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Biogenic Synthesis of Magnetite Nanoparticles from Leaf and Latex Extract of *Calotropis gigantea* for Sunlight Mediated Photocatalytic Degradation of MB Dye

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Key words: Nanoparticles (NPs), Magnetite nanoparticles (MNPs), Green synthesis, Calotropis gigantea, UV-visible Spectroscopy, Phytochemicals, TGA-DTA, VSM and FTIR, Wastewater treatment, Photocatalysis, Dye degradation.

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Abstract

Iron oxide nanoparticles, specifically magnetite (Fe_3O_4-NPs), have become widely used and a significant area of research due to their superparamagnetism and distinctive properties. As a result, scientists are diligently looking into new uses for these nanoparticles. The choice and use of synthesis techniques are important variables that can affect the size and characteristics of the nanoparticles (NPs). The use of toxic chemicals that are absorbed on the surface of the nanoparticles has been linked to a number of negative effects of chemical synthesis methods. The Green synthesis of nanoparticles has emerged as an eco-friendly method in response to environmental concerns, giving researchers the chance to worldwide investigate the potential of various herbs for nanoparticle synthesis. Green synthesis is considered as a novel, rapid, and eco-friendly method for obtaining metallic nanoparticles (NPs). In this study, magnetite nanoparticles (Fe_3O_4-NPs) were successfully synthesized using *Calotropis gigantea* (Akanda) leaf and latex extract. The NPs were identified and characterized by visual observation, Vibrating Sample Magnetometer (VSM), UV–vis spectrophotometry, Fourier Transform Infrared (FTIR) spectroscopy, Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). The UV–vis spectrum showed board absorption without having any strong absorption peak, which confirmed the formation of Fe_3O_4-NPs. FTIR analysis showed the characteristic peak at 602cm^{-1} and 438cm^{-1}, typical for Fe–O bond. The VSM curve doesn't show any hysteresis loop which confirms the superparamagnetic behavior of Fe_3O_4-NPs. The saturation magnetization is 60emu/gm for CG leaf Fe_3O_4-NPs and 53emu/gm for CG latex Fe_3O_4-NPs. TGA confirms the high temperature stability of Fe_3O_4-NPs and the weight loss in TGA curve is due to the decomposition of organic biomolecules acting as a capping agent on the surface of the Fe_3O_4-NPs. The DTA curve shows an endothermic peak for the evaporation and decomposition of water and capping agents. The exothermic peak in DTA curve is due to the high temperature phase transition of Fe_3O_4-NPs to FeO. The photcatalytic activity of Fe_3O_4-NPs for the reduction of methylene blue (MB) dye was demonstrated by using UV–vis spectroscopy. It is expected that the synthesized Fe_3O_4-NPs could be a promising material to treat industrial wastewater via a profitable, sustainable, and eco-friendly approach.

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Introduction

Industries like textiles, leather, plastic, foods, cosmetics, pharmaceuticals, and paper-pulp industries are increasing day by day. Bangladesh has the world's largest textile industry, and they release untreated effluents containing toxic chemicals into oceans, rivers, and canals. This poses a threat to marine life, ecosystems, and biodiversity, as well as to the health of people who rely on these water sources for daily living. The organic dyes present into the effluent of these industries are one of the most serious water pollutants. These dyes have a highly complex structure, due to which they are stable and pose detrimental effects on environment. So, the complete removal of organic dyes from industrial effluents before they are released into the environment (water bodies) is necessary. The degradation of dyes is one of the major challenges in wastewater treatment. Various methods like ozonation, adsorption, electrodialysis, flocculation, etc. are used for the removal of dye from wastewater. These methods are usually costly, slow, and less efficient (Pai *et al.*, 2019).

Degradation of dyes with the help of metal or metal oxide NPs has been explored recently to develop a simple, cost-effective, and environmentally friendly method. Due to their unusual physical, surface chemical, and catalytic properties, metal/metal oxide NPs have attracted great attention (Jain *et al.*, 2005). Low cost, good stability, easy synthesis, high magnetic permeability, and certain unique physiochemical properties make iron oxide NPs of great interest among the various metal oxide NPs. Fe_3O_4-NPs (magnetite NPs) have drawn a lot of attention among the various types of iron oxide nanoparticles, including FeO, α- Fe_2O_3, β- Fe_2O_3, and γ-Fe_2O_3, due to its notable qualities, including superparamagnetic property, biocompatibility, and high surface to volume ratio (Vinayagam *et al.*, 2017). Due to their distinctive qualities, they have become indispensable in a variety of industries, including biomedicine, healthcare, agriculture and food, environmental remediation, energy, defense and aerospace, building and construction, automotive and textiles, and electronics (Dash *et al.*, 2019). Iron oxide nanomaterials are effective at removing both organic and inorganic contaminants from water because of their exceptional properties (Qiu *et al.*, 2011). The superparamagnetic behavior of magnetite nanoparticles (MNPs) is a benefit. The removal of the nanoparticles by the magnetic field after purification makes the purification procedure easier, more affordable, and secure to handle. These particles can be reused, thus making wastewater treatment more cost-effective and sustainable.

For the synthesis of Fe_3O_4 MNPs, a number of techniques have been reported in the literature, including the hydrothermal process Jiao (*et al.*, 2008), sonochemical method Islam *et al.*, (2011), micro-emulsion technique Deng, *et al.*, (2003), electrochemical route Franger *et al.*, (2004), sol-gel technique Unal *et al.*, (2010) and co-precipitation method (Prasad *et al.*, 2016).

However, the aforementioned methods are very expensive, call for expensive equipment, hazardous chemicals, and energy-intensive operating conditions. Additionally, the toxic byproducts produced by chemical methods pollute the environment (Vinayagam *et al.*, 2017).

Increasing attention is being paid to biological methods due to a number of drawbacks of chemical and physical methods. Here, environmentally friendly, cost-effective green synthesis of Fe_3O_4 MNPs has been developed as a substitute for traditional chemical and physical methods. Due to its distinctive qualities, such as the use of plant or biological resources, straightforward protocols, stable, improved NPs, and rapidness, green synthesis is currently becoming a well-known and emerging technique (Dash *et al.*, 2019). Additionally, different phytochemicals found in plant extracts function during the formation of NPs as capping and reducing agents. The rise in research publications in recent years supports the growing acceptance of plant-mediated green synthesis of NPs (Vinayagam *et al.*, 2017).

A survey of earlier literature suggests that extracts from various part of plants such as Carob extract, Carcia papaya hot water extract (Rahmani *et al.*, 2020). Azadirachtaindica hot water extract (Jagathesan *et al.*, 2018). Albiziaadianthifolia hot water extract (Taib*et al.*, 2018). Platanusorientalis L. hot water extract (Sulaiman *et al.*, 2018). Andean blackberry hot water extract (Nurbas *et al.*, 2017). Shanghai white tea (Camellia sinensis) (Kumar *et al.*, 2016). Amaranthusspinosus water extract (Shojaee *et al.*, 2016). Hordeumvulgare aqueous extract (Muthukumar*et al.*, 2015. Carob hot water extract (Awwad *et al.*, 2012). Sargassummuticum (Seaweed) (Mahdavi *et al.*, 2013). Plantain peel extract (Venkateswarlu*et al.*, 2013). Eucalyptus Globulus (Balamurugan *et al.*, 2014). Ocimumsanctum (DaturaInoxiaDas *et al.*, 2014). Centellaasiatica (Lakshmi *et al.*, 2015). Jatropha gosspifolia Karkuzhali *et al.*, 2015). Kappaphycusalvarezi (Seaweed) Yew *et al.*, (2016), etc. have been explored for the synthesis of Fe_3O_4-NPs.

The green synthesis of Fe_3O_4-NPs using the leaf and latex extract of *Calotropis gigantea* has still not been done. *Calotropis gigantea* is abundantly found in various Asian countries and locally known as "Akanda" in Bangladesh. The plant was used to treat fevers, elephantiasis, nausea, vomiting, and diarrhoea as well as skin, digestive, respiratory, circulatory, and neurological disorders. *Calotropis giganta*'s latex has been used as a treatment for cancer, arthritis, and as a snake bite remedy. Numerous plant parts are known to contain substances that serve as capping, reducing, and stabilising agents, such as alkaloids, carotenoids, flavonoids, starch, carbohydrates, essential oils, leguminvicilin, legumelin, vitamin C, oleoresin, gum resin, tannins, terpenes, and phenols (Ramesh *et al.*, 2018).

Here, we investigated for the first time how an extract from the leaf and latex of *Calotropis gigantea* was used as a capping and reducing agent for the synthesis of Fe_3O_4-NPs. Therefore, the primary goals of this study were to (a) synthesizeFe_3O_4-NPs using the leaf and latex extract from *Calotropis gigantea*, and (b) characterize Fe_3O_4-NPs using a variety of spectroscopic methods. UV-visible spectroscopy has been used to investigate the photocatalytic abilities of MNPs created by using *Calotropis gigantea* leaf and latex extracts to break down the Methylene blue (MB) dye in aqueous solutions in the presence of H_2O_2. When exposed to sunlight, the degradation reaction is photocatalytically accelerated.

Materials and methods

Materials used

Calotropis gigantea leaf and latex were collected from the Botanical Garden at University of Rajshahi campus. All reagents used to synthesize the MNPs are ferrous chloride tetrahydrate ($FeCl_2.4H_2O$), ferric chloride anhydrous (anh.$FeCl_3$) and sodium hydroxide (NaOH). Distilled water is obtained from our Bio & Nanotechnology research Laboratory. Hydrogen peroxide (H_2O_2) is used in the photocatalytic reduction of dye for wastewater treatment. The list of chemical used is given in Table-1.

Preparation of Aqueous Extract from Calotropis gigantea Leaf

Fresh leaves of CG were cut into small pieces and washed by tap water with successive washing with distilled water to remove any impurities. Extract was made by taking 20gm of leaves in a 500ml beaker containing 200mL distilled water and boiled at 60°C for 1h. After boiling, the color of the solution changed from watery to yellowish brown color and allowed to cool to room temperature. The extract was filtered using "Double Rings" filter paper to separate leaves from the extract. Finally, the resultant extract was stored at 4°C until further use.

Preparation of Aqueous Extract from Calotropis gigantea Latex

Freshly collected 5mL of CG latex was mixed with 164ml distilled water to get 3% (v/v) solution of it. The solution was stirred for 30min at 80°C. The solution was cooled and filtrated by filter paper. The filtrate was kept at 4°C for further use. The optimum concentration of 3% latex solution was prepared

because greater concentration makes it insoluble in water, and lower concentration was insufficient for nanoparticles synthesis.

Synthesis of Magnetite Nanoparticles

Green Synthesis of Calotropis gigantea Leaf and LatexFe_3O_4-NPs

In this study, magnetite (Fe_3O_4) nanoparticles are synthesized as follows: a 1:2M ratio of ferrous chloride tetra-hydrate ($FeCl_2.4H_2O$) and ferric chloride anhydrate (anh. $FeCl_3$) was dissolved in 100mL of distilled water in a 250mL beaker and heated at 80°C under mild stirring using magnetic stirrer.

For CG leaf Fe_3O_4-NPs, 50mL of CG leaf extract was added slowly after 20 minutes, and the mixture immediately turns into reddish brown color.

Similarly, for CG latex Fe_3O_4-NPs, 125mL of CG latex extract was gradually added after 20 minutes. The mixture was then stirred for 2h at 60°C. After that, the mixture was stirred for two hours at 60°C.

After that, 1M 40ml NaOH solution was added to the mixture with rate 3 mL/min and the reddish brown mixture turns into black color. This is done for allowing the magnetite precipitations uniformly. The black solution was stirred further for about 30 min at 80°C to complete the reaction and get the final black precipitate.

Centrifugation was done at 5000 rpm for 6min repeatedly for 6-7 times to wash the particle with distilled water as well as to remove the heavy biomaterials of AP leaf extract. The magnetite nanoparticles were divided into two parts. In the first part, the magnetite nanoparticles were remained in the distilled water without any additives as prepared. The stability of magnetite suspended nanoparticles in distilled water is for more than two weeks.

This solution can be used for the characterization of the nanoparticles like UV-Vis spectroscopy. In the second part, the magnetite nanoparticles after purification were dried in a vacuum oven for overnight at 70°C. The dried nanoparticles were then crushed into fine powder by mortar.

Characterization of CG-Leaf Fe_3O_4-NPs and CG-Latex Fe_3O_4-NPs

To measure the absorbance, a PG Instruments T60 UV-Visible spectrophotometer was employed. FTIR analysis was conducted using a Perkin Elmer Spectrum 100 FT-IR Spectrometer to demonstrate the presence of the biomolecules required for the synthesis of Fe_3O_4-NPs. Pellets made from powdered dry samples and potassium bromide (KBr) were examined at 400–4000 cm^{-1} wavelengths. Perkin Elmer STA 8000 is a tool used to perform TGA and DTA analyses in order to evaluate thermal stability. A vibrating sample magnetometer (VSM) is used to measure magnetic properties.

Photocatalytic Reduction of Methylene Blue dye

The photocatalytic reduction of MB (Sigma Aldrich) was performed using H_2O_2 (Merck, India) in the presence of both CG leaf and CG latex Fe_3O_4-NPs. In this experiment, 10 mL of MB (10 mg/L) was taken in two clean beakers, which contained 0.4 g/L of CG leaf and CG latex Fe_3O_4-NPs. Subsequently, 10% freshly prepared H_2O_2 was added to both solutions and put under sunlight (97,000 lx, 11:00 a.m. to 1:00 p.m.) was determined via UV–Vis spectroscopy (T60 UV-Visible spectrophotometer) (fig. 1, fig. 2). A sufficient quantity of the dye solution was transferred into a quartz cuvette cell and catalytic performance was monitored by a UV–vis spectrophotometer at a regular interval of time.

Results and discussion

Formation of Fe_3O_4-NPs

The initial identification of the formation of Fe_3O_4-NPs involved three steps: visual observation, magnetic behaviour, and UV-vis spectroscopy.

The main indicator of the formation of Fe_3O_4-NPs was the colour change of the reaction mixture from dark brown to black during the synthesis process (de JesúsRuíz-Baltazar *et al.*, 2019).

Table 1. List of chemicals used.

Chemical name	Purity/Assay	Supplier
Ferrous Chloride Tetrahydrate	98%	Smart Lab (Indoesia)
Ferric Chloride Anhydrous	98%	Sisco Research Laboratories Pvt. Ltd. (India)
Sodium Hydroxide	98.7%	Merck Specialities Pvt. Ltd. (India)
Methylene Blue	82%	Sigma Aldrich
Hydrogen Peroxide	30%	Merck Specialities Pvt. Ltd. (India)

The phytochemicals and iron salts' interaction was what caused the colour change. A ring magnet was used to separate the NPs after the resulting solution had settled, which demonstrated that Fe_3O_4-NPs had indeed formed.

Fig. 1. 10ml MB solution (10mg/L) with 10% H_2O_2 and 4mg/L MNPs.

UV-vis spectral analysis

The UV-vis spectral of both magnetite nanoparticles extracted by CG leaf and latex are shown in fig**.** 3. The characteristic absorption band at 360 nm indicates the formation of Fe_3O_4-NPs which is primarily due to the absorption and scattering of light by Fe_3O_4-NPs (Ramesh *et al.*, 2018). A continuous absorption band was observed in the 200-400 region, which is typical for iron-based NPs (Dhar *et al*, 2021), (Ahmad *et al.*, 2009). The appearance of a broad spectrum is probably due to the reaction between phytochemicals of peel extracts and iron saltsBishnoi *et al.*, 2018). Similar types of UV–vis spectra were previously reported for the Fe_3O_4-NPs synthesized using seaweed (Kappaphycusalvarezii) extract Ramesh *et al.*, (2018) and leaf extract of Calliandrahaematocephala (Sirdeshpande*et al.*, 2018). The high absorption band at 360 nm indicate the formation of a least agglomerated nanosize particles (Ahmad *et al.*, 2009). From the appearance of a broadband and the absence of any hump spectra, it may be concluded that not much size difference was present in the synthesized nanoparticles (Das *et al.*, 2020).

Fig. 2. Solution put under Sunlight.

FTIR Analysis

To investigate the vibrational characteristics and local structure, FTIR (Fourier Transform Infrared) spectra of powder samples with KBr matrices were obtained in the wavenumber range 400-4000 cm^{-1}. All of the FTIR spectra were recorded at room temperature. FTIR spectra (fig**.** 4) of synthesized magnetite nanoparticles were carried out to identify the possible biomolecules in the *Calotropis gigantea* leaf and latex extract responsible for the capping and stabilization of nanoparticles.

The broad peak from 3600 to 2800cm^{-1} is distributed to the overlapping of the O-H stretching (3600 cm^{-1}) vibration of the alcohol, polyphenols, and carboxylic groups, the C-H stretching (2900 cm^{-1}) of the alkane

groups, the NH stretching (3400 cm^{-1}) of the amine groups, and the bending vibration of the NH_2 groups (Awwad *et al.*, 2012), (Mohamed *et al.*, 2014), (Hassan *et al.*, 2017).

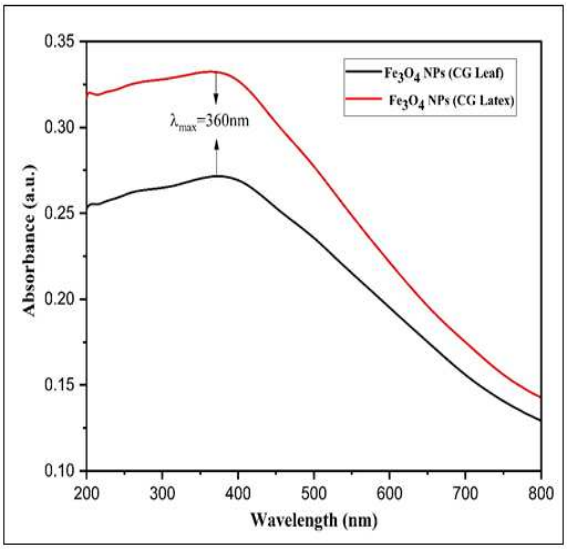

Fig. 3. UV-vis spectra of CG leaf and CG latex Fe_3O_4-NPs.

The weak absorption at 2068.97 cm^{-1} is due to the stretching vibration of C≡C bond (Gawade *et al.*, 2017). The C=O vibration from the carboxylic group (Mohamed *et al.*, 2014), and the N-H bending vibration from the amide-I Das *et al.*, (2012), group give absorption near 1600 cm^{-1}. The broad peak observed at 1633.79 $cm^{-1}$is due to the overlapping of these two vibrations, or we can say it indicates the binding of -NH-C=O to the metal nanoparticles (Harne*et al.*, 2012).

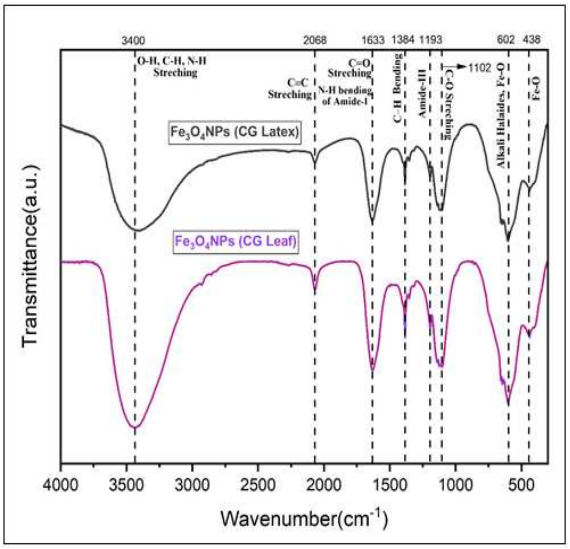

Fig. 4. FTIR curve of CG leaf and CG latex Fe_3O_4-NPs.

The band at 1384 $cm^{-1}$is attributed to the bending vibration of the C-H bond (symmetric bending of CH2 and CH3 deformations) (Mohamed *et al.*, 2014), (Chandhru*et al.*, 2022).

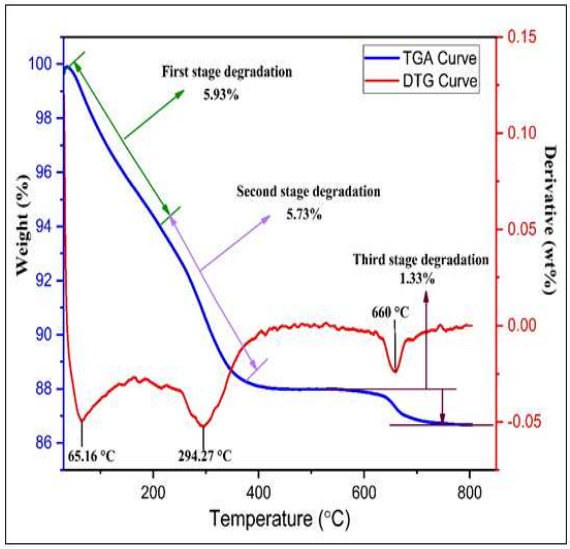

Fig. 5. TGA curve of CG leaf Fe_3O_4-NPs.

The peak observed at 1193 cm^{-1} belongs to the vibration of amide-III. The characteristic band of amide-II seemed to have merged with the intense band of amide-I (1633 cm^{-1}) Mohamed *et al.*, 2014.

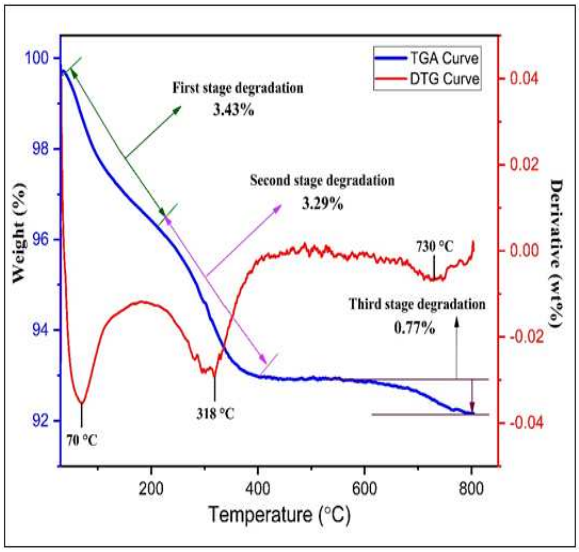

Fig. 6. TGA curve of CG latex Fe_3O_4-NPs.

The C-O stretching of ethers and carboxylic acids, the C-O-C stretching vibration of the aromatic ring, and the C-N stretching of the amine group combine to give a broad peak at 1102 cm^{-1} (Mohamed *et al.*, 2014), (Das *et al.*, 2012).

The small peaks around 650 cm^{-1} are due to the

vibration of alkali halides. The absorption observed at 602cm^{-1} and 438cm^{-1} is attributed to the vibration of the Fe-O bond (Awwad *et al.*, 2012), (Dhar*et al.*, 2021).

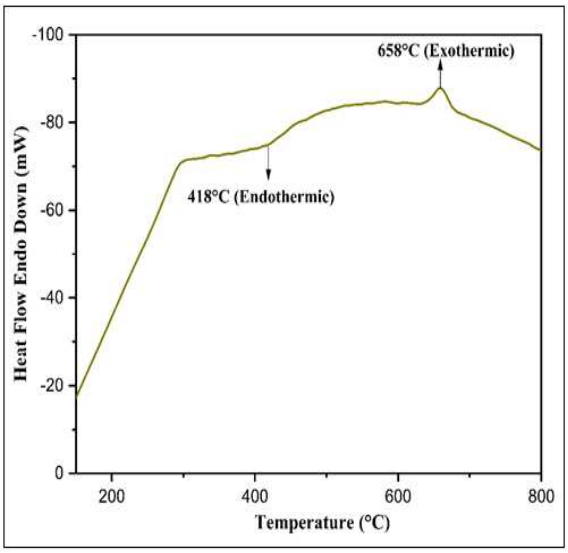

Fig. 7. DTA curve of CG leaf Fe_3O_4-NPs.

Two different absorbances at different wavenumbers may be due to the asymmetric or stretching vibration of Fe-O at a higher number and the symmetric or bending vibration of Fe-O at a lower wave number.

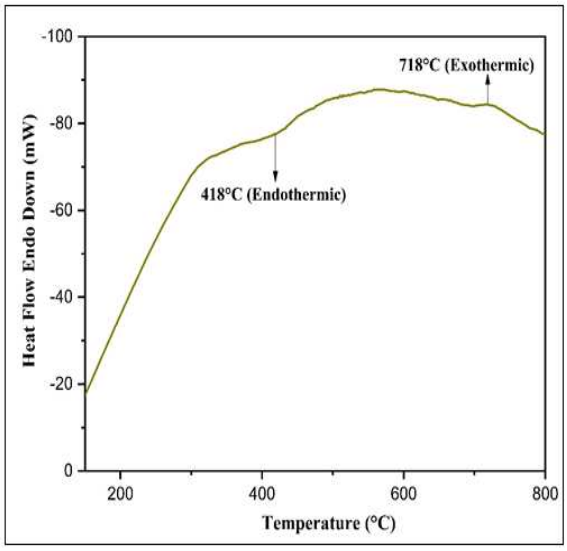

Fig. 8. DTA curve of CG latex Fe_3O_4-NPs.

These results revealed that C-O groups were bonded to the magnetite particle surface as a capping agent. Overall, the observation confirms the presence of protein in the latex and leaf of *Calotropis gigantea*plant, which acts as a reducing agent and stabilizer for magnetite nanoparticles (Awwad *et al.*, 2012). It has been reported that proteins can bind to metal nanoparticles through the free amine groups or carboxylate ions of amino acid residues (Harne *et al.*, 2012).

Fig. 9. MNPs solution before separation.

The shift and broadening of bands observed in the FTIR spectrum of MNPs after biomedical reactions indicate the participation of hydroxyl groups, aldehydes, amines, ketones, and carboxylic acids in biomedical reactions.

Fig. 10. MNPs solution after using a magnet.

The surveillance proves the existence of aldehydes, amines, and phenolic compounds bonded to the surface of MNPs, which enhances the stabilization of MNPs.

The physicochemical properties of *Calotropis gigantea* latex and leaf extracts act as a Bio template

to prevent the aggregation of MNPs.

Thermal analysis

TGA and DTG (derivative thermogravimetric) analysis

Thermal analysis measurement of the synthesized nanoparticles is carried out using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). To determine the thermal stability, decomposition temperature, and decomposition rate of the nanoparticles, TGA analysis was carried out. TGA measurements were carried out in the 30°C to 800°C temperature range at a heating rate of 20°C/min. Fig. 5 and 6 displays the iron oxide nanoparticle's TGA-DTG (derivative thermogravimetric analysis) curve for CG leaf and CG latex Fe_3O_4-NPs respectively.

Three weight loss stages were shown on the TGA plot in the tested temperature range of 30°C to 800°C. In the derivative curve we can easily see the temperature range for this weight losses.

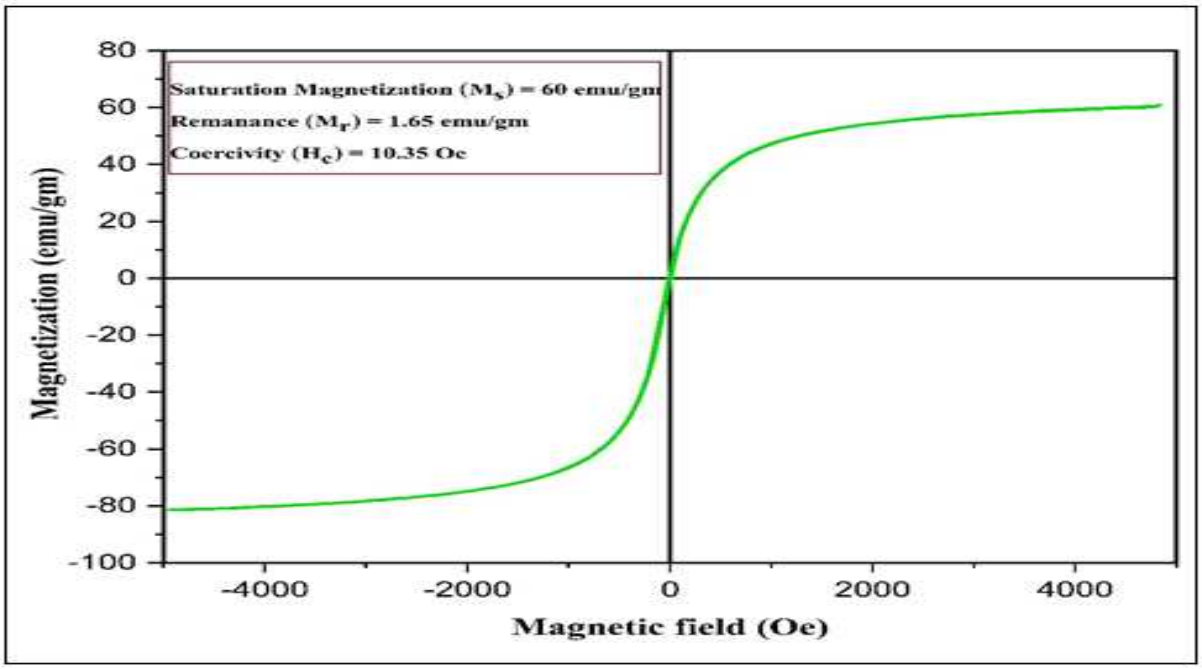

Fig. 11. VSM curve of CG leaf Fe_3O_4-NPs.

Synthesized magnetite nanoparticles showed excellent thermal stability and very less weight loss over a 30-800°C temperature range. This is due to the significant resistance of magnetite nanoparticles against evaporation and phase change at that temperature range (Rajendrachari *et al.*, 2020). In the first step, 5.93% and 3.43% weight loss occurred for CG leaf and CG latex MNPs in the temperature range of 30°C to 220°C indicating the removal of water, organic solvent or residual solvent, physiosorbed and chemisorbed H2O molecules in the sample (Bhuiyan *et al.*, 2020). In second step, decomposition of capping biomolecules takes place at 220°C to 400°C. The weight loss due to the decomposition of capping agent is 5.73% for CG leaf MNPs and 3.29% for CG latex MNPs. The protein of *Calotropis gigantea* leaf and latex extract decomposes completely at temperature higher than 600°C (Shahwan *et al.*, 2011).

The third stage degradation is about 1.33% at temperature of about 660°C (from DTG curve) for CG leaf MNPs and is about 0.77% at temperature of about 730 °C (from DTG curve). This degradation is due to the phase transformation from Fe_3O_4 to FeO (Wustite), as FeO is thermodynamically more stable above 600°C according to the Fe-O phase diagram (Rajendrachari*et al.*, 2020). Further, there was no weight loss observed above 798.70°C and 87.01% for CG leaf MNPs and 92.51% for CG latex MNPs weight

remained at 798.70°C. The results of TGA illustrated that there is a capping of organic biomolecules from akanda leaf and latex extract in the magnetite nanoparticles which weight is around 6% and 4% for CG leaf MNPs and CG latex MNPs respectively. Overall the TGA demonstrated that *Calotropis gigantea*leaf and latex extract existed on the surface of magnetite nanoparticles.

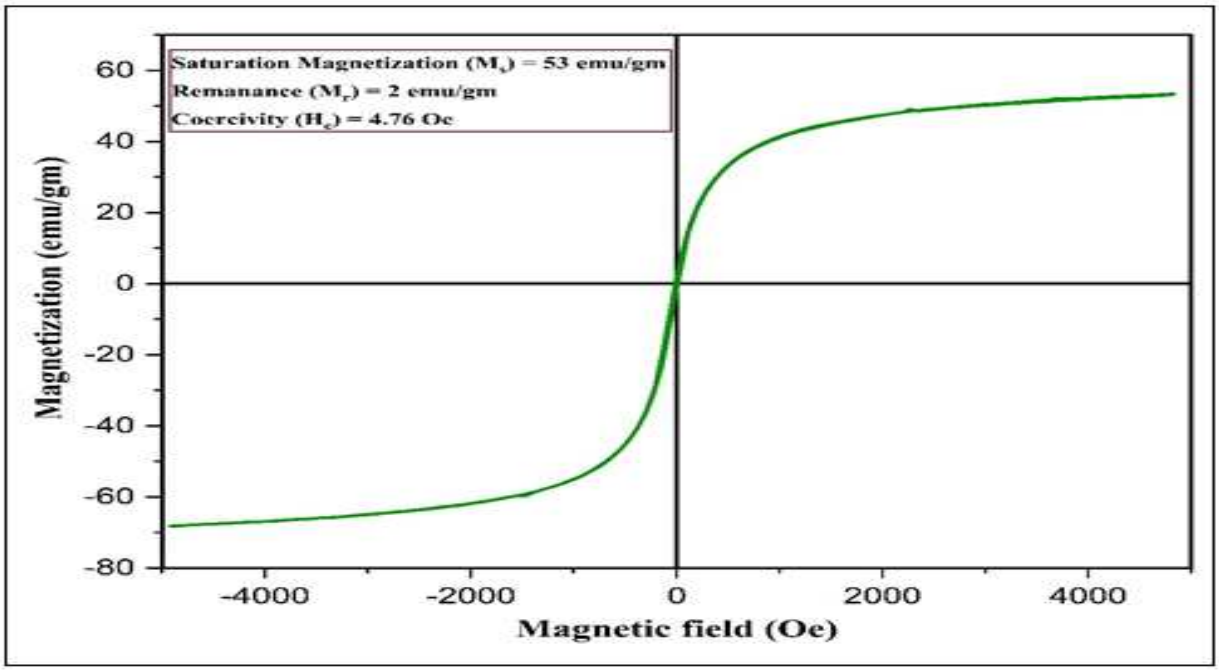

Fig 12. VSM curve of CG latex Fe_3O_4-NPs.

DTA analysis

Differential Thermal Analysis (DTA), a technique used to investigate phase transitions, melting points, and other thermal events of materials, both physical and chemical changes can occur. These changes are classified as endothermic or exothermic based on the heat flow direction. Fig**.** 7 and 8 shows the iron oxide nanoparticle's DTA curve for CG leaf and CG latex Fe_3O_4-NPs respectively. According to DTA curves at 20°C/min heating rate, we can observe endothermic peaks at 480°C both for CG leaf and CG latex MNPs. These endothermic peaks confirm the decomposition of organic matter and carbonaceous materials (Rajendrachari *et al*., 2020). The transition of Fe_3O_4 (iron (II,III) oxide) to FeO (iron(II) oxide) involves a change in the crystal structure, which is a type of phase transition. This specific phase transition is known as the reduction of magnetite (Fe_3O_4) to wüstite (FeO). The reduction of Fe_3O_4 to FeO is an exothermic process. During this transition, iron (II,III) oxide (Fe_3O_4) loses oxygen atoms, and the iron ions rearrange to form iron(II) oxide (FeO). The release of oxygen and rearrangement of the iron ions result in the liberation of energy, which is released to the surroundings in the form of heat. Therefore, an exothermic peak is observed in DTA curve at 658°C and 718°C for CG leaf and CG latex MNPs respectively for the phase transformation from Fe_3O_4 to FeO (Rajendrachari *et al*., 2020), (Jalil *et al*., 2017).

Magnetic properties

The dispersed solutions (fig**.** 9) were treated with magnets externally to demonstrate the magnetic behaviour of CG leaf and CG latex MNPs, and it was discovered that the nanoparticles deposited on the magnet (fig**.** 10). This observation also demonstrated the potential for using a strong magnetic field to separate MNPs following wastewater treatment. Magnetic properties of the synthesized CG leaf MNPs and CG latex MNPs were also studied with the help of VSM (Vibrating sample magnetometer). The magnetic behavior of the materials is strongly dependent on shape, morphology and size which are

greatly influenced by the synthetic procedure (Prasad *et al.*, 2017). Fig. 11 and 12 depicts magnetic hysteresis loop (magnetic field, H versus magnetic moment, M) of CG leaf MNPs and CG latex MNPs at 273 K. The superparamagnetic nature of the nanoparticles were confirmed by the absence of the hysteresis loop (Das *et al.*, 2020). The saturation magnetization for CG leaf MNPs and CG latex MNPs was found to be 60 and 53 emu/gm, respectively.

This value indicates that the synthesized MNPs shows very good magnetic properties when an external magnetic field is applied. The remanent magnetization (Mr) and coercivity field (Hc) gains are 1.65 emu/gm and 10.35 Oe for CG leaf MNPs, and 2 emu/gm and 4.76 Oe for CG latex MNPs.

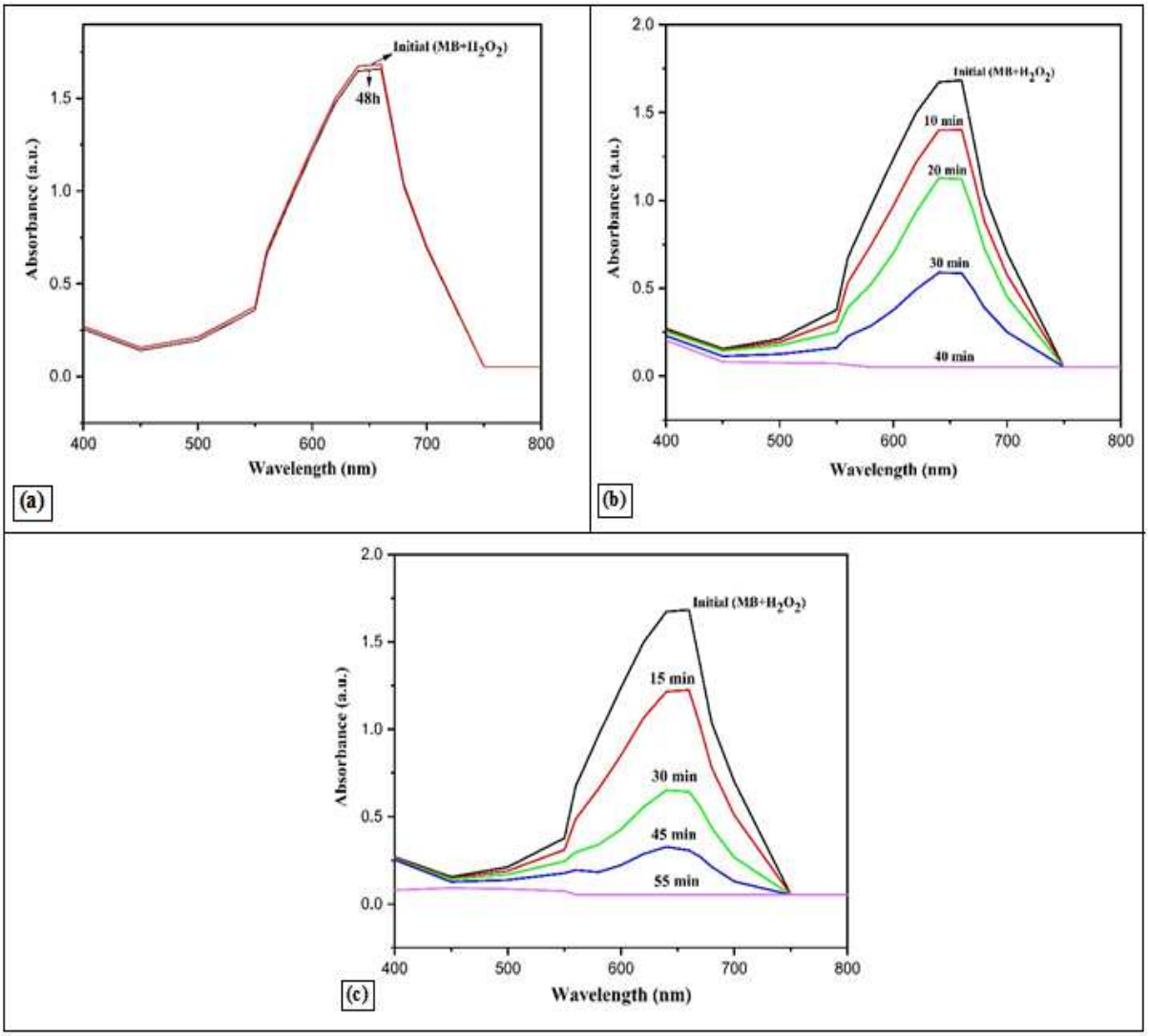

Fig. 13. Photocatalytic reduction of MB to its corresponding product using H_2O_2 (a) MB in dark (b) MB under sunlight in presence of CG leaf MNPs (c) MB under sunlight in presence of CG latex MNPs.

Photocatalytic Reduction of MB Dye

To study the photo oxidation of MB in the presence of H_2O_2 in aqueous solution, CG leaf MNPs and CG latex MNPs were used as photocatalysts.

Under sunlight irradiation, the degradation of methylene blue as a model pollutant was carried out in order to assess the photocatalytic activity of the MNPs (fig. 14). The absorbance and colour of the MB dye are unaffected when there is no MNPs catalyst present (Dhar *et al.*, 2021). Fig. 13 displays the absorption spectra for the reduction of MB dye by H_2O_2 and MNPs in the presence and absence of sunlight.

This observation showed that (i) when the solution was placed in the dark, H_2O_2 and MNPs did not reduce MB efficiently (there was some slight degradation after 48 hours), and (ii) the reduction rate was extremely slow and challenging to measure.

The absorbance intensity of MB (at 660 nm) decreased over time after being exposed to sunlight, and the absorption peaks for CG leaf and CG latex MNPs, respectively, nearly vanished after 40 and 55 minutes, respectively (Fig. 13b and c). Contrary to CG latex MNPS, CG leaf MNP exhibits a faster rate of dye oxidation.

The MB dye was transformed into leuco-MB when the colour of the MB solution changed from blue to colourless. This finding was reasonably consistent with earlier research on the photocatalytic reduction of MB dye by H_2O_2 in the presence of nanocatalyst (Wang *et al.*, 2009).

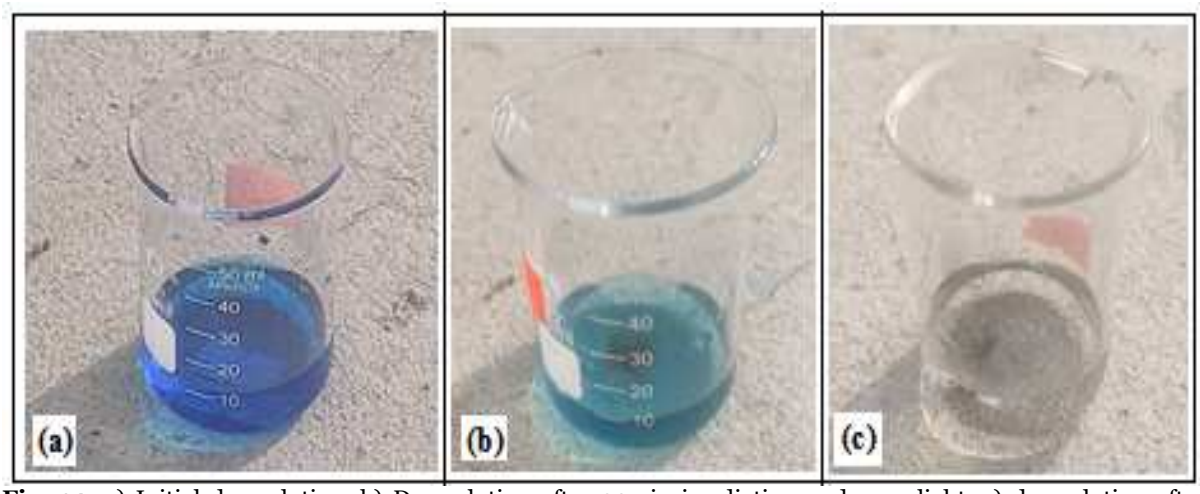

Fig. 14. a) Initial dye solution, b) Dye solution after 20min irradiation under sunlight, c) dye solution after 40min irradiation under sunlight.

Sustainable biosynthesized magnetite has been found to function as a Fenton-like catalyst, capable of degrading a variety of cationic and anionic dyes. This is the mechanism of dye degradation under sunlight (Shahwan *et al.*, 2011). The Fenton reagent, which consists of ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2), is necessary for this degradation process because it causes the hydroxyl radicals (•OH and OOH•) to be produced. These hydroxyl radicals attack and degrade organic pollutants with efficiency.

Conclusion

MNPs were made using a simple and environmentally friendly co-precipitation procedure, ferric and ferrous salts at room temperature, and leaf and latex extract from *Calotropis gigantea*. The phytochemical in the aqueous leaf extract and latex extract of *Calotropis gigantea* can act as a reducing and capping agent for the formation of MNP. The study's methodology is simple and reasonably priced. The technique is also eco-friendly because it doesn't use any harsh chemicals. The nanoparticles were characterised using a variety of methods. The room temperature magnetization curve reveals the superparamagnetic behaviour of the synthesised MNPs. The results of FTIR and TGA-DTA clearly show that organic biomolecules have been coated on the synthesised magnetite nanoparticles.

The dark black colour, continuous absorption peak at a lower wavelength in UV-vis spectra, absorption peak brought on by the Fe-O vibration in FTIR spectra, and lack of a hysterisis loop in the VSM curve all indicate that the synthesised nanoparticle is magnetite. Continuous bands in UV-vis spectra revealed that there aren't many differences in size between the synthesised MNPs. The smaller size of the magnetite nanoparticles is indicated by high saturation magnetization values. The MB dye's degradation in the presence of sunlight proved the

nanoparticles' capacity for photocatalysis. CG leaf extract-based MNPs degrade dye more quickly than CG latex-based MNPs.

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