Preparation, Characterization, and Photocatalytic Activity of Ni-Cd/Al₂O₃ Composite Catalyst

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Abstract

This study was conducted to determine the effect of the radiation source and radiation time on the methylene blue (MB) solution by adding Ni-Cd/Al₂O₃ to the percent degradation of MB. To investigate similar purposes, the pH of the MB solution varied as well. The preparation, characterization, and photocatalytic activity of Ni-Cd/Al₂O₃ are three steps in this research. The Ni-Cd was prepared by mixing Ni(NO₃)₂·6H₂O and Cd(NO₃)₂·4H₂O. Various concentrations of Ni-Cd were mixed with Al₂O₃, then heated, stirred, dried, and calcined to form Ni-Cd/Al₂O₃ powder. The dried powder catalysts were characterized using Field emission scanning electron microscopy (FESEM), Energy-dispersive X-ray spectroscopy (EDS), Brunauer-emmett-teller (BET), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Diffused reflectance spectrometer spectra (DR-UV-Vis). Higher degradation was observed at pH 11, when MB was degraded by 68% and 76% using the 5Ni-2Cd/Al₂O₃ and 6Ni-1Cd/Al₂O₃ catalysts, respectively. The 6Ni-1Cd/Al₂O₃ sample has higher absorption, less surface area, and less band gap; therefore, it has higher performance against degraded MB in the solution. In summary, 6Ni-1Cd/Al₂O₃ is capable of degrading MB and can be utilized in MB dye waste.

Keywords: Photodegradation; Methylene blue; Radiation source; Radiation time; pH


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1. Introduction

Water pollution is an environmental issue related to hazardous wastes and toxics [1]. Several contaminants have a negative impact on the environment, and they are created by the emission of organic water pollutants, leading to a decrease in water quality. These pollutants are caused by various industries, such as primary metals, chemicals, food beverages, textiles, wood, pulp, and paper [2,3]. Organic dye, which is commonly produced from cloth and other industrial processes, is the main pollutant in wastewater [4,5]. There are several dye characteristics that are toxic, carcinogenic, teratogenic, harmful to human health, have high turbidity, and could decrease dissolved oxygen [6].

Methylene blue (MB) dyes, which are commonly used in the textile, printing, and pharmaceuticals industry, produce a high volume of wastewater in the environment and could be a
pollutant. The fact that water is essential for every living thing makes this condition a significant concern. Furthermore, the presence of MB in a water environment could result in eye damage to both humans and aquatic animals [7]. By eliminating and threatening MB dye pollution, there are numerous ways to solve this problem through sedimentation, oxidation, adsorption, filtration, and photocatalytic degradation [8–12]. Photocatalytic degradation is one of the most effective methods to degrade and remove pollutants because of its low cost and highly reactive technique [13–15]. Catalyst concentration, radiation source, time, and pH are all factors that have an impact on photocatalytic degradation [16,17].

Semiconductor materials, like CdS, NiO, TiO$_2$, ZnS and ZnO, have been utilized as photocatalysts [18]. The interfacial properties of the semiconductor bulk could be modified by semiconductor oxides supporting oxides with a precursor compound [19]. The doping of the semiconductor metal is generally used to alter and improve the interfacial surface of the substrate material, improving the photocatalytic degradation reaction.

Numerous studies have been conducted on the synthesis of Ni/Cd materials. Kafeshani et al. [20] synthesized Ni-Cd co-doped SrTiO$_3$ photocatalyst through a co-precipitate method. Doped SrTiO$_3$ with 5wt% Ni-Cd could thoroughly degrade MB after 60 min of irradiation. Khan et al. [21] investigated the synergetic effect of CdTiO$_3$ and NiCdTiO$_3$ on the efficiency of photocatalytic TiO$_2$ nanoparticles. The photocatalytic activity demonstrated that TiO$_2$, CdTiO$_3$, and NiCdTiO$_3$ degraded MB by about 76.59, 82, and 86%, respectively. The presence of Cd and Ni could increase in the photocatalytic activity. This behavior was also found by Kebede et al. [22] that increasing coupled Ni-Cd concentration in BiFeO$_3$ enhanced the photocatalytic activity. Munawar et al. [23] prepared NiO-CdO-ZnO for photocatalytic activity in MB under solar light and found degradation of about 98% in 60 and 90 min illumination.

Al$_2$O$_3$ has also been conducted as a support catalyst in various research due to its low cost [24]. Saffar et al. [25] synthesized novel ZnAl$_2$O$_4$/Al$_2$O$_3$ nanocomposite using sol-gel technique and found maximum MB removal around 70% under conditions: 10 mg/L MB, pH 8.5, 0.05 g of 70 wt% ZnAl$_2$O$_4$/Al$_2$O$_3$. Sodeifian and Behnood [26] synthesizing CuO/Al$_2$O$_3$ nanocomposite assist microwave irradiation in ethylene glycol. 90% of MB dye was successfully removed after 100 min using CuO/Al$_2$O$_3$ nanocomposite prepared with 900 W of microwave. Goudarzi et al. [27] synthesized CuO/ZnO/Al$_2$O$_3$ using Cu(NO$_3$)$_2$, Zn(NO$_3$)$_2$ and Al(NO$_3$)$_3$ with a molar ratio of 8:3:1. The photocatalytic activity shows about 70% of MB degraded after 50 min visible light irradiation. Sangor and Al-Ghouty [28] synthesized nano-g-Al$_2$O$_3$ from Al foil waste for efficient MB adsorption. Increasing the nano-g-Al$_2$O$_3$ concentration would increase the adsorption capacity of MB dye. Moreover, Al$_2$O$_3$ has an MB degradation efficiency of 65% and a rate constant of 8.4×10$^{-3}$ s$^{-1}$ [29].

Nallendran et al. [30] fabricated NiO-CdO and then added it to the methyl orange solution. Presenting NiO-CdO in the methyl orange solution would result in a photodegradation efficiency of around 89.44% when irradiated using visible light for 180 min. Balamurugan et al. [31] also synthesized and characterized CdO-Al$_2$O$_3$-NiO using the precipitation technique. The photodegradation efficiency of CdO-Al$_2$O$_3$-NiO in a metanil yellow solution is higher than Al$_2$O$_3$, CdO, and NiO. The research involved preparing, characterization, and investigating the photocatalytic activity of Ni-Cd/Al$_2$O$_3$ in MB, but it was not observed as stated above. Therefore, this study synthesizes different ratios of the coupled Ni and Cd metal, supported by Al$_2$O$_3$ base material. The Ni-Cd/Al$_2$O$_3$ samples were characterized with FESEM, EDS, BET, XRD, FTIR, and UV/Vis-DR spectroscopy. Various conditions, such as source light, radiation time, and pH, were also conducted for investigated MB degradation.

2. Materials and Methods

2.1 Materials

Commercial powder (NO$_3$)$_2$.6H$_2$O, Cd(NO$_3$)$_2$.4H$_2$O, and Al$_2$O$_3$ were purchased from Merck, while MB (C$_{16}$H$_{12}$CIN$_3$S) was acquired from Fluka Chemie AG CH-9470 Buchs as the starting materials for the study. Distilled water was utilized as a solvent in this experiment.

2.2 Synthesis of Photocatalyst Ni-Cd

The concentration of the Ni varied by 50 and 60 g/L (5 and 6 wt%). At the same time, Cd was varied by 10 and 20 g/L (1 and 2 wt%). 50 g/L of Ni 1 and 20 g/L of Cd were mixed and then designated 5Ni-2Cd. Moreover, 60 g/L of Ni and 10 g/L of Cd were mixed and then defined as 6Ni-1Cd. The mixed solution of 5Ni-2Cd and 6Ni-1Cd (50 mL) was renamed 5Ni-2Cd/Al$_2$O$_3$ and 6Ni-1Cd/Al$_2$O$_3$ after the addi-
tion of 25 g of Al₂O₃. Each mixture solution was heated at 85-90 °C and stirred continuously for 90 min. Subsequently, the catalyst was dried in the oven at 105 °C for 24 h. The photocatalyst was further calcined to activate and remove all the impurities. The activation process was carried out using a tube furnace at 600 °C with a continuous nitrogen flow rate of 20 cm³/min for 2 h. The various dried powder catalysts were used for further investigation. Figure 1 shows the schematic process synthesis of Ni-Cd/Al₂O₃.

2.3 Characterizations

The crystalline phases of Ni-Cd doped Al₂O₃ were examined using field emission scanning electron microscopy (FESEM) equipped with Energy Dispersive x-ray Spectroscopy (EDS) spectra by a Philips XL instrument using 25.0 kV. A Micromeritics Pulse ChemiSorb 2705 using 30% N₂: 70% O₂ was used to analyze Brunauer-Emmett-Teller (BET). The X-ray diffraction (XRD) analysis was carried out by a Siemens Diffractometer D5000 using Cu-Kα radiation at 30 mA and 40 kV. Fourier transform infrared spectroscopy (FTIR) analysis was carried out by a Perkin Elmer instrument using a KBr pelletizer with a scanning region of 400 - 4000 cm⁻¹. Moreover, a l90-diffused reflectance spectrometer was used to perform the UV-Vis spectra.

2.4 Photocatalytic Degradation of MB

2.4.1 Radiation source effect on MB photodegradation

The photodegradation of MB was carried out separately under UV light for 60 min, solar light at 10.00-11.00 AM, and in a dark room for 60 min. The 25 mL solution containing 20 mg/L MB + 50 mg of 5Ni-2Cd/Al₂O₃ was prepared to investigate the effect of the source of radiation photodegradation and then investigated with FTIR. Separately 20 mg/L MB + 50 mg of 6Ni-1Cd/Al₂O₃ was prepared and examined similarly. The percentage degradation of MB dyes was calculated using the following equation [32,33].

\[
\% \text{Degradation} = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\%
\] (1)

where, \( A_0 \) represents Initial absorption, and \( A_t \) represents absorption after \( t \) (min).

2.4.2 Radiation time effect on MB degradation rate

In order to investigate the effect of the radiation time on MB, a 50 mL solution was used with a concentration of 20 mg/L MB. The MB solution was added with 50 mg 5Ni-2Cd/Al₂O₃; another MB solution was added with 50 mg 6Ni-1Cd/Al₂O₃. Furthermore, the solutions were irradiated with UV light. Radiation was carried out for 180 min, and measurement of the degraded percentage of MB was performed.
at 0, 30, 60, 90, 120, 150, and 180 min using Equation (1).

2.4.3 pH Effect on the Degradation of MB

Various 20 mg/L MB of about 50 mL were prepared to determine the pH effect with a pH of 4, 6, 7, 9, 11, and 12. 50 mg of 5Ni-2Cd/Al₂O₃ and 6Ni-1Cd/Al₂O₃ were added to each MB solution. The mixed solution was added 0.1 M HCl until reached desired pH (4 and 6). Moreover, 0.1 M NaOH was added into mixed solution to reach desired pH (7, 9, 11 and 12). Afterward each mixed solution was irradiated with UV light for 90 min.

3. Results and Discussion

3.1 Catalyst Characterizations

3.1.1 FESEM Analysis

The FESEM analysis was carried out on samples of Al₂O₃, 5Ni-2Cd/Al₂O₃, and 6Ni-1Cd/Al₂O₃. The Al₂O₃ result showed non-spherical and non-uniform particles with sharp edges (see Figure 2(a)). Moreover, adding Ni and Cd showed that particles filled the porous space of the Al₂O₃ (see Figure 2(b)). In contrast, the decrease in Cd concentration was not able to cover the porous area of Al₂O₃ (Figure 2(c)). Furthermore, a more compact morphology of CdO-Al₂O₃-NiO was seen in Balamurugan et al.

![Figure 2. FESEM of (a) Al₂O₃, (b) 5Ni-2Cd/Al₂O₃ (c) 6Ni-1Cd/Al₂O₃.](image)

![Figure 3. EDS spectrum of (a) Al₂O₃, (b)5Ni-2Cd/Al₂O₃ and (c) 6Ni-1Cd/Al₂O₃.](image)

<table>
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<th>Element</th>
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<td></td>
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<tr>
<td>O</td>
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<tr>
<td>Al</td>
<td>52.50</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
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<td>Cd</td>
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<td>Total</td>
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Table 1. EDS elemental analysis of samples.

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al. [31] research due to the crushed process after calcination. Isobe et al. [34] found agglomeration between Al$_2$O$_3$ and Ni with several voids fabricated by plasma sintering. Ni particles were observed between Al$_2$O$_3$ based on SEM investigation. Sahu et al. [35] investigated metal recovery from Ni-Cd cake waste residue by the hydrometallurgical route and found Zn, Ni, and Cd agglomerated based on an SEM study. Gürgeç et al. [36] fabricated thin films using NiO-CdO and found perfect agglomeration between them. Therefore, a mixture of Ni-Cd and Al$_2$O$_3$ could form a fusion between them.

3.1.2 EDS analysis

The EDS Spectroscopy was conducted to measure the percentage of element composition in the Al$_2$O$_3$, 5Ni-2Cd/Al$_2$O$_3$, and 6Ni1Cd/Al$_2$O$_3$. Figure 3 shows the EDS spectrum, while Table 1 shows the elements values in Al$_2$O$_3$, 5Ni-2Cd/Al$_2$O$_3$, and 6Ni1Cd/Al$_2$O$_3$. The EDS result for Al$_2$O$_3$ reveals the presence of only Al and O elements. There are no impurities present in this sample. Four elements of the 5Ni-2Cd/Al$_2$O$_3$ and 6Ni1Cd/Al$_2$O$_3$ catalysts were observed in the fabricated samples. When mixed with Ni-Cd, the percentage of Al and O decreased compared to pure alumina. Furthermore, the Ni and Cd in the 5Ni-2Cd/Al$_2$O$_3$ and 6Ni1Cd/Al$_2$O$_3$ composites are confirmed to be perfectly placed in Al$_2$O$_3$. The EDS result suggests that Kebede et al. [22] behave similarly when co-doping Cd-Ni into BiFeO$_3$.

3.1.3 BET surface area analysis

The BET results for Ni-Cd/Al$_2$O$_3$ are displayed in Table 2. The surface of 5Ni-2Cd/Al$_2$O$_3$ is found to be larger than that of 6Ni1Cd/Al$_2$O$_3$. The surface area of the 6Ni1Cd/Al$_2$O$_3$ photocatalyst decreased because the Cd particles did not fill the pores and cover the surface of Al$_2$O$_3$. This phenomenon was confirmed by the surface morphology of the FESEM investigation (Figure 2). Kafesyani et al. [20] found that the more porosity leads to a decrease in sample surface area. Moreover, Liu et al. [37] have similar findings; higher total pore volume leads to a reduced surface area.

3.1.4 XRD analysis

Figure 4(a)–(c) show the diffraction patterns for Ni-Cd doped alumina (Al$_2$O$_3$) samples. Based on the investigation, the Al$_2$O$_3$ phase can be identified in the diffraction pattern in Figure 4(a). In Figure 4(b) and (c), the diffraction pattern shows a peak at $2\theta = 43.20^\circ$, indicating the semi-crystalline and cubic structure of the NiO phase. The peak of the NiO phase is comparable to those found in the study by Vishaka et al. [38]. Moreover, the entrapment of Ni-Cd in alumina led to the disappearance and degradation of several peaks ($2\theta = 27.1$ and $60.8^\circ$). According to earlier research, the CdO phase peaks were found at $2\theta$ of 38.24 and 55.23$^\circ$ [38]. The low Cd content of the samples was probably the cause of the absence of the CdO phase peaks in the Ni-Cd doped Al$_2$O$_3$.

3.1.5 FTIR analysis

FTIR was utilized to determine bond vibrations and demonstrate the presence of metal
oxide in the molecular structure. FTIR can identify the unknown materials and the functional groups present in the samples. The infrared spectra of fabricated Al₂O₃, 5Ni-2Cd/Al₂O₃, and 6Ni-1Cd/Al₂O₃ were recorded in 400-4000 cm⁻¹ in the IR.

Figure 5 provides information on the FTIR spectra of Al₂O₃, 5Ni-2Cd/Al₂O₃, and 6Ni-1Cd/Al₂O₃. The obtained peak at 3900 cm⁻¹ is related to the OH stretching mode [39]. The band received at 3783 cm⁻¹ is associated with the stretching vibration of the hydroxyl groups of alumina [40]. The vibration band around 1624 cm⁻¹ is because of the H₂O deformation vibration [41]. The band related to the symmetric bending vibration of the H₂O molecule is observed at 1597 cm⁻¹ [42]. Two 832 and 562 cm⁻¹ peaks correspond to the AlO stretching vibration bond [43]. The peak at 723 cm⁻¹ is related to the CdO stretching vibration [44]. The band at 678 cm⁻¹ is related to the NH bending mode [30]. The peak associated with the NiO bond is found at 528 cm⁻¹ [30]. The peak attributed to the CdO stretching vibration can be seen at 499 cm⁻¹ [41]. Thus, the NiO, CdO and AlO bonds in the Ni-Cd/Al₂O₃ composite catalyst confirmed their homogeneous mixing.

3.1.6 DR-UV-Vis analysis

The DR-UV-Vis is a technique that collects and analyzes scattered UV-Vis energy and measures the band gap energy of samples. In order to estimate the band gap energy, the absorption value of each specimen obtained was substituted to Planck’s equation [45,46].

\[ E_g = \frac{hc}{\lambda} = \frac{1240}{\lambda} \]  

where, \( E_g \) is the band gap energy, \( h \) is the Planck constant, \( c \) is the velocity of light, and \( \lambda \) is the strong absorption edge.

The band gap energy value of 5Ni-2Cd/Al₂O₃ and 6Ni-1Cd/Al₂O₃ was 4.42 and 3.875 eV, respectively. Farahmandjou and Montagh [40] found that the pure alumina band gap has a value of 4.06 eV. Therefore, the band gap is narrowed by the addition of Ni-Cd. Boschloo and Hagfeldt [47] found that the NiO nanostructure (p-type semiconductor) has an indirect band gap of 3.55 eV. Przeździecka et al. [48] reported the CdO band gap value of 2.55 eV. Moreover, Nallendran et al. [30] found that pure NiO, CdO, and NiO-CdO equal 3.7, 2.47, and 3.1 eV, respectively. The NiO has a higher band gap than the CdO. Therefore, the catalyst with a higher Cd composition would result in a lower band gap, which is a perfect agreement with the present research.

Figure 6 shows the DR-UV-Vis spectra of 5Ni-2Cd/Al₂O₃ and 6Ni-1Cd/Al₂O₃, indicating the influence of Ni and Cd doping on the alumina support in the DR-UV-Vis absorption. Furthermore, the absorption spectrum of 6Ni-1Cd/Al₂O₃ showed a higher absorption at the UV-Vis region than to 5Ni-2Cd/Al₂O₃. This increase in the width of the absorption area indicates a redshift. The number of Ni ions increases as the Ni concentration increases, resulting in an increase in the redshift. In addition to showing a redshift, the two samples of Ni-Cd/Al₂O₃ photocatalysts showed absorbance at 280-320 nm wavelength. An increase in redshift implies an increase in photocatalytic activity. In addition, the maximum shift wavelength of the sample can also be related to the shorter distance between the valence and conduction bands. Thus, the process of forming hole pairs (\( h^+ \)) and electrons is more optimal.

3.2 Photocatalytic Degradation of MB

3.2.1 Radiation source effect on photodegradation of MB

The effect of radiation sources on the MB degradation test aims is to determine the most effective radiation source to produce •OH radicals. Figure 7 shows that the percentage of MB degradation increases if the MB is stored in a dark space, irradiated by UV light and irradiated by solar light. Under dark conditions, MB has a lower degradation rate than UV or solar light radiation. In dark conditions, there is no radiation source; the energy of photons is very low, so too little •OH radicals are regenerated. MB is only absorbed on the surface of the catalyst, not degraded.
Alkaykh et al. [49] discovered that MB degradation in an aqueous solution with MnTiO$_3$ is higher when radiated with solar light than UV. This phenomenon is due to the optimal number of photons required for effective photocatalytic degradation attained under solar light [49]. Moreover, Zhang et al. [50] investigated the degradation of MB by adding pure PEDOT to MB solution under UV light and solar light radiation. They found that solar light radiation has more degradation of MB. The reason for this result is that PEDOT is capable of absorbing light and producing electrons, which leads to the separation and formation of oxyradicals [51]. As a result, the quantity of oxyradicals leads to a higher efficiency of MB degradation under solar light than UV light.

MB irradiated with solar light gives a higher degradation yield than UV light due to solar light having an intensity and wavelength between 310-2300 nm, greater than the wavelength of UV light around 200-380 nm [52–54]. In addition, solar light combines ±45% visible light and ±55% UV light. Therefore, solar light has relatively large energy and can provide photon energy to the photocatalyst [55]. When irradiated to energy above the band gap energy, a photocatalyst will produce holes that are potent oxidizing agents and make •OH radicals. These radicals break down MB into less complex compounds. Kafesyani [20] has preferred a sample with a lower band gap due to its high amounts of electrons, which leads to enhanced photocatalytic activity of the sample. As mentioned, the band gap energy value for 5Ni-2Cd/Al$_2$O$_3$ and 6Ni-1Cd/Al$_2$O$_3$ was 4.42 and 3.875 eV, respectively. Moreover, based on the absorption spectrum of 6Ni-1Cd/Al$_2$O$_3$ showed higher absorption in the UV-Vis region compared to 5Ni-2Cd/Al$_2$O$_3$. Therefore, the 6Ni-1Cd/Al$_2$O$_3$ has a higher MB degradation in various source radiation.

Mebed et al. [56] investigated the degradation of MB by adding PbO-40% Al$_2$O$_3$ nanocomposites under visible and UV-visible light radiation. At 105 min of radiation time, the maximum degradation efficiency for visible and UV-visible light radiation sources are 26.5 and 25.5%, respectively. Compared to the present study, there was less degradation due to the larger band gap caused by Mebed et al. [56] research (4.61 eV). Moreover, Munawar et al. [23] investigated photocatalytic activity by adding NiO-CdO-ZnO in MB under solar light and found degradation of about 90% at 60 min of illumination. Compared to the current research, Munawar et al. [23] achieved higher degradation efficiency due to lower band gap (around 3.24 eV).

Another possible reason for 6Ni-1Cd/Al$_2$O$_3$ having higher MB degradation in various source radiation is due to surface area. Based on BET measurements, 6Ni-1Cd/Al$_2$O$_3$ has a smaller surface area than 5Ni-2Cd/Al$_2$O$_3$. He et al. [10] found that decreased surface area of the catalyst leads to increased MB removal in the solution.

Figure 8 shows the FTIR spectra of MB with the fabricated 6Ni-1Cd/Al$_2$O$_3$ in dark and UV light. The absorption peaks in the spectra have wavelengths that are almost the same. However, the transmittance values are significantly different. The result indicates the adsorption and degradation of MB by the fabricated Ni-Cd/Al$_2$O$_3$ photocatalyst. The FTIR spectrum of MB+6Ni-1Cd/Al$_2$O$_3$ in UV light shows higher IR absorption than that of MB+6Ni-1Cd/Al$_2$O$_3$ in dark conditions.
Based on Figure 8, the obtained peak between 3384-3430 cm\(^{-1}\) is the chemical bonding of the OH group [23]. The vibration band around 1624 cm\(^{-1}\) is caused by H\(_2\)O deformation vibration [41]. Two peaks of 832 and 562 cm\(^{-1}\) are associated with the vibration bond of AlO stretching [43]. The peak of 723 cm\(^{-1}\) is assigned as CdO stretching vibration [44]. The band at 528 cm\(^{-1}\) is associated with the NiO bond [30].

Compared to Figure 8 and 5, there are peaks that are missing at 3900, 3783, 1597, 678, and 499 cm\(^{-1}\). This condition is probably due to the MB degradation process. Tzompantzi et al. [57] found similar behavior with the present research, where several peaks were missing due to degradation using 40 pp of phenol compared to 80 ppm of p-cresol. The comparison between Figures 5 and 8 show that the 6Ni-1Cd/Al\(_2\)O\(_3\) catalyst remains stable after the MB degradation process due to almost similar spectra.

### 3.2.2 Radiation time effect on MB degradation rate

Figure 9 shows the effect of radiation time and catalyst type on MB percentage degradation. It can be seen that the longer the radiation time, the more MB is degraded. Alkaykh et al. [49] found that MB degradation in an aqueous solution by adding MnTiO\(_3\) is increased by increasing the time. This condition is similar to that of solar light and UV radiation [49]. Balamurugan [31] investigated the MB degradation by adding CdO-Al\(_2\)O\(_3\)-NiO nanocomposite in the MB solution and found that MB degradation is increased by increasing the time. Similar behavior was also found in Zhang et al. [50] research when investigating the degradation of MB by adding pure PEDOT in the solution under solar light and UV light. Hence, it can be concluded that with increasing radiation time, more and more photon energy is absorbed by the catalyst on the surface, making it easier to degrade MB. Moreover, the degradation of the 5Ni-2Cd/Al\(_2\)O\(_3\) sample is higher than that of 5Ni-2Cd/Al\(_2\)O\(_3\); this requires further investigation.

The spectrum results for degradation MB with 5Ni-2Cd/Al\(_2\)O\(_3\) and 6Ni-1Cd/Al\(_2\)O\(_3\)-based catalysts are shown in Figure 10. The UV-Vis investigation shows that the peak reduction for 5Ni-2Cd/Al\(_2\)O\(_3\) is 43.21%, while 6Ni-1Cd/Al\(_2\)O\(_3\) is about 24.53% at 675.08 nm in the decomposition of MB. According to Figures 10(a) and (b), no peaks shifted can be found, which suggests there was no generation of intermediates be-

![Figure 9](image_url)

**Figure 9.** Radiation time effect on MB degradation by adding 5Ni2Cd/Al\(_2\)O\(_3\) and 6Ni1Cd/Al\(_2\)O\(_3\) separately.

![Figure 10](image_url)

**Figure 10.** Spectrum of degradation of MB with (a) 5Ni-2Cd/Al\(_2\)O\(_3\) and (b) 6Ni-1Cd/Al\(_2\)O\(_3\) at UV illumination of 312 nm.
between MB molecules and 5Ni-2Cd/Al₂O₃ or 6Ni-1Cd/Al₂O₃ catalyst during the interaction [10].

3.2.3 pH effect on the degradation of MB

In the degradation process, the pH value is essential. The pH value of a solution can affect the Ni-Cd surface charge ionic strength dye properties and the dye adsorption process on Ni-Cd/Al₂O₃ particles. In this study, the pH of the MB solution was maintained at 4, 6, 7, 9, 11, and 12 with a UV light irradiation time for 90 min. The results of pH optimization can be seen in Figure 11.

The decrease in the degradation rate at acidic pH may be due to the high adsorption at low pH. The catalyst surface is covered by dye molecules which causes the absorption of UV radiation on the surface of the catalyst to decrease [58]. In a low pH environment, it is also considered to be saturated with excess H⁺ ions. Thereby inhibiting MB from being absorbed so that under acidic conditions, it can reduce the number of positive charges on the catalyst surface, facilitating the formation of hydroxyl radicals from the active catalyst [59]. An excess of OH anions at higher pH facilitates the photo-degradation of •OH radicals. Changes in pH shift the redox potential of the valence and conduction bands which can affect interfacial charge transfer [58]. The effect of pH can be explained by the acid-base nature of the metal surface, which can be explained by the value of zero-point charge (ZPC). The adsorption of water molecules on the metal surface sites is followed by the dissociation of the charge of the OH− group leading to the chemical equilibrium of the metal hydroxyl group (M–OH) according to the following reactions.

\[
\begin{align*}
\text{M–OH} + \text{H}^+ &\rightarrow \text{M–OH}^{2+} \\
\text{M–OH} &\rightarrow \text{M–O} + \text{H}^+ 
\end{align*}
\]

Equations (3) and (4) show the metal hydroxyl equilibrium reaction [60].

Several conditions, as mentioned in Table 3, have less degradation efficiency than present research. Moreover, Alkaykh et al. [49] found that MB degradation in an aqueous solution by MnTiO₃ is increased by increasing the pH. Tayyebi et al. [61] also found similar behavior when investigating bismuth vanadate’s photoactivity. Therefore, photoactivity depends on pH, and MB degradation increases with increasing pH, which is identical to the present research.

4. Conclusions

Preparation, characterization, and photocatalytic activity of Ni-Cd/Al₂O₃ for MB degradation have been conducted. Due to more porosity, the 6Ni-1Cd/Al₂O₃ had a lesser surface area and higher absorption than the 5Ni-2Cd/Al₂O₃. A light source, time, and varied pH were proven to influence MB degradation. The

Figure 11. Effect of pH on degradation MB solution.

Table 3. Other research findings.

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<th>Result</th>
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<td>1</td>
<td>0.002 g graphene oxide and b-cyclodextrin/graphene oxide to 50 mL MB solution (1.6 mg/L MB)</td>
<td>Degradation efficiency reached the maximum of 73% (at pH value is 7)</td>
<td>Yang et al. [9]</td>
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<tr>
<td>2</td>
<td>Synthesized novel ZnAl₂O₃/Al₂O₃ nano-composite and added it to MB solution</td>
<td>Maximum MB removal around 70% under conditions: 10 mg/L MB, pH 8.5, 0.05 g of 70 wt.% ZnAl₂O₃/Al₂O₃</td>
<td>Saffar et al. [25]</td>
</tr>
<tr>
<td>3</td>
<td>Synthesized nano-g-Al₂O₃ from aluminium foil waste, then 10 mg/L nano-g-Al₂O₃ added in MB solution with various pH values</td>
<td>Optimum degradation at pH 6 with 71% MB removal</td>
<td>Sangor and Al-Ghouti [28]</td>
</tr>
</tbody>
</table>
amount of oxyradicals results in higher efficiency of MB degradation under solar light than UV light. More and more photon energy are absorbed by the catalyst on the surface, making it easier to degrade MB by increasing radiation time. The highest MB degradation is found in pH 11 conditions by adding 6Ni-1Cd/Al₂O₃ catalyst in the solution because the 6Ni-1Cd/Al₂O₃ catalyst has a lower band gap than 5Ni-2Cd/Al₂O₃. Therefore, the 6Ni-1Cd/Al₂O₃ catalyst seems promising applied to the degradation of MB dye waste in industrial wastewater treatment.

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