JFET 27(1) (2023) 65-74

Journal of Faculty of Engineering & Technology

journal homepage: www.pu.edu.pk/journals/index.php/jfet/index

Cestrum Nocturnum Leaf Extract Assisted Biogenic Synthesis of CoO Nanoparticles and their Application in Cationic Dyes Photodegradation

M. Fatima[a], S. Rehmat*[a, b], M. Hassan*[a], M. M. Baig*[a], T. Shahzad[a] and F. Majeed[a]

[a]Department of Chemistry, University of Narowal, Narowal, Pakistan

[b]Department of Chemistry, Government College University Lahore, Lahore, Pakistan

Abstract

The rapid surge in water contamination is considered a significant global environmental challenge in the 21st century, with various sectors like industries, hospitals, domestic sewage, agriculture, livestock, and land leachates contributing to this problem. Among the various pollutants, dyes stand out as the most prevalent organic contaminants, posing harmful effects on all living organisms. To assess the photocatalytic degradation of dyes like crystal violet and methylene blue, we have successfully synthesized cobalt oxide using an extract from the leaves of the Cestrum nocturnum plant, employing the co-precipitation method. We characterized the prepared CoO using FTIR and UV-visible spectroscopy, revealing their exceptional adsorption capabilities and promising performance in removing dyes from water. The bio-synthesized CoO exhibited a 69 % degradation for CV and an impressive 97 % degradation for MB.

Keywords: Wastewater, Textile dyes, Biogenic, Co-precipitation, Photodegradation

1. Introduction

The decline in water sources and the increase in water contamination have been regarded as one of the major environmental problems of the 21st century [1]. Regular use of insufficient potable water leads to poor health, livelihood destruction, and unnecessary suffering for the poor, globally [2]. Water contains various inorganic and organic contaminants such as organic halides, pharmaceutical compounds, fertilizers, phenols, pesticides, surfactants, dyes, etc. [3]. Dyes are the most prevalent type of organic pollutants because of their huge production of synthetic dyes and their wide applications in multiple industries. Dyes are referred to as recalcitrant pollutants. They are named so because of their complex aromatic structure with delocalized electrons and conjugated double bonds which make them chemically stable and remain in the environment for longer periods causing serious health issues like liver and kidney damage, anemia, cancer, respiratory issues, neural and cardiovascular disorders, etc.[4-7]. Because of high efficiency, simplicity, strong reproducibility, and ease of use, photocatalysis is a potential advanced oxidation process (AOP) that is frequently utilized for the photodegradation of organic pollutants [8]. By using sunlight and atmospheric oxygen under ambient conditions, photocatalysis has the potential to degrade organic pollutants into harmless products [9, 10].

Several semiconducting metal oxides such as TiO_2, SnO_2, ZnO, Fe_2O_3, $SrTiO_3$, $ZnGeO_4$, Bi_2O_3, CuO, and WO_3 developed interest in researchers due to their capacity to degrade numerous organic contaminants [11, 12]. Among them, cobalt oxide (CoO) is considered a potential catalyst for photodegradation and for water oxidation that stimulates a wide band gap due to their dual

functionality from other metallic oxides. Moreover, the band gap of CoO is between 2.2 & 2.4 eV and possesses different oxidation states. Among these various possible oxidation states, CoO and Co_3O_4 have gained much consideration because of their structural and redox characteristics [13]. These nanoparticles have applications in capacitors, energy storage systems, lithium-ion batteries, field emission materials, gas sensors, solar selective absorbers, and in catalysis as well etc. [14].

Many physical and chemical methods such as the radiolytic method [15], sol-gel technique, chemical reduction approach [16], and microwave-assisted heating pathways [17] have been developed to synthesize CoO NPs but they are expensive techniques, require high temperature and pressure and use of dangerous and harmful chemicals are involved. They are not favorable to the environment. Currently, scientists are highly interested in creating metal oxide nanoparticles through the utilization of plant extracts. These extracts serve as both capping and reducing agents due to their abundance in bioactive compounds [18]. Green packaging decreases or minimizes the usage and manufacturing of substances that are high-cost, harmful to human health, and produce pollution in the environment. It is a very cheap and comfortable method because it does not require any stabilizing and capping agents [19, 20]. Samuel et al., produced CoO nanoparticles by utilization of Jumbo Muscadine following the co-precipitation method [21]. Siddique et al., synthesized nanoparticles by using the citrus medica plant leaf extract [22].

Cestrum nocturnum, a member of the Solanaceae family, harbors numerous bioactive substances including flavonoids, steroids, glycosides, triterpenes, caffeoyl derivatives, and aromatic compounds. The proteins, glucose, and other bioactive components within the leaf extract play a crucial role in capping metal oxide nanoparticles, while flavonoids stand out as powerful agents for reducing these nanoparticles [23, 24]. Moreover, limited research has been conducted for the fabrication of metal oxide NPs by using this plant extract. So, due to the above said reasons we prepared CoO through the co-precipitation method using the leaf extract of the Cestrum nocturnum plant. Then, CoO was employed to remove different cationic dyes through a photocatalysis reaction.

2. Experimental Work

2.1 Materials

The newly fresh and green leaves of Cestrum nocturnum were taken from the home plantation, Punjab, Pakistan. Cobalt nitrate hexahydrate [$Co(NO_3)_2.6H_2O$] with purity of 98 %, ethanol, sodium hydroxide (NaOH), and dyes were utilized during the whole procedure.

2.2 Equipment and apparatus

The following equipment and apparatus were used in this work: Whatman filter paper no.1, aluminum foil, centrifuge tubes, watch glasses, measuring cylinders, pipette, magnetic stirrer, conical flasks, refrigerator, beakers, weighing balance, centrifuge machine, oven, and mortar and pestle.

2.3 Methodology

2.3.1 Preparation of leaf extract

The Cestrum nocturnum plant was chosen for the current project. Firstly, the fresh, healthy, and green leaves of the plant were washed out with distilled water. The leaves were dried in the oven and then ground to a fine powder. Subsequently, 10 g of this powdered substance were combined with distilled water and subjected to heating at 80 °C for 3 h. After that, the mixture was kept at ambient temperature for cooling, and filter papers having a pore size of 11 µm were used to filter the extract as shown in Figure 1. Then, it was stored in a refrigerator for further procedure [25].

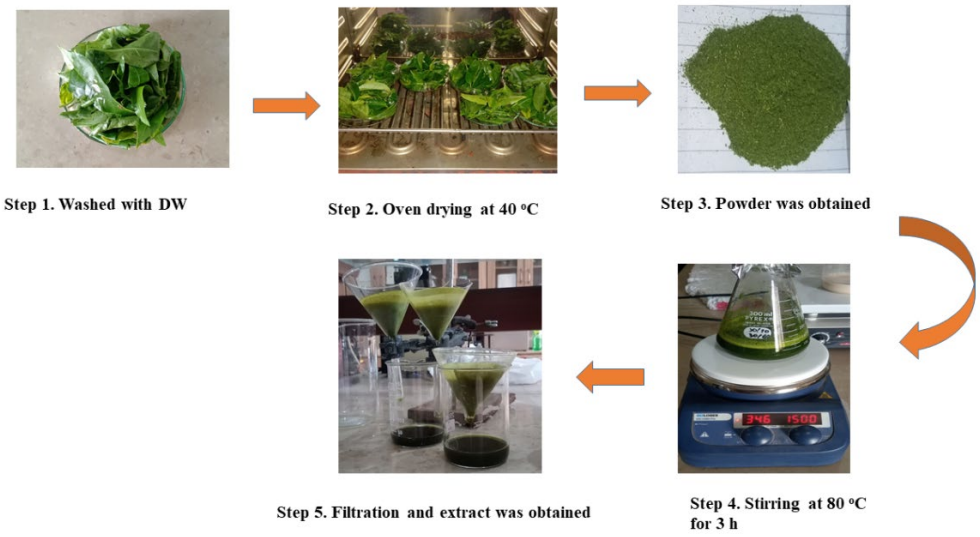

Figure 1: Procedure of leaf extract.

2.3.2 Synthesis of CoO

CoO was fabricated through the co-precipitation method. Combining 10 ml of plant extract with 50 ml of cobalt nitrate solution, the mixture was continuously agitated on a hot plate at 80 °C and then kept overnight at 25 °C. The dark brown color of the solution confirmed the formation of CoO. To eliminate the extract residue, distilled water was used for washing. The obtained product was placed at 100 °C in the oven for 8 h and then calcined for 2 h at 600 °C as shown in Figure 2. The final product was allowed to reach room temperature and then used for photocatalytic experiments and various characterization [26]. For comparison, the same procedure was followed for CoO synthesis (called pristine sample) using NaOH as a reducing agent.

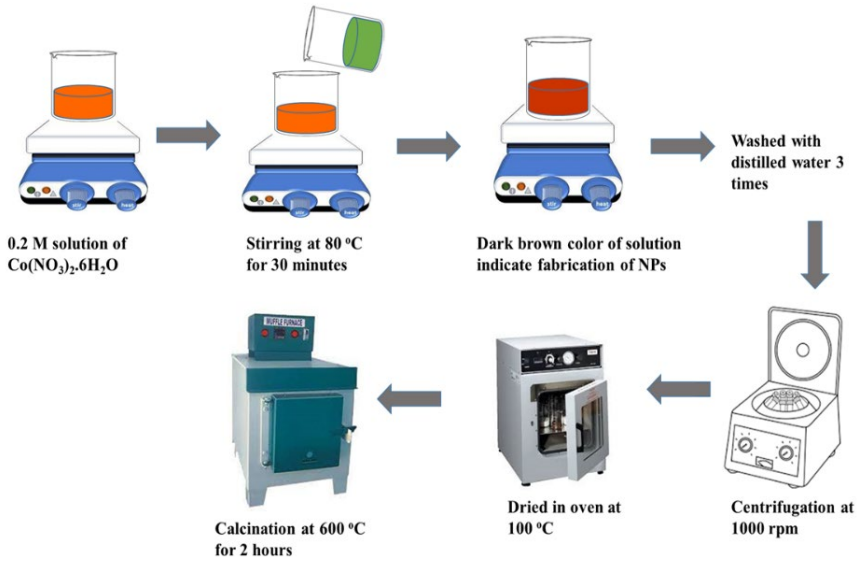

Figure 2: Synthesis of CoO using plant extract.

2.3.3 Mechanism of fabrication of CoO

The bio-reduction process is complex, involving biomolecules in the extract acting as reducing agents. Figure 3 illustrates a potential mechanism for the biosynthesis of CoO utilizing the

bioactive compounds found in C. nocturnum plant extract. Within this process, the reduction of Co^{+2} to Co^{0} occurs due to various phytochemicals present in C. Nocturnum plant extract, notably the flavonoids, serving as potent reducing agents**.** Among these compounds, is quercitrin, an essential photoactive flavonoid containing numerous -OH groups [27]. The major role in the creation of NPs is played by the –OH group [28]. These biomolecules donate electrons to metal ions, leading to their transformation into elemental metal. The resulting atom then serves as a nucleation center, enabling the creation of larger nanoparticles. During the calcination procedure, water molecules are released due to the breakage of the bond between –OH groups and metal salt, and ultimately metal oxide NPs are formed [29].

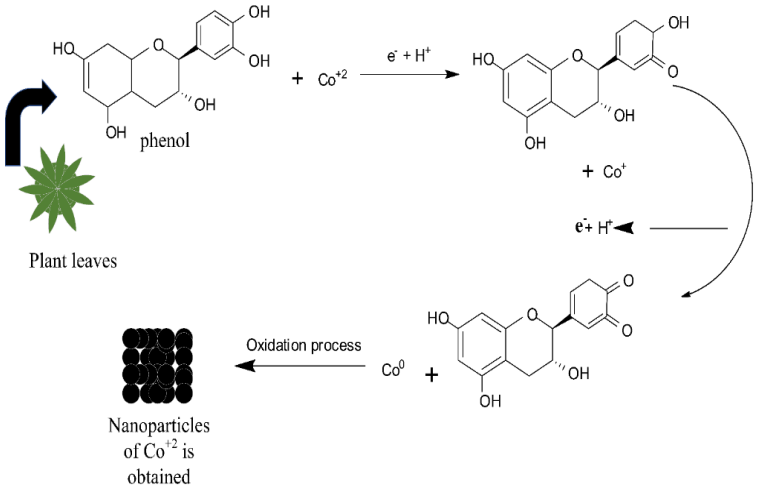

Figure 3: Mechanism of fabrication of CoO.

2.4 Characterization

2.4.1 FTIR analysis

Functional group analysis of prepared CoO was done by Fourier transform infrared (FTIR) spectroscopy using Bruker Alpha-P FTIR Spectrophotometer. The solid samples were dried in a vacuum and placed separately on Pike Miracle ATR cells to cover the ZnSe crystal surface. Afterward, they were scanned in the spectral range of 2500 cm^{-1} to 400 cm^{-1} and we collected an average of 32 scans for each sample, with a resolution of 4.0 cm^{-1}.

2.4.2 Degradation experiment

In the laboratory, we investigated the photodegradation of crystal violet (CV) and methylene blue (MB) dyes using pristine and bio-synthesized CoO. As an energy source, the experiment involved a photocatalytic chamber and visible light. To compare the photocatalytic activity of bio-synthesized CoO with pristine CoO, 20 mg of both samples were added to 30 ml of aqueous solution containing 10 ppm of the dye in different flasks. Subsequently, the solution was agitated without exposure to light for 60 minutes to evaluate the adsorption capacity of CoO. Next, we examined the photocatalytic degradation under visible light (using a 200 W Tungsten bulb) in the photocatalytic chamber. After different time intervals of light exposure, 3 ml samples were withdrawn from each solution and then centrifuged. The degraded amount of MB and CV dye in each sample was measured using a UV-visible spectrophotometer, and the decrease in absorbance indicated dye decolorization. Interestingly, we observed that longer exposure times to visible light resulted in higher levels of dye removal.

A specific formula was employed to calculate the effectiveness of catalytic removal of both dyes given in Eq. (1).

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

C_0 = Concentration of dyes at time (0)

C_t = Concentration of dyes at time (t)

3. Results and Discussion

3.1 FTIR spectra of CoO

Structural characterization of pristine and bio-synthesized CoO was performed in comparison within the range of 2500-400 cm^{-1}.The band that appeared at 656 cm^{-1} in **(b)** was assigned to the Co-O vibrations, providing confirmation of the formation of oxide, using plant extract as previously postulated [30]. As clear from the graph, two extra peaks at 833 & 1313 cm^{-1} were obtained in **(b)** but absent in **(a)**, due to the presence of phytochemicals in plant extract which help in the formation of CoO. The band's vibrations present at 833 cm^{-1} were due to the bending of aromatic compounds present in the plant extract as shown in Figure 4. The peak at 1313 cm^{-1} was due to stretching vibrations of the C-O bond of alcohols which help in the reduction of Co^{+2} into Co^{0} [22].

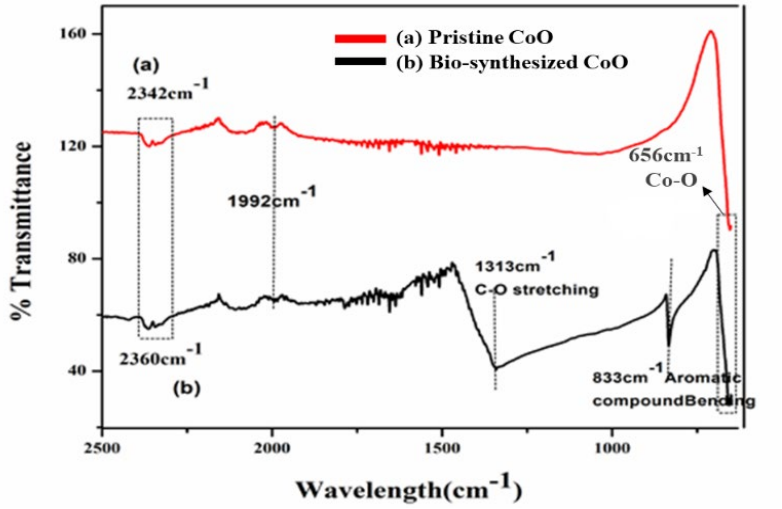

Figure 4: FTIR spectra of CoO.

3.2 Degradation procedures

3.2.1 Methylene blue

From Figure 5, it is confirmed that MB showed maximum absorbance at the wavelength of 664 nm (λ_{max}). From Figure 5 (A & B), results revealed that absorbance of MB under visible light was surprisingly reduced after 15 minutes for bio-synthesized CoO sample as compared to pristine CoO. It's clear from the above graphs (C & D) that the % degradation of MB dye by using bio-synthesized CoO using the plant extract was higher (97%) than pristine CoO (84%) under constant stirring in just 60 minutes.

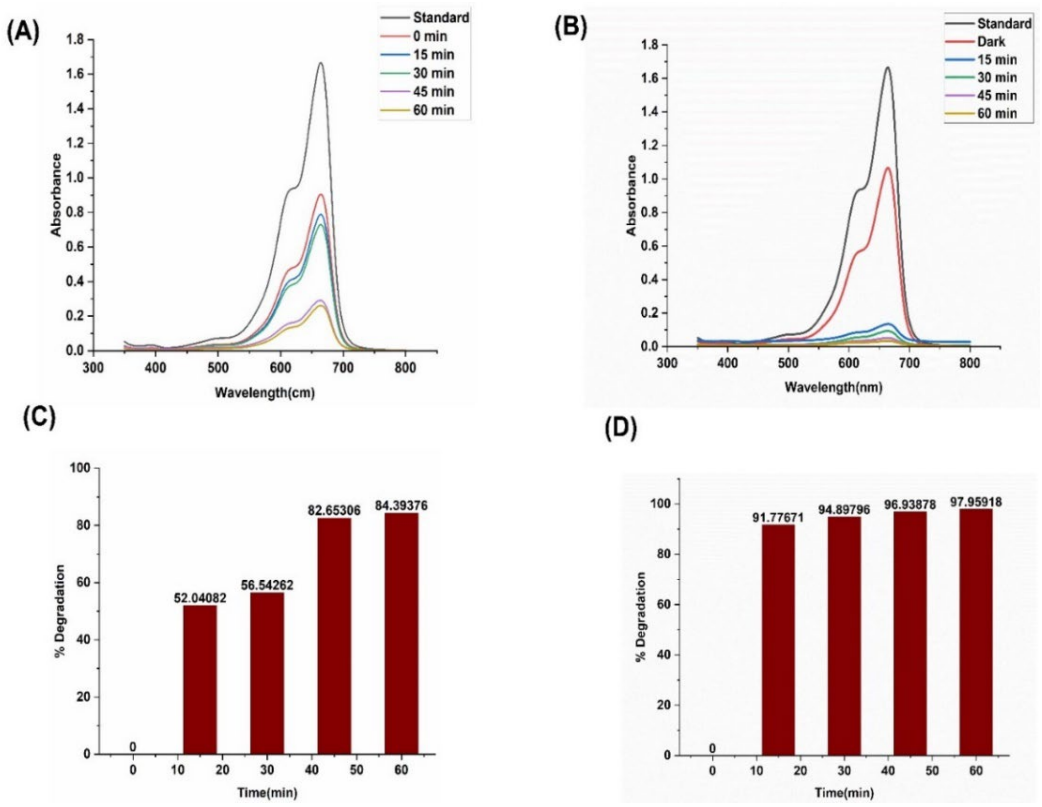

Figure 5: Illustrates the degradation of MB, with A-B showing the degradation profile, and C-D indicating the % degradation for pristine and green CoO.

3.2.2 Crystal violet

The same procedure was carried out for the photodegradation of CV, as for MB. Evaluation of the photocatalytic activity of bio-synthesized CoO (was performed in comparison with pristine CoO. From Figure 6, it is concluded that the % degradation of CV dye by using bio-synthesized CoO was higher than the percentage degradation of pristine CoO under constant stirring for 60 minutes. The % degradation of CV dye reached 61% and 69% for pristine CoO and bio-synthesized CoO, respectively.

3.2.3 Kinetic study

The degradation kinetics of dyes via photocatalysis using the CoO catalysts can be calculated by Eq. (2).

$$-\ln (C_t / C_0) = kt \quad (2)$$

The rate constant "k" represents the pseudo-first-order kinetics ($R^2 > 0.95$), determined using initial (C_o) and at time "t" (C_t) concentrations of dye. The study involved calculating the degradation kinetics of MB and CV dyes using both Pristine CoO and bio-synthesized CoO. The kinetic study revealed that CoO prepared from plant extract displayed a higher rate of removal, degrading 0.05 ppm of MB and 0.03 ppm of CV dye, in one minute. Kinetics analysis showed that the rate constant of bio-synthesized CoO was higher than pristine CoO in both cases as shown in Figure 7.

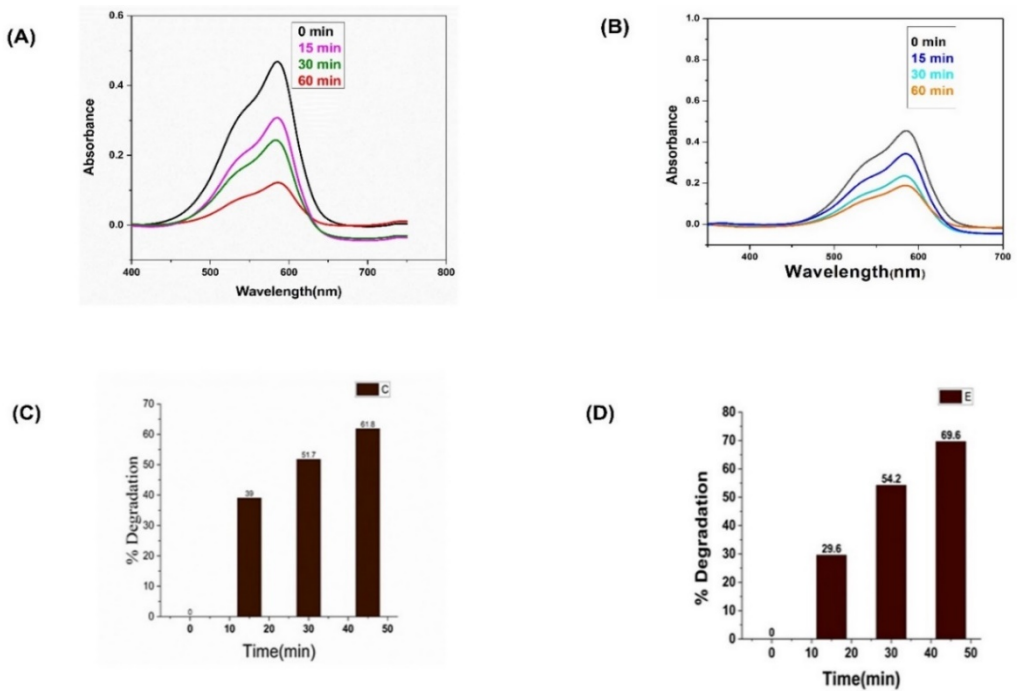

Figure 6: Depicts the photocatalytic degradation of CV dye, with A-B showing the degradation profile, and C-D indicating the % degradation of pristine and bio-synthesized CoO.

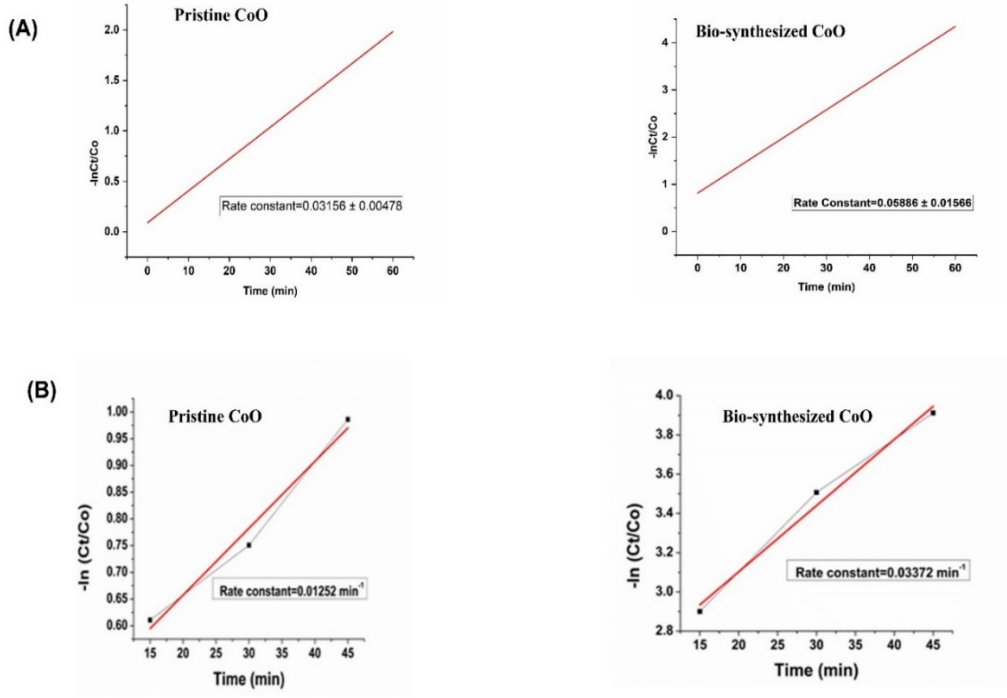

Figure 7: Illustrates the kinetic study of dye degradation, (A) depicts the MB degradation rate, (B) shows the CV degradation rate.

3.2.4 Degradation mechanism

The mechanism of photodegradation involves the creation of electron-hole pairs in the valance band and conduction band. These electrons and holes meet oxygen and water in the solution and

produce radicals which react with dyes and convert them into CO_2 and H_2O [31] as shown in Figure 8.

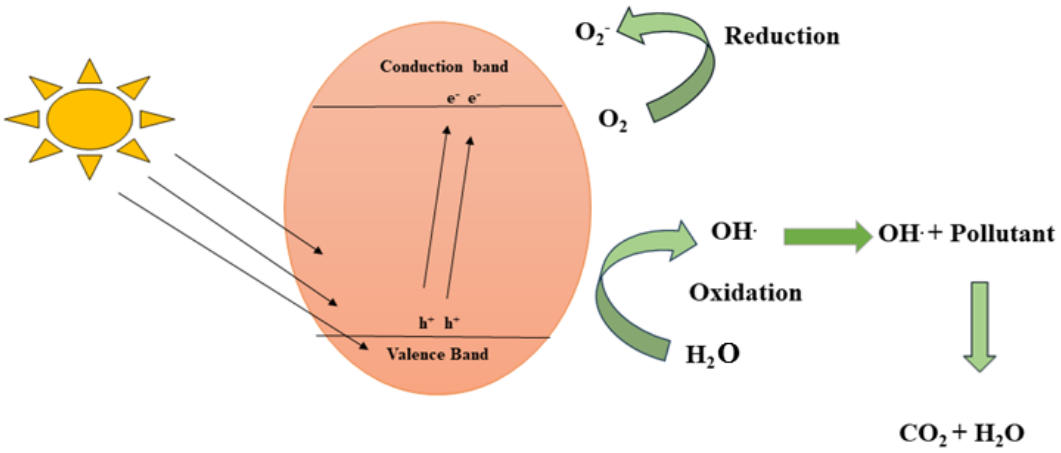

Figure 8: Mechanism of photodegradation of dyes. Reprinted with permission from Ref. [31] Copyright 2011, Elsevier.

4. Conclusions and Future Perspectives

We used an environmentally friendly and straightforward method to successfully produce CoO using an extract of Cestrum nocturnum leaves, ensuring a clean and safe approach. The synthesized CoO showed excellent, considerable, and promising results against crystal Violet and methylene blue. The percentage degradation of CV and MB were found to be 69% and 97%, respectively, in 60 minutes. The biocompatibility of CoO synthesized from leaf extracts and their efficient performance make them usable in multiple applications. In the future, this could potentially be explored for wound healing, targeted drug delivery, tissue engineering, enhanced imaging techniques, reducing the need for chemical fertilizers, crop productivity, and promoting sustainable agriculture.

Acknowledgement
The authors express their gratitude to the Department of Chemistry at the University of Narowal for their valuable contributions to this project.

References

[1]. A. Hayashi et al., "Global evaluation of the effects of agriculture and water management adaptations on the water-stressed population," *Mitig Adapt Strateg Glob Chang*, 18 (2013), 591-618.

[2]. M. A. Hanjra and M. E. Qureshi, "Global water crisis and future food security in an era of climate change," *Food Policy,* 35 (5) (2010), 365-377.

[3]. U. Qumar et al., "Photocatalysis vs adsorption by metal oxide nanoparticles," *J Mater Sci Technol,* 131 (2022), 122-166.

[4]. S. Velusamy et al., "Cover Picture: A review on heavy metal ions and containing dyes removal through graphene oxide‐based adsorption strategies for textile wastewater treatment," *Chem Rec,* 21 (7) (2021), 1569-1569.

[5]. B. Lellis et al., "Effects of textile dyes on health and the environment and bioremediation potential of living organisms," *Biotechnol Res Innov,* 3 (2) (2019), 275-290.

[6]. J. Sharma, S. Sharma, and V. Soni, "Classification and impact of synthetic textile dyes on Aquatic Flora: A review," *Reg Stud Mar Sci,* 45 (2021), 101802.

[7]. S. Pai, M. S. Kini, and R. Selvaraj, "A review on adsorptive removal of dyes from wastewater by hydroxyapatite nanocomposites," *Environ Sci Pollut Res,* 28 (2021), 11835-11849.

[8]. T. Ali et al., "Photocatalytic performance of Fe-doped TiO2 nanoparticles under visible-light irradiation," *Mater Res Express,* 4 (1) (2017), 015022.

[9]. A. Sudhaik et al., "Review on fabrication of graphitic carbon nitride based efficient nanocomposites for photodegradation of aqueous phase organic pollutants," *J Ind Eng Chem,* 67 (2018), 28-51.

[10]. M. Naushad, G. Sharma, and Z. A. Alothman, "Photodegradation of toxic dye using Gum Arabic-crosslinked-poly (acrylamide)/Ni (OH) 2/FeOOH nanocomposites hydrogel," *J Clean Prod,* 241 (2019), 118263.

[11]. M. Zhou et al., "WO3/Ag2CO3 mixed photocatalyst with enhanced photocatalytic activity for organic dye degradation," *ACS Omega,* 6 (40) (2021), 26439-26453.

[12]. A. B. Djurišić, Y. H. Leung, and A. M. C. Ng, "Strategies for improving the efficiency of semiconductor metal oxide photocatalysis," *Mater Horiz,* 1 (4) (2014), 400-410.

[13]. N. Akhlaghi, G. Najafpour-Darzi, and H. Younesi, "Facile and green synthesis of cobalt oxide nanoparticles using ethanolic extract of Trigonella foenumgraceum (Fenugreek) leaves," *Adv Powder Technol,* 31 (8) (2020), 3562-3569.

[14]. M. Hafeez et al., "Green synthesis of cobalt oxide nanoparticles for potential biological applications," *Mater Res Express,* 7 (2) (2020), 025019.

[15]. P. Rani, P. F. Siril, and R. Srivastava, "Cu nanoparticles decorated Cu organic framework based efficient and reusable heterogeneous catalyst for coupling reactions," *Mol Catal,* 433 (2017), 100-110.

[16]. A. Khan et al., "A chemical reduction approach to the synthesis of copper nanoparticles," *Int Nano Lett,* 6 (2016), 21-26.

[17]. S. Felix, R. B. P. Chakkravarthy, and A. N. Grace, *Microwave assisted synthesis of copper oxide and its application in electrochemical sensing* in *IOP Conf Ser Mater Sci Eng,* 2015. IOP Publishing.

[18]. A. Muthuvel, M. Jothibas, and C. Manoharan, "Synthesis of copper oxide nanoparticles by chemical and biogenic methods: photocatalytic degradation and in vitro antioxidant activity," *Nanotechnol Environ Eng,* 5 (2020), 1-19.

[19]. A. Muthuvel et al., "Biosynthesis of gold nanoparticles using Solanum nigrum leaf extract and screening their free radical scavenging and antibacterial properties," *Biomed Prev Nutri,* 4 (2) (2014), 325-332.

[20]. N. Loganayaki, P. Siddhuraju, and S. Manian, "Antioxidant activity and free radical scavenging capacity of phenolic extracts from Helicteres isora L. and Ceiba pentandra L," *J Food Sci Technol,* 50 (2013), 687-695.

[21]. M. S. Samuel et al., "Green synthesis of cobalt-oxide nanoparticle using jumbo Muscadine (Vitis rotundifolia): Characterization and photo-catalytic activity of acid Blue-74," *J Photochem Photobiol B: Biol,* 211 (2020), 112011.

[22]. M. Siddique et al., "Green synthesis of cobalt oxide nanoparticles using Citrus medica leaves extract: Characterization and photo-catalytic activity," *Z Phys Chem,* 235 (6) (2021), 663-681.

[23]. V. U. Ahmad et al., "A spirostanol glycoside from Cestrum nocturnum," *Phytochem,* 30 (9) (1991), 3057-3061.

[24]. Y. Mimaki et al., "Steroidal Glycosides from the Leaves of Cestrum nocturnum," *J Nat Prod,* 65 (12) (2002), 1863-1868.

[25]. J. Singh et al., "Biogenic synthesis of copper oxide nanoparticles using plant extract and its prodigious potential for photocatalytic degradation of dyes," *Environ Rres,* 177 (2019), 108569.

[26]. S. Z. Mohammadi, B. Lashkari, and A. Khosravan, "Green synthesis of Co3O4 nanoparticles by using walnut green skin extract as a reducing agent by using response surface methodology," *Surf Interfaces,* 23 (2021), 100970.

[27]. P. Kumar et al., "Efficient Catalytic Degradation of Selected Toxic Dyes by Green Biosynthesized Silver Nanoparticles Using Aqueous Leaf Extract of Cestrum nocturnum L," *Nanomater,* 12 (21) (2022), 3851.

[28]. M. Imran Din, and A. Rani, "Recent advances in the synthesis and stabilization of nickel and nickel oxide nanoparticles: a green adeptness," *Int J Anal Chem,* 2016 (2016).

[29]. S. Kaur et al., "A smart LPG sensor based on chemo-bio synthesized MgO nanostructure," *J Mater Sci Mater Electron,* 29 (2018), 11679-11687.

[30]. D. C. Onwudiwe, M. P. Ravele, and E. E. Elemike, "Eco-friendly synthesis, structural properties and morphology of cobalt hydroxide and cobalt oxide nanoparticles using extract of Litchi chinensis," *Nano-Struct Nano-Objects,* 23 (2020), 100470.

[31]. M. Y. Ghaly et al., "Treatment of highly polluted paper mill wastewater by solar photocatalytic oxidation with synthesized nano TiO2," *Chem Eng J,* 168 (1) (2011), 446-454.