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## Bio Inspired Green Synthesis of $\text{Fe}_3\text{O}_4$ Magnetic Nanoparticles Using *Cassia Occidentalis* Leaves Extract and Efficient Catalytic Activity for Degradation of 4-Nitro Phenol

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### ABSTRACT

Iron oxide magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$  NPs) are often synthesized using sodium borohydride with aggregation, which is a high cost process and environmentally toxic. To address these issues,  $\text{Fe}_3\text{O}_4$  NPs were synthesized using green methods based on *Cassia occidentalis* leaves (CO). The green synthesized CO- $\text{Fe}_3\text{O}_4$  MNPs was characterized using X-ray diffraction analysis (XRD), transmission electron microscopy (TEM) images, energy-dispersive X-ray spectroscopy (EDS), FT-IR spectroscopy and vibrational sample magnetometer (VSM). The magnetic properties of CO- $\text{Fe}_3\text{O}_4$  MNPs sample clearly exhibits ferromagnetic nature with a saturation magnetization of 15.3 emu/g. Further, the catalytic properties of CO- $\text{Fe}_3\text{O}_4$  MNPs for degradation of 4-Nitrophenol (4-NP) dye in aqueous solution have been investigated by UV-visible spectroscopy. The results show that CO- $\text{Fe}_3\text{O}_4$  MNPs is an efficient catalyst for degradation of 4-NP dye than previously reported ones.

**Keywords:** CO- $\text{Fe}_3\text{O}_4$  MNPs, XRD, TEM, VSM.

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### INTRODUCTION

4-Nitrophenol (4-NP) is considered to be one of the most refractory pollutants in wastewater produced by industries. It can damage the central nervous system, liver, kidney and blood of humans and animals [1–3]. Degradation of the compound to non-dangerous product is difficult because of its high stability and low solubility in water. Its reduction product, 4-aminophenol (4-AP), is very useful and important in many applications that include analgesic and antipyretic drugs, photographic developer,

corrosion inhibitor, anticorrosion lubricant, and so on [4]. As a feasible alternative, 4-NP reduction using metal NPs has recently received much attention owing to their cost effectiveness [5–7]. So, the removal of 4-NP to alleviate sewage pollution from industries is important area of basic and applied research. Nanostructure metal oxides have attracted great attention due to their unusual physical and surface chemical and catalytic properties [8]. Among the various metal oxides, iron oxide ( $\text{Fe}_3\text{O}_4$ ) magnetic nanoparticles are of great interests because their low cost, easy synthesis, good stability, high magnetic permeability and allow for certain unique and abnormal physiochemical properties [9,10]. Because of these outstanding properties, iron oxide nanomaterials are efficient in removing organic and inorganic contaminates in water [11]. Hitherto, a number of methods such as hydrothermal process [12], sonochemical method [13], micro-emulsion technique [14], electrochemical route [15], sol-gel technique [16] and co-precipitation method [17] have been reported in the literature for synthesis of  $\text{Fe}_3\text{O}_4$  MNPs. However, most of these methods suffer from some disadvantages such as high temperature, harsh reaction conditions and long reaction times, the use of expensive, hazardous and toxic capping agents to protect the size and composition of the nanoparticles, the environmental pollution caused by utilization of organic solvents and low yields of the products. Furthermore, the green synthesis has been coming up with as a cost effective and environmentally friendly and alternative to chemical and physical methods. The previous reports suggest that some of the reports are in availability on green synthesis of iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles [18–22]. In the present study, naturally abundant *Cassia occidentalis* leaves were used for the synthesis of  $\text{Fe}_3\text{O}_4$  nanoparticles by the green route. However, in this study, we report *Cassia occidentalis* leaves extract as capping and reducing agent for synthesis of CO- $\text{Fe}_3\text{O}_4$  MNPs. Further, the synthesized CO- $\text{Fe}_3\text{O}_4$  MNPs were characterized by various microscopic and spectroscopic techniques. CO- $\text{Fe}_3\text{O}_4$  MNPs exhibit surface area and larger pore volumes. In this work, we used these CO- $\text{Fe}_3\text{O}_4$  MNPs as typical examples to study their dye adsorption ability which is injurious to the environment and to public health. Hence, we had selected 4-Nitrophenol as the absorbed dye.

## MATERIALS AND METHODS

### *Preparation of the extract*

In a 1000 mL flask, 10 g of dried leaves powdered of *Cassia occidentalis* was mixed to 500 mL double distilled water using magnetic heating stirrer at 70°C for 2 h. The obtained extract centrifuged in 7000 rpm then supernatant was kept to use further.

### *Synthesis of $\text{Fe}_3\text{O}_4$ magnetic nanoparticles*

An aqueous solution of 1 mM iron (III) chloride was used to synthesize  $\text{Fe}_3\text{O}_4$  nanoparticles. 10 mL of *Cassia occidentalis* leaves extract was added to 50 mL of earlier prepared 1 mM salt solution and following this 1.0 M NaOH solution was added until the pH was 6.0 and the formation of CO- $\text{Fe}_3\text{O}_4$  MNPs was marked by the appearance of the intense black precipitate. The resulting solution is cooled to room temperature and the attained black product was isolated by applying an external magnetic field and washed with ethanol and dried in a vacuum oven at 90 °C for 12 h and kept in a stoppered bottle for further use.

### *Reduction of 4-NP by CO- $\text{Fe}_3\text{O}_4$ nanoparticles*

In typical reduction experiments, 25 mL of the newly prepared sodium borohydride solution (0.25 M) were mixed with 25 mL of 4-NP aqueous solution (2.5 mM) and the mixture was then stirred for 1 min at room temperature. 3.0 mg of the CO- $\text{Fe}_3\text{O}_4$  MNPs were subsequently added to the mixture, which was allowed to stir at room temperature until the deep yellow solution became colorless. The reaction progress was monitored by UV–Vis spectroscopy. The yellow color of the solution gradually vanished,

indicating the formation of 4-aminophenol. After completion of the reaction, the catalyst was separated from the reaction system by brief centrifugation, washed with ethanol and dried for the next cycle.

### Characterization techniques

FT-IR measurements of *Cassia occidentalis* leaves extract prepared sample was made with Thermo Nicolet FTIR-200 thermo electron corporations at room temperature. The powder X-ray diffraction (XRD) patterns were obtained using Bruker AXS D8 advanced diffractometer at room temperature using Cu K $\alpha$  ( $\lambda = 0.15406$  nm) radiation generated at 40 kV and 30 mA with scan rate of 0.02° per min from 5 to 80°. Particle size distribution of the sample was determined by transmission electron microscopy (TEM) images were obtained using JEOL JEM-3010 machine operated at 200 kV. Magnetic properties of the samples were carried out using Lakeshore vibrational sample magnetometer (VSM-7410). The magnetic moment vs. magnetic field (M-H) measurements were performed as a function of temperature under zero-field cooled (ZFC) conditions.

## RESULTS AND DISCUSSION

### FT-IR characterization

FT-IR analysis was used to understand the existence of surface functional groups in metallic interactions. Figure 1 shows the FT-IR spectrum of CO-Fe<sub>3</sub>O<sub>4</sub> MNPs. The bands in the region of 3430 cm<sup>-1</sup> were assigned to hydroxyl stretching of poly phenols, 2880 cm<sup>-1</sup> is attributed to the C-H vibration whereas carbonyl stretching frequency peak appears at 1658 cm<sup>-1</sup>, 1398 cm<sup>-1</sup> ascribed to -C=C- stretching frequency. Moreover, the peak at 596 cm<sup>-1</sup> in Figure 1 can be attributed to Fe-O bond suggesting the formation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles [23-28].

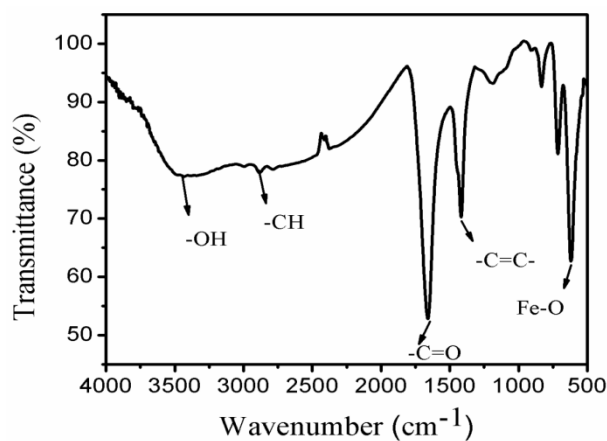


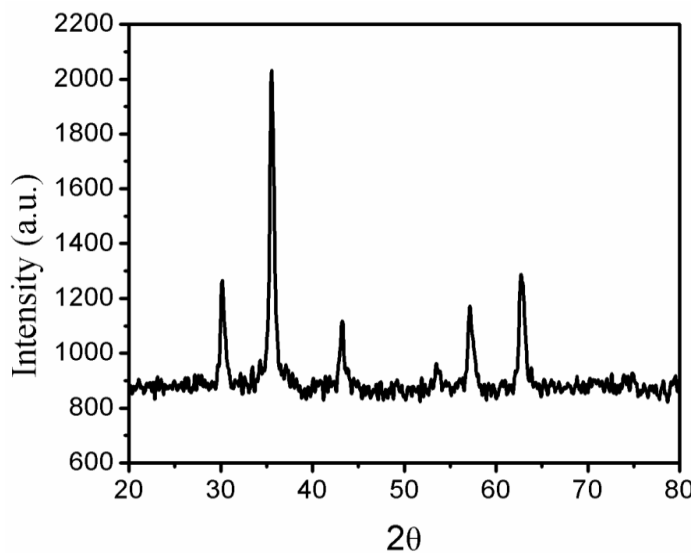
Figure 1: FT-IR spectrum of CO-Fe<sub>3</sub>O<sub>4</sub> MNPs samples

### X-ray diffraction

X-Ray Diffraction was performed to prove the phase of iron oxide nanoparticles. The peaks at 2 $\theta$  values (30.1°, 35.4°, 43.08°, 56.9° and 62.5°) correspond to the planes of (220), (311), (400), (511) and (440) of *Cassia occidentalis* leaves mediated iron oxide nanoparticles (Figure 2). The analyzed diffraction peaks were compared with the JCPDS No. (65-3107) software. The narrow peaks denote that particles were crystalline in nature. The average crystallite size of CO-Fe<sub>3</sub>O<sub>4</sub> MNPs is estimated by applying the Scherres equation as  $D=0.89 \lambda/\beta \cos\theta$  where D is the average particle size,  $\lambda$  is wave length of the CuK $\alpha$  irradiation,

60

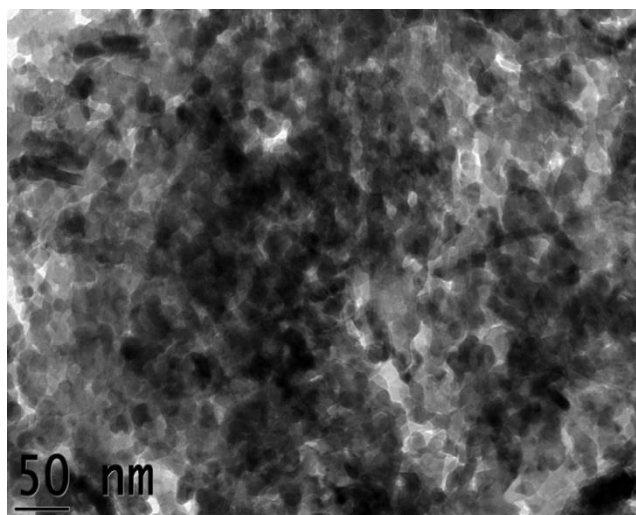
$\beta$  is the full width at half maximum intensity of the diffraction peak and  $\theta$  is the diffraction angle for the (311) peak of iron nanoparticles. The as synthesized  $\text{Fe}_3\text{O}_4$  MNPs resulted in the mean crystallite size of  $\sim 36$  nm which is very close to the TEM results.



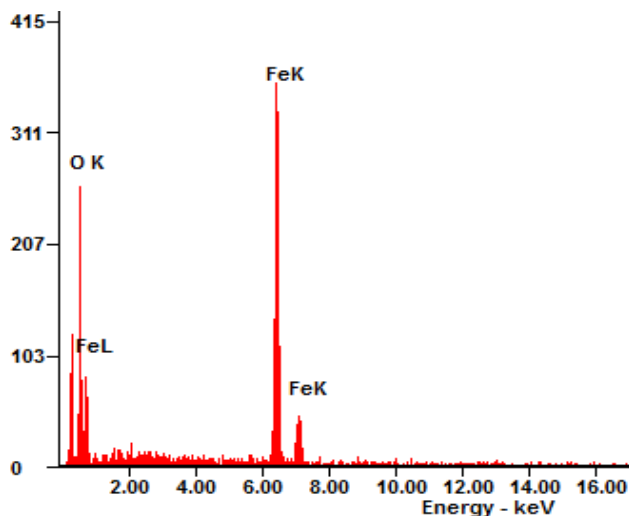
**Figure 2:** The powder XRD pattern of the CO- $\text{Fe}_3\text{O}_4$  MNPs sample.

#### ***TEM and EDX analysis***

Figure 3 revealed that the transmission electron microscope image with scale 50 nm. This TEM image shows that the green synthesized CO- $\text{Fe}_3\text{O}_4$  MNPs were nearly mono-disperse spherical shape and its size range 20 nm to 30 nm. The result of energy dispersive spectroscopy (EDX) analysis was shown in Figure 4. This confirmed the significant presence of elemental iron and oxygen.



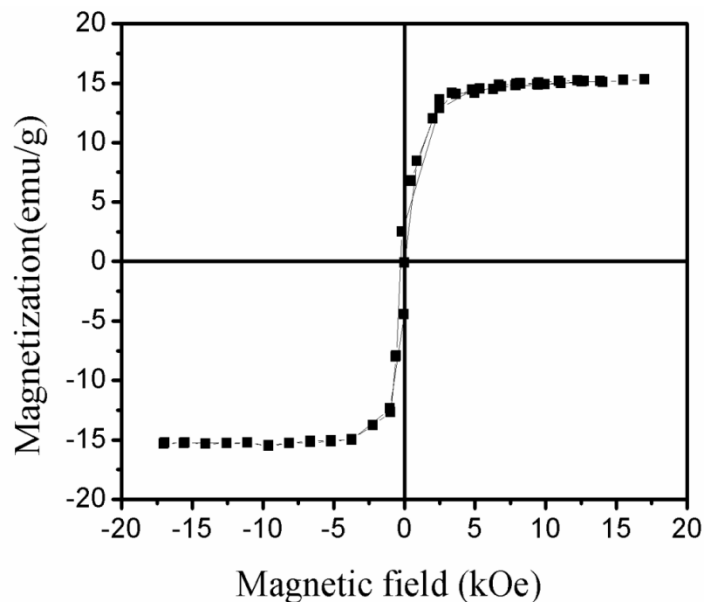
**Figure 3:** TEM images of the CO- $\text{Fe}_3\text{O}_4$  MNPs sample.



**Figure 4:** EDX analysis of the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs sample.

### *Magnetic measurements*

The magnetic properties of as synthesized CO-Fe<sub>3</sub>O<sub>4</sub> MNPs were studied using a vibrating sample magnetometer (VSM) at room temperature (Figure 5) [23-28]. The hysteresis loops indicated that the synthesized CO-Fe<sub>3</sub>O<sub>4</sub> MNPs nanoparticles were ferromagnetic behaviors. In general, particle the saturation magnetization ( $M_s$ ), intrinsic coercivity ( $H_c$ ) and remant magnetization ( $M_r$ ) are determined by VSM. The saturation magnetization ( $M_s$ ), remant magnetization ( $M_r$ ) and coercivity ( $H_c$ ) values are  $15.3 \text{ emu g}^{-1}$ ,  $2.3 \text{ emu g}^{-1}$  and 240 Oe. Herein, very small remant magnetization ( $M_r$ ), it can be easily separated with permanent magnet and re-dispersed into solution quickly without aggregation.



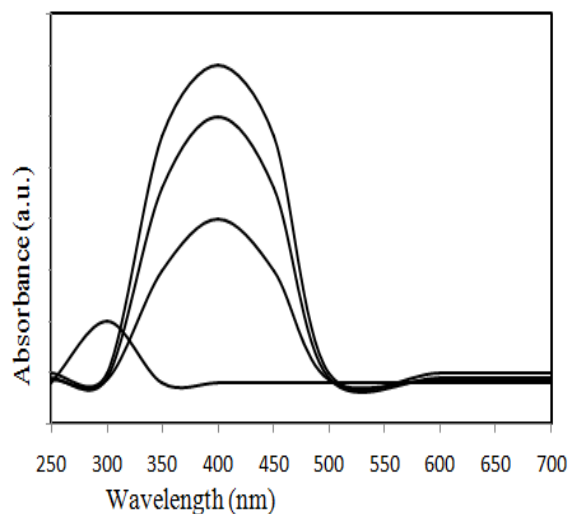
**Figure 5:** M-H hysteresis loop of the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs sample measures at 300 K.

**Activity of the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs for the reduction of 4-NP in water**

The catalytic activities of the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs was evaluated for the reduction of 4-NP in the presence of NaBH<sub>4</sub>. In the first time, the reduction of 4-NP to 4-AP with sodium borohydride (NaBH<sub>4</sub>) as reducing agent in water was used as a model system to quantitatively evaluate the catalytic activity of the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs. The conversion of 4-NP to 4-AP in aqueous medium at room temperature is very fast and simple, with the advantage of the possibility of monitoring by UV-vis spectroscopy and the results are shown in Figure 6. The Solution changed to intense yellow when NaBH<sub>4</sub> was added into 4-NP solution and showed an absorption peak at about 400 nm due to the formation of 4-nitrophenolate ions under alkaline conditions and it did not change as time passed in the absence of catalyst. After the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs was added into the solution containing 4-NP and NaBH<sub>4</sub>, the peak at 400 nm decreased and a new peak appeared at about 300 nm which corresponded to the formation of 4-AP. After about 30 min, the absorption band of 4- nitrophenolate ion at 400 nm disappeared. Thus, indicating that the catalytic reduction occurs at the surface of catalyst. There were two steps of 4-NP reduction; (i) diffusion and adsorption of 4-NP to the catalyst surfaces via-stacking interactions and (ii) electron transfer mediated by the catalyst surfaces from BH<sub>4</sub><sup>-</sup> to 4-NP. The efficiency of the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs for reduction of 4-NP was determined by comparison with other catalytic systems [29–31]. It can be concluded from Table 1 that the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs NPs had significantly higher (or) similar catalytic efficiency comparing to other catalysts.

**Table 1:** Comparison of various catalysts in the reduction of 4-nitrophenol.

Adsorbent	Time (min)	Reference
NiCo <sub>2</sub> alloy microstructure	30 min	29
Fe <sub>3</sub> O <sub>4</sub> @C@Pt	60 min	30
GA-Pt NPs	8 h	31
CO-Fe <sub>3</sub> O <sub>4</sub> MNPs	30 min	Present work

**Figure 6:** (A) UV-vis spectrophotometer spectrum of 4-Nitro phenol in the presence of NaBH<sub>4</sub> and CO-Fe<sub>3</sub>O<sub>4</sub> MNPs with different time intervals (0-30 min).

## CONCLUSION

To the best of our knowledge, we have demonstrated for the first time a novel green synthesis of CO-Fe<sub>3</sub>O<sub>4</sub> MNPs magnetic nanoparticles using *Cassia occidentalis* leaves extract. The FT-IR spectrum exposed that synthesized nanoparticles are CO-Fe<sub>3</sub>O<sub>4</sub> MNPs. The formation nanoparticles morphology of Fe<sub>3</sub>O<sub>4</sub> is confirmed by TEM and the results show that the formation spherical nanoparticles with uniform sizes about 20–30 nm. Beside, powder XRD confirms the iron nanoparticles having FCC structure. In addition the CO-Fe<sub>3</sub>O<sub>4</sub> MNPs present in higher saturation magnetization (~15.3 emu/g) and show excellent magnetic behavior. Eventually, The CO-Fe<sub>3</sub>O<sub>4</sub> MNPs adsorbent shows excellent catalytic activity for degradation of organic dyes in aqueous solution.

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