

Enhanced Photocatalytic Removal of Methylene Blue From Seawater Under Natural Sunlight Using Carbon-Modified n-TiO₂ Nanoparticles

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Abstract

In this study, photocatalytic removal of methylene blue (MB) from natural seawater was examined using carbon-modified titanium oxide (CM-n-TiO₂) nanoparticles under illumination of real sunlight. CM-n-TiO₂ nanoparticles exhibited significantly higher photocatalytic degradation efficiency compared to unmodified n-TiO₂. Photocatalytic removal studies were carried out at different initial dye concentrations (5-30 μM), catalyst dose (0.5-1.5 gL⁻¹), and pH (3-9). The highest removal rate of MB was obtained at the optimal conditions of pH 8 and 1.0 gL⁻¹ of CM-n-TiO₂. The solar photocatalytic removal of MB from seawater using CM-n-TiO₂ obeyed a pseudo-first order kinetics according to the Langmuir-Hinshelwood model.

Keywords: carbon modification, methylene blue, photocatalytic removal, seawater, titanium oxide

1. Introduction

The wastewater from the textile industry is rated as one of the most polluting amongst all industrial sectors, considering the volumes discharged and effluent composition (Bizani, Futianos, Poullos, & Tsiridis, 2005). About 15% of the total amount of dye is lost during the dyeing production process and released in wastewater effluents (Slokar & Le Marechal, 1998). Several classes of dyes are considered as possible carcinogens or mutagens that threaten the entire ecosystem (Flora, Bagnaco, & Zancchi, 1991). Besides this, the presence of these colored compounds, even in trace quantities, is highly undesirable, as it can block both sunlight penetration and oxygen dissolution, which are essential for aquatic life. Therefore, the contamination of seawater with these compounds is a major environmental concern.

Typical classical techniques to remove these compounds, such as adsorption (Rauf, Qadri, Ashraf, & Al-Mansoori, 2009), coagulation (Riera-Torres, Gutiérrez-Bouzán, & Crespi, 2010), ion flotation (Shakir, Elkafrawy, Ghoneimy, Beheir, & Refaat, 2010) and sedimentation (Zodi, Potier, Lapique, & Leclerc, 2010) have inherent drawbacks due to the formation of secondary toxic products that require further treatment. It is therefore crucial to develop an effective and inexpensive method to remove these harmful pollutants safely. Photocatalysis using nanostructured semiconductors has attracted considerable attention in recent years as a potential and economical method for mineralization of organic pollutants in contaminated water to carbon dioxide and water (Stylidi, Kondarides, & Verykios, 2004).

Over the past several years, heterogeneous semiconductor photocatalysis using titanium dioxide has received considerable attention for its application in water splitting to produce hydrogen (Fujishima & Honda, 1972; Khan, Al-Shahry, & Ingler, 2002; Shaban & Khan, 2010; Shaban, 2013), and degradation of organic pollutants (Xu, Killmeyer, Gray, & Khan, 2006; Shaban, El Sayed, El Maradny, Al Farawati, & Al Zobidi, 2013; Shaban, 2013). However, its utilization is limited to the UV region due to its wide band gap (3.0-3.2 eV). Therefore, several attempts were made to extend its optical response to the visible spectral range by doping it with transition metals (Choi, Termin, & Hoffman, 1994; Anpo, 1997), nitrogen (Asahi, Morikawa, Ohwaki, Aoki, & Taga, 2001), and sulphur (Umebayashi, Yamaki, Itoh, & Asai, 2002). Recently, it has been reported that carbon modification of n-TiO₂ lowered its bandgap energy to 2.32 eV, consequently enhanced photoresponse was observed (Khan, Al-Shahry, & Ingler, 2002). Sakthivel and Kisch (2003) observed a fivefold increase in photocatalytic activity of carbon-doped n-TiO₂ as compared to nitrogen-doped n-TiO₂. Xu et al. (2006) reported

that the carbon-modified n-TiO₂ nanoparticles, synthesized by a wet process using a glucose (C₆H₁₂O₆) solution as the carbon source, showed a significantly enhanced photocatalytic activity as compared to regular undoped n-TiO₂.

Although seawater is an increasingly important water source, its behavior as a medium for photocatalytic removal of contaminants has not been studied extensively. Most studies dealing with the photodegradation of dyes using n-TiO₂ have been carried out in distilled water under illumination of UV light sources. On the basis of these considerations, visible light active carbon-modified (CM)-n-TiO₂ nanoparticles were prepared by sol-gel method using carbon-containing precursor as a source of both carbon and titanium without using any external source of carbon. The photocatalytic performance of CM-n-TiO₂ was examined for the photocatalytic removal of methylene blue, an intensely colored cationic dye, from natural seawater under sunlight illumination. The photocatalytic activity of CM-n-TiO₂ was compared with regular n-TiO₂. In succession, the effects of photocatalyst loading, MB concentration, and pH on the photocatalytic removal rate of MB were investigated.

2. Materials and Methods

2.1 Chemicals and Reagents

All chemicals were of analytical grade and were used without any further purification: titanium butoxide (Fluka, 97%); titanium trichloride (Sigma-Aldrich, TiCl₃ 12% in hydrochloric acid (5-12%)); methylene blue (Riedel-De Haën AG) and ethanol (Sigma-Aldrich, HPLC). HCl and NaOH (analytical grade) were used for pH adjustment. Solutions were prepared with ultra-pure water obtained using a Millipore device (Milli-Q).

2.2 Synthesis and Characterization of n-TiO₂ and CM-n-TiO₂ Nanoparticles

Regular (unmodified) titanium dioxide (n-TiO₂) nanoparticles were synthesized by hydrolysis and oxidation of titanium trichloride (TiCl₃) in an aqueous medium. Visible light active carbon-modified titanium dioxide (CM-n-TiO₂) nanoparticles were synthesized by a sol-gel synthesis using titanium butoxide (Ti[O(CH₂)₃CH₃]₄), carbon-containing precursor, as a molecular precursor of TiO₂ as well as a carbon source. The preparation and characterization of carbon-modified titanium oxide (CM-n-TiO₂) and unmodified n-TiO₂ have been reported in details elsewhere (Shaban et al., 2013).

2.3 Photocatalytic Removal Experiments

All solar photocatalytic experiments were carried out at the Faculty of Marine Sciences, Obhur, Jeddah, KSA, in the daytime between 11:00 am and 15:00 pm, during June-July, 2012. Natural seawater samples were collected from Sharm Obhur, Jeddah, KSA. Before spiking with different concentrations of MB, seawater samples were passed through Whatman GFC to remove any solid particles. Experimental set up for photocatalytic degradation consisted of a magnetically stirred 500 mL glass reactor loaded with the seawater solution (400 mL) containing different concentrations of MB ranging from 5 to 30 μM. The synthesized photocatalyst (n-TiO₂ or CM-n-TiO₂) was added with continuous stirring for uniform mixing. The photocatalytic reactor was directly exposed to natural sunlight. The average solar intensity was 1200 Wm⁻², measured by Field Scout Light Sensor Reader (Spectrum Technologies, Inc.) equipped with 3670i Silicon Pyranometer Sensor.

2.4 Sample Analysis

Aliquots of treated seawater samples were regularly withdrawn from the reactor and centrifuged immediately to remove the catalyst. The samples were analyzed using a Shimadzu UV-VIS Spectrophotometer (Model PharmaSpec UV-1700). The photodegradation efficiency (η) was then calculated from the decrease of absorbance of the dye solution at its maximum absorption wavelength (668 nm) as follows:

$$\eta = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

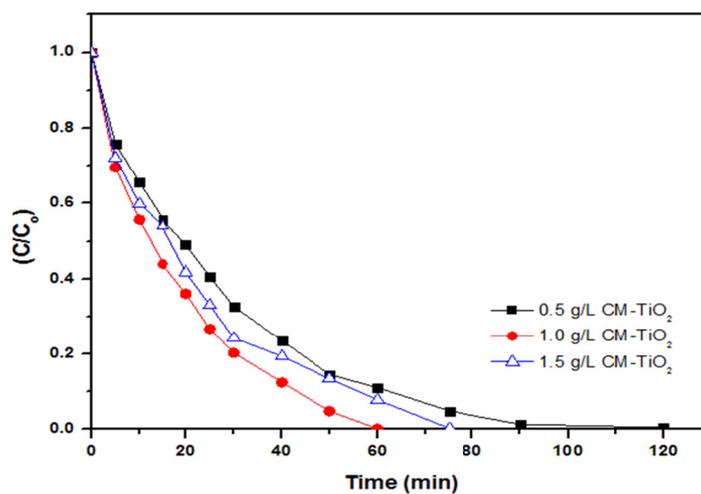
where C₀ represents the initial concentration of the dye solution and C_t represents the concentration of the dye at solar light irradiation time (t).

3. Results and Discussion

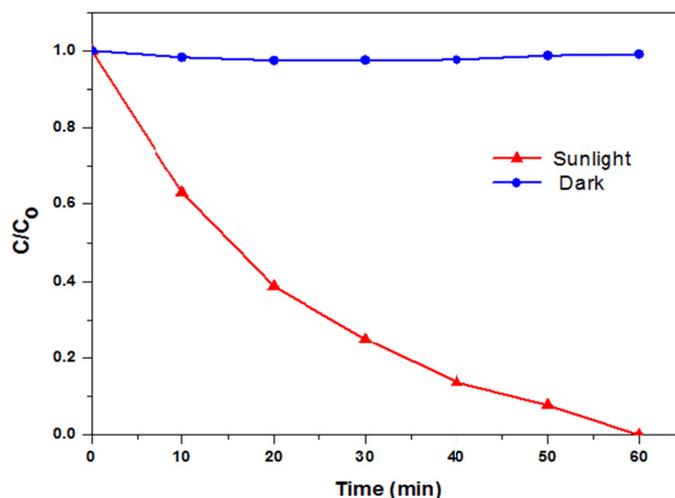
3.1 Effect of Catalyst Dose

To ensure maximum absorption of photons and to avoid an excess amount of catalyst, the optimum catalyst loading must be determined. The influence of CM-n-TiO₂ dose on photodegradation of MB (20 μM) under natural sunlight is shown in Figure 1a. The photocatalytic removal rate of MB increased with increase in catalyst dose from 0.5 to 1.0 gL⁻¹. The increase in catalyst amount increases the number of active sites on the photocatalyst surface thus causing an increase in the number of •OH radicals which can take part in decoloration of the dye solution. Further increase in the catalyst loading to 1.5 gL⁻¹ slightly decreases the degradation

efficiency. This is due to particles aggregation that reduces the surface area available for light absorption (Wang, Ren, Xia, Zhang, & Zhao, 2009). Additionally, the increase of the turbidity of the suspension reduces light penetration which in turn reduces the number of activated sites on the TiO_2 surface. With the overloaded catalyst, these two effects reduce the photocatalytic activity (Merabet, Bouzaza, & Wolbert, 2009). Figure 1b shows the effect of the optimum CM-n-TiO_2 loading (1.0 gL^{-1}) on the removal of methylene blue ($20 \mu\text{M}$) in the absence and presence of sunlight. As can be seen, no obvious degradation of MB in the absence of light, revealing that the decoloration of MB is due to the photocatalytic effect of CM-n-TiO_2 under sunlight illumination rather than the adsorption of MB molecules on the surface of the catalyst in the absence of light.



(a)



(b)

Figure 1. (a) Effect of CM-n-TiO_2 loading on the photocatalytic removal of methylene blue ($20 \mu\text{M}$) under illumination of natural sunlight; (b) Effect of the optimum CM-n-TiO_2 loading (1.0 gL^{-1}) on the removal of methylene blue ($20 \mu\text{M}$) in the absence and presence of sunlight

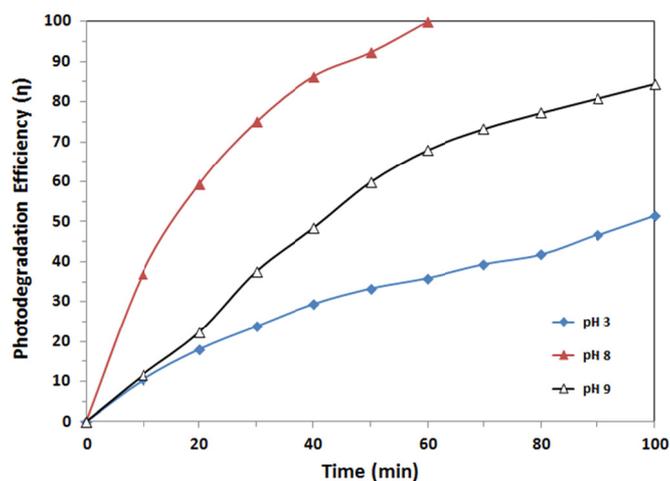
3.2 Effect of Solution pH

The pH of the solution is a key parameter in the photocatalytic degradation of organic pollutants, as it is known to influence the surface charge of the semiconductor, thereby affecting the interfacial electron transfer and the photoredox process (Lu, Roam, Chen, & Huang, 1993). The possible functional groups on TiO_2 surface in water are TiOH_2^+ , TiOH , and TiO^- . The point of zero charge (pH_{pzc}) of TiO_2 is an important factor determining the

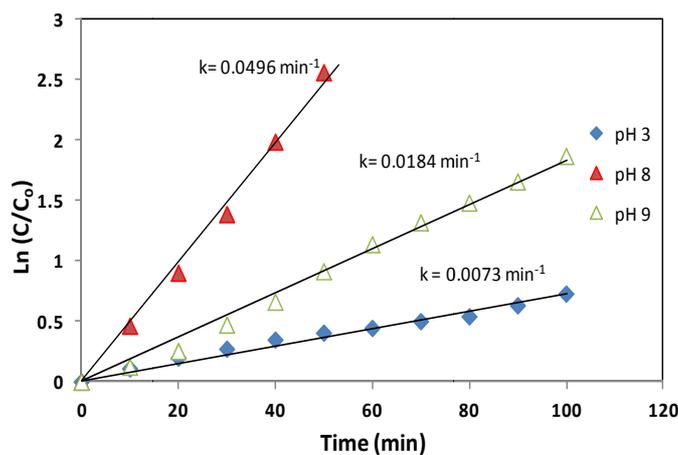
distribution of the surface groups. When $\text{pH} > \text{pH}_{\text{pzc}}$, the surface of TiO_2 is negatively charged with the species TiO^- (Equation (2)), and positively charged with the species TiOH_2^+ at $\text{pH} < \text{pH}_{\text{pzc}}$ (Equation (3)).



In this study, the role of pH in the photocatalytic removal of methylene blue was studied by keeping all other experimental conditions constant and varying the initial pH of the methylene blue solution from 3 to 9. As can be seen in Figure 2a, the photocatalytic degradation efficiency of CM-n- TiO_2 increases with increase in pH from 3 to 8, beyond which the photodegradation efficiency starts to decrease, indicating an optimum pH of approximately 8. At the optimum pH, complete removal of MB was achieved after 60 min, whereas at the same illumination time, removal of 35.9% and 67.9% was observed at pH 3 and pH 9, respectively. The photocatalytic removal rate constant at the optimum pH was found to be 2.9 and 6.8 times those obtained at pH 9 and pH 3, respectively (Figure 2b).



(a)

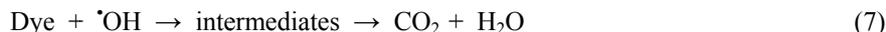


(b)

Figure 2. Effect of pH on photocatalytic removal of methylene blue ($20 \mu\text{M}$) using 1.0 g L^{-1} CM-n- TiO_2 under illumination of natural sunlight (a); Kinetic analysis of photocatalytic removal of MB at the same experimental conditions (b)

The pH of solution affects the formation of hydroxyl radicals as it can be inferred from the following equations (Nikazar, Gholivand, & Mahanpoor, 2008):





Because of the high redox potentials of Equations (5) and (6) in acidic conditions, the formation of hydroxyl radicals will be thermodynamically unfavorable (Tang & Huang, 1995). As a result, the formation of hydroxyl radicals increases with an increase in pH from 3 to 8, leading to an increased photocatalytic degradation efficiency. Besides, since methylene blue is a cationic dye, it is conceivable that at pH 8, which is higher than the point of zero charge (pH_{pzc}) of TiO_2 , its adsorption is favorable on a negatively charged TiO^{-} surface. At pH higher than 8, the formation of carbonate ions is favorable which are effective scavengers of hydroxyl ions and can reduce the efficiency of photodegradation process (Bekbolet & Balcioglu, 1996; Akbal & Onar, 2003).

3.3 Effect of Initial MB Concentration

The effect of the initial MB concentration on its photodegradation rate was investigated over the range of 5 to 30 μM at the optimal conditions of pH 8 and 1.0 g L^{-1} of CM-n- TiO_2 (Figure 3). The photodegradation efficiency was obviously influenced by the initial concentration of MB, the irradiation time required for complete removal of MB under natural sunlight was extended as the initial MB concentration increased. This can be rationalized by considering that, as MB concentration increases, more dye molecules are adsorbed on the surface of TiO_2 , so that fewer number of photons are able to reach the catalyst surface and therefore less amount of $\cdot\text{OH}$ are generated, resulting in a reduction of photodegradation efficiency (Parida, Dash, & Das, 2006). Several studies have reported that high organic substrate loadings induce the formation of intermediates that could be adsorbed onto the catalyst surface and deactivate the active sites (Ahmed, Rasul, Martens, Brown, & Hashib, 2010).

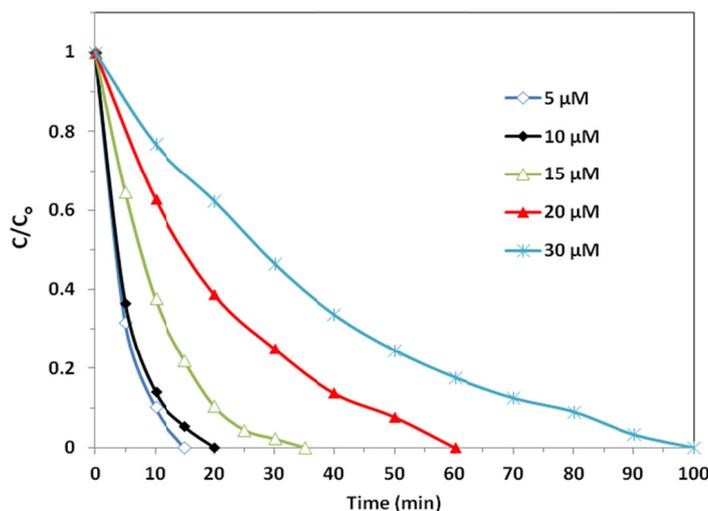


Figure 3. Effect of initial concentration of MB on its photocatalytic removal at pH 8 using 1.0 g L^{-1} CM-n- TiO_2 under natural sunlight

3.4 Photocatalytic Activity of n-TiO₂ and CM-n-TiO₂

The photocatalytic activity of CM-n- TiO_2 was evaluated through a comparison with unmodified n- TiO_2 under the optimal conditions. Figure 4 illustrates the photocatalytic removal of 20 μM of methylene blue under illumination of real sunlight at pH 8 and in the presence of 1.0 g L^{-1} of the photocatalyst. It is clearly observed that the photocatalytic degradation efficiency of CM-n- TiO_2 is higher than that of n- TiO_2 . Complete removal of MB (20 μM) was achieved after 60 min when CM-n- TiO_2 was applied. After the same irradiation time, only 46.4% of MB was degraded using regular n- TiO_2 under the same experimental conditions. The enhanced photoresponse of CM-n- TiO_2 nanoparticles can be attributed to carbon modification of TiO_2 , which in agreement with the previously reported results (Khan et al., 2002; Shaban & Khan, 2010; Shaban et al., 2013). Matsunaga and Inagaki (2006) reported that carbon presents in titanium dioxide particles is assumed to play as a sensitizer in photocatalytic reaction. Additionally, other advanced theoretical studies revealed that carbon doping of n- TiO_2 is responsible for the enhancement in its photoresponse. Wang and Lewis (2005) addressed theoretically the

effects of carbon dopants concentration on the photoresponse of n-TiO₂ in the visible-light region. They found that the substitutional and interstitial carbon dopants incorporated into TiO₂ drastically affected the electronic structure of the material, thus improving its photoactivity. The theoretical findings by Di Valentin, Pacchioni and Selloni (2005) revealed that the presence of substitutional and interstitial carbon in carbon-modified (CM)-n-TiO₂ were found to be responsible for the enhancement of its photoresponse by lowering its main bandgap as well as generating a mid-gap band.

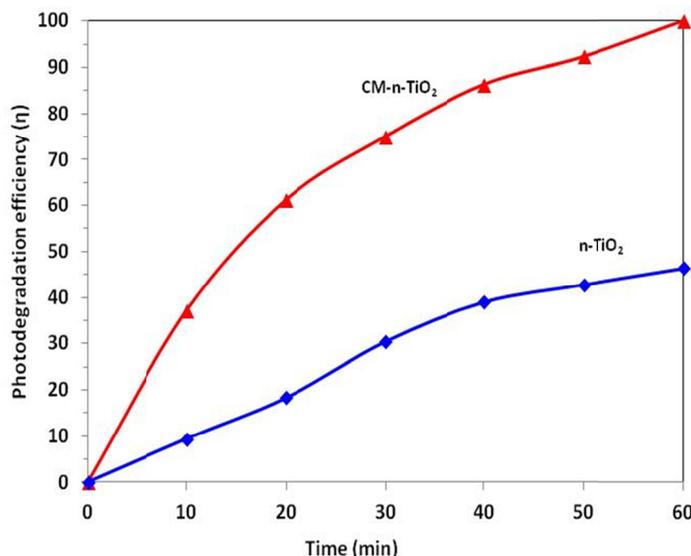


Figure 4. Photocatalytic degradation of methylene blue (20 μM) in the presence of 1.0 g L⁻¹ of CM-n-TiO₂ and n-TiO₂ under illumination of natural sunlight

3.5 Kinetic Studies

The Langmuir–Hinshelwood (L–H) model was used to describe the kinetics of photocatalytic reactions of aqueous organics (Petukhov, 1997; Bayarri, Gimenez, Curco, & Esplugas, 2005; Kusvuran, Samil, Atanur, & Erbatur, 2005). The L–H model relates the degradation rate (r) and reactant concentration in water at time t (C), which is expressed as follows:

$$r = -\frac{dc}{dt} = \frac{k_r K_{ad}}{1 + K_{ad}C} \quad (8)$$

where k_r is the rate constant and K_{ad} is the adsorption equilibrium constant. When the adsorption is relatively weak and/or the reactant concentration is low, Equation (8) can be simplified to the pseudo-first order kinetics with an apparent first-order rate constant k_{app} :

$$\ln\left(\frac{C_0}{C}\right) = k_r K_{ad} t = k_{app} t \quad (9)$$

where C_0 is the initial concentration. Figure 5 shows the plot of $\ln(C_0/C)$ versus illumination time for the photocatalytic degradation of MB (5–30 μM) at the optimal conditions of pH 8 and 1.0 g L⁻¹ of CM-n-TiO₂. The linearity of the plots confirms that the photocatalytic degradation of MB using CM-n-TiO₂ follows the L–H model, and can thus be described by the pseudo-first order kinetics.

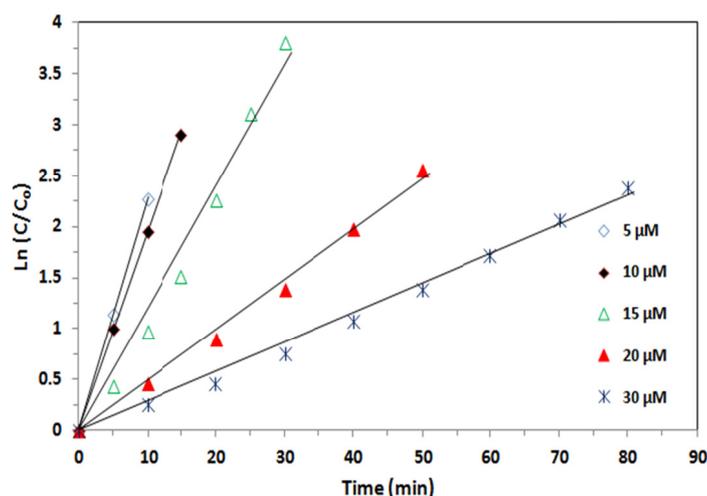


Figure 5. Kinetic analysis of photocatalytic removal of different concentrations of MB at pH 8 using 1.0 g L⁻¹ CM-n-TiO₂ under natural sunlight

Table 1. Apparent first-order rate constant (k_{app}) for different MB concentrations

MB (μM)	k_{app} (min^{-1})	R^2
5	0.2286	0.999
10	0.1953	0.999
15	0.1195	0.9799
20	0.0496	0.9956
30	0.0289	0.9927

Table 1 lists the apparent first-order rate constant (k_{app}) for different MB concentrations (5-30 μM), which were calculated from Figure 5. It is clearly observed that the apparent pseudo-first order rate constant (k_{app}) decreases as the initial MB concentration increases.

The calculation of the half-life time reaction ($t_{1/2}$) when $C = 0.5 C_0$ is one of the most useful means of evaluating the reaction rate of first order kinetics. For a pseudo-first order reaction, the half-life time can be calculated as:

$$t_{1/2} = \ln(2)/k_{app} \quad (10)$$

As can be discerned from Figure 6, the $t_{1/2}$ values for regular n-TiO₂ are 3-6 times those observed using CM-n-TiO₂. These results reflect the significantly enhanced visible light harvesting capability of CM-n-TiO₂ nanoparticles, which can be attributed to the carbon modification.

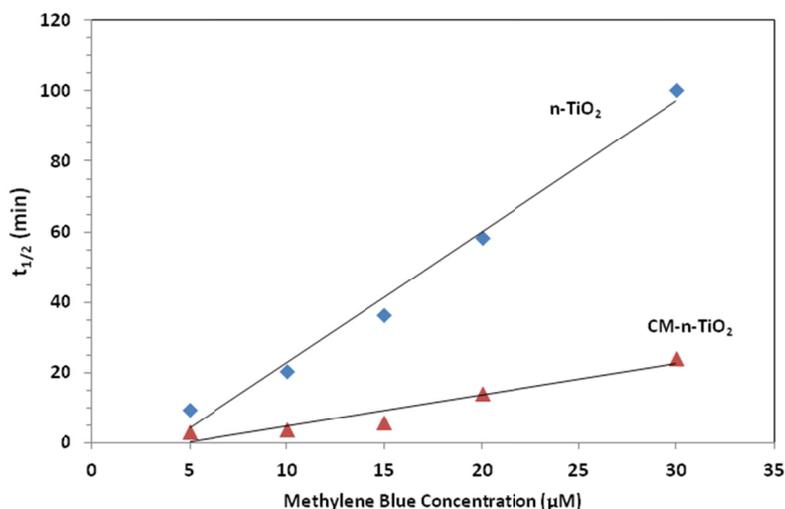


Figure 6. Half-life time reaction ($t_{1/2}$) values versus initial MB concentration in the presence of 1.0 g L^{-1} of CM-n-TiO₂ and n-TiO₂ under illumination of natural sunlight .

4. Conclusions

Carbon-modified (CM)-n-TiO₂ nanoparticles have significantly higher photocatalytic activity compared to unmodified n-TiO₂ towards the photocatalytic removal of methylene blue from seawater under real sunlight, which can be attributed to the carbon modification. The degradation rate of methylene blue was most efficient at the optimum conditions of pH 8 and a catalyst dose of 1.0 g L^{-1} . The photodegradation efficiency of MB was obviously influenced by its initial concentration, the irradiation time required for complete degradation of MB was extended as the initial MB concentration increased. The half-life time reaction ($t_{1/2}$) values for regular n-TiO₂ were found to be 3-6 times higher than those observed using CM-n-TiO₂, reflecting the higher capability of CM-TiO₂ for harvesting the visible light. The solar photocatalytic removal of MB from seawater using CM-n-TiO₂ obeyed a pseudo-first order kinetics according to the Langmuir–Hinshelwood model.

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