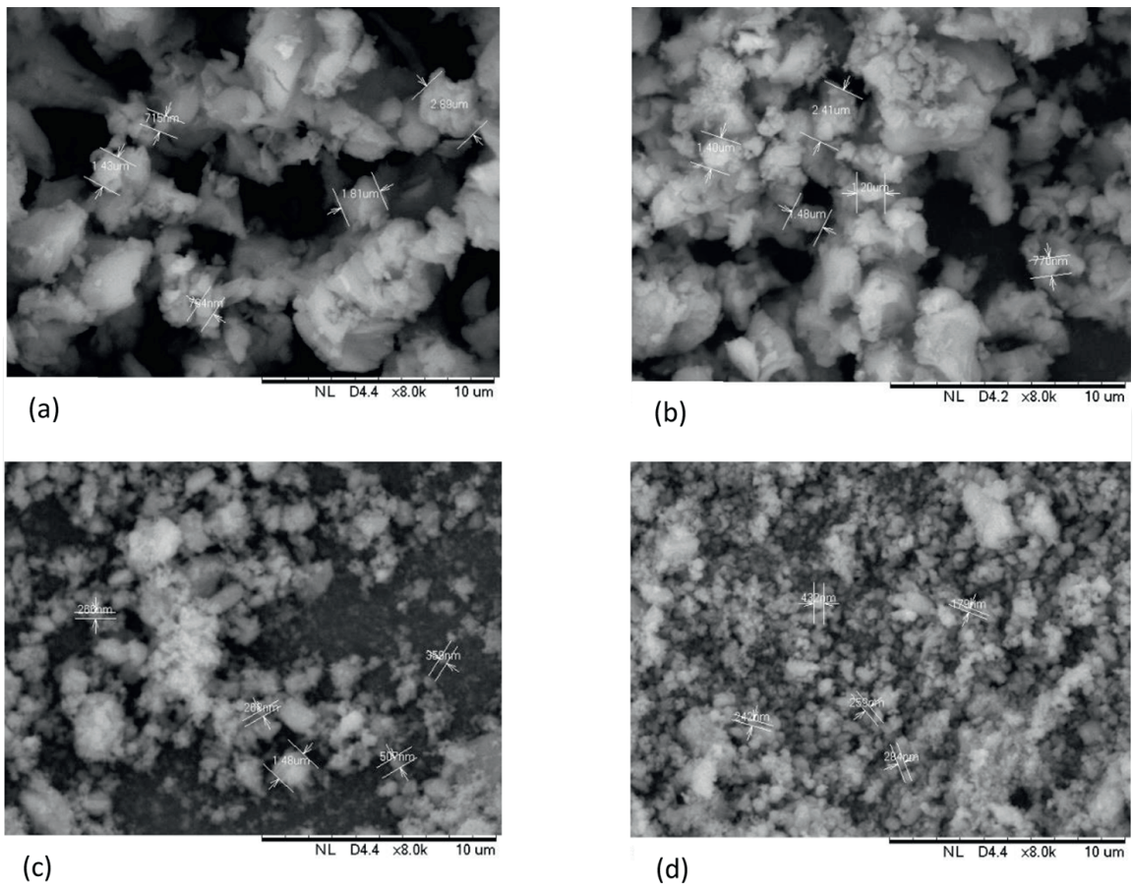
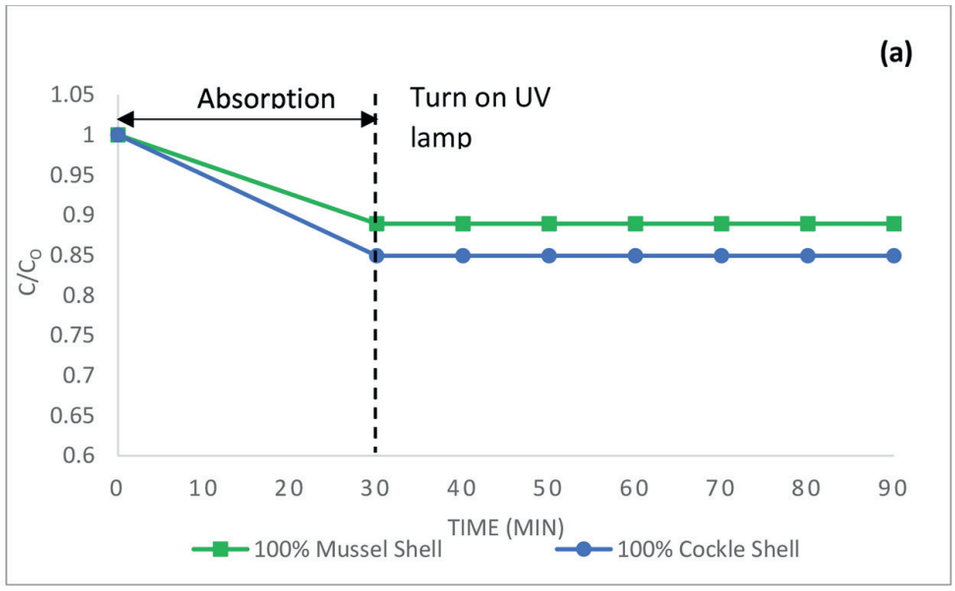
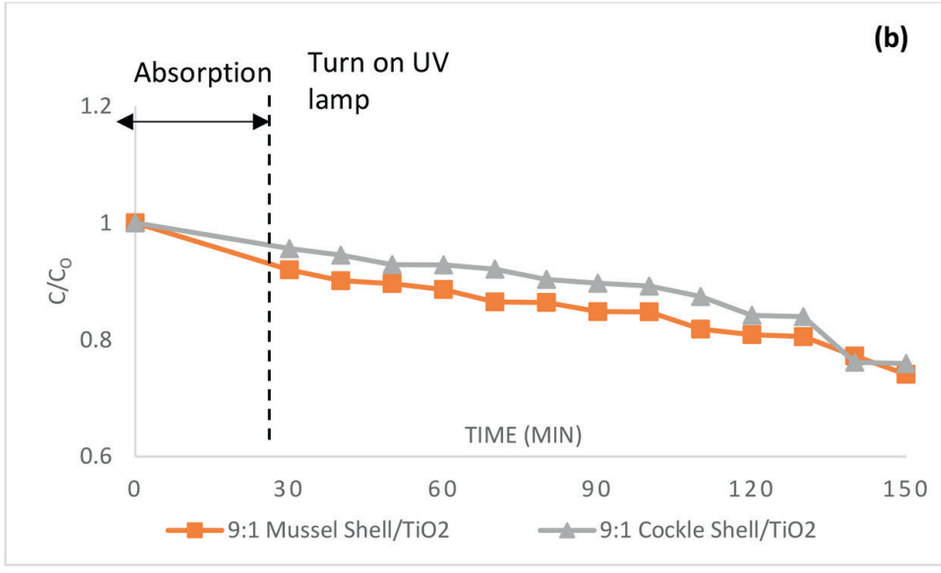


Figure 3.
SEM analysis for (a) cockle shell, (b) mussel shell (c) cockle shell/TiO_2, and (d) mussel shell/TiO_2 composite photocatalyst.





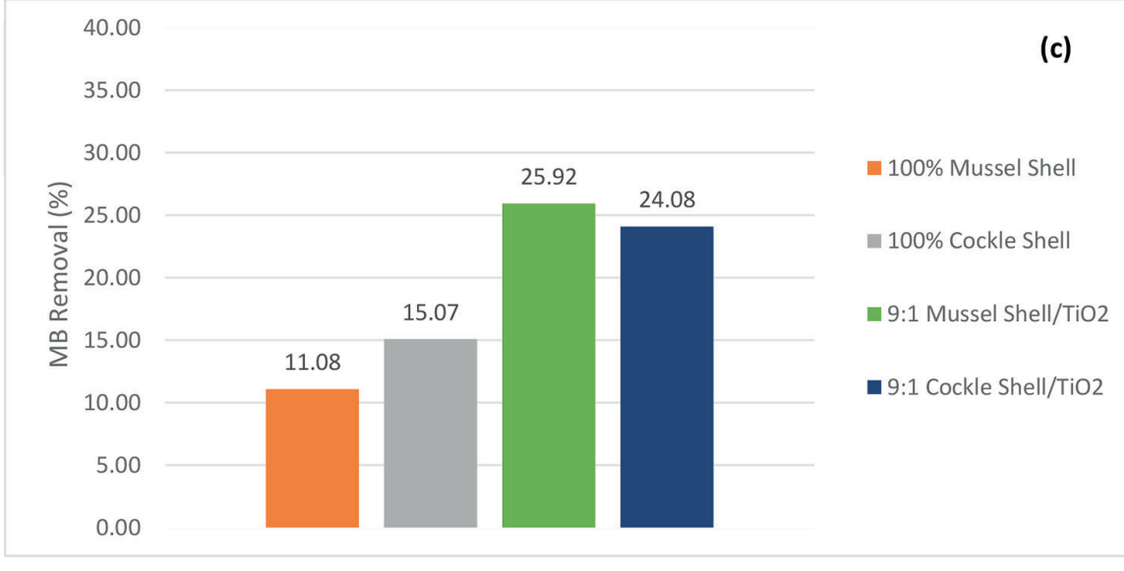


Figure 4.
(a) Normalized absorption and photocatalytic activity for (a) mussel and cockle shell, (b) for composite photocatalyst, and (c) percentage MB removal.

3.2 Performance of methylene blue removal

The removal of MB was carried out under UV illumination for 150 min, the photocatalytic efficiency of the composite photocatalyst was determined and the result is shown in **Figure 4**. When the cockle and mussel shell was used as an adsorbent, there was no photocatalytic degradation of the MB solution, which was as expected (**Figure 4a**). By comparison of the composite photocatalyst, mussel shell/TiO_2 exhibited the highest adsorption and achieved 25.92% of MB photocatalytic degradation compared to cockle shell/TiO_2 (**Figure 4b** and **c**). It is interesting to note that the particle size of the mussel shell/TiO_2 composite photocatalyst is smaller than cockle shell/TiO_2, which gives a higher surface area for adsorption and photocatalytic activity takes place.

4. Conclusion

By using the solid-state dispersion (SSD) method, photocatalyst composites made of cockle shell/TiO_2 and mussel shell/TiO_2 were successfully prepared. Using a suspension system and methylene blue as a model pollutant, we investigated the adsorption and photocatalytic activity of the material. The mussel shell/TiO_2 composite photocatalyst with the smallest particle size gives the highest MB removal when compared to the cockleshell/TiO_2 photocatalyst. Therefore, mussel shells have the potential to be utilized as useful materials for the removal of reactive dyes compared to cockle shells. In order to increase the MB removal, it would be suggested that the particle sizes or mussel shells should be nanosized and integrated with TiO_2 to form nanocomposite photocatalysts.

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