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Table 1 is available in the Supplementary Files section.

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Green synthesis of Li-doped Mn₃O₄ nanoparticles using *Madhuca longifolia* leaf extract for enhanced photocatalytic, electrochemical and antimicrobial applications

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Abstract

In this study, lithium (Li) doped Mn₃O₄ nanoparticles (NPs) were successfully synthesized via a green and eco-friendly route using *Madhuca longifolia* (*M. longifolia*) leaf extract as a reducing and stabilizing agent. The structural, morphological and optical properties of the synthesized nanoparticles were systematically characterized using standard analytical techniques. The formation and structural properties of the synthesized nanoparticles were confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction analysis. In XRD analysis confirms a crystalline phase with an average crystallite size of 29.6 nm, as calculated using the scherrer equation. The Williamson-Hall (W-H) plot however, indicates a broad size of 45.26 nm. It suggests the presence of lattice strain. These are indicating successful incorporation of Li ions into the Mn₃O₄ lattice. UV-Visible spectroscopy revealed the optical absorption behavior and band gap characteristics of the nanoparticles. This reveals the optical band gap of 3.05 eV, indicates suitable for photocatalytic applications. Transmission Electron Microscopy (TEM) analysis demonstrated nanoscale particle size with relatively uniform morphology. Energy Dispersive X-ray Analysis (EDAX) confirmed the elemental composition and purity. Electrochemical studies using cyclic voltammetry demonstrated good redox behavior with an average specific capacitance of 216.43 F/g, indicating promising energy storage performance. The biosynthesized NPs exhibited notable antimicrobial activity against *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Candida albicans*. Furthermore, the photocatalytic performance showed efficient degradation of both cationic and anionic dyes, achieving 77.6% degradation of methylene blue (MB) and 80.91% degradation of methyl orange (MO). The enhanced performance is attributed to Li doping which improves charge separation and reduces electron – hole recombination. Overall, this work demonstrates an eco-friendly synthesis route and highlights the multifunctional potential of Li doped Mn₃O₄ NPs for environmental remediation, antimicrobial and energy storage applications.

Key words: Li doped Mn₃O₄ NPs; Phyto-mediated synthesis; Williamson-Hall analysis; Supercapacitor performance; Photocatalysis; Antimicrobial activity

1. Introduction

Transition metal oxides have emerged as versatile functional materials owing to their tunable electronic structure, mixed oxidation states, and wide range of technological applications [1, 2]. Among these, manganese oxide (Mn_3O_4) has gained considerable attention due to its natural abundance, environmental compatibility, and pseudocapacitive behavior. The hausmannite structure of Mn_3O_4 enables rapid and reversible redox reactions, making it a promising electrode material for next-generation supercapacitors. However, its practical performance is often limited by relatively low electrical conductivity and moderate ion-diffusion kinetics. To overcome these limitations, cation doping has been widely explored as an effective strategy to enhance structural stability, electronic conductivity, and electrochemical activity [3-4]. In this context, lithium (Li) doping is particularly attractive. The incorporation of Li^+ ions into the Mn_3O_4 lattice can modify the electronic environment, create additional defect sites, improve charge mobility, and facilitate faster ion transport. Such lattice modifications significantly enhance the electrochemical response, making Li-doped Mn_3O_4 nanoparticles superior candidates for high-performance supercapacitor electrodes. Beyond energy-storage applications, Mn_3O_4 -based nanomaterials have also shown promising antibacterial properties, attributed to mechanisms such as reactive oxygen species (ROS) generation, membrane disruption, and controlled release of metal ions. Doping can further amplify these effects by increasing surface activity, electrical interactions, and catalytic efficiency. The growing global challenge of microbial infections and antibiotic resistance highlights the need for efficient, safe, and cost-effective alternative antimicrobial agents. Li-doped Mn_3O_4 nanoparticles offer a unique dual-functionality, combining enhanced electrochemical behavior with potent antibacterial activity [5-8].

The specific size of the nanoparticle can alter magnetic, conducting, chemical, and electronic properties. Metal oxide nanoparticles are synthesized via various methods like Physical method, chemical method and biological method [9, 10]. In physical method [11] include these techniques Mechanical milling, Laser ablation and sputtering methods [12-14] etc., The chemical method include the techniques like Sol-gel, Chemical co-precipitation, Hydrothermal and Micro emulsion methods [15-18] etc., In these methods are using toxic chemicals and toxic reagents. It contaminates water, air and other environmental pollutions using hazardous chemical reducing agents. Biological synthesis methods employ plant extracts, bacteria, fungi and algae for nanoparticle preparation. These act as bio reducing agents and as a fuel in the biosynthesis method. Biosynthesis methods are eco-friendly non-toxic and reducing the particle size controlled [19, 20].

The metal oxide nanoparticles are wide range of applications. Many metal oxides are water purifier in garments waste water treatment. The wide bandgap materials act as a supercapacitor in optoelectronics field. The doped nanoparticles are high electrical conductivity and optical conductivity. These act as super capacitors and improved photocatalytic property. ZnO , CuO , TiO_2 , MnO_2 , WO_3 , MgO , GO , Bi_2O_3 , SnO_2 , SnS_2 , NiO , Mn_3O_4 , Al_2O_3 , NiTiO_3 , SrTiO_3 and BaTiO_3 are the transition metal oxide NPs. These Transition metal oxides are highly active and improved Super capacitance and Photocatalysis activities. In doped metal oxides are dramatic increases in supercapacitor property and

enhanced photocatalytic property. These nanoparticles are synthesized via bio route improve the quantum confinement effect for particle size control.

In this study, Li-doped Mn_3O_4 nanoparticles were synthesized using a biological approach. The structural, morphological, and optical properties were systematically investigated to understand the effect of Li incorporation on Mn_3O_4 . The nanoparticles were further evaluated for their supercapacitor performance through electrochemical techniques and were tested against pathogenic bacterial strains to assess their antibacterial activity. The results demonstrate the multifunctional potential of Li-doped Mn_3O_4 nanoparticles for integrated applications in energy storage, Photocatalysis and biomedical fields.

2. Experimental

2.1 Chemicals used

Manganese sulphate, Lithium sulphate, Sodium Hydroxide pellets, Acetone, Double distilled water, Whatman No.1 filter paper were purchased from Sigma-Aldrich .

2.2 Plant materials and extraction

Fresh leaves of *Madhuca longifolia* were collected from botanical gardens in Udangudi, Tamil Nadu, India. The leaves were thoroughly cleaned by washing with tap water followed by three rinses with double-distilled water to remove surface impurities. The washed leaves were air-dried at room temperature in the absence of light. Subsequently, the dried leaves were pulverized into a fine powder using a mixer grinder and stored at room temperature until further use. For aqueous extract preparation, 15 g of the powdered leaves were added to 150 mL of double-distilled water and heated at 80 °C for 3 h. After cooling to room temperature, the extract was filtered through Whatman No. 1 filter paper. The filtrate was stored in an airtight container at 4 °C for subsequent experimental studies.

2.3 Biological synthesis of Li doped Manganese oxide nanoparticles

Lithium-doped manganese oxide ($\text{Li-Mn}_3\text{O}_4$) nanoparticles were synthesized using a green biosynthesis approach. Initially, a 1 M manganese sulfate solution was stirred for 30 min to obtain a clear and homogeneous precursor solution. A 6 wt% lithium sulfate solution was then added dropwise to the manganese sulfate solution under continuous stirring. Subsequently, 30 mL of *Madhuca longifolia* leaf extract was added dropwise, and the resulting reaction mixture was vigorously stirred at 80 °C for 3 h. The pH of the mixture was should be maintained using 1M NaOH solution into dropwise added. The appearance of a white precipitate confirmed the formation of Li-doped Mn_3O_4 nanoparticles. The obtained precipitate was collected and washed sequentially with acetone, ethanol, and distilled water to remove unreacted precursors and residual organic compounds. The purified precipitate was calcined in a muffle furnace at 400 °C for 3 h. After calcination, the resulting Li-doped Mn_3O_4 nanopowder was cooled to room temperature and stored in an airtight container for subsequent characterization studies.

3 Results and discussions

3.1 Structural analysis

3.1.1 XRD analysis

The prepared Li-doped Mn_3O_4 nanoparticles were subjected to powder X-ray diffraction (XRD) analysis to determine the crystal structure, lattice parameters, and phase purity, as well as to identify the corresponding reflection planes. The XRD pattern was recorded over a 2θ range of 20° – 80° . The observed diffraction peaks were indexed to the crystallographic planes (112), (200), (103), (211), (004), (220), (105), (312), (321), (215), and (400), which are in good agreement with the standard JCPDS card No. 01-080-0382 [21]. The XRD results confirm that the Li-doped manganese oxide nanoparticles crystallize in a tetragonal structure [22]. The diffraction pattern provides both the diffraction angles (2θ) and the corresponding intensities for each reflection, and the recorded XRD pattern is shown in Figure 1(a). The interplanar spacings (d-values) corresponding to the observed diffraction peaks were calculated using Bragg's law:

$$n\lambda = 2d\sin\theta \quad (1)$$

Where d is the interplanar spacing, θ is the Bragg angle, n is the order of diffraction, and λ represents the X-ray wavelength. The broadening of the diffraction peaks indicates the nanocrystalline nature of the synthesized Li-doped Mn_3O_4 nanoparticles.

The average crystallite size (D) was calculated using Debye-Scherrer's formula.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Where K is a constant and it is equal to 0.9, λ - wavelength of X-rays ($1.5406 \text{ \AA}$),

B is the Full width at half maximum, θ is Bragg's angle. The average crystallite size of the Li-doped Mn_3O_4 nanoparticles is found to be 29.6 nm .

The dislocation density (δ) was calculated using the following formula:

$$\text{Dislocation density, } \delta = \frac{1}{D^2} \quad (3)$$

where D is the average crystallite size.

The dislocation density of Li-doped Mn_3O_4 NPs is calculated to be, $\delta = 11.41 \times 10^{14}/\text{m}^2$. The microstrain (ϵ_s) generated within the lattice is expressed as,

$$\epsilon = \frac{\beta}{4\tan\theta} \quad (4)$$

Where β is the line broadening at FWHM in radians, θ is the Bragg's angle in degrees. The calculated values of the microstrain of the Li-doped Mn_3O_4 nanoparticles, with an average value of 0.0047601.

3.1.2 W-H plot

The Williamson–Hall analysis was employed to evaluate the crystallite size and lattice strain of Li-doped Mn_3O_4 nanoparticles. The linear fitting of $\beta\cos\theta$ versus $4\sin\theta$ indicates that peak broadening arises from both finite crystallite size and microstrain induced by Li incorporation into the Mn_3O_4 lattice. The following equation represents the W-H plot:

$$B \cos\theta = \frac{k\lambda}{D} + 4\epsilon \sin\theta \quad (5)$$

The Williamson-Hall plot was constructed by plotting four $\sin\theta$ on the X-axis and $\beta\cos\theta$ on the Y-axis, resulting in a straight-line pattern [23]. From this plot, the microstrain was determined from the slope, while the crystallite size was calculated based on the Y-axis intercept. The W-H plot for the sample is shown in Figure 1(b). From the W-H plot, the values of microstrain (ϵ) are 0.00397, and the average crystallite size (D) of the sample is found to be 45.26 nm. The comparison data for Debye-Scherrer's and W-H plot was shown in table 1.

3.2 FTIR analysis

Fourier transform infrared (FTIR) spectroscopy was employed to investigate the functional groups and metal–oxygen bonding present in the biosynthesized Li-doped Mn_3O_4 nanoparticles. The FTIR spectrum of Li-doped Mn_3O_4 nanoparticles are shown in figure 2. The strong bands observed at 523 and 619 cm^{-1} are attributed to the Mn–O stretching vibrations of $\text{Mn}^{2+}\text{--O}$ and $\text{Mn}^{3+}\text{--O}$ bonds in the tetragonal spinel structure of Mn_3O_4 , confirming the formation of the metal–oxygen framework. The slight variation in band position compared to pure Mn_3O_4 indicates lattice distortion induced by Li^+ incorporation. The absorption band at 1114 cm^{-1} is associated with Mn–O–Mn bending vibrations and possible lattice defects generated by Li doping. The band at 1469 cm^{-1} is assigned to C–O stretching vibrations arising from residual carbonate species or adsorbed atmospheric CO_2 . The peak at 1629 cm^{-1} corresponds to the H–O–H bending vibration of molecularly adsorbed water on the nanoparticles surface. A weak band appearing at 2341 cm^{-1} is attributed to asymmetric stretching of CO_2 molecules adsorbed from the ambient atmosphere. The band at 2918 cm^{-1} is assigned to C–H stretching vibrations, originating from trace organic residues remaining from the synthesis process. The broad absorption band centered at 3412 cm^{-1} is due to the O–H stretching vibration of surface hydroxyl groups and adsorbed moisture [24–26]. The FTIR results confirm the formation of Mn_3O_4 nanoparticles and suggest that Li^+

doping induces local lattice distortion without introducing additional impurity phases, consistent with the XRD observations.

3.3 UV-Visible analysis

The UV–Visible absorption spectrum of biosynthesized Li-doped Mn_3O_4 nanoparticles was recorded over the wavelength range of 200–1200 nm. Figure 3(a) illustrates the absorbance spectrum of Li-doped Mn_3O_4 nanoparticles, exhibiting significant absorption in the visible region [27]. A distinct absorption edge observed at 316 nm. Figure 3(b) presents the corresponding transmittance spectrum of the Li– Mn_3O_4 bionanoparticles. The transmittance data reveal a lower cut-off wavelength around 316 nm, which is consistent with the absorbance results. This characteristic behavior confirms the nanoscale nature of the synthesized Li– Mn_3O_4 particles. In addition, the optical reflectance (R), which represents the fraction of incident light, reflected from the nanoparticle surface. It can be estimated from the UV–Visible data. The calculation is carried out using the given relation:

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (6)$$

Figure 3(c) and (d) present the variation of reflectance and refractive index with respect to wavelength for the synthesized sample. The refractive index (n), which describes the propagation of light within the material, is an important optical parameter. It can be estimated using the following relation:

$$n = \left(\frac{1}{T} + \left(\frac{1}{T} - 1 \right) \right) \quad (7)$$

Here, T represents the transmittance of the biosynthesized Li– Mn_3O_4 . The optical band gap (E_g) was determined from the absorption spectrum, and the optical absorbance coefficient (α) in the vicinity of the absorption edge was calculated using Tauc's relation,

$$(ah\nu)^n = A(h\nu - E_g) \quad (8)$$

In this context, h denotes Planck's constant, ν represents the frequency of the incident photons, A is a proportionality constant, and E_g corresponds to the optical band gap. Figure 3(e) shows the Tauc's plot, from which the optical band gap of the sample was estimated to be 3.05 eV. The extinction coefficient (k) was subsequently determined using the following relation:

$$k = \frac{\alpha\lambda}{4\pi} \quad (9)$$

Here, λ denotes the wavelength of the incident photons and α represents the absorption coefficient. The calculated extinction coefficient (k) was plotted as a function of wavelength, as illustrated in Figure 3(f). The dielectric constant (ϵ_c) can be expressed as:

$$\varepsilon_c = \varepsilon_r - i\varepsilon_i \quad (10)$$

Where ε_r is the real part of the dielectric constant, and ε_i is the imaginary part. These components can be calculated using the following relations:

$$\varepsilon_r = n^2 - k^2 \quad (11)$$

$$\varepsilon_i = 2nk \quad (12)$$

Here, n denotes the refractive index, and k represents the extinction coefficient. These parameters collectively provide a comprehensive understanding of the optical properties of the biosynthesized Li-Mn₃O₄ NPs .

The real and imaginary components of the dielectric constant describe distinct optical characteristics of the biosynthesized Li-Mn₃O₄ NPs. The real part is associated with the propagation of light within the medium, whereas the imaginary part corresponds to the absorption of optical energy. Figure 4(a) and (b), illustrates the variation of ε_r and ε_i as functions of photon energy for the synthesized nanoparticles. The plots reveals that both ε_r and ε_i exhibit similar trends, indicating a consistent correlation between the dielectric response and the energy-dependent behavior of the particles. The optical conductivity of the prepared biosynthesized Li-Mn₃O₄ NPs was subsequently calculated using the following relation:

$$\sigma_{op} = \frac{\alpha n c}{4\pi} \quad (13)$$

Here α represents the absorption coefficient, n denotes the refractive index and c is the velocity of light. Figure 4(c) shows the variation of optical conductivity as a function of photon energy for the Li-Mn₃O₄ nanoparticles. It is observed that optical conductivity increases as photon energy increases, and decreases correspondingly at lower photon energies. The electrical conductivity (σ_{el}) can be related to the optical conductivity (σ_{op}) and the absorption coefficient (α) through the following expression:

$$\sigma_{el} = \frac{2\lambda \sigma_{op}}{\alpha} \quad (14)$$

This relationship establishes a link between the electrical conductivity of the material and its optical properties, particularly its absorption behavior. Figure 4(d) illustrates the variation of electrical conductivity as a function of photon energy for the Li-Mn₃O₄ nanoparticles. It is

observed that the electrical conductivity decreases with increasing photon energy within the visible region. This reduction in electrical conductivity suggests that the material exhibits dielectric characteristics, indicating a resistance to charge transport under the influence of an external electric field. Such behavior is characteristic of insulating materials, which show limited electrical conduction at higher photon energies in the visible spectrum [28, 29].

3.4 Morphological analysis

3.4.1 TEM and EDAX analysis

Figure 5(a-d) shows the TEM images of biosynthesized Li doped Mn_3O_4 NPs. It clearly reveals that the prepared Li doped Mn_3O_4 nanoparticles are quasi-spherical shaped and irregular agglomerated NPs. This property provides a higher density of electro active sites. It's facilitating improved redox reactions. The interconnected nanoparticle network enhances electron transport pathways resulting in pronounced redox peaks in the cyclic voltammetric curves. However, excessive agglomeration may limit electrolyte ion diffusion slightly affecting the overall capacitance. The irregular and agglomerated morphology enhances light absorption due to multiple scattering effects. It provides abundant surface-active sites for photocatalytic reactions. The particle – particle interaction within agglomerates can also facilitate charge transfer, Thereby reducing electron hole recombination. Figure 5 e) illustrates the SAED pattern of bio-synthesized Li- Mn_3O_4 NP. It confirms the fringes of the TEM images indicate the d-spacing value of XRD analysis. Figure shows the EDAX analysis of Li doped Mn_3O_4 NPs. This confirms the presence of Mn and O elements with no detectable impurities. The successful incorporation of Li into the crystal structure inferred based on the synthesis conditions. Li was further corroborated by XRD and other characterization techniques [30 -32].

3.5 Electrochemical analysis

Cyclic voltammetry was employed for the electrochemical characterization of the Li-doped Mn_3O_4 nanoparticles. This technique evaluates the electrochemical properties of Li-doped Mn_3O_4 nanoparticles by applying a varying potential and measuring the resulting current. CV provides insight into understanding the charge storage capabilities, redox

behavior, and overall electrochemical performance of the Li-doped Mn₃O₄ nanoparticles, which are essential for their applications in energy storage, sensors, and other electrochemical devices [33, 34]. CV is commonly used to investigate electron transfer processes under various conditions. It is a powerful tool for evaluating the stability of electrode materials by optimizing electrolyte types and concentrations. Fig. 6 shows the cyclic voltammetry curves for the synthesized nanoparticles. The data reveal that the area enclosed by the current-potential curve is larger, representing enhanced electrochemical reaction activity of the synthesized nano oxides. From the CV plots, the specific capacitance (C_s) is calculated using the following relation.

$$C_s = \frac{A}{2mK\Delta v} \quad (15)$$

where A is the area under the CV curve, m is the mass of active material on the electrode, ΔV is the potential window, and K is the scan rate. The high C_s value observed for the sample indicates that Li-doped Mn₃O₄ is a promising electrode material for high-performance supercapacitors. This finding suggests that Li-doped Mn₃O₄ nanoparticles possess strong potential for application in energy storage devices, such as supercapacitors, due to their enhanced electrochemical properties. The CV mechanism of Li-doped Mn₃O₄ nanoparticles is described here. The CV curves exhibit well defined redox peaks corresponding to the reversible Mn²⁺/Mn³⁺ transition. This indicates that the Li doped NPs exhibit promising pseudocapacitive behavior. The incorporation of Li enhances electrical conductivity and introduces additional active sites, facilitating faster charge transfer and ion diffusion [35 -37]. The cyclic voltammetry reveals that the average specific capacitance C_s of bio Li doped Mn₃O₄ NPs are 216.43 F/g. We noted that the specific capacitance decreases by the scan rate increases. Based on the CV profile, the charging and discharging behavior of Li-doped Mn₃O₄ in a KOH alkaline electrolyte within the potential window of -1.0 to 1.1 V can be summarized as follows:



During the charging process, the manganese species undergoes oxidation, typically from a lower to a higher oxidation state. Mn²⁺ into Mn³⁺ it involves the adsorption of hydroxyl ions.



During discharge, the Mn^{3+} species is reduced back to Mn^{2+} as electrons are released back in to the system.



3.5.1 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) analysis was carried out to investigate the charge transport properties of Li doped Mn_3O_4 nanoparticles. From the figure 6 b) shows a small intercept in the high frequency region corresponds to low solution resistance (R_s). It indicates good ionic conductivity of Li doped Mn_3O_4 electrolyte. A depressed semicircle observed in the mid frequency region represents the charge transfer resistance (R_{ct}). It suggests moderate electron transfer kinetics at the electrode-electrolyte interface. The Warburg impedance shows in the 45° straight line, it confirms the diffusion controlled ion transport within the electrode material. The deviation from an ideal vertical line indicates pseudocapacitive behavior of Li doped Mn_3O_4 NPs [38, 39]. The EIS analysis confirms the prepared Li doped Mn_3O_4 NPs are exhibits combined diffusion controlled and capacitive charge storage behavior.

3.6 Antibacterial activity

The antibacterial pathogenises of the biosynthesized Li doped Mn_3O_4 NPs are shown in figure 7. It was using a *Staphylococcus aureus* (gram positive), *Pseudomonas aeruginosa* (gram negative) and *Candida albicans* as a fungus. The concentrations of bio synthesized Li- Mn_3O_4 NPs are evaluated as 5,25,50 and 100 $\mu\text{g/ml}$. The high inhibition zone was observed in pathogenises of *P.aeruginosa* and *S.aureus*. The inhibition zone value was near 13mm , it was well activity against gram positive and gram negative. Also, against fungus like *Candida albicans* is moderate zonal activity for 11mm. The antibacterial activity suggests the concentrations increases with inhibition zone increases [40, 41]. The inhibition zones of different concentrations are shown in figure.

3.7 Photocatalytic activity

To evaluate the photocatalytic activity of Li-doped Mn_3O_4 NPs, the degradation of aqueous cationic dye like MB and anionic dye like MO solutions under natural sunlight

irradiation was examined. Figure 8 a) illustrates the photocatalytic degradation of MB and MO dyes. The results confirm that Li doping enhances the photocatalytic performance of Mn_3O_4 photocatalysts [42, 43]. Upon 90 min of sun light exposure, the photocatalytic efficiencies of MB and MO using Li-doped Mn_3O_4 as the photocatalyst reached 77.6% and 80.91%, respectively, as shown in Figure 8 b). The reaction can be represented by equations (5) and (6).

$$\text{Degradation efficiency \%} = (C_0 - C_t / C_0) \times 100$$

$$dC/dt = kC_t$$

Where C_0 , C_t , and k are the concentrations of MB and MO and rate constant of the reaction, respectively. Figure 8 c) and d) presents the rate constant and degradation efficiency of Li-doped Mn_3O_4 NPs. The subscript t denotes the time interval. By integration, the equation could be transformed as follows (equation (7)).

$$\ln C_0/C_t = kt \quad (16)$$

The change in $\ln(C_0/C_t)$ for each dye is plotted against irradiation time (t) in Figure 8(b). This relationship appears linear and indicates that the photo degradation of MO can be well explained by the first-order pseudo reaction. The degradation efficiency was hiegher for the anionic dye Methyl orange. The anionic dye was compared to cationic dye like as methelene blue. It has attributed to the stronger electrostatic attraction between anionic MO dyes. The surface of prepared bio Li-doped Mn_3O_4 NPs are resulting in enhanced adsorption and faster photocatalytic degradation [44, 45].

4. Conclusion

The green nanotechnology used to prepare bio Li-doped Mn_3O_4 NPs using the leaves extract of *Madhuca longifolia*. The powder XRD pattern revealed that the prepared NPs are tetragonal structure. The Powder XRD pattern shows the prepared material has crystalline nature. The average crystallite size was calculated using Debye-Scherrer's formula and compared by W-H plot. The Mn-O stretching vibrations, Mn-O-Mn bending, C-O stretching O-H bending vibrations and their functional groups are observed by FTIR analysis. The optical band gap and other optical parameters are carried out by UV-Visible analysis. The HR-TEM analysis was successfully confirms the irregular and agglomerated morphology and

ED's analysis confirms the bio Li-doped Mn₃O₄ NPs. The average specific capacitance of a material is 216.43 F/g. The EIS analysis confirms low solution resistance, moderate charge transfer resistance and dominant diffusion controlled pseudocapacitive behavior of the Li doped Mn₃O₄ electrode. The anti bacterial activity of a bio NPs are well against gram positive and gram negative bacteria. The anionic and cationic dye removal properties of bio NPs depends on their surface charge, functional groups and interaction mechanisms with dye molecules. This research highlights the strong potential of these materials as multifunctional candidates for environmental remediation applications.

Author contribution statement

G.Emerson Robin performed the synthesis, characterizations and data analysis.

V.Saththeesh assisted in experimental work and data interpretation.

P.Selvarajan supervised the research and reviewed the manuscript.

All authors contributed to writing and approved the final manuscript.

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Declaration of competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on a reasonable request.

Ethical issues

Not applicable

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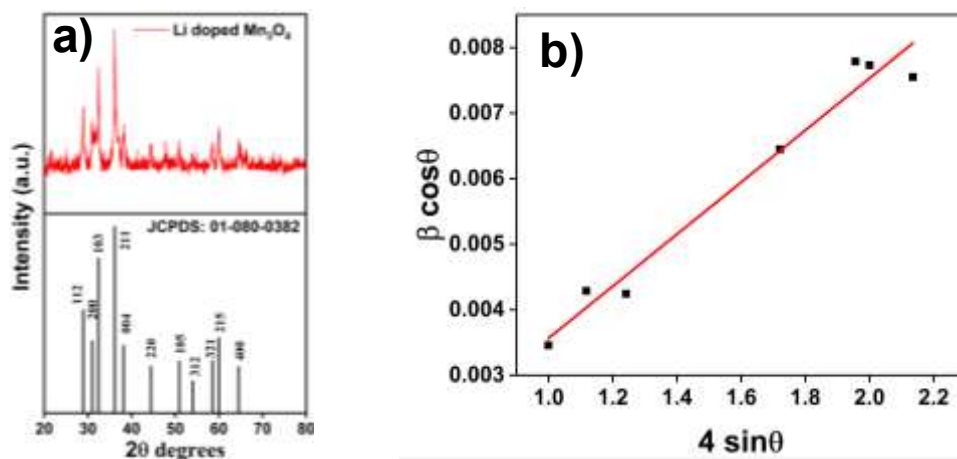


Fig: 1 a) XRD spectrum of Li doped Mn_3O_4 NPs b) W-H plot of Li doped Mn_3O_4 NPs

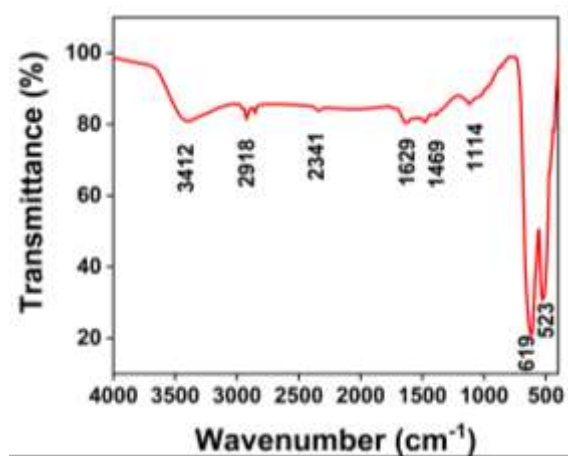


Fig: 2 FTIR spectrum of Li doped Mn_3O_4 NPs

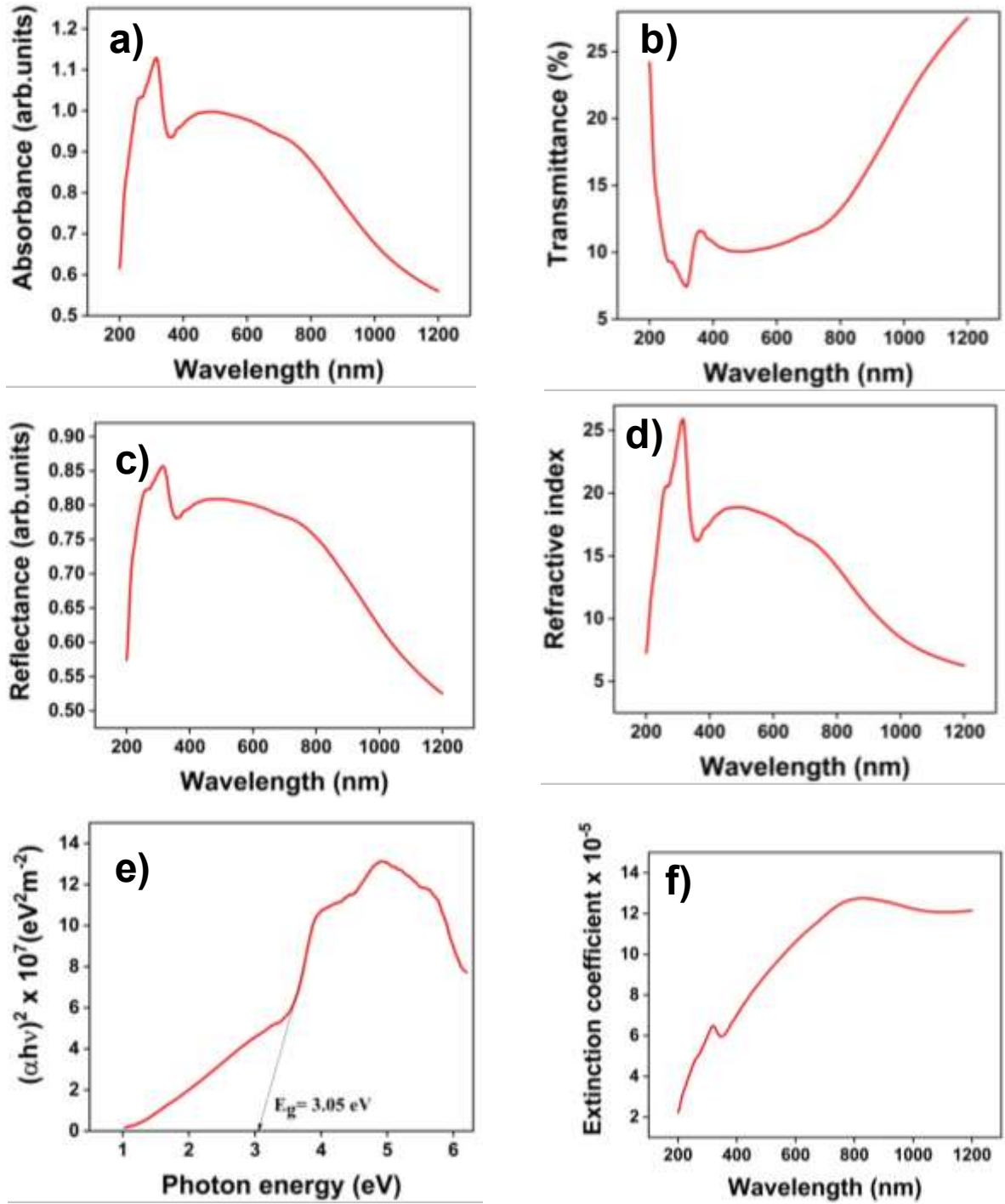


**Fig: 3 Optical graph of a) Absorbance spectrum b) Transmittance spectrum
c) Reflectance spectrum d) Refractive spectrum e) Tauc's plot f) Extinction coefficient**

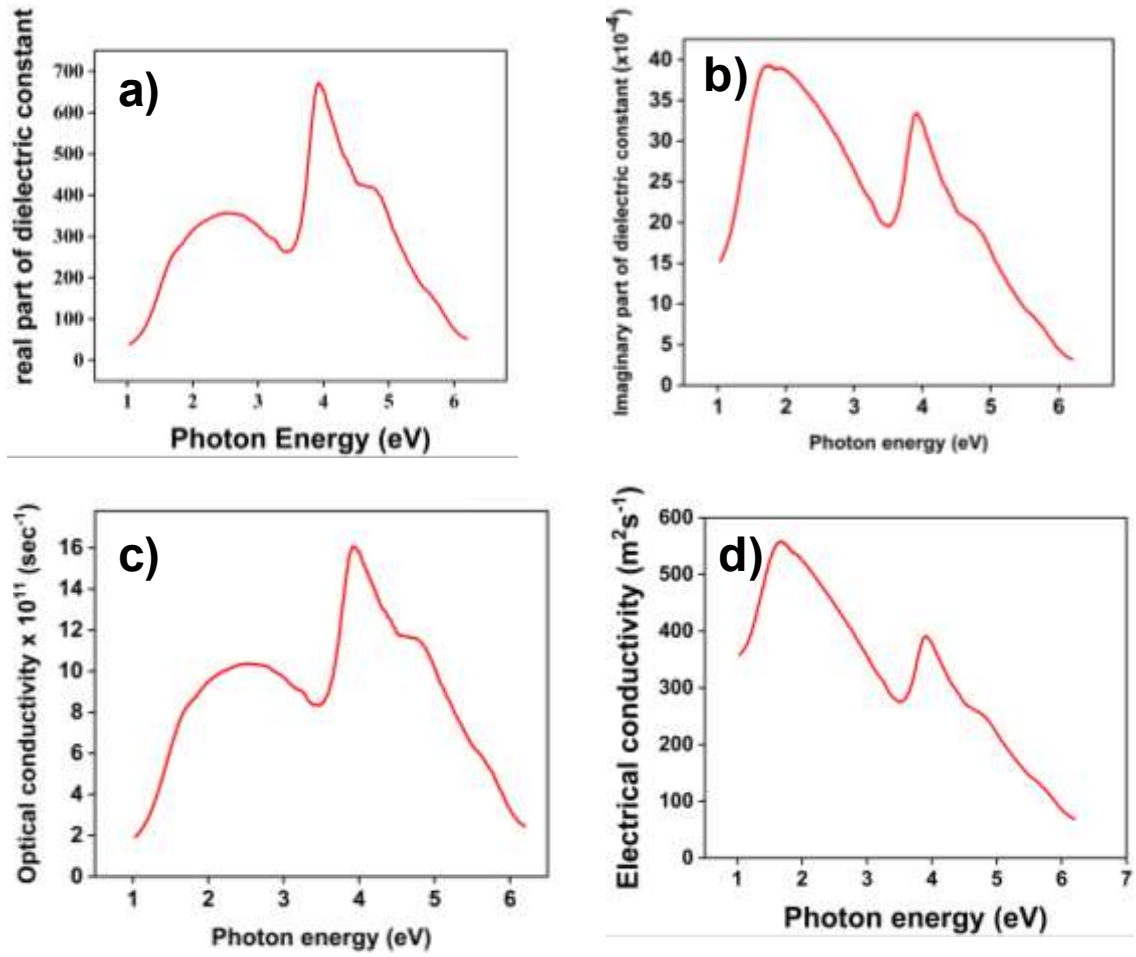


Fig: 4 Optical graph of a) Real part of dielectric constant b) Imaginary part of dielectric constant c) Optical conductivity d) Electrical conductivity

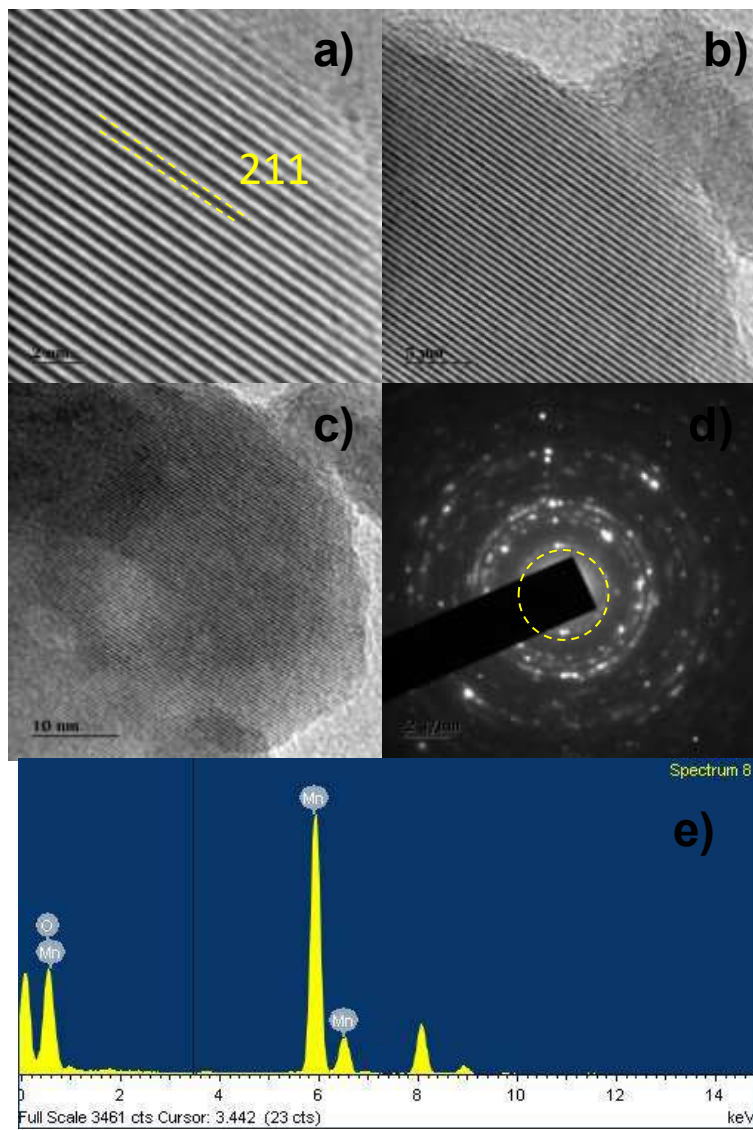


Fig: 5 a-d) TEM images of Li doped Mn_3O_4 NPs e) EDAX spectrum of Li doped Mn_3O_4 NPs

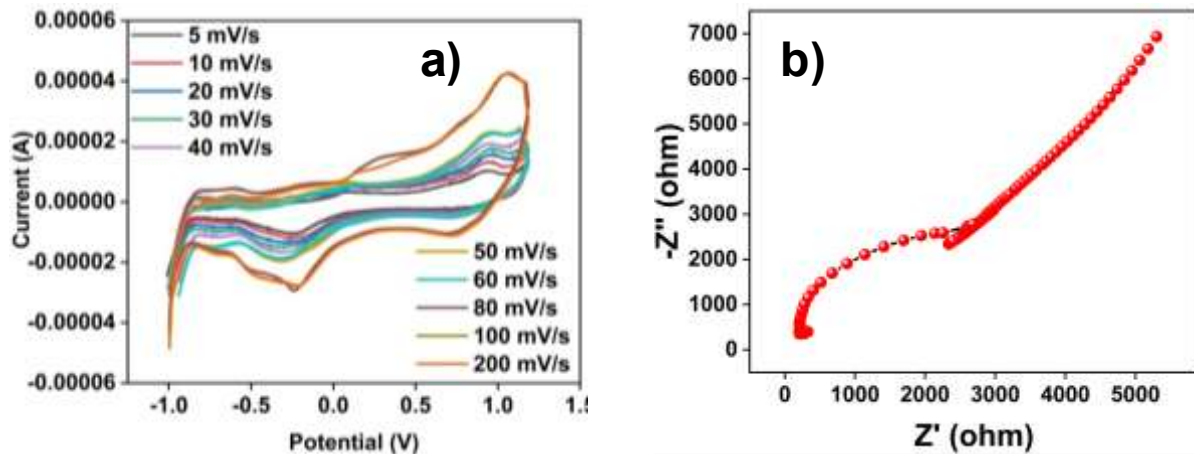


Fig: 6 a) CV curves of Li doped Mn_3O_4 NPs at different scan rates b) impedance spectrum

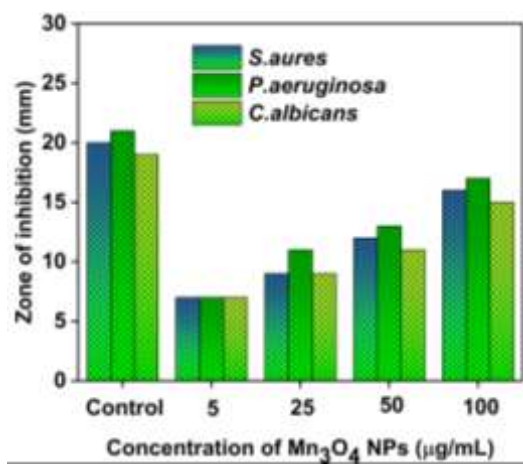


Fig: 7 Anti microbial activity of Li doped Mn_3O_4 NPs

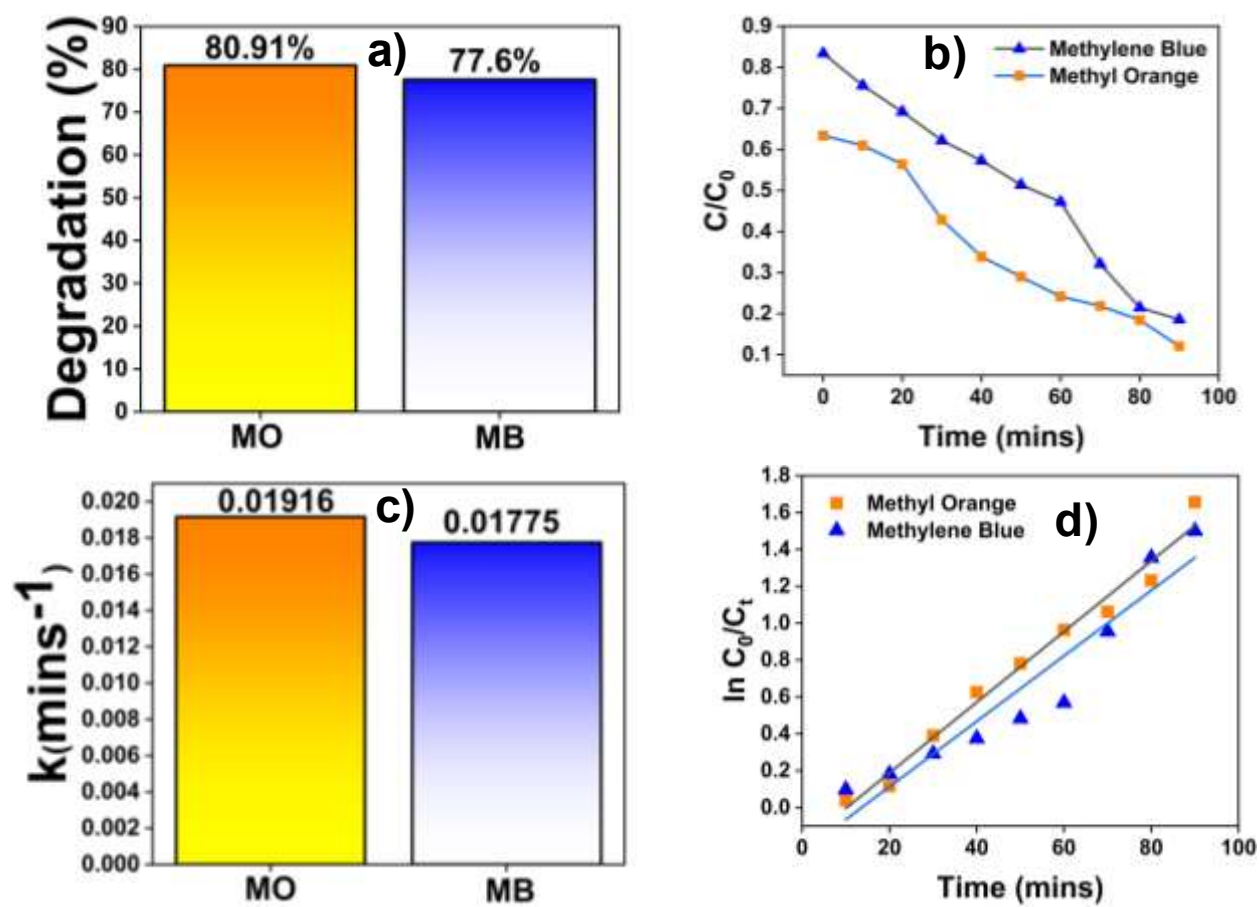


Fig: 8 Photocatalytic activities of Li doped Mn_3O_4 NPs a) rate curve b) kinetic curve
c) rate constant d) degradation efficiency of MB and MO dyes

Supplementary Files

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