

Removal of Methylene Blue Dye from Aqueous Solution Using a Newly Synthesized TiO₂-SiO₂ Photocatalyst in the Presence of Active Chlorine Species

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Abstract. Industrialization and urbanization demand high amount of water consumption, which contributes to their polluted condition. Thus, there is a need to develop a sustainable wastewater remediation technique in order to provide sustainable use of clean water for future generations without ramifications to the economic sectors. The newly synthesized TiO₂-SiO₂ photocatalyst was used to remediate Methylene Blue contaminated aqueous solution in the presence of active chlorine species. The doping of SiO₂ into TiO₂ enhanced the removal rate of Methylene Blue dye from the solution by increasing the surface area, thermal stability and surface acidity of the TiO₂. The active chlorine species further enhanced the removal rate of Methylene Blue dye from the solution by contributing more reactive species, chlorine radicals, which broke down the dye molecules. The experiments were conducted via Taguchi analysis. The findings show that combining TiO₂, SiO₂ and active chlorine species enhanced the removal percentage of Methylene Blue dye compared to using TiO₂ alone by 70%. About 70% of 50ppm Methylene Blue was degraded by 1 g of TiO₂-SiO₂ in the presence of 0.3 ppm Ca(OCl)₂ under 9 Watts solar irradiation within 3 hours. The enhanced dye removal method brings photocatalysis a step closer to sustainable wastewater remediation methods.

1. Introduction

Sunlight or solar energy is a well known renewable energy and largest source of carbon neutral energy [1]. Approximately 95% of UV-A and 5% of UV-B reaches the Earth's surface since ozone and oxygen absorb majority UV-B and UV-C [2]. The UV wavelength (100-400 nm) consists of UV-C (100-280 nm), UV-B (280-315 nm) as well as (315-400 nm) [2-4]. The titanium oxide, TiO₂, is a well known photocatalyst, utilized widely in numerous catalyzed reactions including photocatalysis, oxidation, Fischer-Tropsch reaction [5] delivery of drug, chemical sensors as well as photovoltaic cells [6]. The SiO₂ addition into TiO₂ enhances TiO₂ suspension in aqueous solution, enhances the adsorption of pollutants [7], induce high mechanical and thermal stability [5].

In previous research done by our team, 10 ppm of Methylene Blue (MB) was successfully removed from simulated wastewater using Solar/HOCl treatment method. Active chlorine species produced due to addition of HOCl was utilized as chemical oxidant due to its simplicity, strong oxidation and disinfection capability and low cost. Optimum conditions required for remediation of MB using 9 Watts solar irradiation was at pH 4, lower HOCl dosage as well as high initial concentration of MB. In order to further enhance the removal efficiency of MB from simulated wastewater using solar irradiation, in this we study we included photocatalyst, TiO₂-SiO₂.



In this study, commercial P-25 TiO₂ doped with SiO₂ was synthesized via sol gel method in order to increase the surface area and acid properties [8]. MB dye was utilized as a model dye to analyze the photo activity of TiO₂-SiO₂. The Taguchi design was employed to study the influence of different parameters on removal efficiency of MB [9]. Taguchi design was employed because compared to full factorial design, the number of experiments required for Taguchi method is lowered [9].

2. Materials and Methods

2.1. Preparation of TiO₂-SiO₂

Commercial TiO₂ (Degussa P25) and TEOS precursor were used to prepare TiO₂-SiO₂ photocatalyst. SiO₂ sol was prepared by addition of 22.2 mL of TEOS, to a mixture of 29.2 mL ethanol, 7.2 mL distilled water and 0.4 mL of 3.6% of hydrochloric acid followed by stirring at 90°C in air for 1 hour. 0.2g of Degussa TiO₂ was added to a mixture of SiO₂ sol which was subsequently diluted with absolute ethanol in order to yield a final volume of 50 mL. The resulting sol was dried in air at 80°C for 24 h [10]. Dried TiO₂-SiO₂ were stored in small clean screw cap vials for subsequent experiments [11]. The synthesized TiO₂-SiO₂ was later irradiated with UV-B, UV-C and Solar lamps in order to facilitate the formation of Ti-O-Si bond. Calcium hypochlorite (Ca(OCl)₂) salt was utilized to prepare stock aqueous chlorine solutions and were filtered through a 0.45 µm filter [12]. All free chlorine solutions were prepared by dilution of the calcium hypochlorite stock solution with distilled water in glassware protected from light to minimize free chlorine photodecay [13].

2.2. Photo-activation of TiO₂-SiO₂

Photoactivation of TiO₂-SiO₂ was conducted inside a beaker placed on a hotplate to enable constant stirring of the solution using a magnetic stirrer. Three different types of lamps emitting UV-C, UV-B and Solar were utilized to activate the TiO₂-SiO₂. The height of UV lamps were adjusted so that the height of the MB solution is equal or more than midpoint of the lamps for maximum exposure [11]. The photocatalyst was added into MB solution and stirred using magnetic stirrer for 40 min in the dark to achieve adsorption equilibrium and uniformity of the reaction system [14]. All the experiments were conducted using batch photo-reactor [15]. 250 mL of simulated Methylene Blue wastewater (10, 30 or 50 ppm) was prepared and TiO₂-SiO₂ (0.5, 1.0 or 1.5 g) was added. After 40 min of adsorption, 50 mL of prepared HOCl (0.1, 0.2 or 0.3 ppm) solution was added. 9 Watts of Solar lamp was used to irradiate the solution. At every 10 min intervals, the dispersion was extracted and filtered to separate the photocatalyst particles. Any changes in the concentration of MB after the experiments were tracked using a Perkin Elmer Lambda 25 UV-Vis spectrophotometer [16]. The removal efficiency of MB was calculated from the peak intensity of the characteristic absorption band of MB at 665 nm. The removal efficiency of MB was calculated using [17]:

$$\text{Removal Efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

In which C₀ (mg L⁻¹) and C_t (mg L⁻¹) represent the initial concentration of dye and concentration at a particular time, respectively.

2.3. Taguchi Design

First, the outcome characteristic (removal efficiency of MB dye) was identified, and process parameters that are to be investigated (effect of different wavelength irradiated TiO₂-SiO₂, HOCl dosage, TiO₂-SiO₂ dosage as well as initial concentration of MB) are selected [18-19]. Second, the amount of levels of each parameters are selected. Next, suitable orthogonal array (OA) was selected and the parameters were assigned to the orthogonal array. Forth, experiments were conducted based on the arrangement of the orthogonal array. The experiments were conducted twice and average value was determined and used for the analysis. Fifth, the analysis on the obtained data were conducted and analyzed using analysis of variance (ANOVA). In this study, four parameters were selected to study removal efficiency of MB using Taguchi design. Taguchi orthogonal array L₉ (3⁴) with three levels for each factor [20] was utilized in order to analyze the impact of four factors (effect of irradiated TiO₂-SiO₂, HOCl dosage, TiO₂-SiO₂ dosage as well as MB concentration) on the removal efficiency of Methylene Blue dye. It should be

noted that in the orthogonal arrays, for each level of any factor, each level in the factor occur equal number of times in which gives a balanced design [9]. Following are the different levels for each factor, (1) Different wavelength utilized to irradiate TiO₂-SiO₂ (UV-C/ 100-280 nm, UV-B/ 280-315 nm, & solar/ 280-700 nm), (2) HOCl dosage (0.1, 0.2 & 0.3 ppm) (3) TiO₂-SiO₂ dosage (0.5, 1.0 & 1.5 g) and lastly initial concentration of MB (10, 30 & 50 ppm). UV-A (315-400 nm) was not included in the study since the natural sunlight consists of UV-A [21]. The experiments were conducted twice for each experiment to ensure accuracy and the average response is shown in the table [19]. The influence of the parameters on MB removal efficiency were investigated through analysis of variance (ANOVA) with 95% confidence level [9, 22].

3. Results & Discussion

3.1. Effects of parameters on the removal efficiency of MB dye

No significant change in MB concentration was determined under solar irradiation without the presence of TiO₂-SiO₂ [23]. Following Table 1 and Table 2 show selected factors and their levels (Coded and Actual). All the Taguchi experiments showed removal of MB from aqueous solution with removal efficiency ranging from 82.6-99.3%. From the analysis of UV-Vis absorbance peaks of Methylene Blue, the characteristic peaks of MB appears at 665 nm, 293 nm and 246 nm. The peak at 665 nm represents dimethylamino group / thiazine (the chromophore), as well as peaks at 293 nm and 246 nm represent the benzene rings in the MB molecule [24-25]. At the end of all 9 experiments, the dominant peak at 665 nm decreases due N-demethylation and deamination of MB, while the peaks at 293 nm and 256 nm decrease due to cracking of benzene ring [24].

As shown in the Fig. 1-4, highest removal efficiency of Methylene Blue was achieved when lower wavelength (UV-C/ 100-280 nm) was used to irradiate TiO₂-SiO₂ (UV-C), lower HOCl dosage, lower concentration of Methylene Blue as well as higher amount of TiO₂-SiO₂ dosage.

Table 1. Selected factors and their levels (actual)

Factors	Symbol	Level		
		1	2	3
Different wavelength irradiated TiO ₂ -SiO ₂ (Factor A)	-	UV-C irradiated TiO ₂ -SiO ₂	UV-B irradiated TiO ₂ -SiO ₂	Solar irradiated TiO ₂ -SiO ₂
HOCl dosage (Factor B)	ppm	0.1	0.2	0.3
TiO ₂ -SiO ₂ dosage (Factor C)	g	0.5	1.0	1.5
Conc. of MB (Factor D)	ppm	10	30	50

Table 2. Taguchi L₉ (3⁴) orthogonal array of selected factors (coded)

Standard	Run Order	Factor A	Factor B	Factor C	Factor D	Removal efficiency (Average)
2	1	1	2	2	2	97.2
5	2	2	2	3	1	99.3
6	3	2	3	1	2	82.6
8	4	3	2	1	3	85.3
4	5	2	1	2	3	92.7
3	6	1	3	3	3	95.9
1	7	1	1	1	1	97.5
7	8	3	1	3	2	97.0
9	9	3	3	2	1	95.1

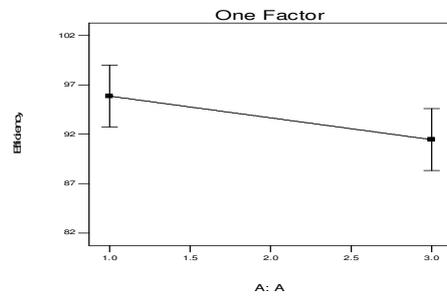


Figure 1. Factor A

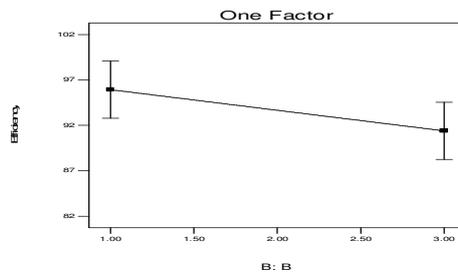


Figure 2. Factor B

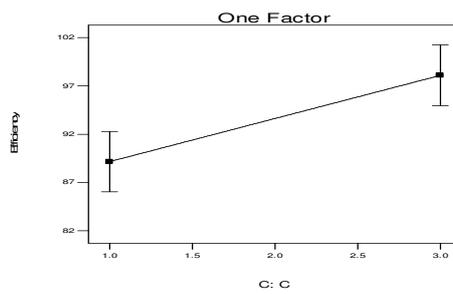


Figure 3. Factor C

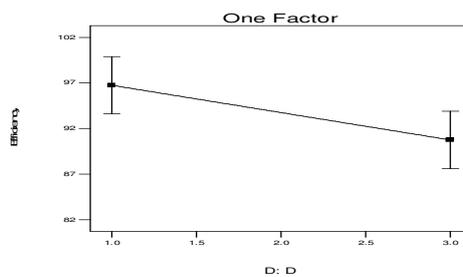


Figure 4. Factor D

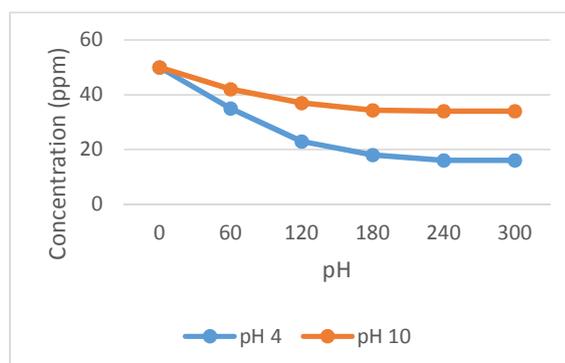


Figure 5. Concentration vs pH (50 ppm of Methylene Blue was degraded by 1 g of $\text{TiO}_2\text{-SiO}_2$ in the presence of 0.3 ppm $\text{Ca}(\text{OCl})_2$ under 9 Watts solar irradiation within 3 hours)

Table 3. Analysis of variance

Source	Sum of Squares	Df	Mean Square	F value	p-value Prob>F
Model	233.57	4	58.39	6.33	0.0507
A	29.04	1	29.04	3.15	0.1506
B	30.83	1	30.83	3.34	0.1415
C	119.71	1	119.71	12.98	0.0227
D	54.00	1	54.00	5.86	0.0728

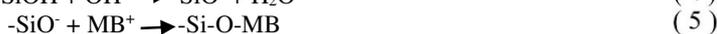
This shows that the newly synthesized $\text{TiO}_2\text{-SiO}_2$ has good photo degradation ability in relative to low MB concentration [24, 26]. At low initial concentration of MB, maximum amount of dye molecules adsorbed on $\text{TiO}_2\text{-SiO}_2$ dosage leading to high adsorption efficiency [26]. However, at high concentration of MB, lower adsorption efficiency was reported due to saturation of active sites on the adsorbent's surface [26].

The maximum adsorption percentage was achieved at 1.5 g of $\text{TiO}_2\text{-SiO}_2$ because more active sites are available as the dosage increased from 0.5 to 1.5 g. If the dosage is further increased, it may cause aggregation of adsorption sites and increased diffusion path length which may decrease the availability of total available surface area of adsorbent [26]. From the Fig. 2, it shows that increasing the HOCl dosage decreases the removal efficiency of MB from simulated wastewater. This may due to pH of the solution which was alkaline (pH 10). At $\text{pH} < 3$, Cl_2 is the main chlorine species HOCl in the region $3 \leq \text{pH} \leq 7$, and OCl^- at $\text{pH} > 7$ in which among these, HOCl is the strongest oxidant and the predominant species at pH 4 [27]. Hence, another experiment was conducted to investigate the effect of HOCl at pH 4 as shown in Graph 1. About 70% of 50ppm Methylene Blue was degraded by 1 g of $\text{TiO}_2\text{-SiO}_2$ in the presence of 0.3 ppm $\text{Ca}(\text{OCl})_2$ under 9 Watts solar irradiation within 3 hours for pH 4 while 32% for pH 10. The effectiveness of 254 nm radiation (UV-C) was attributed to the shorter penetration capability of the higher energy photons [28]. Compared to UV-A, UV-B and solar irradiation, UV-C contributed the most to chemical or morphological modification on the surface of $\text{TiO}_2\text{-SiO}_2$ by creating uniformly distributed pores and formation of large amount of Ti-O-Si bonds. The Table 3 consists of "p" values that is used to investigate the statistical significance of each parameter [19, 29]. It was found that only factor C ($\text{TiO}_2\text{-SiO}_2$ dosage) exhibit significant influence on removal efficiency of MB from simulated wastewater.

3.2. Mechanism of TiO₂-SiO₂

It was reported that TiO₂ either successfully or partially incorporated with amorphous SiO₂ through Si⁴⁺ entering the TiO₂ lattice fringes [30]. This is due to smaller size of Si⁴⁺ ionic radii (0.039 nm) compared to TiO₂ (0.068 nm) which enables Si⁴⁺ ions enter into crystal lattice of TiO₂ as a substitute for Ti⁴⁺ [30]. In the TiO₂-SiO₂, the SiO₂ acts as an excellent adsorbent due to enormous amount of acid sites as well as hydroxyl groups on its amorphous surface [31]. The SiO₂ on the surface of TiO₂ acts as favored adsorption sites for dye molecules, thus bringing the pollutant molecules within close proximity to high [•]OH concentration leading to enhanced photo degradation rate [10, 32]. In addition, there is a possibility of other ROS (e.g., superoxide anion) production enhanced due to surface modification using SiO₂ [32].

The mechanism of TiO₂-SiO₂'s superhydrophilicity is still not explained well. Three possible explanations for this enhanced property are; 1) enhanced surface roughness cause an increase in hydrophilicity, 2) Changes in the surface structure (either chemically or morphologically) caused conversion of Ti⁴⁺ sites to Ti³⁺ sites via conduction band electron trapping which is favors the dissociative water adsorption, 3) increased surface acidity of Si-O-Ti bonds at the interfaces lead huge amount of hydroxyl groups on the surface [10]. The possible interaction that occur during adsorption of MB dye molecules onto adsorbents surface are the electrostatic interaction between negatively charged surface of the adsorbent and positively charged active site of dye molecule; dipole-dipole H-bonding interaction between -OH groups present on the surface of the adsorbent and the electronegative residue (N lone pair) in MB⁺ molecules; as well as Yoshida H- bonding interaction between silanol -OH groups, large number of -OH groups present on the TiO₂ surface and the active sites of MB⁺ dye (aromatic ring) [26]. The existence of silanol groups on the surface of SiOH and these groups are able to interact with MB molecules. At low pH values, the H⁺ and MB⁺ compete with each other for adsorption sites and there is repulsive force between the positive charged TiO₂-SiO₂ and MB⁺. However with increasing pH, the silanol groups on the surface increases which then interact with MB⁺. Moreover, the amount of negatively charged adsorption sites increases at alkaline condition, which favors the cationic MB adsorption [33].



Meso-macroporous TiO₂-SiO₂ film exhibited higher photo degradation compared to silica-etched TiO₂ and dense TiO₂ films. The higher degradation rate is attributed to meso-macroporous structure and TiO₂-SiO₂ hybridization [6]. The doping of SiO₂ onto TiO₂ enhances the photo degradation efficiency of MB dye molecules due to the SiO₂'s ability to adsorb the dye molecules in the vicinity of TiO₂ photo active centre as well as its ability to block the recombination of photo generated holes and electrons from TiO₂. The pores offer larger surface area with greater possibility of target pollutant attack by a higher number of oxidizing agents such as positive holes h⁺_{VB} and [•]OH formed between holes and HO[•] groups on the surfaces of TiO₂ or H₂O as well as reducing agents such as electrons, e⁻_{CB} and the superoxide radical anion, O₂^{•-} formed due to the reaction of O₂ adsorbed on the TiO₂ surface or dissolved in H₂O and photogenerated electron [6].

Two degradation pathway of MB dye molecule under solar light irradiation [23];

- i) Self-sensitized reaction: Direct photon absorption by MB, excitation of MB molecule, injection of electron from MB into conduction band of TiO₂, electron reacts with O₂ to produce super oxide radical which oxidize MB molecules.
- ii) Excitation of TiO₂: photon absorption by TiO₂, electron excitation from valence band into conduction band to create e⁻/h⁺ pairs. The electron reacts with O₂ to produce super oxide radical and holes oxidize H₂O to produce OH radicals which oxidize the MB molecules.

4. Conclusion

The TiO₂-SiO₂ acts as an excellent adsorbent and photocatalyst which can work effectively under natural sunlight. The enhanced photocatalytic activity of UV irradiated TiO₂-SiO₂ is due to the narrowed bandgap aided by production of many HO[•] free radicals, larger surface area as well as more active sites for dye adsorption of TiO₂-SiO₂. Combination of crystalline nature, high amount of hydroxyl groups and porosity are the main contributors for high photocatalytic activity by TiO₂-SiO₂. Compared with non-irradiated TiO₂-SiO₂, irradiated TiO₂-SiO₂ exhibited higher removal efficiency of MB. Taguchi analysis showed that removal efficiency of MB decreases with increasing irradiated TiO₂-SiO₂, HOCl dosage and initial concentration of MB. However, removal efficiency of MB increases with increasing TiO₂-SiO₂ dosage. From the ANOVA analysis, TiO₂-SiO₂ dosage significantly influences the removal efficiency of MB.

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