Remediation of Cationic Dye Simulated Wastewater Using Photolysis: Parametric and Kinetic Studies

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In this study, the photodegradation of methylene blue (MB) simulated wastewater was investigated using three types of UV lamps emitting UV-A, UV-B, UV-C and a solar lamp emitting solar irradiation, as the source of light to enable the destruction of MB molecules by photochemical reactions. From the experimental data, UV-C irradiation proved to be the most effective irradiation light source that resulted in 96.7% degradation of MB after 5 h of irradiation, while solar irradiation treatment on the simulated dye wastewater degraded 29.6% of MB after 5 h of exposure and proved to be an encouraging option for this treatment as sunlight is a renewable, green energy source. COD analysis percentage of 83.3% achieved after 60 min proved the effectiveness of using this treatment option. Kinetic studies showed that all experiments fulfilled first-order kinetics (the correlation coefficient ranged between r=0.7495 to 0.998) for MB photo degradation.

Key words: Dye; photolysis; pretreatment; methylene blue; photodegradation; biochemical degradation; textile

Environmental pollution caused by the effluents from industrial wastewater is one of the major concerns among the developing countries [1-3]. Manufacturing of dyes worldwide has exceeded one million tons [4]. The wastewater from the textile industry are characterized mainly by their dark colour resulting from the high amounts of dyes inside them [5]. The release of those coloured wastewaters in the environment is a source of pollution and eutrophication [6] and can produce dangerous byproducts when the pollutants undergo oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase [7].

It is highly perturbing that about 1.5% of total production of colourants from textile industry may be released to wastewaters during synthesis and processing operations [8]. The wastewater from textile-based industries must be treated before being discharged into the environment. Biological treatment has been widely used to deal with the wastewater. However, aerobic and anaerobic degradation treated effluent still contains aromatic amines which are Received: May 2017; Accepted: July 2017

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known to be carcinogenic and mutagenic to human beings [4]. Biodegradation alone is not efficient enough to completely break down the complex organic molecules due to the variation of concentration and the wide range of pH [9].

Thus there is a need for the combination of treatment methods in order to accelerate the biodegradation rate of recalcitrant dye molecules [4]. Past researchers have reported the combination of different treatment methods, for instance, adsorption-Fenton [9] and adsorption-biodegradation [10].

In this study, we investigated the application of photolysis as a pre-treatment method which could be applied before the biochemical degradation of dye wastewater. Synergistic effect of photolysis and biodegradation treatment of wastewater from textile industry offers a cost-effective remediation method which produces effluent with zero organic molecules as well as eco-friendly alternative to conventional physicochemical treatment methods [10].

The definition of photolysis given by Joseph and co-workers [11], was the use of UV irradiation (either UV-A, B or C) without the presence of any catalyst, to irradiate a polluted aqueous solution. Photolysis utilizes photons, from a light source, to break the bonds present in pollutant molecules; thus helps to break down the complex molecules into smaller molecules [12]. This can directly break the chromophore bond in dye molecules thus remove the colour from the aqueous solution [13]. The photolysis reaction can be represented by the following equation [14]:

Photon + dye + (oxygen) \longrightarrow decolourization

Photolysis has been proven as an efficient pretreatment method before biological treatment [4]. Sun *et al.* [4] utilized only UV-C (24 Watts at a wavelength of 253.7 nm) as the source of photons to break down the acid orange 7 dye molecules before they undergo biodegradation. Keen *et al.* [15] reported that combination of photo-oxidation (photolysis/ H_2O_2) and biodegradation synergistically mineralize Carbamazepine, a recalcitrant pharmaceutical compound, into CO₂.

UV photolysis has long been used to eliminate chlorinated and nitrated aromatics, phenols, halogenated aliphatics, end products of metal finishing, oil, and steel processing, and other hazardous wastes present in water [16–17]. Direct photolysis in natural water involves the transformation of a chemical resulting from the direct absorption of a solar photon while indirect photolysis involves the transformation of a chemical due to energy transfer from naturally occurring photosensitizers or due to reactions with transient oxidants such as hydroxyl radicals, molecular oxygen in a singlet electronic state ("singlet oxygen"), and peroxy radicals. Both triplet state photosensitizers and transient oxidants result from the absorption of solar photons by chromophoric dissolved organic matter (CDOM) and nitrate ion. Both direct and indirect photolysis can contribute significantly to the dissipation of a chemical in waters [18].

MB was chosen as model dye due to its ability to absorb both at UV and visible region [19]. MB, a

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heterocyclic aromatic dye, was used as the model dye. MB can be found in a variety of wastes and different contaminated water sources, such as fresh waters of rivers and lakes, seawater, or even drinking waters such as tap waters [20].

In the present work, we report the photodegradation of MB dye by four radiation sources UV-A, UV-B, UV-C and solar lamps. It should be noted that these four radiation sources represented different wavelengths as follows; UV-C - 254 nm, UV-B - 311nm, UV-A - 365 nm as well as solar lamp - maximum at 610 nm [21].

EXPERIMENTAL SECTION

Preparation of Stock Solution

MB was purchased from Aldrich and used without further treatment. All samples were prepared in distilled water. MB was added to distilled water to obtain a 1000 mg l⁻¹ stock solution. MB solutions with different concentrations for specific experiments were prepared using distilled water [21–22].

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Light Sources

Four different radiation lamps (UV-C, UV-B, UV-A, and Solar) were used as the source of photons. According to the manufacturer's specification, the intensity of each light was 10 mW/cm² with a total radiating surface of 86.4 cm² for each lamp. A total of three lamps were used as the radiation source; giving a total of 30 mW/cm² irradiation [21–22].

Photolysis Experiment

The set-up of this photolysis experiment was known as Batch Photo-reactor which is under a closed condition to maintain the temperature and avoid the interference of natural light. All dark and photochemical experiments were performed in a batch photoreactor [21-23]. Figure 1 shows the setup for the photolysis experiment.

A 4 ppm MB solution (500 ml) at the approximate pH 5 was placed in a 1000 ml beaker and irradiated with 27 Watts lamps while performing the batch experiment. The lamps were placed in quartz lamp

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Figure 1. Schematic diagram of the photolysis photoreactor.

sheets and fitted at the centre of the beaker. The lamps were switched on for 20 min before to the start of each experiment to bring the low-pressure mercury lamp to the working temperature. The experiment was carried out at room temperature [21–23].

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The experiments were conducted in duplicates [24], each for five hour with liquid samples collected at every hour. The decomposition of MB was monitored by measuring the absorbance at regular intervals of time [25] by using UV-Vis spectrophotometer (Lambda 25 UV-vis Spectrophotometer) at λ max of 665 nm [14]. A control experiment known as the dark reaction was conducted by keeping the solution under the same conditions as other experiments but without the irradiation [26].

Chemical Oxygen Demand Analysis

Chemical oxygen demand (COD) analysis was done using the COD Digester (Hanna COD Digestor) to show the difference in the amount of organic matter before and after the photolysis [27]. COD indicates how much oxygen is required to oxidize the sample and is considered as a potential measure of the reactivity of organic carbon in the sample with another oxidizer: hydroxyl radical [28]. According to Nawi and Zain [29], high COD content of a water sample indicates the presence of high organic matter.

Data Analysis

Degradation efficient. The absorption spectra were obtained, and the rate of degradation was observed regarding the change in intensity of absorption peak at 665 nm [30]. Equation 1 was used to calculate the degradation efficiency of MB solution at appropriate reaction time [26].

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Degradation efficiency (%) = $\frac{(C_o - C_t)}{C_o} \times 100$

Where,

 C_{o} = Initial concentration of MB at t = 0 min C_{t} = Concentration of MB at t min

Reaction Order

Many researchers have reported that most degradation curves obey the first order kinetics [21, 31]. Thus, the first order kinetics was used to study the kinetics of MB degradation. The first-order rate constants were calculated from the linear fitting of a plot of $\ln (C_0/C_t)$ against time (t) as shown below [21, 31–32]:

$$\ln \frac{C_{\rm t}}{C_{\rm o}} = k_{\rm t}$$

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where, C_o and C_t represent the concentration of the dye in solution at time zero and time of *t* of irradiation respectively, and *k* represents the apparent rate constant [33–34].

RESULTS AND DISCUSSION

Effect of Radiation Source

Figure 2 shows the dark reaction and the photodegradation of MB at different types of irradiation. Based on the UV analysis, no significant degradation of MB was observed for the dark experiment. However, there was a slight fluctuation in the concentration of MB. This is because MB first dissociates into MB⁺ and Cl⁻ which causes a decrease in the concentration is maybe due to the reverse process between MB⁺ and Cl⁻ and due to the regeneration of MB in the presence of atmospheric oxygen [35, 36].

In contrast, all four types of irradiation show only decrease in concentration of the MB indicating that photodegradation of MB had occurred. This proved the need for irradiation (both UV and solar) for photodecomposition of MB. Vaiano *et al.* 2015 documented degradation of spiramycin, a pharmaceutical compound, under solar (400–550 nm) and UV-A (365 nm) irradiation. MB molecules undergo reduction and decolourization to become leuco-methylene blue (LMB) [20, 37] under UV and solar irradiation as shown in Figure 3.

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This result is supported by Tennakone *et al.* [35] where in the study it was proven that MB underwent detectable direct photodegradation by energetic UV photons.

Figure 4 shows the degradation efficiency of MB solution under different types of irradiation. Almost 80% of MB was degraded within 1 h using UV-C irradiation meanwhile the total degradation efficiency of MB after 5 h using UV-A, UV-B and solar were only 12.07, 38.24, and 29.56, respectively. This high degradation ability of UV-C wavelengths is due to its photons with sufficient energy to break a broad range of organic bonds, and are therefore capable of creating radicals as reported by [28].

Furthermore, the effectiveness of 254 nm radiation (UV-C) is also attributed to the shorter penetration capability of the higher energy photons [38]. Lower the wavelength of UV irradiation, higher the energy of photons, higher the degradation efficiency. This has been proven by results obtained by this study. Petrovic *et al.* [39] also documented that photodegradation of chlorophyll was faster under UV-B (300 nm) irradiation compared to visible irradiation (400–800 nm) because UV-B consists photons with higher energy compared to visible irradiation.

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Figure 2. Concentration of MB against time graph for the dark reaction and different types of irradiation. (The experimental conditions were 4 ppm of MB aqueous solution (500 ml) at its natural pH).

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Figure 4. Degradation efficiency of MB aqueous solution under different types of irradiation. (The experimental conditions were 4 ppm of MB aqueous solution (500 ml) at its natural pH).

Table 1 shows the rate of degradation varies with different types of irradiation. It was observed that the photodegradation of MB just follows the first order reaction equation, $\ln C_0/C_t = k_t$ as reported by Zhai *et al.* [40]. According to Table 1, the rate of degradation of MB was highest under UV-C irradiation (0.648 hr⁻¹) followed by UV-B (0.092 hr⁻¹), solar (0.069 hr⁻¹) and UV-A (0.024 hr⁻¹).

Based on Table 1, the degradation of dye occurs at a faster rate with solar light (0.069 hr⁻¹) in comparison to UV-A light (0.024 hr⁻¹) which was also reported by Kansal *et al.* [41]. It seems that the lower the wavelength of the radiation, the better efficiency of degradation is obtained [38].

Effect of Contact Time

It is evident that the MB concentration in the aqueous solutions decreases with the irradiation time showing MB decompose under UV irradiation [32, 42]. The constant reduction in the intensity of blue colour was observed over time. According to Khan *et al.* [31] and Ong *et al.* [43], the percentage of removal increases with increasing irradiation time.

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With longer exposure to UV irradiation, more MB molecules can absorb energy from photons which aids them to decompose. Furthermore, more hydroxyl radicals will be generated when the exposure time is longer. The generation of hydroxyl radicals is crucial

Experimental conditions	Equation	Rate constant (hr ⁻¹)	R ²
UV-A	y = -0.024x - 0.025	0.024	0.844
UV-B	y = -0.092x - 0.069	0.092	0.924
UV-C	y = -0.648x - 0.768	0.648	0.803
Solar	y = -0.069x -0.006	0.069	0.998

Table 1. Linear regression results for different types of irradiation in $\ln (C_{\nu}/C_{o})$ versus time curves.

in photodegradation process as it oxidizes the organic pollutants to some simple intermediates [43].

Effect of Initial Concentration

Based on Figure 5, the photodegradation rate for the MB dye decreased with increasing initial concentration of the dye [44, 45]. When the initial concentration of MB is 2 ppm, the degradation efficiency can reach about 94% within 60 minutes compared to the initial level of 10 ppm which only degrade 48% in the same duration. The possible explanation for this behaviour is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorbed by MB in lower concentration [41, 46].

Figure 6 shows the degradation efficiency of MB at different initial concentrations. According to the Figure 6, the degradation efficiency of 10 ppm of MB is lowest compared to other concentrations because the available free radicals are not sufficient where some of the molecules have no chance to be oxidized when MB is present at high levels [47, 48]. The degradation rate is related to the likelihood of the formation of hydroxyl radicals and those reacting with MB molecules. The likelihood of reactions between MB and oxidizing species also increased with the initial concentration of the dye, while the degradation ratio decreased with further increases in the MB concentration, maybe due to the shielding of the UV light by the high dye concentration. Thus, the light triggered generation of hydroxyl radicals also decreased [44].

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Figure 5. Concentration of MB against the function of time for different initial concentration. (The experimental conditions were 500 ml of MB aqueous solution at its natural pH irradiated with UV-C).

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Figure 6. Degradation Efficiency of MB aqueous solution under different initial concentrations. (The experimental conditions were 500 ml of MB aqueous solution at its natural pH irradiated with UV-C).

Table 2 shows the linear regression results for photodegradation of MB under different initial concentrations. Based on Table 2, the rate constant decreases when there is an increase in the concentration of MB. This can be explained by the fact that the increase of the dyes initial concentration caused a decrease in the light transmittance of the system, resulting in a reduction in the generation of hydroxyl radicals, leading to a decreasing rate of dye photo degradation of MB [49].

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Effect of pH

Figure 7 shows the photodegradation of MB at different pH. A decrease in MB concentration in all three experiments at different pH was observed. The wide difference in removal of MB dye molecules in basic solutions in comparison with acidic solutions appeared to be highly significant based on Figure 7 where the highest degree of photodegradation of MB occurred in basic condition (pH 10) [50,51].

Experimental conditions	Equation	Rate constant (min ⁻¹)	R ²
2 ppm	y = -0.050x + 0.049	0.050	0.988
4 ppm	y = -0.027x + 0.052	0.027	0.985
6 ppm	y = -0.018x + 0.068	0.018	0.984
8 ppm	y = -0.013x + 0.032	0.013	0.992
10 ppm	y = -0.011x + 0.037	0.011	0.988

Table 2. Linear regression results for different initial concentration in $\ln(C_t/C_0)$ versus time curves.

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Figure 7. Concentration of MB against time graph for different pH. (The experimental conditions were 4 ppm of MB aqueous solution (500 ml) irradiated with UV-C).

Figure 8 shows the degradation efficiency of MB at different pH. The higher degradation efficiency of MB in alkaline solution (as in Figure 8) is because alkaline pH facilitates hydroxyl radical formation due to the presence of a large amount of hydroxide ions in alkaline conditions and hydroxyl radicals enhance the photodegradation of MB [52, 53]. Moreover, since MB is a cationic dye, its decomposition is favoured at high pH values [50, 54].

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Table 3 shows linear regression results for different pH. Based on Table 3, the reaction rate constant had a higher value at pH 10 than pH 7, indicating hydroxyl radical attack represents the main reaction in photodegradation of MB [52, 55]. Since hydroxyl radicals are the major oxidant for dye degradation, therefore, the excess hydroxyl radicals accelerate the degradation rate [41, 56]. This phenomenon is widely accepted as principal oxidizing

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Figure 8. Degradation Efficiency of MB aqueous solution under different pH. (The experimental conditions were 4 ppm of MB aqueous solution (500 ml) irradiated with UV-C).

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Experimental conditions	Equation	Rate constant (min ⁻¹)	R ²
pH 4	y = -0.0476x + 3.5269	0.0476	0.9835
рН 7	y = -0.0503x + 2.965	0.0503	0.9029
pH 10	y = -0.0509 + 2.4617	0.0509	0.7495

Table 3. Linear regression results for different pH in $\ln (C_t/C_o)$ versus time curves.

species responsible for degradation process at neutral or high pH levels and results in enhancement of the efficiency of the process [41]. Another reason for higher degradation efficiency of MB at an alkaline solution is that the MB sensitized reactions are more efficient at pH greater than 8 [57].

The lowest value of the rate constant was obtained at pH 4, where the greatest concentration of inorganic anion (HCl) was added to adjust the pH [8]. According to Mitrovic *et al.* [8], the poor performance of acidic solution on the degradation of MB is due to the amount of added conjugated base, Cl-. This anion can react with hydroxyl radicals leading to inorganic radical ions which exhibit a much lower reactivity than hydroxyl radicals. Hence it does not participate in the dye degradation. There is also a severe competition between the dye and the anion concerning to hydroxyl radicals as shown in the Equation 3:

$$Cl^{-} + OH \longrightarrow ClHO^{-}$$
 (3)

According to Mills and Wang [58], the oxidized form of MB, i.e., MB^{+} , which appears to be quite stable and is easily reduced back to MB in acidic solution causing low degradation efficiency and causing poor performance of acidic solution in photodegradation of MB.

Optimum Conditions

Based on the previous experiment results in this study, optimum conditions required to degrade MB

effectively were chosen for further analysis. Figure 9 shows the absorption spectrum of MB solution at optimum conditions. The peak at 665 nm had disappeared, proving the cleavage of conjugated bonds, which thus made the dye colourless. In the ultraviolet region, the absorbance values were out of the range. Once the dye was broken down into simpler colourless aromatic compounds, these compounds could have given peaks in the ultraviolet region [59]. A mixture of N-demethylated analogs of MB broadens the absorption spectra in the visible region. Besides, a parallel decrease in intensities and slight blue shift of the bands located at 292 nm also could be observed; these are caused by the N-demethylated degradation of the phenothiazine [60]. After 60 min of UV-C irradiation, no other spectral features were evident in the absorption spectra, indicating that the MB degraded entirely.

Figure 10 shows the change in colour from intense blue to very light blue during 60 min of UV irradiation. This showed that even though the direct photolysis did not completely degrade the MB to carbon dioxide and water, but it could be used as pretreatment of textile wastewater to decrease the level of pollutants in wastewater thus lowering the wastewater treatment cost.

Chemical Oxygen Demand Analysis

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The experiment with optimum conditions was further analyzed for COD value. COD was utilized as an indicator to measure the dosage of pollutants in water in this study [9]. A higher COD values mean more severe pollution, for 100% discolouration may

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Figure 9. The absorption spectrum of MB solution at optimum conditions.



Figure 10. The change in colour of MB before and after irradiation with UV-C. (4.1 a shows the MB solution before irradiation;

4.1 b shows the MB solution after irradiated with UV-C for 60 min in alkaline condition and4.1 c shows the decrease in intensity of blue colour throughout the experiment).

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not mean the whole removal of organics. Dyes may degrade into intermediates with low molecules, which might be more toxic and refractory than the initial pollutant itself, instead of H_2O and CO_2 directly [9]. The percentage of COD removal was calculated to be 83.33%. The COD removal was lower than the photodegradation measured by the spectrophotometric method which might be due to the formation of uncoloured intermediates or by-products during the photolysis [53]. This means the MB dye decomposed first to smaller organic intermediates that could still contribute to the COD values but not the colour of the irradiated solutions [29].

Degradation Mechanism of MB

The absorption of light leads to destruction or transformation of the MB which absorbs the light energy. In consequence, absorption diminishes the concentration of the MB which, in turn, changes the rate of light absorption, leading to the interplay between these two properties [61]. The mechanism of the photolysis of MB is based on the fact that the MB Remediation of Cationic Dye Simulated Wastewater Using Photolysis: Parametric and Kinetic Studies

molecules undergo photochemical reactions, by which molecules are broken down into smaller molecules, merely through the absorption of light [38, 57].

It is known that UV-C wavelength corresponds to photon energy (6.7 eV) which is higher than the bond dissociation energy (BDE) of water molecules and can dissociate water to form hydroxyl radicals. The BDE data of MB molecules and water are shown in Table 4. It could be seen that the BDE of MB molecules were much smaller than the photon energy of UV-C radiation as well as water molecules. According to the BDE theory, the lower the BDE is, the less powerful the chemical bond is and the easier it is for old bonds to break and new bonds to form. Compared with water molecules, MB molecules can more easily to be destructed by energetic photons [62].

According to Manu and Chaudhari [59], once the dye was broken down, simpler colourless aromatic compounds are formed as shown in Figure 11.

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Molecule bonds	Bond energy (kcal/mol)	Bond energy (eV)
CH ₃ N(CH ₃)C ₆ H ₅	70.8	3.07
N(CH ₃) ₂ C ₆ H ₅	93.2	4.04
C ₆ H ₅ -NH-C ₆ H ₅	87.4	3.79
C ₆ H ₅ SC ₆ H ₅	76.0	3.30
C ₆ H ₅ NH ₂	102.6	4.45
НОН	120.2	5.21

 Table 4. BDE in a MB and water molecule.

The chemical bonds corresponding to the given BDE are shown as "---".



Figure 11. Degradation of MB under direct photolysis.

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In basic aqueous solutions under solar light irradiation, highly reactive hydroxyl radicals can be formed through monoelectronic reduction of MB+ by the hydroxyl ion as shown in Figure 12 [63].



Figure 12. Formation of hydroxyl radical by MB⁺.

The hydroxyl radicals generated then can react with MB molecules causing degradation of the dye as shown in Figure 13.



Figure 13. Degradation of MB by hydroxyl radicals.

MB was found to act as a photosensitizer in many research papers as it possesses triplet states of appropriate energies for sensitization of oxygen [19, 64, 65, 66]. According to Swati and Meena [67], MB is a suitable photosensitizer to degrade azo dyes. The photosensitizing property of MB works through two mechanisms labeled type I and II, depending on the process by which the excited photosensitizer returns to the ground state [68]. Type I mechanism involves

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hydrogen-atom abstraction or electron-transfer between the excited sensitizer and a substrate, yielding free radicals. These radicals can react with oxygen to form an active oxygen species such as the superoxide radical anion. In a type II mechanism, singlet oxygen is generated via an energy transfer process during a collision of the excited sensitizer with triplet oxygen [64]. Mechanism of sensitizing property of MB was given as follows in Figure 14 [58, 64].

Figure 14 shows the sensitizing mechanism of MB under UV irradiation where MB represents MB molecule, ${}^{1}MB^{*}$ is the MB in a singlet ground state, ${}^{3}MB^{*}$ is the MB in a triplet excited state, MB⁺ is the oxidized MB molecule, O_{2} .⁻ is the superoxide anion, O_{2} molecular oxygen, ${}^{3}O_{2}$ is the triplet ground state oxygen, and ${}^{1}O_{2}$ is the singlet excited oxygen.

In a nutshell, the energetic photons and the highly reactive oxygen species (O_2 - & HO·) can be said to be responsible for degradation of MB under UV irradiation.

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Kinetic Analysis

All the experiments were tested for the kinetic equation for a first-order reaction. Since a good linear relationship was observed between $\ln (C_t/C_o)$ and time (*t*) plot for the experiments, the apparent rate constant (*k*) was calculated by fitting the linear plot [69]. Based



Figure 14. Mechanism of MB photosensitizer.

on Table 1, 2 and 3, degradation kinetic data revealed high correlation to irradiation time (the correlation coefficient ranged between r = 0.7495 to 0.998), fitted well with the first-order kinetics.

CONCLUSION

This study suggested the potential use of photolysis as a pretreatment of MB contaminated textile wastewater. MB, a phenothiazine dye, is an intense blue colour dye which is highly soluble in water. It was proven that photolysis without catalyst also aided in degradation of MB dye. The absorption spectrum of MB obtained via UV-Vis spectrophotometer proved the disappearance of the maximum peak which indicated the degradation of MB into simpler molecules. UV-C was proven to be the most effective irradiation for the photodegradation of MB. Through observation, the intensity of blue color of the MB solution was found to decrease when irradiated with UV-C. It was found that the direct solar irradiation could also be used to degrade the MB contaminated textile water. In a tropical country like Malaysia, intense sunlight is available throughout the year and, hence it could be effectively used for photodegradation of MB in wastewater. Moreover, there was no material deterioration in the case where sunlight was used as the radiation source. Through observation, it was found that the longer the exposure of MB solution to UV irradiation, the greater the extent of degradation observed. The constant decrease in the intensity of the blue colour was observed over time. The lower the initial concentration of MB solution the greater the degradation efficiency observed. The best pH required for better photodegradation of MB was found to be pH 10 (alkaline condition). The COD analyzer proved that the amount of organic pollutants decreased after the photolysis experiment which further emphasizes the potential use of photolysis in wastewater treatment system.

ACKNOWLEDGEMENTS

This research was supported by the Centre of Research and Innovation of Universiti Putra Malaysia in collaboration with the Centre of Research and Innovation of Universiti Malaysia Sabah (Grant No. RACE0008-ST-2013) and is gratefully acknowledged. Remediation of Cationic Dye Simulated Wastewater Using Photolysis: Parametric and Kinetic Studies

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