Optimisation of Methyl Orange Photodegradation Using TiO$_2$-Zeolite Photocatalyst and H$_2$O$_2$ in Acid Condition

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Abstract. This paper discusses an optimisation of methyl orange photodegradation using TiO$_2$-zeolite photocatalyst and H$_2$O$_2$ (with condition of pH 2, 10 ppm, UV light). A 15 mmol TiO2 in 1 gram activated zeolite was used. The influence of H$_2$O$_2$ concentration (4, 8, 12, 16%) and irradiation time (20, 30, 40, 50, 60 minutes) was also investigated, as well as initial methyl orange concentration (10, 20, 30 ppm) toward reaction rate constant. As the H$_2$O$_2$ concentration increase, the photodegradation percentage is also increased until it reaches optimum condition (H$_2$O$_2$ 12% for 10 ppm MO solution). Identical effect also showed by the irradiation time in which an optimum point reached at 60 minutes (for 10 ppm MO solution) and 50 minutes (for 20 and 30 ppm MO solutions). Moreover, the higher initial MO concentration used, the lower reaction rate constant obtained. The highest rate constant was shown by MO solution of 10 ppm. The reuse of TiO$_2$-Zeolite photocatalyst remains effective and efficient in photodegradation of methyl orange in solution for up to 4 times.

Keywords: methyl orange, photocatalyst, TiO$_2$-zeolite, H$_2$O$_2$.

1. Introduction

The textile industry as one of the developing industries has a large contribution to water pollution. The most abundant compounds (60 – 70 %) in textile waste are azo dyes [1]. Methyl orange is one of the azo dyes that are often used as textile dyes and have different structure depends on the acidity (Figure 1). Non-biodegradable methyl orange can produce several environmental pollution problems by releasing toxic and carcinogenic compounds in the waters [2]. Waste treatment has been widely developed, one of which is the photocatalytic degradation method using semiconductors [3]. The advantage of the photocatalytic process compared to traditional chemical oxidation processes or biological processes is that it is able to degrade various chemical compounds, can be applied to liquid or gas mediums, and has the potential to utilize sunlight as a substitute for UV light [4]. Photocatalysts are irradiated with wavelengths of 100-400 nm to activate electrons from the valence band to the conduction band in order to form holes (positive charges) in the valence band (h$^+$cb) and electrons in the conduction band (e$^-$_cb) [5].

The efficiency of photocatalysts in waste processing can be viewed from its ability to degrade waste repeatedly. Based on the research by Pekakis, et al. [6] TiO$_2$ can be reused to degrade textile waste until the 3rd usage. The catalytic activity of semiconductors can be increased through development of a porous material, such as zeolite [7-9].
Improved zeolite performance can be carried out by deploying transition metals which have $d$ orbitals that have not been fully filled or transition metal oxides [5]. Zeolite carries TiO$_2$ so that it can decrease the surface area of solids due to aggregation of its oxides on the surface of the solid so that it covers the pores of natural zeolite [10]. The ability of photocatalytic metal oxides will increase if the particle size is very small. Faghihian and Bahranifard reported [8] that the development of TiO$_2$ in zeolites was able to increase percentage of Safranin-O degradation by 69% compared to not-incorporated TiO$_2$.

Hydroxyl radicals play an important role in the process of photocatalytic degradation. The addition of H$_2$O$_2$ can increase the rate of degradation of compounds because it is effective in generating hydroxyl radicals and inhibiting electron hole recombination [11]. Research conducted by Rashed and El-Amin [12] showed that the concentration of methyl orange had an effect on the degradation process using TiO$_2$ photocatalysts. The greater the concentration of methyl orange, the degradation reaction rate constants will decrease. The duration of irradiation affects the amount of hydroxyl radicals produced to degrade dyes. The longer the reaction, the more interaction occurred between photons and photocatalysts.

![Figure 1. Structures of methyl orange salt in different pH condition (acid = red, base = yellow).](image)

This study focuses on the effect of irradiation time and H$_2$O$_2$ concentration on the photodegradation of methyl orange using TiO$_2$-zeolite photocatalysts and the effect of the initial concentration of methyl orange on degradation rate constants. Possible reuse of the photocatalyst and its effectiveness in photodegradation of methyl orange is also discussed.

2. Materials and Methods

2.1. Materials

All chemicals were laboratory grade and used without further treatment as obtained from the supplier (except zeolite from local market), namely TiO$_2$, HCl, ethanol, AgNO$_3$, H$_2$O$_2$, and methyl orange.

2.2. Preparation of TiO$_2$-Zeolite

Zeolite was grinded into powder and washed with distilled water, followed by drying it in an oven at 110°C for 2 hours. A 45 g of dry zeolite was activated by soaking it in HCl 0.4 M. The mixture was shaken at 100 rpm for 4 hours, then filtered off. The zeolite then washed with distilled water again until it is free from chloride ion (the filtrate was tested with AgNO$_3$ 1M). The activated zeolite then dried at 110 °C for 2 hours.

A 6 g of activated zeolite mixed with 7.2 g of TiO$_2$ (15 mmol TiO$_2$ / g zeolite) was added with 6 mL of 99% ethanol. The mixture was stirred for 5 hours at room temperature. The mixture then dried at 120 °C for 5 hours. Dry TiO$_2$-zeolite were grinded and sieved with a 200 mesh sift and then the powder was calcined at 400-500 °C for 5 hours.
2.3. Effect of $H_2O_2$ in photodegradation of methyl orange with TiO$_2$-zeolite

Five samples of methyl orange solution (25 mL, 10 mg/L, pH 2) were prepared. Sample no 1 did not use any photocatalyst and $H_2O_2$. Sample no 2, 4, and 5 were added with TiO$_2$-zeolite photocatalyst. A 1 mL of 4% $H_2O_2$ was added to sample no 3, 4, and 5. Samples 1-4 were irradiated in a UV reactor for 40 minutes. The fifth sample was closed and stand at room temperature without light for 40 minutes. Another solution of methyl orange (25 mL, 10 mg/L, pH 6) was also prepared. This solution was added with 50 mg of TiO$_2$-zeolite photocatalyst and 1 mL of 4% $H_2O_2$. This solution was also inserted into the UV reactor together with the five samples.

After treatment, the photocatalyst was separated from the methyl orange solution by decantation. The pH of the solution after treatment was measured. The concentrations of methyl orange after treatment (pH 6) were measured by UV-Vis spectrophotometer at 460 nm. Degradation percentage of methyl orange was determined based on Eq. 1 ($Co$ = methyl orange concentration before irradiation, $Ct$ = methyl orange concentration after irradiation):

$$\text{% degradation} = \frac{Co - Ct}{Co} \times 100\%$$

(Eq. 1)

2.4. Effect of $H_2O_2$ concentration in photodegradation of methyl orange with TiO$_2$-zeolite

Four samples of methyl orange solution (25 mL, 10 mg/L, pH 2) were prepared. All solutions were added with 50 mg of TiO$_2$-zeolite photocatalyst and 5 mL $H_2O_2$ with concentrations of 4, 8, 12 and 16% and then irradiated in the UV reactor for 40 minutes. After that, the photocatalyst was separated from the methyl orange solution by decantation. The pH of the solution after treatment was measured. The concentrations of methyl orange after treatment (pH 6) were measured by UV-Vis spectrophotometer at 460 nm. Degradation percentage of methyl orange was determined based on Eq. 1.

2.5. Effect of irradiation time in photodegradation of methyl orange with TiO$_2$-zeolite

Five series of methyl orange solution (25 mL, pH 2) with concentrations of 10, 20, and 30 mg/L were prepared. To each sample, 50 mg of TiO$_2$-zeolite photocatalyst and 5 mL $H_2O_2$ with 8% $H_2O_2$ was added. For each concentration, the solution then irradiated in the UV reactor for 20, 30, 40, 50 and 60 minutes. Next, the photocatalyst was separated from the methyl orange solution by decantation. The pH of the solution after treatment was measured. The concentrations of methyl orange after treatment (pH 6) were measured by UV-Vis spectrophotometer at 460 nm. Degradation percentage of methyl orange was determined based on Eq. 1.

2.6. Effect of initial methyl orange concentration in the rate constant of methyl orange photodegradation

The results from subsection 2.5 above was then used to make an equation to study the relationship between time as the $x$ axis and $\ln(Co/Ct)$ as the $y$ axis. The rate constant ($k$) of methyl orange photodegradation was calculated based on Eq. 2 ($Co$ = methyl orange concentration before irradiation, $Ct$ = methyl orange concentration after irradiation):

$$\ln \left( \frac{Co}{Ct} \right) = kt$$

(Eq. 2)

2.7. Effectiveness of reusing TiO$_2$-zeolite photocatalysts in methyl orange photo degradation

Six samples of methyl orange solution (25 mL, 10 mg/L, pH 2) added with 50 mg of TiO$_2$-zeolite photocatalyst and 5 mL of $H_2O_2$ 8% were prepared. All samples were then irradiated in a UV reactor for 60 minutes. After decanting the solution, 5 mL solution was taken out and the pH was adjusted to 6. The concentrations of methyl orange after treatment were measured by UV-Vis spectrophotometer at 460 nm. Degradation percentage of methyl orange was determined based on Eq. 1.

The photocatalyst that has been used was added with 50 mL distilled water and the solution was shaken for 5 hours. After filtering off, the precipitate dried in an oven at 110°C for 2 hours. Dry TiO$_2$-
zeolite photocatalyst was weighed and reused in the degradation of methyl orange (4 samples, 25 mL, 10 mg/L, pH 2) with a ratio of methyl orange:TiO$_2$-zeolite:8% H$_2$O$_2$ = 5:10:1.

3. Result and Discussion

3.1. Synthesis of TiO$_2$-Zeolite

Acid activation process was performed for zeolite to increase crystallinity, acidity, surface area [13], total pore volume and decrease the mean radius of the pore [14], while impregnation of TiO$_2$ was confirmed by XRF analysis in which the TiO$_2$ content in zeolite after impregnation was increased from 0.76 ± 0.11% to 82.04 ± 0.16 %. Other metal oxides remain present in TiO$_2$-zeolite with four highest content are 13.4 ± 0.1% (SiO$_2$), 1.58 ± 0.01 (CaO), 1.23 ± 0.003% (Fe$_2$O$_3$), and 0.978 ± 0.003% (K$_2$O). It is expected that the high amount of TiO$_2$ dispersed on the zeolite surface influences the degradation process of methyl orange. The more TiO$_2$ dispersed on the surface of zeolite, the more OH radicals produced on the surface of the photocatalyst.

3.2. Effect of H$_2$O$_2$ in photodegradation of methyl orange with TiO$_2$-zeolite

Different treatments were conducted to study the effect of H$_2$O$_2$ in photodegradation of methyl orange with TiO$_2$-zeolite, the results are presented in Figure 2. Treatment of methyl orange irradiated by UV without addition of any H$_2$O$_2$ and TiO$_2$-zeolite (treatment 1) give a baseline information on photodegradation percentage. It also indicates that although it gives 8.33% degradation after 40 hours irradiation, UV light has limited ability to break the double bond, thus addition of H$_2$O$_2$ and TiO$_2$-zeolite may have a role to increase the photodegradation percentage.

Figure 2. Different treatments in photodegradation of methyl orange with TiO$_2$-zeolite (1 = MO + hv + pH 2; 2 = MO + TiO$_2$-zeolite + hv + pH 2; 3 = MO + H$_2$O$_2$ + hv + pH 2; 4 = MO + TiO$_2$-zeolite + H$_2$O$_2$ + dark + pH 2; 5 = MO + TiO$_2$-zeolite + H$_2$O$_2$ + hv + pH 2; 6 = MO + TiO$_2$-zeolite + H$_2$O$_2$ + hv + pH 6)

Degradation of UV-assisted methyl orange with addition of H$_2$O$_2$ (treatment 3) give degradation percentage of 18.89%. Compare to treatment 1, the degradation percentage is increase due to H$_2$O$_2$ produces •OH when UV light was used. The hydroxyl radical helps degrading methyl orange (MO) into methyl orange degradation compounds (MO’s) as shown in the following equation:

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH}
\]
\[
\text{MO} + 2 \cdot \text{OH} \rightarrow \text{MO’s}
\]
Meanwhile, UV-assisted methyl orange with addition of TiO$_2$-zeolite photocatalyst (treatment 2) give higher degradation percentage of 37.42%. This is possible due to TiO$_2$ which absorbs photons produces holes in the valence band and then excite its electrons in the conduction band. The holes react with H$_2$O to form •OH and H$^+$. The electrons in the conduction band react with dissolved oxygen to form superoxide radicals. The superoxide radical can react with H$_2$O to form perhydroxyl radicals. These hydroxyl radicals, superoxide, and perhydroxyl are compounds that degrade the methyl orange [15, 16], as shown in the following equation:

\[
\text{TiO}_2 + h\nu \rightarrow e^- + h^+
\]
\[
h^+ + \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{H}^+
\]
\[
e^- + \text{O}_2 \rightarrow \text{O}_2^-
\]
\[
\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{OH}^-
\]

The amount of TiO$_2$ in the photocatalysts allows the activity of TiO$_2$ dispersed in zeolites. Development of TiO$_2$ in zeolite increases the surface area hence large amounts of e$^-$ and H$^+$ are formed when photons arrive on the surface of the photocatalyst. Therefore, the more H$^+$ formed, the more superoxide and hydroxyl radicals produce.

Based on the results of UV-DRS characterization using the TiO$_2$-N photocatalyst carried out by Risca et al [17], the photocatalyst experienced a band gap energy reduction of 0.01 eV, which mean that the photocatalyst can be active under visible light radiation. This is confirmed by the result of treatment 4 in which in dark condition, methyl orange concentration only reduced by 20% although TiO$_2$-zeolite photocatalyst and H$_2$O$_2$ was incorporated. In dark conditions, less •OH to degrade methyl orange were formed because the absence of photons as an energy source. In dark conditions, only adsorption process occurs by TiO$_2$-Zeolite particles [17]. Formation of •OH by H$_2$O$_2$ is still possible due to the nature of H$_2$O$_2$ which is unstable and easily reduced, but the amount of OH produced in dark conditions is very limited and insufficient to degrade methyl orange.

Degradation of methyl orange at pH 2 (treatment 5) shows higher degradation percentage of methyl than at pH 6 (treatment 6) because methyl orange is anionic which tends to interact with positively charged photocatalyst surfaces. The coulomb repulsion between the negatively charged surface of the photocatalyst and the hydroxide ion causes the formation of hydroxyl radicals to be inhibited thus the degradation percentage is decreased.

### 3.3. Effect of H$_2$O$_2$ concentration in photodegradation of methyl orange with TiO$_2$-zeolite

Figure 3 shows the influence of H$_2$O$_2$ concentration in photodegradation of methyl orange with TiO$_2$-zeolite with condition of MO solution 10 ppm at pH 2. As the concentration increase from 4 to 12 %, photodegradation percentage is also increase significantly. This is because the as the H$_2$O$_2$ concentration increased, the amount of OH radicals that produced in the solution is getting higher [18].

![Figure 3. Relationship between H$_2$O$_2$ concentrations and methyl orange photodegradation.](image-url)
The •OH radical oxidation potential is higher than other oxidizers (2.8 V), thus •OH is very effective in degrading organic compounds. Upon using higher \( \text{H}_2\text{O}_2 \) concentration, the photodegradation percentage of MO declined about 10% due to excess \( \text{H}_2\text{O}_2 \) inhibits the rate of degradation. \( \text{H}_2\text{O}_2 \) can react with OH radicals to form dihydroxyl radicals [18]. Study by Abo-Farha [16] suggest that the addition of excess \( \text{H}_2\text{O}_2 \) would result in \( \text{H}_2\text{O}_2 \) reacting with •OH and hole in the valence band. As a result, the amount of •OH in the solution is reduced which eventually decrease the degradation percentage of methyl orange. The reactivity of \( \text{HO}_2^- \) radicals with organic compounds is weaker than that of •OH and it also has a tendency to disproportionate to produce \( \text{H}_2\text{O}_2 \) and oxygen, as follows:

\[
\text{HO}_2^- + \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{•OH}
\]

A statistic F test shows that \( \text{H}_2\text{O}_2 \) concentrations had an effect on the degradation percentage of methyl orange. The optimum \( \text{H}_2\text{O}_2 \) concentration to degrade methyl orange 10 mg/L at pH 2 is 8% with an error rate of 1%.

### 3.4. Effect of Irradiation Time on Degradation of Methyl Orange with TiO\textsubscript{2}-Zeolite Photocatalyst

Photodegradation percentage of methyl orange increases as longer irradiation time applied. The interaction between photons, \( \text{H}_2\text{O}_2 \) and TiO\textsubscript{2}-zeolite photocatalysts is directly proportional to the duration of irradiation. Hence, the longer the irradiation time, the greater the interaction, resulting in more OH radicals. For MO concentration of 10 ppm, the optimum irradiation time is 60 minutes (76.94%), whereas for concentrations of 20 and 30 ppm, the optimum irradiation times are 50 minutes (Figure 4).

![Figure 4. Relationship between irradiation time and methyl orange photodegradation.](image)

Formation of radicals •OH is rapid and the active side is available for adsorption in large quantities at the beginning of the reaction. After a certain time, the remaining active side is difficult to fill because of the repulsion force between molecules on the surface with bulk phase. Therefore, the degradation percentage tends to be constant after some time [12].

### 3.5. Effect of initial methyl orange concentration in the rate constant of methyl orange photodegradation

The concentration of methyl orange at 10 ppm gives the highest reaction rate constant as shown in Table 1 with a slope of 0.015/minutes. As the methyl orange concentration increases, lower reaction rate constant was observed. This is due to higher concentration of methyl orange solution can block the UV light to reach the photocatalyst surface. Hence, the amount of OH radicals produced is becoming less, causing slower degradation rate.

According to Chong, et al. [19], increasing the concentration of dyes resulting in lower formation of OH radicals on the surface of the catalyst. This is because the active side was covered by the dye as a
result of physical adsorption. Several studies also suggest that the reaction rate of photocatalytic degradation of dyes can be explained by model using kinetic rate constants in pseudo-first order [20].

### Table 1. Methyl Orange Degradation Rate Constants Table with Early Methyl Orange Concentration Variations.

| No | Concentration MO (mg/L) | Degradation Rate Constants (minute⁻¹) | Correlation Coefficient (R²) |
|----|-------------------------|--------------------------------------|-----------------------------|
| 1  | 10                      | 0.015                                | 0.973                       |
| 2  | 20                      | 0.010                                | 0.972                       |
| 3  | 30                      | 0.009                                | 0.941                       |

**Figure 5.** Relationship of Ln (C₀ / Cₜ) to Time for variation of initial methyl orange concentration

#### 3.6. Effectiveness of reusing TiO₂-Zeolite Photocatalyst in Methyl Orange Degradation

Based on Figure 6, it is observed that TiO₂-zelite photocatalysts on the second to fourth uses are still able to degrade methyl orange and give almost the same result as that of the first use of TiO₂-zelite photocatalyst. On the surface of TiO₂-zelite photocatalyst, TiO₂ can aggregated and causing an increase of pore finger rate or reduced pore volume. Thus, resulting in decrease in photocatalytic activity of TiO₂-zelite. Formation of h⁺vb and e⁻cb on the photocatalyst surface can occur in large numbers, so that photocatalytic activity does not change with the presence of formed TiO₂ aggregates. Therefore, TiO₂-zelite photocatalyst can be used in methyl orange photodegradation repeatedly (four times) without reducing its effectiveness significantly.

**Figure 6.** Relation of the Use of TiO₂-Zeolite Photocatalyst to Percentage of Methyl Orange degradation
4. Conclusion
Optimisation of methyl orange photodegradation using TiO$_2$-Zeolite photocatalyst and H$_2$O$_2$ (with condition of pH 2, 10 ppm, UV light) were studied. The influence of H$_2$O$_2$ concentration and irradiation time was also investigated, as well as initial methyl orange concentration toward reaction rate constant. As the H$_2$O$_2$ concentration increase, the photodegradation percentage is also increased until it reaches optimum condition (H$_2$O$_2$ 12% for 10 ppm MO solution). Identical effect also showed by the irradiation time in which an optimum point reached at 60 minutes (for 10 ppm MO solution) and 50 minutes (for 20 and 30 ppm MO solutions). Moreover, the higher initial MO concentration used, the lower reaction rate constant obtained. The highest rate constant was shown by MO solution of 10 ppm. The reuse of TiO$_2$-Zeolite photocatalyst remains effective and efficient in photodegradation of methyl orange in solution for up to 4 times.

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