Aluminum-Doped Cobalt Ferrite as an Efficient Photocatalyst for the Abatement of Methylene Blue

Naseem Abbas 1, Nida Rubab 2, Natasha Sadiq 1, Suryyia Manzoor 1,*, Muhammad Imran Khan 3,*, Javier Fernandez Garcia 4,* 5, Isaias Barbosa Aragao 5, Muhammad Tariq 1, Zeeshan Akhtar 6 and Ghazala Yasmin 1

1 Institute of Chemical Sciences, Bahauddin Zakariya University, Multan 60800, Pakistan; dr.naseem.abbas@bzu.edu.pk (N.A.); natashasadiq007@gmail.com (N.S.); mtnazir@yahoo.com (M.T.); ghazala31pk@yahoo.com (G.Y.)
2 Department of Physics, Bahauddin Zakariya University, Multan 60800, Pakistan; nidarubab491@gmail.com
3 School of Energy and Power Engineering, Xi’an Jiaotong University, 28 West Xianning Road, Xi’an 710049, Shaanxi, China
4 School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK
5 C2P2 (CNRS-UMR 5265), Université Claude Bernard Lyon 1, ESCPE Lyon, 43 Boulevard du 11 Novembre 1918, CEDEX, 69626 Villeurbanne, France; aragao.isaias@gmail.com
6 Department of Applied Chemistry and Chemical Technology, University of Karachi, Karachi 75270, Pakistan; zakhtar@uok.edu.pk
* Correspondence: suryyia878@gmail.com or suryyia.manzoor@bzu.edu.pk (S.M.); raoimranishaq@gmail.com (M.I.K.); j.fernandezgarcia@leeds.ac.uk (J.F.G.)

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Abstract: The present study is aimed to access the photodegradation efficiency of methylene blue dye using CoFe2O4 and Co0.1Al0.03Fe0.17O0.4 nanoparticles. The synthesis of spinel ferrites nanoparticles was performed by a facile sol-gel method. The synthesized nanoparticles were characterized by FTIR, XRD, SEM, EDS, Nitrogen adsorption/desorption and UV–Visible spectroscopy. The XRD studies confirmed the spinel cubic structure of ferrite. It was also found that the crystallinity increases at an annealing temperature of 800 °C. The application of these nanoparticles for methylene blue’s photocatalytic degradation was explored and also the optimization of several parameters involving dye’s concentration, amount of catalyst and pH of the solution was done. Photocatalytic degradation of methylene blue showed that at pH 11, using 200 W visible light bulb and in 120 min; 93% methylene blue dye was degraded by using 0.1 g of Co0.1Al0.03Fe0.17O0.4.

Keywords: aluminum-doped cobalt ferrite; sol-gel synthesis; methylene blue; photocatalytic degradation

1. Introduction

Pollution is unquestionably among the most serious and prevailing dangers of the modern world that have been threatening the biosphere for decades and to overcome this menace, immediate preventive measures are necessary [1,2]. Water pollution caused by dyes is a global concern and their removal through cost-effective and eco-friendly techniques is a challenging task [3,4]. Several industries that employ dyeing procedures, e.g., textile, leather and paper, contribute significantly to water pollution due to the excessive use of toxic compounds like dyes, which eventually enter the ecosystem, affecting the surrounding flora and fauna either directly or indirectly [5]. They can also affect our drinking water supplies since they are not easily degraded through natural or biological methods. Additionally, their toxicity poses a danger to the environment, they can form a layer above the sea-water (or freshwater) surface and block the sunlight, which is one of the most relevant components
for the survival of aquatic life. This is due to the inefficiency of the dyeing process in which the dyes are still present in their waste due to their high stability in water [6].

Methylene blue (MB), C₁₆H₁₈N₃SCl, an organic dye used in the industry, is well-known to cause water pollution [7]. It is linked to numerous health issues in humans—such as irritation of digestive tract resulting in anaemia, nausea, vomiting, and diarrhoea—and enhance eutrophication [8] which results in a misbalance of the aquatic ecosystem that may cause catastrophic effects to fauna and flora [9]. Previously, chemical coagulation, biological, and adsorption methods were used to treat industrial waste but these approaches do not completely degrade MB in water, and nowadays the advanced oxidative processes (AOPs) have become the most commonly used methods for wastewater treatment [10]. In this process, the generation of active radical species (OH) takes place from common oxidants such as O₃, H₂O₂, and O₂. For the improvement in the dye removal efficiency, AOPs are modified with the doping of transition metal salts and by irradiation with different light sources (e.g., ultraviolet, visible light, and γ rays) as well as ultrasonic waves with the aim of increasing the generation rate of OH.

In this study, the efficient photocatalytic degradation method is used to degrade MB dye by using aluminum-doped spinel ferrite nanoparticles as photocatalysts [11] because they are stable and present high catalytic activity due to their small bandgap [12]. The wide use of ferrite as nanocatalyst [13] is due to their cost-effectiveness, stability, facile preparation, stability towards harsh conditions, and its docile nature towards further modifications [14,15]. The ferrite nanocatalysts are generally nontoxic or slightly phytotoxic only if freshly prepared NPs are released into water [16,17]. Then, both doped and undoped ferrites have gained a great interest in catalysis [18], and for this study, undoped CoFe₂O₄ and doped Co₀.1Al₀.03Fe₀.17O₀.4 were synthesized, characterized and used for the photocatalytic degradation of MB dye in the presence of visible light. Several parameters affecting the catalytic activity were also optimized.

2. Experimental

2.1. Synthesis of Undoped CoFe₂O₄ and Doped CoAlₓFe₂−ₓO₄

Aluminum-doped cobalt nanoferrites, CoAlₓFe₂−ₓO₄, in which x is 0.1, 0.2, 0.3, 0.4 and 0.5 have been synthesized by the sol-gel combustion method [19]. All the reagents used for the synthesis were of analytical grade and were used as received. The 100 mL of each aqueous solution of the nitrates [0.1 M Co (NO₃)₂·6H₂O, 0.5 M Fe (NO₃)₂·9H₂O, and 0.2 M Al (NO₃)₂·9H₂O] was prepared and mixed followed by the slow addition of 9 g citric acid (chelating agent). To precipitate out nanoferrites, the pH was adjusted to 8 by using a 32% ammonia solution. Afterward, the water was evaporated and the solution was converted into a wet gel by constant heating at 70 °C. After some time, the gel underwent self-ignition, transforming the sample to ash, which was ground and annealed at 800 °C for 5 h, using a heating rate of 20 °C min⁻¹.

All materials were characterized using standard techniques and were used for MB dye degradation.

2.2. Characterization

2.2.1. X-ray Diffraction (XRD)s

XRD served to determine the phases and crystallinity of the synthesized nanoferrite samples over a 2θ range of 10° to 80°. XRD was performed on a Raigaku D/Max 3A Model 1981 using CuKα radiation at room temperature. Debye–Schererrer formula was applied for the calculation of average crystallite size given in Equation (1) [20]:

\[ D = \frac{(0.9\lambda)}{(\beta \cos \theta)} \] (1)
where “D” presents average crystallite size, “θ” is Bragg’s angle, “β” serves for full width half maximum (FWHM) and λ is the wavelength of the X-ray (CuKα is 1.54051 A). The lattice parameter of the spinel ferrites was determined by Equation (2):

\[ a = \frac{d(h^2 + k^2 + l^2)^{1/2}}{2} \]  

where “a” represents lattice constant, “d” is interplanar spacing, and h, k and l are Miller indices. Unit cell volume is found out by Equation (3):

\[ V = a^3 \]

where “a” is the lattice parameter and V is the cell’s volume.

2.2.2. SEM-EDS Analysis

SEM-EDS analysis was performed using NOVA NANO Scanning Electron Microscope equipped with an Energy-Dispersive Spectrophotometer (EDS). Particle size and their distribution were calculated using the Image J and Origin Pro software, while the elemental analysis of CoFe₂O₄ and Co₀.₁Al₀.₃Fe₀.₁₇O₀.₄ with different compositions was determined through EDS.

2.2.3. Nitrogen Adsorption/Desorption Studies

The surface area was calculated through the N₂ sorption isotherms on a Nova Station A. Around 0.3 g of each sample were used and analysis was performed at liquid nitrogen bath temperature.

2.3. Degradation of MB Dye Using Synthesized Spinel Ferrites

For the photocatalytic degradation assays, a dark photocatalytic reactor was used to avoid outside illumination and, when required, a reflective surface was used inside. Visible light bulbs containing tungsten filament (Philips 100 W and 200 W) were applied as a source of photons; it was connected at the top of the reactor chamber. The reaction chamber was a simple wooden box whose inside walls were covered with aluminum foil (Figure 1). The photocatalytic degradation of MB dye with undoped (CoFe₂O₄) and doped (Co₀.₁Al₀.₃Fe₀.₁₇O₀.₄) cobalt ferrite nanoparticles was estimated by quantification of the MB dye using a UV–Vis spectrophotometer. Photocatalysts were taken into a beaker containing the MB solution and put inside the photoreactor. After attaining the adsorption equilibrium (A₀) (about 30 min), the light was turned on to study the photocatalytic conversion of the MB dye solution. After a time-lapse of 30 min, an aliquot was taken using a centrifuge machine. The MB dye’s concentration after irradiation was determined by measuring the absorbance intensity of each aliquot at the dye maximum absorption λ, i.e., 665 nm, by using an ultraviolet-visible spectrophotometer (SHIMADZU 1800). The dye’s % degradation was then found by using Equation (4):

\[ \% \text{ Degradation} = (A₀ - A/A₀) \times 100 \]  

where

A₀ is MB dye’s initial absorbance
A is MB dye’s final absorbance, after irradiation.
2.4. Optimization of Different Variables Affecting Degradation of MB Dye

2.4.1. Effect of Time

Illumination time is considered a prime factor affecting the dye's degradation. The role of illumination time on dye's percentage (%) degradation was studied at different time periods till equilibrium was established while keeping other variables constant, i.e., catalyst amount 0.5 g and 10 mg/L MB dye solution.

2.4.2. Effect of pH

The effect of pH on methylene blue dye photocatalytic degradation was considered in the pH range of 3–11 using 100 mL of 10 mg/L of the initial concentration of MB dye and a dose of 0.5 g under visible light for 120 min. MB solution's pH was adjusted either through 0.1 M HCl or 0.1 M NaOH. Moreover, the pH of the MB dye solution was found out before and after the photocatalytic degradation process.

2.4.3. Effect of Dose of Catalyst

To determine the role of the amount of catalyst, dosages of nanoferrites were varied from 0.05 g to 0.2 g. Different amounts of catalysts were taken in beakers containing 100 mL MB dye having a concentration of 10 mg/L and pH 11. This sample was kept in the photoreactor for a time duration of 120 min, and stirred by a magnetic stirrer (400 rpm). A plot of % degradation of methylene blue dye for various catalyst doses vs. time was drawn.

2.4.4. Effect of Initial Concentration of MB Dye Solution

The effect of the initial concentration on photodegradation process was studied by using the fixed photocatalyst dose of 0.1 g at varying initial concentrations of MB dye ranging from 5 mg/L to 30 mg/L, from a stock solution of 100 mg/L with pH 11 under visible light for 120 min. Later, the graph was plotted as the % degradation vs. time.
2.4.5. Effect of Intensity of Light

For this purpose, the variation in light intensity with respect to the changing distance between the light source and the solution containing the catalyst was investigated. 100 Watts and 200 Watts visible light bulbs were utilized for photocatalytic degradation by using 10 mg/L dye concentration, at pH 11 with 0.1 g catalyst dose for 120 min.

2.5. Photostability Studies

Photostability studies of the CoAlFe$_2$O$_4$ were carried out to determine its durability following the procedure described by Bashir et al. [21]. The FTIR spectrum of the unused photocatalyst was taken in the first step. In the next step, photocatalyst was employed for the degradation of dye, then washed and reused in the same manner for 5 consecutive cycles. The FTIR spectrum of the washed photocatalyst after 5 runs was taken again.

3. Results and Discussion

3.1. Synthesis of CoFe$_2$O$_4$ and Doped CoAlFe$_2$O$_4$

Synthesized catalyst was of a grayish-black powder and magnetic in nature, whose physical appearance is shown in Figure 2.

![Figure 2. The final appearance of the catalyst.](image)

3.2. Characterization

3.2.1. SEM Analysis

Figures 3 and 4 present the SEM images of the synthesized undoped and doped samples. From Figure 3, it can be observed that the particles show a uniform pattern in the doped sample as compared to the undoped sample. Moreover, the undoped sample is not in a well-ordered form while the doped sample is in a well-ordered form. Further from Figure 5, it can be observed that the average grain size slightly decreases upon doping of Al$^{3+}$ ion from 46.51 nm for CoFe$_2$O$_4$ [22] to 36.21 nm for Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{0.4}$. 
Figure 3. SEM image of undoped CoFe2O4 at a resolution of 5 μm.

Figure 4. SEM images of Co0.1Al0.03Fe0.17O0.4 at a resolution of 5 μm.
3.2.2. XRD Analysis

XRD patterns of cobalt ferrite \( \text{CoFe}_2\text{O}_4 \) is shown in Figure 6. All the peaks were indexed within a single-phase spinel structure with few percentages of \( \alpha\text{-Fe}_2\text{O}_3 \). X-Powder Software was used to study the XRD pattern and crystalline phases were identified by correlation with reference data from JCPDS Card No. 22108 for Cobalt ferrites (\( \text{CoFe}_2\text{O}_4 \)). The spectrum showed peaks at 2\( \theta \) (23.48, 30.12, 35.46, 36.74, 43.07, 53.49, 56.81, 63.03) which are attributed to hkl values \((111), (220), (311), (222), (400), (422), (511), (440)\) and proves the ferrite’s spinel cubic structure. The additional XRD peaks that can be seen in Figures 6 and 7 were assigned to \( \alpha\text{-Fe}_2\text{O}_3 \) (JCPDS Card No. 33–664) as an associated phase [23].

Figure 7 presents the XRD diffraction spectrum of \( \text{Co}_{0.1}\text{Al}_{0.03}\text{Fe}_{0.17}\text{O}_{0.4} \). Generally, pure aluminum-doped cobalt ferrites exhibit seven peaks, which were located in the 2\( \theta \) range of \((10^\circ–80^\circ)\). It can also be observed that the most intense peak appeared at 2\( \theta = 35^\circ \) (311), which suggests the spinel structure of ferrites. The analysis using X-Powder software shows the crystalline phases of spinel ferrites have a perfect match with reference data of JCPDS Card No. 86-2267, and a small percentage of \( \alpha\text{-Fe}_2\text{O}_3 \), which proves that cubic spinel lattice has been successfully doped with \( \text{Al}^{3+} \) ions. The XRD
pattern shows peaks at 2θ(23.74, 29.89, 35.52, 43.14, 54.16, 57.10, 62.99), which are accredited to (111), (220), (311), (400), (422), (511) and (440) of the spinel cubic structure of ferrite [24]. The peak (311) is the highly diffracted peak of cubic spinel ferrite and its intensity determines the crystallinity of this cubic structure. From the Debye–Scherrer formula, the average crystallite size of CoFe2O4 was 37 nm and 21.6 nm for Co0.1Al0.03Fe0.17O0.4, shown in Table 1. The lattice parameter decreases with the insertion of Al on the structure, from 8.38615 Å for the undoped to 8.3387 Å to the doped one. This effect is classic when a larger atom, Fe3+ (0.67 Å), is substituted by a smaller one, Al3+ (0.51 Å), thus changing all cell parameters.

Figure 6. X-ray diffraction spectra of CoFe2O4.

Figure 7. X-ray diffraction spectra of Co0.1Al0.03Fe0.17O0.4.
Table 1. XRD results of CoFe$_2$O$_4$ and Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{0.4}$.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample</th>
<th>Lattice Parametera (Å)</th>
<th>Average Crystalline Size (nm)</th>
<th>Volume of Cell (Å$^3$)</th>
<th>Inter Planar Spacing (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CoFe$_2$O$_4$</td>
<td>8.38615</td>
<td>37</td>
<td>589.77</td>
<td>2.515</td>
</tr>
<tr>
<td>2</td>
<td>Co$<em>{0.1}$Al$</em>{0.03}$Fe$<em>{0.17}$O$</em>{0.4}$</td>
<td>8.3387</td>
<td>21.6</td>
<td>579.82</td>
<td>2.501</td>
</tr>
</tbody>
</table>

3.2.3. Energy-Dispersive X-ray Spectroscopy

Figure 8 is representative of the EDS spectra showing the presence of Co, Al, Fe, and oxygen.

![Energy-dispersive X-ray spectra of CoFe$_2$O$_4$ and Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{0.4}$](image)

Table 2. Nitrogen adsorption/desorption results of undoped and doped ferrites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Average Pore Radius (Å)</th>
<th>Total Pore Volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>9.217</td>
<td>17.80</td>
<td>0.013</td>
</tr>
<tr>
<td>Co$<em>{0.1}$Al$</em>{0.03}$Fe$<em>{0.17}$O$</em>{0.4}$</td>
<td>14.865</td>
<td>27.69</td>
<td>1.261.26</td>
</tr>
</tbody>
</table>

Figure 8. Energy-dispersive X-ray spectra of CoFe$_2$O$_4$ and Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{0.4}$.
3.2.4. Nitrogen Adsorption/Desorption Studies

Nitrogen adsorption/desorption studies were performed to determine the surface area, pore volume, and pore radius (Table 2, Figure 9).

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>Average Pore Radius (Å)</th>
<th>Total Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe₂O₄</td>
<td>9.217</td>
<td>17.80</td>
<td>0.013</td>
</tr>
<tr>
<td>Co₀.₁Al₀.₃Fe₀.₁₇O₀.₄</td>
<td>14.865</td>
<td>27.69</td>
<td>1.261.26</td>
</tr>
</tbody>
</table>

![Graph showing nitrogen adsorption/desorption studies of CoFe₂O₄ and Co₀.₁Al₀.₃Fe₀.₁₇O₀.₄](image)

**Figure 9.** Nitrogen adsorption/desorption studies of CoFe₂O₄ and Co₀.₁Al₀.₃Fe₀.₁₇O₀.₄.

From the data in Table 2, it can be observed that a slight increase in the surface area occurred in the case of doped ferrite as compared to the undoped material.

3.2.5. FTIR of Cobalt Ferrite

The FTIR spectrum of cobalt ferrite is shown in Figure 10. The frequency bands at 443.91 cm⁻¹ (95.04% T) and 530.33 cm⁻¹ (93.23% T) were due to the stretching vibrations of metal oxides in octahedral group complex Co (II)-O²⁻ and tetrahedral group complex Fe (III)-O²⁻ of cobalt ferrite, which proves the spinel structure of ferrite. The frequency band at 787.72 cm⁻¹ in the FTIR spectrum of cobalt ferrite was attributed to Co-O vibrations where Co ions were in a tetrahedral position. The band at 906.97 cm⁻¹ is related to CoOOH hydration of water. The band at 1058.46 cm⁻¹ and 1196.95 cm⁻¹ was characteristic of the CoFe₂O₄ system and it was due to residual FeOOH. Bands that were present between 1500 cm⁻¹ and 3000 cm⁻¹ were due to the bending of the absorbed water molecules on the
structure of spinel ferrite, i.e., 1584.24 cm\(^{-1}\) and 2105.27 cm\(^{-1}\). It was observed that differences in band positions were expected because of different bond lengths of Fe\(^{3+}\)-O\(^{2-}\) ions which were distributed at octahedral and tetrahedral sites [25].

![Figure 10. FTIR of cobalt ferrite CoFe\(_2\)O\(_4\).](image)

3.2.6. FTIR of Aluminum-Doped Cobalt Ferrite

The FTIR spectrum of aluminum-doped cobalt ferrite shown in Figure 10 confirms the spinel structure of ferrite nanoparticles. The transmission spectrum of aluminum-doped cobalt ferrite shows two bands (\(v_1, v_2\)). The characteristic peak which was in the range of 400–600 cm\(^{-1}\) represents the presence of the M-O stretching vibration band. These bands were very susceptible to changes in the interaction between cations and oxygen in tetrahedral and octahedral sites [26]. The high-frequency band at 533.68 cm\(^{-1}\) shows stretching vibrations of tetrahedral groups. Lower frequency band near 406.01 cm\(^{-1}\) shows the stretching mode of octahedral M-O groups in ferrites. The reason behind the difference in the location of both frequency bands was due to different distances of Fe\(^{3+}\) ion in octahedral and tetrahedral complexes. Figure 11 illustrates that aluminum doping shifts lower frequency bands towards higher frequency bands.
3.3. Adsorption of MB on the Surface of Synthesized Catalysts

The adsorption phenomenon of MB on the surface of Co$_{0.5}$Al$_{0.3}$Fe$_{1.7}$O$_{0.4}$ is shown in Figure 12. Results, clearly, indicate that adsorption equilibrium was obtained in 30 min.
3.4. Photocatalytic Activity of Synthesized Catalysts

The photocatalytic activity of different synthesized catalysts is shown in Figure 13.

![Figure 13. The plot of % Photodegradation of MB dye by different photocatalysts.](image)

From Figure 13 it can be observed that undoped cobalt ferrite CoFe$_2$O$_4$ showed only 45% degradation efficiency while samples with 15% aluminum (Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{0.4}$) doped cobalt ferrite presented maximum degradation efficiency, however a further increase of aluminum doping decreases the degradation efficiency of the catalyst which might be due to distortion in the crystal structure of the catalyst. As Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{0.4}$ showed maximum efficiency, so aluminum-doped cobalt ferrite is taken for further optimization. Results were compared with the efficiency of other catalysts for degradation of MB but Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{0.4}$ showed a 10–15% higher efficiency [27–29].

3.5. Optimization of Different Variables Affecting the Degradation of MB Dye

3.5.1. Effect of Time

Illumination time is a key factor in an efficient photodegradation of dye. The impact of illumination time on dye’s percentage degradation was studied at a different time interval at pH 11 with a 0.5 g catalyst (shown in Figure 14). The addition of Al favors the formation of hole–electron pairs, which is linked to the formation of the radical intermediates, thus mediating the photodegradation process. Results confirmed that 120 min was enough to degrade dyes up to a maximum of 83% using the doped catalyst which was higher than that of undoped one (58%) [30,31].
3.5.2. Effect of pH

The pH of the solution plays a significant role in photodegradation as it affects the charge on the catalyst’s surface which in turn influences the adsorption of dye [32]. From Figure 15, it can be observed that maximum photocatalytic degradation occurred in alkaline pH and minimum in acidic medium. The maximum percentage of degradation was observed at pH 11. As discussed in the literature, it is due to the cationic nature of methylene blue dye that its surface becomes protonated in acidic pH which happens because of the adsorption of H⁺ ions. Therefore, it results in repulsion between dye molecules and photocatalyst. The increase in pH from acidic to alkaline causes a reduction in the repulsion between catalyst and dye molecules. This results in bringing the dye close to the catalytic surface, hence increasing photocatalytic degradation of dye. However, at pH higher than 11, the negative charge appears again on the surface of the catalyst and increase in repulsion between the catalyst’s surface and the dye may occur [33,34].

The role of pH in photodegradation of dye is associated with multiple phenomena [35]. The adsorption characteristics of the dye also change with pH and affect the surface characteristics of semiconductors [36]. Positive holes react with hydroxide ions which can form hydroxyl radicals. Hence, positive holes are the prime oxidation species at low pH, whereas at neutral or high pH levels, hydroxyl radicals are considered as the predominant species [37]. In alkaline solution, OH is easily generated by hydroxide ions present on the semiconductor surface [38]. It is also necessary to neutralize the pH of treated water by using different chemical methods.

![Figure 14. % degradation of MB dye by undoped and doped photocatalysts.](image-url)
3.5.3. Effect of Catalyst Dose

In photodegradation of dye; optimization of catalyst dose is shown in Figure 16. The optimum dose was calculated for the efficient removal of dye. The amount of catalyst required will depend upon the configuration of the reactor, light intensity, type of the dye targeted, type and morphology of particles of the catalyst [39,40].

Figure 15. Percentage degradation of MB dye at different pH in varying time intervals using $\text{Co}_{0.1}\text{Al}_{0.03}\text{Fe}_{0.17}\text{O}_{0.4}$.

Figure 16. The plot of percentage degradation of MB by varying catalyst amounts in different time intervals.
From Figure 16, it is clearly observed that 0.1 g catalyst amount showed maximum degradation. Further increase in catalyst dose caused a decrease in photocatalytic degradation of dye. The decreasing efficiency with an increase in dose might be because the light penetration to all the catalyst sites will become difficult due to an increase in turbidity caused by an increasing amount of photocatalyst and light scattering effect.

3.5.4. Effect of Initial Concentration of MB Dye Solution

The optimization of the effect of the initial concentration of MB dye was also evaluated and results are presented in Figure 17.

It is obvious that 10 mg/L dye solution gave maximum degradation, however, above this, the increase in concentration caused a decreased degradation of methylene blue which might be due to unavailability of active sites for adsorption and decrease in hydroxyl OH radicals due to an increase in turbidity and as a result degradation decreased [41,42].

3.5.5. Effect of Intensity of Light

The results presented in Figure 18 describe that the photodegradation increases with an increase in the intensity of light [43–45] which might be due to the increase of OH radicals with high energy photons. The high intensity also results in a temperature rise which further helps the formation of free radicals.

![Figure 17. Percentage photodegradation of MB at varying concentrations of dye with respect to time.](image-url)
Figure 18. Percentage photodegradation of MB at various light intensities; in the presence of 100 and 200 watts visible light bulb.

Moreover, the photostability studies confirmed the durability of Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{0.4}$ as shown in Figure 19. Even after 5 consecutive cycles, no prominent change in the FTIR spectra taken before and after the cycles were observed which confirm its reusability. The most characteristic band appeared in a range of 400–600 cm$^{-1}$ that represents the M-O stretching vibration band and can be observed in both the spectra. A minor band also emerged in Spectrum 2 which might be due to the presence of some minute amount of impurity left adsorbed on the catalyst’s surface.

Figure 19. FTIR spectra of Co$_{0.1}$Al$_{0.03}$Fe$_{0.17}$O$_{4}$ before (1) and after 5 cycles (2) using as photocatalyst.
Different photocatalysts have been reported in the literature for the purpose of photodegradation of methylene blue. The competency of aluminum-doped cobalt ferrite was found comparable to those already synthesized modified spinel ferrite. A comparison of the efficiency of the different photocatalyst is given in Table 3.

Table 3. A comparison of different modified spinel ferrite with Co0.1Al0.3Fe1.7O4.4.

<table>
<thead>
<tr>
<th>Types of Synthesized Photocatalyst</th>
<th>Size (nm)</th>
<th>Pollutant/</th>
<th>pH</th>
<th>Contact Time (min)</th>
<th>Catalyst Dose (g/L)</th>
<th>Pollutant (mg/L)</th>
<th>Light Source</th>
<th>Removal Efficiency</th>
<th>Cycle</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe2O4/TiO2</td>
<td>64</td>
<td>MB</td>
<td></td>
<td>180</td>
<td>0.5</td>
<td>20</td>
<td>Vis</td>
<td>40%</td>
<td>3</td>
<td>[46]</td>
</tr>
<tr>
<td>Ni0.5Zn0.5Fe2O4</td>
<td>-</td>
<td>MB</td>
<td>5</td>
<td>56</td>
<td>1</td>
<td>5</td>
<td>UV-Vis</td>
<td>55%</td>
<td>-</td>
<td>[47]</td>
</tr>
<tr>
<td>FeCuO/TiO2</td>
<td>35</td>
<td>MB</td>
<td></td>
<td>240</td>
<td>0.2</td>
<td>10</td>
<td>UV</td>
<td>50%</td>
<td>3</td>
<td>[48]</td>
</tr>
<tr>
<td>Co0.5Zn0.5Ni0.5Fe2O4:TiO2</td>
<td>-</td>
<td>MB</td>
<td>80</td>
<td>1</td>
<td>12.79</td>
<td>UV-Vis</td>
<td>12.66%</td>
<td>-</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>Co0.1Al0.3Fe1.7O4.4</td>
<td>40</td>
<td>MB</td>
<td>11</td>
<td>120</td>
<td>0.5</td>
<td>10</td>
<td>Vis</td>
<td>83%</td>
<td>5</td>
<td>Current work</td>
</tr>
</tbody>
</table>

3.5.6. Kinetic Modeling

According to Zhang et al., the pseudo-first-order or second-order kinetic models are not only facile but can also accommodate any rate law expression [50]. Therefore, these two models were followed to determine the rate of reaction. Figure 20 presents the graphs obtained for both kinetic models. The regression coefficient (R^2) value for the pseudo-first-order was 0.974, while for the second order, the obtained value was 0.998. It can hence be inferred from the regression R^2 value, that the degradation followed second-order kinetics.

![Figure 20](image_url)

Figure 20. Plots of (a) pseudo-first-order (b) second-order kinetic models for photocatalytic degradation of methylene blue using Co0.1Al0.3Fe1.7O4.4.
4. Conclusions

A series of aluminum-doped cobalt ferrites with compositional formula CoAl$_x$Fe$_{2-x}$O$_4$ ($x = 0.1$ to $0.5$) was prepared and studied for the photodegradation of dye. The homogenous nanosized spinel ferrites were obtained through the sol-gel method. Due to Al$^{3+}$ doping crystallite size and lattice parameter decreases and crystallite size found to be $21.6$ nm to $37$ nm. An FTIR spectrum confirms the cubic spinel structure of ferrites. Cobalt ferrite possessed a surface area of $9.217$ m$^2$/g whereas that of aluminum-doped cobalt ferrite was $14.865$ m$^2$/g. The SEM histograms confirmed that synthesis on nanoparticles ranging from $10$ to $120$ nm having maximum size distribution $40$–$50$ nm EDS data confirm the presence of Co, Fe, O and Al participating cations. For maximum efficiency of doped aluminum spinel ferrite, $10$ mg/L solution of MB dye, $0.1$ g catalyst at pH $11$ in $200$ watts was required for $120$ min. The synthesized NP may be used in wastewater treatment of dyes industry by designing different sieves using such adsorbents on the pathway of their wastewater.

Author Contributions: N.A. and S.M. supervised the research project. N.R. and N.S. carried out the experimental work as part of their Mphil theses. M.I.K., J.F.G., I.B.A., M.T., Z.A. and G.Y. contributed to the conceptualization, data analysis and interpretation, article editing and proof reading, as well as provision of resources for chemical characterization. All authors have read and agreed to the published version of the manuscript.

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