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Synthesis, Characterization and Antimicrobial Activity of Magnetite (Fe_3O_4) Nanoparticles by the Sol-Gel Method

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Abstract: Transition Metal Oxide (TMO) nanoparticles have emerged as promising materials for various applications including colour imaging, magnetic recording media, soft magnetic materials, heterogeneous catalysis, and different field of biomedical science. Apart from the TMO, Fe_3O_4 nanoparticles hold great promise in a variety of biomedical uses such as drug delivery, cell separation, and MRI imaging. Magnetite (Fe_3O_4) nanoparticles exhibit their potential as antimicrobial agents due to their unique properties and interactions with microorganisms. This study focuses on the synthesis, characterization, and evaluation of the antimicrobial activity of magnetite (Fe_3O_4) nanoparticles prepared using the sol-gel method. The Fe_3O_4 nanoparticles were synthesized through a facile and cost-effective sol-gel route, involving the ferric nitrate and ethanol as precursors. Different characterization techniques, including Energy-Dispersive X-ray Spectroscopy (EDAX), X-ray diffraction (XRD), and UV-VIS NIR spectroscopy were employed to analyse the compositional analysis, crystalline structure, and optical properties of the nanoparticles. The EDAX and XRD analysis confirmed that the synthesized nanoparticles are near to stoichiometry and formation of single-phase magnetite nanoparticles. The obtained bandgap of synthesized nanoparticles is 5.03 eV. Furthermore, the synthesized Fe_3O_4 nanoparticles were evaluated for their antimicrobial efficacy against a panel of including both Gram-positive (e.g., Staphylococcus aureus) and Gram-negative (e.g., Enterobacter aerogenes) bacteria. Investigations into the nanoparticles biocompatibility and long-term effects would be crucial for their safe and effective utilization in real-world applications.

Keywords: magnetite (Fe_3O_4) nanoparticles; sol-gel method; optical properties

1. Introduction

Transition metal oxide nanoparticles turned out to be widely explored for many applications such as color imaging, magnetic recording, soft magnetic materials, sensors, supercapacitors, heterogeneous catalysis, and different fields of biomedical applications. Magnetite (Fe_3O_4) is natural mineral of iron oxide. The multiple phases of iron oxides are important in academic and industrial research areas. In recent years, there has been a growing interest in the synthesis and characterization of magnetite nanoparticles due to their unique properties and wide range of applications [1]. Magnetite nanoparticles are composed of iron oxide and exhibit magnetic behavior, making them attractive for various fields such as drug delivery, cell separation, imaging (MRI) and in vivo therapy technology [2-3]. Magnetite possesses FCC structure, where Fe has mixed valency of Fe^{2+} and Fe^{3+}. Chemical formula of magnetite can be written as $[Fe^{3+}]_{tetra}\,[Fe^{2+}Fe^{3+}]_{octa}O_4$, which falls to Inverse spinel group [4]. Magnetite can be synthesized using several methods including co-precipitation [5], micro-emulsion [6], thermal decomposition [7], hydrothermal [8], ultrasonic [9], sol-gel [10] methods. The sol-gel method is a chemical method for synthesizing various nanostructures, especially metal oxide nanoparticles. The sol-gel method is cost-effective and allows for good control over the chemical composition as well as surface area of the nanoparticles. The purpose of this work is the preparation of magnetite nanoparticles via sol-gel method. The elemental composition, structural analysis, optical properties, and antimicrobial activity of the synthesized magnetite nanoparticles were investigated.

2. Materials and Methods

- Materials

From LOBA Chemicals the ferric nitrate (Fe $(NO_3)_3{\cdot}9H_2O$ and ethanol (C_2H_5OH) of analytical grade were obtained. The materials were used without any further purification.

- Synthesis of Magnetite nanoparticles

In this process first, 1.0 M ferric nitrate dissolved in 20 ml ethanol and was vigorously stirred for 2 hours at 50°C. Then the prepared sol was heated to 70°C to obtained brown gel. The gel was aged at room temperature for about 1 hour and then the xerogel was annealed at 200°C for 3 hours in furnace. The calcined sample was crushed as fine powder by using mortar pestle. Finally, brown color magnetite nanoparticles were successfully synthesized.

- Characterization

The EDAX characterization of synthesized magnetite nanoparticles was carried out for determination of elemental composition. The X-ray diffraction spectroscopy (XRD) (Bruker, D8 Advance) is used to determination of structural analysis of magnetite nanoparticles. The absorption spectra of the magnetite nanoparticles were determined by UV-VIS spectroscopy (Perkin Elmer, LAMBDA 1050+). Antimicrobial activity of synthesized magnetite nanoparticles was evaluated by standardized test, aiming to establish the minimum inhibitory concentration.

3. Results and Discussion Conclusions

In order to describe elemental composition of magnetite (Fe_3O_4) nanoparticles, EDAX characterization was employed. In table 1 shows that the EDAX analysis of magnetite nanoparticles, which shows that the atomic weight % of Fe is 53.38 and the atomic weight % of O is 46.62 in the Fe_3O_4. It closes to the Stoichiometric composition of Fe_3O_4. EDAX image of magnetite nanoparticles shown in Figure 1.

Table 1. Percentage of elements in magnetite (Fe_3O_4) nanoparticles from EDAX.

Element	Weight%
O K	24.7
Fe K	75.3

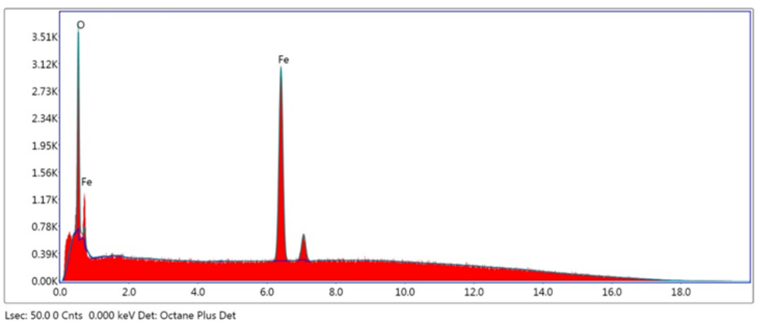

Figure 1. EDAX Image of magnetite (Fe_3O_4) nanoparticles.

In order to describe the structural property of magnetite (Fe_3O_4) nanoparticles, the X-ray diffraction (XRD) was employed. The X-ray diffraction (XRD) pattern of magnetite (Fe_3O_4) nanoparticles as shown in figure 2. The diffraction peaks at 2θ= 9.77°, 17.99°, 21.64°, 24.36°, 31.40°, 35.75°, 40.20°, 45.93°, 52.77°, 62.47°, 70.82° can be assigned to (1 0 0), (1 1 1), (2 0 0), (2 1 0), (2 2 1), (3 1 1), (3 2 1), (3 3 0), (4 2 2), (4 4 0), (6 2 0) respectively. crystal structure of obtained magnetite (Fe_3O_4) nanoparticles is cubic and the lattice parameter obtained is a=b=c = 8.409 A^0 and the obtained data is well match with JCPDS No: 019-0629.

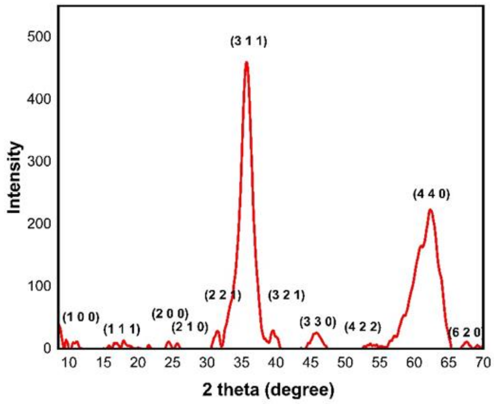

Figure 2. XRD image of magnetite (Fe_3O_4) nanoparticles.

In order to describe the optical property of magnetite (Fe_3O_4) nanoparticles, UV-visible spectroscopy was employed. The optical parameters such as absorbance spectra, absorption coefficient, refractive index, extinction coefficient optical band gap, Urbanch energy, Skin depth. The produced magnetite (Fe_3O_4) nanoparticles were found to have absorption peaks within the typical UV-vis absorption range, with a lower absorption wavelength of 203 nm being observed.

The relation between the absorption coefficient (α) and the incident photon energy (hν) can be determined by using Tauc's relationship as follows [11]:

$$\alpha h\nu = \alpha_0(h\nu - E_g)^n \quad (1)$$

where α_0 is a constant and known as the band tailing parameter, Eg is the optical energy gap and n is also constant which is known as the power factor of the transition mode. Direct optical bandgap is shown in figure 3, which obtained is 5.03 eV. Indirect optical bandgap is shown in figure 4, which obtained is 3.38 eV.

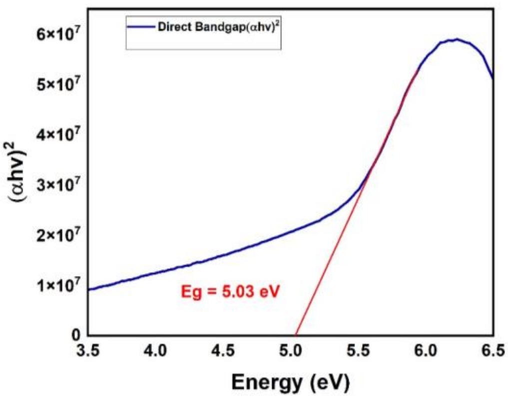

Figure 3. Direct optical bandgap of magnetite (Fe_3O_4) nanoparticles.

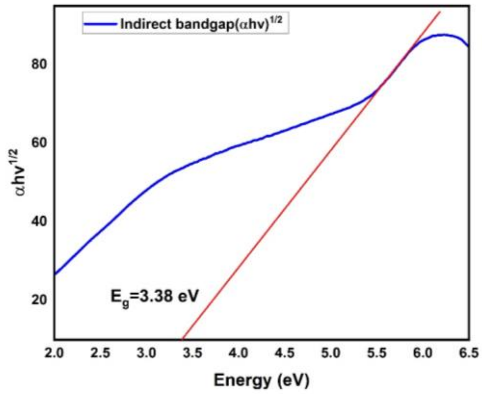

Figure 4. Indirect optical bandgap of magnetite (Fe_3O_4) nanoparticles.

The optical density the absorbance is proportional to both the thickness of samples and the concentration of the absorbing material. The optical density of the magnetite nanoparticles can be estimated by using this simple equation[11]:

$$\mathbf{D_{opt} = \alpha t} \quad (2)$$

where t is the thickness of the sample. Figure 5 shows the plot of the optical density (D_{opt}) against the incident photon energy (hν), which is obtained is 1.34 eV. The skin depth (δ) is related to the absorption coefficient (α) by the following simple relation[11]:

$$\boldsymbol{\delta = \frac{1}{\alpha}} \quad (3)$$

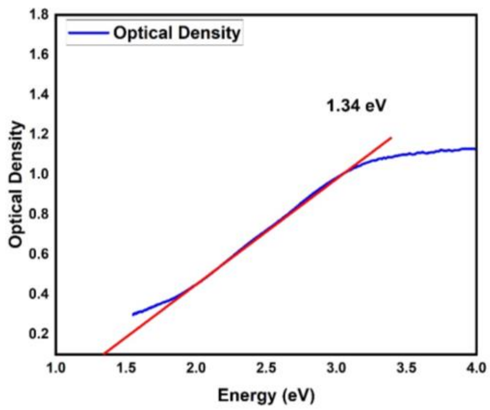

Figure 5. plot of the optical density (D_{opt}) against energy (hν) of magnetite (Fe_3O_4) nanoparticles.

Figure 6 shows plot of skin depth against energy(hν), which is obtained is 3.29 eV. The Urbach energy is calculated by ln α against Energy (hν) plot, which is shown in figure 7. The Urbach energy of magnetite nanoparticles given by following relation[11]:

$$\boldsymbol{\alpha = \alpha_0 \exp\left(\frac{E}{E_U}\right)} \quad (4)$$

where E_U is Urbanch energy; E is photon energy and α_0 is constant. The Urbach energy of magnetite (Fe_3O_4) nanoparticles is 1.36 eV.

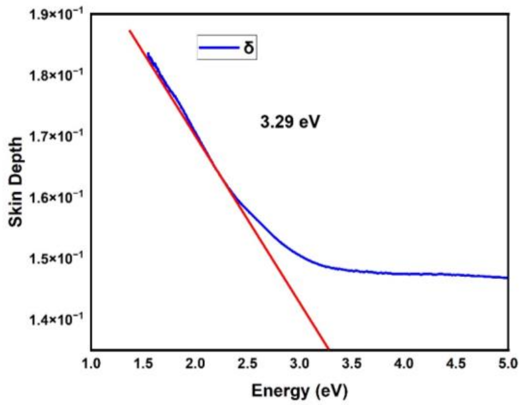

Figure 6. Plot of skin depth against energy (hν) of magnetite (Fe_3O_4) nanoparticles.

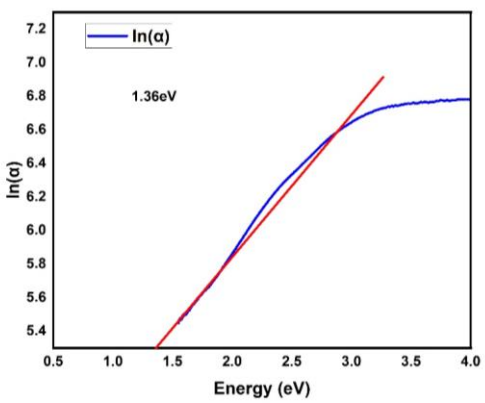

Figure 7. Plot of ln α against Energy (hν) of magnetite (Fe_3O_4) nanoparticles.

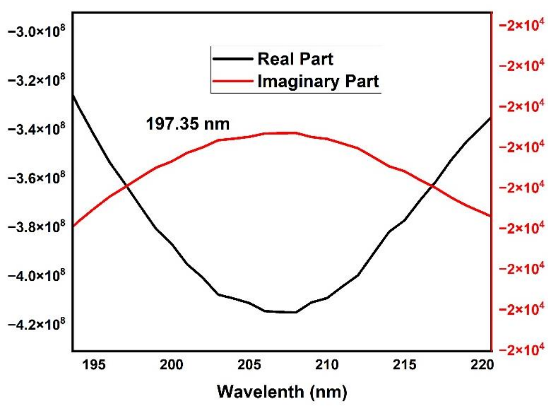

Figure 8. Plot of complex dielectric constant against wavelength of magnetite (Fe_3O_4) nanoparticles.

- Antimicrobial activity

The antimicrobial activity of the magnetite (Fe_3O_4) nanoparticles was assessed by agar well diffusion method. The bacterial cultures *Staphylococcus aureus* and *Enterobacter aerogenes* were poured over N-agar plates with 1% (W/V) top agar. The plates were allowed to be solidified at room temperature and 4 wells were bored by sterile cup borer. For the antimicrobial activity demonstration following concentration of Fe_3O_4 nanoparticles were selected – 200 ug ml^{-1}, 150 ug ml^{-1}, 100 ug ml^{-1}, and 50 ug ml^{-1}. The agar wells were filled up with magnetite (Fe_3O_4) nanoparticles solution. The antimicrobial activity was evaluated based on zone of inhibition appear around agar well and the diameter was measured in mm. As shown in figure 9.(a) the magnetite (Fe_3O_4) nanoparticles effectively inhibited the growth of *Enterobacter aerogenes* and *Staphylococcus aureus* at higher concentrations. The inhibitory effect is concentration depended and the minimum threshold for the growth inhibition was found to be between 100-150 ug ml^{-1}. The result indicates that magnetite (Fe_3O_4) nanoparticles synthesised in house have potential to be used as a bacteriostatic as well as bactericidal agent.

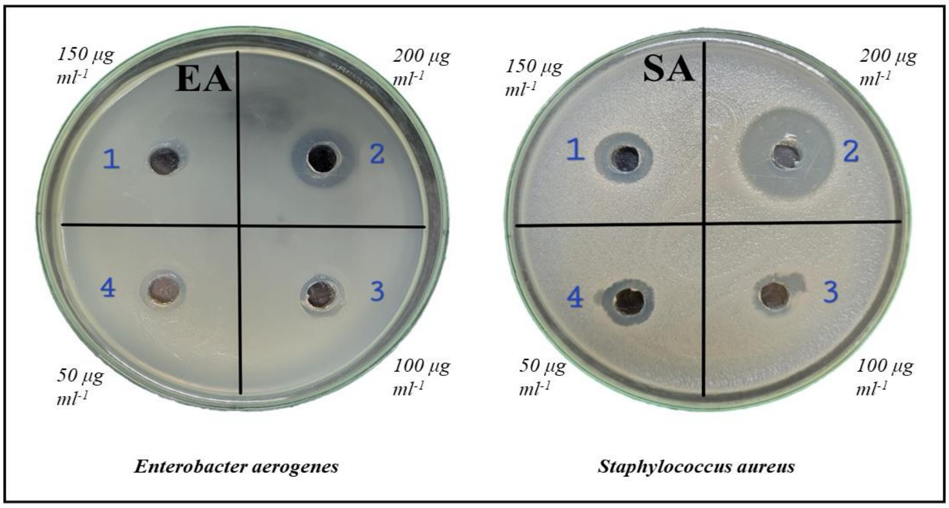

Figure 9. (a) Antimicrobial activity of Magnetite (Fe_3O_4) nanoparticles against Enterobacter aerogenes and Staphylococcus aureus.

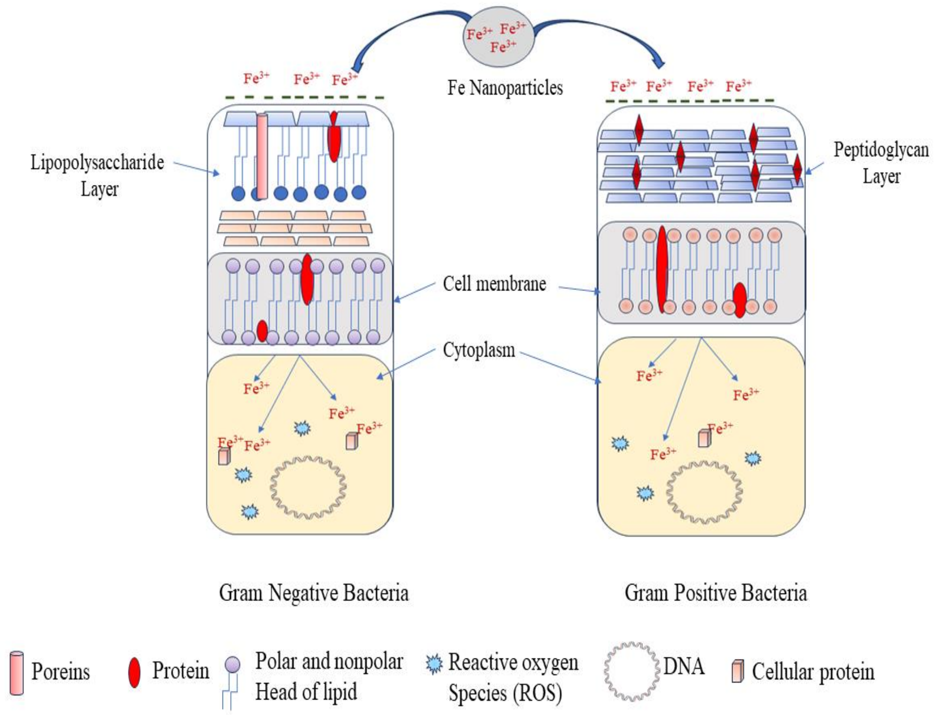

Figure 9. (b) Proposed mechanism of antimicrobial action of Magnetite (Fe_3O_4) nanoparticles. Fe^{3+} ions are attracted to negatively charged lipopolysaccharide layer in gram negative bacteria and peptidoglycan layer of gram-positive bacteria. After entering the cell, metal nanoparticles can disrupt cell membrane, block cellular proteins, disrupt cellular DNA, and generate ROS species which can lead to death of the microorganism.

4. Conclusion

Magnetite (Fe_3O_4) nanoparticles were prepared by sol-gel method at 200°C. The Sol-gel method offers several advantages for preparation of magnetite (Fe_3O_4) nanoparticles. The EDAX analysis of magnetite nanoparticles, which shows that the atomic weight % of Fe is 53.38 and the atomic weight % of O is 46.62 in the Fe_3O_4. It closes to the Stoichiometric composition of Fe_3O_4. XRD shows that Crystal structure of obtained Fe_3O_4 nanoparticles is cubic and the lattice parameter obtained is a=b=c = 8.409 A^0 and the obtained data is well match with JCPDS No: 019-0629. From UV-Visible obtained direct optical bandgap is 5.03 eV and indirect optical bandgap is 3.38 eV. The Urbach energy of magnetite (Fe_3O_4) nanoparticles is 1.36 eV. The result indicates that magnetite (Fe_3O_4) nanoparticles synthesised in house have potential to be used as a bacteriostatic as well as bactericidal agent.

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