A Facile Plant Mediated Synthesis of Magnetite Nanoparticles Using Aqueous Leaf Extract of Ficus hispida L. for Adsorption of Organic Dye

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Abstract: A facile and eco-friendly method for the synthesis of magnetite nanoparticles (Fe₃O₄ NPs) via Co-Precipitation in the presence of aqueous leaf extract of Ficus hispida L. The optical, crystalline, structural morphology and magnetic behaviour of the synthesized Fe₃O₄ NPs were characterized by Ultraviolet-Visible (UV-Vis), Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). The absorption spectrum reveals the peak at 379 nm, which confirm the formations of Fe₃O₄ NPs. XRD results reveals the formation of phase pure Fe₃O₄ NPs with cubic inverse spinel structure with crystallite sizes of 11.04 nm. The FESEM and TEM images clearly show that the spherical shape of Fe₃O₄ NPs with average particles size of 10.96 nm. Bright circular rings in the selected area electron diffraction (SAED) pattern showed good crystallinity. VSM results show super paramagnetic behaviour of Fe₃O₄ NPs. The synthesized Fe₃O₄ NPs have potential to adsorption of Methylene Blue(MB)

Keywords: Magnetite nanoparticles, Green Synthesis, Ficus hispida L. leaf, Methylene Blue dye.

I. Introduction

During the past two decades metal oxide nanomaterials have attracted a great attention due to their unique optical, electrical, magnetic and electronic properties.[1] Especially, the magnetic metal oxide nanoparticles received much attention for a wide range of applications such as catalysis, biosensors, ferrofluids, high density magnetic storage media, separation and purification of biomolecules.[2-6]. Among all magnetic metal oxides, magnetite (Fe₃O₄) have emerged potential candidates for advance technological applications due to their low toxicity, biocompatibility and super paramagnetic behaviour.[7-9]. Upto now, various morphologies, such as nanorods, nanowires, nanofibers, nanoflowers, nanotubes, nano cage, and nanoparticles have been prepared for Fe₃O₄ NPs by several chemical and physical approaches such as Co-Precipitation, hydrothermal, thermal decomposition of iron carbonyls, poloyl, electrochemical deposition, spray and laser pyrolysis and sono chemical method.[10-20]. In all these methods, synthesis of Fe₃O₄ NPs uses toxic or potentially hazardous materials and requires more energy. Moreover, Fe₃O₄ NPs can easily aggregated below their critical particle size and limits their applications. Numerous approaches have been reported for the preparation of aggregate free Fe₃O₄ NPs by the use of surface capping agents such as polymers, long chain organic capping agents. However, these capping agents have a potential toxicity to the environment and public health. Therefore, it is highly desirable to develop simple bio-compatible and green methods for synthesis of Fe₃O₄ NPs. More recently, use of biomaterials such as microbial, fungi and plant extracts for the preparation of variety of metal oxide nanoparticles due to their nontoxic nature and eco-friendly. The plant extract assisted synthesis of Fe₃O₄ NPs has been quite limited and few plant extracts mediated works have been reported. For example, Tridax procumbens, Artemisia annua, leaf extract of Perilla frutescens and carica papaya and also seed extract of grape proanthocyanidin.[21-25]. So far no reports were available for synthesis of Fe₃O₄ NPs using the aqueous leaf extract of Ficus hispida L. In this work, for the first time, we have synthesized Fe₃O₄ NPs via plant mediated green synthesis approach using aqueous leaf extract of Ficus hispida L. The synthesis carried out in an aqueous medium, aqueous leaf extract of Ficus hispida L. act as reducing and capping agent for Fe₃O₄ NPs. As prepared Fe₃O₄ NPs using aqueous leaf extract of Ficus hispida L were characterized by range of spectroscopic and microscopic techniques such as UV-Visible(UV-Vis), Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), and Transmission electron microscopy (TEM) and Vibrating sample magnetometer (VSM).
II. Experimental

2.1 Materials
Analytical grade Iron (II) sulfate hepta hydrate (FeSO₄·7H₂O), Iron (III) chloride hexa hydrate (FeCl₃·6H₂O), NH₃ Methylene blue were purchased from Merck, India and used without further purification. The leaves of Ficus hispida L. were collected from forest of Chintapalli, Andhra Pradesh, India. Milli-Q water was used throughout the synthesis process.

2.2 Preparation of plant extract
The fresh leaves of Ficus hispida L. washed thoroughly with running tap water and followed by Milli-Q water to remove the dust, adhering soil and the leaves were dried under shade for 15 days and make powdered using blender. The extract was prepared by dissolving 5 grams of leaf powder in 100 mL of Milli-Q water and boiled at 60 °C for 20 min. Then the aqueous leaf extract was filtered through the Whatman NO.1 filter paper to separate out the broth and the filtrate was stored at 4 °C for the preparation of Fe₃O₄ NPs.

2.3 Synthesis of Fe₃O₄ NPs
Fe₃O₄ NPs were synthesized based on co-precipitation method in the presence of aqueous leaf extract of Ficus hispida L. as a capping agent. In a typical synthesis, 2:1 molar ratio of FeCl₃·6H₂O (0.11 g) and FeSO₄·7H₂O (0.556 g) were dissolved in a 85 mL Milli-Q water under ultrasonication in a 250 mL Erlenmeyer flask at room temperature. Then the reaction was allowed for 60 minutes to proceeded at 80 °C with constant stirring under nitrogen atmosphere. Then, 10 mL of 5 % aqueous leaf extract of Ficus hispida L. was quickly added in to the above reaction mixture and 5 mL of 25% NH₃ was added drop wise to the reaction mixture to adjust the pH = 10. The formation of Fe₃O₄ NPs was marked by the appearance of a black precipitate, and the Fe₃O₄ NPs were separated by centrifuging at 5000 rpm. The product was washed periodically with Milli-Q water and ethanol and then dried in the vacuum at room temperature.

2.4 Characterization
The absorption spectra of as prepared Fe₃O₄ NPs were recorded using a Shimadzu (2450 – SHIMADZU) spectrometer. Fourier transform-infrared (FTIR) spectra were recorded in the range of 4000-400 cm⁻¹ with a SHIMADZU-IR PRESTIGE-2 Spectrometer. Powder samples were mixed thoroughly with potassium bromide (KBr) and pressed into thin pellets. The powder X-ray diffraction (XRD) patterns were obtained by PANalytical X’pert pro dıffractometer at 0.02 degree/sec scan rate with Cu-kα radiation (1.5406 A°, 45 kV, 40 mA). Morphology of Fe₃O₄ NPs was investigated by using FESEM (FESEM, Zeiss Ultra-60) equipped with X-ray energy dispersive spectroscopy (EDS). TEM images were obtained (TEM model FEI Technai 20 U Twin) at an accelerating voltage of 120 and 200 kV. The room temperature magnetization of Fe₃O₄ NPs was measured using vibrating sample magnetometer (VSM Lakeshore 665, USA).

2.5 Batch mode adsorption studies
Batch adsorption efficiency of synthesized Fe₃O₄ NPs experiments was carried out at room temperature (300 K) using Methylene Blue as a model water pollutant. Typically, 50 mg of Fe₃O₄ NPs was mixed with 50 mL of known concentration of dye solution. The solution pH was adjusted by HCl (0.1 M) or NaOH (0.1 M). The flask was stirred for the specified time period and sample from each flask was withdrawn at the desired time of reaction. The synthesized Fe₃O₄ NPs were recovered by an external magnet. The residual dye concentration was determined by UV-Visible spectrophotometer by measuring the absorbance at a wavelength of maximum (λmax= 664 nm) absorbance of MB. The amount of adsorbed MB (q) onto synthesized Fe₃O₄ NPs was expressed in mg of dye per gram of Fe₃O₄ NPs, as shown in the Eq. (1):

\[ q = \frac{(C_0 - C)V}{m} \]  

(1)

Where q is adsorption capacity of MB in (mg g⁻¹) at time t, C₀ represents the initial MB concentration in mg L⁻¹, C is the concentration of MB in mg/L after adsorption at a time ‘t’, V is the volume of MB solution in L, and m is the mass of synthesized Fe₃O₄ NPs in grams. The adsorption phenomenon was evaluated by adsorption isotherms and kinetic models.

III. Result And Discussion
Fe₃O₄ NPs were prepared via co-precipitation method by adding a base (25% NH₃) to an aqueous mixture of Fe³⁺ and Fe²⁺ salts at a 2:1 molar ratio in presence of the aqueous leaf extract of Ficus hispida L. The phytochemicals present in the aqueous leaf extract of Ficus hispida L. are responsible for the formation of Fe₃O₄ NPs. After addition of 25% NH₃ and stirring the reaction mixture for 1 h, the colour of the reaction mixture of Fe²⁺ and Fe³⁺ salts and aqueous leaf extract of Ficus hispida L. turned from light rose red to black, which indicates the formation of Fe₃O₄ NPs. The UV-Vis absorption spectra of synthesized Fe₃O₄ NPs and aqueous

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leaf extract of *Ficus hispida* L. were depicted in Fig 2. The aqueous leaf extract of *Ficus hispida* L. has a strong absorption bands at 235 and 265 nm which are attributed to the presence of terpenoids, alkaloids, phenolic acid, flavonoids, tannins and carbohydrates in aqueous extract. The characteristic absorption band at 379 nm indicates the formation of Fe$_3$O$_4$ NPs which is primarily due to the absorption and scattering of light by Fe$_3$O$_4$ NPs. Moreover, the absence of the leaf extract peak of *Ficus hispida* L. at 235 and 265 nm in the Fe$_3$O$_4$ NPs spectrum clearly indicates terpenoids, alkaloids, phenolic acid, flavonoids, tannins and carbohydrates phytochemicals act as reducing and capping agent for synthesis of Fe$_3$O$_4$ NPs.

![Fig. 1 Images of Ficus hispida L. plant](image)

The plant *Ficus hispida* L. belongs to the Moraceae family and its leaves used as an indigenous traditional medicine [26]. The extracts of all parts of the plant have been reported to be antidiysenteric and to have activity against jaundice, hypoglycemic activity, antidiabetic activity and hemorrhage [27-29]. Leaf extract of *Ficus hispida* L. contains alkaloids, carbohydrates, proteins, amino acids, sterols, phenols, flavonoids, glycosides, saponins, and terpenes. Phytochemicals present in leaf extract of *Ficus Hispida* L. can used as reducing and capping agent for the formation of magnetite nanoparticles.

3.1 UV-Vis, XRD Characterization of as prepared Fe$_3$O$_4$ NPs

The UV-Vis absorption spectra of both aqueous leaf extract of *Ficus hispida* L. and synthesized Fe$_3$O$_4$ NPs were depicted in Fig 2. The characteristic absorption peak observed at 379 nm which indicates the formation of Fe$_3$O$_4$ NPs. As the concentration of bark extract increases, the absorption intensity of synthesized Fe$_3$O$_4$ NPs also increases.

![Fig. 2 The UV–vis spectra of 5% aqueous leaf extract of Ficus hispida L. and Fe$_3$O$_4$ NPs synthesized using 5% aqueous leaf extract of Ficus hispida L. at 350 K, and P[H] = 10 respectively.](image)
(220), (311), (400), (422), (511), (440) and (533) planes of inverse cubic spinel phase of pure Fe$_3$O$_4$ NPs (JCPDS 19-0629). The intense reflection at (311) plane in contrast to the other of planes may specify the growth direction of the nanocrystals.

The average crystallite sizes of the Fe$_3$O$_4$ NPs were estimated by the Scherrer equation

$$D = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (Eq.1)

Where $D$ is particle diameter size, $K$ is a constant equals 1, $\lambda$ is wavelength of X-ray source (0.1541 nm), $\beta$ is the full width at half maxima (FWHM) and $\theta$ is the diffraction angle corresponding to the lattice plane. The average crystallite size of Fe$_3$O$_4$ NPs according to Scherrer equation with the width of (311) plane is found to be 11.04 nm.

![Powder XRD patterns of Fe$_3$O$_4$ NPs](image)

**Fig. 3** Powder XRD patterns of Fe$_3$O$_4$ NPs synthesised using aqueous leaf extract of *Ficus hispida* L.

### 3.2 Morphology

Surface morphology as synthesised Fe$_3$O$_4$ NPs was investigated by FESEM and TEM. Representative FESEM images of Fe$_3$O$_4$ NPs depicts in Fig.4 (a-c). FESEM images of Fe$_3$O$_4$ NPs show spherical shape. Fig 5(d) show the EDS spectrum of Fe$_3$O$_4$ NPs and it shows that the presence of Fe and O atoms with 63.75%, 29.37% weight value respectively. EDS spectrum also reveals that the presence of C (6.87) % are the source of leaf extract of *Ficus hispida* L.

![FESEM images and EDS spectrum](image)

**Fig.4** (a, b and c) FESEM images and (d) Energy dispersive X-ray spectroscopy (EDS) of Fe$_3$O$_4$ NPs synthesized using aqueous leaf extract of *Ficus hispida* L.
TEM images of Fe$_3$O$_4$ NPs synthesized using aqueous leaf extract of *Ficus hispida* L. represent in Fig 5(a-b). As can be seen in Fig 5(a-b), the morphology of the Fe$_3$O$_4$ NPs was found to be cubic morphology with an average particle size 10.96 nm. It is very close to crystallite size (11.04). The selected area electron diffraction (SAED) pattern of the Fe$_3$O$_4$ NPs shows in Fig 5 (c). The ring-like diffraction pattern indicates that the as synthesized Fe$_3$O$_4$ NPs are crystalline. The size distribution histogram of synthesized Fe$_3$O$_4$ NPs shows in Fig 5 (d).

![Fig 5](a and b) Representative TEM images and (c) Selected Area Electron Diffraction (SAED) and(d) size distribution histogram of Fe$_3$O$_4$ NPs synthesized using aqueous leaf extract of *Ficus hispida* L.

### 3.3 Magnetic property

The magnetic property of synthesized Fe$_3$O$_4$ NPs was measured at room temperature by a Vibrating sample magnetometer (VSM). The magnetization curve of the synthesized Fe$_3$O$_4$ NPs is presented in Fig.6. The sigmoidal shape of VSM curve of the synthesized Fe$_3$O$_4$ NPs without hysteresis loop demonstration of super paramagnetic behaviour with the saturation magnetization (Ms) value 100 emu/g at room temperature.

![Fig. 6](The room temperature magnetization curve of Fe$_3$O$_4$ NPs synthesized using aqueous leaf extract of *Ficus hispida* L.)
3.4 FTIR characterisation of as prepared Fe\textsubscript{3}O\textsubscript{4} NPs

FTIR spectra were recorded to identify the functionalities found on aqueous leaf extract of *Ficus hispida* L. and Fe\textsubscript{3}O\textsubscript{4} NPs. As shown in Fig 7(a-b), both FTIR spectra of and Fe\textsubscript{3}O\textsubscript{4} NPs obtained from aqueous leaf extract of *Ficus hispida* L. and aqueous leaf extract of *Ficus hispida* L. extract have close similarities, with some marginal shifts in peak position, clearly indicate the presence of phytocomponents in the leaf extract act as a reducing and capping agent to the Fe\textsubscript{3}O\textsubscript{4} NPs. The phytocatalytic analysis of aqueous leaf extract of *Ficus hispida* L. based on FTIR spectrum strongly suggested the presence of flavonoids, tannins, carbohydrates and polyphenols, which were mainly responsible for the preparation of the Fe\textsubscript{3}O\textsubscript{4} NPs. The FTIR spectrum of the aqueous leaf extract of *Ficus hispida* L. exhibited characteristic stretching frequencies at 3423,2926,2360,1622,1436,1315,1054,889,781,668 cm\textsuperscript{-1}.

The characteristic band at 3423, 2926, 1622 cm\textsuperscript{-1} are ascribed to the presence of O-H group of the phenolic compound, C-H group of alkane, C=C group of terpenoids respectively. In the case of synthesized Fe\textsubscript{3}O\textsubscript{4} NPs, a there was a shift in the absorbance peak of O-H group from 3423 to 3402 cm\textsuperscript{-1} indicates O-H group of the phenolic group involved in the capping of Fe\textsubscript{3}O\textsubscript{4} NPs. There was also shift in the absorbance peak of C=C group of terpenoids from 1622 to 1628 cm\textsuperscript{-1}. Also, a characteristic additional peak formed at 584 cm\textsuperscript{-1} was observed for in the case of Fe\textsubscript{3}O\textsubscript{4} NPs which are due to characteristic stretching vibration of Fe-O. Hence, FTIR analyses were suggested that the effective capping of *Ficus hispida* L. leaf extract to synthesized Fe\textsubscript{3}O\textsubscript{4} NPs.

![FTIR spectra of (a) Fe\textsubscript{3}O\textsubscript{4} NPs synthesised using aqueous leaf extract of *Ficus hispida* L. and (b) aqueous leaf extract of *Ficus hispida* L.](image)

IV. Adsorption Studies

The time-dependent UV–vis absorption spectra of MB in the solution at time ‘t’ after the adsorption by synthesized Fe\textsubscript{3}O\textsubscript{4} NPs is shown in Fig. 8. The adsorption after 180 min there was not observed a further reduction of MB peak at 664 nm which ascribed to adsorption equilibrium was attained at the end of 180 min. Fig. 9 (a-b) is depicted that at the adsorption equilibrium (180 min), adsorption of Fe\textsubscript{3}O\textsubscript{4} NPs for MB [at 300 K, pH = 11], were found to be 91 %, 89%, 80% for concentration of 5 mgL\textsuperscript{-1}, 10 mgL\textsuperscript{-1}, 15 mgL\textsuperscript{-1} MB respectively.

![The UV–Vis absorption spectra of MB (10 mgL\textsuperscript{-1}) adsorbed by synthesized Fe\textsubscript{3}O\textsubscript{4} NPs at different time](image)
The Freundlich isotherm (Eq. 7) can be expressed as:

\[ q_e = k_f \cdot C_e^1/n \]

The correlation coefficient (R²) of the pseudo-second-order kinetic model was also investigated.

\[ t/q_t = 1/k_2 \cdot q_e^2 + (1/q_e) \cdot t \]

Where k₂ (g/mg min⁻¹) is the pseudo-second-order rate constant, qₑ (mg/g) and qₜ (mg/g) are the amounts of the MB adsorbed at time t and at equilibrium. k₁ (min⁻¹) was determined from the slope of the plot of log (qe-qt) vs t (Fig. 10(a)) and it was obtained that the correlation coefficient value (R²) is 0.9825. Moreover, to validate the kinetic of adsorption of MB pseudo-second-order kinetic model was also investigated.

\[ C_e/q_e = C_e/Q_0 + 1/Q_b L^* \]

Where \( q_e \) (mg/g) is the equilibrium adsorption capacity of MB on the adsorbent, \( C_e \) (mg/L) is the equilibrium concentration of MB in the solution, \( Q_0 \) (mg/g) is the maximum capacity of adsorbent, and \( L^* \) (L/mg) is the equilibrium constant relating to the enthalpy of process. Fig.10(c) shows that the experimental data well fitted to the Langmuir adsorption isotherm and it was found to be 16.39344mg/g maximum adsorption capacity. The correlation coefficient (R²) and equilibrium constant (bₒ) values were found to be 0.9875 and 0.98387 respectively. Besides, dimensionless factor (R_L) of the Langmuir adsorption isotherm parameter calculates using Eq. 5. The R_L value was obtained 0.179618 which is in between 0 and 1. This indicates that the adsorption process more likely proceeds through electrostatic interaction of MB and surface of synthesized Fe₃O₄ NPs, also called by chemisorption process.[31]
log$q_e = \log k_f + \frac{1}{n} \log C_e$  \hspace{1cm} (Eq.7)

$q_e\text{(mg/g)}$, is the equilibrium adsorption capacity of MB on the synthesized Fe$_3$O$_4$ NPs, $k_f\text{(mg/g)}$, 1/n are Freundlich constants representing the adsorption capacity (adsorption coefficient) at unit equilibrium concentration, and adsorption intensity. The value of Freundlich constant ‘n’ is 2.01 indicating that MB favorably adsorbed on synthesized Fe$_3$O$_4$ NPs. The correlation coefficient values of Langmuir model ($R^2$=0.9875) more close to unity than Freundlich model ($R^2$=0.8883), which indicates that the experimental data best fit with the Langmuir isotherm. The monolayer adsorption maximum adsorption capacity ($Q_0$) of synthesized Fe$_3$O$_4$ NPs was found to be 16.39344 mg/g. This figure indicates that the Ficus hispida L. assisted synthesized Fe$_3$O$_4$ NPs has comparative adsorption efficiency towards organic dyes.

![Fig.10](image)

**Table 1**: The kinetic parameters calculated from Pseudo-first and Pseudo second order kinetics model on adsorption of MB onto the synthesized Fe$_3$O$_4$ NPs

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<thead>
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<th>Parameters</th>
<th>Initial concentration of dye</th>
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<td>$q_e\text{,exp. (mg/g)}$</td>
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<tr>
<td>$k_1$ ($\text{min}^{-1}$)</td>
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<tr>
<td>$q_{\text{cal}}$ (mg/g)</td>
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<td>$R^2$</td>
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<tr>
<td>$k_2$ (g/mg/min)</td>
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<tr>
<td>$q_{\text{cal}}$ (mg/g)</td>
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</tr>
<tr>
<td>$R^2$</td>
<td>0.93528</td>
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</table>

**Table 2**: The Langmuir and Freundlich adsorption Isotherm parameters for adsorption of MB on synthesized Fe$_3$O$_4$ NPs

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Parameters</th>
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<td>$Q_0$ (mg/g)</td>
<td>$b_L$ (L/mg)</td>
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<td>0.98387</td>
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<tr>
<td>Freundlich Isoterm</td>
<td>$1/n$</td>
<td>$k_f$ (mg/L$^{1/n}$ g$^{-1}$)</td>
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<tr>
<td></td>
<td>0.497</td>
<td>7.413102</td>
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</table>

**V. Conclusion**

We have synthesized for the first time Fe$_3$O$_4$ NPs using aqueous leaves extract of Ficus hispida L. The synthesised Fe$_3$O$_4$ NPs have shown characteristic absorption band at 379 nm. XRD study of the synthesised Fe$_3$O$_4$ NPs has shown cubic inverse spinel structure with crystallite sizes of 11.04 nm. The FESEM and TEM images were clearly shown that the spherical shape of Fe$_3$O$_4$ NPs with average particles size of 10.96 nm. The
obtained magnetite nanoparticles exhibited super paramagnetic behaviour with the saturation magnetization (Ms) value 100 emu/g at room temperature. The synthesized Fe₃O₄ NPs have potential to adsorption of MB.

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### References


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