Int. J. Nano Dimens., 13 (3): 335-343, Summer 2022

ORIGINAL ARTICLE

Synthesis and characterization of Cobalt Oxide nanoparticles using *Momordica charantia* and its photocatalytic activity

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Received 11 April 2022; revised 25 May 2022; accepted 05 June 2022; available online 11 June 2022

Abstract

Synthesizing plant-derived nanoparticles attract attention due to both their broad spectrum biological applications and sustainable production. This paper describes the production of Cobalt oxide nanoparticles (Co_3O_4 NPs) using M. charantia leaf extract. The UV–Vis absorption spectrum of them has peaks at 309 and 595nm. FTIR spectroscopy reveals bands at 580cm^{-1} and 667cm^{-1} and confirms the formation of Co_3O_4. The particle size was determined by XRD to be between 44.68 and 89.20nm. The Field Emission Scanning Electron Microscopy (FESEM) showed that Co_3O_4 NPs were irregular in shape and between 40 and 90nm in size. Further, the dye degrading capacity of this nanoparticle was ascertained. The dye degrading capacity of Co_3O_4 NPs exhibited was 81.50% obtained at 90 minutes of light irradiation.

Keywords: *Dye Degradation; FESEM; Green Synthesis; Momordica Charantia; Photocatalytic Activity; XRD.*

How to cite this article

Alwin David S., Doss A., Powel Praveen Pole R., Pushpabai Kumari Pushpa Rani Th., Padma Latha Reshmi R., Rajalakshmi R. Synthesis and characterization of Cobalt Oxide nanoparticles using Momordica charantia and its photocatalytic activity. Int. J. Nano Dimens., 2022; 13(3): 335-343.

INTRODUCTION

Nanomaterials are fine sized particles measured at nanoscale having efficiency in catalytic reaction, non-linear optical activity, thermal conductivity and chemical stability attributed to its increased surface area to volume ratio. Particles with diameter less than 100 nm are considered as nanomaterials and they known to contain special properties [1-4]. Nanoparticles are of paramount importance as they are known for their innumerable applications over different fields including engineering, medicine, catalysis and environmental remediation. The generation of metallic nanoparticles can be achieved through physical, chemical and biological methods [5] and these methods fall under two categories such as top-down approach and bottom-up approach [6]. The process of nanoparticle generation in top-down approach is through size reduction of the material, whereas in the case of bottom-up approach, involves self-assembly of particles of atomic size to grow to nano size particle [7].

Synthesizing nanoparticles by chemical methods require chemicals such as metallic precursors, stabilizing and reducing agents and certain physical methods as well employed such as microwave irradiation, ultrasonication, electrochemical approaches *etc*. for the size reduction of the material [8-11]. There are certain disadvantages present in the physical methods such as consuming long time to achieve thermal stability, lot of energy consumption for temperature increase around source material,

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needs a lot of space for tube furnaces [12]; in chemical methods, employ reducing agents and organic solvents become toxic to the environment [13]. As an alternative to this, the development of methods such as green synthesis of nanoparticles receive attention due to its superiority in terms of less chemical usage, production at short time, cost-effectiveness and environmentally compatible [14]. The biological synthesis of nanoparticles is mediated by bacteria, fungi, algae and plants. Plants are considered important in this regard, because they known to contain bioactive principles those reduce metal ions biologically to their elemental forms in nanoscale size and act as capping agent prevents aggregation so that the stability of the nanoparticle is maintained as well. There are a number of biogenic nanoparticles of metals such as Cu, Zn, Fe, Au, Ag, etc. with different applications in various fields are evident. However, Co_3O_4 nanoparticles are, economical as compared to other costly nanoparticles [15-16], suitable p-type semiconductors those have been widely used in super capacitors, lithium-ion batteries, photovoltaic cells, sensor systems, electrocatalysis, and photocatalytic degradation [17-18]. Among them, the photocatalytic activity exhibited by Co_3O_4 nanoparticles, degrades organic water pollutants such as dyes by oxidation process with the involvement of light is of paramount importance environmentally [19]. Dyes are considered important industrially and the waste products, in most cases, released into the environment causes pollution. These wastes products are let out to the water bodies seem to be non-biodegradable and carcinogenic, as they have not been treated to non-toxic form previously [20].

Based on this scenario, the present study reports the green synthesis of Co_3O_4 NPs by using the bitter gourd, *M. charantia*, leaf extract. Though the literature survey revealed the usage of other different plant derivatives [21], *M. charantia* assumes importance as it is shown to have anticarcinogenic, antimicrobial activity, antileukemic, antitumorous, antifungal, antiprotozoal, antiviral, antiparasitic, hypoglycemic, anti-obesity, anti-ulcer, and immune stimulant properties [22, 23]. Natural healthcare practitioners have used this to treat diabetes, high cholesterol, cancer, viral infections, and bacterial infections. Proteins, triterpenes, alkaloids, steroids, and other phenolic compounds are the important components of *M. charantia* that are responsible for the therapeutic qualities [24, 25]. As the main objective, this study attempted to assess the photocatalytic activity of Co_3O_4 NPs on the degradation of methylene blue dye.

MATERIALS AND METHODS

Chemicals

Cobalt (II) chloride hexahydrate, Methylene blue, was obtained from Merck Chemicals. All glass wares were cleaned thoroughly with tap water and rinsed with double distilled water.

Collection and processing of plant material

The fresh aerial parts of *M. charantia* were collected from Tuticorin, Tamilnadu, India and taxonomically identified in the Department of Botany, V. O. Chidambaram College, Tuticorin. The herbarium specimen was deposited at the Department of Botany, V. O. Chidambaram College, Tuticorin. Fresh leaves were excised and grounded to fine powder in a Mechanical Blender. Aqueous extraction was performed on the fine plant powder, while rest was stored for further use.

Biosynthesis of cobalt oxide nanoparticles

For the biosynthesis of cobalt oxide nanoparticles, 0.1 M $CoCl_2.6H_2O$ solution was prepared in 100 ml. Then, 25 ml of aqueous leaf extract was mixed with 75 ml of 0.1M $CoCl_2.6H_2O$ solution. This solution was heated for 2 hours at 110°C. The Co_3O_4 NPs formed were then filtered, dried, and calcinated for 2 hours at 450°C. For the synthesis of 0.2M and 0.3M Co_3O_4 NPs, various concentrations of $CoCl_2.6H_2O$ solution and freshly prepared *M. charantia* leaf extract were used.

Characterization of Co_3O_4 NPs

The characterization of synthesized cobalt oxide nanoparticles were carried out by following methods. UV-Visible spectrometer (JASCO V–650, Japan), analysis was performed by spectrophotometer at resolutions of 1nm between 200 and 800 nm. The functional groups of synthesized cobalt oxide nanoparticles falling in the range of 450 cm^{-1} to 4000 cm^{-1} were observed by FTIR (Thermo Scientific Nicolet iS5, USA). The size and purity of the cobalt oxide nanoparticles were observed powder X-ray diffraction (XRD – XPERT-PRO, INDIA). The morphology and topography of the synthesized nanoparticles were analyzed by Field Emission Scanning Electron Microscopy, with

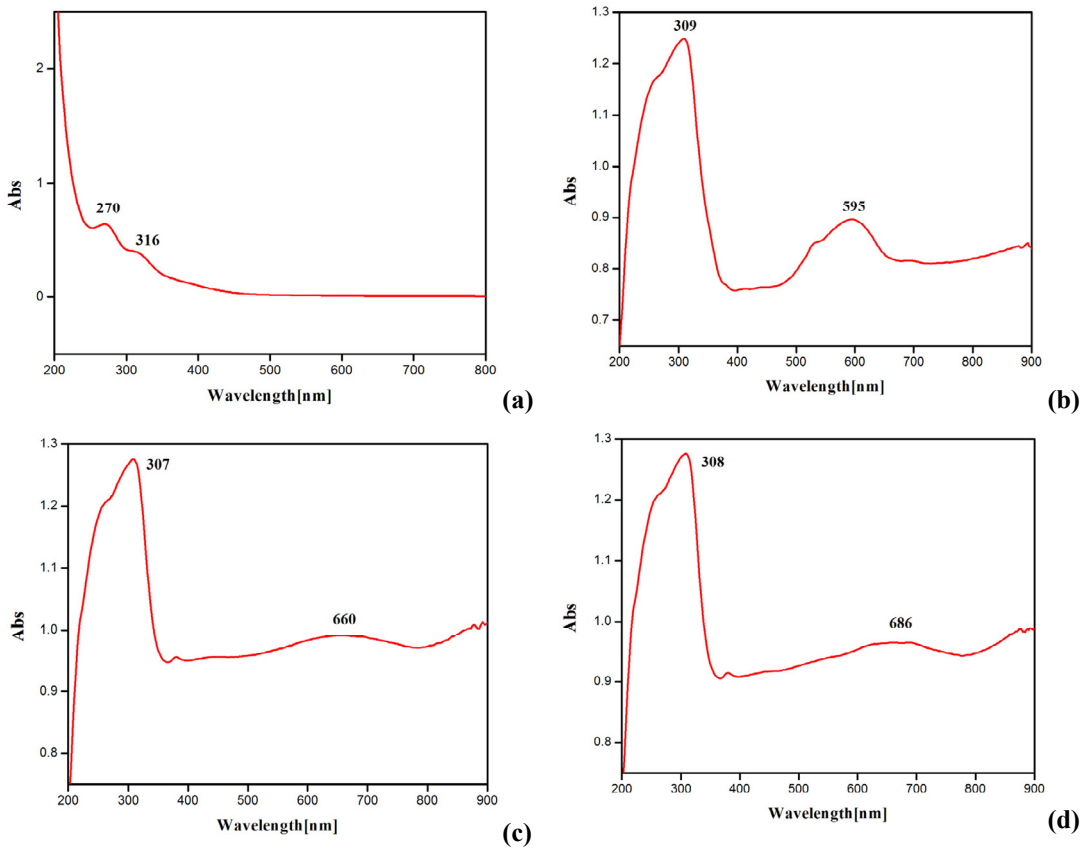


Fig. 1. UV-Visible diffuse reflectance spectroscopy (a) *M. charantia* leaf extract; (b) 0.1 M Co_3O_4 NPs; (c) 0.2 M Co_3O_4 NPs; (d) 0.3 M Co_3O_4 NPs.

EDAX (Energy Dispersive X-ray) (FESEM, TESCAN MIRA3 XMU model, Czech Republic.

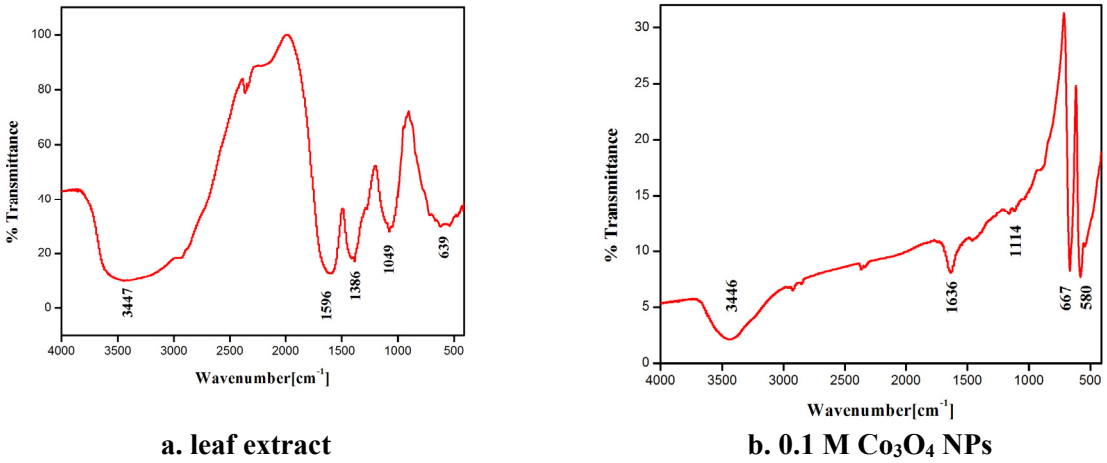
Photocatalytic degradation studies

In this experiment, 100mL of 1 x 10^{-5} M Methylene blue dye solution was placed in a beaker and exposed to direct sunshine for photocatalytic degradation. Approximately 10 mg of Co_3O_4 NPs were added to the solution and thoroughly mixed in a magnetic stirrer. The dye solutions were detached from the sorbent by centrifugation after the samples were taken at periodic intervals. By assessing dye absorbance at maximum wavelengths with a JASCO spectrophotometer and computing from the calibration curves, dye concentrations in the supernatant solutions were estimated.

RESULTS AND DISCUSSION

The UV-Visible spectrum is one of the important preliminary techniques in the characterization of synthesized nanoparticles. The UV-Visible spectrum of *M. charantia* leaf extract (Fig. 1a) reveals absorption bands at 270nm and 316nm originating due to π → π* transitions, revealing the presence of phenolic compounds responsible for the green synthesis of Co_3O_4 NPs. The UV-Visible spectra of green synthesized Co_3O_4 NPs are shown in Fig. 1 (b–d), which exhibit two absorption bands in the wavelength ranges of (i) 307–309 and (ii) 595–686 nm. The formation of Co_3O_4 NPs is confirmed by the presence of the first band near the UV region, which is attributed to the $O^{2-} \rightarrow Co^{2+}$ charge transfer process, and the second absorption band near the green region, which is attributed to the $O^{2-} \rightarrow Co^{3+}$ charge transfer.

With regard to the activity of phenolic compounds which are responsible for the synthesis of Co_3O_4 NPs, the results of this study found to be concordant with the observation (the absorption spectra present between 270-686 nm) reported by Sharma *et al.* [26], whereas in the



a. leaf extract **b. 0.1 M Co_3O_4 NPs**

Fig. 2. FTIR spectrum of crude leaf extract (a), and nanoparticles (0.1 M Co_3O_4) (b).

case of the confirmation of Co_3O_4 NPs synthesis, the present study results which is not in line with those observed (the bands formed near 300–360 and 480–530 nm) by Sharma *et al.* [26]. This may be reasoned to the effect of bioactive molecules present in the different plant material used in different studies.

FTIR analysis

The FTIR spectroscopy of *M. charantia* leaf extract (Fig. 2a) reveals well-known peaks at 639, 1049, 1386, 1596, and 3447 cm^{-1}, respectively, due to C-H out of plane bending, C–N stretching (aliphatic amines), C-H group (aromatic), C=O stretching, and O–H stretching. The majority of the infrared bands in the leaf extract seem to be due to the presence of alkaloids, triterpenes, steroids, proteins, and other phenolic compounds. The C-H group (aromatic), C=O stretching, and O–H stretching show prominent peaks at 1114, 1636, and 3446 cm^{-1} in the FTIR spectrum of Co_3O_4 NPs [27-28]. The stretching vibration peak of the carbonyl group shifted from 1596 to 1636 cm^{-1} according to the IR absorption spectra. The shift from 1596 to 1636 cm^{-1} could indicate that the product of gallic acid after the reduction of the precursor is a quinoid compound, because phenolic compounds are easily oxidised to form quinones. The stretching vibration of the metal oxygen bonds (v (Co-O) in the spinel lattice is visible in the FT-IR spectra of Co_3O_4 NPs at 580 and 667 cm^{-1} (Fig. 2b). The band at 580 cm^{-1} is due to Co^{3+} in an octahedral hole and, the latter band at 667 cm^{-1} for Co^{2+} in a tetrahedral hole [29].

X-ray diffraction analysis

The particle size of the Co_3O_4 NPs as estimated using the Scherrer formula is in the range of 44.68 - 89.20 nm. According to the Scherrer formula, the average size of the Co_3O_4 NPs is 66.05 nm. The XRD peaks at 2θ values of 19.03°, 31.33°, 36.87°, 44.88°, 59.43° and 65.25° can be attributed to the (111), (220), (311), (400), (511) and (440) crystalline planes of face-centered-cubic (FCC) structure of Co_3O_4 NPs, respectively which matched with JCPDS No. 00 - 042 - 1467. The XRD pattern (Fig. 3) clearly shows that the Co_3O_4 NPs synthesized in this study are crystalline in character [30].

Field Emission Scanning Electron Microscopy

The FESEM images (Fig. 4a & b) reveal that the product consists primarily of nano clusters with a panoramic view. However, closer inspection exposes that these nanoclusters are made up of smaller nanoparticles with irregular shapes and varying sizes. These Co_3O_4 NPs is around 40 and 90 nanometers in size.

Energy dispersive X - ray analysis

The elemental composition of the synthesized Co_3O_4 NPs was confirmed using EDAX study. Cobalt and oxygen signal peaks in the EDAX spectrum conclude that the prepared nanoparticles are Co_3O_4 NPs (Table 1; Fig. 5).

Elemental mapping

The uniform distribution of cobalt and oxygen in the Co_3O_4 NPs is acknowledged by elemental mapping (Fig. 6).

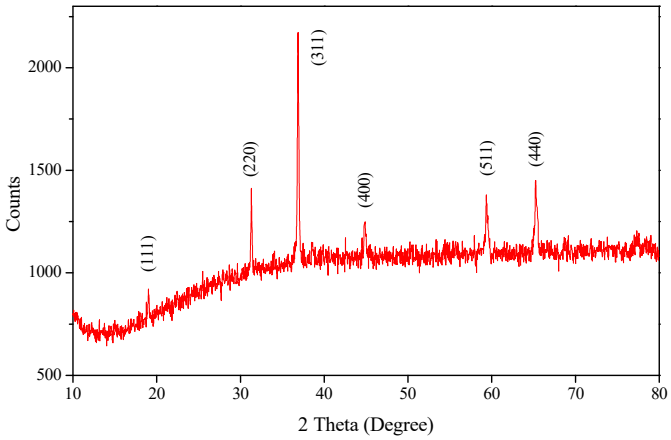
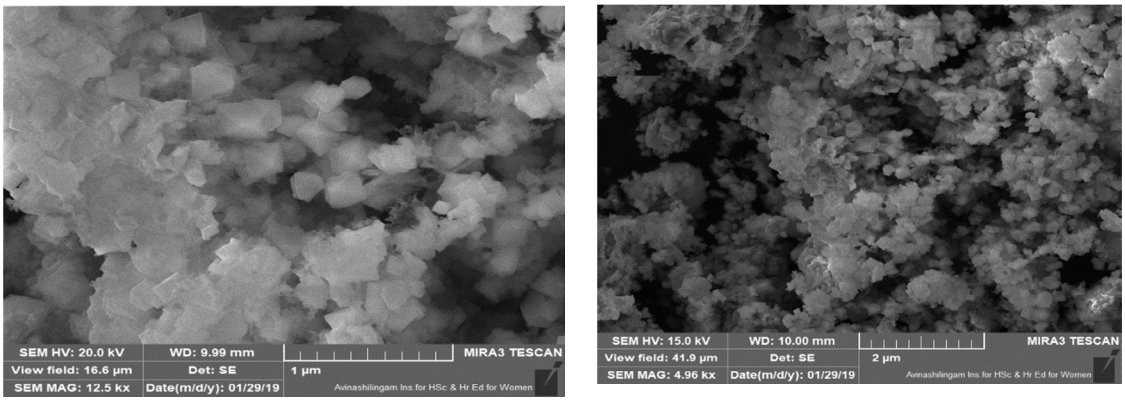


Fig. 3. XRD pattern of 0.1 M Co_3O_4 NPs.



a. 1 µm scale a. 2 µm scale

Fig. 4(a, b). FESEM image analysis of cobalt oxide nanoparticles.

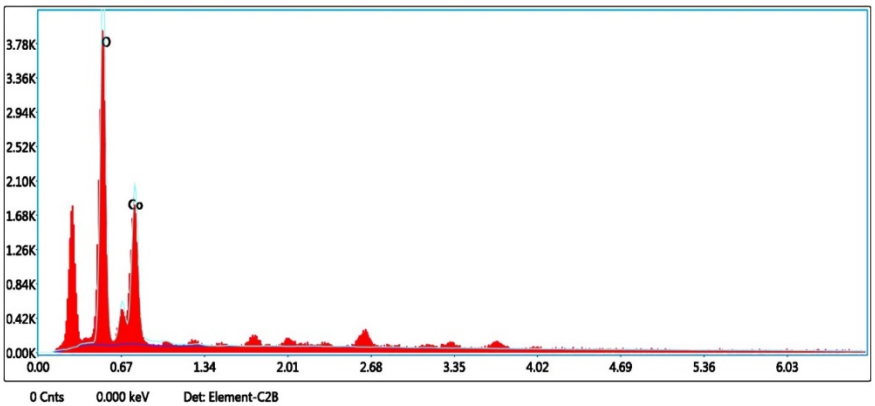


Fig. 5. EDAX spectrum of Co_3O_4 NPs.

Table 1. EDAX analysis of cobalt oxide nanoparticles.

Element	Weight %	Atomic %
Co	55.32	25.16
O	44.68	74.84
TOTAL	100.00	100.00

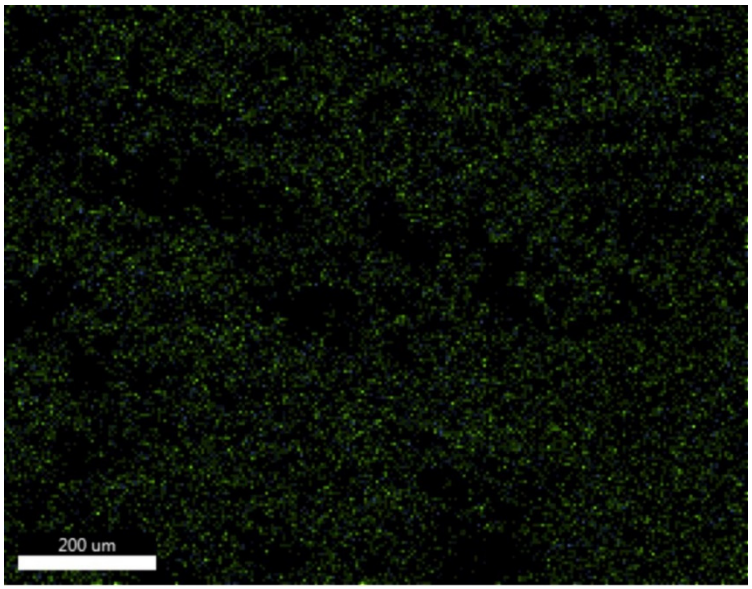


Fig. 6. Elemental map of (●) Oxygen (●) Cobalt.

Photocatalytic activity

The photocatalytic activities of the Co_3O_4 NPs were evaluated by tracing the absorbance of methylene blue dye in an aqueous solution under sun light. Possible mechanism for the degradation of methylene blue dye can be given as follows

Catalyst surface (Irradiation) $\rightarrow e^- + h^+$

$h^+ + H_2O \rightarrow OH^\bullet + H^+$

$e^- + O_2 \rightarrow O_2^{\bullet\,--}$

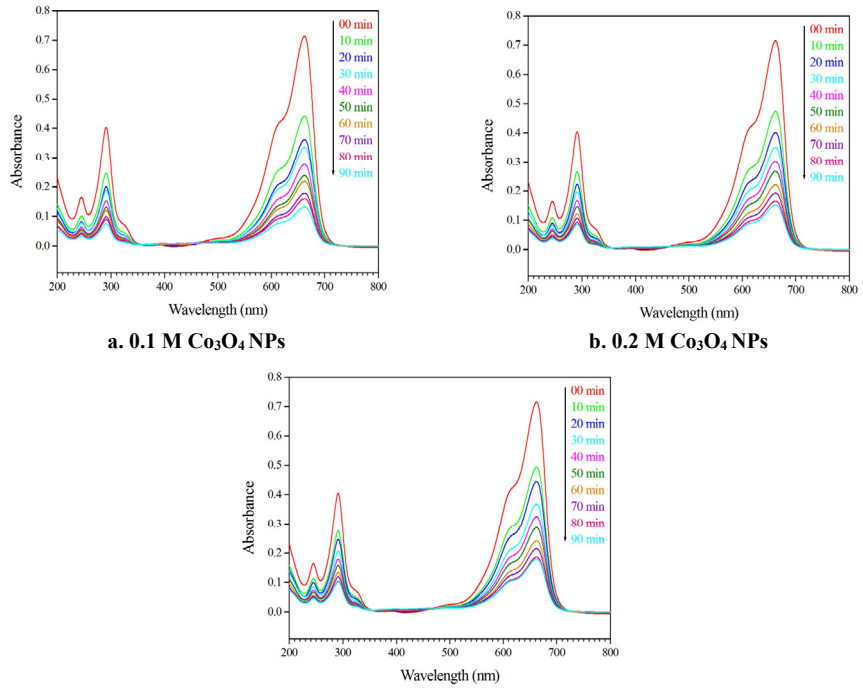
$OH^\bullet$ + dye $\rightarrow$ Oxidative product

After 90 minutes of irradiation (Fig. 7 a, b, c), the maximum absorbance of methylene blue dye at about 662 nm gradually decreased from 0.71455 to 0.13218. The percent of degradation of methylene blue dye is 81.50 percent within 90 minutes.

Percentage of degradation = $C_o - C/ C_o$ X 100
C_O = initial concentration of the dye
C = concentration of the dye at a selected time

On comparison, the results reported by different studies using green synthesized Co_3O_4 NPs on methylene blue dye degradation capacity of 79% reported to be observed in 60 minutes according to Aragaw *et al.* [31]; whereas in case of using Co_3O_4 NPs synthesized by different conventional methods, took long time on methylene blue dye degradation observed between 76 and 99% achieved in 4-8 hours which were reported by Warang *et al.* [32]. But, in general, the phytogenic Co_3O_4 NPs found to contain, visible light driven, good photocatalytic activity that degrades different dye stuffs. Saeed *et al.* [33] reported a degradation percentage of 53 for methylene orange dye achieved at 120 minutes. A dye degradation percentage of 78.5 achieved in 50 minutes for RBO_3R dye, reported by Bibi *et al.* [34].

The present study observed that initially there is an increase in the percentage of decolonization of methylene blue dye and then decreased as the time proceeds, as shown by the plot of Absorbance



a. 0.1 M Co_3O_4 NPs

b. 0.2 M Co_3O_4 NPs

c. 0.3 M Co_3O_4 NPs

Fig. 7 (a, b, c). UV-Visible spectra of MB dye degraded by different concentrations.

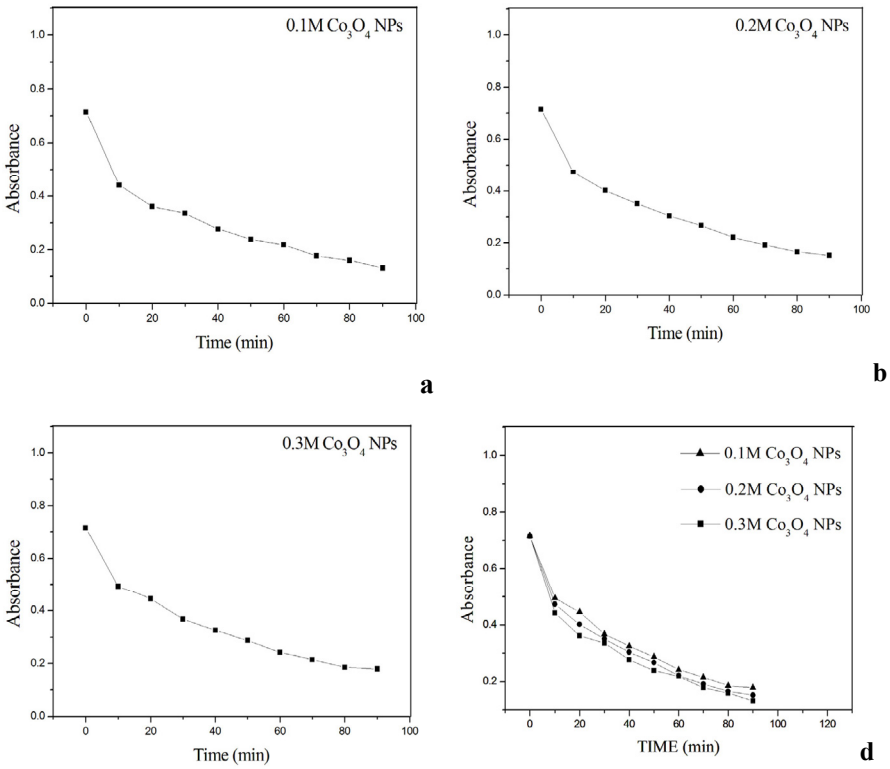


Fig. 8 (a, b, c, d). Plot of Absorbance Vs Time.

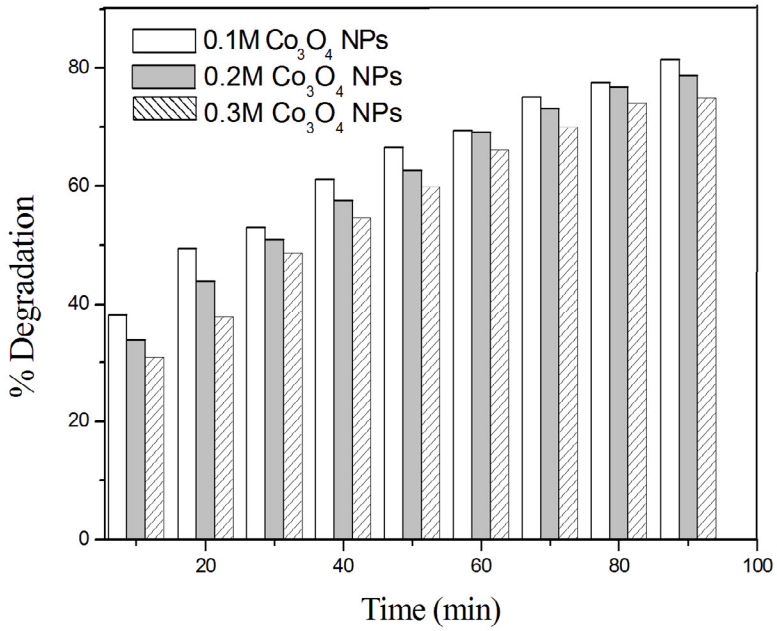


Fig. 9. Plot of percentage of degradation Vs Time.

Vs Time (Fig. 8a, b, c & d and Fig. 9). Probably, this is because as the dye concentration increases, more dye molecules become adsorbed on the catalyst surface. This masks the active site surface and allowing fewer photons to reach the catalyst surface, in turn, reduces the photocatalytic efficiency [19]. Methylene blue dye degradation by 0.1 M Co_3O_4 NPs is higher than that of 0.2 M Co_3O_4 NPs and 0.3 M Co_3O_4 NPs. The results indicate that the photocatalytic activity of 0.1 M Co_3O_4 NPs is the best among the three different concentrations. Hence, though textile dyes are considered one among the major groups of environmental pollutants and the conventional remediation methods are found to be ineffective, the present study ascertains the biogenic Co_3O_4 NPs are efficient in environmental remediation.

CONCLUSION

The biosynthesis of Co_3O_4 NPs using *M. charantia* leaf extract has been demonstrated with possible role of phenolic compounds as reducing agent. The formation of Co_3O_4 NPs is confirmed by absorption bands centered between 307-309nm and 595–686nm. The presence of a Co – O bond is revealed by two sharp bands in the FT-IR spectra at 580 and 667 cm^{-1}. The presence of highly crystalline and face-centered cubic structure Co_3O_4 NPs with an average particle size of 66.05 nm is confirmed by XRD pattern. FESEM reveals that Co_3O_4 NPs are irregular in shape, with sizes ranging from 40 to 90 nm. Of the three concentrations, 0.1M, 0.2M and 0.3M of Co_3O_4 NPs were tested, the photocatalytic activity of 0.1M Co_3O_4 NPs is observed to be the best, and it can degrade methylene blue dye by 81.50 percent in 90 minutes. In essence, (i) compared to traditional physical and chemical methods of Co_3O_4 NPs synthesis, the biological method appears to be economically smart and environmentally safe option for developing photocatalysts and (ii) the green synthesized Co_3O_4 NPs are efficient in dye degradation as well.

FUNDING

The present research work did not receive any grant from funding agencies in the Government/ Non-Government sectors.

ACKNOWLEDGMENTS

This research has no acknowledgment.

CONFLICTS OF INTEREST

The authors declare no conflict of interest

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