Article

Heterogeneous Photocatalytic Chlorination of Methylene Blue Using a Newly Synthesized TiO₂-SiO₂ Photocatalyst

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Abstract: The titanium dioxide-silicon dioxide (TiO₂-SiO₂) nanocomposite used for the study was synthesized using a sol-gel method followed by UV-treatment. The physicochemical properties of the synthesized catalyst, TiO₂-SiO₂ were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) and photoluminescence (PL). The photocatalytic degradation of methylene blue (MB) dye was evaluated in the presence of TiO₂-SiO₂ and reactive chlorine species (RCS) under experimental conditions. By comparing the important reaction processes in the study, including photocatalysis, chlorination and photocatalytic chlorination, it was found out that the process of photocatalytic chlorination had the highest photodegradation efficiency (95% at 60 min) of the MB under optimum reaction conditions (MB = 6 mg L⁻¹, catalyst = 0.1 g and pH = 4). The enhanced removal of MB from the aqueous medium was identified because of the synergy between chlorination and photocatalysis activated in the presence of TiO₂-SiO₂. The mechanism of the photocatalytic chlorination process was scrutinized in the presence of various RCS and reactive oxygen species (ROS) scavengers. Based on the experimental data attained, Na₂S₂O₃ exhibited the highest inhibitory effect on the degradation efficiency of MB, indicating that the RCS is the main contributor to visible light-induced photodegradation of MB.

Keywords: TiO₂-SiO₂; solar photocatalysis; chlorination; MB; parametric study; ROS

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1. Introduction

In a recent United Nations (UN) report, around 80% of total wastewater is released directly into nearby land before any proper and prior degradation procedure. This causes severe water pollution and affects the natural ecosystem and public health [1]. The increasing population in the world and rapid industrialization are the primary reasons for the requirement for clean drinking water for human consumption. The reuse of wastewater can mitigate the problem of reduced availability of fresh water in the future to some extent [2]. In recent years, especially during the past ten years, the field of wastewater treatment has progressed rapidly as a remedy to the challenges, including the nonavailability and scarcity of fresh water.

The textile industry is one of the largest industries which generates hazardous coloured contaminants into natural water sources by the discharge of about 10–15% of total dye consumed. Dye molecules consist of different functional groups including NH₂, COOH,

and SO_3 , which might cause health issues in humans. Apart from that, most dye molecules are highly soluble in water, recalcitrant and nonbiodegradable [3]. Therefore, a technology capable of remediating and recycling textile wastewater at a low cost is required. In the quest to refine the wastewater produced by the textile industry, numerous methods have been developed in the past few decades. For instance, since the discovery by Fujishima in 1972 about water splitting, thousands of articles have been published about the wastewater remediation by TiO_2 and various other semiconductor oxide catalysts [4].

Advanced oxidation processes (AOPs) are those that employ in situ generation of hydroxyl radicals ($\text{HO}^\bullet$). The $\text{HO}^\bullet$ radicals are nonselective, highly reactive, able to react with a number of recalcitrant organic pollutants and possess high oxidizing potential. These factors enable the $\text{HO}^\bullet$ radicals to achieve complete mineralization of various hazardous compounds such as herbicides, phenolic compounds, chlorinated organics, pharmaceuticals, dyes and by-products [3,4]. Photocatalysis is considered an efficient and progressing technology to mitigate the issue of water pollution by using photocatalytic transformation from solar light to chemical energy [5]. In this study, a photocatalytic process considered as one of the most effective AOPs was used for photodegradation of the target pollutant. Our previous studies using the photolysis process yielded satisfactory results [6–8]. TiO_2 is favoured because of its low maintenance cost and enhanced stability, and is more energy efficiency compared with that of another semiconductor, ZnO [9]. Low activity under visible light and having a very short life span of photoinduced charge carriers, are the two major drawbacks of TiO_2 photocatalysis [10]. Therefore, extensive research interest has been paid to the improvement of the photocatalysis process.

The incorporation of SiO_2 onto the catalyst TiO_2 results in an enhancement of the band-gap energy value of the resultant TiO_2 - SiO_2 composite. The quantum-size effect enhances the band-gap energy value as well as interface interaction occurring between the oxide phases, with either an SiO_2 matrix or SiO_2 support effect. Incorporating SiO_2 onto the catalyst, TiO_2 also enhances the adsorption of more target pollutant molecules to the proximity of the photoactive centre of TiO_2 resulting in the degradation of a greater number of target pollutants. The result is an enhanced rate of degradation for the target pollutant in the presence of visible-light irradiation. As there are more active adsorption sites on the surface of the TiO_2 - SiO_2 catalyst composite, there is a reduction in recombination of photogenerated holes and electrons, thereby increasing the chance of photogenerated holes to reach the active surface sites. This enhances photocatalytic activity in the presence of TiO_2 [11]. In this study, SiO_2 was incorporated onto TiO_2 to reduce the distance between dye molecules and the photogenerated $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$, so that the $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals could effectively break down the dye molecules.

UV/chlorine is one of the AOP processes, and chlorine is a widely used disinfectant [12]. This technique can oxidize a large number of recalcitrant organic compounds such as dye molecules, pharmaceutical products and microorganisms etc. [13]. Apart from that, UV/chlorine is economical, efficient, and easy to use [2,13]. Chlorination is common because it is cost-effective, even though it cannot achieve the complete removal of pollutants [2]. It has been reported that for the degradation of dyes and other organics, the presence of Cl^- could be very effective in improving the degradation rate [14,15]. The enhancement in the degradation rate in the presence of UV/chlorine can be demonstrated by a synergy between the highly reactive $\text{HO}^\bullet$ and reactive chlorine species formed in situ, including $\text{Cl}^\bullet$ and $\text{Cl}_2^{\bullet-}$. There is also the presence of active chlorine species such as HClO and Cl_2 which can contribute to the bulk of the solution [16,17]. Thus, in this study, we combined chlorination and photocatalysis to achieve complete mineralization of MB molecules in an aqueous system under solar light.

2. Experimental

2.1. Chemicals

Methylene blue (MB) powder was obtained from Sigma (St. Louis, MO, USA). Titanium dioxide (TiO_2) Degussa (Evonik, Essen, North Rhine-Westphalia, Germany) P25 was

purchased from Nanoshel (Wilmington, DE, USA). Tetraethyl orthosilicate (TEOS), a precursor for Si, was purchased from Aldrich (St. Louis, MO, USA). Ethanol absolute ($\geq 99.5\%$) was purchased from VWR Chemicals (Radnor, PA, USA). Calcium hypochlorite [$\text{Ca}(\text{OCl})_2$] was provided by Sigma-Aldrich. Hydrochloric acid (HCl) was supplied by Fisher Scientific (Waltham, MA, USA), and sodium hydroxide (NaOH) was purchased from RCI Labscan (Pathumwan Bangkok Thailand). The radical scavengers nitrobenzene (10 mM), benzoquinone (10 mM) and sodium thiosulfate (10 mM) were attained from Sigma-Aldrich. Nitrobenzene, benzoquinone and sodium thiosulfate were used to scavenge HO , O_2^- and RCS, respectively.

2.2. Synthesis of TiO_2 - SiO_2 Nanocomposite

The facile sol-gel process was employed in incorporating SiO_2 (TEOS) to commercial Degussa P25 TiO_2 nanoparticles. The TiO_2 - SiO_2 nanocomposite was prepared as follows. In the specified method, 0.2 g of P25 nanoparticles were put into a prepared SiO_2 solution and then diluted with ethanol. The reaction was performed at room temperature with continuous stirring for 1 h. Resultant TiO_2 - SiO_2 nanocomposites were harvested by filtration with PTFE 0.45 μm , washed thoroughly with ethanol and dried at a temperature of 80°C in a hot air oven for 24 h [11,18,19]. A powder was attained.

The newly synthesized TiO_2 - SiO_2 was UV-treated with UV-C (9 Watts, 10 mW cm^{-2}) for 2 weeks at room temperature under continuous stirring. After the UV treatment, the attained composite (denoted as UV-treated TiO_2 - SiO_2) was filtered using PTFE 0.45 μm filter, dried and stored in a vial.

2.3. Material Characterization

Crystallographic analyses and phase analyses were carried out by X-ray powder diffractometry (Philips X'pert Pro, Andover, MA, USA) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$). Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer unit with a wavenumber range of $4000\text{--}800\text{ cm}^{-1}$ to identify surface functional groups of the samples. Ultraviolet-visible diffuse reflectance spectrometry (UV-vis DRS) of the test samples was performed using a Cary 100 diffuse reflectance spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) to determine the optical band gap (E_g) of the samples. Photoluminescence measurements were conducted using a PL spectrophotometer (Perkin Elmer, Waltham, MA, USA) to evaluate the charge carrier recombination rates of the samples.

2.4. Photocatalytic Reactions

In each experiment, 0.1 g of the catalyst powder (TiO_2 , TiO_2 - SiO_2 or UV-treated TiO_2 - SiO_2) was dispersed into 250 mL of an aqueous solution of Methylene Blue (MB, $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, 6 mg L^{-1}) and was then stirred for 40 min under dark conditions to achieve adsorption equilibrium. Once the adsorption equilibrium was attained, 100 ppm of HOCl solution was poured into the MB solution. Next, the test solution was exposed to UV-visible irradiation using a 9 Watts solar power lamp (10,000 K daylight photon energy) for the MB degradation study. The lamp was placed inside quartz and immersed in the MB solution as shown in Figure S1a. Aliquots were removed from the solution every 10 min and filtered for the UV-vis spectroscopic study (Cary 60 UV-vis spectrophotometer; Agilent Technologies) to quantify degradation at the time of irradiation. The presence of chemical scavengers was analyzed to identify the major contributors during photocatalysis.

3. Results and Discussion

3.1. Photocatalytic Activity Measurements

The TiO_2 - SiO_2 nanocomposite was prepared using the sol-gel technique. Figure S1b schematically illustrates the preparation scheme of the catalyst. The attained TiO_2 - SiO_2 was UV-treated to enhance surface hydroxylation [19,20] and crystallinity of the TiO_2 - SiO_2 .

The phase composition of the samples was identified by XRD characterization; the diffraction data evolved are shown in Figure S2 which exhibits the presence of both anatase

and rutile phases in all three samples (TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$) [21]. The diffraction peaks at $2\theta = 25.3^\circ$ (101 plane), 37.8° (004 plane), 48.0° (200 plane) and 55.1° (211 plane) are attributed to crystal planes of anatase. Meanwhile, the diffraction peaks at $2\theta = 27.4^\circ$ (110 plane), 36.1° (101 plane) and 54.1° (211 plane) are accredited to crystal planes of rutile [22,23]. As observed, upon adding SiO_2 , the $\text{TiO}_2\text{-SiO}_2$ diminishes the intensity of the anatase peak (101), indicating reduced crystallinity [24,25]. However, upon UV treatment, the UV-treated $\text{TiO}_2\text{-SiO}_2$ displayed an intensified anatase peak (101), indicating enhanced crystallinity of the anatase phase.

Since XRD cannot detect amorphous phases, FTIR analysis was carried out to detect chemical bonds irrespective of their crystallinity [21]. The FTIR spectrum of the UV-treated $\text{TiO}_2\text{-SiO}_2$ was compared with $\text{TiO}_2\text{-SiO}_2$ and TiO_2 in Figure S3. The broad peak at 3400 cm^{-1} depicts the stretching mode of water and hydroxyl groups. The peak located at 940 cm^{-1} represents the characteristic stretching vibration of Ti-O-Si bonds. The bands located at 1250 cm^{-1} and 1090 cm^{-1} represent the asymmetric vibration of the Si-O-Si mode. Compared to $\text{TiO}_2\text{-SiO}_2$, the UV-treated $\text{TiO}_2\text{-SiO}_2$ exhibits enhanced intensity of peaks reflecting Si-O-Si and Ti-O-Si bonds. The enhanced intensity of the peak in the FTIR spectrum indicates the formation of more bonds [26]. The increased intensity of the 1077 cm^{-1} and 938 cm^{-1} peaks upon UV-C irradiation pinpoints the formation of more Si-O-Si bonds and Si-O-Ti bonds through the oxidation of incompletely hydrolysed organic groups and enhancement of the interaction between TiO_2 and SiO_2 nanoparticles [20]. Based on Figure S3, at 3400 cm^{-1} , compared to TiO_2 , the IR absorption for $\text{TiO}_2\text{-SiO}_2$ in this region is more intense, which indicates a greater amount of adsorbed water/OH groups on the surface [27]. Meanwhile, the UV-treated $\text{TiO}_2\text{-SiO}_2$ showed maximum intensity at 3400 cm^{-1} denoting that UV treatment facilitates the generation of more surface hydroxyl groups on the surface of $\text{TiO}_2\text{-SiO}_2$. The enhanced number of surface hydroxyl groups further improves the photocatalytic activity of $\text{TiO}_2\text{-SiO}_2$ under the visible region [28].

UV-vis diffuse-reflectance spectra (DRS) of the test sample were evaluated to determine the optical band gap (E_g) energy value of the catalysts, including TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$. The identified band gap energies (E_g) of the photocatalysts were estimated by the equation $(Ah\nu)^2 = K(h\nu - E_g)$, where $h\nu$ represents the energy of a photon (eV), A epitomizes the absorption coefficient, and K and E_g represent a constant and the band gap respectively. The band gap of the samples can be determined by extrapolating the linear part of the spectra in a graph of $(Ah\nu)^2$ versus the photon energy [23]. Figure 1 displays the plot of $(\alpha h\nu)^2$ versus $h\nu$ for the TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$. The band gaps (E_g) obtained for TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$ were 3.30, 3.35 and 3.40, respectively. The UV-vis DRS data demonstrated that SiO_2 incorporation results in a slight improvement of the light absorption properties of the P25 nanoparticles [21].

In addition, photoluminescence analysis was employed to determine the charge carrier recombination behavior of the samples.

Figure 2 illustrates the PL spectra of TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$. The PL intensities were reduced upon addition of SiO_2 and further diminished with UV-treatment, indicating that the rate of recombination of the charge carrier also diminished upon UV-treatment of $\text{TiO}_2\text{-SiO}_2$. The UV-treated $\text{TiO}_2\text{-SiO}_2$ exhibited superior suppression of electron-hole recombination compared to $\text{TiO}_2\text{-SiO}_2$ due to enhanced crystallinity, as observed in the XRD pattern. The smaller number of surface defects reduces the possibility of electron-hole recombination. The diminished recombination of photo-generated electron-hole pairs leads to more electrons and holes being available for photocatalytic reactions [29]. This can lead to enhanced photocatalytic activity of the composite since the electrons and holes can be efficiently converted to $\text{O}_2^{\bullet-}$ and $\text{HO}^\bullet$, which can efficiently break down MB molecules.

Figure 1. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$.

Figure 2. PL spectra of TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$.

Photocatalytic activities of various catalysts, including TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$, in degradation involving photocatalysis were identified to find investigate the influence of catalyst, SiO_2 and UV-treatment under various photocatalytic reaction processes. The photocatalytic degradation of MB studied in the presence of solar light irradiation is shown in Figure 3. During the first 40 min in the dark, UV-treated $\text{TiO}_2\text{-SiO}_2$ exhibited the highest adsorption (25%) in comparison with TiO_2 (7%) and $\text{TiO}_2\text{-SiO}_2$ (10%). After 60 min of solar irradiation, the UV-treated $\text{TiO}_2\text{-SiO}_2$ also demonstrated the highest MB removal efficiency (68%) in comparison to TiO_2 (32%) and $\text{TiO}_2\text{-SiO}_2$ (44%). It was evident from a study [30] that the molar ratio of the $\text{TiO}_2\text{-SiO}_2$ composite clearly influences the degradation performance of the specific catalyst. The synthesized materials appear to be more active in dark conditions than in fresh TiO_2 , whereas in the presence of light irradiation, all the catalysts exhibited significant enhancement in the degradation process.

The $\text{TiO}_2\text{-SiO}_2$ composite showed higher activity, and the rate of its enhancement increased, by increasing the molar ratio of $\text{TiO}_2\text{-SiO}_2$. In this study, a molar ratio of 9:1 for the $\text{TiO}_2\text{-SiO}_2$ composite was more active in the photocatalytic process. The enhancement of photocatalytic activity of UV-treated $\text{TiO}_2\text{-SiO}_2$ is attributed to the enhanced surface area, surface hydroxyl groups, crystallinity and diminished charge carrier recombination rate of the UV-treated $\text{TiO}_2\text{-SiO}_2$ in comparison with TiO_2 and $\text{TiO}_2\text{-SiO}_2$.

Figure 3. Graph of concentration versus time for TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$. Conditions: $[\text{MB}] = 6 \text{ mg L}^{-1}$, $[\text{catalyst}] = 0.1 \text{ g}$ and $\text{pH} = 5$.

Before starting functional evaluation of the parametric study, several studies were performed for comparing the efficiency of degradation of MB under various degradation processes, such as photolysis, chlorination, photocatalytic oxidation by TiO_2 , photocatalytic oxidation by $\text{TiO}_2\text{-SiO}_2$, photocatalytic oxidation by UV-treated $\text{TiO}_2\text{-SiO}_2$ and photocatalytic chlorination by UV-treated $\text{TiO}_2\text{-SiO}_2$. Figure 4 shows the effect of MB degradation efficiency for each process. MB degradation was lowest (5%) during direct photolysis under solar irradiation. The degradation efficiency of MB through chlorination, photocatalytic oxidation by UV-treated $\text{TiO}_2\text{-SiO}_2$ and photocatalytic chlorination by UV-treated $\text{TiO}_2\text{-SiO}_2$ were found to be 30, 68 and 85%, respectively.

MB degradation by chlorination occurs exclusively in the liquid phase. The dominant RCS generated during the solar/chlorine process are chlorine radicals ($\text{Cl}^\bullet$), secondary chlorine oxides ($\text{ClO}^\bullet$) and dichloride anions $\text{Cl}_2^{\bullet-}$. These RCS species react with the MB molecules and break down the molecules under solar irradiation. Photocatalytic oxidation by TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$ is initiated by the photon absorption by TiO_2 and the electrons from valence bands jumps to conduction bands.

The photogenerated electrons and holes react with dissolved oxygen and water molecules resulting in the generation of superoxide anions ($\text{O}_2^{\bullet-}$) and hydroxyl radicals ($\text{HO}^\bullet$). The generation of these radicals is shown in Figure S4. MB degradation by chlorination and photocatalytic oxidation by UV-treated $\text{TiO}_2\text{-SiO}_2$ occurs on the photocatalyst's surface and in the liquid phase by using direct and indirect mechanisms. The RCS generated through photolysis of HOCl and ROS generated by photo excitation of TiO_2 work together in visible light-induced MB degradation.

Figure 4. Comparison of the degradation efficiency of MB under different processes (i.e., photolysis, chlorination (with photolysis), photocatalytic oxidation by TiO₂, photocatalytic oxidation by TiO₂-SiO₂, photocatalytic oxidation by UV-treated TiO₂-SiO₂ with photocatalytic chlorination). Conditions: [MB] = 6 mg L⁻¹, 250 mL, [catalyst] = 0.1 g and pH = 5.

3.2. Effect of Initial pH

The pH of the aqueous solution is an essential parameter controlling both adsorption and photodegradation processes. This is because any change in the solution pH influences the surface charge of the photocatalyst by protonation and deprotonation phenomena [31–33]. The effect of the initial pH of MB solution (acidic, neutral, and alkaline) on the photocatalytic chlorination of MB was studied at pH 4, 7 and 10. The results are presented in Figure 5 and the kinetic data are listed in Table S1.

Figure 5. Graph of concentration versus time for different initial pH values. Conditions: [MB] = 6 mg L⁻¹ and [UV-treated TiO₂-SiO₂] = 0.1 g.

Modifying the pH of the solution strongly influenced the amount of MB adsorbed by the photocatalyst. As observed in Figure 3, during the adsorption process, the highest adsorption efficiency of MB was achieved at pH 10 while the highest degradation efficiency was achieved at pH 4. The enhanced adsorption of MB on the surface of the UV-treated

TiO₂-SiO₂ in alkaline medium can be explained in terms of the photocatalyst's point zero charge. Figure S5 portrays a schematic diagram displaying the change in the surface charge of the UV-treated TiO₂-SiO₂ based on its point of zero charge (pH_{PZC} = 5.5). At pH > pH_{PZC}, the surface of UV-treated TiO₂-SiO₂ is negatively charged and at pH < pH_{PZC}, the surface of UV-treated TiO₂-SiO₂ is positively charged. Therefore, the adsorption of the MB⁺ cationic dye is favored at pH > pH_{PZC} (alkaline condition) due to the presence of a large number of active sites such as TiO[−], HO[−] and SiO[−] [34,35].

As observed in Table S1, the degradation rate constant for photocatalytic chlorination of MB was highest at pH 4 (0.041 mg L^{−1} min^{−1}), followed by pH 10 (0.0128 mg L^{−1} min^{−1}) and pH 7 (0.0117 mg L^{−1} min^{−1}). This is because the HOCl species, which exists predominantly at pH 4, is a more potent oxidant than the OCl[−] species, which exists predominantly at pH 10. Furthermore, Yin et al. (2018) [36] documented that HOCl has a larger quantum yield of about 1.0–1.5 compared to OCl[−], which has a quantum yield of 0.87–1.3.

The difference in the reactivity of RCS in different pH media can be further explained by reactivity of the RCS species being highly pH dependent due to its speciation according to the equilibrium as shown in Equation (1) [37–39]:

The dominant species generated during the UV/chlorine process are chlorine radicals (Cl[•]), secondary chlorine oxides (ClO[•]) and dichloride anions Cl₂^{−•} in acidic medium. The formation of these RCS upon solar irradiation is shown in the following Equations (2)–(5) [34].

One of the advantages of employing RCS to assist the photocatalytic activity of UV-treated TiO₂-SiO₂ is the presence of more radicals, especially HO[•], Cl[•], ClO[•] and Cl₂^{−•} (in acidic medium), whereas only HO[•] and O₂^{−•} radicals are generated in the UV/TiO₂ and UV/H₂O₂ remediation system [39]. Owing to this, the highest photodegradation efficiency of MB was attained at pH 4.

Moreover, Yin et al. (2018) [35] documented that fewer radicals (i.e., HO[•] and Cl[•]) are produced by increasing the pH of the solution during the UV/Cl₂ process. Thus, the neutral and alkaline conditions had only 50% and 52% degradation efficiency of MB compared to the acidic condition (92%). Compared to pH 7, pH 10 demonstrated a rather higher degradation efficiency of MB because of the formation of more HO[•] radicals in the presence of TiO₂ upon photon absorption. It has been widely documented that the photocatalytic activity of TiO₂ is optimum in an alkaline medium [40,41]. In a nutshell, the visible light assisted photocatalytic chlorination of MB is most efficient at pH 4 compared to pH 7 and 10.

3.3. Effect of Initial Concentration

The influence of the initial concentration of MB on its degradation by the photocatalytic chlorination method was evaluated with various concentrations of MB (2, 4, 6 and 8 ppm) in the presence of the optimized initial pH of 4 and UV-treated TiO₂-SiO₂ dosage of 0.1 g. Figure 6 illustrates the effect of various initial concentrations of MB solution on the photocatalytic chlorination of MB. Furthermore, the kinetic data obtained from different experiments, employing different concentrations of MB are given in Table S2. At first, the photodegradation efficiency of MB increased from 79% to 91% when the initial concentration of MB was increased from 2 to 6 ppm, and then plummeted to 88% at the highest concentration of MB. Similarly, the rate constant calculated during the degradation

of MB increased from $0.0251 \text{ mg L}^{-1} \text{ min}^{-1}$ to $0.0411 \text{ mg L}^{-1} \text{ min}^{-1}$ by increasing the initial concentration of MB from 2 to 6 mg L^{-1} and then decreased to $0.0349 \text{ mg L}^{-1} \text{ min}^{-1}$ at 8 mg L^{-1} .

Figure 6. Graph of concentration versus time for different initial concentration of MB. Conditions: [UV-treated $\text{TiO}_2\text{-SiO}_2$] = 0.1 g and $\text{Ph} = 4$.

The elevated degradation rates from 2 to 6 mg L^{-1} presented in Table S2 are due to enhanced reactions amongst the ROS, RCS and MB molecules [26]. The degradation of MB diminishing at high concentration (8 ppm) might be due to competition between the MB molecules and their intermediate products for the available ROS and RCS since at higher initial MB concentration the intermediates' concentrations are also enhanced, which reduce the MB degradation rate [40]. In addition, as the MB concentration increases, it absorb more photons and hereby decreases the availability of overall solar radiation received by the UV-treated $\text{TiO}_2\text{-SiO}_2$ nanoparticles. As a result, this slows down the generation of ROS in the presence of UV-treated $\text{TiO}_2\text{-SiO}_2$ and also the formation of RCS by the process of HOCl photolysis. In effect, the increased initial concentration of MB inhibits the overall reaction and the degradation rate by itself [42].

3.4. Effect of Dosage of UV-Treated $\text{TiO}_2\text{-SiO}_2$

The optimization of photocatalyst loading is essential to avoid excessive usage of the photocatalyst and to ensure maximum absorption of photons [30,43]. Similarly, loading of the UV-treated $\text{TiO}_2\text{-SiO}_2$ also plays a crucial part in the visible light induced photocatalytic system for the degradation of MB in the presence of RCS. The UV-treated $\text{TiO}_2\text{-SiO}_2$ dose was varied from 0.05 g to 0.20 g . Figure 7 shows the effect of catalyst dosage on MB degradation by photocatalytic chlorination under solar irradiation. The kinetic data from different experiments in which the dosage of photocatalyst was varied are reported in Table S3. As depicted in Figure 7, the corresponding MB photodegradation efficiencies were found to be 85.32, 90.76, 91.22 and 91.81% for 0.05, 0.10, 0.15 and 0.20 g , respectively. This clearly implies a very minimal effect of increasing the photocatalyst dosage [44].

Based on the results in Table S3, the rate constant obtained from the degradation of MB was found to be enhanced from a value of $0.033 \text{ mg L}^{-1} \text{ min}^{-1}$ to $0.0424 \text{ mg L}^{-1} \text{ min}^{-1}$ by the increasing dosage of UV-treated $\text{TiO}_2\text{-SiO}_2$ from a value of 0.05 g to 0.20 g . The boost in the removal efficiency of MB molecules with increasing UV-treated $\text{TiO}_2\text{-SiO}_2$ dosage occurred because of the presence of enormous amounts of surface-active sites, thereby increasing the number of $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals generated [45]. Apart from that, with increasing dosage of catalyst, the exposed surface area for MB adsorption also increased, thereby enhancing degradation of adsorbed MB molecules by both ROS and RCS radicals.

Figure 7. Graph of concentration versus time for different dosage of catalyst. Conditions: [MB] = 6 mg L⁻¹ and pH = 4.

3.5. Effect of Various Scavengers on MB Degradation

Numerous studies were conducted in the presence of different ROS as well as RCS inhibitors including nitrobenzene, benzoquinone and sodium thiosulfate to scrutinize the effect of ROS and RCS involved in MB degradation in the visible region. Radical scavengers, nitrobenzene (10 mM) and benzoquinone (10 mM) were employed to quench the HO• and O₂^{-•} radicals, respectively [34,38,46]. According to Yin et al. (2018) [35], nitrobenzene was found to be more reactive in the presence of HO• ($k = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), whereas it was less reactive or unreactive in the presence of RCS and/or free chlorine. In addition, excess sodium thiosulfate, Na₂S₂O₃, was employed to quench the effect of RCS to evaluate the contribution of RCS towards visible light-induced photodegradation of MB [47].

As displayed in Figure 8, the photodegradation of MB was primarily due to RCS, and then by HO• radicals. According to Kong et al. (2018) [38], the degradation of gemfibrozil (GFRZ) and bezafibrate (BZF) was also mainly due to RCS and HO• radicals. The author reported that RCS contributed about 80% and 70% to degradation of GFRZ and BZF, respectively. However, in this study, it was found out that the RCS, HO• and O₂^{-•} radicals contributed about 52, 20 and 11%, respectively, to the visible light induced photo degradation of MB molecules in the aqueous system. The highest contribution of RCS in the photodegradation of MB under solar irradiation in acidic medium was due to the generation and efficient oxidative reaction of the RCS, such as Cl₂^{-•}, Cl•, ClO• and ClOH^{-•} radicals. Similarly, Kamath & Minakata (2018) [46] documented that the degradation of acetone was induced by both HO• and RCS such as Cl₂^{-•}, ClO•, ClOH^{-•} and Cl• radicals. Overall, these results revealed that the enhanced adsorption of MB on the surface of the UV-treated TiO₂-SiO₂ and the RCS generated by the HOCl photolysis might be crucial steps in the photocatalytic chlorination process.

3.6. Spectral Changes during the Photocatalytic Chlorination of MB

The spectrum of degradation obtained during the photocatalytic chlorination of MB at a reaction time of 60 min was recorded and evaluated by absorption spectrophotometry and is shown in Figure S6. Three absorbance peaks of MB at 245, 290 and 660 nm were seen in the absorbance spectrum. The peaks at 245 and 290 nm are due to the absorbance of the $\pi \rightarrow \pi^*$ transition, while the peak at 660 nm is due to the absorbance of the $n \rightarrow \pi^*$ transition [48]. As observed in Figure S6, prolonged illumination with a solar lamp remarkably promoted the photocatalytic degradation of MB up to 95% [42]. Apart from the rapid decrease in the initial UV absorbance of the peak at 660 nm [49], a reduced and shifted peak was also

observed because of the degradation of MB molecules by the process of photocatalytic reaction in the presence of UV light irradiation [41]. In this study, 95% removal efficiency of MB was achieved under 60 min of solar irradiation (10 mW cm^{-2}). This was mainly due to the generation of more ROS such as $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals and RCS species which readily react with MB molecules under visible light.

Figure 8. Graph of concentration versus time for different radical scavengers. Conditions: $[\text{MB}] = 6 \text{ mg L}^{-1}$, $[\text{catalyst}] = 0.1 \text{ g}$ and $\text{pH} = 4$.

Figure S7 shows a schematic diagram of visible light-induced photocatalytic chlorination of MB. The reaction occurs via three major processes, i.e., adsorption of MB on the surface of the photocatalyst, photo induced formation of ROS and RCS radicals, and reaction between the radicals and the MB molecules. During the adsorption process, the SiO_2 nanoparticles adsorb MB molecules in the bulk solution by the electrostatic attraction between the surface $\text{Si-O}^{\delta-}$ groups and positively charged MB^+ cations. The resultant adsorbed MB molecules enrich the surface of SiO_2 nanoparticles. Under solar irradiation, the $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ radicals generated by the anatase TiO_2 nanoparticles and RCS generated by the HOCl photolysis attack the pre-enriched MB molecules on the surface of SiO_2 [45]. The highly reactive $\text{HO}^\bullet$ radicals possess a very short lifetime, i.e., 10^{-9} s [50]. Since the SiO_2 concentrates the MB molecules near the active centers of TiO_2 through adsorption, the UV-treated TiO_2 - SiO_2 composite can efficiently capture and utilize the short-living $\text{HO}^\bullet$, which are localized onto the surface of TiO_2 for photodegradation of MB in the visible region [51]. Apart from that, the generation of RCS due to the photolysis of HOCl highly contributes to the photodegradation of MB in the visible region. It is widely documented that TiO_2 exhibits poor photocatalytic activity in the visible region [20,52]; hence, the RCS, i.e., $\text{Cl}^\bullet$, $\text{ClO}^\bullet$ and $\text{Cl}_2^{\bullet-}$ radicals generated assist in the visible light-induced photocatalytic activity by the UV-treated TiO_2 - SiO_2 . The MB molecules are decomposed into smaller molecules and finally into CO_2 , H_2O and minerals as shown in Figure S7. Consequently, SiO_2 can be regenerated in the system itself by the presence of nearby anatase crystals, and the MB molecules can be re-adsorbed. At this point, the anatase crystals can attack the re-adsorbed MB molecules. These continuous and repetitive processes significantly enhance the efficient use of the ROS and RCS radicals [49].

4. Conclusions

A sol-gel process was employed to incorporate SiO_2 with commercial Degussa-P25 TiO_2 followed by UV-C treatment for 2 weeks. The characteristics of the commercial TiO_2 , the newly prepared TiO_2 - SiO_2 and UV-treated TiO_2 - SiO_2 were analysed and compared

with each other. The crystallinity, functional groups, band gap and photoluminescence of the TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$ were scrutinized to recognize characteristics that contribute the most to photocatalytic activity in visible region. The visible light-induced photocatalytic activity of UV-treated $\text{TiO}_2\text{-SiO}_2$ was assisted by the presence of RCS, including free chlorine (Cl_2 , HOCl , OCl^-) and chlorine radical species ($\text{Cl}^\bullet$, $\text{Cl}_2^{\bullet-}$) formed in the system. Compared to TiO_2 and $\text{TiO}_2\text{-SiO}_2$, UV-treated $\text{TiO}_2\text{-SiO}_2$ had the highest adsorption efficiency, exhibiting the highest photodegradation efficiency of MB in the visible region. Apart from that, the enhanced surface area, surface hydroxyl and crystallinity of UV-treated $\text{TiO}_2\text{-SiO}_2$ enabled efficient removal of MB from the aqueous system under solar irradiation in comparison with TiO_2 and $\text{TiO}_2\text{-SiO}_2$. The photodegradation of MB molecules by UV-treated $\text{TiO}_2\text{-SiO}_2$ proceeds through dominant adsorption of Si-OH groups followed by oxidation and reduction process by $\text{HO}^\bullet$, $\text{O}_2^{\bullet-}$, $\text{Cl}^\bullet$, $\text{ClO}^\bullet$ and $\text{Cl}_2^{\bullet-}$ radicals. The influences of various parameters, i.e., initial pH of solution, initial concentration of MB, and dosage of photocatalyst were investigated to identify the competency of the method for the total mineralization of MB. The maximum efficiency for the removal of MB was achieved in an acidic medium (pH 4), with the highest initial concentration of MB and the highest initial dosage of UV-treated $\text{TiO}_2\text{-SiO}_2$.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal12020156/s1>, Figure S1: (a) Schematic set-up of the photoreactor (b) Schematic diagram of $\text{TiO}_2\text{-SiO}_2$ preparation steps via sol gel method; Figure S2: XRD pattern of TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$; Figure S3: FTIR spectra of the TiO_2 , $\text{TiO}_2\text{-SiO}_2$ and UV-treated $\text{TiO}_2\text{-SiO}_2$; Figure S4: Schematic diagram of TiO_2 photocatalysis; Figure S5: Schematic diagram of adsorption mechanism of MB molecule onto UV-treated $\text{TiO}_2\text{-SiO}_2$; Figure S6: UV-vis absorbance spectrum of photocatalytic chlorination of MB. Conditions: $[\text{MB}] = 6 \text{ mg L}^{-1}$, $[\text{UV-treated TiO}_2\text{-SiO}_2] = 0.1 \text{ g}$ and $\text{pH} = 4$. Samples were extracted every 10 minutes; Figure S7: Schematic diagram of visible light induced photocatalytic chlorination of MB molecule; Table S1: Degradation efficiency (DE%) (except for adsorption), first-order constants and correlation coefficients of the MB degradation experiments with different initial pH; Table S2: Degradation efficiency (DE%) (except for adsorption), first-order constants and correlation coefficients of the MB degradation experiments with different initial concentration of MB; Table S3: Degradation efficiency (DE%) (except for adsorption), first-order constants and correlation coefficients of the MB degradation experiments with different dosage of catalyst.

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