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Research Article

TiO_2/Zeolite Coal Fly Ash Nanocomposite for Photodegradation of Naphthol Blue Black Dye: Optimization and Mechanism under Visible Light

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Abstract

Naphthol Blue Black (NBB) is a water-insoluble synthetic azo dye with a molecular weight of 616.49 g/mol that requires alkaline treatment for solubility and poses environmental risks by reducing water quality, increasing BOD and COD, and disrupting aquatic ecosystems. The TiO_2/Zeolite Fly Ash nanocomposite represents a promising material for the photocatalytic degradation of NBB. Analysis of the TiO_2/zeolite fly ash nanocomposites revealed the presence of Ti-O-Si and Ti-O-Al functional groups, along with a suitable band gap energy value of 2.85 eV for visible light consumption. The average particle size is 62-75 nm, with a relatively high crystallinity of 95.64%. The insertion of TiO_2 into the surface of the zeolite changes the size of the catalyst from 62-75 nm to 10 nm and 98.2% crystallinity. An emphasis was placed on the key parameters governing the degradation process. The test results showed that the degree of degradation increases at lower pH, while changes in catalyst dosage and initial dye concentrations do not significantly affect the degradation of NBB. The addition of H_2O_2 demonstrates the increasing degradation efficiency. The optimum operating process was carried out by adding 1.2 % (v/v) of H_2O_2, the pH 2, 0.1% (w/v) of catalyst, an initial concentration NBB of 12 mg/l, and irradiating under visible light for 75 minutes. It was a short period to produce the best conditions for degrading 12 mg/l naphthol blue-black, with a degradation efficiency of 99.68%. The rate of photodegradation kinetics had a reaction rate constant of 0.0312 min^{-1} and was followed a pseudo-first-order Langmuir-Hinshelwood. From the results, it was found that adsorption is an essential factor in the photodegradability of the dye. The linear transform of the Langmuir isotherm curve was further used to determine the characteristic parameters, which included the maximum absorbable dye quantity Q_{max}=11,8217 mgg^{-1}. LC-MS/MS analysis identified the compounds formed through the photocatalytic degradation of naphthol blue-black dye into lower-molecular-weight molecules, such as benzoic acid, maleic acid, and phenol, which can gradually break down naturally into carbon dioxide and water.

Keywords: Fly ash, naphtol blue black, photodegradation, TiO_2/Zeolite Nanocomposite, TiO_2/Zeolite

1. INTRODUCTION

Naphthol Blue Black (NBB) is one of the synthetic azo dyes with a molecular formula of $C_{22}H_{14}N_6Na_2O_9S_2$ and a molecular weight of 616.49 g mol^{-1} [1]. This black powder dye is stable at room temperature and incompatible with substantial reducing and oxidizing agents. Naphthol dyes' primary properties include polygenic, monogenic, and insoluble in water but in boiling concentrated pyridine. Since naphthol compounds are not soluble in water, NaOH must be added to transform them into naphtholate [2]. Synthetic dye pollution can drastically lower the quality of water, raise BOD and COD levels, interfere with photosynthesis, impede plant growth, and contaminate aquatic food chains [3].

Utilizing semiconductor photocatalytic capabilities is one way to combat water contamination caused by substances such as dyes and turbidity. The two categories of photocatalysts are heterogeneous and homogeneous photocatalysis. Oxidants such as ozone and H_2O_2 are used in homogeneous photocatalysis, whereas semiconductors exposed to light are used in heterogeneous photocatalysis. One relatively recent oxidation technique for wastewater treatment is heterogeneous photocatalysis [4]. Photocatalytic degradation is now garnering more attention. Common photocatalytic materials are oxide semiconductors. Due to its high photocatalytic effectiveness, TiO_2 has garnered significant interest in addressing environmental challenges such as water and air purification. Some modifications of TiO_2 with metal ions like Fe, Co, Mn, and Cr are often employed to increase optical and structural qualities [5–7]. Meanwhile, some experiments modifying TiO_2 with zeolite indicate improved characteristics. Zeolite has a significantly higher capacity for adsorption than other porous materials, such as bentonite and activated carbon [8,9]. Meanwhile, the modest TiO_2 surface area of 9.492 m^2/g renders it an inadequate photocatalytic material in terms of efficiency and adsorption capacity[10]. Natural zeolite modified by ZnO demonstrate the higher degradation efficiency of NBB than ZnO itself [11].

Kusumawardani et al. used the sol-gel procedure to successfully modify zeolite coal fly ash by including a TiO_2 semiconductor as an adsorption-photocatalysis material at 14 hours of aging time. The resulting nanocomposite exhibits optical and physical properties that make it suitable for the photodegradation of dyes and organic pollutants. The TiO_2/Zeolite nanocomposite has a band gap of 2.5 eV and can transfer its activity from UV to visible light. In addition, this nanocomposite has an average particle size of 9 nm, which can affect its chemical activity, as a smaller particle size leads to a larger surface area [12]. However, no further research has been conducted on the photodegradation ability of this material in the process of lowering the concentration of synthetic dyes, particularly those that are water insoluble.

This work will synthesize and characterize TiO_2/Zeolite Coal Fly Ash nanocomposite [12], then optimize the photodegradation process of naphthol blue black dye (NBB) by employing the TiO_2/Zeolite Coal Fly Ash nanocomposite. The effects of H_2O_2 addition, solution pH, nanocomposite dose, initial dye concentration, and irradiation period will all be varied during the investigation. UV-vis spectrophotometry will be used to measure the dye concentrations at the beginning and the end. Results are examined utilizing degradation kinetic parameters, such as the Langmuir-Hinshelwood equation. Additionally, the study will utilize LC-MS/MS to analyze and identify the end products of naphthol blue-black dye photodegradation.

2. RESEARCH METHODS

Instruments and Materials

Titanium tetra-isopropoxide (TTIP) is a TiO_2 precursor, and coal fly ash is from PT. PLTU PJB UP Paiton Malang as a Zeolite Precursor, Ethanol pro analysis from Merck, Naphthol Blue Black Dye from Himedia, Hydrogen Peroxide (H_2O_2) 30% from Merck, $NaOH_{(s)}$ from Merck, $HCl_{(l)}$ from Merck, and distilled water.

Mortar, furnace, oven, porcelain cup, funnel, analytical balance, spatula, magnetic stirrer, pH meter, halogen lamp (Philips, 1000 watts), aluminum foil, centrifuge (spin plus), filter paper, and glassware commonly used in laboratories. The instruments used were Fourier Transform Infra-Red (Shimadzu), UV-Vis DRS spectrophotometer (Analytic Jena), UV-Vis Spectrophotometer (Genesys 10 UV), Scanning Electron Microscopy (SEM-Phenom Pro-X), X-Ray Diffractometer (X'Pert MPD) and Liquid Chromatography-tandem Mass Spectrometry (Waters, USA).

Synthesis of Zeolite from Coal Fly Ash Using a Combination of Alkali Fusion and Hydrothermal Method

Coal fly ash, weighing 60 grams, was cleaned, ground in a mortar, and heated in a furnace at 800 °C for 2 hours to remove any organic impurities that might be present in the fly ash waste. Afterward, the fly ash was washed by adding 300 mL of 10% HCl. The mixture was then heated in an oven at 140 °C for 2 hours. The mixture was filtered and washed three times with distilled water. The filtrate was then dried in an oven at 120 °C for 6 hours[13]. The washed fly ash, weighing 60 grams, was mixed with 96 grams of NaOH (in a 1:1.6 weight-to-weight ratio) and crushed in a mortar until fine [14]. The resulting mixture was placed in a porcelain crucible and heated in a furnace at 550 °C for 2 hours. Afterward, the fly ash was crushed in a mortar and mixed with 600 mL of distilled water. The mixture was then heated in an oven at 110 °C for 8 hours. The mixture was lifted, filtered, washed with distilled water three times, and dried again in an oven at 105 °C for 4 hours [15].

Synthesis of TiO_2/Zeolite Coal Fly Ash Nanocomposite using the Sol-Gel Method

The first step involved mixing 150 mL of titanium tetra-isopropoxide, 300 mL of pro-analytical ethanol, and 750 mL of distilled water. The mixture was stirred vigorously for 4 hours until a gel was formed. The gel was dried in an oven at 105 °C for 12 hours to remove absorbed water and organic residues. The resulting xerogel was ground in a mortar and then dried in a furnace at 350 °C for 1 hour.

The synthesis continued by mixing 30 grams of TiO_2 and 15 grams of zeolite (obtained from coal fly ash) into 300 mL of distilled water. The mixing was performed using a magnetic stirrer at 1500 rpm. The resulting mixture was then allowed to stand for 14 hours for aging time. The solid material obtained was filtered, washed with distilled water three times, and dried in an oven at 100 °C for 1 hour, followed by calcination at 500 °C for 2 hours [16].

Characterization of Zeolite from Fly Ash and TiO_2/Zeolite Coal Fly Ash Nanocomposite

The zeolite and TiO_2/zeolite nanocomposite were characterized using Fourier Transform Infrared (FT 1000) to analyze chemical compounds based on their infrared absorption at wavelengths ranging from 400 to 4000 cm^{-1}. The results showed absorption bands related to specific functional groups and chemical bonds. The TiO_2/zeolite nanocomposite was characterized using DRS (Diffuse Reflectance Spectroscopy) to determine the light absorption and band gap energy. The samples were prepared, and their reflectance was measured over the 200-800 nm wavelength range. The band gap energy of the sample was calculated using the Kubelka-Munk equation[12]. The crystal phase, crystallinity, and crystal size are determined by X-ray Diffraction (XRD). Fourier Transform Infrared (FTIR) spectroscopy was used to analyze bonds and functional groups while Scanning Electron Microscopy (SEM) was used to identify the nanocomposite material's morphology.

Effect of H_2O_2 Addition

Optimization was carried out by introducing a 100 mL solution of 10 mg/L NBB into a reactor and adding 0.4, 0.8, 1.2, and 1.6% (v/v) of H_2O_2 [17]. Subsequently, 0.3 grams of the TiO_2/zeolite nanocomposite was added. The mixed solution was stirred and illuminated with a 1000 W halogen lamp for 60 minutes. Afterward, the mixed solution was centrifuged to separate the TiO_2/zeolite powder from the tested solution. The intensity of the color in the photodegraded solution was measured by its absorbance using a UV-Vis spectrophotometer at a wavelength of 614 nm.

Optimization Operating Process and Kinetic Study for NBB Photodegradation

Photocatalytic degradation was obtained by adding nanocomposites containing 10 mg/l NBB to the sample solution. Halogen lamps are utilized as lighting sources. The reaction vessel is magnetically stirred. To examine the impacts of the technique, a range of circumstances were used, including varied pH levels (2, 3, 4, 5, and 6), catalyst dosages (0.5, 1, 2, 3, 4, and 5 g/1), initial NBB concentrations (10, 12, 14, 16, 18, and 20 mg/L) and exposure times of roughly 90 minutes with 15-minute intervals. A Shimadzu UV-Vis Spectrophotometer was used to quantify the photocatalytic breakdown of NBB. **Figure 1** shows a model of a photocatalytic degradation reactor.

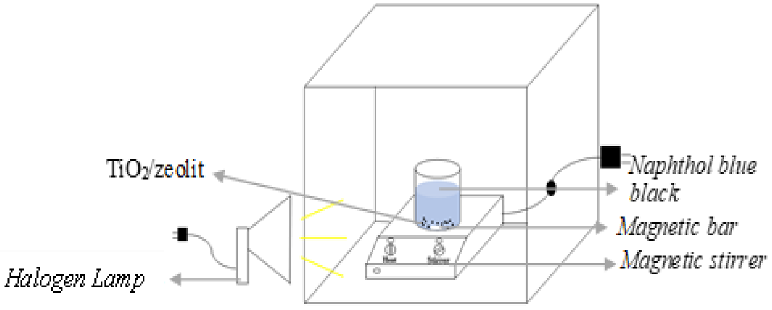

Figure 1. Reactor Model of the Photocatalytic Degradation Process

Equation (1), the percentage of photocatalytic activity was calculated using the percentage of degradation (% D), the sample's initial concentration (mg/l) prior to halogen irradiation, and the final concentration (mg/L) after halogen irradiation. The following concentration values were entered into the efficiency formula using NBB. By incorporating nanocomposites with a concentration of 10 mg/l NBB into the sample solution, photocatalytic degradation was achieved. Halogen lamps are used as 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 of 0,1; 0,2; 0,3; and 0,4 % (w/v), and exposure times of roughly 75 minutes with 15-minute intervals.

Eq. (1) calculates the degradation percentage (% D), which is the difference between the sample's initial concentration (mg/L) prior to halogen irradiation, and its final concentration (mg/L) following halogen irradiation, thereby determining the percentage of photocatalytic activity. The following concentration values were entered into the efficiency formula using NBB:

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

The determination of chemical reaction kinetics and the degradation rate constant is carried out by degrading naphthol blue-black solution under optimal conditions in a reactor with time variations of 15, 30, 45, 60, and 75 minutes. The absorbance is measured using a UV-Vis spectrophotometer. Subsequently, the reaction order is determined using the Langmuir-Hinshelwood kinetic model, along with the degradation rate constant.

Determination of the Degraded Products by LCMS/MS Study

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

Table 1. Specification of UPLC-MS/MS QToF

Part	Spesification	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 Hybride*)
Mass Spectrometer	Xevo G2-S QToF (Waters, USA)	*Quadropole time-of-flight mass spectrometry*

3. RESULT AND DISCUSSIONS

Synthesis and Characterization TiO_2/Zeolite Coal Fly Ash

Zeolite from coal fly ash waste is prepared by treating it with a hydrochloric acid solution to remove metal oxides and other impurities since these metals can dissolve in acid [13]. The fly ash obtained from this treatment is then fused with NaOH, which acts as an activator during the fusion process. The fly ash's silica and alumina content interact with NaOH to create water-soluble silicate and aluminate ions. A more significant amount of NaOH is used than fly ash because the higher the NaOH content in the mixture during the fusion process, the more Na^+ ions will react, forming sodium silicate and aluminates. These Na^+ ions create a porous zeolite structure. Subsequently, a hydrothermal process is carried out by heating at 110 °C for 8 hours to refine and homogenize the formed zeolite crystals. The crystalline structure of zeolite is achieved by transitioning from the liquid phase to the solid phase. Zeolite is obtained as a brownish and fine particle.

TiO_2 was synthesized from titanium (IV) isopropoxide as a precursor using the sol-gel method, followed by the addition of zeolite synthesized from coal fly ash waste. The TiO_2 crystals obtained are then combined with synthetic zeolite and water in a 2:1:20 ratio (w/w/v). A more substantial and more rigid gel network is formed during this aging process. Additionally, the aging process aims to the condensation and polymerization processes to facilitate the formation of stronger Ti-O-Ti bonds [18]. The calcination step is intended to create new bonds, specifically Ti-O-Ti bonds with zeolite, as during high-temperature heating (calcination), the Ti-O-Ti bonds contract and attach to the surface of the zeolite, particularly the silica part [19]. **Figure 2** shows the result of each step of synthesizing TiO_2/zeolite Nanocomposite from coal fly ash. FTIR spectroscopy was used to investigate the substance's functional groups and bonds. **Figure 3** shows the characteristic absorption of functional groups in the synthesized zeolite and TiO_2/zeolite nanocomposite.

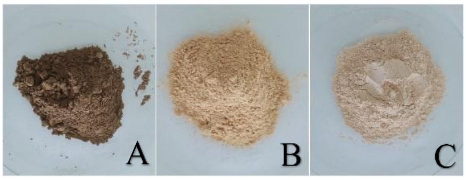

Figure 2. (A) Fly Ash, (B) Zeolite, (C) TiO_2/Zeolite Nanocomposite

Sharp absorption peaks are also observed at the wavenumber of 945.58 cm^{-1}, which is attributed to the non-symmetric stretching of Si-O-Si and Al-O-Al groups in the tetrahedral SiO_4 and AlO_4 structures that form the basic framework of zeolite [19]. The absorption at the wavenumber of 1647.27 cm^{-1} indicates the presence of OH bonds in water molecules adsorbed by zeolite NaX [20]. The incorporation of TiO_2 on the zeolite surface, as seen in Figure 3b, results in an absorption peak at the wavenumber of 658 cm^{-1}, characteristic of Ti-O and Ti-O-Ti bonds associated with TiO_2. A sharp absorption peak is observed at the wavenumber of 968.40 cm^{-1}, which is caused by incorporating Ti into the zeolite structure. In this case, the wavenumber of 968.40 cm^{-1} represents the absorption of Ti-O-Si and Ti-O-Al bonds, forming the TiO_2/zeolite nanocomposite compound [21]. Additionally, there is an absorption peak at the wavenumber of 1637.29 cm^{-1}, which results from Ti-OH bonds arising from the interaction of Ti metal with water [22].

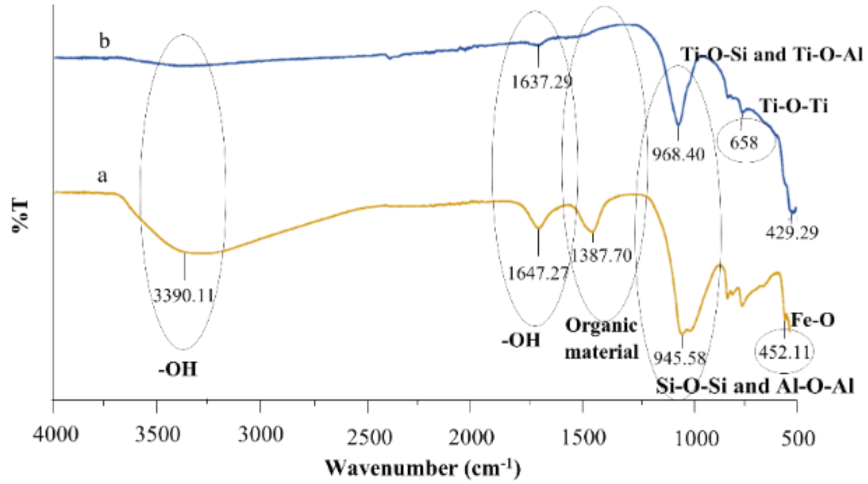

Figure 3. FTIR Spectrum (a) Zeolite Synthesized from Coal Fly Ash Waste; (b) TiO_2/Zeolite Nanocomposite

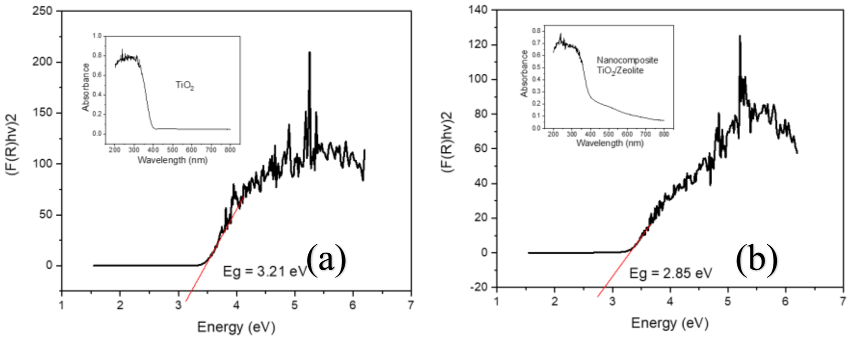

Figure 4. Tauc Plot and Absorbance Spectrum of (a) TiO_2 (b) TiO_2/Zeolite Nanocomposite.

Characterization using UV-Vis DRS was performed to gather information about the light absorption characteristics in the UV-visible region and determine the synthesized materials' band gap energy. The Tauc plots for TiO_2 and the TiO_2/Zeolite nanocomposite can be seen in **Figure 4**. The analysis found that the band gap energy of pure TiO_2 was 3.22 eV, which is characteristic of anatase-phase TiO_2. However, this value indicates one of the limitations of TiO_2 as a semiconductor: due to its wide band gap, it can only operate under UV light. This restricts its applications in photocatalysis under visible light conditions. In contrast, the TiO_2/Zeolite nanocomposite synthesized from fly ash demonstrated a reduced band gap energy of 2.85 eV. This reduction indicates successful material modification, shifting TiO_2's operating range from the UV region to the visible light region. This shift enhances the nanocomposite's potential for broader applications, including photocatalysis under sunlight and other visible light sources.

Figure 5 shows the X-ray diffraction patterns of the zeolite, TiO_2 Degussa and the TiO_2/zeolite nanocomposite. According to JCPDS data No. 38-0237, the zeolite spectrum has a peak intensity of 6° at 2θ, indicating a zeolite-X. The average particle size of zeolite determined using the Debye-Scherer equation is 62-75 nm, with a relatively high crystallinity of 95.64%. This finding indicates that zeolite-X production was successful in the absence of hydroxy sodalite. Meanwhile, TiO_2 peaks are generated around 25 °C, which is a common feature of anatase crystals. The insertion of TiO_2 into the surface of the zeolite changes the size of the product from 62-75 nm to 10,3 nm and 98.2% crystallinity. **Figure 6** depicts the shape of TiO_2/zeolite as revealed by SEM. Figure 6a shows that the particle zeolite-X is spherical and porous. This study demonstrates the properties of zeolite-X as an adsorbent. Meanwhile, Figure 6b illustrates the successful formation of the TiO_2/zeolite composite. The research confirms that TiO_2 is dispersed on the surface of the zeolite and covers its pores, thereby validating the effective synthesis of the TiO_2/zeolite composite.

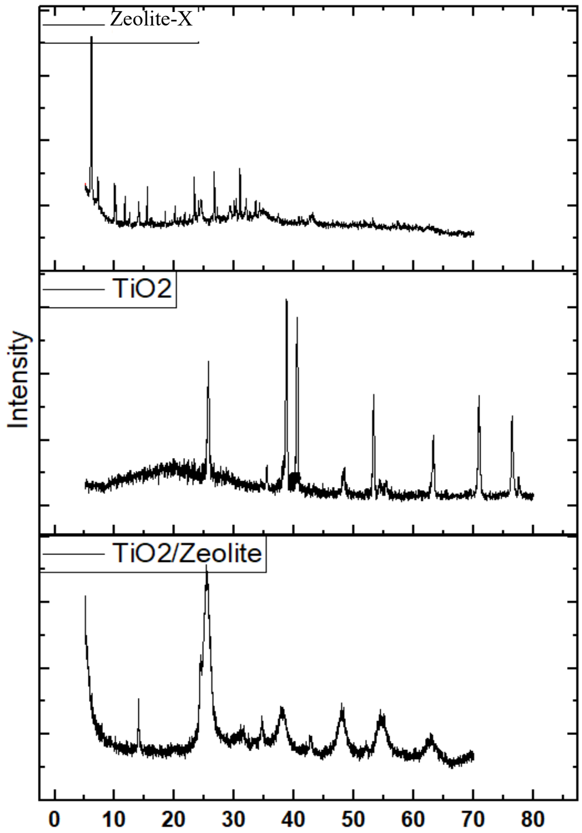

Figure 5. X-ray Diffraction Patterns of zeolite, TiO_2, and the Nanocomposite TiO_2/Zeolite

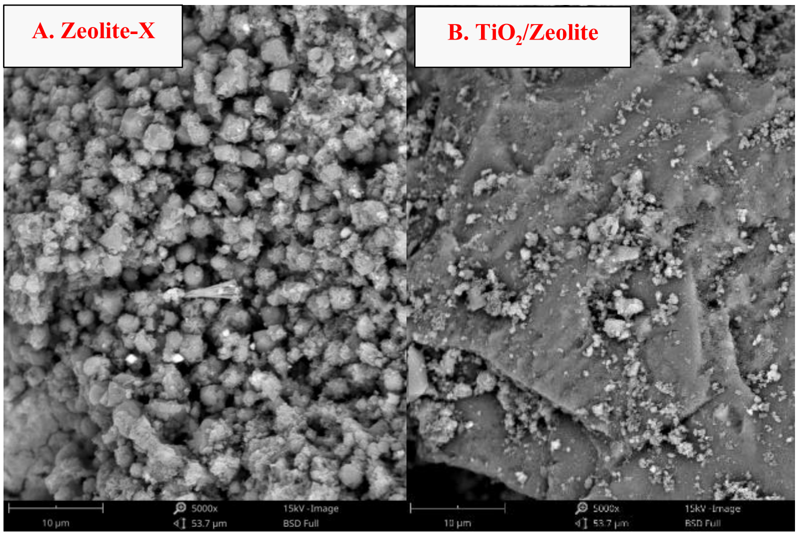

Figure 6. Transformation of Morphology Material: A. Zeolite-X to B. TiO_2/Zeolite Nanocomposite at a Magnification of 5000×

Effect of Adding H_2O_2 30%

The effect of H_2O_2 presence was also investigated by adding H_2O_2 dose (ml) to a 100 ml solution. The highest degradation percentage, 10.89%, is achieved when 1.2 % of H_2O_2 is added, as shown in **Figure 7**. Adding H_2O_2 can enhance the effectiveness of Naphthol Blue Black dye photodegradation catalyzed by TiO_2/zeolite. This is because the addition of H_2O_2 leads to the formation of more hydroxyl radicals, which play a crucial role in degrading Naphthol Blue Black into degradation compounds [23]. When 1.6% of H_2O_2 is added, the percentage of photodegradation decreases to 7.13%. This decrease is attributed to the excess H_2O_2 inhibiting the photodegradation rate. An excess of H_2O_2 leads to more hydroxyl radicals (•OH), which react with H_2O_2 to form less reactive per-hydroxyl radicals (HO_2•). Consequently, the •OH radicals decrease, affecting the degradation of the dye and causing a reduction in degradation [23].

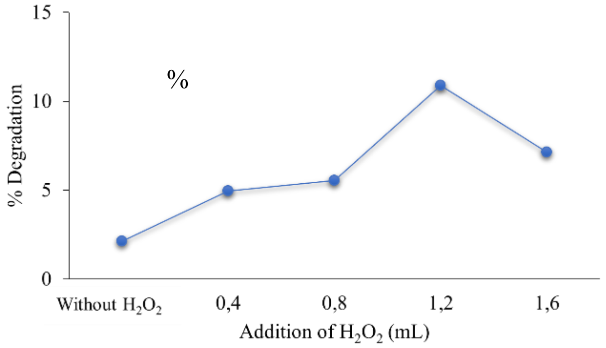

Figure 7. Percentage Degradation Curve of Naphthol Blue Black Solution with Different H_2O_2 Additions

Optimization Operating Process of NBB Photodegradation

Optimization of the operating process is carried out by adjusting several factors, such as pH, catalyst dose, initial dye concentration, and irradiation period. The pH value is one factor that influences the Naphthol Blue Black degradation process. This is because the pH level significantly affects the degradation rate of Naphthol Blue Black [24].

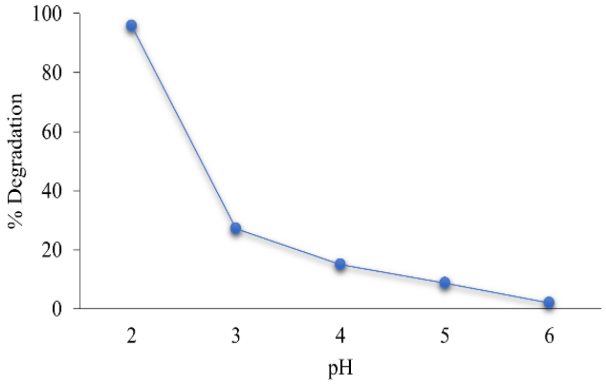

Figure 8. Percentage Degradation Curve of Naphthol Blue Black Solution at Various pH Variations with the Addition of 1.2 mL H_2O_2 30%

In **Figure 8**, it can be observed that pH values influence the photodegradation process of the Naphthol Blue Black solution. The optimum pH is 2. This is an extremely low pH, resulting in the highest degradation percentage of 95.77%. Naphthol dye solution dissolves completely at its original pH, causing its structure to be stable and more resistant to degradation. When an acid is added, the dye solution becomes neutral, reducing its solubility in water, which makes its structure less stable and more susceptible to degradation[2].

One factor that affects the efficiency of the photodegradation process is the amount of catalyst dosage used. **Figure 9** shows that the most effective catalyst dosage for the photodegradation process is 0.1 % (w/v) dye solution, resulting in a degradation percentage of 98.10%. The percentage of degradation increased from the prior 0.05-gram dose to 97.33%. This is because increasing the amount of catalyst used increases the amount of light radiation absorbed and the number of active sites available. However, this study found that extra TiO_2/zeolite nanocomposites reduced the degradation percentage of NBB. The decrease in degradation percentage is caused by the increasing turbidity of the solution due to the scattering of the TiO_2/zeolite nanocomposite in the naphthol blue-black solution, reducing the amount of light that reaches the active side of the nanocomposite. This results in fewer hydroxyl radicals (•OH) being generated, thereby reducing the photodegradation process of the dye[25].

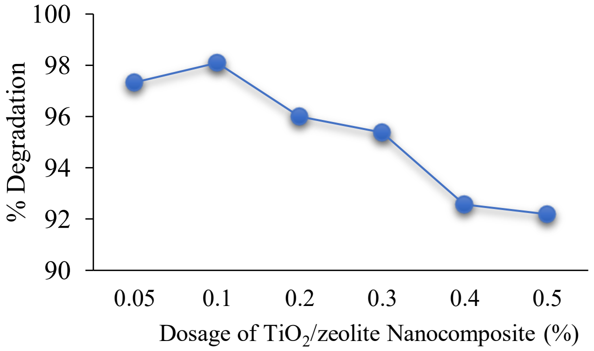

Figure 9. Percentage Degradation Curve of Naphthol Blue Black Solution at Various Catalyst Dosage Variations with pH = 2 and Addition of H_2O_2 = 1.2%

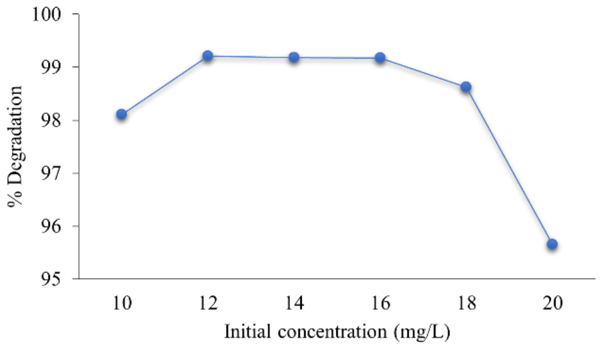

Figure 10. Degradation Curve of Naphthol Blue Black at pH 2, H_2O_2 (1.2%), and Catalyst (0.1%) Across Initial Concentrations

The concentration of NBB varied to determine the optimum concentration for degradation by the TiO_2/zeolite nanocomposite. The optimum concentration was 12 mg/L, achieving a degradation efficiency of 99.21%. Higher dye concentrations increase molecules, as the data in **Figure 10** indicates. The abundance of molecules causes competition among naphthol blue-black molecules to be adsorbed by the TiO_2/zeolite catalyst, leading to a reduction in the adsorption process [26].

The Naphthol Blue Black photodegradation time was optimized to determine the ideal period for dye degradation. **Figure 11** illustrates that as the photodegradation duration increases, the degradation percentage also increases. This is because extended exposure to radiation increases the energy reaching the catalyst, creating more hydroxyl radicals (•OH), which are more active in destroying the dye[27].

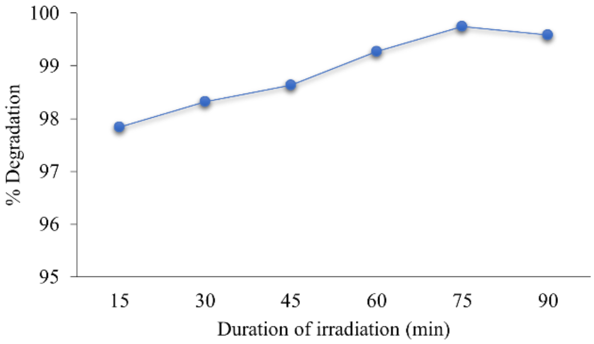

Figure 11. Degradation Curve of Naphthol Blue Black at 12 mg/L, pH 2, H_2O_2 (1.2 mL), Catalyst (0.1 g), and Varying Irradiation Times

The degradation percentage begins to increase at 15 minutes reaching a degradation percentage of 97.78% and then reaches its optimum at 75 minutes with a degradation percentage of 99.68%. This result illustrates show the relationship between irradiation time and the change in concentration of the degraded dye over time. This is consistent with the pseudo-first-order Langmuir-Hinshelwood kinetic model, where an increase in irradiation time leads to an increase in dye degradation. The decrease in degradation percentage at 90 minutes is due to the increasing formation of hydroxyl radicals (•OH), which react with H_2O_2 to form hydroxyl radicals (HO_2•). Therefore, the hydroxyl radicals (•OH) responsible for degrading the dye decrease[23].

Kinetics Study and Rate Constant

The determination of heterogeneous photocatalytic reaction rates generally uses the Langmuir-Hinshelwood equation following pseudo-first order and pseudo-second order reaction rate orders[28]. **Figure 12** provides clear evidence that the kinetics of the photodegradation of naphthol blue-black dye follow a pseudo-first-order reaction mechanism. This is substantiated by the strong linearity observed in the kinetic plot, as indicated by the high R^2 value of 0.9044, which signifies a robust fit to the first-order reaction model. The linear transform of the Langmuir isotherm curve was further used to determine the characteristic parameters which were: maximum absorbable dye quantity Q_{max}=11,8217 mgg^{-1}. From the results, it was found that adsorption is an essential factor in the photodegradability of the dye. The slope of the linear relationship, corresponding to the rate constant (k), is determined to be 0.0312 min^{-1}. This rate constant quantitatively describes the speed of the photodegradation process, signifying that the concentration of naphthol blue-black dye decreases steadily over time under the specified experimental conditions. The relatively high R^2 value underscores the reliability of the pseudo-first-order approximation, suggesting that the photodegradation reaction proceeds efficiently and consistently.

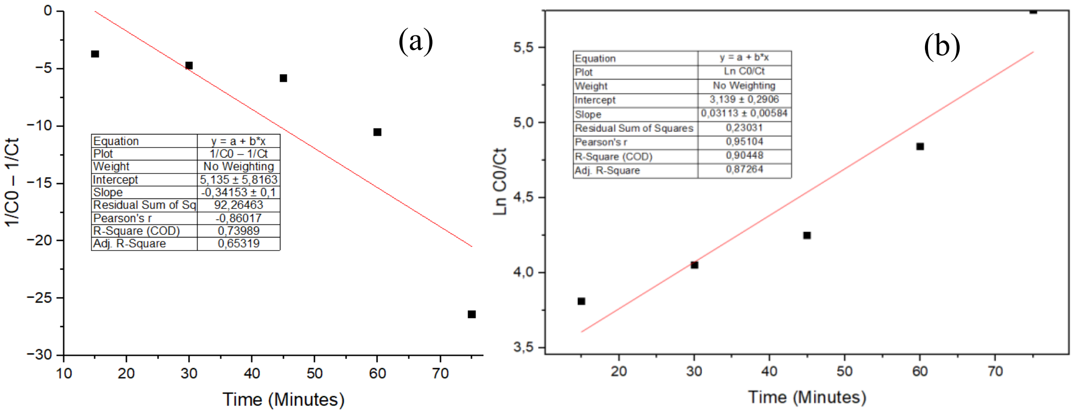

Figure 12. Reaction Kinetics for the Photodegradation of Naphthol Blue Black using TiO_2/Zeolite Nanocomposite, Illustrating (a) the Pseudo-first-order Model and (b) Pseudo-second-order Model

Furthermore, these findings highlight the potential application of this kinetic model in optimizing the photodegradation process for environmental or industrial purposes, particularly in the degradation of synthetic dyes. Changes in the solution's color can visually indicate the degradation process. In this case, the color of the naphthol blue-black dye solution transitions from blue to clear, signifying the occurrence of photodegradation. This visible change is a significant marker of the reaction's progress under specific conditions.

The final products resulting from the photodegradation of naphthol blue-black were analyzed using LC-MS/MS QToF. These products were identified based on the interpretation of mass spectrometry peak fragmentation and molecular ions, providing valuable insights into the molecular changes occurring during degradation. The analysis produced a UPLC chromatogram at the initial stage, as shown in **Figure 13**. This chromatographic data, processed through the MS/MS detector, revealed parent ions (main degradation compounds) at low energy (4 volts). At energy levels (25–60 volts), fragment ions were generated higher, representing new compounds formed due to the molecular breakdown of the parent ions. Additionally, **Figure 14** presents the mass spectra of the major degradation intermediates detected. These spectra offer crucial information about the degradation pathways and compounds formed during photodegradation

Table 2. Chromatogram Data and Spectra for the Photodegradation of Naphthol Blue Black

Retention time (min)	Parent ion (M^+) (m/z)	Fragment ion (M^+) (m/z)
1,11	157	83
6,86	330	251, 223, 195, 79
10,58	251	195, 149, 121
11,47	393	305, 277, 94, 80
11,78	375	347, 301, 257, 117

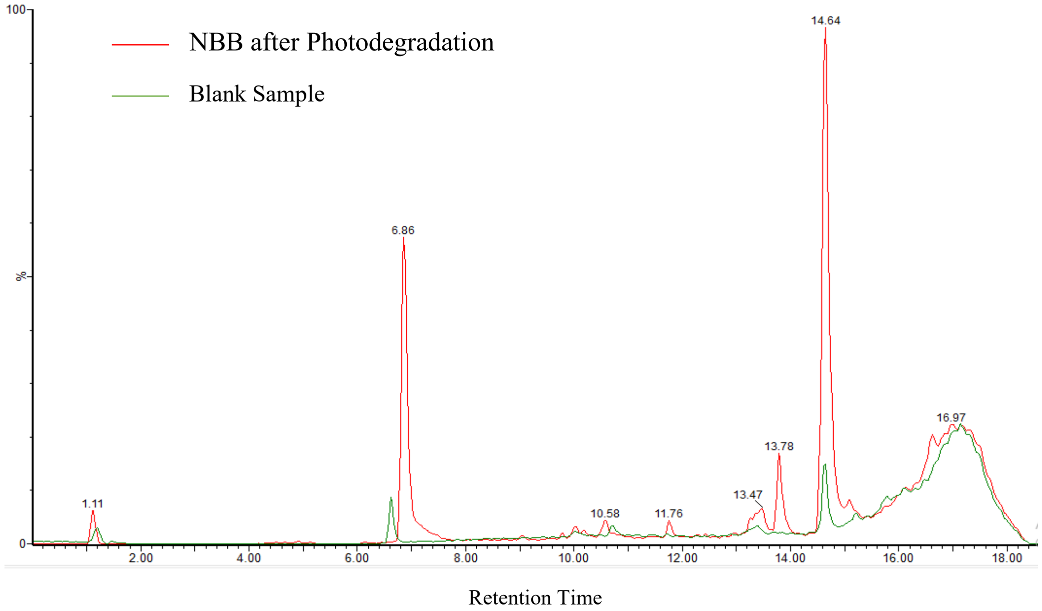

Figure 13. UPLC Chromatogram for the Photodegradation Products of Naphthol Blue Black under Optimal Conditions

Table 2 presents the molecular mass-to-charge ratios (m/z) determined by the LC-MS/MS instrument, along with the fragmentation patterns of the major photodegradation products of Naphthol Blue Black. Studies have shown that the primary degradation products of NBB elute within the first 12 minutes of chromatographic analysis. For instance, a previous study reported that significant peaks corresponding to degradation products appeared at retention times in the range 9 to 10 minutes. These peaks were associated with ions such as m/z 481.05, indicating cleavage at the azo linkage, and m/z 286.75, suggesting further breakdown products [29,30]. Focusing on this retention time window allows researchers to capture the most abundant and relevant degradation intermediates, facilitating a clearer understanding of the degradation pathway. The retention times at 14.64 and approximately 17 minutes showed peaks with the highest abundance. However, these peaks were also present in the chromatogram data of the blank sample, indicating that the compounds at these retention times are not derived from the pure photodegradation of Naphthol Blue Black. Therefore, it is crucial to distinguish between genuine degradation products and artifacts arising from the analytical process. Implementing rigorous system cleaning protocols and validating methods to ensure specificity can help mitigate such interferences, ensuring accurate interpretation of degradation pathways in LC-MS/MS analyses.

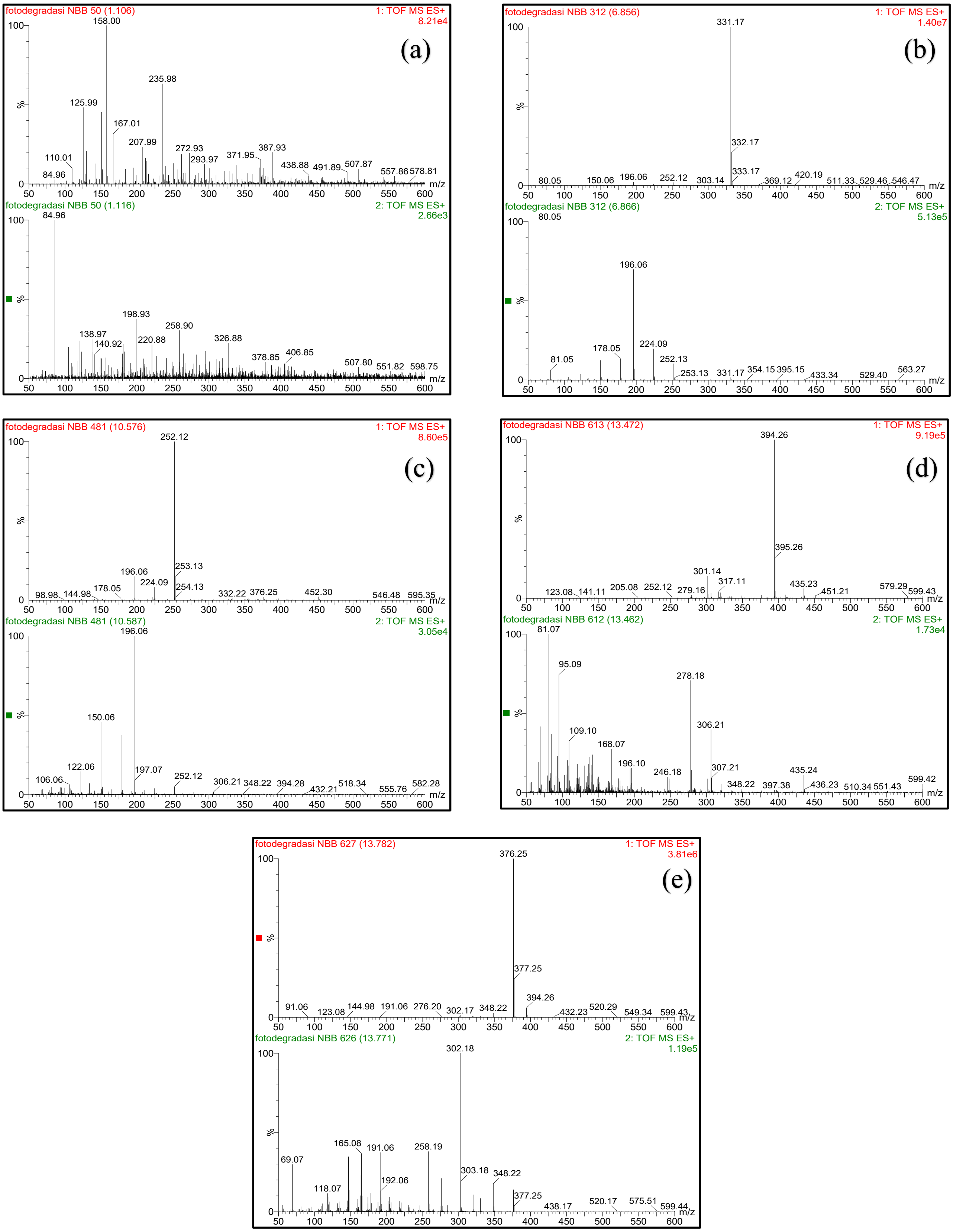

Figure 14. The Mass Spectra of the Major Detected Degradation Intermediates Identified by LCMS/MS QToF According to Retention Time: (a) 1,11 min; (b) 6,86 min; (c) 10,58 min; (d) 13,47 min; dan (e) 13,78 min.

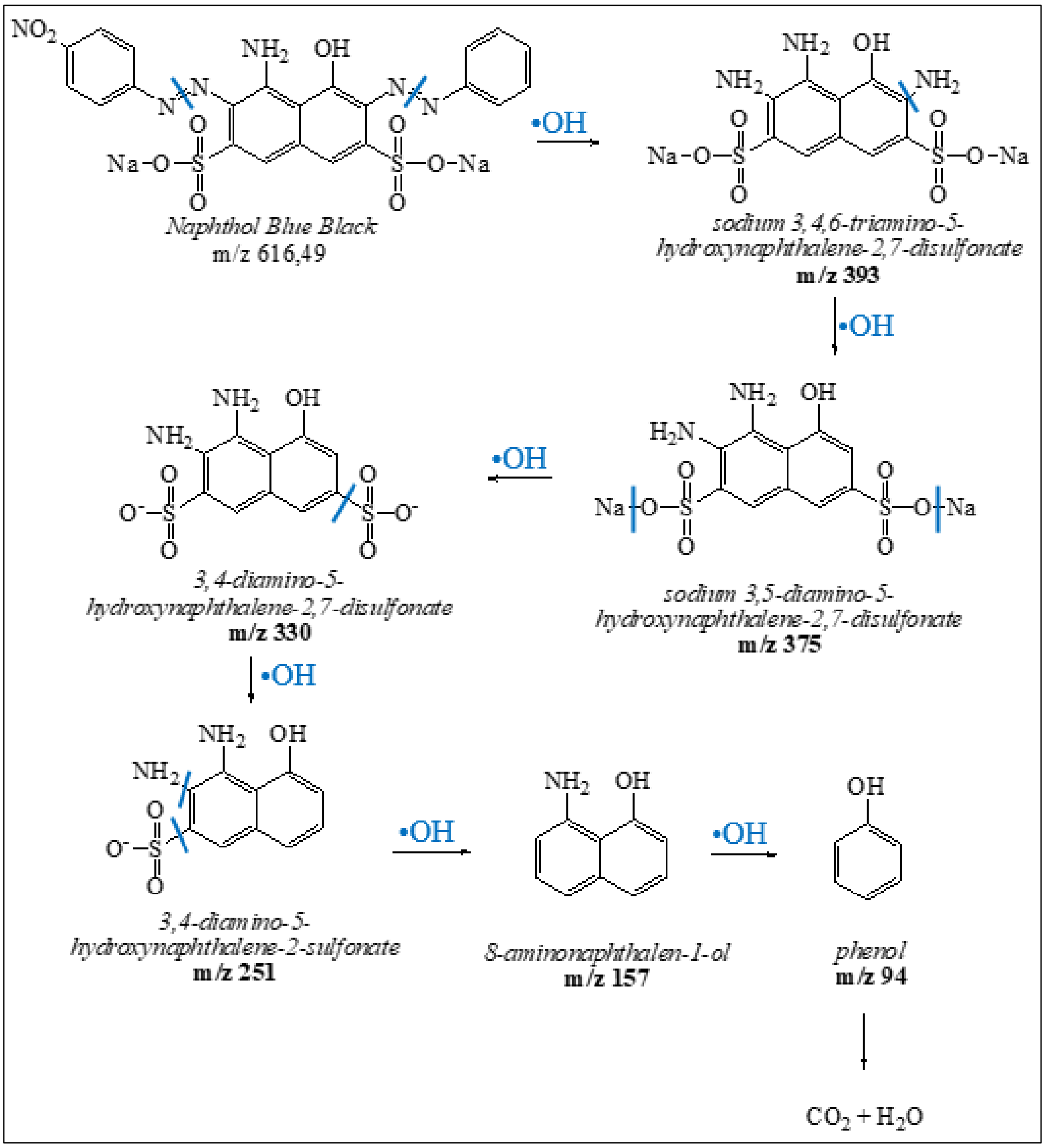

Figure 15. Possible Pathway of Naphthol Blue Black Photodegradation using TiO_2/zeolite under Visible Light

In this study, the LC-MS/MS apparatus operated in positive MS mode, specifically utilizing the $(M-H)^+$ ionization technique. This approach measures the analyte's molecular mass (M^+) minus one hydrogen atom (H ion), represented in the molecular formula detected by the mass spectrometer. The detailed information obtained from the measured m/z values, combined with the analysis of molecular structure fragmentation, facilitates the prediction of potential photodegradation pathways for Naphthol Blue Black under photocatalytic conditions. The mechanism underlying the photodegradation of this azo dye is hypothesized to involve two primary processes. The first step involves the reductive cleavage of the azo bond within the dye molecule, which significantly reduce its visible absorption spectrum and subsequent color fading. The second step involves an oxidative transformation of the resulting intermediate compounds into more straightforward degradation products. These products are ultimately mineralized into harmless end products, completing the photodegradation process [31].

4. CONCLUSION

Based on the findings, it can be concluded that the TiO_2/zeolite nanocomposite was effectively synthesized, with characterization data indicating the presence of Ti-O-Si and Ti-O-Al functional groups. The obtained band gap energy value was 2.85 eV, allowing it to operate under visible light. The average particle size of is 62-75 nm, with a relatively high crystallinity of 95.64%. The insertion of TiO_2 into the surface of the zeolite changes the size of the product from 62-75 nm to 10 nm and 98.2% crystallinity. The degree of degradation increases at lower pH, while changes in catalyst dosage and initial dye concentrations do not significantly influence the degradation of NBB. The optimum operating process was carried out by adding 1.2 % (v/v) of H_2O_2, the pH 2, 0.1% (w/v) of catalyst and an initial concentration NBB of 12 mg/l, and irradiating under visible light for 75 minutes. The photodegradation kinetics followed a pseudo-first-order model, specifically the Langmuir-Hinshelwood kinetic model, with a reaction rate constant of 0.0312 min^{-1}. This rate constant quantitatively describes the rate of photodegradation, which indicates that the concentration of naphthol blue-black dye declines continuously over time under the stated experimental conditions. The LC-MS analysis confirmed degradation after visible irradiation and detected photodegradation products, providing experimental evidence for the generation of hydroxyl radicals and the associated reduction in molecular weight of organic compounds, such as benzoic acid, maleic acid, and phenol, which can gradually break down naturally into carbon dioxide and water.

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