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Photocatalytic Degradation of Methylene Blue Dye Using Ultraviolet Light Emitting Diodes

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This study was focused on the application of ultraviolet light emitting diodes (UV-LED) as an alternate source for the photocatalytic degradation of methylene blue (MB), which was used as a model compound. A simple reactor arrangement was made to carry out the photocatalytic degradation of methylene blue dye. The photocatalytic activity of P-25 Degussa TiO_2 was evaluated using UV-LED reactor. The decomposition of MB dye in aqueous solution by TiO_2 photocatalytic process with the UV-LED was found to be technically feasible. The effects of various parameters such as catalyst loading, initial dye concentration, pH, and addition of H_2O_2 on decolorization and degradation have been investigated to find the optimum conditions. The complete mineralization of MB dye (3.12×10^{-5} M) was confirmed by chemical oxygen demand analysis. Results demonstrated that the UV-LED/ TiO_2 process can effectively degrade methylene blue dye with optimum conditions.

1. Introduction

In the past 40 years, extensive research efforts have been devoted to the development of heterogeneous photocatalytic technology for eliminating organic and inorganic pollutants.^{1–8} Usually, semiconductor particles with suitable band gap and flat band potentials/energy levels are used as photocatalysts. The semiconductors such as TiO_2 , ZnO , Fe_2O_3 , CdS , ZnS , and ZrO_2 are employed. Among the semiconductors, titanium dioxide (TiO_2) is the most widely used photocatalyst because of its suitable flat band potential, chemical stability, nontoxicity, and high photocatalytic activity.^{4,9–14} The excitation of TiO_2 generates highly reactive electron–hole pairs that in turn produce highly potent radicals (such as $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$) to oxidize organic and inorganic pollutants. However, the optimum reactor design and operational conditions are the major concerns for the development and potential application of the photocatalytic process. It is worth mentioning that all the previous work on photocatalytic degradation/removal of pollutants from wastewater have been carried out with broad spectral radiation sources such as UV lamps and TiO_2 as a photocatalyst. The traditional UV source is a mercury vapor high-pressure lamp, which is a gas discharge source.^{15–17} Several problems are associated with the use of UV lamps emitting over a broad spectral wavelength range. For example, the long-term power instability due to overheating of lamps during the operation, low photonic efficiency, and longer exposure time (h) for complete mineralization of pollutants are the major drawbacks associated with UV lamps as a source of irradiation;¹⁸ other drawbacks of using this source are that it needs high voltage to generate a strong electric field and free electrons in the gas in the initial stage and the filling gas must have a fairly low ionization energy, have sufficient vapor pressure, be inert, and have an excited state at a low enough level that the resonance radiation appears at UV wavelength, and have shorter lifetime. Also, the mercury used in this source, which is specified as a hazardous air pollutant (HAP) by the U.S. Environmental Protection Agency, can damage the brain and kidneys. The new, safer, and energy-efficient alternative for the gas discharge sources is ultraviolet

light emitting diodes (UV-LED). Light-emitting diodes are p-n junction devices made of gallium arsenide (GaAs), gallium arsenide phosphide (GaAsP), gallium phosphide (GaP), or indium gallium nitride (InGaN). Three semiconductor layers were deposited on a substrate, with an active region that lies between the p- and n-type semiconductor layers. Current flow in a LED is one-directional (forward biased); therefore, the electrons and holes move into the active region and are recombined to emit light through a process called electroluminescence. This implies that the electron–hole pair drops into a more stable state, releasing energy by emission of a photon. The light output is linearly proportional to the current within its active region. A LED is a directional light source, with the maximum emitted power in the direction perpendicular to the emitting surface. Another advantage of using UV-LED is that their lifetime is 100000 h, whereas in the case of gas discharge sources it is 1000 h.

Recently, some researchers demonstrated the photocatalytic degradation of red 22 dye and perchloroethylene using specifically designed reactor setup with UV-LED.^{19–21} Until now, there have been no reports on the use of UV-LED as a source, for photocatalytic degradation of methylene blue in a dispersion medium in a small reactor setup. The main objective of this study is to explore the possibility of UV-LED as a UV source for the photocatalytic degradation of dyes in a dispersion medium because it is economical and contains no hazardous material. It is a long-term UV light source for the development of a miniaturized photocatalytic experimental setup. In this study, we report the first time use of UV-LED as a source for photocatalytic degradation of methylene blue using a simple experimental setup. The photocatalytic activity of standard photocatalyst P-25 Degussa was evaluated using 5 number of UV-LED locally fabricated reactor. The effects of various parameters such as catalyst loading, initial dye concentration, pH, and addition of H_2O_2 on decolorization and degradation have been investigated to find optimum conditions.

2. Experimental Section

2.1. Chemicals and Reagents. Methylene blue, procured from s.d. Fine Chem Ltd., Mumbai, India, was chosen as a

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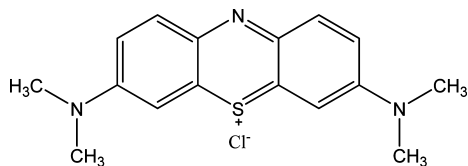


Figure 1. Structural formula of methylene blue.

simple model of a series of thiazin dyes largely used in the industry. Methylene blue is a heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}ClN_3S$. It has many uses in a range of different fields. At room temperature it appears as a solid and is odorless and a dark green powder, which yields a blue solution when dissolved in water. Its structure is given in Figure 1. When dissolved in water, the UV–visible spectrum of MB showed three absorption maxima. The first band was observed at 246 nm and then 291 nm and more intensely 663 nm. The absorption maxima wavelength of MB ($\lambda_{\max} = 291$ and 663 nm) was used for the analysis during degradation and decolorization of MB dye, respectively. The natural pH of the aqueous dye solution is 6.5. The pH of the solutions was adjusted using H_2SO_4 or NaOH.

Standard chemical reagents for chemical oxygen demand (COD) measurements were purchased from E. Merck India Ltd., Mumbai, India. The double-distilled water was used to prepare experimental solutions.

Titanium dioxide (P-25) was purchased from Degussa Corporation, Germany. It has an average particle size of 30 nm and a BET specific surface area of $55 \text{ m}^2 \cdot \text{g}^{-1}$. The anatase and rutile percentages were 70% and 30%, respectively. Titanium dioxide (P-25) was used as a catalyst without further modification.

2.2. Components and Power Supply. UV-LEDs used for this work were p-n junction devices made of indium gallium nitride (InGaN). They emit blue UV light. The operating temperature range of UV-LED is -25 to 85°C . The optical risetime for this UV-LED is 30 ns. The UV-LED has a diameter of 5 mm and irradiation wavelength in the range of 390–410 nm. The luminous intensity of each LED is 350 mcd and the radiant flux is in the range of 10–12 mW at 20 mA.²¹ The switch mode power supply of 0–60 V, 0–6 A, manufactured by ISO-TECH and to limit the current resistor of 220 Ω , was procured at a local market.

2.3. UV-LED Source Photocatalytic Reactor. The photocatalytic activities of commercial standard P-25 Degussa TiO_2 catalysts were determined by studying the degradation of an aqueous solution of methylene blue dye in a simple indigenously made photocatalytic reactor. The photocatalytic reactor consists of a 125 mL glass beaker and 5 UV-LED mounted acrylic sheet (Figure 2). The LEDs were mounted on an acrylic sheet in a circular path. All the LEDs were connected in series and attached to a d.c. power supply through a current limiting resistor. All photocatalytic experiments were carried out under similar conditions by keeping the same voltage and current. This LED-mounted acrylic sheet was held at 1 cm above the mixture of catalyst and methylene blue dye solution.

2.4. Experimental Procedure. In a typical experiment, a suspension containing the required amount of the TiO_2 catalyst (P-25 Degussa) and 25 mL of an aqueous methylene blue dye solution was ultrasonicated for 2 min and then stirred for 30 min in the dark prior to irradiation of UV light; to determine the adsorption on the catalyst, a 2 mL sample was withdrawn by syringe for analysis. The reaction mixture was stirred for continuous dispersion of catalysts. The concentration of methylene blue dye in the bulk solution prior to irradiation was used as the initial value for the measurements of methylene blue dye

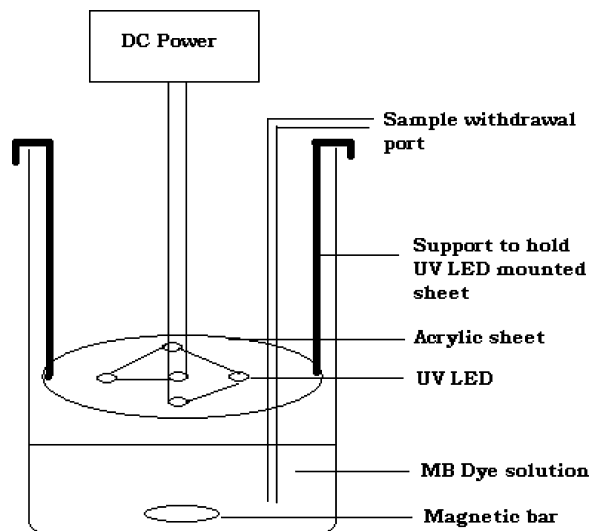


Figure 2. Experimental setup.

degradation. At each interval of 1 h, a 2 mL sample was withdrawn by syringe from the irradiated suspension. The catalyst was separated by centrifugation from the aqueous solution prior to analysis. The concentration of methylene blue dye ($\lambda_{\max} = 291$ and 663 nm) in the solution was determined using a calibration curve of methylene blue (concentration vs absorbance) prepared with known concentrations using a Cary 500 UV–vis spectrophotometer (Varian, Palo Alto, CA).

3. Results and Discussion

3.1. Photocatalytic Activity. There are so many reports on the degradation of organic contaminants and dyes using a mercury vapor lamp as a UV source and solar light.^{15,16,22–25} It is reported that the photocatalytic rates of degradation dye under UV light irradiation are higher than those under solar light.¹⁸ For photocatalytic degradation, mainly a low, medium, or high mercury pressure vapor lamp is used as a UV source. The constraints with UV sources are that they need higher energy and cooling, are large in size, and contain hazardous mercury. UV-LEDs are free of toxic chemicals (e.g., mercury), are small in size, and consume less energy than a traditional lamp. So in this study we have used the simple reactor arrangement based on UV-LED sources, for the photocatalytic degradation of methylene blue. The experiments were carried out to study the effect of dye concentration, amount of catalysts, pH, and addition of hydrogen peroxide. All these experiments were carried out using 5 UV-LED.

3.2. Photodegradability. To study the photodegradability, experiments were carried out under the following conditions: (i) MB dye solution with the UV-LED light in the absence of photocatalyst; (ii) MB dye solution under irradiation of UV-LED light with Degussa photocatalyst. The concentration of MB dye was $3.12 \times 10^{-5} \text{ M}$ and the amount of photocatalyst was 1.2 g/L. The results are shown in Figure 3. The color of MB after the addition of catalyst was blue under dark conditions. The results demonstrated that in the absence of photocatalysts the degradation and decolorization of MB dye was 12% and 15%, respectively, while in the case of the reaction in the presence of catalyst complete degradation and decolorization take place in 6 h time and the color of the reaction mixture solution changed from blue to milky white. In the presence of photocatalyst without UV-LED light irradiation, about 10–15% decrease in concentration was observed from absorbance measurements. This is due to the adsorption of dye molecule

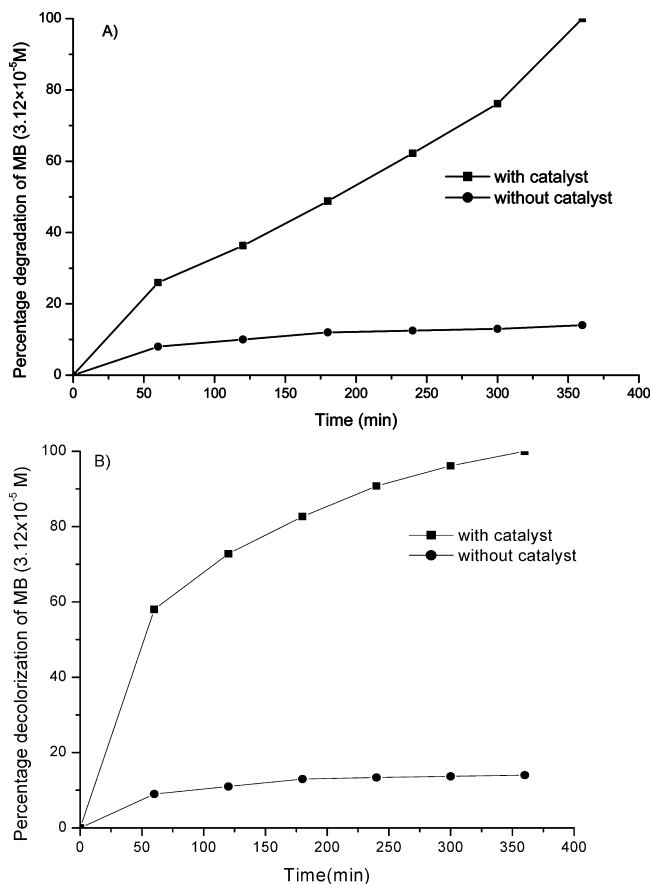


Figure 3. (A) Degradation and (B) decolorization of MB dye (3.12×10^{-5} M) with and without catalyst in the presence of UV-LED light irradiation.

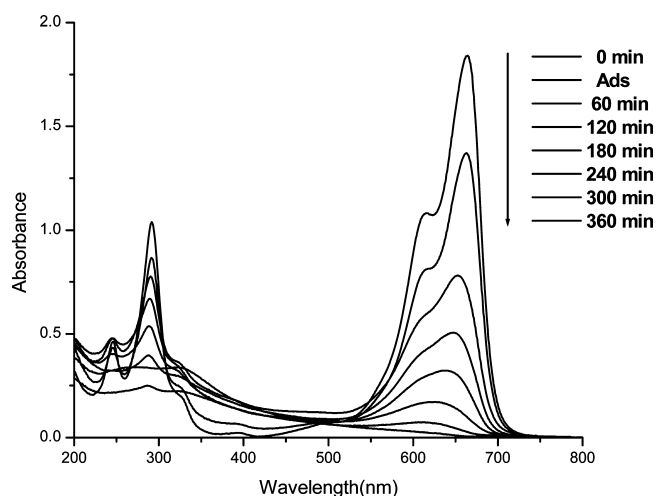


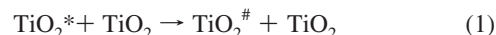
Figure 4. UV-visible spectra of MB dye (3.12×10^{-5} M) after treatment with photocatalyst P-25 Degussa (1.2 g/L) under irradiation of UV-LED light.

on the surface of TiO₂. Figure 4 shows the UV-visible spectra of MB dye (3.12×10^{-5} M) after treatment with photocatalyst P-25 Degussa (1.2 g/L) under irradiation of UV-LED light.

3.3. Chemical Oxygen Demand. To confirm the complete degradation of methylene blue (3.12×10^{-5} M), the COD was determined. There was no significant difference in the COD when only UV-LED light (without photocatalyst) was irradiated on MB solution but reduction in COD value was observed with catalyst. Results demonstrated that the initial COD of MB dye (3.12×10^{-5} M) was 35 mg/L, which was reduced to zero after

6 h in the presence of UV-LED light, whereas in the case of the reaction without catalyst the COD reduced from 35 to 32 mg/L only (Table 1). These results are similar to our earlier reported work, which showed a decrease in COD by photocatalytic degradation of MB using TiO₂-coated Na-Y and HY zeolite in the presence of UV light.²⁶ The reduction in COD values also confirms the photocatalytic degradation of methylene blue using the P-25 Degussa photocatalyst under irradiation of UV-LED light. The decrease in COD showed the same trend as that observed by a UV-visible spectrophotometer.

3.4. Effect of Catalyst Loading. Many reports suggest that the amount of catalyst plays a major role in the degradation of organic compound or dyes in photocatalytic degradation. To avoid the use of excess catalyst, it is necessary to find the optimum loading for the efficient removal of dye or organic compound. So it is necessary to optimize the amount of catalyst to obtain the highest photocatalytic activity. To study the effect of the amount of catalysts, we have varied the amounts from 0.2 to 1.6 g/L. The concentration of methylene blue dye (ca. 6.25×10^{-5} M) was kept the same in all these experiments. Figure 5 shows the effect of the amount of catalyst on the degradation of 6.25×10^{-5} M dye in the presence of UV-LED light irradiation. The result demonstrated that the increase in percentage decolorization and degradation of MB dye was lowest in the case of 0.2 g/L catalyst and it was increased up to 1.2 g/L sharply from 45% to 86% and from 34% to 79%, respectively, in 6 h. This has been explained on the basis of the fact that as the catalyst load increases, the turbidity of the solution increases, resulting in a decrease in UV light penetration and photoactivated volume.²⁷ When the photocatalyst amount surpassed 1.2 g/L, the degradation rate decreased because a further increase in catalyst loading caused light scattering and a screening effect while reducing the specific activity of the catalyst. Part of the catalyst surface probably became unavailable for photon absorption and dye adsorption under such conditions, thus bringing little stimulation to catalytic reaction.²⁸ The results suggest that an optimal amount of the catalyst is necessary for enhancing the degradation rate and reducing needless waste, and in this experiment the optimal amount is 1.2 g/L. Thus, the decreased percentage degradation at higher catalyst loading may be deactivation of activated molecules by collision with ground state molecules. Shielding by TiO₂ may also take place (eq 1).



where TiO₂^{*} is the TiO₂ with active species adsorbed on its surface and TiO₂[#] the deactivated form of TiO₂.

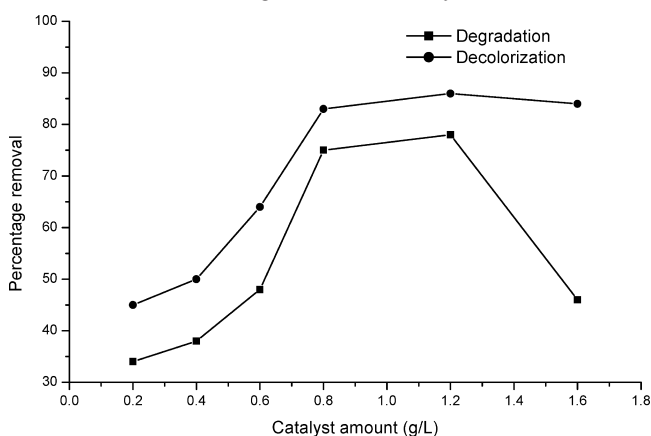
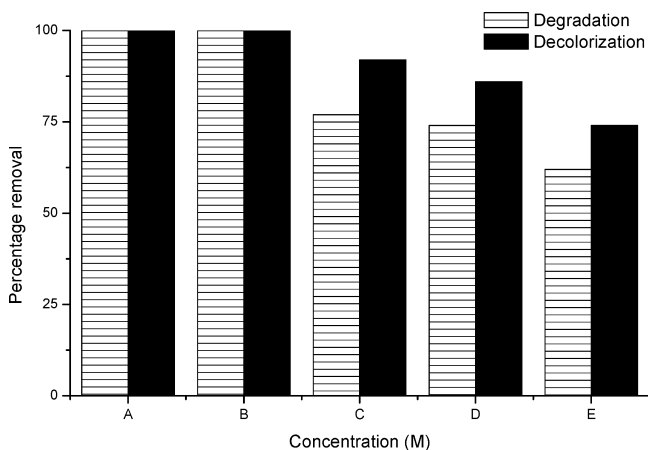
Hence, an optimum catalyst has to be added to avoid unnecessary excess catalyst and also to ensure total absorption of solar photons²⁹ for efficient photocatalytic degradation. These results, although interesting, are based on the assumption that the catalyst particles were of the same size, had the same optical properties, and were uniformly and equally illuminated.

3.5. Effect of Dye Concentration. The dye concentration also plays a major role in the photocatalytic degradation. The effect of dye concentration on the photocatalytic activity of P-25 Degussa under UV-LED light irradiation has been investigated in the range of 1.56 – 7.82×10^{-5} M with optimum catalyst loading. The results are shown in Figure 6. Similar results have been reported for the photocatalytic degradation of dyes using UV and solar light.^{30,31} Results demonstrated that with the increase in dye concentration from 1.56 to 7.82×10^{-5} M, the decolorization and degradation were 100% in the case of 1.56 and 3.12×10^{-5} M concentration of MB dye and after it was reduced from 100% to 75% and from 100% to 62%, respec-

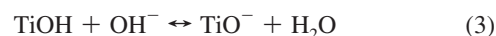
Table 1. Percentage Degradation, Decolorization, and COD Values of MB Dye (3.12×10^{-5} M)

UV-LED light irradiation time (h)	percentage removal					
	degradation		decolorization		COD value (mg/L)	
	without catalyst	with catalyst	without catalyst	with catalyst	without catalyst	with catalyst
0	0	0	0	0	35	35
1	3	26	10	58	34	26
2	3	36	11	72	34	23
3	4	49	12	83	33	18
4	7	62	13	91	33	14
5	10	76	14	96	32	09
6	12	100	15	100	32	00

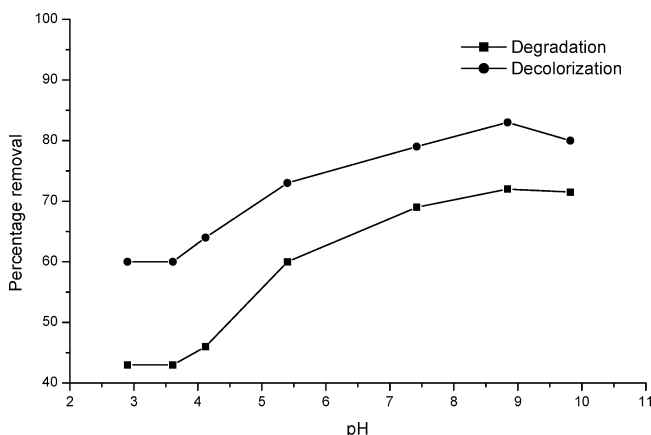
tively, with an increase in concentration of dye in 6 h irradiation of UV-LED light. The possible explanation for this behavior is that as the initial concentration of the dye increases, the path length of photons entering the solution decreases and in low concentration the reversed effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration.³² The same effect was observed by Matthews during the photocatalytic degradation of methylene blue dye with TiO_2 catalysts.³³ The effect of concentration of dye on photocatalytic degradation of MB dye in the presence of UV-LED light irradiation suggests that as the initial concentration of the dye increases, the requirement of catalyst surface needed for the degradation also increases; since illumination time and amount of catalyst are constant, the $\cdot\text{OH}$ radical (primary oxidant) formed on the surface of TiO_2 is also constant. So the relative number of free radicals attacking the dye molecules decreases with increasing amount of catalyst.^{34,35}

**Figure 5.** Photocatalytic degradation and decolorization of MB (6.25×10^{-5} M) using different amounts of catalyst.**Figure 6.** Photocatalytic degradation and decolorization of different concentrations of MB dye: (A) 1.56×10^{-5} M, (B) 3.12×10^{-5} M, (C) 4.69×10^{-5} M, (D) 6.25×10^{-5} M, and (E) 7.82×10^{-5} M.

3.6. Effect of pH. According to the literature, the pH of the solution is by far the major factor influencing the rate of the photocatalytic process^{36,37} because of its multiple roles: (i) The ionization state of the TiO_2 surface according to the following reactions:



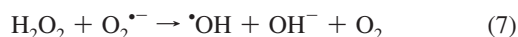
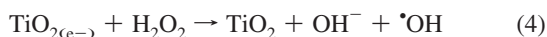
(ii) Thus, the TiO_2 surface is positively charged in acidic media, whereas it is negatively charged under alkaline medium. For these reasons, the experiments were carried out to find the optimal pH of the reaction mixture for degradation of MB (6.25×10^{-5} M). The examined range of pH was from 2.9 to 9.82. In all experiments, the pH was adjusted by the addition of appropriate amounts of NaOH or H_2SO_4 solutions. The catalyst amount was 1.2 g/L. The initial pH of the solution was 6.5. It is evident from the results that when the pH of the solution is decreased from 6.5 to 2.9, the percentage of degradation and decolorization decreased as well; this may be due to the acidic solution retraining the adsorption of dye. In contrast, when the pH value of the solution is increased from 6.5 to 9.82, it is observed that up to pH 8.84 of the solution there was increase in percentage of degradation and decolorization; this is because in alkaline medium the surface area of photocatalyst possesses much negative charge (changing the acidic degree of the catalytic surface), which is beneficial to MB adsorption on the photocatalyst (Figure 7). Further increase in pH resulted in a decrease in the percentage of degradation and decolorization. This may be due to the higher adsorption of MB dye on the surface of the catalyst taking place when the pH of the solution is above 8.84, which leads to inhibition of light penetration. The results indicated that the pH value of the solution was the key factor for dye degradation.

**Figure 7.** Effect of pH on degradation and decolorization of MB (6.25×10^{-5} M).

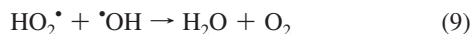
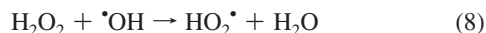
3.7. Effect of Addition of H₂O₂. To enhance the photocatalytic degradation activity, increasing the hydroxyl radical concentration is required. The investigation was carried out to study the effect of the addition of H₂O₂ (5–20 mmol) to increase the hydroxyl radical in the reaction mixture. The result demonstrated that the enhancement in the decolorization and degradation of MB dye (6.25×10^{-5} M, catalyst weight: 1.2 g/L) takes place after the addition of H₂O₂.

The results indicate that the percentage of decolorization and degradation was 100% with the addition of 5 mmol of H₂O₂ within 2 h, then it was reduced with an increase in the amount of H₂O₂ to 10 mmol, and it reached 100% within 1 h. When the amount of H₂O₂ was further increased above 10 mmol, no further enhancement in the photocatalytic activity with respect to time and complete decolorization and degradation took place in 1 h.

The enhancement in decolorization and degradation by the addition of H₂O₂ increases the concentration of hydroxyl radical since it inhibits the e⁻, h⁺ recombination according to the following equations:^{38,39}



At high H₂O₂ dosage the removal rate decreases because of its hydroxyl radical scavenging effect.



4. Conclusions

The photocatalytic degradation study was carried out in the presence of UV-LED light irradiation using a simple photocatalytic reactor in dispersion medium. The degradation of MB dye in aqueous solution by a TiO₂ photocatalytic process under irradiation of UV-LED light was found to be technically feasible under optimum experimental conditions. The results demonstrated that with use of only 5 UV-LED 100% degradation and decolorization of 3.12×10^{-5} M MB dye can be achieved in 6 h time. The optimal catalyst loading is 1.2 g/L; with an increase in dye concentration, the degradation and decolorization was reduced, and the optimum pH was 8.84. These results demonstrate that UV-LED may be a good alternative light source for the degradation of dyes and can be utilized in different geometries of photocatalytic reactors as they are small, thus not requiring any cooling arrangement. Further studies on the development of photocatalytic reactors based on this work using a higher number of UV-LED is in progress to achieve a higher concentration of dyes and organic compound.

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