Titanium Dioxide/Polyvinyl Alcohol/Cork Nanocomposite: A Floating Photocatalyst for the Degradation of Methylene Blue under Irradiation of a Visible Light Source

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ABSTRACT: Photocatalytic degradation by the titanium dioxide (TiO2) photocatalyst attracts tremendous interest due to its promising strategy to eliminate pollutants from wastewater. The floating photocatalysts are explored as potential candidates for practical wastewater treatment applications that could overcome the drawbacks posed by the suspended TiO2 photocatalysis system. The problem occurs when the powdered TiO2 applied directly into the treated solution will form a slurry, making its reuse become a difficult step after treatment. In this study, the immobilization of titanium dioxide nanoparticles (TiO2 NPs) on the floating substrate (cork) employing polyvinyl alcohol (PVA) as a binder to anchor TiO2 NPs on the surface of the cork was carried out. Characterizations such as Fourier transformer infrared, X-ray diffraction (XRD), ultraviolet−visible spectroscopy (UV−vis), zeta potential, photoluminescence spectroscopy, femtosecond to millisecond time-resolved spectroscopy, ion chromatography, and scanning electron microscopy−energy-dispersive X-ray spectroscopy (SEM−EDX) analyses were employed. XRD analysis revealed the formation of anatase-phase TiO2 NPs. The results demonstrated that the crystallite size was 9.36 nm. The band gap energy of TiO2 NPs was determined as 3.0 eV. PL analysis verified that TiO2 NPs possessed a slower recombination rate of electron−hole pairs as compared to anatase TiO2. The result was attributed by the behavior of photogenerated charge carriers on TiO2 NPs, which existed as shallowly trapped electrons that could survive longer than a few milliseconds in this study. Furthermore, SEM−EDX analysis indicated that TiO2 NPs were well distributed on the surface of the cork. At the optimal mole ratio of TiO2/PVA (1:8), the TiO2/PVA/cork floating photocatalyst degraded at 98.43% of methylene blue (MB) under a visible light source which performed better than under sunlight irradiation (77.09% of MB removal) for 120 min. Besides, the mineralization result has measured the presence of sulfate anions after photocatalytic activities, which achieved 86.13% (under a visible light source) and 65.34% (under sunlight). The superior photodegradation performance for MB was mainly controlled by the reactive oxygen species of the superoxide radical (•O2−). The degradation kinetics of MB followed the first-order kinetics. Meanwhile, the Langmuir isotherm model was fitted for the adsorption isotherm. The floating photocatalyst presented good reusability, resulting in 78.13% of MB removal efficiency even after five cycles. Our TiO2/PVA/cork floating photocatalyst fabrication and high photocatalytic performance are potentially used in wastewater treatment, especially under visible light irradiation.

1. INTRODUCTION

Wastewater effluents from industrial and domestic sources often contain high concentrations of organic chemicals which continuously trigger major environmental issues. Dyes are one of the wastewater sources which are widely used in the textile, printing, and food industries.1 Generally, 30−40% of the residual dyes are expected to be released by textile industries into the aqueous system as effluents without proper treatment. However, dyes can hamper human health due to their negative attributes such as being toxic and potentially carcinogenic.2 Several attempts have been explored to resolve these short-comings.3 Among them, methods such as sorption, chemical precipitation, membrane filtration, ion exchange, coagulation, photocatalysis, oxidation or reduction, and solvent extraction...
have been developed to overcome this hazard. As such, photocatalysis is observed to be the most popular technique. It is an excellent approach to degrade the toxic pollutants from an aqueous system due to its high efficiency, nontoxicity, and the formation of nonhazardous secondary pollutants only. Several types of semiconductor photocatalysts have been documented in previous studies such as titanium dioxide (TiO$_2$), zinc oxide (ZnO), and copper oxide (CuO). Since Fujishima and Honda discovered the photolysis of water on the crystal titania electrode in 1972, advanced research on this promising photocatalyst of TiO$_2$ has been explored. The advantages offered by TiO$_2$ include having high chemical inertness and low toxicity and being cheap and environmentally friendly.

The TiO$_2$ system has one significant obstacle to its real application: it becomes active at ultraviolet light irradiation which is attributed to its large band gap energy of 3.2 eV. To circumvent the drawback, modification of the photocatalyst by shifting the absorption onset of TiO$_2$ to the visible light region ($\lambda > 400$ nm) is one of the solutions. Therefore, efforts to narrow its band gap energy were initiated. In our previous work, we have successfully synthesized TiO$_2$ nanoparticles (NPs) using the green chemistry sol–gel method. It has been reported that the obtained TiO$_2$ NPs resulted in 3.0 eV of band gap energy and have good photocatalytic activity in the visible light region. This performance is ascribed to the presence of surface defects (Ti$^{4+}$ species and oxygen vacancies).

Generally, TiO$_2$ powder is applied directly to the treated solution forming a slurry. The filtration or separation of the used TiO$_2$ after treatment becomes more challenging due to its extremely small particle size. Therefore, the immobilization of TiO$_2$ NPs on the floating substrates is explored as an alternative approach to solve the problem. The floating substrates are lightweight materials that are considered a carrier to float on the surface of water.

Previsously, different types of TiO$_2$ NP-based floating substrates such as polymer perlate, graphite, vermiculite, glass, and cork were studied. For instance, the B–N–TiO$_2$/expanded perlate floating photocatalyst was fabricated by the sol–gel method, resulting in 94.0% efficiency degradation of rhodamine B (RhB) dye for 3 h under visible light irradiation. Meanwhile, An and co-workers have reported the immobilization of TiO$_2$/Ag$_2$PO$_4$ particles onto the hollow glass microspheres that acted as a floating substrate using (3-aminopropyl)-tiethoxysilane as a binder. The floating photocatalyst achieved 96% degradation of methylene blue (MB) after 90 min under visible light irradiation. Both mentioned models have shown that the expanded perlate and hollow glass microspheres could degrade 70% and 75% of the dye after five cycles, respectively.

In addition, 1H,1H,2H,2H-perfluoroctyltrithoxysilane was reported as a binder and hydrophobic agent to synthesize TiO$_2$-coated hollow glass microspheres. Owing to the strategy of TiO$_2$ immobilization on the floating substrates, the floating photocatalysts showed great recovery and reusability. This benefit is attributed to the good attachment of the catalyst on the floating substrate and is dependent on the fabrication method of the floating photocatalyst and the binder. The floating photocatalyst can be exposed to maximum light irradiation and has sufficient oxygenation, resulting in high photocatalytic performance. In addition, the floating photocatalyst gives access to a large specific surface area.

In our work, cork was employed as the floating substrate to immobilize TiO$_2$ NPs onto the substrate. Cork possesses good traits such as lightweight, low heat conduction, and high corrosion resistance. Polyvinyl alcohol (PVA) was utilized as a binder to anchor TiO$_2$ NPs on the surface of the cork. Besides, MB was selected as a model pollutant for photodegradation analysis. Thus, the adopted approach was facile, cost-effective, and efficient for developing the TiO$_2$/PVA/cork floating photocatalyst. Cork utilized in this study would allow this floating photocatalyst to provide a potential platform for wastewater treatment applications, especially for the degradation of dyes under the visible light irradiation.

2. EXPERIMENTAL SECTION

2.1. Materials. Titanium(IV) peroxide, TTIP, with a purity of ≥97% was purchased from Sigma-Aldrich, Co., USA. Soluble starch was purchased from System Laboratory Chemicals & Reagents, Malaysia. Ammonium solution, NH$_4$OH, was obtained from Merck KGaA Analytics, EMD Millipore, Co., Germany. PVA with average molecular weight $M_n = \sim 14,000$ and spray paint (MC821 dark Nyatoh) were obtained from BDH Chemicals Ltd, Poole, England and Nippon Paint Malaysia, Gelugor, Malaysia, respectively. MB was obtained from QREC, Grade AR, (Asia) Sdn. Bhd, Malaysia. Universal Saxophone sax neck cork was procured from Luckyolita.my. All chemicals were used as received without further purification.

2.2. Synthesis of TiO$_2$ NPs Using Green Synthesis. TiO$_2$ NPs were prepared by the sol–gel method using titanium(IV) isoproxide, TTIP, as a precursor based on the previous study, where 5.0 g of soluble starch was dissolved in 150 mL of boiling distilled water. Then, 3 mL of TTIP was added to the starch solution that was stirred homogeneously for 5 min at 85 °C. Next, ammonia solution (NH$_4$OH) was slowly added dropwise to the solution while stirring for 30 min until the pH reached 9. The obtained white precipitate was separated by centrifugation at 8500 rpm for 10 min, washed five times with distilled water to achieve pH 7, and dried in an oven at 50 °C for 24 h. The white powder was finally calcined at 500 °C for 2 h.

2.3. TiO$_2$/PVA/Cork Floating Photocatalyst Preparation. A 0.5 g cork was weighed and cut into small pieces for preparation of the TiO$_2$/PVA/cork floating photocatalyst at a 1:8 mol ratio of TiO$_2$/PVA. A mixture of 50 mL of distilled water and PVA (0.050 mol) was heated and stirred vigorously for 1 h until the PVA dissolved. PVA acted as a binder to anchor the TiO$_2$ NPs on the surface of the cork. Then, 0.5 g of cork and TiO$_2$ NPs (0.006 mol) were added to the mixture and stirred vigorously for another 1 h. The treated cork was collected and dried at 60 °C for 3 h before being stirred vigorously in distilled water for 1 h to eliminate the excess TiO$_2$ NPs. The treated cork was left to dry at room temperature. Spray paint was next applied to the cork to form a hydrophobic layer around the outside of the cork. The method was repeated for mole ratios (TiO$_2$/PVA) of 1:6 and 1:10.

2.4. Characterization. The photocatalysts were analyzed using a variety of techniques. X-ray diffraction (XRD) (PW 3040/60 XPERT PRO, PANalytical, Netherland) was used to identify the crystal structure and crystalline phase of the samples using Cu Kα ($1.541$ Å) radiation in the range 2θ = 10–90°. Fourier transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm$^{-1}$ using a PerkinElmer Model System 2000 spectrophotometer (USA) with KBr pellets at room temperature. The band gap was determined by ultraviolet–visible (UV–vis) diffuse reflectance spectra (DRS) using a PerkinElmer Lambda 35 spectrometer (USA) equipped with a Labsphere RUSAPE-20 integration sphere with BaSO$_4$ as a reference standard. Surface morphologies of the samples were observed by scanning electron microscopy (SEM) using a...
Quanta FEG 650 scanning electron microscope (UK). Energy-dispersive X-ray spectroscopy (EDX) analysis was also performed during the SEM measurements to determine the chemical compositions of the samples. The lifetime of charge carriers for the samples was measured using a PerkinElmer LS 55 luminescence spectrometer (USA) with an excitation wavelength of 300 nm. The transient absorption spectrum from 6000 to 1000 cm\(^{-1}\) was measured with a laboratory-built spectrometer (Japan) as reported in a previous study.\textsuperscript{20} Briefly, TiO\textsubscript{2} powder fixed on a CaF\textsubscript{2} plate (2 mg/cm\(^2\)) was irradiated with a 450 nm laser pulse (Continuum, Surelite I, duration: 6 ns, power: 5 mL, and repetition rate: 5 Hz), and the change in the IR transmittance was measured. The surface charge of TiO\textsubscript{2} NPs before and after adsorption was measured by a Zetasizer Nano S and ZS (Malven Instrument Ltd., United Kingdom) for point of zero charge (pH\textsubscript{ZPC}) determination.

2.5. Evaluation of Photocatalytic Activities. The photocatalytic activity of the TiO\textsubscript{2}/PVA/cork floating photocatalyst was determined by the decomposition of MB under light source irradiation. The floating photocatalyst (0.5 g) was mixed with 200 mL of MB solution (6 ppm). The mixture was stirred for 1 h under dark conditions to reach adsorption–desorption equilibrium before being exposed to a visible light source (luminosity between 100 and 110 klux) and sunlight (luminosity between 80 and 90 klux). Samples were collected every 15 min with a nylon syringe filter (Ø = 25 mm and pore diameter 0.22 µm) for 2 h to study the degradation efficiency. The filtrate was analyzed using a LAMBDA 25 UV–visible spectrophotometer (Shimadzu, Japan), with the concentration of MB in the solution based on the intensity of the MB peak at 664 nm. Three different mole ratios (TiO\textsubscript{2}/PVA) of the floating photocatalysts, 1:6, 1:8, and 1:10, were investigated using the visible light source. The photocatalytic activity of the optimized floating photocatalyst was also measured under sunlight irradiation for comparison. The following equation was used to calculate the efficiency of MB removal

\[
R = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}
\]

where \(C_0\) is the initial concentration of MB solution and \(C_t\) represents the concentration of MB solution during irradiation. The mean and standard deviation reported for the degradation of MB under sunlight and a visible light source with an irradiance of 1000 W/m\(^2\) (luminosity between 100 and 110 klux) and sunlight (luminosity between 80 and 90 klux). The adsorption study was conducted based on previous studies, by mixing 0.5 g of the floating photocatalyst with 200 mL of MB solution of initial concentration, \(C_{0,MB}\), 2, 4, 6, 8, and 10 ppm under stirring in the dark for 1 h.\textsuperscript{21} A sample was collected every 5 min, and the absorbance of MB was evaluated at 664 nm using a LAMBDA 25 UV–visible spectrophotometer until the solution reached equilibrium, and \(C_1\) was then recorded. The amounts of MB adsorbed were determined from the concentrations in solution before and after adsorption.

2.7. Mineralization Study. Ion chromatography (IC) analysis was used to study the mineralization of the degradation process by measuring the concentration of the sulfate anion (SO\textsubscript{4}\(^{2-}\)) after 2 h of photocatalytic reaction under visible light irradiation. This evaluation used a Metrohm 792 Basic IC for anion detection with a Metrosep A Supp 5–150 column. A mobile phase of 1.00 mmol L\(^{-1}\) sodium carbonate with 3.20 mmol L\(^{-1}\) sodium bicarbonate and 100 mmol L\(^{-1}\) sulfuric acid was used as the first and second eluent, respectively. The injection flow rate and volume were 0.70 mL min\(^{-1}\) and 20.0 µL, respectively.

2.8. Scavenging Study. Scavenging tests were undertaken to distinguish the reactive radical species responsible for the photodegradation of MB. Methanol (10% v/v of MeOH), silver nitrate (0.2 M of AgNO\textsubscript{3}), acetonitrile (100% v/v of ACN), sodium pyruvate (0.2 M of C\textsubscript{3}H\textsubscript{4}NaO\textsubscript{2}), and ascorbic acid (0.2 M of C\textsubscript{6}H\textsubscript{8}O\textsubscript{6}) were applied as scavengers for the photogenerated holes (h\(^{+}\)), electrons (e\(^{-}\)), hydroxyl radicals (•OH), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), and singlet oxygen (1\textsuperscript{O}2), respectively. For AgNO\textsubscript{3}, the scavenging effect was similar to the superoxide radicals (•O\textsubscript{2}\textsuperscript{-}).\textsuperscript{22}

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Analysis. The X-ray diffraction (XRD) pattern of TiO\textsubscript{2} NPs is illustrated in Figure 1. The Miller indices of the reflections are indicated.

![Figure 1. XRD spectrum of the as-synthesized TiO\textsubscript{2} NPs. The Miller indices of the reflections are indicated.](https://doi.org/10.1021/acsomega.1c01458)
expressed as the relationship between the peak width and the crystallite size, as shown below

\[
\tau = \frac{K\lambda}{\beta \cos \theta}
\]  

(2)

where \( \tau \) is the average crystallite size of the solid particle, \( K \) is the Scherrer constant (0.9), \( \lambda \) is the X-ray wavelength (0.154 nm), and \( \beta \) is the full width at half maximum intensity. The (101) peak at \( 2\theta = 25.29^\circ \) is the most intense reflection, Figure 1. The \( \tau \) value estimated from this was 9.36 nm. This value shows that the calcined TiO\(_2\) NPs have a smaller crystallite size than pure anatase TiO\(_2\) (12.96 nm).\(^{24}\)

### 3.2. FTIR Analysis

Figure 2 displays the FTIR spectrum of TiO\(_2\) NPs. A wide absorbance between 3500 and 3250 cm\(^{-1}\) in the FTIR spectrum, attributed to –OH stretching of TiO\(_2\) NPs, was observed, demonstrating the presence of absorbed water.\(^{23}\)

The prominent peak at 1629 cm\(^{-1}\) is from the bending of adsorbed water Ti–OH, and the weaker peak at 1386 cm\(^{-1}\) is assigned to the stretching vibrations of Ti–O modes. The peak at 554 cm\(^{-1}\) corresponds to a Ti–OH bond.\(^{26–28}\) These results verified the successful synthesis of TiO\(_2\) NPs using a green approach.

### 3.3. Microstructure and Morphology

The morphology and the presence of specific elements in plain cork and the optimized TiO\(_2\)/PVA/cork floating photocatalyst were studied by SEM–EDX analysis. The SEM image of plain cork, in Figure 3a,b, shows porous and cellular structures of hexagonal shape in a honeycomb arrangement. The SEM image of the TiO\(_2\)/PVA/cork floating photocatalyst is given in Figure 3c,d. Figure 3d shows the appearance of spherical TiO\(_2\) NPs on the surface. Based on the FESEM image of TiO\(_2\) NPs from our previous work, the size of TiO\(_2\) NPs was measured as 64.19 ± 2.6 nm. These data were further confirmed with high-resolution transmission electron microscopy analysis that showed the size of TiO\(_2\) NPs to be in the range of 20–70 nm.\(^{29}\) EDX data of the TiO\(_2\)/PVA/cork floating photocatalyst, summarized in Table 1b, show the presence of Ti (1.69 wt %) and increased O content (31.98 wt %) as compared to the untreated cork in Table 1a. This observation indicates that the TiO\(_2\) NPs are distributed on the surface of the floating photocatalyst.

### 3.4. Optical Spectroscopy

The optical properties of the TiO\(_2\) NPs were determined by UV–vis DRS. The absorption spectrum of the synthesized TiO\(_2\) NPs is shown in Figure 4, and the inset of Figure 4 shows the band gap evaluated using Kubelka–Munk theory.\(^{29}\) The absorbance edge of the TiO\(_2\) NPs was red-shifted to a longer wavelength of 407 nm which corresponds to a band gap of 3.0 eV. Pure anatase TiO\(_2\) has a wide band gap of 3.2 eV, which restricts its application under visible light as it can only be activated by ultraviolet light irradiation.\(^{30}\) The band gap has been successfully reduced from 3.2 to 3.0 eV in the TiO\(_2\) NPs. The decrease in the band gap
energy could be due to the formation of new energy levels below the conduction band (CB) induced by Ti$_3^+$ ions and oxygen vacancies. Important, the shift in the band gap shows that the TiO$_2$ NPs could work in the visible light region during the photocatalysis process.

3.5. Photoluminescence Analysis. Photoluminescence (PL) emission was employed to investigate the transfer behavior of the electron–hole pairs in the TiO$_2$ NPs. The TiO$_2$ NPs are compared with anatase TiO$_2$ in Figure 5, at an excitation wavelength of 300 nm. The profile of the emission spectra showed that each sample has the highest intensity around 420 nm, indicating the charge-transfer transition of Ti$^{4+}$. This observation is similar to that of Mathew and co-workers who reported that the highest emission peak at 421 nm from surface-state emissions is due to the recombination of trapped electron–hole pairs in TiO$_2$ NPs. The TiO$_2$ NPs showed a weaker PL signal, suggesting that it has a slower recombination rate of electron–hole pairs than bulk anatase TiO$_2$. It is postulated that the presence of Ti$^{3+}$ ions in the TiO$_2$ NPs acts as electron traps, to inhibit the recombination of electrons and holes. Thus, the lifetime of the charges increases, and this contributes to the enhanced photocatalytic performance, described below.

3.6. Zeta Potential (Isoelectric Point, IEP). The determination of the point of zero charge (pHpzc) is crucial to estimate the charge on the NPs during the photodegradation of contaminants. The zeta potential was analyzed using a suspension in distilled water at room temperature to predict the stability of TiO$_2$ NPs. The point where the zeta potential equals zero is the isoelectric point (IEP). The dispersion of semiconductor NPs in water or an organic solvent can cause the −OH surface groups to be protonated or deprotonated, forming surface-charged groups of −OH$_2^+$ or −O$^-$, respectively. For example, when the pH of working solution is lower than the IEP, it will form Ti−OH$_2^+$ and the surface obtains a positive charge (eq 3).

$$\text{Ti}−\text{OH} + \text{H}^+ \rightarrow \text{Ti}−\text{OH}_2^+ \quad \text{pH < IEP}$$

whereas Ti−O$^-$ will be formed if pH is higher than the IEP, and the surface obtains a negative charge (eq 4).

$$\text{Ti}−\text{OH} + \text{OH}^- \rightarrow \text{Ti}−\text{O}^- + \text{H}_2\text{O} \quad \text{pH > IEP}$$

Figure 6 presents the zeta potential of TiO$_2$ NPs versus the pH of the initial solution, indicating that the point of zero charge (pHpzc) or IEP of TiO$_2$ NPs was pH 5.57. Meanwhile, the MB solution had a pH of 5.99 which is higher than the IEP of TiO$_2$ NPs. The MB solution can be considered as a cationic dye. Since the TiO$_2$ NPs have a negative surface charge, electrostatic attraction occurred between them and the MB, promoting the smoothness of the photocatalytic process. The performance of the photocatalyst was significantly affected by the pH of the solution when photocatalysis took place on the surface of the NPs. The present results are in good agreement with those for TiO$_2$ NPs synthesized by the sol–gel method with titanium tetrachloride (TiCl$_4$) as a precursor. We observed an MB degradation efficiency of 93 and 97% at pH 7 and 10, respectively. The observed pH dependence can be attributed to the presence of negative charge on the surface of the TiO$_2$ NPs.

3.7. Photocatalytic and Adsorption Studies. 3.7.1. Evaluation of the Photocatalytic Activity of the TiO$_2$/PVA/Cork Floating Photocatalyst. The effect of different mole ratios of TiO$_2$/PVA on the photocatalytic activity of the TiO$_2$/PVA/cork floating photocatalyst was compared by determining the rate of photodegradation of MB under the visible light source. After 2 h of exposure to visible light, the percentage degradation of the MB solution for mole ratios of 1:6, 1:8, and 1:10 of TiO$_2$/PVA were 95.47, 98.43, and 92.73%, respectively, as illustrated in Figure 7. Therefore, the floating photocatalyst with the 1:8 TiO$_2$/PVA mole ratio showed better photodegradation performance than those with 1:6 and 1:10 ratios.

The floating photocatalyst with the lowest mole ratio of TiO$_2$/PVA (1:6) showed a decline in degradation efficiency. This observation was attributed to the low PVA content, which reduced the probability of TiO$_2$ NPs being incorporated on the surface when photocatalysis took place on the surface of the NPs. The e–f$^{+}$f$^{*}$ efficiency of MB under the irradiation of the light source with TiO$_2$/PVA mole ratios of 1:6, 1:8, and 1:10 (n = 3) was 93 and 97% at pH 7 and 10, respectively.
The enhancement in the photocatalytic activity was also attributed to the role of Ti$^{4+}$ ions as electron traps, thereby reducing the rate of electron–hole pair recombination as reported by Zhou and co-workers. This behavior enhances the high photodegradation performance. The PL measurements presented in Section 3.5 indicated that the TiO$_2$ NPs have lower intensity than bulk anatase TiO$_2$, confirming slower charge transfer. Furthermore, the synthesis of TiO$_2$ NPs by a sol–gel method proved to be an effective strategy to extend the absorption of TiO$_2$ to the visible light region, reducing the band gap to 3.0 eV. The high surface area of active sites exposed to the light irradiation could also boost the photodegradation performance. Overall, we found that the TiO$_2$/PVA/cork was an active floating photocatalyst when illuminated by a visible light source.

### 3.7.2. Photocatalytic Activity under a Visible Light Source and Sunlight

For comparison, the performance of the optimized TiO$_2$/PVA/cork floating photocatalyst was evaluated under sunlight and visible light irradiation for 2 h. In both cases, a noticeable change in the solution color was observed, indicating the change in the MB concentration. Sunlight is composed of the visible light, infrared (IR), and UV light and contains more infrared (55%) than visible light (43%). In contrast, the visible light source provides predominantly visible light with very little IR and UV radiation. Therefore, the higher degradation efficiency of MB was 98.43% under visible light irradiation compared to sunlight (77.09%) in Figure 9 as the absorption of TiO$_2$ sample falls in the visible light region.

The greater photodegradation rate of MB was obtained under the irradiation of the visible light source (0.0336 min$^{-1}$) compared to sunlight (0.0114 min$^{-1}$), as shown in Figure 10. This observation was similar to the $R^2$-value, whereby the obtained values for visible light irradiation (0.9582) were higher than those for sunlight (0.9421), as shown in Table 3. As observed in Section 3.7.1, the photodegradation of MB showed first-order reaction kinetics. These results gave further evidence that the photocatalytic degradation under visible light irradiation was better than sunlight irradiation.

Both light intensity and radiation wavelength influenced the photodegradation rate of the pollutants. In this work, the luminosity for sunlight was 80–90 klux, whereas for the visible light source, it was 100–110 klux, indicating a higher penetration of visible light into the MB solution. Consequently, it activated the catalyst on the surface and increased the degradation rate. This is in good agreement with Ahmed and co-
workers who reported that the degradation efficiency of MB increased from 82.97 to 99.90% with an increase in visible light intensity from 43.4 to 176 mV cm$^{-2}$, respectively, when employing Fe–Ni/SiO$_2$ as the photocatalyst.

3.7.3. Mineralization Study. Since the MB removal based on the absorbance (discoloration) is insufficient to express the scope of its mineralization, IC analysis was also conducted. IC was performed to identify residual sulfate (SO$_4^{2-}$), since it has been previously reported that this is a good indicator for the mineralization of MB. A sulfur atom is at the center of the aromatic heterocycle in MB. Therefore, the presence of sulfate anions demonstrates the oxidative cleavage of the aromatic rings. The percentage of sulfate anions was 86.13 and 65.34% under visible light and sunlight, respectively, after 2 h of irradiation time, as shown in Table 3. However, the amount of sulfate generated was slightly less than the amount of MB removed as estimated by absorption spectroscopy due to the dye adsorption capability of the TiO$_2$/PVA/cork floating photocatalyst. This finding is consistent with a previous study, which reported a TiO$_2$/calcium alginate floating photocatalyst that degraded 88.97% of tartrazine dye with a low total organic carbon mineralization of 77.42% after 180 min under UV light irradiation. Additionally, 95% of MB was removed after 240 min of UV light irradiation with a TiO$_2$/LDPE floating photocatalyst; however, the mineralization was relatively low (35%). When compared to the studies mentioned above, the TiO$_2$/PVA/cork floating photocatalyst displayed the highest mineralization of MB under visible light irradiation for 2 h.

3.7.4. Adsorption Isotherm Analysis. The adsorption study is significant to provide a useful explanation of the interaction between adsorbent and dye molecules. It is applied to measure the maximum adsorption capability of the adsorbent. Therefore, the Langmuir and Freundlich isotherm models were introduced to analyze the MB adsorption data. Experimental results for the adsorption isotherms were obtained using eqs 5 and 6 for the Langmuir and Freundlich models, respectively.

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

(5)

$$\ln q_e = \ln K_f - \frac{1}{n} \ln C_e$$

(6)

For the Langmuir model, a graph of $C_e/q_m$ against $C_e$ was plotted as illustrated in Figure 11. The result showed that the value of maximum adsorption capacity ($q_m$) was 51.55 mg/g and the Langmuir adsorption equilibrium constant ($b$) was 5.24 L/mg. For the Freundlich model, the graph of $\ln q_e$ against $\ln C_e$ was plotted, as illustrated in Figure 12. The values of the adsorption capacity ($K_f$) and adsorption intensity ($n$) were 44.23 mol g$^{-1}$ and $-2.845$, respectively.

![Figure 10. First-order linear transform ln($C_0/C_t$) of MB degradation plots against time for the irradiation of the visible light source and sunlight with a mole ratio of 1:8.](image)

![Figure 11. Langmuir isotherm showing the variation of adsorption ($C_e/q_m$) against the equilibrium concentration ($C_e$) for adsorption of the TiO$_2$/PVA/cork floating photocatalyst.](image)

![Figure 12. Freundlich isotherm showing the variation of adsorption (ln $q_e$) against the equilibrium concentration (ln $C_e$) for adsorption of the TiO$_2$/PVA/cork floating photocatalyst.](image)

Table 3. Rate Constants, Correlation Coefficients, and Percentage Degradation of MB for Mole Ratios of TiO$_2$/PVA, 1:8 under Irradiation of Sunlight and the Visible Light Source

| type of irradiation of light | rate constant, $k$ (min$^{-1}$) | $R^2$ | degradation of MB (%) | mineralization, SO$_4^{2-}$ content (%) |
|-----------------------------|----------------------------------|-------|------------------------|----------------------------------------|
| sunlight                    | 0.0114                           | 0.9421| 77.09                  | 65.34                                  |
| visible light               | 0.0336                           | 0.9582| 98.43                  | 86.13                                  |
NPs have higher active sites, and thus, it could lead to higher adsorption capacity of the MB molecules.\textsuperscript{3,43}

The $R_l$ value was calculated as 0.202 by applying eq 7. Since the value of $R_l$ was within the range of 0 and 1.0, it was defined as a favorable adsorption isotherm.

$$R_l = \frac{1}{1 + bC_e} \quad \text{(7)}$$

3.8. Scavenging Study. Reactive oxygen species (ROS) such as the photogenerated holes (h\textsuperscript{+}), electrons (e\textsuperscript{-}), and hydroxyl radicals (\textsuperscript{\cdot}OH) are notable in the photodegradation of MB. Methanol (MeOH), silver nitrate (AgNO\textsubscript{3}), acetonitrile (ACN), sodium pyruvate (C\textsubscript{3}H\textsubscript{3}NaO\textsubscript{3}), and ascorbic acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{6}) were used as scavengers for the photogenerated holes (h\textsuperscript{+}), superoxide radicals (\textsuperscript{\cdot}O\textsubscript{2}\textsuperscript{-}), hydroxyl radicals (\textsuperscript{\cdot}OH), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), and singlet oxygen (\textsuperscript{\cdot}O\textsubscript{2}), respectively. Figure 13 depicts the free radical scavenging results. Comparison of the degradation between the absence and presence of scavengers demonstrated that AgNO\textsubscript{3} remarkably restricted the degradation of MB. The use of AgNO\textsubscript{3} showed the highest reduction (70.02%) in the photodegradation of MB followed by C\textsubscript{6}H\textsubscript{8}O\textsubscript{6} (77.23% of MB removal), C\textsubscript{3}H\textsubscript{3}NaO\textsubscript{3} (80.21% of MB removal), MeOH (92.04% of MB removal), and ACN (93.96% of MB removal). Thus, this observation verified that the \textsuperscript{\cdot}O\textsubscript{2}\textsuperscript{-} played a dominant role in the photodegradation of MB.

3.9. Proposed Mechanism of Methylene Blue Degradation. Efficient charge separation is the predominant element to measure the photocatalytic performance of a semiconducting photocatalyst. Therefore, it is significant to determine the value of the CB and valence band (VB) potentials of the TiO\textsubscript{2} photocatalyst using the following equations\textsuperscript{44}

$$E_{VB} = \chi + 0.5E_g - E^e$$  \hspace{1cm} \text{(8)}

$$E_{CB} = E_{VB} - E^e$$  \hspace{1cm} \text{(9)}

where $E_{CB}$ and $E_{VB}$ are CB and VB edge potential, respectively, $\chi$, $E^e$, and $E_g$ represent the electronegativity of the semiconductor, the free electrons energy on the hydrogen scale (4.5 eV), and the band gap energy of the semiconductor, respectively. The electronegativity of TiO\textsubscript{2} is calculated as follows

$$\chi = [\chi(A)^a \chi(B)^b \chi(C)^c]^{1/(a+b+c)} \quad \text{(10)}$$

where $a$, $b$, and $c$ represent the number of the atoms in the compound, whereas the electronegativity of the Ti and O atoms is calculated as the atomic electron affinity and the first ionization energy. The value of $\chi$ of TiO\textsubscript{2} is determined to be 5.82. $E_{CB}$ and $E_{VB}$ are estimated to be $-0.18$ and $+2.82$ eV, respectively.

The findings obtained from the scavenging study can be used to propose a potential mechanism of MB photodegradation, whereby the \textsuperscript{\cdot}O\textsubscript{2}\textsuperscript{-} plays a dominant role in photodegradation of MB, followed by \textsuperscript{1}O\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, and *OH. Initially, the light irradiation activates the TiO\textsubscript{2} NPs causing migration of electrons from the VB to the CB and subsequently forming positively charged holes in the VB \textsuperscript{11}. The photogenerated electrons and holes create ROS, whereby the e\textsubscript{CB}\textsuperscript{-} reacts with adsorbed O\textsubscript{2} to form \textsuperscript{\cdot}O\textsubscript{2}\textsuperscript{-} (superoxide anion), eventually generating H\textsubscript{2}O\textsubscript{2} due to the combination of the strong oxidative species (\textsuperscript{\cdot}O\textsubscript{2}) with H\textsuperscript{+} from the solution \textsuperscript{12} and \textsuperscript{13}. Then, \textsuperscript{\cdot}O\textsubscript{2}\textsuperscript{-} will degrade MB molecules into harmless products such as CO\textsubscript{2} and water \textsuperscript{14}. The photoinduced reduction of H\textsubscript{2}O\textsubscript{2} generates hydroxyl radicals (\textsuperscript{\cdot}OH) that are responsible for the MB degradation \textsuperscript{15}. Meanwhile, the photogenerated holes (h\textsuperscript{+}) are predicted to produce hydroxyl radicals (\textsuperscript{\cdot}OH) which will degrade MB molecules into harmless products such as CO\textsubscript{2} and water \textsuperscript{16} and \textsuperscript{17}. Additionally, singlet oxygen (\textsuperscript{\cdot}O\textsubscript{2}) species are generated by the reaction of h\textsuperscript{+} with \textsuperscript{\cdot}O\textsubscript{2}\textsuperscript{-}, which subsequently degrade MB \textsuperscript{18}.\textsuperscript{45} Furthermore, h\textsuperscript{+} also can degrade MB directly \textsuperscript{19}. This observation indicates that the generated free radicals including \textsuperscript{\cdot}O\textsubscript{2}, \textsuperscript{1}O\textsubscript{2}, and \textsuperscript{\cdot}OH can degrade MB molecules into harmless products such as CO\textsubscript{2} and water due to their feature as strong oxidizing agents.\textsuperscript{46}

A localized gap of Ti\textsuperscript{3+} is formed below the CB. Then, the electron can be trapped by Ti\textsuperscript{3+} to create an isolated Ti\textsuperscript{3+} (eq \textsuperscript{20}). The Ti\textsuperscript{3+} sites react with O\textsubscript{2} and form \textsuperscript{\cdot}O\textsubscript{2}\textsuperscript{-} which assists in the photodegradation of MB \textsuperscript{21}. Based on our previous work, X-ray photoelectron spectra data showed the existence of Ti\textsuperscript{4+} and Ti\textsuperscript{3+},\textsuperscript{12,47} suggesting the occurrence of self-doped TiO\textsubscript{2} with the presence of Ti\textsuperscript{3+}. In addition, the localized gap of Ti\textsuperscript{3+} is attributed to shallowly trapped electrons that can improve the transfer efficiency of electrons and lead to the enhanced lifetime of the photogenerated carriers.\textsuperscript{48,49} Therefore, the behavior of photogenerated charge carriers on the photocatalyst either predominantly present as free and shallowly trapped electrons or as deeply trapped electrons and holes in TiO\textsubscript{2} was identified by femtosecond to millisecond time-resolved visible to mid-IR absorption spectroscopy. In our study, an in-house-built spectrometer was employed.\textsuperscript{20} Figure 14 shows the transient absorption spectrum of the as-synthesized TiO\textsubscript{2} NPs, revealing that the intensity of free and shallowly trapped electrons (<3000 cm\textsuperscript{-1}) was higher than that of the deeply trapped electrons (>4000 cm\textsuperscript{-1}). The depth of the electron trap is predicted to be much shallower than 0.1 eV due to the fact that strong absorption was observed at the low wavenumber limit at 1000 cm\textsuperscript{-1}.\textsuperscript{50} Furthermore, this observation showed the high number of surviving free electrons (<3000 cm\textsuperscript{-1}) in the microsecond region. This observation suggests that the free and shallowly trapped electrons were generated even under visible light irradiation. These charge carriers could survive longer than a few milliseconds. Hence, they could induce the photocatalytic reactions observed in this work that could be attributed from slower recombination of electron and hole rates.

The possible pathway for the degradation of MB is illustrated in 11 and Scheme 1.
3.10. Reusability of the TiO$_2$/PVA/cork Floating Photocatalyst. Photocatalyst recycling capacity is a crucial requirement in wastewater treatment applications. The development of immobilized TiO$_2$ NPs on the floating substrates (cork) has been suggested to overcome the filtration issue. Therefore, recycling and stability tests of the floating photocatalyst were evaluated by conducting five cycles of photocatalytic activities under visible light irradiation. Figure 15 depicts that the degradation efficiency was at 78.13% after five cycles. The slight decline occurred after the first cycle due to the fixation of MB on the surface of the photocatalyst which could block the active sites and might also be due to loss of TiO$_2$ NPs from the cork surface.$^{26,51}$ The loss of catalyst materials might take place during the washing and filtration process.$^{35}$ However, this observation proved that the floating photocatalyst has good recycling performance due to a good binder of PVA and could be reused five times.

4. CONCLUSIONS

A TiO$_2$/PVA/cork floating photocatalyst was developed by applying PVA as a binder to bind TiO$_2$ NPs to cork. The optimal mole ratio of TiO$_2$/PVA (1:8) showed higher percentage degradation of MB, 98.43% under visible light irradiation as compared to 77.09% under sunlight. Besides, the benefit of low band gap energy (3.0 eV) contributed to the high photo-degradation performance of MB also in the visible light region. The reason for this good trait was the presence of surface defects (Ti$^{3+}$ and oxygen vacancies) in TiO$_2$ NPs. Furthermore, the O$_2$\(^{-}\) anion was identified as the main ROS for degrading MB. Other features of the TiO$_2$/PVA/cork floating photocatalyst, such as easy separation from the treated aqueous system and its good reusability (78.13% of MB removal after five cycles), contributed to various prospects in the photocatalytic applications, especially under the irradiation of a visible light source. Our unique floating photocatalyst can be dedicated to other potential model pollutants such as pesticides and phenols.

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Figure 14. Transient absorption spectrum of the as-synthesized TiO$_2$ NPs measured in 20 Torr N$_2$ after 450 nm laser pulse (5 mL/pulse at 5 Hz) irradiation. The negative signal at 3500–2800 cm$^{-1}$ is due to the desorption of water.

Figure 15. Reusability test of the TiO$_2$/PVA/cork floating photocatalyst (n = 3).
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