

RESEARCH ARTICLE

Cobalt Oxide Nanoparticles for Visible-Light Photocatalytic Degradation of Methylene Blue

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ABSTRACT: Cobalt oxide (Co_3O_4) nanoparticles were synthesized using a hydrothermal method, providing a simple and efficient route to obtain highly crystalline nanomaterials. The structural and optical properties of the nanoparticles were confirmed through various characterization techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy, and photoluminescence (PL). XRD analysis revealed that the Co_3O_4 nanoparticles had a cubic spinel structure with an average crystallite size of 64.86 nm. FTIR measurements provided insights into the chemical bonding, showing prominent metal-oxygen stretching and bending vibrations. Optical analysis using UV-Vis spectra and PL studies demonstrated the material's ability to absorb light, with significant absorption around 265 nm and a UV emission peak at 335 nm. The photocatalytic degradation of methylene blue dye under visible light irradiation was tested, with Co_3O_4 showing a degradation efficiency of 60%. These results highlight the potential of Co_3O_4 nanoparticles for environmental applications, particularly in wastewater treatment, where efficient dye removal under visible light is critical. The hydrothermal synthesis method and excellent photocatalytic performance of Co_3O_4 nanoparticles suggest their promising role in future photocatalytic applications.

Keywords: Cobalt oxide nanoparticles, Visible-light photocatalysis, Methylene blue degradation

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1. INTRODUCTION

Nanostructured materials have garnered significant attention in recent years due to their wide-ranging applications in fields such as catalysis, energy storage, sensors, and environmental remediation [1, 2]. Among these, metal oxides, particularly cobalt oxide (Co_3O_4), have shown remarkable potential due to their unique structural, electronic, and photocatalytic properties [3, 4]. Metal oxides can exhibit a range of behaviors, including metallic, semiconducting, or insulating properties, making them versatile materials for various applications [5]. Their capabilities are further enhanced when engineered at the nanoscale, where phenomena such as quantum confinement and increased surface area improve their performance in electronic, optical,

and catalytic processes [6, 7].

Cobalt oxide (Co_3O_4) is a p-type semiconductor with a spinel structure, which consists of both Co^{2+} and Co^{3+} ions [8]. This mixed oxidation state is a key feature that contributes to the material's excellent catalytic, electrochemical, and photocatalytic performance [9, 10]. The ability of Co_3O_4 to undergo redox reactions, switching between the Co^{2+} and Co^{3+} states, allows it to act as an effective catalyst in various oxidation and reduction processes [11, 12]. The presence of these dual oxidation states is particularly useful in photocatalytic applications, where cobalt oxide nanoparticles can absorb light and generate reactive species capable of breaking down pollutants [13].

Photocatalysis has emerged as an environmentally friendly and efficient method for degrading organic pollutants in water [14, 15]. The process involves a photocatalyst absorbing light energy, usually from the ultraviolet or visible spectrum, to generate electron-hole pairs [16]. These charge carriers then interact with water

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molecules or oxygen to produce reactive oxygen species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide anions ($\text{O}_2\bullet^-$), which are highly effective in degrading toxic organic compounds [17]. Cobalt oxide nanoparticles are particularly suitable for photocatalytic applications because they can absorb visible light, which comprises a large portion of the solar spectrum [18, 19]. The ability of Co_3O_4 to harness visible light, combined with its efficient redox properties, makes it a promising candidate for photocatalytic degradation of pollutants [20].

One of the most significant environmental challenges today is the contamination of water bodies by organic pollutants, especially synthetic dyes [21]. Methylene blue (MB), a synthetic dye used extensively in textile, pharmaceutical, and paper industries, is a major pollutant found in wastewater [22]. Methylene blue is resistant to natural degradation processes, and its persistence in the environment poses risks to aquatic ecosystems and human health [23]. It can cause harm to marine organisms, while also being toxic to humans at high concentrations, leading to respiratory problems and skin irritation [24]. Thus, effective methods to remove methylene blue from water are essential for environmental protection [25]. Traditional water treatment methods are often insufficient to degrade methylene blue, prompting interest in alternative techniques such as photocatalysis [26].

Cobalt oxide nanoparticles have shown excellent potential in degrading methylene blue under visible light irradiation [27]. The photocatalytic degradation of methylene blue using Co_3O_4 nanoparticles follows a general mechanism where the catalyst absorbs visible light, promoting electrons from the valence band to the conduction band [28]. This creates electron-hole pairs that, in turn, produce ROS capable of breaking down methylene blue into less harmful products such as water and carbon dioxide [29]. The efficiency of this process depends on several factors, including the size, morphology, crystallinity, and surface area of the nanoparticles [30, 31].

Nanostructured Co_3O_4 offers several advantages over its bulk counterparts in photocatalytic applications [32]. At the nanoscale, cobalt oxide's high surface area allows for more active sites where dye molecules can adsorb and degrade [33]. Additionally, the small particle size facilitates better charge separation, reducing the recombination of electron-hole pairs, which is a major issue in photocatalysis [34, 35]. These characteristics enhance the overall photocatalytic efficiency of Co_3O_4 , making it a more effective solution for pollutant degradation [36]. To further improve the photocatalytic properties of Co_3O_4 , researchers have explored strategies such as doping with other metals, coupling with different semiconductors, and modifying the surface of the nanoparticles [37, 38].

The hydrothermal synthesis method is widely employed for producing cobalt oxide nanoparticles because it allows for precise control over the particle size, morphology, and crystallinity [39]. This method involves the reaction of cobalt precursors in an aqueous solution under high temperature and pressure, resulting in uniform nanoparticles with well-

defined structures [40]. Hydrothermal synthesis is considered environmentally friendly and scalable for industrial production, making it an ideal method for synthesizing Co_3O_4 nanoparticles [41]. By adjusting the reaction conditions, such as temperature, reaction time, and precursor concentration, the size and crystallinity of the Co_3O_4 nanoparticles can be fine-tuned to optimize their photocatalytic performance [42].

Several recent studies have focused on improving the photocatalytic efficiency of cobalt oxide by modifying the synthesis conditions and incorporating additional elements to enhance light absorption and electron transfer [43]. For instance, doping Co_3O_4 with transition metals, such as copper or iron, has been shown to improve its photocatalytic activity by altering its electronic structure [44, 45]. Additionally, combining Co_3O_4 with other semiconductors, such as titanium dioxide (TiO_2) or zinc oxide (ZnO), can create heterojunctions that enhance charge separation and increase photocatalytic efficiency [46]. Surface modifications with organic or inorganic groups also help improve the light absorption properties of Co_3O_4 , further boosting its photocatalytic performance [47, 48].

In this paper, we present the synthesis of cobalt oxide (Co_3O_4) nanoparticles via a hydrothermal method and evaluate their photocatalytic performance for the degradation of methylene blue under visible light. The synthesized Co_3O_4 nanoparticles are characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible (UV-Vis) spectroscopy, and photoluminescence (PL) spectroscopy to assess their structural and optical properties. The photocatalytic efficiency of the nanoparticles is studied by monitoring the degradation of methylene blue dye under visible light irradiation.

2. EXPERIMENTAL DETAILS

Cobalt oxide nanoparticles were synthesized using a hydrothermal method. Initially, a cobalt precursor (cobalt chloride, CoCl_2) was dissolved in distilled water to form a clear solution. The concentration of the cobalt precursor was adjusted according to the desired final product yield. Urea, serving as a precipitating agent, was then added to the solution and stirred continuously for 2 hours to ensure homogeneity. The resulting mixture was transferred into a sealed Teflon-lined stainless steel autoclave to prevent the escape of any reactants or products. The autoclave was subsequently heated to 150°C and maintained at that temperature for the duration of the hydrothermal process under self-generated pressure. After completion of the hydrothermal treatment, the autoclave was allowed to cool down naturally to room temperature. The obtained cobalt oxide product was separated by centrifugation to isolate the solid material from the remaining solution. The solid was then thoroughly washed several times with ethanol and distilled water to remove any unreacted precursors or residual impurities. The purified cobalt oxide product was dried at 80°C for 24 hours to remove moisture. To enhance the

crystallinity, the dried product was annealed at 450°C for 2 hours under ambient conditions. The resulting material was then collected for further characterization and analysis.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction (XRD) Analysis

The XRD pattern of Co_3O_4 nanoparticles synthesized via the hydrothermal method provides clear evidence of the crystal structure and phase purity of the material. All observed diffraction peaks are in agreement with the standard Joint Committee on Powder Diffraction Standards (JCPDS) card no. 80-1536, confirming the formation of a pure Co_3O_4 spinel phase (Figure 1). The characteristic diffraction peaks at 2θ values of 31° , 36.46° , 44.5° , 59.18° , and 65.08° correspond to the (220), (311), (400), (511), and (440) crystal planes, respectively, which are typical of a cubic spinel structure. Among these diffraction peaks, the (311) plane exhibits the highest intensity, suggesting a preferential crystal growth orientation along this direction. The prominent intensity of this peak further supports the high degree of crystallinity in the synthesized Co_3O_4 nanoparticles [23]. The average crystallite size was estimated using the Debye-Scherrer equation:

$$D = 0.92\lambda / \beta \cos\theta \quad (1)$$

where D is the crystallite size, λ is the X-ray wavelength (0.15406 nm), β is the full width at half maximum (FWHM) of the most intense diffraction peak, and θ is the Bragg angle. Using this formula, the average particle size of the Co_3O_4 nanoparticles was calculated to be approximately 64.87 nm. The small particle size and high crystallinity are indicative of the successful synthesis of nanoscale Co_3O_4 with controlled morphology.

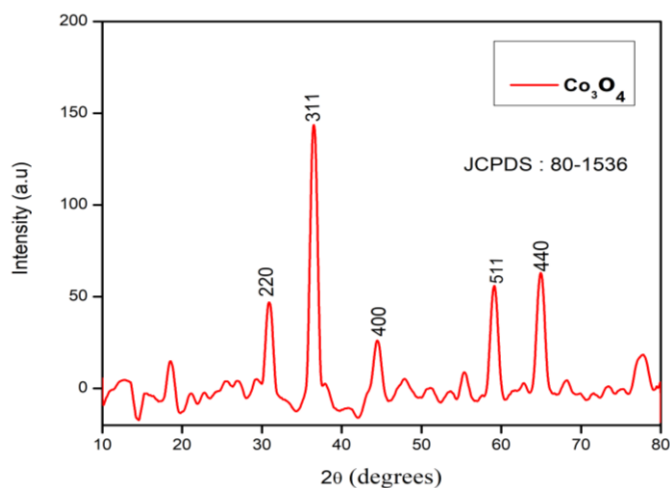


Fig. 1. Typical XRD pattern of the prepared Co_3O_4 nanoparticles.

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectroscopy was used to identify the functional groups present on the surface of the Co_3O_4 nanoparticles and confirm the formation of the metal oxide. The FTIR spectrum of the Co_3O_4 sample shows several characteristic peaks (Figure 2). A broad absorption peak around 3434 cm^{-1} corresponds to the O–H stretching vibration, which is attributed to adsorbed water molecules on the nanoparticle surface during the preparation process. The peak at 1629 cm^{-1} can be associated with bending vibrations of water molecules. More importantly, two strong absorption bands were observed at 664.69 cm^{-1} and 568.74 cm^{-1} , which correspond to the metal-oxygen (M–O) stretching and bending vibrations, respectively. These bands are characteristic of the spinel Co_3O_4 structure, confirming the successful formation of cobalt oxide nanoparticles with well-defined crystalline properties. The presence of these M–O bands further indicates the high purity of the sample, as no other significant peaks from impurities were detected.

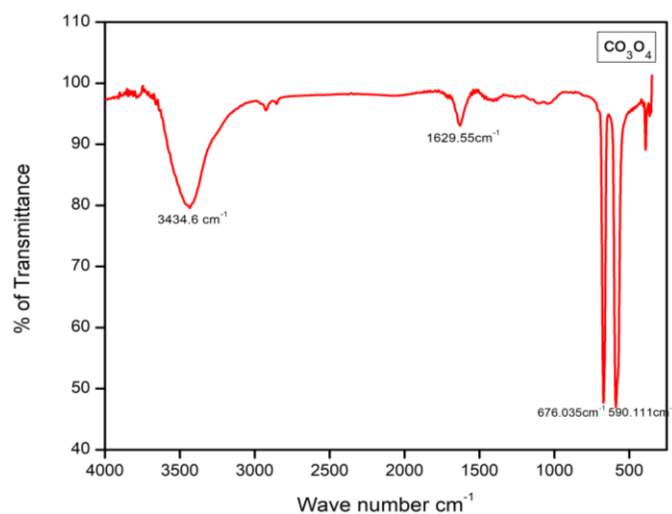


Fig. 2. Typical FTIR spectrum of the prepared Co_3O_4 nanoparticles.

3.3. UV-Visible Spectroscopy

The optical properties of Co_3O_4 nanoparticles were examined using UV-Visible spectroscopy. The UV-Vis absorption spectrum reveals a strong absorption peak at 265 nm, corresponding to the electronic transition from the valence band to the conduction band (Figure 3). This absorption edge in the UV region confirms that Co_3O_4 nanoparticles can effectively absorb UV light, which is typical for semiconductors with photocatalytic properties. The annealing process plays a significant role in influencing the optical properties of the nanoparticles. After annealing, the crystallite size increased, which directly affects the band gap energy by reducing it due to the improved crystallinity. This

behavior is well-documented, as annealing tends to enhance the crystallinity and reduce defects, resulting in lower band gaps [33]. To further quantify the optical band gap, the absorption data was analyzed using the Tauc relation:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, and A is a constant. For Co_3O_4 , a direct band gap transition is assumed ($n = 2$), and the estimated band gap energy was found to be approximately 1.78 eV (Figure 4). This value is consistent with other reported band gaps for Co_3O_4 nanoparticles, further confirming the suitability of Co_3O_4 for photocatalytic applications under visible light [28-30].

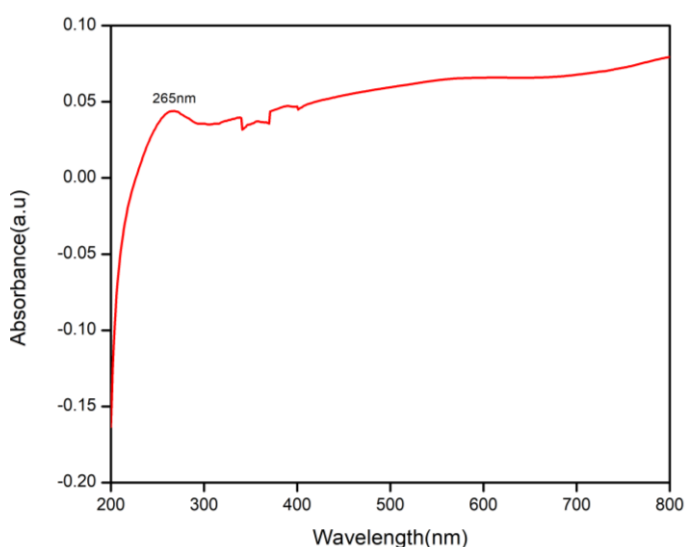


Fig. 3. Typical UV-Visible spectrum of the prepared Co_3O_4 nanoparticles.

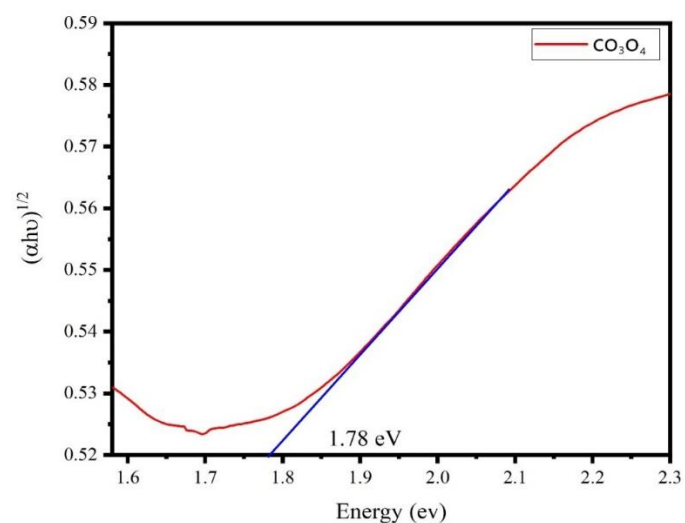


Fig. 4. Tauc plot for the energy band gap of the prepared Co_3O_4 nanoparticles.

3.4. Photoluminescence (PL) Studies

The optical characteristics of Co_3O_4 nanoparticles were investigated using room-temperature photoluminescence (PL) spectroscopy. By exciting the nanoparticles at a wavelength of 330 nm, their emission behavior was studied. The PL spectrum revealed a distinct UV emission peak at 335 nm, which corresponds to the recombination of photo-generated electron-hole pairs (Figure 5). This peak is indicative of the electronic transitions occurring within the Co_3O_4 nanoparticles and reflects their energy band structure. The UV emission suggests that Co_3O_4 nanoparticles possess favorable optical properties, making them potentially useful in optoelectronic applications. Additionally, the observed emission wavelength aligns with the intrinsic properties of Co_3O_4 , particularly its band gap energy, which is consistent with previous findings from UV-Vis spectroscopy [35-38]. The intensity of the emission peak also provides insights into the quality and crystallinity of the synthesized nanoparticles. Stronger emission generally implies fewer defects and better crystallinity, while weaker or broadened peaks can indicate the presence of structural defects or impurities. The relatively sharp UV emission observed in this study suggests that the Co_3O_4 nanoparticles possess high crystallinity with minimal defects, which is crucial for their potential use in photocatalytic and optoelectronic applications.

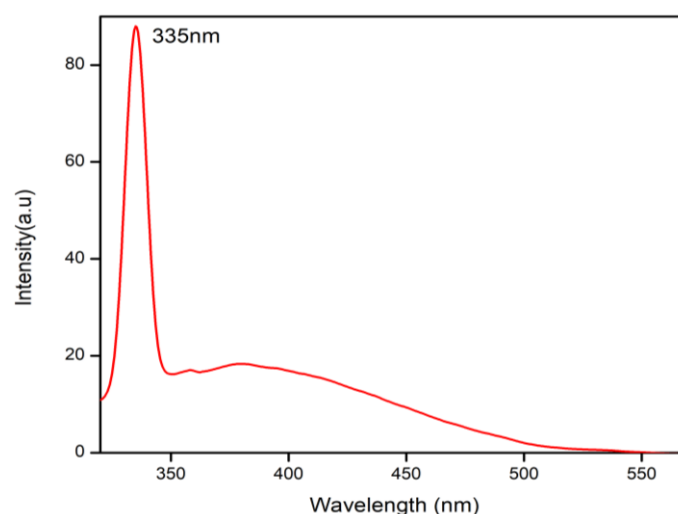


Fig. 5. Typical room-temperature photoluminescence (PL) spectrum of the prepared Co_3O_4 nanoparticles.

3.6. Photocatalytic Studies

The photocatalytic performance of Co_3O_4 nanoparticles was evaluated by studying their ability to degrade methylene blue (MB), a common organic dye, under sunlight. In this experiment, a 5 ppm methylene blue solution was prepared by mixing 25 ml of dye with 75 ml of distilled water. The solution was then stirred while a known amount of Co_3O_4

catalyst was added. The suspension was exposed to sunlight, and the degradation of methylene blue was monitored by measuring the change in absorbance over time using UV-Vis spectroscopy (Figure 6). The absorption spectra showed a gradual decrease in the characteristic absorbance peak of methylene blue at 665 nm as the reaction proceeded. This decrease in absorbance corresponds to a reduction in the concentration of methylene blue, indicating the successful photocatalytic degradation of the dye in the presence of Co_3O_4 nanoparticles.

The photocatalytic efficiency (η) was calculated using the following equation:

$$\eta = \frac{C_0 - C}{C_0} \times 100 \quad (3)$$

where C_0 is the initial concentration of methylene blue, and C is the concentration at a given time. Based on the experimental data, the photocatalytic efficiency of the Co_3O_4 nanoparticles was found to be approximately 60%. This moderate efficiency suggests that Co_3O_4 nanoparticles are effective photocatalysts for the degradation of organic pollutants under sunlight, though there is potential for improvement by optimizing the nanoparticle synthesis or experimental conditions.

Several factors contribute to the observed photocatalytic activity of Co_3O_4 nanoparticles. First, their ability to absorb visible light due to their suitable band gap energy (~ 1.78 eV) makes them highly responsive to solar radiation. Upon irradiation, Co_3O_4 nanoparticles generate electron-hole pairs, which initiate redox reactions that break down the dye molecules. The transition between Co^{2+} and Co^{3+} within the spinel structure plays a key role in these redox processes, facilitating the transfer of electrons and enhancing the catalytic activity. Additionally, the small size of the nanoparticles (~ 64.87 nm, as determined from XRD data) increases the surface area available for interaction with the dye molecules, further promoting the degradation process. The high crystallinity of the Co_3O_4 nanoparticles, as confirmed by XRD and PL studies, also contributes to their photocatalytic performance by reducing the recombination

rate of electron-hole pairs, thereby enhancing the efficiency of the photocatalytic process.

4. CONCLUSION

Co_3O_4 nanoparticles were successfully synthesized using the hydrothermal method, exhibiting notable structural, optical, and photocatalytic properties. The XRD analysis confirmed the spinel cubic structure of Co_3O_4 , with diffraction peaks that correspond to standard values from the JCPDS database. The crystalline size, calculated using the Debye-Scherrer formula, demonstrated the formation of well-defined nanoparticles. FTIR spectroscopy further confirmed the presence of surface functional groups, including M-O bonds, with prominent stretching frequencies at 664.69 cm^{-1} and 568.74 cm^{-1} , indicating the integrity of the cobalt oxide structure. Optical studies provided key insights into the properties of the nanoparticles. UV-Visible spectroscopy revealed an absorption peak at 265 nm, which corresponds to the transition of electrons within the Co_3O_4 structure. Photoluminescence studies, with an excitation wavelength of 330 nm, exhibited a UV emission peak at 335 nm, reflecting the high crystallinity and efficient electron-hole recombination of the nanoparticles. In addition to their structural and optical properties, the Co_3O_4 nanoparticles demonstrated photocatalytic activity in the degradation of methylene blue dye under sunlight, achieving an efficiency of 60%. This photocatalytic performance highlights the potential of Co_3O_4 as a catalyst for environmental applications, particularly in water purification. Overall, the hydrothermal method proved effective for producing Co_3O_4 nanoparticles with desirable properties, making them promising candidates for applications in photocatalysis and optoelectronic devices. Further optimization could enhance their efficiency and broaden their applicability in various technological fields.

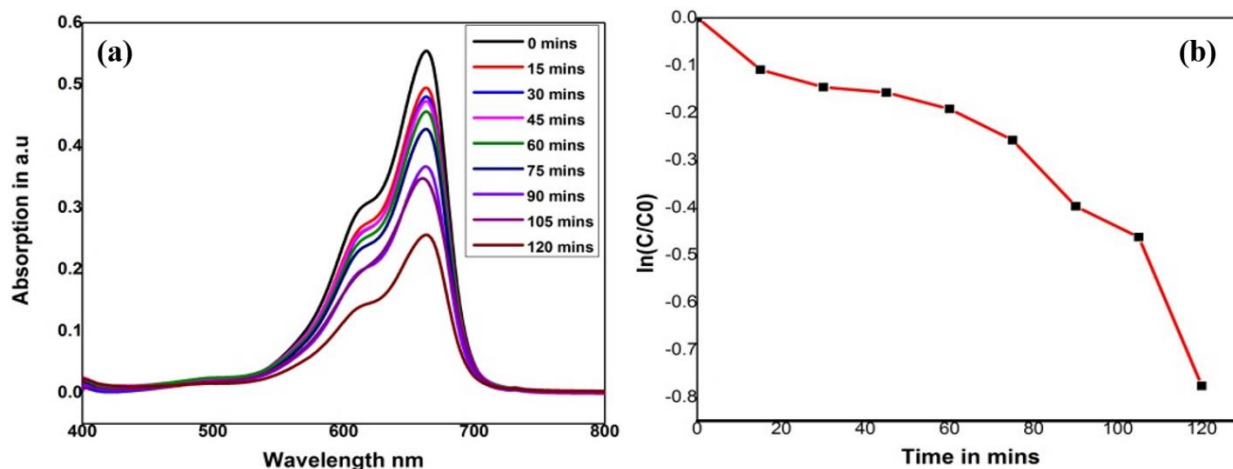


Fig. 6. (a) Absorption spectra of methylene blue aqueous solution degraded by Co_3O_4 nanoparticles. (b) Plot for degradation rate.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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