RESEARCH PAPER

# Synthesis and Characterization of $CoFe_2O_4$ Nanoparticles and Its Application in Removal of Reactive Violet 5 from Water

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ABSTRACT

Because of its unique features, including optical, magnetic, and crystalline properties, $CoFe_2O_4$ magnetic nanoparticles have gotten a lot of interest in photocatalytic process. In this work, $CoFe_2O_4$ magnetic nanoparticles is applied to effective removal of Reactive Violet 5 as a water organic pollutant. For this purpose, the $CoFe_2O_4$ magnetic nanoparticles is fabricated by a hydrothermal method at 170 °C for 12 h. Then, the crystalline structure, shape and size of the prepared $CoFe_2O_4$ nanoparticles are characterized by X-ray powder diffraction (XRD) and scanning electron microscope (SEM) methods. The performance of any photocatalyst depends on optical band gap energy of photocatalyst. So, the optical properties of the prepared $CoFe_2O_4$ nanoparticles are investigated by the UV-Vis spectroscopy. The optical band gap of $CoFe_2O_4$ magnetic nanoparticles (2.41 eV) lead to excellent photocatalytic properties of $CoFe_2O_4$ nanoparticles. The obtained results showed that the prepared $CoFe_2O_4$ nanoparticles could effectively degrade Reactive Violet 5. The 76.4% of Reactive Violet 5 was degraded in 75 minutes under visible light irradiation.

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## INTRODUCTION

Simultaneously with advance going of human social and economic life, new challenges are emerged in human life that these challenges can face significant risks to human life. One of the main problems in this regard is the problems created for the environment and its destructive effects on the all aspects of human life [1-3].

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In recent years, with increasing expansion of the paint and paper industries, various organic pollutants have increasingly entered the environment. The presence of these pollutants can cause a series problems and pose major challenge to the health of drinking water [4-8]. To eliminate these pollutants, various methods such as filtration [9, 10], electrochemical oxidation [11, 12], ozonation [13, 14], and photocatalytic process [15-17] have been applied. Among these process, the photocatalytic method has received a lot of attention because it uses free sunlight to remove organic pollutants. One of the main reasons for this attention lies in the greenness of this method. Because this method use green energy and also produces non-toxic products during the process. This becomes even more important when it is noted that that other methods often produce toxic products during the process that can subsequently cause other containments [18-20].

Photocatalysts are semiconductor-based compounds that can trigger specific chemical reactions by absorbing visible and ultraviolet light. In this regard, semiconductors can be used to degradation of water organic pollutants [21, 22]. The photocatalytic activity of semiconductors depends on the optical band gap intensively. So, providing semiconductor with desired optical properties for photocatalytic process is the vital step in the process [23, 24]. In recent years, with growing development of nanotechnology and nanoscience, various nanomaterials have contributed to the photocatalytic process in this regard. Therefore, one of the ways to improve the optical properties of semiconductors is to reduce particle size and reach nanoscale. Transition metal oxide-based semiconductors are attractive candidates that can effectively degrade pollutants [25, 26]. Ferrites with the formula $MFe_2O_4$ commonly include metal cations such as barium [27, 28], calcium [29], cobalt [30, 31], copper [32], magnesium [33], manganese [34], and nickel [35]. Ferrites are an important group of these compounds that due to their unique properties have found many applications in the degradation of various water pollutants. Sufficient optical band gap, spinel crystal structure, chemical and thermal stability, high specific surface area and attractive magnetic behavior make them excellent photocatalyst option [36]. Also, the physical and chemical properties of ferrite-based nanostructures depend on the synthesis route intensively [37].

Sneha Singh et al. prepared ruthenium doped $CoFe_2O_4$ nanostructures via sol-gel route with different amount of ruthenium. The findings revealed that the ruthenium doping improves the crystalline structure and magnetic behavior of cobalt ferrite. The photocatalytic activity of the prepared $CoRu_xFe_{2-x}O_4$ were studied against organic dyes under visible light. The obtained results confirmed that doping of ruthenium into $CoFe_2O_4$ nanomaterials make it superior photocatalyst. They reported that the excellent magnetic properties of prepared ruthenium doped cobalt ferrite lead to facilitate separation and reuse of photocatalyst [38].

In this work, $CoFe_2O_4$ nanoparticles was synthesized via hydrothermal rout at 170 °C for 12 h. The crystalline structure of prepared cobalt ferrite was investigated via XRD pattern. The purity of prepared samples was studied via EDS analysis. Also, the morphological and magnetic properties of samples were studied via SEM and VSM analysis respectively. Finally the photocatalytic activity of prepared $CoFe_2O_4$ nanoparticles was investigated via photodegradation of Reactive Violet 5 under visible light irradiation.

## MATERIALS AND METHODS

### *Precursors and materials*

All starting materials and chemicals were purchased from a Sigma-Aldrich with synthesis grade and used without further purification. FT-IR was applied for the investigation of functional groups (Nicolet Magna-550/ KBr pellets). The structural composition of nanocomposites was performed by an X-ray diffractometer device using Ni-filtered Cu Ka radiation (Philips-X'pertpro). Investigation of surface morphology was studied by SEM images (model: LEO-1455VP). The magnetic measurement of samples was obtained by VSM.

### *Preparation of $CoFe_2O_4$ nanoparticles*

First of all, $CoFe_2O_4$ nanoparticles were prepared through the hydrothermal method by adding $Co(NO_3)_2.6H_2O$ and $Fe(NO_3)_2.9H_2O$ as precursor materials at 1:1 molar ratios in DI water (60 ml). The hydrothermal synthesis procedure has been explained in detail elsewhere [39]. After that, the as-prepared sodium hydroxide solution [10 M] was added to the above mixture by dropping. Next, the whole mixture was kept in a Teflon-lined stainless



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steel autoclave for 12 h at 170 °C. Upon completion of the time reaction, the solid was separated by an external magnet and then, washed with ethanol and DI water several times. Finally, the resulting solid was dried at 65 °C overnight.

*Photocatalytic test*

Typically, a 30 ppm of Reactive Violet 5 solution was provided. Then 0.1 g of prepared $CoFe_2O_4$ nanoparticles was added to the Reactive Violet 5-containing solution and the obtained mixture was transferred to dark box under stirrer for 30 minutes. To provide the solution oxygen-saturated via the reaction, air was introduced into the prepared mixture via a pump. Then $CoFe_2O_4$ nanoparticles was filtered from the mixture, and the concentration of Reactive Violet 5 was determined through a UV-Vis spectrophotometer. To calculate the Reactive Violet 5 degradation efficiency, Eq. 1 was utilized:

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

## RESULTS AND DISCUSSION

The $CoFe_2O_4$ nanoparticles were investigated in terms of purity and structural composition by applying the XRD approach. The XRD pattern of $CoFe_2O_4$ nanoparticles is shown in Fig. 1. The observed peaks corresponded to a standard reference (JCPDS= 00-003-0864), and it confirms the formation of a single-phase with a cubic shape [40]. In addition, $CoFe_2O_4$ nanoparticles Miller's index is observed. According to the Debye-Scherrer equation (D= kλ/βcosθ), the crystallite size was measured at approximately 38 nm.

FT-IR test was used for the detection of functional groups of sample and is shown in Fig. 2. The main peak at 574 $cm^{-1}$ is related to metal-oxide vibration which is overlap with each other. Besides, two bonds at 3435 $cm^{-1}$ and 1635 $cm^{-1}$ related to the stretching and bending absorption of water, respectively.

EDS analysis was carried out to determine the elemental composition of $CoFe_2O_4$ nanoparticles (Fig. 3). EDS information shows the percentage of oxygen, iron, and cobalt in the structural composition. So, data approved the formation of $CoFe_2O_4$ nanoparticles without any impurities. Elemental mapping reveals the homogenous dispersion of O, Fe, and Co elements into their corresponding structural composition (Fig. 3).

The magnetization property of as-prepared $CoFe_2O_4$ nanoparticles was investigated with VSM analysis. The resulting data was shown in

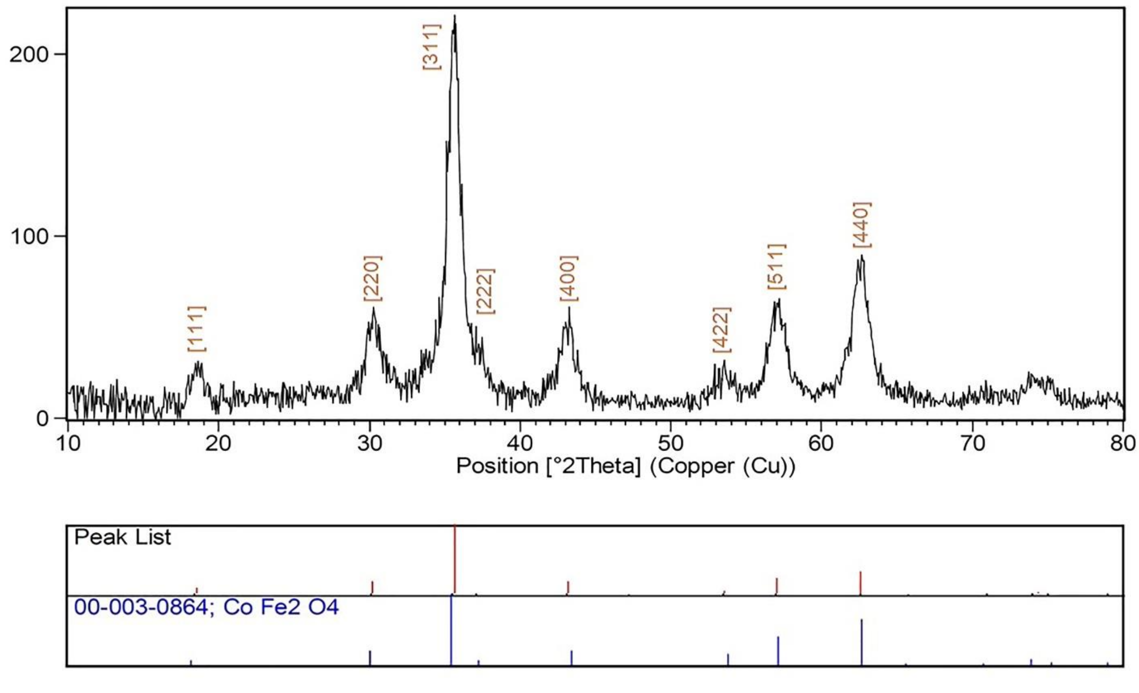


Fig. 1. The XRD graph of $CoFe_2O_4$ nanoparticles

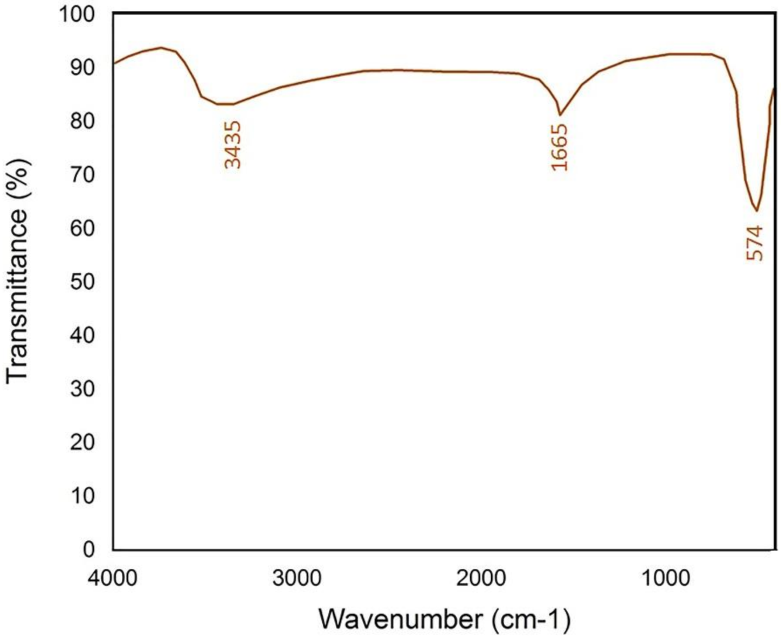


Fig. 2. FT-IR spectrum of $CoFe_2O_4$ nanoparticles

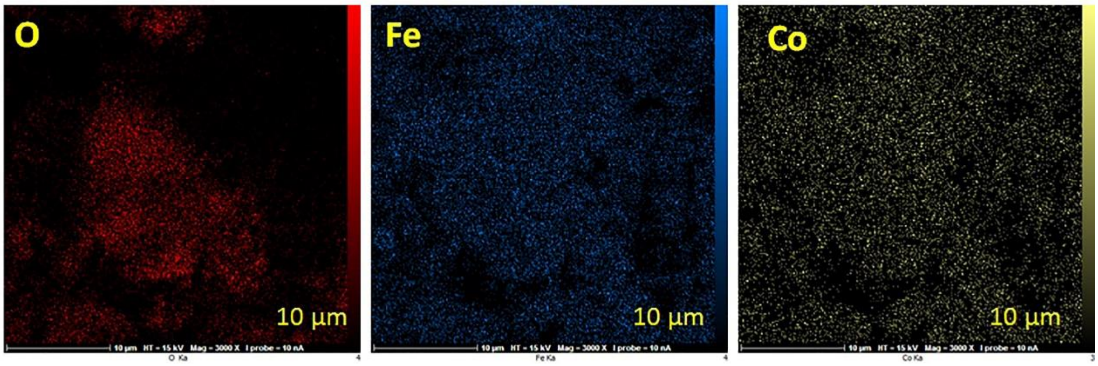


Fig. 3. The elemental mapping of $CoFe_2O_4$ nanoparticles

Fig. 4. Based on the resulting curve, the magnetic property was reported about 45 (emu/g).

The morphologies of as-prepared $CoFe_2O_4$ nanoparticles were investigated by the FE-SEM technique. FE-SEM images of the sample are shown in Fig. 5. It can be seen that the obtained average particle sizes (78.87 nm) are clearly in the nanostructure range with agglomeration.

The performance of any photocatalyst depends on optical band gap energy of photocatalyst. The UV-Vis analysis is shown in Fig. 6a. Optical band gap energy of prepared $CoFe_2O_4$ nanoparticles is shown in Fig. 6b. The optical band gap ($E_g$) was measured by the Tauc equation (Eq. 2):

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

where hν is the photon energy; α is absorbance, B is a constant attributed to the photocatalyst; and n equal either 2 or ½ for direct transition and indirect transition, respectively [41]. As well as known, the optical band gap for the absorption peak determined by extrapolating the linear portion of the $(\alpha h\nu)^n$ – hν curve to zero as shown in Fig. 7b. The band gap values of prepared $CoFe_2O_4$ nanoparticles was determined 2.41 eV.

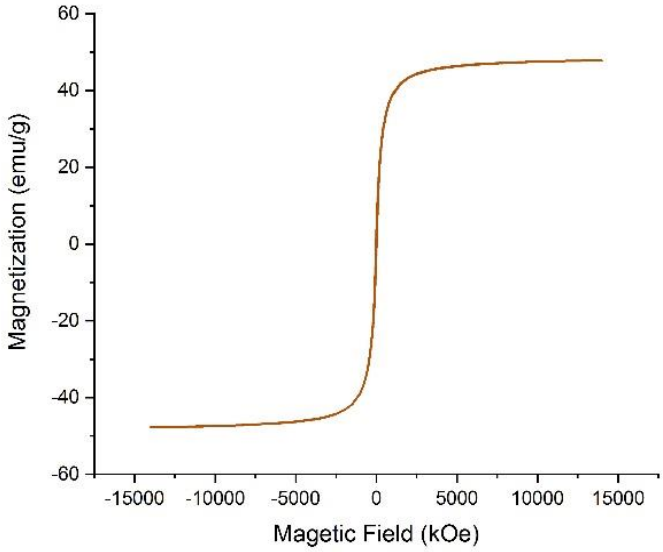


Fig. 4. VSM curve of $CoFe_2O_4$ nanoparticles

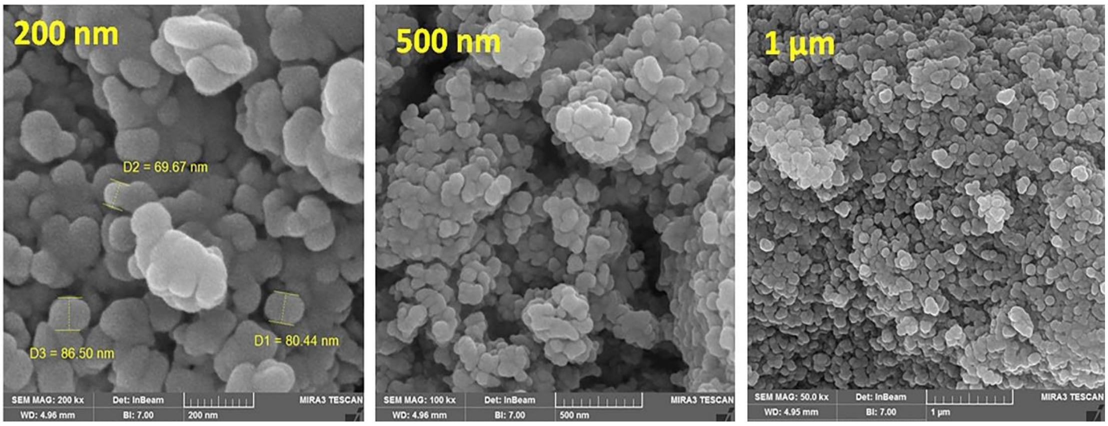


Fig. 5. FE-SEM images of as-prepared $CoFe_2O_4$ nanoparticles

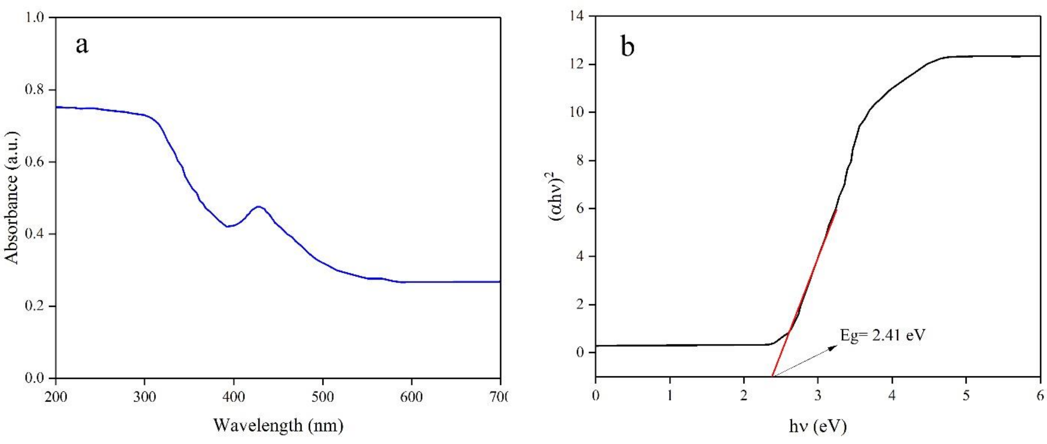


Fig. 6. a) UV-Vis analysis b) optical band gap of prepared $CoFe_2O_4$ nanoparticles

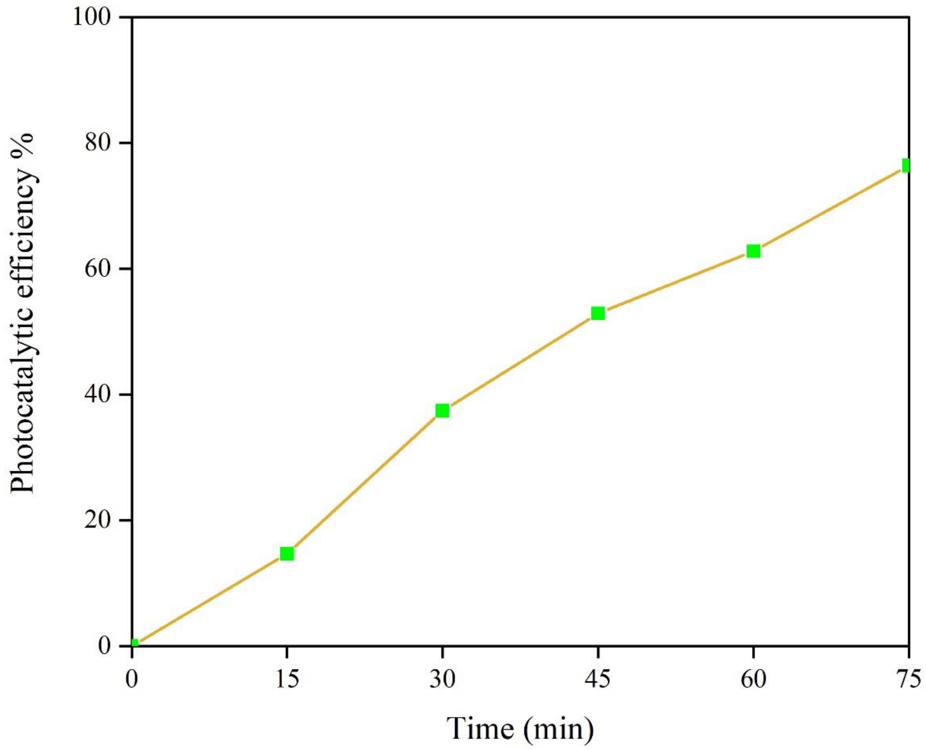

Fig. 7. Photodgradation of Reactive Violet 5 under visible light after 75 min.

Fig. 7 shows the photocatalytic activity of prepared cobalt ferrite nanoparticles against Reactive Violet 5 under visible light after 75 minutes. As well as seen, the 76.4% of Reactive Violet 5 was degraded after 75 min. $CoFe_2O_4$ have been approved to be effective photocatalysts by utilizing light energy to form electron/hole pairs on the $CoFe_2O_4$ surface. The electron/hole pairs are then facilities oxidation and reduction reaction, which lead to the make the reactive oxygen species (ROS), such as $O_{2\bullet}^-$ and •OH which then further aid in the degradation of Reactive Violet 5.

## CONCLUSION

In conclusion, the $CoFe_2O_4$ nanoparticles was applied as a new magnetic nano photocatalyst to removal of the Reactive Violet 5 from waste water. The magnetic nano photocatalyst was prepared via hydrothermal method at 170 °C for 12 h. Then, the structural properties, shape and size of prepared $CoFe_2O_4$ nanoparticles were determined via X-ray powder diffraction (XRD), scanning electron microscope (SEM), vibrating-sample magnetometer (VSM) technique. The optical was calculated 2.41 eV through Tauc equation via assistance of UV-Vis spectroscopy. Results showed that the $CoFe_2O_4$ nanoparticles could act as an excellent photocatalyst for degradation of Reactive Violet 5 from the waste water. The degradation mechanism was provided via reactive oxygen species ($O2\bullet^-$ and •OH) which then further lead to photodegradation of Reactive Violet 5.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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