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PHOTODEGRADATION OF NEW METHYLENE BLUE N IN AQUEOUS SOLUTION USING ZINC OXIDE AND TITANIUM DIOXIDE AS CATALYST

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Abstract. In this study, ZnO and TiO_2 are used as photocatalyst to degrade the dye, New Methylene Blue N (NMBN). The photodegradation rate was measured using UV-Visible spectrophotometer. In this study, New Methylene Blue N showed absorption values at $\lambda = 590$ nm and $\lambda = 286$ nm. UV lamp ($\lambda = 354$ nm) is used in the photodegradation process. Results showed that ZnO is a better photocatalyst compared to TiO_2. The degradation by ZnO showed that 81% of NMBN was degraded at $\lambda = 590$ nm and 77.75% at $\lambda = 286$ nm. In contratst, the degradation using TiO_2 was 25.68% at $\lambda = 590$ nm and 26.37% at $\lambda = 286$ nm. The percent degradation of New Methylene Blue N is 88.89% and 68.94% at $\lambda = 590$ nm and $\lambda = 286$ nm respectively when H_2O_2 was added. A mixture of ZnO and TiO_2 in the ratio of 85: 15 (0.085 g: 0.015 g) is the most optimum ratio for the mixed photocatalyst where the degradation percentage of NMBN are 96.97% and 93.61% at $\lambda = 590$ nm and $\lambda = 286$ nm. The addition of Cu^{2+} metal ion gave the highest percentage of degradation (83.83% at $\lambda = 590$ nm) compared to other metal ions. The addition of Pb^{2+} gave the highest percentage of degradation at $\lambda = 286$ nm with 81.25% degradation of the dye. The optimum condition was achieved at pH 5.90, which gave the highest percentage degradation, 92.84% and 89.30% at $\lambda = 590$ nm and $\lambda = 286$ nm respectively.

Keywords: New Methylene Blue N; photodegradation; aqueous; ZnO; TiO_2

Abstrak. Dalam kajian ini, ZnO dan TiO_2 digunakan sebagai fotomangkin dalam pendegradasian pewarna New Methylene Blue N (NMBN). Kadar fotodegradasi diukur menggunakan alat spektrofotometer UV-Vis. Dalam kajian ini, New Methylene Blue N menunjukkan nilai serapan pada $\lambda = 590$ nm dan $\lambda = 286$ nm. Lampu UV ($\lambda = 354$ nm) digunakan dalam proses fotodegradasi. Dalam proses degradasi menggunakan ZnO menunjukkan 81.42% NMBN terdegradasi pada $\lambda = 590$ nm dan 77.75% pada $\lambda = 286$ nm. Sebaliknya, degradasi menggunakan TiO_2 adalah 25.68% pada $\lambda = 590$ nm dan 26.37% pada $\lambda = 286$ nm. Peratus degradasi New Methylene Blue N ialah 88.89% dan 68.94% pada masing-masing $\lambda = 590$ nm dan $\lambda = 286$ nm apabila ditambahkan dengan H_2O_2. Campuran ZnO dan TiO_2 dalam nisbah 85: 15 (0.085 g; 0.015 g) merupakan campuran fotomangkin yang paling optimum iaitu dengan peratus degradasi NMBN sebanyak 96.97% dan 93.61% pada $\lambda = 590$ nm dan $\lambda = 286$ nm. Penambahan ion logam Cu^{2+} memberikan peratus degradasi tertinggi berbanding ion logam lain iaitu 83.83% pada $\lambda = 590$ nm. Penambahan ion logam Pb^{2+} memberikan peratus degradasi tertinggi pada $\lambda = 286$ nm iaitu 81.25% pewarna terdegradasi. Keadaan optimum dicapai pada pH 5.90, dengan peratus degradasi tertinggi iaitu 92.84% dan 89.30% pada masing-masing $\lambda = 590$ nm dan $\lambda = 286$ nm.

Kata kunci: New Methylene Blue N; fotodegradasi; larutan; ZnO; TiO_2

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1.0 INTRODUCTION

TThe textile industry produces large quantities of highly coloured effluents. These aqueous effluents are generally toxic and resistant to destruction by biological treatment methods such as using micro organisms, which was used to decompose the sludge into smaller compounds. Azo dyes, such as New Methylene Blue N or basic blue 24, are widely used in the textile industry [1]. The worldwide annual production of these dyes is over 7×10^5 tonnes [2]. Among these dyes, azo dyes constitute the largest and the most important class of commercial dyes. Over 50% of all dyes used in industry are azo dyes. Azo dyes are characterized by the presence of nitrogen to nitrogen double bonds (N = N). The color of azo dyes was determined by the azo bonds and their associated chromophores and auxochromes [3].

The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of the biological process. In an Environmental Protection Agency (EPA) study, eleven of the eighteen azo dyes passed through the Activated Sludge Process were untreated [4]. While the physical processes, such as coagulation and adsorption, merely transfer the pollutant from wastewater to another media and cause a secondary pollution. Traditional oxidation processes such as ozonation and chlorination are only effective in destroying some classes of dyes [5].

As a results of these problems, Advanced Oxidation Processes (AOPs) have been considered as an effective technology in treating organic chemicals including dyes in wastewater [6]. Advanced Oxidation Processes include photo catalysis systems such as a combination of a semiconductor (TiO_2, ZnO, Al_2O_3, WO_3, etc.) and UV light. ZnO appears to be a suitable alternative to TiO_2 since its photodegradation mechanism has been proven to be similar to TiO_2 [7]. Zinc oxide is an n-type semiconductor with many attractive features. Zinc oxide with a wide band gap of 3.17 eV as compared to TiO_2 (E_{bg} anatase = 3.2 ev), is capable to generate hydroxyl radicals in sufficient quantity and it is transparent to most of the solar spectrum. The synthesized ZnO was also shown to absorbed more UV light than any other powders. This means that the high UV absorption efficiency leads to the generation of more electrons and holes. These electrons and holes are considered the main species involved in the photodegradation process. The general scheme of the photocatalytic destruction of an organic compounds begin with its excitation by suprabandgap photons, and continues through redox reactions where $^{\bullet}OH$ radicals formed on the photocatalyst surface, play a major role as shown in Equations (1) – (4):

$$ZnO/TiO_2 \rightarrow ZnO/TiO_2\ (h^+ + e) \quad \ldots 1$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad \ldots 2$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad \ldots 3$$

$$e + O_2 \rightarrow {}^{\bullet}O_2^- \quad \ldots 4$$

This research is a model study of the real treatment of textile wastewater that is contaminated by New Methylene Blue N. The degradation process was carried out using mixture of TiO_2 and ZnO in aqueous solution. Metal ions was added to the system to act as a co-catalyst in this reaction. The reaction was carried out under UV light (λ = 354 nm) and solar light. The wavelength of the absorption is measured at 286 nm and 590 nm. The degradation rates are measured quantitatively by UV-Vis spectrophotometer. Decolourization is directly affected by photodegradation process. In this paper, factors such as the effect of metal ions, H_2O_2, pH and a mixture of catalysts that effects the photodegradation of methylene blue N will be discussed.

2.0 EXPERIMENTAL

2.1 Reagents and Chemicals

New Methylene Blue N and zinc chloride double salt was obtained from Fluka Chemika and used without further purification. Zinc oxide, ZnO AR was obtained from Emory Laboratory Chemicals while TiO_2 (anatase) with particle size 0.20 – 0.25 μm and 99.0% purity was obtained from Sigma Chemical Co. Distilled water was used in all the experiments. Hydrogen Peroxide (33% w/v, density 1.11 g/mL) was obtained from J.T Baker Inc. Metal ions, Co^{2+} and Cu^{2+} used in all the experiments were obtained from Emory Laboratory Chemicals, USA. Sodium hydroxide, NaOH and hydrochloric acid, HCl were obtained from Sigma Chemical Co, USA.

2.2 Apparatus

Photocatalytic tests were performed in a pyrex glass cylinder batch photoreactor with a volume of 1000 mL. The UV light source was powered with 100 volt, 6 Watt and l = 354 nm. The tests were also carried out in sunlight. An electrical magnetic stirrer with magnetic bar was used continuously so that TiO_2 and ZnO can be uniformly dispersed in the solution when the sample was degraded by UV light. UV-Vis Spectrophotometer Shimadzu 1601PC was used to monitor the dye concentration.

2.3 Effect of TiO_2 and ZnO on the Photodegradation Process

New Methylene Blue N dye (100 mL 100 ppm) and different ratio of TiO_2 and ZnO was placed in a photoreactor. Eight different ratios of TiO_2 and ZnO used in this study are shown in Table 1. An electrical magnetic stirrer was used continuously in the reaction so that TiO_2 and ZnO can be uniformly dispersed in the solution. After stirring the solution for 5 minutes, 5 mL of the sample was collected and labeled as sample at 0 minute. The sample was then covered and the light source was switched on. Samples were collected using 10 mL plastic syringe at different time interval (15, 30, 60, 90, 120, 150, 180, 240 minutes) until 300 minutes. The concentration of the dye was determined from the absorbance observed at λ = 590 nm and 286 nm using

Table 1 Ratio of TiO_2 and ZnO used in the photodegradation tests

Ratio (TiO_2 : ZnO)	Ratio in gram (g TiO_2 : g ZnO)
2 : 98	0.002 : 0.098
3 : 97	0.003 : 0.097
5 : 95	0.005 : 0.095
10 : 90	0.010 : 0.090
15 : 85	0.015 : 0.085
20 : 80	0.020 : 0.080
100 : 0	100 : 0
0 : 100	0 : 100

UV-Vis spectrophotometer.The percentage degradation (% D) was calculated using Equation (5).

$$\text{Percentage degradation, } = \frac{A_0 - A_t}{A_0} \times 100 \quad \ldots 5$$

where A_0 = absorbance at t = 0 minute
A_t = absorbance at t minute

2.4 Effect of Metal Ions and Hydrogen Peroxide on the Photodegradation Process

New Methylene Blue N (20 mL 100 ppm), 10 mL 1×10^{-3} M of H_2O_2 and 10 mL 1×10^{-3} M of metal ions were prepared individually. The solution was then poured into a 100 mL volumetric flask and distilled water was added up to the calibration mark. The solution was transferred into the photoreactor and 0.015 g of TiO_2 and 0.085 g of ZnO (15:85) were added. The solution was homogenized using an electrical magnetic stirrer before the light source was switched on. Samples (5 mL) were taken at 15 minutes interval and tested with UV-Vis spectrophotometer. The reaction was repeated using New Methylene Blue N (20 mL 100 ppm), 10 mL 1×10^{-3} M of H_2O_2 and 0.10 g of ZnO to study the effect of H_2O_2.

2.5 Effect of pH on the Photodegradation Process

After obtaining the optimum condition for the degradation process of New Methylene Blue N, Pb^{2+} was found to be the best metal ion at λ = 286 nm. Thus, five solutions consisting of 20 mL 100 ppm of New Methylene Blue N, 10 mL 1×10^{-3} M of H_2O_2 and 10 mL 1×10^{-3} M of Pb^{2+} were prepared. Five solutions with different pH values (pH 3.70, pH 5.90, 8.20, 10.63 and pH 12.11) were degraded under UV-light radiation. Solution with pH 3.70 was obtained by adding HCl, while pH 8.20, pH 10.63 and pH

12.11 were obtained by adding NaOH into the solution. The solution was then diluted and the photodegradation procedure was repeated as above.

3.0 RESULTS AND DISCUSSION

3.1 Effect of TiO_2 and ZnO on the Photodegradation Process

In this experiment, New Methylene Blue N exhibited an absorption peaks at $\lambda = 590$ nm and $\lambda = 286$ nm. The method used to determine the best photocatalyst in degrading New Methylene Blue N was to mix a certain amount of TiO_2 and ZnO together into the aquous sample. According to Figures 1 and 2, the best catalyst to degrade the

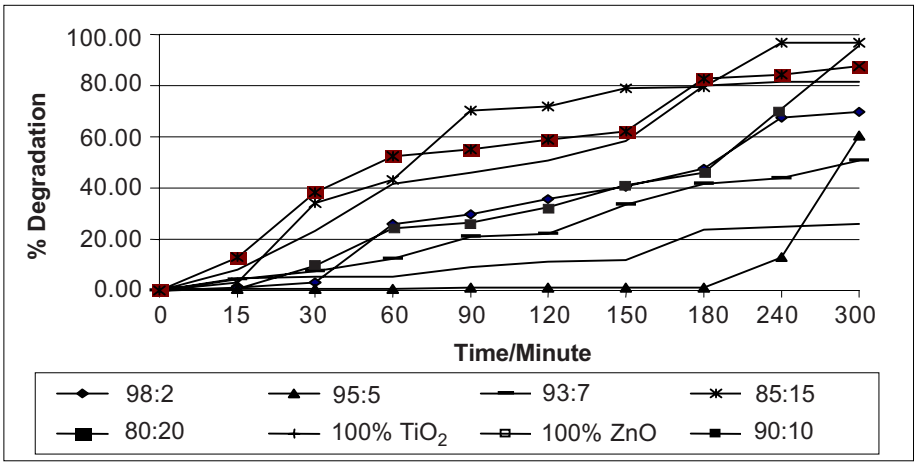

Figure 1 Effect of various ratios of TiO_2 and ZnO on the percent of degradation of methylene Blue N, at 590 nm

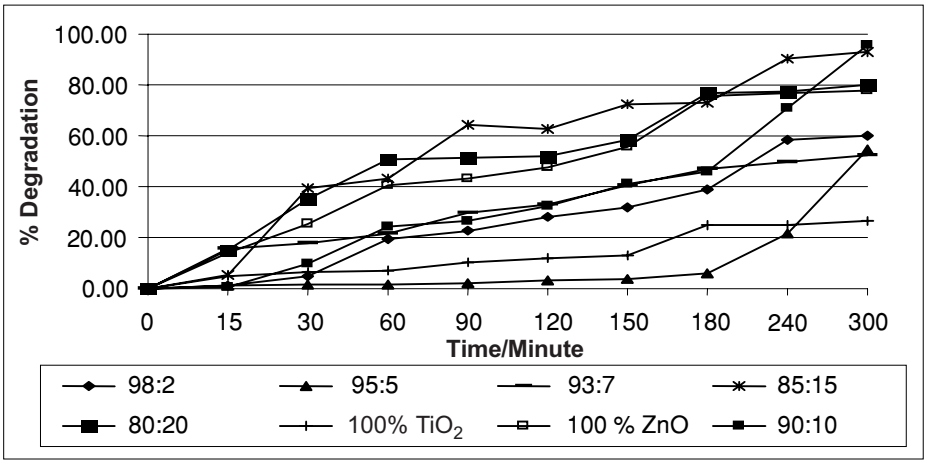

Figure 2 Effect of various ratios TiO_2 and ZnO on the percent of degradation of methylene Blue N, at 286 nm

sample is the catalyst with a ratio of 15: 85 (0.015 g TiO_2: 0.085 g ZnO) after 300 minutes irradiation time. The percentage degradation when 85% of ZnO (85: 15) was used in the photocatalyst mixture was 96.97% and 93.01% at λ = 590 nm and 286 nm respectively. Pure TiO_2 gave only 25.68% degradation while pure ZnO is better with 77.75% of the dye degraded at λ590 nm. Percentage degradation of Methylene Blue N using various ratios of ZnO and TiO_2 at 300 minutes is shown in Table 2.

Table 2 Percentage of degradation from various ratios of ZnO and TiO_2 at 300 minutes

Ratio (ZnO : TiO_2)	λ = 286 nm	λ = 590 nm
85 : 15	93.01%	96.97%
90 : 10	88.48%	95.43%
80 : 20	80.05%	87.62%
100 : 0	61.42%	77.75%
98 : 2	59.83%	69.5%
95 : 5	54.39%	60.28%
93 : 7	52.60%	50.60%
0 : 100	26.37%	25.68%

· pH solution = 5.9 to 3.76

The reason for a higher activity of ZnO is due to its lower band gap energy of 3.17 eV as compared to TiO_2 anatase at 3.20 eV. Since the value of ZnO band gap energy is smaller than TiO_2, the quantum efficiency of ZnO powder is also smaller than TiO_2 powder and hence more excitation of the electron have been reported for ZnO. More electron and positive holes were produced at the ZnO surface as compared to TiO_2. ZnO is also found to degrade acid brown 14 of azo dye more efficiently than TiO_2, suggesting that it absorbs large fraction of energy and absorption of more light quanta than TiO_2 [8]. Therefore more degradation is also assumed to occur by using a mixture of two catalysts containing more ZnO rather than TiO_2. The photocatalyst with an optimum ratio of 85 : 15 was the best catalyst. It gave a synergy effect, which might reduce the band gap energy to produce more electron-hole pairs. If the amount of co-catalyst is higher than the optimum value, the properties of TiO_2 become more dominant thus lowering the rate of photodegradation. TiO_2 powder was also found to degrade other substrate less efficiently such as 2,4,-DDE, 40.48% [9] and nitrophenol, 32% [10]. In contrast paraquat dichloride was degraded efficiently up to 100% after 180 minutes irradiation [11].

3.2 Effect of Metal Ions and Hydrogen Peroxide on the Photodegradation Process

The addition of powerful oxidizing species such as hydrogen peroxide to titanium dioxide or zinc oxide suspensions is well known procedure and in many cases lead to

an increase in the photooxidation rate. H_2O_2 is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation (Equation 6). It also produces $^{\bullet}OH$ radicals upon irradiation according to Equation (7).

$$e + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- \quad \ldots 6$$

$$H_2O_2 + h\nu \rightarrow {}^{\bullet}OH + OH^- \quad \ldots 7$$

Results obtained from this experiment showed that the percentage photodegradation increment was not significant whereby only 88.89% was recorded with the addition of H_2O_2 compared to 81.42% without H_2O_2 for ZnO at λ = 590 nm. At λ = 286 nm the percentage observed was 68.94% with H_2O_2 compared to 61.42% without H_2O_2 after 300 minutes. However these values were lower if compared to the results obtained from the optimum mixture of catalyst which was 96.97% at λ590 nm and 93.01% at λ = 286 nm.

Theoretically, the presence of metal ions can delay the recombination process of the generated electrons and holes as shown in Equations (8) and (9). Therefore, the percent degradation of methylene Blue N is expected to rise. However, the results obtained in this experiment do not confirm to the theory when a mixture of catalyst was added (ZnO : TiO_2 = 85 : 15).

$$M^{n+} + e \rightarrow M^{(n-1)+} \quad \ldots 8$$

$$M^{(n-1)+} + h^+ \rightarrow M^{n+} \quad \ldots 9$$

Since the optimum ratio of the photocatalyst was used in the reactions, the results obtained here must be compared to the optimum mixture of photocatalyst which consisted of TiO_2 and ZnO and not with either TiO_2 or ZnO. The results showed that all the metal ions gave a detrimental effect on the activity of the mixed catalyst. Copper ion, Cu^{2+} is the best ion giving the highest percentage of degradation when the absorption at λ = 590 nm (83.83 %) nm was measured while Pb^{2+} ion was the best ion for λ = 286 nm (81.25 %) (refer to Figures 3 and 4). These values however were lower compared to the reaction without the presence of metal ion, which were recorded as 96.97% at λ = 590 nm and 93.01% at λ = 286 nm. This means that the presence of metal ions gave detrimental effect to the activity of the photocatalyst when a second catalyst was added in this system. In contrast, the presence of H_2O_2 and Fe^{2+} ion increased the percentage of degradation of 2,4'-DDE using ZnO and TiO_2 with 95 : 5 ratio as a mix catalysts [9]. In previous studies, the presence of metal ions in the photodegradation using pure catalyst such as TiO_2 or ZnO increases the activity of the catalyst [11]. Litter [12] also found that metal ions increase the percentage of organic compound elimination in the photodegradation process by using only TiO_2 or ZnO. The results obtained using different systems showed that the effect of metal ions on the percentage degradation was not solely dependent on the type of catalyst but also on the type of

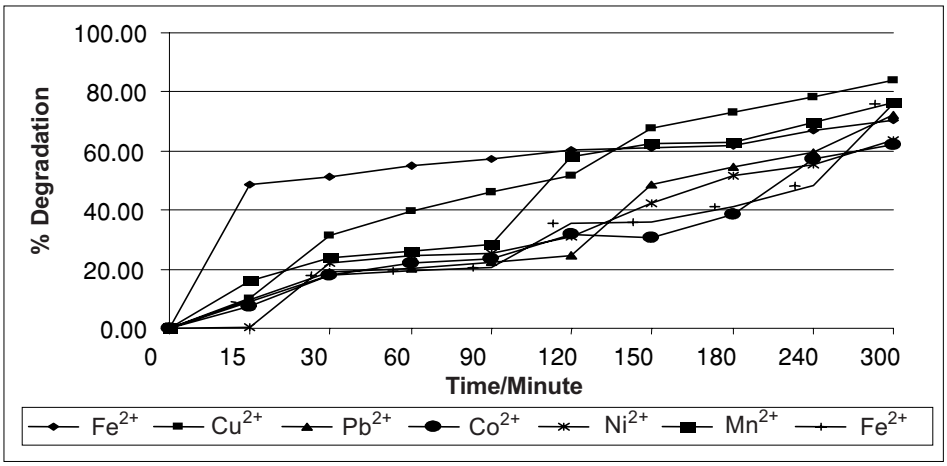

Figure 3 Effect of metal ions on the percent of degradation of Methylene Blue N, at 590 nm

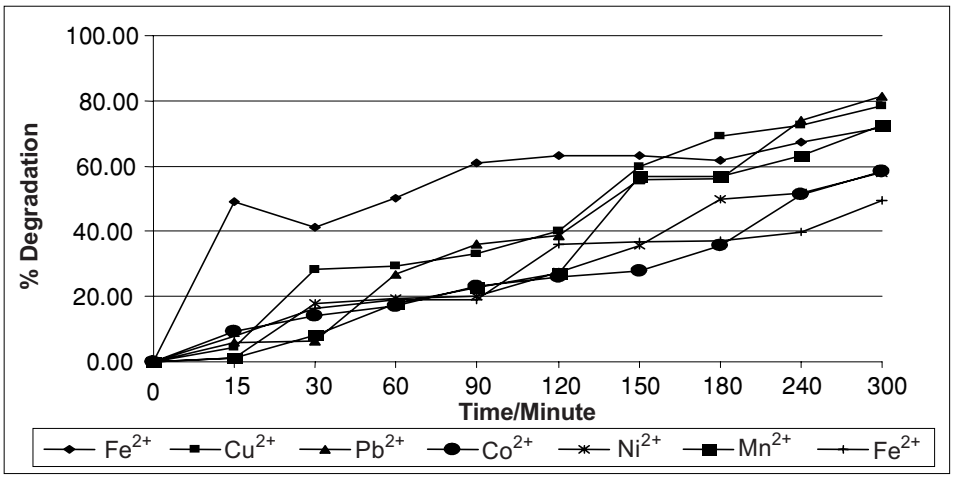

Figure 4 Effect of metal ions on the percent of degradation of Methylene Blue N, at 286 nm

substrate used. The order of metal ions in degrading the Methylene Blue N is as below:

$$Cu^{2+} > Pb^{2+} > Mn^{2+} > Fe^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+}$$

The result obtained can be explained using the standard reduction potential data, $E°_{SRP}$. Ion with highly positive value of $E°_{SRP}$ is expected to increase the amount of pollutant degraded. Cu^{2+} ion with the highest value ($E°_{SRP} = +0.34$ eV) is found to be the best metal ion, but the rest of the metals do not obey the general rules. This means that the SRP data is not the only factor affecting the activity of the catalyst, but other factors such as the substrate or the pH values of the system must also be considered.

3.3 Effect of pH on the Photodegradation Process

pH plays an important role both in characterizing the textile wastes and the generation of the hydroxyl radicals. Hence, attempt has been made to study the influence of pH in the degradation of dye at the pH range of 3 – 12. In all the experiments reported here, a sharp drop of the pH solution from 5.90 to 3.76 was observed within 15 minutes of the reaction, and then remained constant (refer Figure 5). The drastic drop in pH at the early part of the reaction is probably due to the formation of some carboxylic acid intermediates that could not be characterized. There are two factors that lead to the pH drop from 5.90 to 3.90. One of the factors is the generation of HSO_4^- and NO_3^- ion during the mineralization of New Methylene Blue N [13]. Both HSO_4^- and NO_3^- can contribute to the acidity of the solution. The other factor is the formation of carboxylic acid as an intermediate such as hydrocumanic acid.

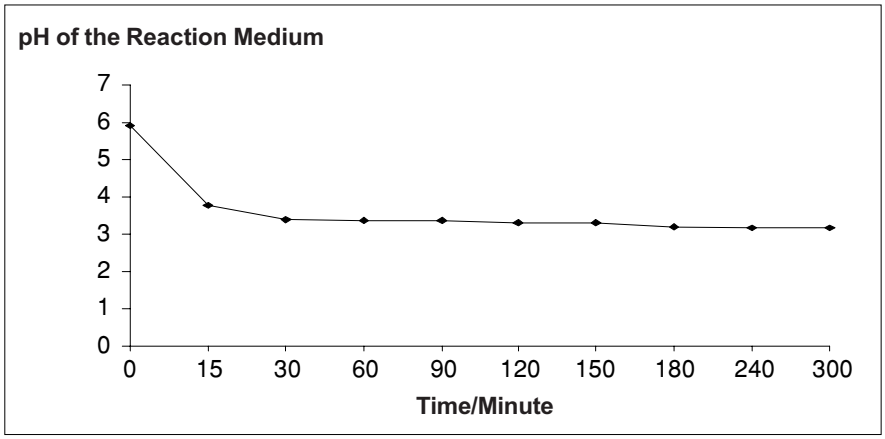

Figure 5 Change of pH during the normal photodegradation of New Methylene Blue N with catalyst, ZnO : TiO_2 = 85:15, [Dye] = 1×10^{-4} M, [$[Pb^{2+}]$ = 1×10^{-3} M and $[H_2O_2] = 1 \times 10^{-3}$ M

Theoritically, the TiO_2 surface is positively charged in acidic media (pH < 6.8) and negatively charged under alkaline condition (pH > 6.8) but for ZnO the surface is positively charged below pH 9 [8]. Therefore the results would be expected to give a higher percentage degradation at pH above 9 because the dye used is positively charged which is easily absorbed at a negatively charged surface.

However, according to Figures 6 and 7, the highest percentage of degradation occurred at pH 5.90, which is the normal pH observed in all experiments. The values are 92.84% at λ = 590 nm and 89.30% at λ = 286 nm. At pH 3.70 the percentage is lower which is 83.66% (590 nm) and 63.27% (286 nm). This is due to the scavenging effect of the $^{\bullet}OH$ radicals by H^+ that eventually reduced the active species involved in the

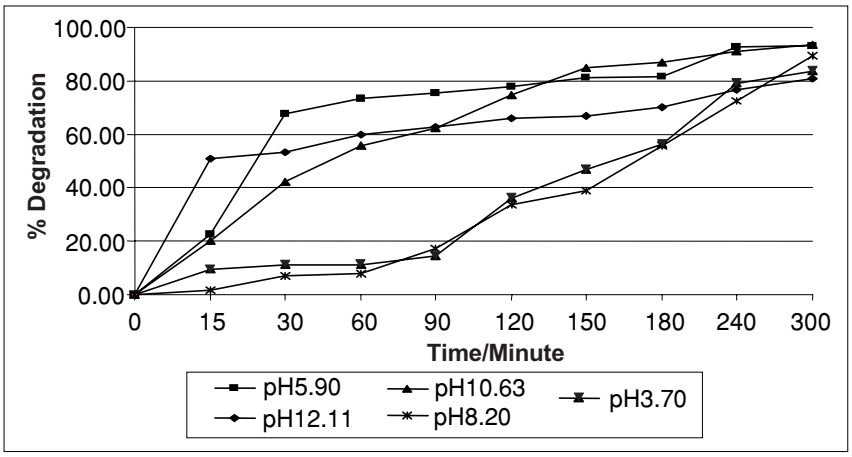

Figure 6 Effect of and pH on the percent of degradation of Methylene Blue N, at 590 nm

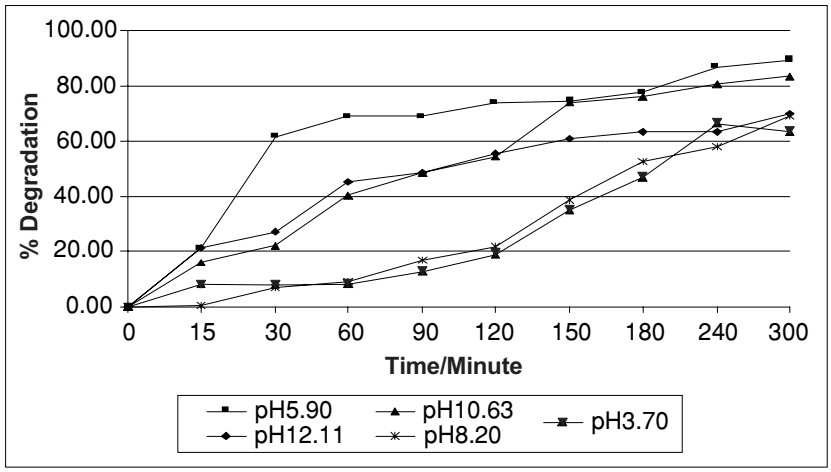

Figure 7 Plot percent of Degradation at different pH values against time at 286 nm

photodegradation process. At higher pH, the percentages are also lower because the formations of the •OH radical become slow due to the formation of metal hydroxide.

4.0 CONCLUSION

The results show that 0.015 g TiO_2 and 0.085 g ZnO (15: 85) was the optimum ratio of TiO_2 and ZnO mixture to degrade Methylene Blue N. Any amount greater or less than the optimum ratio, decreased the activity of the catalyst. The addition of metal ions and H_2O_2 gave a detrimental effect on the photodegradation process. Cu^{2+} is the best metal ion to degrade New Methylene Blue N and the best pH to degrade the

sample is at normal pH, 5.90. The optimum discolouration of New Methylene Blue N was achieved after 5 hours illumination in the presence of 0.015 g TiO_2, 0.085 g ZnO, at pH 5.90.

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