



## OPTIMIZATION AND MECHANISM ELUCIDATION OF CATALYTIC PHOTODEGRADATION METHYLENE BLUE BY TiO<sub>2</sub>/ZEOLITE COAL FLY ASH NANOCOMPOSITE UNDER H<sub>2</sub>O<sub>2</sub> PRESENCE

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### ABSTRACT

The synthetic dye methylene blue is utilized in many industries. However, it harms the aquatic ecosystem. Methylene blue causes wastewater to become colored. If this colored waste is released into the environment, clean, colorless water will become colored. This work uses a zeolite coal fly ash/TiO<sub>2</sub> nanocomposite to enhance the process and identify the photodegradation mechanism of Methylene Blue (MB). Our group has successfully synthesized this nanocomposite using a developed method, improving the materials' capacity for both photodegradation and adsorption. This study has proved nanocomposite performance to degrade methylene blue as a synthetic dye by optimizing the effects of H<sub>2</sub>O<sub>2</sub> addition, catalyst dosage, pH, initial concentration of methylene blue, and irradiation period. The maximum photodegradation in this investigation was observed at a pH of 12 with a nanocomposite dose of 3 g/l and an addition of 8 ml/l of H<sub>2</sub>O<sub>2</sub>, and in this study, degradation efficiency reached 100% for an 18 mg/l MB concentration in a short period of 75 minutes. With a reaction rate constant of 0.0601 min<sup>-1</sup>, the reaction kinetics were described by a pseudo-first-order reaction kinetics model. UPLC-MS/MS QToF analysis revealed the result of chemicals produced by photocatalytic degradation of methylene blue fragmentation into simpler molecules.

### INTRODUCTION

Methylene blue is a synthetic dye commonly used in various industries, including textiles, paper, and pharmaceuticals. Because of its toxicity and persistence, it is categorized as a cationic dye or a water pollutant. The primary sources of methylene blue pollution include industrial discharges, particularly from dyeing and printing processes, as well as improper disposal of waste from laboratories and medical facilities. Several methods for removing methylene blue from water can be categorized into physical, chemical, and biological processes. Coagulation, activated charcoal adsorption, and ultrafiltration have been used to address the issue of dye wastewater (Bethi et al., 2016; Desmiarti et al., 2019). These methods, however, do not cause any damage because they merely move the dyes in wastewater to solid media

that need more processing (Priya. et al., 2020). As the technique frequently necessitates higher operational costs regarding chemicals, installation, and comparatively longer processing times, this method has been considered less effective (Saqib et al., 2019).

Additionally, undegraded compounds remain in the environment, leading to the accumulation of these compounds in nature. Photocatalytic degradation is currently attracting more attention. Common photocatalytic materials are oxide semiconductors (Vossoughi et al., 2014). Among many semiconductor materials, TiO<sub>2</sub> has attracted significant attention in addressing environmental issues such as water and air purification due to its high photocatalytic efficiency (Kusumawardani & Iryani, 2021; Kusumawardani et al., 2022). Some modification of TiO<sub>2</sub> using metal ions is commonly used to improve the optical and structural properties



of Fe, Co, Mn, and Cr (Kusumawardani & Syahputri, 2019; Zhang et al., 2019). Meanwhile, other studies of modifying TiO<sub>2</sub> using zeolite show better properties (Maraschi et al., 2014; Peng et al., 2017). Zeolite exhibits a significantly greater capacity for adsorption than other porous materials like activated carbon and bentonite. In the meantime, a small TiO<sub>2</sub> surface area of 9.492 m<sup>2</sup>/g makes it an ineffective photocatalytic material in terms of both efficiency and adsorption capacity (Deshmukh et al., 2020). On the other hand, zeolite is an inexpensive microporous material.

Our group has successfully synthesized TiO<sub>2</sub>/Zeolite coal fly ash nanocomposite (Kusumawardani et al., 2023). Considering all measurement results, the synthesized nanocomposite material has the lowest band gap energy of 2.50 eV, the largest surface area of 189.483 m<sup>2</sup>/g, and an average particle size of 9 nm, which is still within the nanometer range (Hu et al., 2010). This size can influence how effectively the material works regarding its chemical activity because a smaller particle size leads to a larger surface area (Huang et al., 2020). Therefore, our team has successfully developed this synthesis method to enhance the properties of nanocomposite, a combination material of adsorbent zeolite from coal fly ash and titanium dioxide as a photocatalyst. However, its performance must still be proven, especially for degrading dyes, due to its properties in enhancing the active side's capacity to come into contact with other compounds.

In this study, we develop the operating process of photocatalytic degradation for methylene blue (MB) removal using TiO<sub>2</sub>/zeolite coal fly ash nanocomposites. The pH, initial concentration of MB, nanocomposite dose, and irradiation period are factors in photodegradation that influence the dye decolorization process. Methylene blue removal will be evaluated under 1000-watt halogen light and measured by UV-visible spectrophotometer. Moreover, it is advised to run the photodegradation process under H<sub>2</sub>O<sub>2</sub> to improve results because it functions as an oxidizing agent and accelerates the generation of OH radicals (Liu et al., 2018). Ultimately, a degradation mechanism was postulated based on the LCMS/MS data, and the degraded products were identified by UPLC-MS/MS QToF analysis.

## MATERIALS AND METHOD

### Materials and Instrumentation

The materials used are TiO<sub>2</sub>/zeolite nanocomposites from coal fly ash from our previous study (Kusumawardani et al., 2023), methylene blue grade for analysis, H<sub>2</sub>O<sub>2</sub> 30% (p.a), NaOH 30% (Merck), HCl 10% (Merck). UV-visible spectrophotometer (Shimadzu UV-vis) was applied to determine the concentration of methylene blue before and after the photodegradation process. UPLC-MS/MS QToF (Waters, USA) was used to identify the intermediate product at optimum degradation.

### Method

#### *Effect of H<sub>2</sub>O<sub>2</sub> Presence*

A study of the effect of H<sub>2</sub>O<sub>2</sub> addition was carried out by adding 0, 4, 8, 12 ml/l H<sub>2</sub>O<sub>2</sub> 30% and 3g/l nanocomposite into 100 ml methylene blue (MB) at an initial concentration of 10 mg/l under visible light irradiation for 60 minutes. The absorbance was measured with a UV-Vis Spectrophotometer at a wavelength of 662 nm.

#### *Optimization Operating Process for MB Photodegradation*

By incorporating nanocomposites with a concentration of 10 mg/l MB into the sample solution, photocatalytic degradation was achieved. Halogen lamps were used as the light sources. There is magnetic stirring in the reaction vessel. In order to investigate the effects of the process, a variety of conditions were applied, including different pH levels (5, 7, 9, 11, 12, and 13), initial MB concentrations (13, 15, 18, and 19 mg/l), catalyst dosages (1,00; 2,00; 3,00; dan 4,00 mg/l), and irradiation period of roughly 75 minutes with 15-minute intervals. Utilizing a Shimadzu UV-Vis Spectrophotometer, the photocatalytic degradation of MB ( $\lambda_{\text{max}}=662$  nm) was quantified. Figure 1 depicts a model of a photocatalytic degradation reactor.

Using Eq. (1), which takes into account the percentage of degradation (% D), the sample's initial concentration (C<sub>0</sub>) prior to halogen irradiation, and the final concentration (C<sub>t</sub>) following halogen irradiation, the percentage of photocatalytic activity was determined. The following concentration values were entered into the efficiency formula using methylene blue :

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

### Determination of the Degraded Products by LCMS/MS Study

A total of 5 µl of clear degradation solution was filtered with a 0.2 µm filter and injected into the sample holder and the UPLC column. The mobile phases used were formic acid (A) and acetonitrile + 0.05% formic acid (B), with a 0.2 ml/min flow rate. The QToF-MS detector read the separation results to obtain chromatogram peaks, which were then interpreted using the *Masslynx* application. The specification of LCMS/MS is shown as Table 1.

## RESULT AND DISCUSSION

### Effect of H<sub>2</sub>O<sub>2</sub> Presence

Different concentrations of H<sub>2</sub>O<sub>2</sub> were added to MB solution (0, 4, 8, and 12 ml/l) and exposed to halogen lamp radiation for 60 minutes to observe the effects of H<sub>2</sub>O<sub>2</sub> presence. The nanocomposites were added at 3 g/l. According to this investigation, there was more degradation when H<sub>2</sub>O<sub>2</sub> was

present. In line with Figure 2, 94.6% showed the highest degradation of MB at 8 ml/l, whereas only 85.2% of the photodegradation occurred without H<sub>2</sub>O<sub>2</sub>. The highest degradation MB removal occurred from the initial concentration of 10 mg/l to 0.5323 mg/l as the final concentration. It has been concluded earlier that this represents the optimum dosage of H<sub>2</sub>O<sub>2</sub>. The result shows that faster photocatalytic degradation is caused by H<sub>2</sub>O<sub>2</sub>, which accelerates the degradation process. Higher production of •OH radicals is the result. During the photodegradation process, numerous organic compounds were successfully oxidized into CO<sub>2</sub> and H<sub>2</sub>O by the most potent and significant oxidizing species, the OH• radicals. By generating OH• radicals, the oxidizing agent plays a significant role in breaking these organic molecules, increasing the quantum yield. TiO<sub>2</sub>/zeolite provides an advantage for photocatalytic degradation in the presence of H<sub>2</sub>O<sub>2</sub> by generating OH• radicals through H<sub>2</sub>O<sub>2</sub> dissociation (Wicaksono et al., 2020). The primary cause of the enhanced MB degradation could be attributed to the rapid decrease in electron-hole pair recombination over the photocatalyst surface, which is achieved by producing more OH• (Zul et al., 2020).

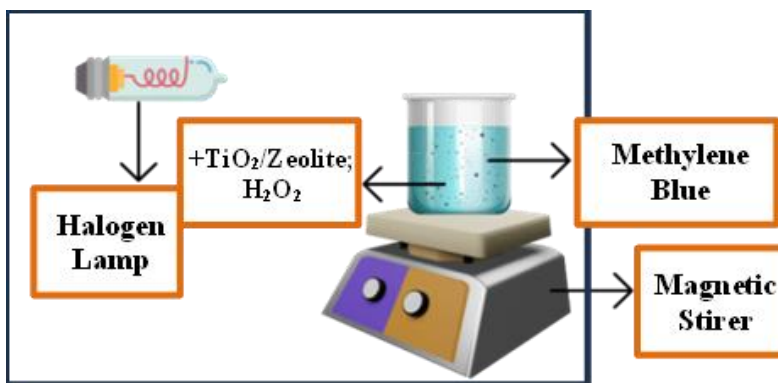


Figure 1. Reactor Model of the Photocatalytic Degradation Process

Table 1. Specification of UPLC-MS/MS QToF

Part	Specification	Details
LC System	ACQUITY UPLC H-Class system (Waters, USA)	UPLC (Ultra Performance Liquid Chromatography)
LC Column	ACQUITY BEH c18 (1.8 µm 2.1 x 50 mm; Waters, USA)	UPLC Column BEH (Ethylene Bridge Hybrid)
Mass Spectrometer	Xevo G2-S QToF (Waters, USA)	Quadrupole time-of-flight mass spectrometry

Meanwhile, a H<sub>2</sub>O<sub>2</sub> dose of 12 ml/l reduced the chemical efficiency to 89.5%. The reason might be either the interaction between •OH and H<sub>2</sub>O<sub>2</sub> or the combining of two •OH radicals to generate H<sub>2</sub>O<sub>2</sub>. Both interactions reduced the likelihood of MB being attacked by •OH, decreasing MB oxidation efficiency (Catalkaya & Kargi, 2007). However, without adding H<sub>2</sub>O<sub>2</sub>, the nanocomposite performed well in decolorizing 10 mg/l methylene blue. It reveals that the high addition of H<sub>2</sub>O<sub>2</sub> does not mean that the effectiveness of the treatment will be high but that there will be an optimal amount of H<sub>2</sub>O<sub>2</sub>.

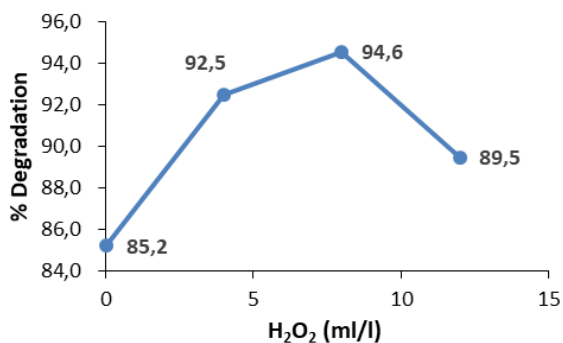


Figure 2. Effect of Variation of H<sub>2</sub>O<sub>2</sub> Dosages at MB Initial Concentration 10 mg/l

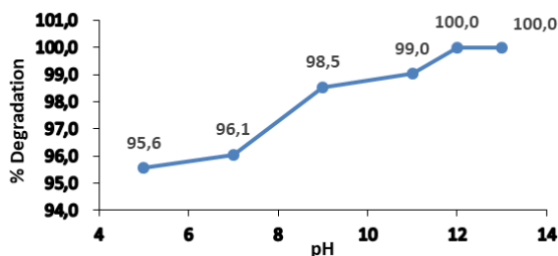


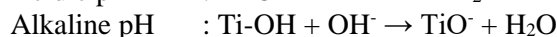
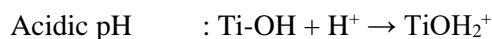
Figure 3. Effect of pH Solution, MB Initial Concentration 10 mg/l

### Effect of pH Solution

pH solution can affect the photocatalytic degradation process in producing hydroxyl radicals. Hydroxyl radicals have high reactivity in the oxidation process. Thus, the more hydroxyl radicals produced, the more methylene blue dye will be degraded. Determination of the optimum pH was done by varying the pH of the methylene blue solution from the acidic to alkaline pH range, namely pH 5, 7, 9, 11, 12, and 13. Figure 5 shows that the highest efficiency value at pH 12 is 100%. This result proved that the more the pH value rises, the more the degradation rate increases; this is

because, in acidic conditions, the surface of TiO<sub>2</sub> will be positively charged; otherwise, in alkaline conditions, it will be negatively charged.

The photocatalyst surface is positively charged in acidic solutions and negatively charged in alkaline solutions. So, it was not surprising to see an increase in the adsorption of dye molecules (positively charged) on the surface of the photocatalyst in an alkaline solution and, therefore, increases the degradation efficiency (Sohrabnezhad, 2011). In other words, at low pH, the diffusion of cationic dyes on the surface of the photocatalysts is reduced because the surface of the photocatalysts is more flexible, and the repulsive forces are due to the decreased adsorption. Therefore, the effectiveness of MB removal will be decreased at acid pH.



Following treatment with the TiO<sub>2</sub>/zeolite nanocomposite, the MB 10 mg/l showed almost no UV-visible absorption at pH 12. This result showed that the MB was almost completely removed from the solution; however, the removal mechanisms may have involved TiO<sub>2</sub>/Zeolite oxidative degradation or adsorption.

### Effect of Initial Concentration of Methylene Blue

The degradation efficiency of the dye decreased with the increase in the initial dye concentration to more than 10 mg/l and the optimum at 18 mg/l. Some studies reported that modification of TiO<sub>2</sub> using zeolite increases the specific surface area higher than modification using metal ions (Kusumawardani et al., 2023; Susanti et al., 2021). This condition will impact the photodegradation process, including the parameter of the initial concentration of dyes. The results are shown in Figure 4. The decrease in % degradation with increasing color saturation can be due to two reasons. More dye molecules were added to the photocatalyst's surface as its color increases, more decreased in the number of active sites. Consequently, fewer hydroxyl radicals will be produced as there is more room on the product's surface. Furthermore, a decrease in the number of photons that reach the catalyst's surface may result from intensifying the color. The fewer photons that

excite the photocatalyst particles, the more light the dye molecules absorb. As a result, photodegradation's efficiency is reduced. This result reveals that nanocomposite TiO<sub>2</sub>/zeolite coal fly ash can degrade higher concentration methylene blue than TiO<sub>2</sub> modified by metal ion due to the higher specific surface area of 189.483 m<sup>2</sup>/g (Kusumawardani et al., 2022; Kusumawardani & Syahputri, 2019; Pava-Gómez et al., 2018; Zhang et al., 2019).

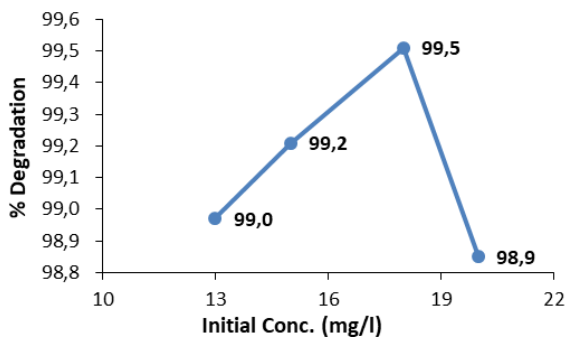


Figure 4. Effect of MB Initial Concentration

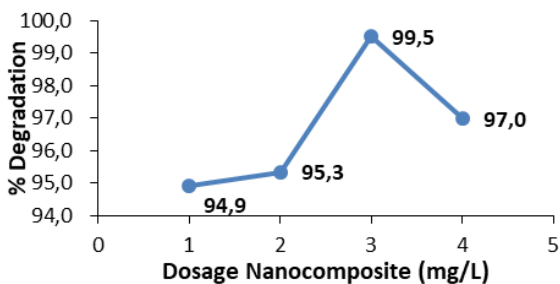


Figure 5. Effect of Nanocomposite Dosages, MB Initial Concentration 18.00 mg/l

### Effect of Nanocomposite Dosages

Photocatalytic degradation of MB was studied at catalyst dosages of 1, 2, 3 and 4 g/l under optimum concentration of 18 ppm MB, H<sub>2</sub>O<sub>2</sub> 12 ml/l and pH 12. Figure 5 shows the effect of the nanocomposite on the methylene blue photocatalytic decolorization process. The activity results increased from 94.9% to 99.5% when the nanocomposite dose was increased from 1 g/L to 3 g/L. This result demonstrated that more methylene blue dye was degraded when the dosage of TiO<sub>2</sub>/zeolite nanocomposite is increased due to the number of active sites available for dye degradation under optimal radiation penetration through suspension. However, the decolorization activity started declining at 4 g/l of the nanocomposite.

Another possibility for the decrease in %D is that the nanocomposite dosage was already saturated, breaking down the methylene blue dye when added. In this case, an excessive dose of added nanocomposite would lead to attenuation, decreasing the degradation percentage (Rauf et al., 2010). Therefore, an optimum catalyst dose was 3 g/l.

### Effect of Irradiation Period

The methylene blue photocatalytic decolorization process can be affected by the duration of exposure to visible light. This study used a halogen lamp as a light source for 75 minutes at intervals of absorption measurement MB every 15 minutes. The result is shown in Figure 6. The highest percent degradation was obtained at 75 minutes, which was 100%. There was almost no UV-vis absorption for the MB 18 mg/l. This result showed that exposure time has a significant effect and was an important aspect of the overall photocatalytic process. It was found that the absorption value of the color decreases with the irradiation time, thus indicating the change in the solution of the color. A reduction in the dye solution's absorption value may involve a process of photodegradation efficiency.

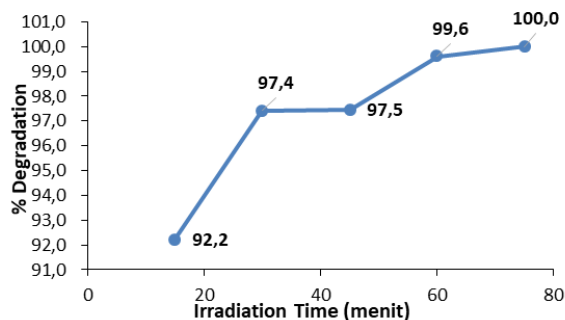


Figure 6. Effect of Irradiation Time, MB Initial Concentration 18.00 mg/l.

This study reveals that the nanocomposite TiO<sub>2</sub>/zeolite coal fly ash has a short period to degrade 100% methylene blue. However, this result should be ensured by advanced analysis using LCMS/MS to prove the degradation of methylene blue fragmentation into simpler molecules.

### Kinetic Study Degradation of MB

This work utilized a pseudo-first-order reaction approach to analyze the kinetics of the

methylene blue photocatalytic decolorization reaction. When one substance is present in very high concentrations, such as in the degradation reaction between an organic substance and a catalyst, the pseudo-first-order reaction kinetics approach is frequently employed (Zuhaela et al., 2021). A pseudo-first-order reaction linear curve made by plotting  $-\ln [C_t/C_0]$  against time (t). On the other hand, the chemical kinetics studies also calculated for zero and pseudo-second-order reactions in this study.

The rate constants indicated that the model fitted well with the experimental data. The correlation coefficients ( $R^2$ ) was as high as 0.9. Figure 7b shows the greatest linear regression value (0.9111). The reaction rate constant is the comparative value of the reaction rate, calculated using the slope value of the  $-\ln [C_t/C_0]$  curve plot against time (t), which is 0.0785 minutes<sup>-1</sup>. The greater the reaction rate constant value, the faster

the reaction will run. A good linear relationship with  $R^2$  indicates that the photocatalytic degradation process of dyes conforms to pseudo-first-order reaction kinetics (Zuhaela et al., 2021).

#### Determination of the Degradation Products by LCMS/MS Study

The MB solution was treated by TiO<sub>2</sub>/zeolite nanocomposite system, and the color of the MB solution gradually decreased as the reaction progressed, indicating that the MB concentration decreased. Figure 8 shows the decolorization of methylene blue after photodegradation at optimum process parameters. This condition can be attributed to the destruction of molecular assemblies or the destruction of chromophores (Su et al., 2019). Apart from the UV-visible studies, the degradation of organic dye MB was confirmed by LCMS/MS studies.

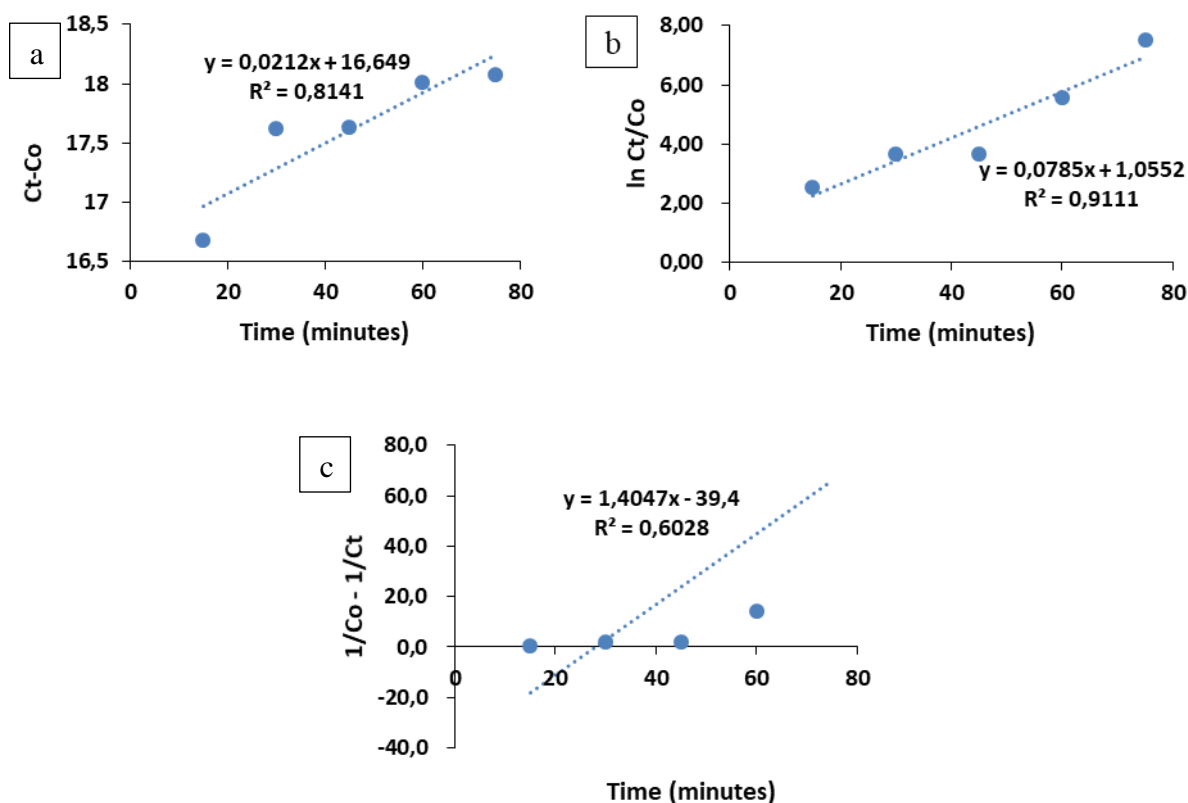


Figure 7. Reaction Kinetics, a)  $C_t - C_0$  Graph vs. Time in Zero-order Reaction; b)  $\ln C_t/C_0$  Graph vs. Time in The First-order Reaction; c)  $\ln 1/C_0 - 1/C_t$  Graph vs. Time in The Second-order Reaction.

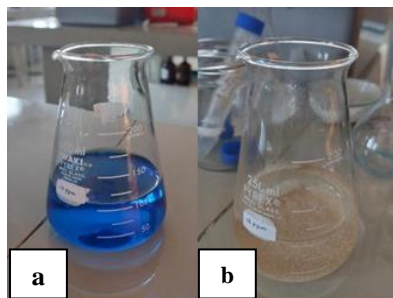


Figure 8. a) MB 18 mg/l before Photodegradation Process, b) MB after Photodegradation Process, %D = 100% (Under H<sub>2</sub>O<sub>2</sub> 8 ml/l; pH=12; Nanocomposite Dose 3g/l; and Irradiation Time = 75 minutes)

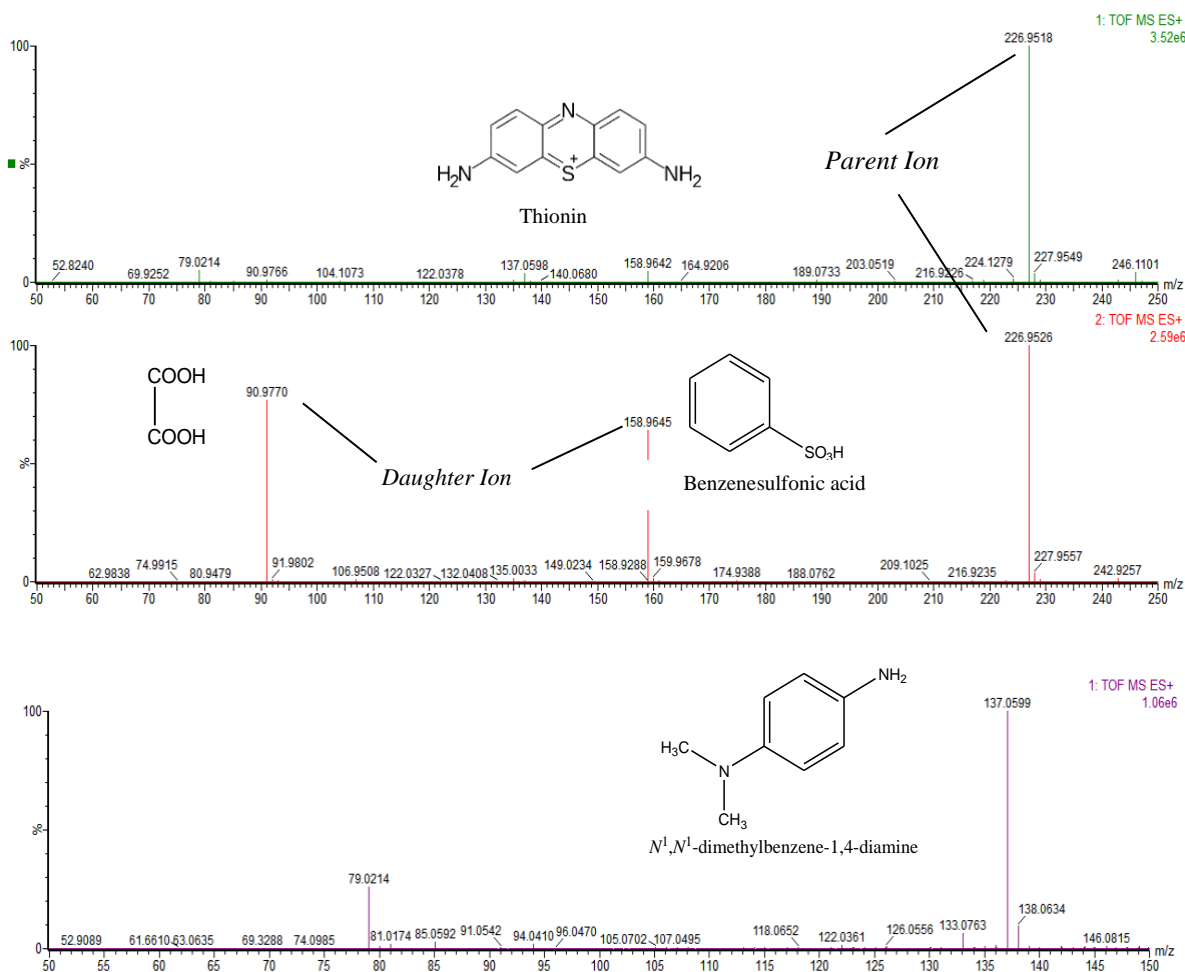


Figure 9. Mass spectra of the major detected degradation intermediates identified by LCMS/MS QToF

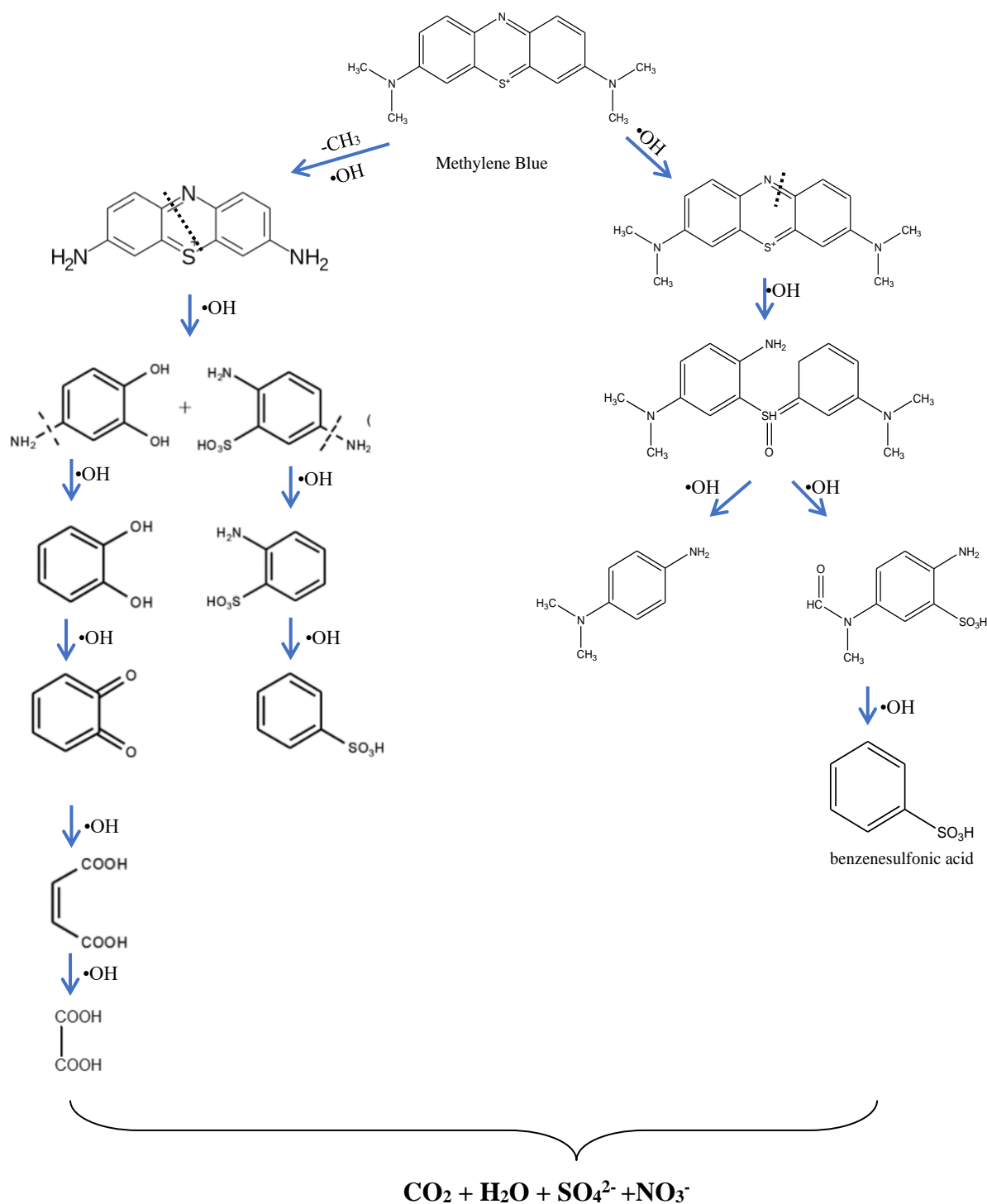


Figure 10. Proposed Degradation Pathway of MB by TiO<sub>2</sub>/Zeolite Nanocomposite

Thionin, produced due to the demethylation process, was identified in the mass spectrum of the metabolite that eluted at 227 m/z (Kishor et al., 2021). Methylene blue was reduced to thionin at

alkaline pH, and demethylation was observed (Sohrabnezhad et al., 2010). Figure 10 illustrates the analysis and description of the MB degradation mechanism based on the intermediate and final

products found. The MB molecule simultaneously broke down in two different ways. The majority of Cl<sup>-</sup> may ionized and existed in the detached state when MB dissolves. N-CH<sub>3</sub>, whose bond energy is 70.8 kcal/mol, has the lowest value (Wang et al., 2014). The -CH<sub>3</sub> was first broken and oxidized to produce HCHO or HCOOH. After the remaining structure's oxidation, C-S and C-N were broken; these organic intermediates in solution underwent additional oxidation until they were ultimately converted into CO<sub>2</sub>, H<sub>2</sub>O, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>.

## CONCLUSIONS

In conclusion, the TiO<sub>2</sub>/zeolite coal fly ash nanocomposite at dose of 3 g/l, pH 12, and dose of H<sub>2</sub>O<sub>2</sub> 8 ml/l has proven to reach 100% degradation for 18 mg/l methylene blue under visible irradiation in a short period of 75-minutes. The highest R<sup>2</sup> = 0.9111 and reaction rate constant 0.0785 minutes<sup>-1</sup> were achieved during the decolorization of MB using the photocatalysis degradation technique. In this case, the pseudo-first-order reaction is more appropriate than the zero and pseudo-second-order reactions. Compounds involved in photocatalytic decolorization identified by LCMS/MS QToF. The MB molecule simultaneously broke down in two different ways. The results demonstrated how methylene blue broke down into more basic substances. The more basic chemical intermediates in the solution underwent additional oxidation until they eventually changed into CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>.

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