Immobilized carbon-doped TiO\(_2\) in polyamide fibers for the degradation of methylene blue

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**ABSTRACT**
The discharge of dyes in the textile industry leads to several hazardous effects on the environment. One of the most effective methods on treating dye-contaminated wastewater is photocatalytic degradation. TiO\(_2\) has been widely used as a photocatalyst for wastewater treatment. Since the light absorption of TiO\(_2\) is in the UV light range, however, doping of TiO\(_2\) with a non-metal or metal element is needed to improve its absorption in the visible light range. In this study, TiO\(_2\) photocatalyst was doped with carbon using sucrose as a carbon+electron ratio of 0.75:1 and 1:1. The surface area of TiO\(_2\) after doping with carbon improved to two times the TiO\(_2\) surface area. Additionally, the band gap energy of TiO\(_2\) was successfully reduced to 2.38 eV after doping with carbon. In order to avoid the secondary pollutant problems, the carbon-doped TiO\(_2\) was then immobilized with polyamide fibers at 1 wt%, 2 wt% and 3 wt% to facilitate recollection of the photocatalyst. A photodegradation test was performed by degrading methylene blue under visible light irradiation using 70 W halogen lamps with a total of 5 hours of time interval readings. The highest percentage degradation was recorded at 82.67% using immobilized 2 wt% 1:1 carbon-doped TiO\(_2\) in polyamide fibers.

**1. Introduction**

Textile effluents contain a large variety of dyes and chemical substances which raise environmental challenges for effective treatment [1]. In recent years, emissions of pollutants are increasing, especially from textile factories which release several hazardous dyes and cause serious environmental problems that affect human health and aquatic life [1]. Furthermore, dyes released into a water source impede light penetration, retard photosynthesis...
activity, and contaminate drinking water, which making it unfit for human consumption [1].

Photocatalysis is considered to be one of the most effective techniques for degrading aqueous phase impurities, either chemical or biological [2]. Titanium dioxide (TiO$_2$) is one of the most studied photocatalysts amongst the other elements because of its photo-stability, relatively low cost, and low toxicity as well as its ease of production and use [3,4]. Titanium dioxide also has high chemical stability when exposed to acidic and basic compounds [5]. However, titanium dioxide has its own major drawbacks as well, one of which is a wide bandgap that responds only to ultraviolet light that has a wavelength below 387 nm and allows absorption of only a small portion of the solar spectrum [6]. Additionally, titanium dioxide has a low quantum yield of excitations between electron-holes which lead to fast recombination and consequently reduce its catalytic activity for removal of harmful pollutants in waste water treatment [7].

One countermeasure that can be taken to enhance its visible-light photocatalytic activity is doping of TiO$_2$ with metal ions such as Cu, Co, Ni, Cr, Mn, Fe, or Au, or with non-metal ions such as B, N, C, S, F, P or I which can lead to successful methods of narrowing the band gap and improving the electron-hole separation under visible-light irradiation [8]. Nevertheless, metal-ion dopants have the negative effect of causing thermal instability of the catalyst, and they are also often toxic, which leads to a high possibility of producing secondary water contamination. Therefore, the most favourable and best type of dopant for use as an alternative for increasing photocatalytic activity is a non-metal dopant. Previous research on the use of carbon as a dopant or additive in TiO$_2$ systems have been widely performed to degrade organic pollutants such as methylene blue [9], methyl orange [10,11], bisphenol A [10], rhodamine B [12–15], p-nitrophenol [16], dimethylhydrazine [17], ciprofloxacin [18], rosebengal dye [19], tetracycline hydrochloride [20], ammonia nitrogen [21], and stearic acid [22]. The doping of carbon in the TiO$_2$ matrix could narrow the band gap through modification of the electronic band structure of TiO$_2$ by forming a valence band-tail state [23]. Carbon is also known to increase the surface area, act as a photosensitizer to transport photogenerated electrons to the conduction band, and adsorb organic pollutants on photocatalysts [23].

The immobilization of photocatalysts on substrates has been widely performed to facilitate the recollection of materials and avoid secondary pollutant problems, which involve the escape of photocatalysts into a water environment [24]. The immobilization of carbon-doped TiO$_2$ on a support has been performed using carbon nanofibrous film [14], a metal organic framework (MOF) [15], and activated carbon [25]. The support materials help TiO$_2$ in degrading pollutants by improving adsorption, and also by adding other functions to a system such as stability, mechanical strength, and reusability [14].

Polyamide is a widely used polymer in the textile industry due to its excellent properties such as high impact resilience, toughness, high flexibility, and excellent resistance to abrasion, organic solvents and water [26]. The immobilization of TiO$_2$ in polyamide affects its properties and functions, including its photocatalytic performance, surface area, and adsorption. This technique also eliminates the need to separate the catalyst particles from treated wastewater and allows contaminated water to be treated constantly. A previous study on immobilizing carbon-doped TiO$_2$ in polyvinyl pyrrolidone (PVP) fibers was conducted by Mondal et al. [27] to degrade naphthalene; an improvement in degradation was shown when carbon-doped TiO$_2$ was immobilized in PVP fibers. In this study, polyamide was used as polymeric fiber support for carbon-doped TiO$_2$. A previous study by Zhang et al. [28] utilizing polyamide fibers to immobilize Fe-doped TiO$_2$ showed the improvement of methylene blue degradation under sunlight and UV irradiation. Additionally, polyamide fibers provide composites with mechanical strength, such as improved breaking force and elongation [28].

In past decades, electrospinning was an extensively used technology for electrostatic fiber formation which utilized electrical forces to provide polymer fibers with various diameters ranging from 2 nm to numerous micro-meters [29]. In this study, the electrospinning method was utilized to synthesize polyamide fibers with embedded carbon-doped TiO$_2$. TiO$_2$ was doped with carbon to improve its light absorption in the visible light spectrum, and immobilized in polyamide fibers to avoid secondary pollutant problems. The product was then used to degrade methylene blue as a model for organic pollutants. The doping with carbon showed increasing absorbance of light by TiO$_2$ in the higher visible light range, followed by increases in the surface area and degradation of methylene blue under irradiation from the visible light source.

2. Methodology

2.1. Materials

Titanium tetraisopropoxide (TTIP), C$_2$H$_5$OH (absolute ethanol), HNO$_3$, sucrose, polyamide 6 (MW: 262.35 g/mol), formic acid, acetic acid, and methylene blue were purchased from Sigma Aldrich (USA).

2.2. Preparation of carbon-doped TiO$_2$ nanoparticles

TiO$_2$ and carbon-doped TiO$_2$ nanoparticles were synthesized using a hydrothermal technique. The TTIP, C$_2$H$_5$OH, HNO$_3$ and sucrose as a carbon source were used as raw materials. The detailed process can be described as
follows: 8 ml of TTIP was added to an ethanol and distilled water mixture under constant stirring conditions. Sucrose as a carbon source was then dissolved in the TTIP solution at ratios of 1:0.75 and 1:1 with respect to the weight of TiO$_2$. After adjusting the pH value of the solution to 6–7, the mixture was entered into the autoclave and heated at 200°C for 5 hours. The suspended solid was then filtered and washed a few times with distilled water. After washing, the suspended solid was dried overnight at 180°C. The solid precipitate was then calcined at a temperature of 400°C for 3 hours in a furnace.

### 2.3. Synthesis of immobilized carbon-doped TiO$_2$ in polyamide fibers

A polymer solution was prepared by mixing formic acid (99.9%–100% pure) and glacial acetic acid (98%–100% pure) at a ratio of 1:1, followed by adding 14 wt% polyamide 6 pellets to the solution under stirring at 180 rpm at 60°C overnight to achieve homogenous mixing. The polymer solution was then placed in a commercial syringe (10 mL) fitted with a steel needle with a constant diameter (1 mm). An electrospinning process was conducted at a constant high voltage of 20 kV (Glassman PS/FC30P04, USA). A syringe pump (Syringepump, USA) was used to feed the polymer solution into the needle tip at a rate of 0.4 mL/hr, and the electrospun fibers were collected using an aluminium sheet. The distance between the needle and collector was kept at a constant 15 cm. The immobilization of carbon-doped TiO$_2$ in polyamide 6 fibers was prepared by varying the concentration of carbon-doped TiO$_2$ (1 wt%, 2 wt% and 3 wt%). The carbon-doped TiO$_2$ was dispersed in the polymer solution under constant stirring. The photocatalyst samples were abbreviated as seen in Table 1.

### 2.4. Analysis

The surface morphologies of carbon-doped TiO$_2$ nanoparticles and polyamide fibers were examined using field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) (Ultra 55 Carl Zeiss, Germany). The band gap energy of the photocatalyst was determined using a Lambda 35 UV-Vis diffuse reflectance spectrophotometer (DRS) (Perkin Elmer, USA) at wavelengths of 280–800 nm. Fourier-transform infrared spectroscopy (FT-IR) analysis (Perkin Elmar Spectrum One, USA) was conducted to investigate the functional groups contained in the photocatalyst and recorded in the 4000–500 cm$^{-1}$ range. The crystallinity and phases of the samples were characterized with X-ray diffractometer (XRD) spectroscopy using a XPert$^2$ Powder & Empyrean PANalytical with Cu Ka irradiation ($\lambda$ = 1.54), at diffraction angles (20) from 10° to 70°, step size of 0.01°/step, and an exposure time of 1s/step. The surface area and pore size of the samples were analysed using N$_2$ physisorption analysis. The samples were degassed at 200°C, followed by N$_2$ adsorption-desorption isotherm measurements at −196°C (Micromeritics ASAP 2020, USA).

### 2.5. Degradation of methylene blue

The photocatalytic reaction was conducted through degradation of methylene blue under visible light radiation in an apparatus constructed in house. The visible light was provided by two 70 W halogen lamps (Philips, Netherlands). 0.1 g of the photocatalyst was added to 70 mL (5 ppm) of methylene blue under vigorous magnetic stirring. The photocatalyst solution was left in the dark for 30 min to reach an adsorption-desorption equilibrium of methylene blue. At 30, 60, 120, 180, 240 and 300 min time intervals, 5 mL of the solution was taken out and centrifuged at 4000 r/min for 5 min for testing for methylene blue degradation using a UV-Vis spectrophotometer at 664 nm. Comparative trials were carried out under the same conditions using polyamide fibers and immobilized carbon-doped TiO$_2$ in polyamide. The percentage degradation of methylene blue can be calculated using the below equation:

$$\text{% degradation} = \frac{C_0 - C_t}{C_0} \times 100\%$$

where $C_0$ is the initial concentration and $C_t$ is the concentration at different time intervals.

The weight of the fibers was measured after usage to determine the loss of composite during the experiment. The recyclability of composite fibers was determined for the Polyamide-2 wt% C/TiO$_2$ (1:1) due to its superior performance. The composite was regenerated by soaking in DI water for 1 hour, a process that was repeated two times, followed by drying at 40°C overnight after usage. The regenerated composite was then used for degradation of methylene blue. This experiment was repeated five times to observe the recyclability of the composite.

### 3. Results and discussion

#### 3.1. Structure and functional groups

The crystallinity of TiO$_2$ and the carbon-doped TiO$_2$ samples are shown in Figure 1(a). Highly crystalline anatase TiO$_2$ was formed for all the TiO$_2$ samples as shown by the sharp peaks, where the addition of
carbon did not change the phase of TiO$_2$. Anatase peaks can be found at 2$\theta$ positions of 25.57°, 38.24°, 48.28°, 54.9° (duplet), and 63° which represent the direction of [101], [004], [200], [105] and [211], and [204] [30–32]. This result shows close agreement with previous studies on carbon-doped TiO$_2$, in which formation of anatase was found with or without the presence of carbon [12]. The addition of carbon to favour the formation of anatase was also shown in previous studies [11,12,17,20], where the addition of carbon improved anatase formation and inhibited rutile formation. Figure 1(b) shows specifically in the diffraction range between 23° and 28°. It is apparent that there is a slight shifting of the peak [101] to a higher degree for carbon-doped TiO$_2$ which indicates doping with carbon by replacing the oxygen atom in TiO$_2$ [11,17,18].

This result is supported by FTIR analysis in Figure 2(a). The functional groups of bending vibrations of Ti-O-Ti and bending vibrations of OH groups adsorbed onto the TiO$_2$ surface are shown for all the samples by peaks at 743 cm$^{-1}$ and 1621 cm$^{-1}$, respectively [33,34]. Carbon-doped TiO$_2$ samples show an additional peak at 1714 cm$^{-1}$, which can be attributed to stretching of the C = O bond [35,36]. Interestingly, the intensity of the Ti-O-Ti peak in C/TiO$_2$ (1:1) starts to decrease and a peak appears at 1070 cm$^{-1}$, which can be attributed to Ti-O-C [20,35,36]. Hence, the bonding of TiO$_2$ and C was induced by increasing the addition of carbon to TiO$_2$.

When carbon-doped TiO$_2$ was immobilized in polyamide fibers, FTIR analysis observed only the functional groups of polyamide (Figure 2(b)), where the peaks at 3302 cm$^{-1}$ and 3301 cm$^{-1}$ were attributed to N-H stretching. TiO$_2$ in the polymer matrix can be shadowed or covered by polyamide, and hence the functional groups of TiO$_2$ are not visible in the composite system.

### 3.2. Morphology and surface area

The morphologies of synthesized TiO$_2$ and carbon-doped TiO$_2$ are shown in Figure 3. A granular nanoparticle shape is shown for all the samples, where the size ranges from 14–17 nm. The granular nanoparticle shapes are irregular and agglomerated. The EDS analysis (Figure 3(f)) for carbon-doped TiO$_2$ with a sucrose-to-TiO$_2$ ratio of 1:1 shows the existence of carbon peaks with atomic ratios of the elements of 7.97% C, 26.39% Ti, and 65.63% O. This result is supported by FTIR and XRD analyses, which show the bonding of carbon with TiO$_2$. The shapes and sizes of the nanoparticles produced in this study using sucrose are similar to results obtained with previous methods using different carbon sources such as phloroglucinol, resorcinol, glycerol, ethylene glycol [13], and pine cone [20]. The electrospun polyamide fibers are shown to be smooth fibers without a beaded formation in Figure. 4(a,b). When the carbon-doped TiO$_2$ was electrospun with polyamide, nanoparticles can be seen to be present extensively alongside the surface of the fibers (Figure. 4(c–e)). The
agglomeration of coarse particles can be observed in Figure 4(e), which shows the presence of carbon-doped TiO$_2$ on the surface of the fibers and creates coarse surface of fibers. This can be caused by higher viscosity of the polymeric solution when the nanoparticles are added and spun [37]. The existence of carbon-doped TiO$_2$ in polyamide fibers can be detected using EDS analysis where atomic percentages of carbon, titanium, and oxygen were found at 8.36%, 22.05%, and 69.6%, respectively (Figure 4(f)). The particle size of carbon-doped TiO$_2$ shows a range of 15–18 nm (Figure 4(d)). Surface area analysis of the samples shows type IV isotherms with hysteresis loops for desorption and adsorption, especially for C/TiO$_2$ (1:1) (Figure 5(a,c,e)), which indicates a mesoporous character. The surface area values for TiO$_2$, C/TiO$_2$ (0.75:1), and C/TiO$_2$ (1:1) are 48.36 m$^2$/g, 39.1 m$^2$/g, and 101 m$^2$/g, respectively. The surface area improved by more than two times with the addition of sucrose at a 1:1 ratio to TiO$_2$. Similar results for improvement in surface area with carbon-doping were found for ZnO and TiO$_2$ in previous studies, which might be caused by restrained growth of TiO$_2$ in the presence of carbon [11,38,39]. It is known that materials with higher surface areas provide better photocatalytic efficiency in terms of surface reaction performance by providing more reaction sites [17,40]. The pore volume of TiO$_2$ also increased when carbon was doped, with the values observed at 0.057 cm$^3$/g, 0.053 cm$^3$/g, and 0.21 cm$^3$/g for TiO$_2$, C/TiO$_2$ (0.75:1), and C/TiO$_2$ (1:1), respectively. The pore size values for the samples were recorded at 5.13 nm, 5.8 nm, and 8.36 nm for TiO$_2$, C/TiO$_2$ (0.75:1), and C/TiO$_2$ (1:1), respectively. Higher pore volume values give higher adsorption sites for pollutants to be adsorbed on the surfaces of photocatalysts [12].

### 3.3. Photocatalytic degradation

The effect of carbon addition on the light absorbance of TiO$_2$ is shown in Figure 6. Doping with carbon improved the sensitivity of TiO$_2$ in the visible light range by...
decreasing the band gap energy. Based on the Kubelka-Munk theory, the band gap can be determined from \((\alpha h\nu)^2\) vs \(h\nu\), where \(\alpha\) is the absorption coefficient, \(h\) is the Plank’s constant, and \(\nu\) is the frequency of radiation. The band gap values for TiO\(_2\), C/TiO\(_2\) (0.75:1), and C/TiO\(_2\) (1:1) are around 3.05 eV, 2.88 eV, and 2.38 eV, respectively. This may result from the presence of carbon as impurities in the TiO\(_2\) system, which induced intermediate states. These results show close agreement with those of previous studies where the optical response improved in the visible light range, allowing the material to utilize more photoenergy and generate more charges [18].

Figure 7 shows the results of photocatalytic decomposition of methylene blue over carbon-doped TiO\(_2\) prepared at different carbon ratios. It was found that the photocatalytic activity increased with increases in the sucrose-to-TiO\(_2\) ratio increased up to 1:1. The results for photocatalytic activity for TiO\(_2\) at 0.5 h (under dark stirring) and 1 h after the experiment show that there is no change in the concentration of the methylene blue solution; hence, no photodegradation has occurred yet between these two time intervals. The degradation for TiO\(_2\) started after 1 h, with 20% of the degradation found after 2 h of the experiment. The degradation kept increasing after 4 h, where it was 37.96%. After 5 h, 39.63% degradation was achieved. In comparison with TiO\(_2\), both samples of carbon-doped TiO\(_2\) showed better photodegradation performance. Carbon-doped TiO\(_2\) samples showed methylene blue removal even after only 0.5 h of the experiment (under dark stirring) with results of 18.15% and 21.51% for sucrose-to-TiO\(_2\) ratios of 0.75:1 and 1:1, respectively. The degradation then increased to 47.87% and 60.08% for sucrose-to-TiO\(_2\) ratios of 0.75:1 and 1:1, respectively, after 5 hours of the experiment. The degradation of methylene blue was improved when the ratio of sucrose increased from 0.75

**Figure 5.** N\(_2\) adsorption-desorption isotherms of (a) TiO\(_2\), (c) C/TiO\(_2\) (0.75:1), and (e) C/TiO\(_2\) (1:1). Pore size distribution of (b) TiO\(_2\), (d) C/TiO\(_2\) (0.75:1), and (f) C/TiO\(_2\) (1:1).
As can be seen from Figure 6, the light absorption of TiO$_2$ was extended to the visible light range when carbon was loaded, with the band gap reduced from 3.05 eV to 2.38 eV. The extension of light absorption caused more electrons to become excited to the conduction band under visible light irradiation, which improves the degradation of methylene blue [15]. This result shows close agreement with previous research on incorporating carbon into the TiO$_2$ matrix [15,41,42]. Since C/TiO$_2$ (1:1) shows the highest degradation of methylene blue, it is then immobilized in polyamide fibers at 1 wt%, 2 wt%, and 3 wt%, as shown in Figure 8. In determining the adsorption ability of polyamide, adsorption started after 0.5 h for 10.62% and achieved 32.12% after 5 h of adsorption. When carbon-doped TiO$_2$ was incorporated into polyamide fibers, increased degradation of methylene blue was observed due to the photocatalytic effect. The degradation of methylene blue reached 74.4%, 82.67%, and 79.5% for 1 wt%, 2 wt%, and 3 wt% addition of carbon-doped TiO$_2$. It can be seen that the highest degradation was found at 2 wt% carbon-doped TiO$_2$ (C/TiO$_2$ (1:1)). The degradation experienced a slight decrease when the amount of carbon-doped TiO$_2$ was increased to 3 wt%. This may be due to the agglomeration of photocatalyst particles, since it is a challenge to distribute the particles evenly during the electrospinning process. Immobilized carbon-doped TiO$_2$ in polyamide fibers shows better overall performance in photodegradation compared to a non-immobilized photocatalyst. The adsorption ability of polyamide helps the methylene blue to be adsorbed on the surface of the composite, which is then degraded by the carbon-doped TiO$_2$. The photodegradation of every photocatalyst sample fits the pseudo first-order kinetics, with $R^2$ values of 0.94, 0.87, 0.96, 0.94, 0.94, and 0.95 for TiO$_2$, C/TiO$_2$ (0.75:1), C/TiO$_2$ (1:1), polyamide, polyamide-1 wt% C/TiO$_2$ (1:1), polyamide-2 wt% C/TiO$_2$ (1:1), and polyamide-3 wt% C/TiO$_2$ (1:1), respectively.

### 3.4. Recyclability performance

Immobilization of C/TiO$_2$ (1:1) in polyamide fibers contributes to minimum loss of the composite, with around 93% of the composite recollectable after 5 hours of the experiment. This result supports the aim of immobilization, which is to facilitate the recollection of the composite and minimize its loss. The recyclability of composite fibers in Figure 9 shows excellent performance of the material, where 58.7% methylene blue degradation can
still be achieved after reuse of the composite fibers in five experiments.

4. Conclusion

TiO$_2$ is one of the most effective photocatalysts used in wastewater treatment since it provides the benefits of low-toxicity, chemical stability and environmental friendliness. Doping of TiO$_2$ with carbon improved its surface area from 48.36 m$^2$/g to 101 m$^2$/g. The morphologies of nanoparticles with sizes ranging from 14–18 nm were observed for TiO$_2$ and carbon-doped TiO$_2$. The band gap of TiO$_2$ was reduced from 3.05 eV to 2.38 eV, making the photocatalyst more sensitive to the visible light range. The photodegradation of methylene blue reached 60.08% for carbon-doped TiO$_2$ after 5 hours of the experiment. This performance was successfully increased by immobilizing carbon-doped TiO$_2$ in polyamide fibers, due to the adsorption ability of the fibers. The photodegradation of methylene blue achieved 82.67% when 2 wt% carbon-doped TiO$_2$ was embedded in polyamide fibers. Thus, immobilization of carbon-doped TiO$_2$ in polyamide fibers is an effective method for use in wastewater treatment.

**Highlights**

- Doping of TiO$_2$ with carbon improved the surface area of TiO$_2$ to 101 m$^2$/g and the light response of TiO$_2$ to the visible light range with a band gap of 2.38 eV.
- Photodegradation of methylene blue was performed using a 70 W halogen lamp as a visible light source, where 60.08% degradation was achieved by carbon-doped TiO$_2$. 

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**Figure 8.** (a) Pseudo second-order kinetic model and (b) photodegradation profile of methylene blue using immobilized photocatalyst samples.

**Figure 9.** Recyclability of polyamide-2 wt% C/TiO$_2$ (1:1).
• Immobilization of carbon-doped TiO₂ in electrospun polyamide fibers improved the methylene blue degradation to 82.67%.

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