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Synthesis of doped Nickel Ferrite with Copper- $NiCuFe_2O_4$, its structure elucidation and Photocatalytic study-eco-friendly nature a step towards interdisciplinary research

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Abstract

My work is based on study of $NiCuFe_2O_4$, which is a mixed metal Ferrite. This Copper doped Nickel Ferrite has been synthesised by Citrate Gel method, which has resulted in a crystalline homogeneous sample of appreciable yield. A non magnetic dopant Cu is added to $NiFe_2O_4$ crystals, which causes modifications in structural, and physical properties. Structure determination is carried out by XRD technique, which confirmed the cubic structure a=b=d, α=β=γ= 90°. SEM image showed the formation of tetragonal and octahedral grains with irregular morphology and the particle size was determined from micrograph and was found to be between 28-58 nm. The IR analysis confirms spinel structure and proves the incorporation of dopant Copper into Ferrite structure. The photocatalytic activity of $NiCuFe_2O_4$ was determined using two dyes methyl orange, methylene blue which have well resolved spectrum. This method involves measurement of optical density values at fixed time intervals which gradually go on decreasing thus indicating that $NiCuFe_2O_4$ is capable of dye degradation, and therefore can be employed for purification of waters which are contaminated with organic based toxic substances. This reveals its ecofriendly nature, in dealing with water pollution thus contributing towards Interdisciplinary research. The degradation of the two dyes was studied with $NiFe_2O_4$, the absorbance values slowly decreased which indicated that photocatalytic activity of $NiFe_2O_4$ is less than $NiCuFe_2O_4$ and doping by Copper enhances dye degradation. It is one of the promising photocatalyst for treatement of waste waters.

Keywords: Precursor, Citric acid, Dopant, Morphology, Agglomerates, Crystalline, Dye degradation, Photocatalyst, Waste waters.

Introduction

The rich physical properties of Ferrites are of great interest in fundamental science[1].

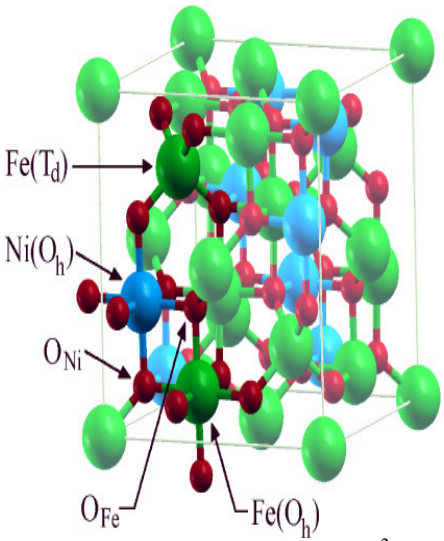


Figure-1: Structure of $NiFe_2O_4$[2].

Ferrites are superior to other magnetic materials for use at higher frequency as they exhibit high electrical resistance combined with ferromagnetic behaviour[3]. $NiFe_2O_4$ finds its way in electronic devices because of high permeability at high frequency, high electrical resistivity, mechanical hardness, chemical stability and reasonable cost[3].

Nickel Ferrite has low Eddy current losses. $NiFe_2O_4$ when doped with copper there are structural and morphological changes produced. These have found to be softer magnetic materials[1].

It has a cubic close packed structure.: i. $NiFe_2O_4$ is an inverse spinel in which divalent Ni^{+2} ions occupy the octahedral sites and trivalent Fe^{+3} ions are distributed among tetrahedral and octahedral sites $(Fe^{III})^{tetr}$ $(Ni^{II}Fe^{III})^{oct}O_4$ [4]. ii. $NiFe_2O_4$ when doped with Copper results in NiCu Fe_2O_4 which is also an Inverse Spinel, Cu^{+2} ions displace some of Ni^{+2} from the octahedral sites depending upon the ratio, accordingly changing the surface morphology and reactivity $(Fe^{III})^{tetr}(Ni^{II}$ $Cu^{II}Fe^{III})^{oct}O_4$[5].

$NiFe_2O_4$ and Copper doped Nickel Ferrites have been synthesized by Citrate Gel method.

Synthesis by Citrate Gel method

$NiFe_2O_4$: $NiCl_2.6H_2O$ and Ferric amm sulphate were mixed in the ratio of 1:2 and this was heated till it melts, to this (4 times amount) Citric acid was added, and further heated till it formed a sticky gel like substance. This was cooled and sintered in a furnace at 1000°C for 6 hrs, further cooled and weighed, Yield was reported as 16 gms.

(Weights corresponding to 0.05M $NiCl_2.6H_2O$, 0.1M Ferric amm sulphate and 0.2 M Citric acid were taken.)

$Ni_{0.5}Cu_{0.5}Fe_2O_4$: $NiNO_3.6H_2O$, $Cu(NO_3)_2.3H_2O$ and Ferric amm sulphate were mixed in the ratio of 0.5:0.5:2 and this was heated till it melts, to this (4 times amount) Citric acid was added, and further heated till it formed a sticky gel like substance. This was cooled and sintered in a furnace at 1000°C for 6 hrs, further cooled and weighed, Yield was reported as 7.4 gms.

(Weights corresponding to 100ml 0.05M $NiNO_3.6H_2O$,0.05M $Cu(NO_3)_2.3H_2O$ 0.2M Ferric amm sulphate and 0.4 M Citric acid were taken.)

$Ni_{0.4}Cu_{0.6}Fe_2O_4$: $NiNO_3.6H_2O$, $Cu(NO_3)_2.3H_2O$ and Ferric amm sulphate were mixed in the ratio of 0.4:0.6:2 and this was heated till it melts, to this (4 times amount) Citric acid was added, and further heated till it formed a sticky gel like substance. This was cooled and sintered in a furnace at 1000°C for 6 hrs, further cooled and weighed, Yield was reported as 7.2 gms.

(Weights corresponding to 100 ml 0.04M $NiNO_3.6H_2O$, 0.06M $Cu(NO_3)_2.3H_2O$ 0.2M Ferric amm sulphate and 0.4 M Citric acid were taken).

$Ni_{0.2}Cu_{0.8}Fe_2O_4$: $NiNO_3.6H_2O$, $Cu(NO_3)_2.3H_2O$ and Ferric amm sulphate were mixed in the ratio of 0.2:0.8:2 and this was heated till it melts, to this (4 times amount) Citric acid was added, and further heated till it formed a sticky gel like substance. This was cooled and sintered in a furnace at 1000°C for 6 hrs, further cooled and weighed, Yield was reported as 6.8 gms.

(Weights corresponding to 100ml 0.02M $NiNO_3.6H_2O$, 0.08M $Cu(NO_3)_2.3H_2O$ 0.2M Ferric amm sulphate and 0.4 M Citric acid were taken.)

X-ray Analysis

XRD analysis was carried out and the d values (interplanar spacing) were determined with the help of Bragg's law

$n\lambda = 2d\sin\theta$ [6].
Where: n = order of reflection of x-ray, λ = wavelength, d = interplanar spacing, θ = angle of reflection.

Table-1: $NiFe_2O_4$

2θ	30	35.65	37	43	53	57.5	62.5
Calc d values	2.99	2.53	2.42	2.11	1.734	1.61	1.49
Std d values	2.948	2.507	2.409	2.08	1.694	1.606	1.482

Table-2: $Ni_{0.5}Cu_{0.5}Fe_2O_4$

2θ	30.64	35.76	35.6	43.24	45.34	57.28	24.26
Calc d values	2.93	2.51	2.53	2.12	2.0	1.63	3.68
Std d values	2.948	2.507	2.56	2.08	2.08	1.609	

Table-3: $Ni_{0.4}Cu_{0.6}Fe_2O_4$

2θ	30.62	35.4	35.86	43.74	35.64	35.6	43.42	45.86	57.12
Calc d values	2.93	2.54	2.51	2.076	2.53	2.53	2.09	1.98	3.22
Std d values	2.98	2.56	2.48	2.08	2.56	2.56	2.08	2.08	1.609

Table-4: $Ni_{0.2}Cu_{0.8}Fe_2O_4$

2θ	23.3	30.32	35.52	37.1	45.14	57.12
Calc d values	3.83	2.95	2.54	2.43	2.014	1.62
Std d values		2.98	2.56	2.48	2.08	1.609

XRD patterns of sintered sample of $NiFe_2O_4$ exhibit typical reflections of (220) (311), (222) (400) (511) and (440) planes. The d values of $NiFe_2O_4$ in Table1 match with the standard ones as given in JCPDS files 10-0325 [7]. The lattice parameters calculated by $a=d\ (h^2+k^2+l^2)^{1/2}$ as a= 8.34 A^o [8].

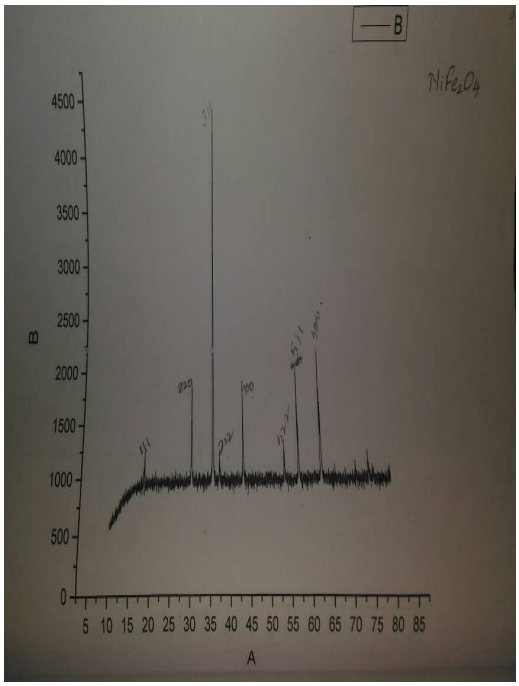


Figure-2: XRD of $NiFe_2O_4$

In Figure-2 the diffraction peaks are sharp which indicates the product as monophasic crystalline. The (311) reflection line of highest intensity can be used to find out the particle size by De-bye Scherrer formula $D= 0.9\lambda / \beta\cos\theta$ [9] where $\lambda = 1.54A^o$, β is the full width at half maxima of the peak having highest intensity observed at 2θ 35.65, the particle size was found to be 500nm.

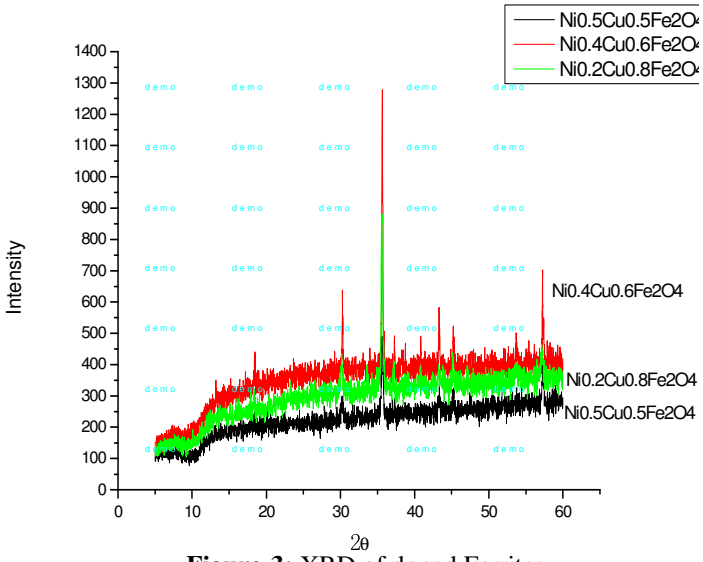


Figure-3: XRD of doped Ferrites.

In Figure-3 the XRD peaks are broad which indicates that the grain size is well within nanoscale. These are indicative of formation of nano size particles[1]. The XRD peaks confirm the formation of cubic spinel structure, which is consistent with standard data in JCPDS card No 074-2081 [1]. Further the XRD patterns show no excess phases indicating that almost all copper atoms have been placed in the Cubic lattices[1]. The particle size for the three doped Ferrites is determined with De Bye Schherer formula. This indicates that substitution of Copper has indeed brought about a reduction in crystallite size. Extra peaks indicate formation of Haematite Fe_2O_3 [1]. The lattice parameters calculated by $a=d\ (h^2+k^2+l^2)^{1/2}$ as a= 8.33+/-0.01 A^o [8].

$D= 0.9\lambda / \beta\cos\theta$

For $Ni_{0.5}Cu_{0.5}Fe_2O_4$ at peak of 2θ 35.6 which is around 28nm
For $Ni_{0.4}Cu_{0.6}Fe_2O_4$ at peak of 2θ 35.62 is found to be 58.5nm.
For $Ni_{0.2}Cu_{0.8}Fe_2O_4$ at peak of 2θ 35.6 is found to be 40nm

Scanning Electron Microscopy

SEM image of the $NiFe_2O_4$ sample sintered at 1000^{o}C was taken. This image clearly depicts the formation of agglomerates with irregular morphology[9]; the cohesion of grains is due to magnetic attraction. The SEM micrographs do not focus on exact grain boundaries and cannot determine the exact particle size[1].

Figure-4: $NiFe_2O_4$

SEM of Doped samples: SEM images of doped samples depict remarkable changes in the microstructures as proportion of Ni, Cu are varied. The powders of three samples have uniform grains different from SEM of $NiFe_2O_4$ which confirms the formation of $NiCuFe_2O_4$. The doped samples have an average particle size ranging from 28-58 nm[7]. The images clearly depict formation of spherical and tetragonal grains, which are uniformly distributed but not highly agglomerated[7].

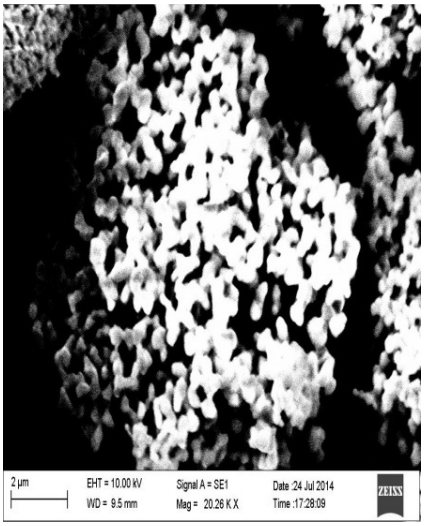


Figure-5: $Ni_{0.5}Cu_{0.5}Fe_2O_4$

Figure-6: $Ni_{0.4}Cu_{0.6}Fe_2O_4$

Figure-7: $Ni_{0.2}Cu_{0.8}Fe_2O_4$

Infra Red Spectroscopy

Interpretation: The vibrational Frequencies of various bonds were recorded in the region 400-4000 cm^{-1}. In Figure-8 for $NiFe_2O_4$ the absorption band around 3905 cm^{-1} is characteristic of O-H stretching frequency, the band localized at 1581cm^{-1} is indicative of H-O-H bending vibrations. The peaks around 578cm^{-1} and 468cm^{-1} coresspond to vibrations of tetrahedral and octahedral M-O bonds. The vibrational frequency of tetrahedral cluster is higher than octahedral cluster which proves that tetrahedral bonds are shorter and octahedral bonds are longer in length.

In the doped Ferrites the bands in range 3600-4000cm^{-1} become more distinct.

In Figure-9 for $Ni_{0.5}Cu_{0.5}Fe_2O_4$ the Tetrahedral vibrations are at 580 cm^{-1}, and the octahedral vibrations are around 464 cm^{-1}.

In Figure-10 for $Ni_{0.4}Cu_{0.6}Fe_2O_4$ the Tetrahedral vibrations are around 586 cm-1 and the octahedral vibrations are around 447 cm^{-1}. In Figure-11 for $Ni_{0.2}Cu_{0.8}Fe_2O_4$ the Tetrahedral vibrations are around 576 cm-1 and the octahedral vibrations are around 464cm^{-1}.

As the concentration of dopant Cu increases the frequency of tetrahedral stretching bonds decreases and become more intense which is due to redistribution of Fe^{+3} ions in tetrahedral and octahedral sites and the bands due to octahedral bonds are spread over range which proves that dopant Copper is well incorporated into Ferrite Cubic lattice.

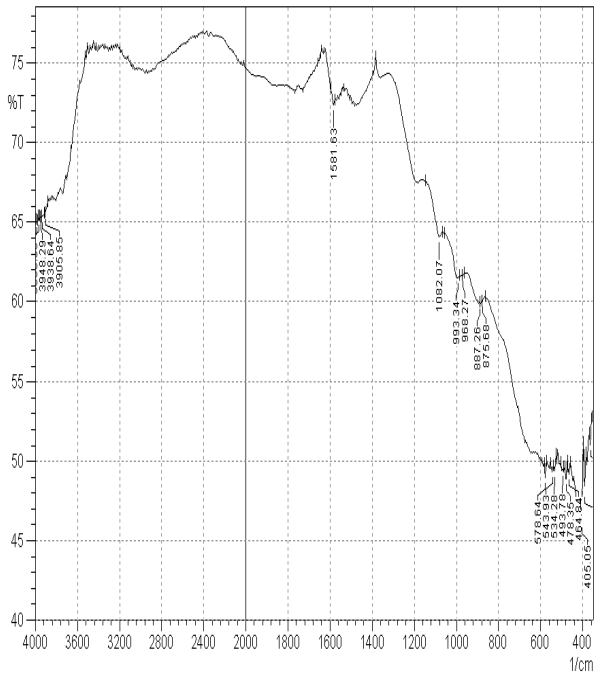


Figure-8: $NiFe_2O_4$

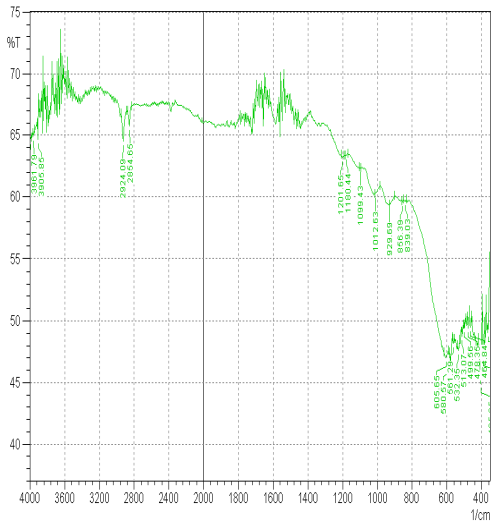


Figure-9: $Ni_{0.5}Cu_{0.5}Fe_2O_4$

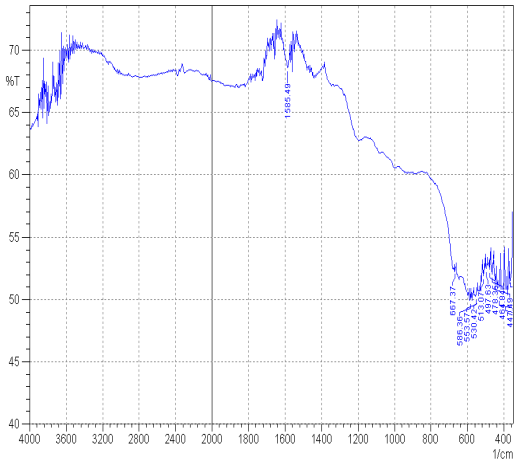


Figure-10: $Ni_{0.4}Cu_{0.6}Fe_2O_4$

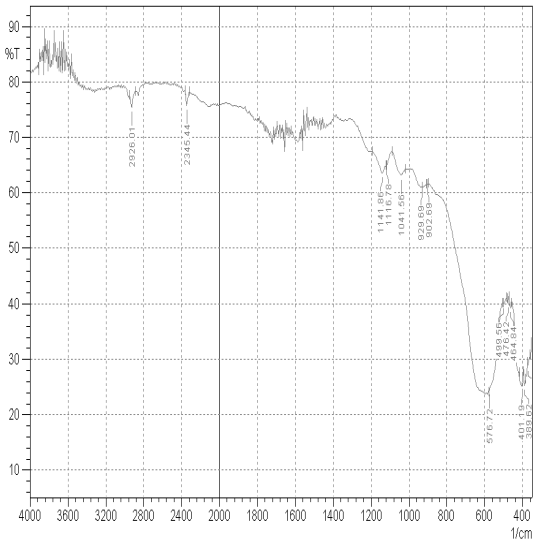


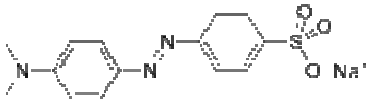
Figure-11: $Ni_{0.2}Cu_{0.8}Fe_2O_4$

Photocatalysis

Dye degradation is a process in which a large dye molecule is broken down into smaller fragments[10]. To demonstrate the photocatalytic activity, two dyes; methyl orange and methylene blue were used, as they have well resolved spectrum in visible region[11].

Methyl orange: 20 ppm Methyl orange was prepared and 25 ml of this was taken separately in 3 different labelled beakers and to the first two beakers 0.1g of $NiFe_2O_4$, and doped Ferrites were added and third one was labeled as blank. These beakers were then was kept in sunlight and after every half an hour optical density measurements were done at 507 nm.

Figure-12: Methyl orange and Methylene Blue kept in sunlight.



$C_{14}H_{14}N_3NaO_3S$[12]

Table-5: OD measurement using Methyl orange.

Time in minutes	O.D Blank	O.D $NiFe_2O_4$	O.D $Ni_{0.5}Cu_{0.5}Fe_2O_4$
0	0.1	0.85	0.98
30	0.1	0.8	0.88
60	0.1	0.78	0.79
90	0.1	0.72	0.67
120	0.1	0.67	0.59
150	0.1	0.63	0.48
180	0.1	0.60	0.39
210	0.1	0.57	0.32
240	0.1	0.52	0.27

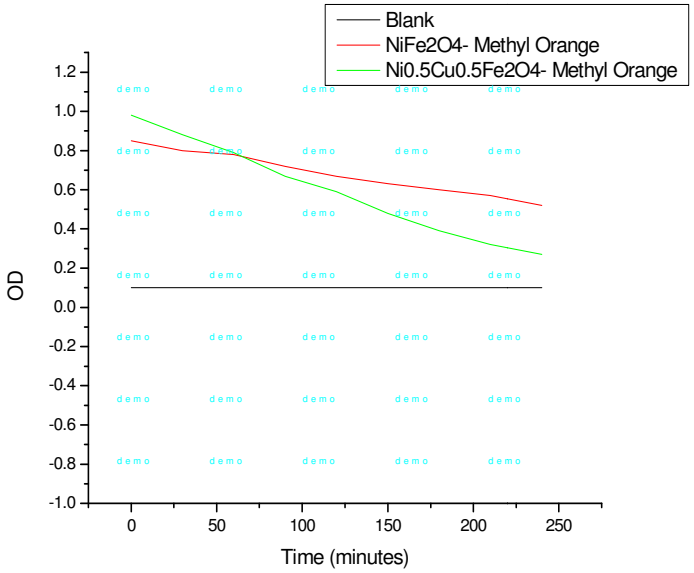
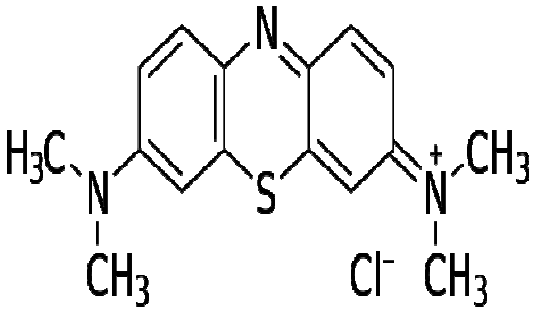


Figure-13: Degradation of Methyl Orange.

The optical density values of dye solution containing $NiFe_2O_4$ showed slow decrease in optical density values, while the dye solution containing $Ni_{0.5}Cu_{0.5}Fe_2O_4$ showed steady decrease which revealed that it is able to carry degradation of Methyl orange dye to much greater extent than $NiFe_2O_4$. i. Methylene Blue, ii. 5 ppm Methylene blue was prepared and 25 ml of this was taken separately in 3 different labelled beakers and to the first two beakers 0.1g of $NiFe_2O_4$, and doped Ferrites were added and third one was labeled as blank. iii. These beakers were then was kept in sunlight and after every half an hour optical density measurements were done on spectrophotometer at 668 nm.



$C_{16}\ H_{18}\ C_1N_3\ S$[13]

The optical density values of dye solution containing $NiFe_2O_4$ showed slow decrease in optical density values; while the dye solution containing $Ni_{0.5}Cu_{0.5}Fe_2O_4$ showed steady decrease which revealed that it is able to carry degradation of Methylene dye to much greater extent than $NiFe_2O_4$.

Copper doped $NiFe_2O_4$ is found to be a promising photocatalyst and can be employed for waste water treatement[13].

Table-6: OD meserment using Methylene Blue.

Time in minutes	O.D. Blank	O.D. $NiFe_2O_4$	O.D $Ni_{0.5}Cu_{0.5}Fe_2O_4$
0	0.1	1.57	1.64
30	0.1	1.52	1.57
60	0.1	1.47	1.50
90	0.1	1.43	1.44
120	0.1	1.39	1.37
150	0.1	1.35	1.29
180	0.1	1.31	1.20
210	0.1	1.28	1.15
240	0.1	1.24	0.09

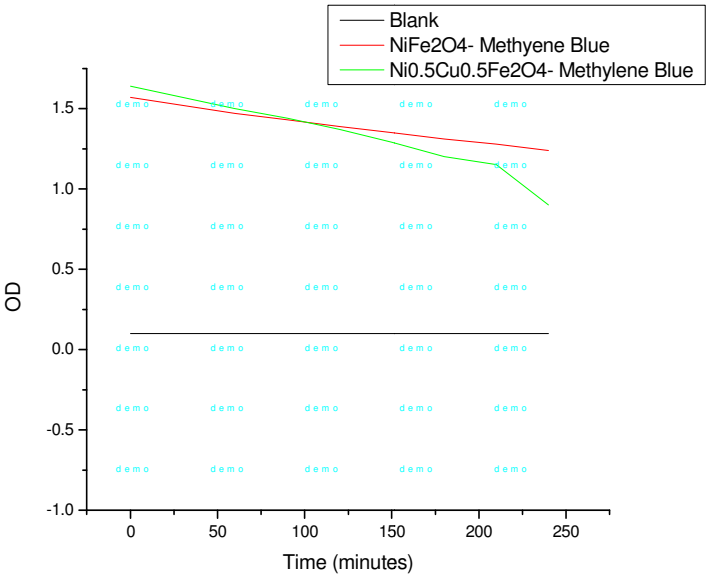


Figure-14: Degradation of Methylene Blue.

Results and discussion

The Citrate Gel method employed for preparing $NiFe_2O_4$ and Copper doped Nickel Ferrites has resulted in better yield. The XRD pattern of $NiFe_2O_4$ shown distinct peaks and line broadening at 35.65 m and the data matches with the standards as given in JCPDS files 10-0325, this again confirms the product to be a monophase crystalline one. The doped samples have broadened peaks, due to reduction in particle size, Calculations by De Bye Scherrer formula confirms nanograins of the doped samples. The doped Ferrites have even smaller sized nano grains which indicates that addition of Copper

dopant causes more reduction in size. The SEM image of $NiFe_2O_4$ shows formation of agglomerates, while that of doped samples, reveals formation of uniform nano sized grains. The IR spectra of $NiFe_2O_4$ shows the vibration of (Fe^{+3}----O) tetrahedral and (Ni^{+2} ---- O) octahedral bonds, and spectra of doped samples clearly shows that Copper is well incorporated in the Cubic Ferrite structure. Dye degradation study reveals that doping of Copper increases the photocatalytic power of Nickel Ferrites due to reduction in particle size. Therefore these compounds can be effectively used in treatement of waste waters.

Conclusion

Citrate Gel method is found to be suitable for preparation of doped Nickel Ferrites giving good yield. Addition of a non magnetic dopant Copper to $NiFe_2O_4$ causes Nickel and Copper ions to redistribute in the octahedral sites. The doped Ferrites have been prepared in three different varying compositions , as the ratio of Ni^{+2} and Cu^{+2} varies their distribution in the octahedral sites varies, thus affecting the surface morphology as shown by variation in SEM imges. SEM image reveals formation of agglomerates. Doped Ferrites are found to be promising photocatalyst for treatement of polluted waters containing organic based pollutants and effluents from textile industries.

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