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DNA/EDTA Assisted Synthesis of FeO-MnO Nanocomposites: Structural, Optical characterization and its Biological applications

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ABSTRACT

Nanosized Iron – Manganese Oxide Nanocomposites were prepared by co-precipitation method using Deoxyribonucleic acid(DNA)/Ethylenediaminetetraacetic acid(EDTA) as surfactants and its structural, morphological and optical characteristics were studied by X-Ray diffraction (XRD), SEM, Fourier Transform Infrared Spectroscopy (FT-IR),and UV-Visible spectroscopy. The average crystallite size was found to be minimum values 27.96&39.52nm for DNA and EDTA samples, respectively. Antimicrobial activity of the samples were investigated against a Gram-positive bacteria Staphylococcus aureus, a Gram-negative bacteria Pseudomonas aeruginosa **using agar- well diffusion method and a fungus Candida Albicans. Zone of inhibition values also calculated to determine susceptibilities of bacteria to drugs.**

Keywords: Capping agent, FeO-MnO Nanocomposites, Reactive oxygen species, Zone of inhibition,

1. INTRODUCTION

Nanocomposites are a type of high-performance material that has its own set of qualities and unique designs. Nanocomposites are emerging materials with new multifunctional properties that are influenced by the morphology and interfacial properties of individual components. Many technological applications demand mixed transition metal oxide nanocomposites, and these mixed metal oxide materials frequently comprise one or more transition-metal elements whose ionic radii and oxidation states are critical for defining their overall characteristics.

The current work presents a thorough overview of the synthesis technique, characterizations, and resistance against microorganisms, with an emphasis on the synthesis of mixed transition metal oxide nanocomposites using two distinct capping agents. Nanocomposites of transition mixed oxides exhibit a wide range of features, including a high anisotropy constant, size-dependent optical and magnetic properties, super spin glass state, and Superparamagnetism, among others.Mixed magnetic oxides have a wide range of uses, including magnetic recording, MRI contrast agent, ferrofluid, site-specific drug delivery, magnetic tunnel junction-based sensor, photo catalyst, gas sensor, and hot-gas absorbent material. The azo dye Acid Red B was shown to be successfully removed from water using MnFeO magnetic nano particles as an excellent adsorbent. [1-4]. Manganese ferrite's properties are strongly dependent on its composition, morphology, and size, which are often closely linked to the preparation conditions and the use of suitable surfactants. To prepare single-domain MnFeO nanoparticles, a variety of preparation procedures have been devised, including hydrothermal, combustion route, co-precipitation, sol-gel, mechano-chemical, solvo-thermal, and reverse micelle [5,6]. The co-precipitation procedure was utilized here for the fabrication of mixed oxide nanocomposites. The process is simple and inexpensive, and the particle size may be altered by changing reaction parameters such temperature, pH, and ionic strength induced by non-complexing salt [7]. Iron oxides and Manganese oxides are suited for numerous applications in many sectors due to their nontoxic, inexpensive, stable, and environmentally acceptable nature.

Due to its basic significance and potential wide range of applications, the synthesis and fabrication of mixed metal oxide nanocomposites with various morphologies and sizes has generated a great deal of interest in recent years.

Because of their high surface energy and magnetism, nanoparticles usually agglomerate. The choice of the surface coating agent, which is used to avoid agglomeration of the nanoparticles, has a big impact on their stability. Another benefit of this capping agent control is that it enables one to modify the nanoparticles for a certain application. DNA and EDTA are two significant capping agents employed in this investigation. The double helix structure of DNA functions as an excellent stabilizing agent as well as a template for nano particles. The use of a capping agent prevents agglomeration by effectively protecting the nuclei's surface as soon as they form, preventing them from interacting directly with the solution. Capping agents are typically compounds with longer chains [8]. Antimicrobial effects are being widely investigated due to a huge increase in bacterialresistance to commonly used antibiotics. The interfacial and surface characteristics can be altered in the presence of chemical substances. By retaining particle charge and altering the outermost layer of the particle, such chemicals can indirectly stabilize against coagulation and aggregation. They have a positive surface charge to make it easier for them to adhere to the bacteria's negatively charged surface, perhaps increasing the bactericidal impact [9]. In this study, biologically synthesized nanoparticles were found to be more effective in inhibiting bacteria.

2. EXPERIMENTAL

A. Materials

Nanocomposites of Fe-Mn oxide have been synthesized by chemical co-precipitation method by using their respective metal chlorides, sodium hydroxide and DNA/EDTA as capping agent.The conditions have been standardized and optimized. The choice of correct molarity results in the yield of good nanoparticles.

B. Methods

Preparation of Samples

In the present work the samples were prepared by chemical co-precipitation method by using chemical and biological surfactants (EDTA and DNA). The samples prepared are nanoparticles of Iron-Manganese oxide at a specific stoichiometric ratio by using two capping agents, which helps to study the role of capping agents in determining the size and morphology of the prepared samples.By varying capping agents two samples were prepared. Forthe preparation, iron (III) chloride and manganese (II) chloride were used as cationic precursors, at their respective molarity is dropped in to DNA/EDTA solution having very low molarity.

Sodium hydroxide solution as an anionic precursor is used to adjust the pH of the solution to enable precipitation. All the chemicals are of AR grade and use double distilled water. The rate of dropping is adjusted at 10ml/hr under constant stirring of 5hours using a magnetic stirrer. A precipitate is obtained is washed with alcohol and distilled water several times and then dried.On heating at the required temperature the hydroxide precursor decomposes in to Iron-manganese oxide. In this present study samples are heated at 600^{o}C.In the present work two different samples were prepared. They are named as SD16 (0.1m $MnCl_2$+0.1m $FeCl_2$and DNA), SE16(0.1m $MnCl_2$+0.1m $FeCl_2$and EDTA).

Characterization of the samples

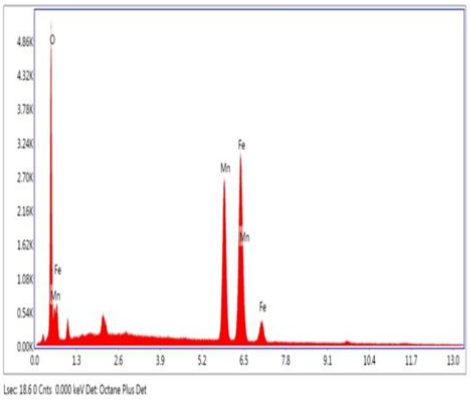
After the synthesis of the sample it is essential to find the elemental composition. Here we used Energy dispersive X-ray analysis to find the composition of the sample. In EDS analysis by measuring the amount of energy of X-Rays released by a specimen during the electron beam collision,we can identify the atoms present in the specimen. The XRD measurements of the prepared samples were done using XPERT-PRO model X-ray diffractometer using CuKα radiation of wavelength λ=1.5406A^0 at 40KV and 100mA at a scanning rate of 5^0/min.

The average particle size of the nanocrystalline samples can be measured from the X-ray line broadening analysis without taking instrumental correction to line broadening .The FTIR studies of all the samples were carried out in a Perkin-Elmer FTIR spectrometer between 300 cm^{-1} to 4000cm^{-1} .Absorption spectra of the samples are taken at room temperature with the help of a JascoV550 UV/Vis-NIR spectrophotometer. Optical studies were performed by measuring the transmittance of the samples wavelength range λ (200-850nm) using the spectro photometer.

3. RESULTS AND DISCUSSION

C. Compositional analysis(EDS)

The elemental composition and purity of the samples were confirmed by EDS analysis and peaks obtained are shown in the fig. The EDS spectrum indicates the presence of Fe, Mn and O in the sample. Thus EDS spectrum confirms the purity and stoichiometry and composition of the prepared samples.



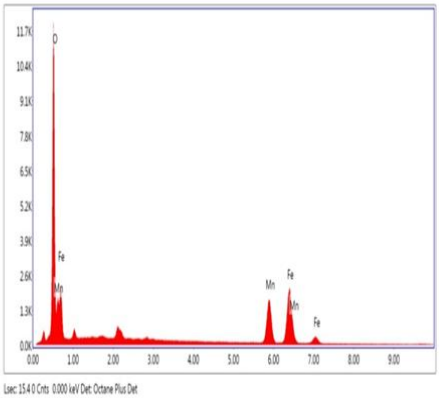


Figure.1 **Figure.2**

Figure.1&2 shows EDS spectrum of FeO-MnO by using DNA/EDTA as capping agent

D. X-ray Diffraction Analysis(XRD)

Figure shows the XRD pattern of Iron-Manganese Oxide nanoparticles synthesized using a biomolecule DNA and a chemical compound EDTA as surfactants. In SD1 the phase separation between α-$Fe_2O_3$and Mn_2O_3 is clearly visible and the formation of the mixed/binary nanocomposite was confirmed. XRD patterns of these two samples show two prominent peaks from the planes (104) and (110) along with weak intense peaks from (116), (024), (012), (300), (125), (113). The presence of these peaks revealed the rhombohedral phase of hematite in two samples and match with ICDD Card No: 710-636. The most intense diffraction peak from (104) at 2θ=330 confirms the formation of both phases in the sample. The intense peak from the planes (104), (440) and other peaks from (211), (400), (522), (322) confirms the orthorhombic phase of Mn_2O_3 with ICDD Card No: 240-508. The XRD analysis of above samples indicates the formation of α-Fe_2O_3 /Mn_2O_3 nanocomposite with pure crystalline nature. A nanocomposite is a mixture of different phases of materials hence its XRD pattern shows diffraction peaks related to all phases present in it. Peak broadening in both cases depends upon the crystallite size and strain developed in them. In the case of EDTA capped sample SE1 shows mixed phase with rhombohedral and orthorhombic crystal system. The XRD results indicates that DNA as surfactant led to the formation of nanoparticles with good crystallinity with no impurity phase. From this XRD data, the particle size and the micro strain have been calculated.The XRD results indicate that DNA as surfactant led to the formation of nanoparticles with good crystallinity with no impurity phase.

The average crystallite size can be calculated using Scherrer equation. The crystallite size of the particles were calculated using Debye Scherrer's formula,

$$D=K\lambda/\beta\cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where β = full width half maximum (FWHM), K = grain shape dependent constant (0.9), λ= wavelength of incident beam, θ = Bragg Reflection angle in degree. The obtained crystallite sizes of the particles were 27.96nm and 39.52nm for SD1 and SE1respectively.

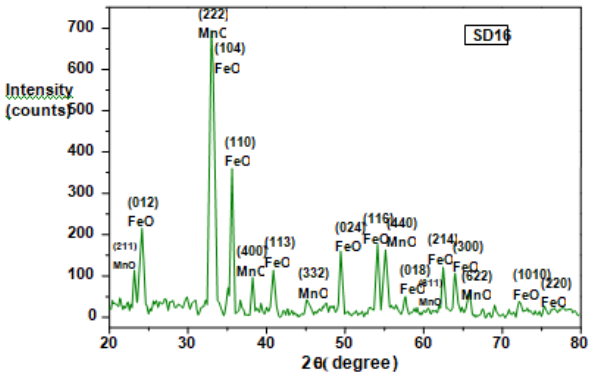


Figure.3XRD patterns of the sampleSD1 sample

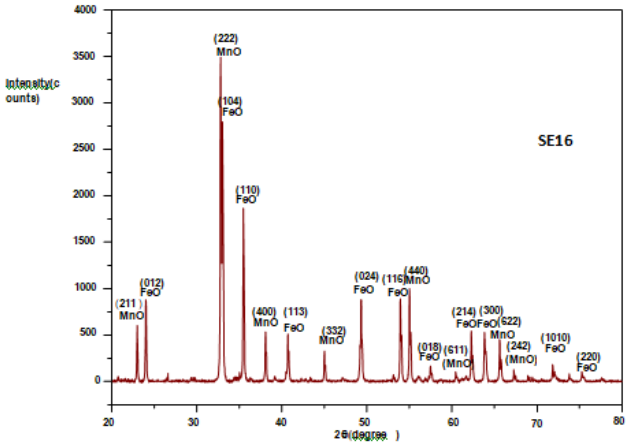


Figure.4 XRD patterns of the sample SE1 sample

E. Fourier Trans form Infrared Spectroscopy (FTIR)

FTIR Spectroscopy gives information about molecular vibration or transition between vibration and absorption energy level. Absorption of radiation in the infrared region results in the excitation of bond deformation, either stretching or bending vibration occurs at certain quantized frequencies. FTIR spectrum of nanocomposites using different capping agents annealed at 600^0C are shown in fig.5.The broad peaks around the point h (3300-3405$cm^{-1)}$ indicates the presence of stretching vibration of intermolecular hydrogen bond(O-H)bond[10]. Peaks appearing below 700$cm^{-1}$are due to metal oxide bonds. The band around b (517$cm^{-1)}$ and a (428cm^{-1})is attributed to the Fe–O stretching and bending vibration mode of α-Fe_2O_3respectively[11]. The weak band near f (1600 cm^{-1}) is assigned to H–O–H bending vibrations mode. The appearance of such peak is representative of adsorbed water molecules on the external surface of α-Fe_2O_3sample during handling to record FTIR spectra. These observations provided the evidence of the hygroscopic nature of the sample. Another broad band at 1379cm^{-1}, is due to the metal coordinated carboxylic ion (COO^{-}).

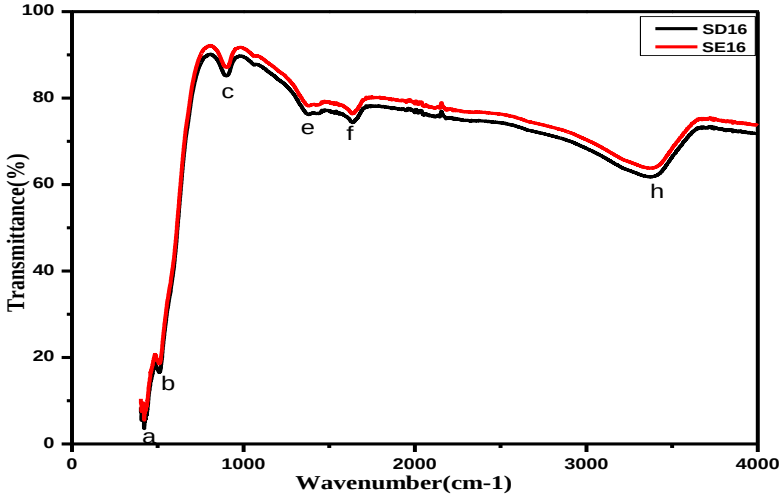


Figure.5. FTIR spectrum of the samples SD1&SE1

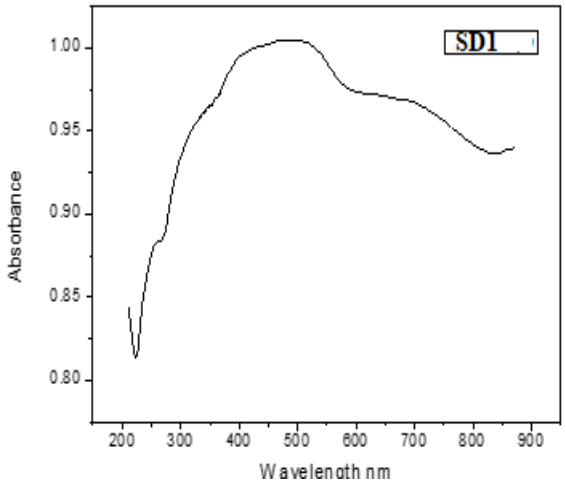
F.UV-Visible Spectroscopy

UV-Vis absorbance spectrum of functionalized DNA/EDTA capped FeO-MnO nanocomposite is as depicted in Fig.6&8.The optical properties of nano composite materials differ from those of the components commonly used to make composites.The absorption edge is extended to visible range of spectra due to the inclusion of manganese oxide in to the iron oxide matrix, as seen by the UV-Visible absorption spectrum. It may make use of the visible part of the sun's rays for a variety of purposes.

The Kubelka-Munk method employs for the determination of bandgap of the nanostructures. Plotting the Kubelka-Munk function versus photon energy yields the bandgap value. As depicted in fig.7&9, the linear section of the curve is extrapolated to the photon energy axis, yielding the bandgap value.
The bandgap of the material is calculated using the relation,

F(R) hυ=A (hυ -Eg) ᵑ…….. (2)

Where F(R) is the Kubelka –Monk function
The band gap values of SD1 and SE1 are found to be 1.91 and 1.94eV respectively. In the case of SE1&SD1 samples Band gap energy of the materials increases due to the quantum confinement effect. However, the band gap of nanocomposites formed decreases compared to individual metal oxides. The bandgap of the material is reduced if visible light absorption increases.



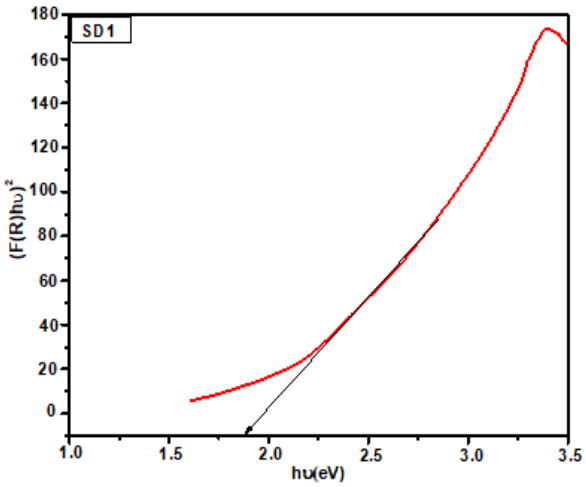
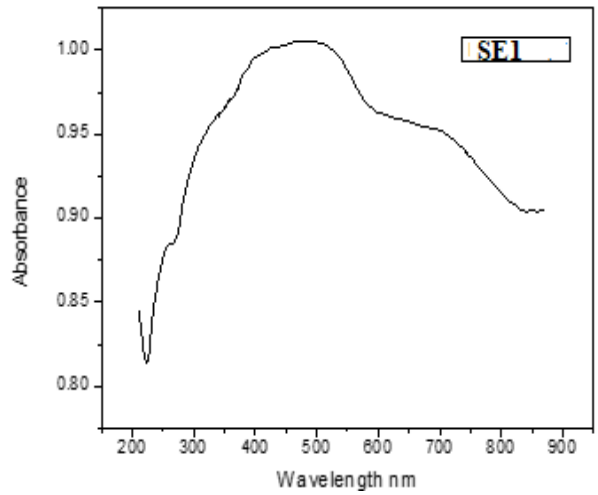


Figure. 6. **Figure.7.**

Figure.6&7UV-Visible Absorption spectra and Tauc plot of the samples SD1



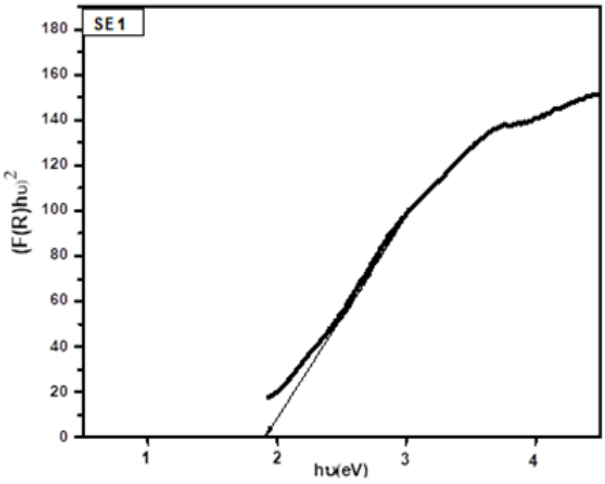


Figure. 8. **Figure.9.**

Figure.8&9 UV-Visible Absorption spectra and Tauc plot of the samples SE1

G.Field Emission Scanning Electron Microscope (FESEM)

With high-resolution imaging, FESEM pictures of mixed oxide nanostructures were obtained to analyze surface textures thoroughly. Fig.10 shows that nearly all of the nanoparticles are spherical in form with limited aggregation. This is due to the fact that the incorporation of manganese oxide into the hematite matrix affected the grain growth of the FeO lattice. Because of its versatility, various modes of imaging, wide range of magnifications help the easy interpretation of the images taken in FESEM.

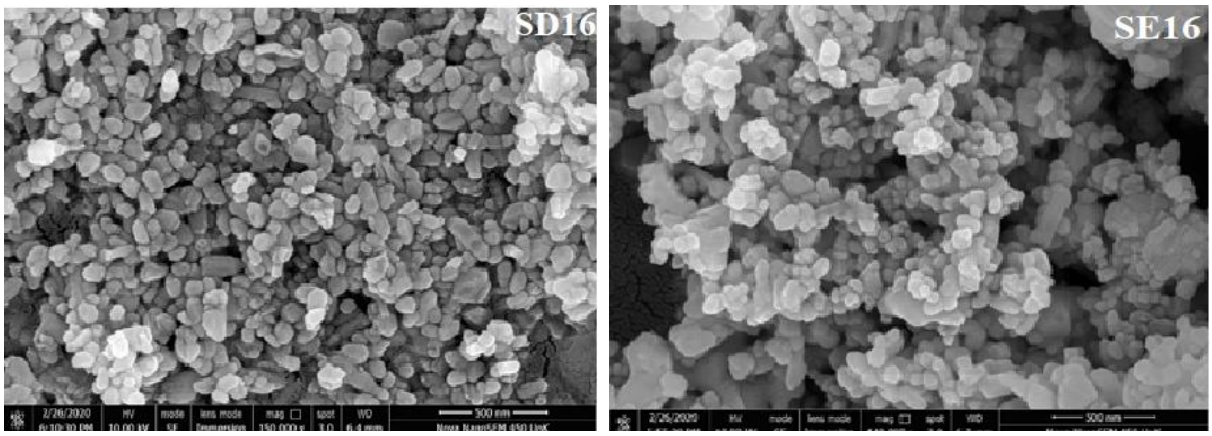


Figure.10. FESEM images of samples SD1, SE1

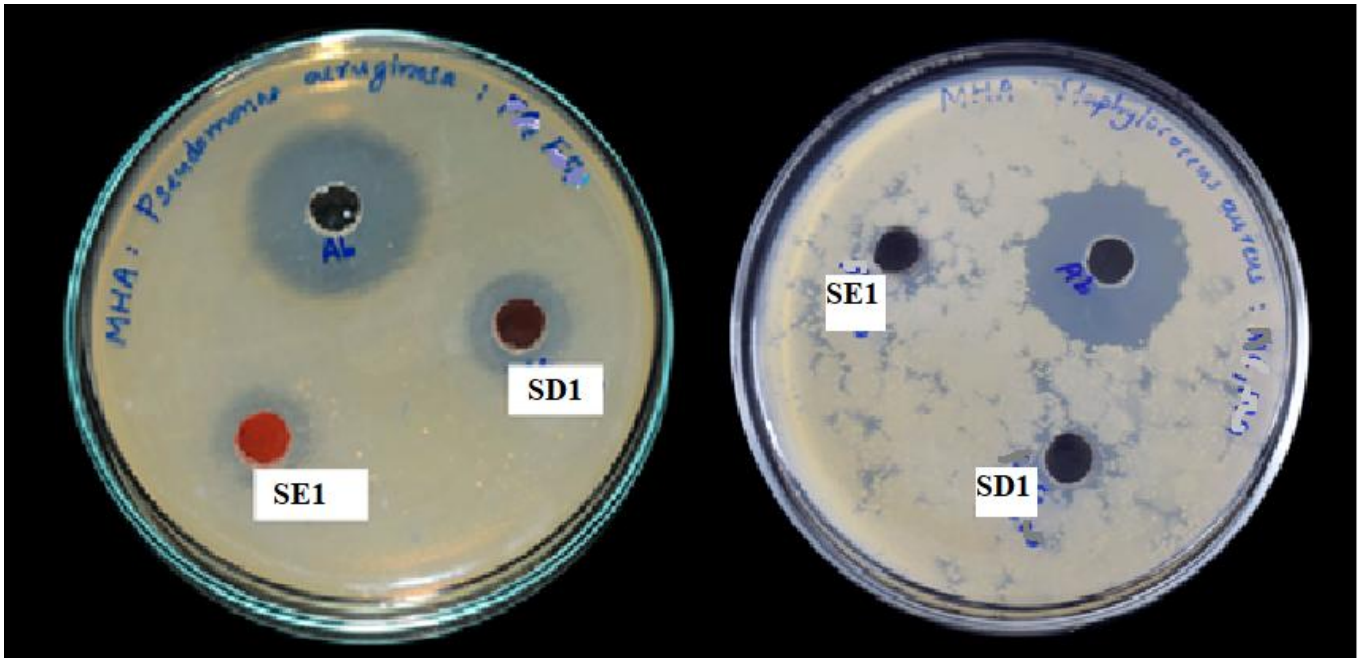
H. Antimicrobial activity

The antimicrobial activity was performed on DNA/EDTA stabilized Iron- manganese oxide nanoparticles against a gram-positive Staphylococcus aureus.a gram-negative bacteria Pseudomonas aeruginosa and a fungus Candida Albicansby agar- well diffusion method. The zone of inhibition was compared to a well-known commercial antibiotic Streptomycin and Clotrimazole. In this method wells of approximately 10mm was bored using a well cutter and a specific concentrations of sample such as 500µg/mL, was added. The plates were then incubated at 37°C for 24 hours. The antimicrobial activity was assayed by measuring the diameter of the inhibition zone formed around the well. The results of the quantitative antibacterial assessment by agar- well diffusion method are shown in table 1 .It was observed that the inhibition zone of DNA stabilized Iron manganese oxide nanoparticles was higher than the EDTAstabilized Iron manganese oxide nanoparticles for all bacterial and fungal strains. The synthesized nanoparticles exhibited the strongest antibacterial activity against Pseudomonas aeruginosa thanStaphylococcusaureus in 500µg/mL concentration.The diameter of the Zone of Inhibition (ZOI) of studied pathogen and samples at different concentrations were presented in table.1. Here, we also found an inverse dependence between particle size and activity. It was reported that the diameter of the inhibition zone higher than 6mm exhibits better antibacterial activity [12].On the basis of observed results, the nanocomposite ofSD1 powder could be a very good material for disinfectant purposes.

Table.1 The diameter of the Zone of Inhibition (ZOI) obtained for the antimicrobial activity of prepared samples

Samples	Amount (µg/mL)	Diameter of Inhibition Zones(mm)		
		Staphylococcus Aureus (Gram positive)	Pseudomonas aeruginosa (Gram Negative)	Candida Albicans (Fungus)
Streptomycin	100	28	27	…..
Clotrimazole	100	…..	…..	34
SD1	500	11	16	21
SE1	500	5	15	16

Morphological or surface altered iron oxide nanoparticles can produce excellent toxicity against Gram-negative bacterial cells. The possible mechanism of action of a bio-nano composite involves the direct and indirect interaction of nanoparticles.In the direct interaction, Fe^{3+} and Mn^{2+} cationic nanoparticles released from the nanostructures directly interact with the anionic bacterial surface, and adhesion of nanoparticles to the bacterial surface takes place. Nanoparticle binding to the microbial cell membrane is aided by a strong electrostatic attraction between nano-bio surfaces, which breaks the cell membrane and leads to microbial infection. In indirect interaction, ROS production of nanoparticles may cause oxidative stress which leads to membrane disruption, mitochondrial dysfunction, and DNA damage.It was also reported that in the presence of H_2O_2, manganese oxide can generate hydroxyl-free radicals which adversely affects microbial cells. [13].



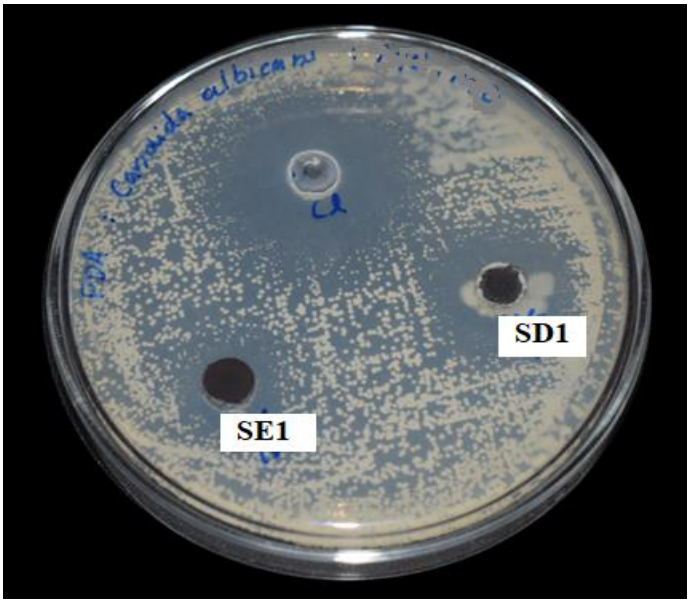


Figure.11. Inhibition zones obtained for (a) Pseudomonas aeruginosa (b) Staphylococcus aureus
Figure.12. Inhibition zones obtained for Candida Albicans

Bicationic mixed nanostructures with high electrostatic charge densities provide high proximity to microbial cells. Synthesized mixed metal oxide nanocomposites have been shown to have antimicrobial properties, indicating that they can be used as bioactive materials. Due to the interaction with the negatively charged biological membrane, the synthesized compounds have a small particle size, which increases their stability in the presence of biocatalysts and improves their antibacterial activity.

CONCLUSION

Highly stable nanocomposites of FeO-MnO synthesized by co-precipitation method by using DNA/EDTA as surfactants. The structural, morphological and optical characteristics and defense against microbial were studied by using chemical and biological surfactant. Manganese ion concentration and capping agent affected the particle size as well as optical properties. Over all characteristics of the sample is improved by adopting biological capping agents for

the synthesis.It is seen that biologically synthesized nanoparticles possess an enormous potential as an antimicrobial agent and can be pursued as an important material for future studies.

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REFERENCES

[1]. Carta D., Casula M. F., Floris P., Falqui A., Mountjoy G., Boni A., Sangragoria C. and Corrias A., "Synthesis and microstructure of manganese ferrite colloidal nanocrystals". Phys. Chem. Chem. Phys., 12 (2010) 5074-5083.
[2]. Kim D. H., Nikles D. E. and Brazel C. S., "Synthesis and Characterization of Multifunctional Chitosan- $MnFe_2O_4$ Nanoparticles for Magnetic Hyperthermia and Drug Delivery". Materials, 3 (2010) 4051-4065.
[3]. Mozaffari M., Behdadfar B., and Amighian J., "Preparation and Characterization of Manganese Ferrite Nanoparticles via Co-precipitation Method for Hyperthermia". Iranian J. Pharmaceutical Sciences, 4(2) (2008)115-118.
[4]. Sam S. and Nesaraj A. S., "Preparation of $MnFe_2O_4$ Nanoceramic Particles by Soft Chemical Routes". Int. J. Appl. Sci. Eng., 9(4) (2011) 223-239.
[5]. Rafique M. Y., Li-Qing P., Javed Q., Iqbal M. Z., Hong-Mei Q., Farooq M. H. Zhen-Gang G. and Tanveer M., "Growth of monodisperse nanospheres of $MnFe_2O_4$ with enhanced magnetic and optical properties". Chin. Phys. B, 22 (10) (2013) 107101- 107107.
[6]. Deraz. N. M, Alarifi. A., "Controlled Synthesis, Physicochemical and Magnetic Properties of Nano-Crystalline Mn Ferrite System". Int. J. Electrochem. Sci., 7 (2012) 5534-5543.
[7]. Gnanaprakash G., Philip J. and Raj B., "Effect of divalent metal hydroxide solubility product on the size of ferrite nanoparticles". Materials Letters, 61 (2007) 4545-4548.
[8]. Javed, R., Zia, M., Naz, S. et al. Role of capping agents in the application of nanoparticles in biomedicine and environmental remediation: recent trends and future prospects. J Nanobiotechnol **18,** 172 (2020).
[9]. Linlin Wang, Chen Hu, and Longquan Shao,"The antimicrobial activity of nanoparticles: present situation and prospects for the future**",**Int J Nanomedicine. 2017; 12: 1227–1249.
[10]. Debasish Sarkar, Kalyan Mandal and Madhurai Mandal "Synthesis of chainlike α-Fe2O3 Nanoparticles in DNA template and their characterization", Nano Science and Nanotechnology Letters, 3, (2011), 170 – 174.
[11]. Patsalas P, Logothetidis S and Metaxa C, "Optical performance of nanocrystalline transparent ceria films", Applied Physics Letters, 81, (2002), 466.
[12]. Karthik K, Dhanuskodi S, Gobinath C, Prabu Kumar Seetharaman and Sivaramakrishnan S, "Multifunctional properties of microwave assisted CdO– NiO–ZnO mixed metal oxide nanocomposite: enhanced photocatalytic and antibacterial activities", J Mater Sci: Mater Electron, 29, (2018), 5459.
[13]. Sourov Chandra, Pradip Das, Sourav Bag, Radhaballabh Bhar and Panchanan Pramanik, "Mn_2O_3 decorated graphene nanosheet: An advanced material for the References 172 photocatalytic degradation of organic dyes", Materials Science and Engineering: B, 177, 2012, 855-861.