Ni Substituted MgMn Nanoferrites as Antibacterial Agent for Biotextile Application

M. S. Revathy, S. R. Chitra, R. Suman, S. Shenbagavalli, S. Jeyavijayan, T. Theivashanthi

Abstract: Biological aspects of nanoferrite incorporation is growing in demand in textile industries. In this regard the present study focuses on the synthesis of nanoferrite with Nickel substitution by Coprecipitation route. Structural studies of the nanoferrites was analyzed using X-ray diffraction. The chemical analyses determined by TEM, was in good agreement with that of XRD analysis. Thermal analysis by TG/DTA inferred that nanoferrites were thermally stable due to Ni dopants added with the compounds. $MgMnNiFe_2O_4$ nanoferrites on cotton fabrics was subjected antibacterial assay on various pathogenic microorganism and exhibits the zone of inhibition. The fabricated nanoferrites on cotton fabrics showed great durability evidenced by their antibacterial activities even after 20 washing cycles. Hence, the functionalized cotton fabrics could be used as a potential antibacterial agent.

Keywords: Antibacterial activities, Co-precipitation, Ferrites, TEM, TGA XRD.

I. INTRODUCTION

Ferrite compounds has generic formula XFe_2O_4 where X being a divalent metal ion (Fe^{2+},Ni^{2+},Mg^{2+},Mn^{2+},Zn^{2+},Cu^{2+}). Nanoparticulate ferrites has credible properties such as uniform size of the particle and narrow size distribution, non-toxic, antimicrobial, biocompatibility, biodegradability and chemical inertness. These properties makes it a desirable candidate for multifarious applications like drug delivery, ferrofluids, medical imaging, magnetic data storage, sensors, catalytic, microwave applications [1,2]. Recent investigated literatures of nanoferrite particle, claims that it can be applied in biomedical field due to its antibacterial properties.

For the preparation of the identified ferrite compound coprecipitation liquid phase route is best suited due to desirable stoichiometry, process done at low temperature, rapid, doesn't require sophisticated instruments.

Herein we present, substitution of Ni^{2+} on Mg-Mn ferrites using simple technique of coprecipitation. The structural characterization was performed with XRD and the effect of Ni^{2+} ions on morphological and thermal properties for the development of antimicrobial textiles was analyzed with SEM and TGA respectively.

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II. EXPERIMENTAL

The study seeks to address, a series of ferrites $Mg_{0.40}Mn_{0.60-x}Ni_xFe_2O_4$ [$0.00 \leq x \leq 0.45$] prepared with the appropriate stoichiometric amounts of Ni using chemical co-precipitation method owing due to its relative easy reaction process, good quality control over the particle dimension and shape[3].

The chosen precursors $MgSO_4.7H_2O$, $MnSO_4.H_2O$, $NiSO_4.6H_2O$ and $FeCl_3$ (0.2M) for the study were made into aqueous solutions in 100 ml DM(Demineralized) water. The alkaline NaOH of 3M concentration was added gradually to the former aqueous bath. Under constant stirring, the temperature was optimized to 70 °C waited for obtaining a clear solution. The settled precipitate was carefully collected and was dried. Finally, ultrafine particles of Mg0.40Mn0.60-xNixFe2O4 were prepared. Similar process was repeated for the different concentrations of x = 0, 0.15, 0.25, 0.35 and 0.45.

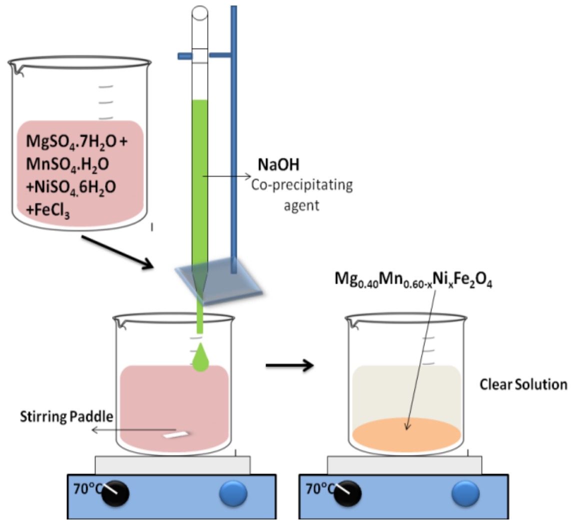

Fig.1. Schematic illustration of synthesis process

Steps involved in the synthesis are co-precipitation and ferritization. Solid hydroxides of metals in the form of nanoferrites were obtained by the co-precipitation of metal cations in alkaline medium. Solid solution of metal hydroxides was transformed to complex nickel substituted nanoferrites when subjected to heating in the alkaline medium.

III. RESULTS AND DISCUSSION

A. Structural Studies

For the structural characterization and formation of single spinel phase, all the samples were characterized by XRD analysis using Philips X'pert PROPANalytic X-ray diffractometer which uses CuKα as a radiation source, was used to confirm the formation of spinel phase, operated maximum resolution. TABLE- I yields the parameters values of $Mg_{0.40}Mn_{0.60-x}Ni_xFe_2O_4$for different concentrations (*x*). The measured density as well as X-ray density of the prepared samples was estimated using the relation,

$$\rho_m = \frac{m}{r^2 h} \quad (1)$$

$$\rho_x = \frac{8M}{Na^3} \quad (2)$$

where m, the mass; r, the radius; h, height; M, the molecular weight of the samples; N, the Avogadro's number and a, the lattice constant.

In the compositions of the nanoferrite, there was a notable observance of decrement in the values of lattice parameters with the reduction in Mn concentration. Also, there was an increment in Ni concentration. Likewise, average crystallite size was found to depend on Mn (*x*) concentration. The value shows decrement with decrease in the concentration of Mn due to the fact that, larger Mn ionic radius could be replaced by smaller Ni ionic radius (i.e) larger metal ions might have been substituted with relatively smaller metal ions. This observation was in good agreement with other research reports[4].

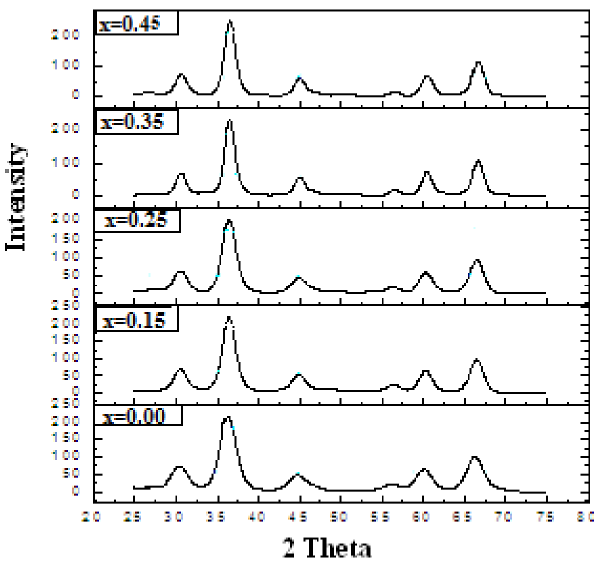

Fig. 1. Typical XRD patterns of $Mg_{0.40}Mn_{0.60-x}Ni_xFe_2O_4$ $(0.00 \le x \le 0.45)$ nanoferrites

Table- I: Lattice parameters of the prepared nanoferrites

Parameters	Compositions of x				
	0.00	***0.15***	***0.25***	***0.35***	***0.45***
D (nm)	9.52	14.25	14.12	9.88	9.50
a (Å)	8.415	8.433	8.429	8.4209	8.402
$V(A)^3$	595	599	598.12	596	594
ρ_x (X-Ray Density)	5.85	5.81	5.814	5.838	5.84
ρ_m (Measured Density)	4.41	4.39	4.397	4.41	4.42

B. Morphological Studies

Morphological studies of TEM explained the complete picture of the nanoferrites and are shown in Fig.2.

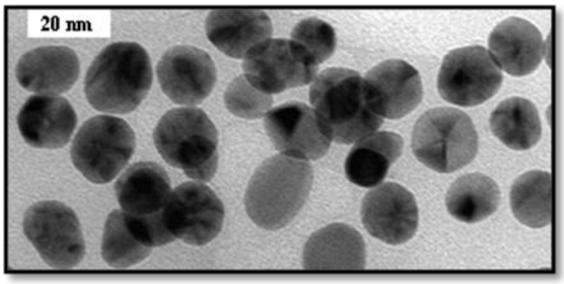

Fig. 2. TEM image for $Mg_{0.40}Mn_{0.60-x}Ni_xFe_2O_4$ nanoferrites with the compositions of x=0.45

In the image there were uniform distribution and less agglomeration of homogenous spherical particles with size of 20 nm and in line with the agreement of XRD analysis.

C. Thermal Analyses

TGA/DTA spectra have been recorded in temperature range from 25 to 800 °C at a heating rate of 10˚C per min using Thermo-Gravimetric Analyzer with Differential thermal analyzer (SII Nanotechnology Inc., Japan, EXSTAR 6000 TG/DTA). Thermogravimetry is an extensively used tool for thermal stability, decomposition temperature, temperature of desorption and drying, oxidative stability determination of the synthesized product[5]. Usually, powder samples ranging from 8 mg to 10 mg were weighed and heated from 50 to 800 °C. During this process temperature difference and weight loss were recorded as a function of temperature.

The TG/DTA/DTG plots for the synthesized ferrites are shown in Fig. 3. From TG analysis we observed that all the samples have been observed to possess weight loss in four steps. The very first weight loss around 100 ^{o}C could be attributed to initial dehydration, loss of mass is due to vapourization of surface water molecules and more loss of mass around 250 ^{o}C due to vaporization of trapped water molecules.

The temperatures of respective weight losses have been observed to increase with increasing Ni concentration. In DTA thermogram, the weight loss below 150 °C is linked with an endothermic DTA peak occurred due to absorbed water loss. The first exothermic peak at around 250 °C in the DTA curve, go together with a very large weight loss (around 25%) in the TGA thermogram. During this period small weight loss occurred in the temperature range 250°C to 500 °C along the second DTA exothermic peak, which is probably due to the removal of excess water (if any). Beyond this temperature the material began to degrade. Theoretical weight loss, % and Experimental weight loss, % of the prepared samples were calculated and tabulated in Table- II.

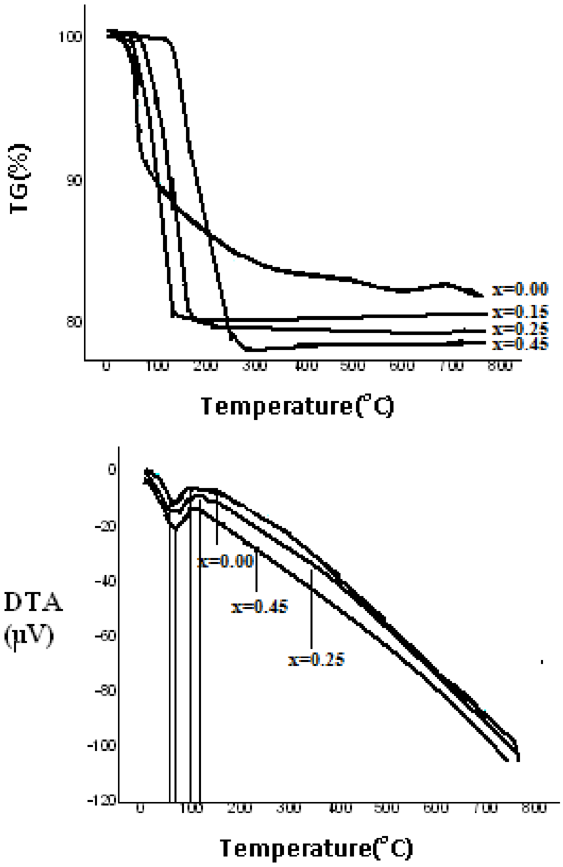

Fig. 3. Typical TGA/DTA profiles of the samples

Table- II: Theoretical Weight Loss, % And Experimental Weight Loss, % Of The Prepared Samples

x	Temperature of dehydration	Theor. weight loss, %	Experimental weight loss, %
0.00	90	7.47	7
0.15	120	20.12	19.5
0.25	180	21.8	20.5
0.35	210	22.3	21.5
0.45	250	22.6	22.25

D. Antibacterial assay

The antibacterial activities of the prepared nanoferrites of dissimilar concentration were tested against the pathogens like *Pseudomonas fluorescens*, *Proteus mirablis*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Escherichia coli* and *Enterobacter aerogenes* were inoculated in nutrient broth and kept in shaker for overnight incubation. Antibacterial activities were evaluated by measuring inhibition zones. Different concentrations of synthesized nanoferrites were loaded on cotton fabrics to study their antibacterial activities by agar based diffusion method. The loaded plates were incubated at 40 °C for 24 hours and inhibition zones developed around the discs was measured[6]. The nanoferrites treated on cotton fabrics were evaluated for their antibacterial activities before and after washing.

The test organisms, bacterial strains are *Proteus mirablis* [**MTCC 3310**], *Staphylococcus aureus* [**MTCC 87**], *Enterococcus aerogenes* [**MTCC 111**], *Escherichia coli* [**MTCC 64**], *Klebsiella pneumoniae* [**MTCC 39**], *Pseudomonas fluorescens* [**MTCC 103**] were procured from IMTECH(Institute of Microbial Technology). Agar based diffusion method was carried out for anti-bacterial evaluation [7].

Table- III: Antibacterial activities of $MgMnNiFe_2O_4$ ferrite particles

Organism	Antibacterial activities (Zone of inhibition in cm)			
	25 μg/ml	50 μg/ml	75 μg/ml	100 μg/ml
Proteus mirablis	-	1.3	1.8	1.9
Staphylococcus aureus	-	1.8	1.9	2.0
Enterococcus aerogenes	-	1.6	1.7	2.4
Escherichia coli	-	1.4	1.8	2.2
Klebsiella pneumoniae	-	1.0	1.4	1.7
Pseudomonas fluorescens	-	0.8	1.5	1.8

- Recording of Zone of inhibition

Nanoferrites treated on cotton fabrics (10 mm × 10 mm) were used. Steps involved for observation

1. Selection of bacterial stains (Gram positive : *Staphylococcus aureus*, *Bacillus subtilis*, *Streptococcus* sp. and Gram negative: *Escherichia coli*, *Proteus mirablis*, *Klebsiella pneumonia*)
2. Inoculation of bacterial pathogens in sterile nutrient broth.
3. Incubation of plates for 24 hours at 40 °C
4. Recording of zone of inhibition around the fabrics.

E. Antibacterial reduction % (After washing)

The nanoferrites treated on cotton fabrics were evaluated for their antibacterial activities before and after washing. $MgMnNiFe_2O_4$ particles coated and uncoated fabrics were taken individually in 3000 ml sterile Schott Duran flasks and 1 ml of overnight grown bacterial suspension was added.

Percentage reduction(PR) of each bacterium was estimated by the formulae:

$$PR = \frac{[100(B-A)]}{B} \qquad (3)$$

where A and B are the total number of bacteria recovered from nanoferrites untreated and treated on fabrics respectively. $MgMnNiFe_2O_4$ nanoferrites wash durability treated on cotton fabrics was assessed after 5, 10 and 15 wash cycles using neutral soap (5% Hiclean, HiMedia) at 40 ± 2°C for 45 minutes with a material to liquid ratio of 1:50. Then subsequent rinsing and drying was repeated to a maximum of 15 wash cycles. The prepared nanoferrites showed greater inhibitory activity against all the experimental strains with 50μg/ml and above concentrations are shown in Fig. 4 and Table- III.

Table- IV: Effect of wash cycles on antibacterial activities of cotton fabrics loaded with particles

Organism	Antibacterial activity (Reduction percentage %)			
	Before washing	*After 5 washes*	*After 10 washes*	*After 15 washes*
Proteus mirablis	99.81	98.63	96.13	94.32
Staphylococcus aureus	99.52	98.54	96.11	94.43
Enterococcus aerogenes	99.78	98.85	96.34	94.87
Escherichia coli	99.37	98.78	96.14	95.53
Klebsiella pneumonia	99.45	98.76	96.17	95.02
Pseudomonas fluorescens	99.12	97.76	95.23	92.98

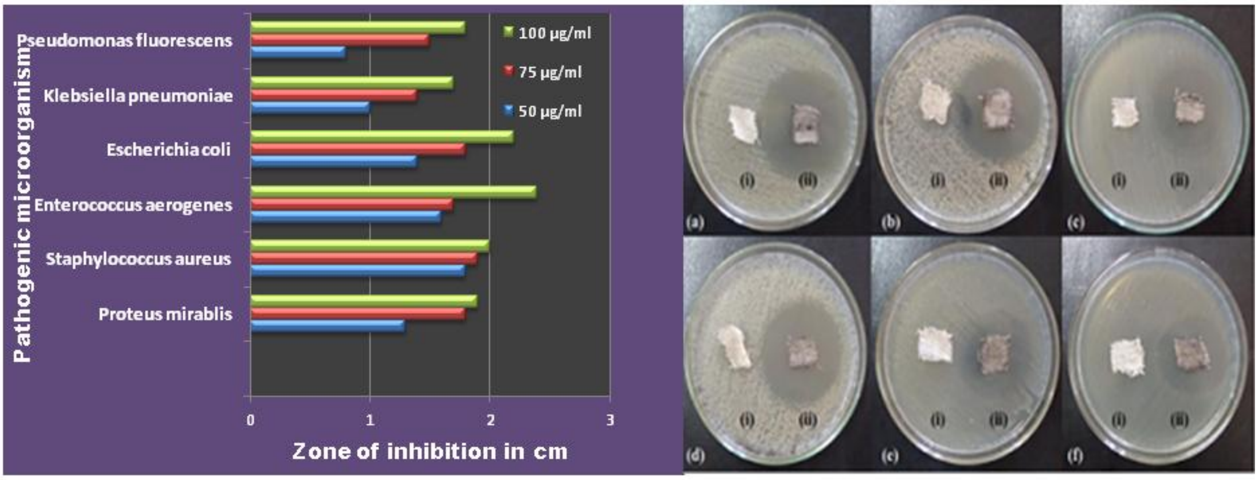

Fig. 4. Antibacterial activities on cotton fabrics with coated and uncoated particles (I) 25 µg/ml; (II) 50 µg/ml; (a) Proteus mirablis, (b) Staphylococcus aureus, (c) Enterococcus aerogenes, (d) Escherichia coli,(e) Klebsiella pneumoniae, (f) Pseudomonas fluorescens

It is obvious from the Table- III that antibacterial activity of the zone of inhibition = 100 µg/ml is found to be higher in *Escherichia coli* and *Enterococcus aerogenes* than those of other concentrations. However lesser activity is recorded on *Pseudomonas fluorescens*. The antibacterial properties of $MgMnNiFe_2O_4$ nanoferrites treated on cotton fabrics were evaluated against selected Gram positive and Gram negative bacteria.

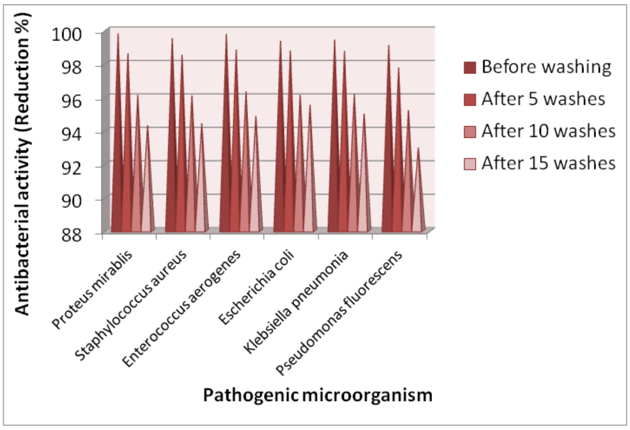

Fig. 5. Antibacterial responses in effect of wash cycles of cotton fabrics loaded with particles

The antibacterial efficiency of the prepared nanoferrites treated on cotton fabrics was studied using agar diffusion assay and the results were shown in Fig. 5 and TABLE- IV. Furthermore preceding studies have indicated that the smaller $MgMnNiFe_2O_4$ particle size, the greater the efficacy in inhibiting the growth of bacteria than other's reports[8,9]. conversely nanoferrites of $MgMnNiFe_2O_4$ were formerly reported to act both as bactericidal agent and also bacteriostatic agent possibly thereby limiting their biomedical use.

IV. CONCLUSION

The results on the investigations of the nanoferrites demonstrate that Ni substituted MgMn nanoferrite particles inhibited the growth of bacteria at very low concentrations. The influence of $MgMnNiFe_2O_4$ nanoferrites and morphology of the nanostructure is significant for the antimicrobial activity of the prepared particles which is an important aspect for textile industries. Thus, the application of these nanoferrites as antibacterial agent will be very precious for biomedical and industrial applications.

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