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Photocatalytic degradation of organic pollutant using Copper substituted calcium ferrite

T. L Ajeesha[1], Ashwini Anantharaman[2], Mary George[3], Mary Teresita V[4]
[1, 2, 3, 4,] *Department of Chemistry, Stella Maris College*

Abstract: ***The magnetic and optical properties of $Ca_{1-x}Cu_xFe_2O_4$ nano ferrites have fascinated the attention of researchers. Copper substituted calcium ferrite with composition (x=0.2, 0.4, 0.6, 0.8, 1.0) was prepared by coprecipiation method. The prepared compositions were subjected to structural, optical and magnetic properties. X-ray diffraction studies reveal the formation of orthorhombic phase and the lattice constant increases with increase in calcium concentration from (x=0.2 to 0.8) Transmission Electron microscope (TEM) technique was used to study the morphology of the synthesized ferrites. The hysteresis loop confirms the magnetic behavior of the prepared composition. The adsorption and desorption measurement was studied from Brunauer-Emmett-Teller (BET) technique. The parameters such as magnetization, coercivity and retentivity are also calculated. The photocatalytic degradation of the synthesized ferrites using Methylene blue was also studied.***
Key words: Ferrites; co-precipitation; Optical properties; photo degradation.

I. INTRODUCTION

The presence of hazardous contaminants in water poses dangers for human and environment exposure that result in health issues and environmental damages. Adsorption of activated carbon, chlorination, ultrafiltration and ozonation treatment have been used to reduce this hazardous contaminants. But all the above treatments require high cost. Therefore, Usage of ecofriendly semiconducting catalyst is used for the Photodegradation of dyes and pollutants [1]. Ferrites are well known for their tremendous applications in the field of magnetic and electronic materials [2-6]. The ferrites has an advantage of displaying the optical absorption for the low energy photons and of exhibiting the well suited electronic structure desirable for photocatalytic applications .Additionally the spinel related oxide photocatalysts exhibit enhanced efficiency due to the available extra catalytic sites of their crystal lattices. $CaCuFe_2O_4$ is a semiconductor spinel ferrite, with high chemical stability which makes it a good applicant for visible light responsive photocatalytic material [7-10]. There are several methods like the hydrothermal, ceramic, auto-combustion, mechanical milling, Sol-gel and co-precipitation techniques by which ferrite nanoparticles are usually prepared. The co -precipitation method has more advantages than the other methods [11-14]. In our present work we have proposed to synthesize Copper substituted Calcium ferrite by co-precipitation method and to study their structural, optical, magnetic properties and photo catalytic degradation of methylene blue dye.

II. MATERIALS AND METHODS

Nanosized Ca_{1-x} $Cu_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1) spinel ferrite was prepared by chemical co-precipitation method. Calcium nitrate ($Ca(NO_3)_2$), Copper nitrate ($Cu(NO_3)_2$) and Ferric nitrate ($Fe(NO_3)_3$) are dissolved separately in 50 mL deionized water and stirred well. The solution is kept for stirring and 2M NaOH is added drop-wise maintaining the pH at 13. The solutions were heated at 80 °C for 3 hours until a brown precipitate was obtained. The precipitate was centrifuged and washed with deionized water. The product thus obtained was annealed at 75 °C for 24 hours in a hot air oven. The annealed samples were calcined at 650°C in a muffle furnace for 8hours to obtain $CaCuFe_2O_4$ nanoparticles.

III. RESULTS AND DISCUSSION

A. Powder –XRD diffraction studies

The structural properties of the synthesized $CaCuFe_2O_4$ ferrites were studied from the diffraction pattern. (Fig .1) obtained from XRD technique (Bruker AXS D8 Advance and temperature ranging from 170 °C to +450 °C).The existence of the (220), (311), (011), (320), (400), (422), (511), (440) major lattice planes in the XRD patterns confirms the formation of single phase pseudo cubic structure of orthorhombic regularity with space group pbnm .The average crystallite sizes D are calculated from the characteristics of the (320) XRD peaks through the Scherrer formula in the range of 12-40 nm. The synthesized $Ca_{1-x}Cu_xFe_2O_4$ nanomaterial have inverse spinel structure in which half of the Fe^{3+} ions fill the tetrahedral site and rest occupy the octahedral site with the Ca^{2+} ions in Calcium ferrite [15].

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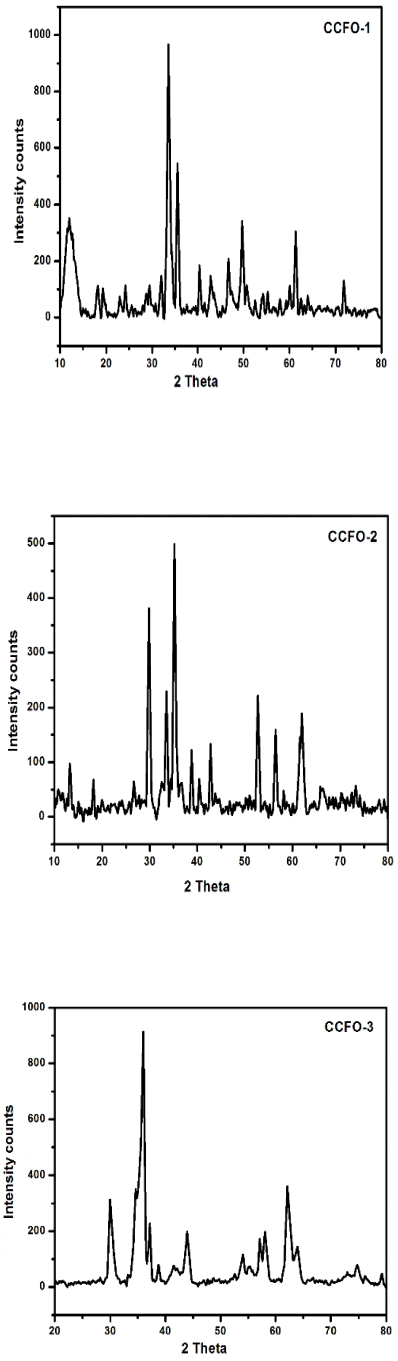

Fig. 1 PXRD pattern for CCFO nanocomposites

B. FT-IR studies

The FT-IR spectra (Perkin Elmer model Spectrum RXI) of the synthesized Copper substituted Calcium ferrites was studied from 400–4000 cm^{-1},which helps to figure out the nature of chemical bonding . The spinel absorption band at 480 cm^{-1} and 579 cm^{-1} are attributed to the stretching vibrations due to the interaction of oxygen and cations in Ca-O and Fe-O bonds. The bands at 849,709 cm^{-1} are due to O-Fe-O, Fe-OH and bands at 453 cm^{-1} corresponds to Fe-O bonds The band at 1003 cm^{-1} corresponds to metal – alloy (Fe-Ca) and bands at 636 cm^{-1} attributes to Fe-O bonds due to the presence of Ferrite skeleton . The common broad bands at 3423 and 1644 cm^{-1} are assigned to the O-H stretching vibrations [15].

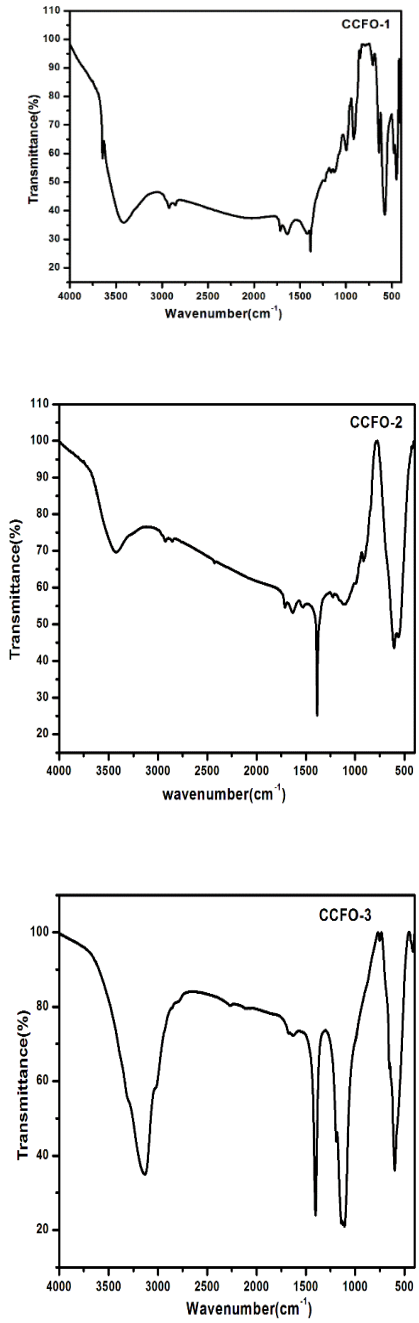

Fig. 2 FT-IR spectra for CCFO nanocomposites

C. TEM Analysis

TEM (Jeol/JEM 2100 and magnification ranges from 2000 X–1500000 X) images (Fig.3) showed the morphology of the synthesized spinel ferrites. The pictures showed that the materials were mesoporous in nature as the particle size of the material ranges between 2-100 nm. The images indicate the aggregation of the material with spherical and irregular morphology of $CaCuFe_2O_4$ nanocomposites. These high diameter pictures depicts the high degree of agglomerations. This may result the formation of heterogeneous surface. Selected area electron diffraction pattern (SAED) showed a single crystalline diffraction ring indicating the spinel structure of Ca_{1-x} $Cu_xFe_2O_4$ oxide.

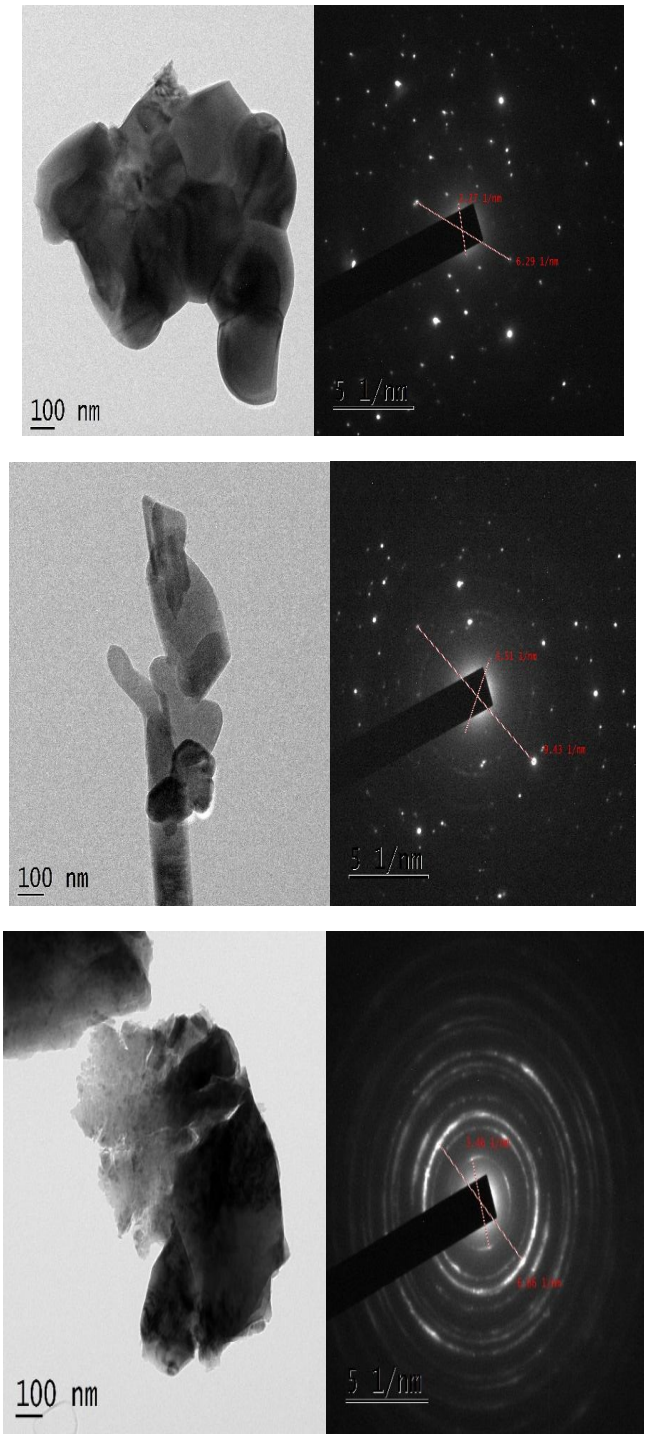

Fig. 3 TEM image for CCFO nanocomposites

D. BET Analysis

The porosity and N_2 adsorption-desorption measurements were analyzed from BET analysis (Quantachrome Instrument). The measurement was carried out at –195ºC (77 K) for $Ca_{1-x}Cu_xFe_2O_4$ ferrites. The technique provides the surface area, pore volume and the pore diameter. Fig represents the porous material exhibiting type II and III isotherm and found to be mesoporous in nature. The bending of cure at 0.365 m^2/g is due to the multi-layer absorption and there is increase in porosity and surface area are due to the substitution of Copper metal. Table 1 shows the absorption and desorption of the synthesized $CaCuFe_2O_4$ oxide respectively. The Fig.4, confirms the absence of narrow pore size distribution of the synthesized nanomaterial.

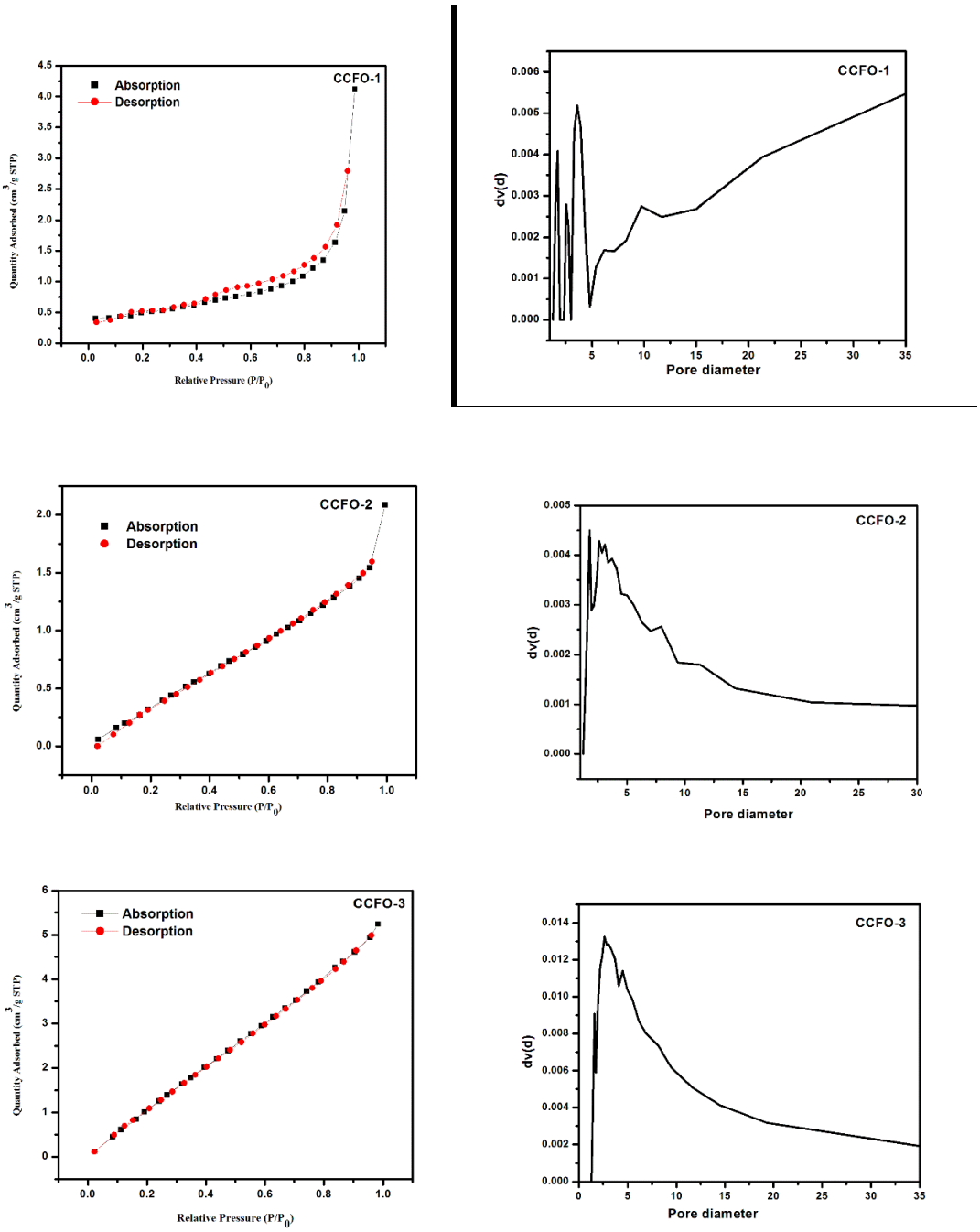

Fig. 4 BET graph for CCFO nanocomposites

Table I BET Parameters for CCFO nanocomposites

Compound name	Surface area	Total pore volume	Average pore diameter
CCFO-1	2.82 m^2/g	0.005 cc/g	1.75 nm
CCFO-2	3.57 m^2/g	0.003 cc/g	1.79 nm
CCFO-3	8.31 m^2/g	0.010 cc/g	1.59 nm

E. VSM Studies

The magnetic properties of nanocomposites were studied using a vibrating sample magnetometer (VSM) Lakeshore VSM 7407 with magnetic field 2.5 T at room temperature (303 K). (Fig. 5) The hysteresis curve of the synthesized $Ca_{1-x}Cu_xFe_2O_4$ nanomaterials showed weak ferromagnetic behaviour, which indicates that the synthesized $CaCuFe_2O_4$ are soft ferrites. The coercivity was found to be 663.66 G, 345.86 G and 503.69 G for CCFO-1, CCFO-2 and CCFO-3 respectively. The squareness ratio value of the hysteresis loops along with magnetic parameters are represented in Table 2.

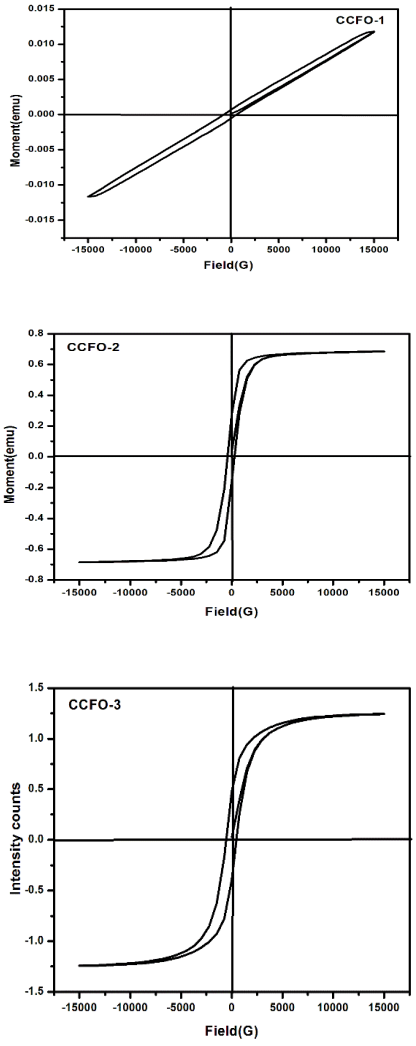

Fig. 5 Hysteresis loop for CCFO nanocomposites

Table II
Magnetic parameters of CCFO nanocomposites

Compound name	Coercivity (Hci)	Magnetization (Ms)	Retentivity (Mr)	Squareness ratio(M_r/M_s)
CCFO-1	663.66 G	11.720E-3 emu	615.79E-6 emu	52.54
CCFO-2	345.86 G	0.68569 emu	0.21595 emu	0.314
CCFO-3	503.69 G	1.2431 emu	0.43547 emu	0.350

F. Optical Studies

The optical studies were done by using Bruker UV-Visible spectrometer. The absorption edge of the as synthesized materials were found to be 365 nm, 545 nm and 766 nm for CCFO-1, CCFO-2 and CCFO-3 respectively (Fig.6). The band gap of 3.39 eV, 2.27 eV corresponds to CCFO-1, CCFO-2 nanomaterials which may be due to metal to ligand charge transfer. The band gap of CCFO-3 was found to be 1.61eV which might be due to the octahedral field splitting between t_2g and eg of iron orbitals.

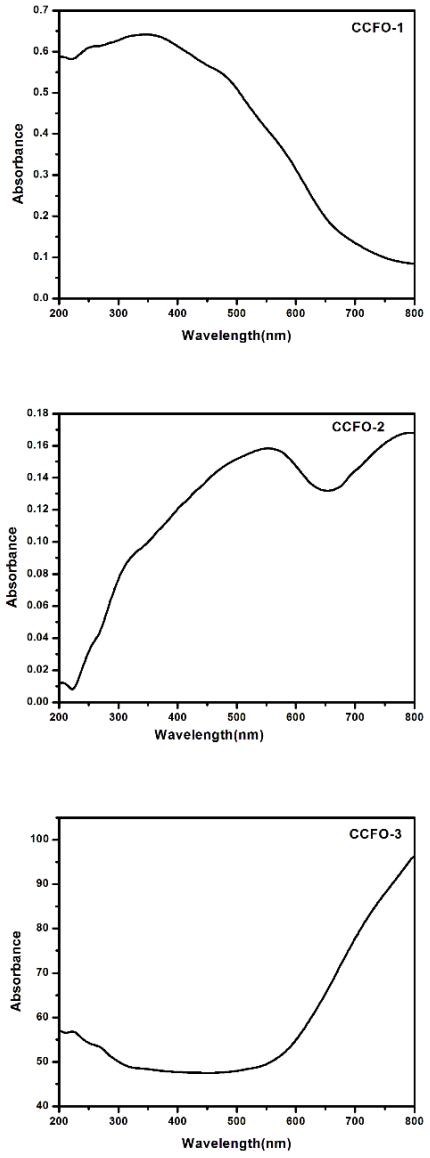

Fig. 6 UV-Visible spectra for CCFO nanocomposites

G. Photocatalytic Studies

The photocatalytic experiment was carried out by taking 100 mg of the catalyst and 100 mL of 25 ppm methylene blue dye solution. The photocatalytic reaction media was left for stirring for 30 min to attain adsorption equilibrium before the illumination of UV-lamp. The percentage of decolourization was observed at 4.3%, 3.7% and 5.3% for CCFO-1, CCFO-2 and CCFO-3 spinel oxides respectively. The photo catalytic studies was performed for three hours under UV-lamp irradiation and the samples were drawn every 30 minutes and measured with UV-Visible spectrophotometer. Absorption spectra (Fig.7) showed 92% degradation for $Ca_{1-x}Cu_xFe_2O_4$ spinel ferrites in 180 minutes due to the combination of several factors such as crystallite size and band gap value. This reduction in absorption indicated the clear photocatalytic activity of the synthesized nanocatalysts. Fig. 7.1 showed linear plot for

CCFO-1, CCFO-2, CCFO-3 nanocomposites, which indicates the photocatalytic degradation followed by pseudo first order kinectics. Fig. 7.2 showed the degradation efficiency of $Ca_{1-x}Cu_xFe_2O_4$ spinel oxides. The following equation was used to determine the percentage degradation of the nanocomposites.

$$\% \text{ Degradation} = C_O - C_t / C_O$$

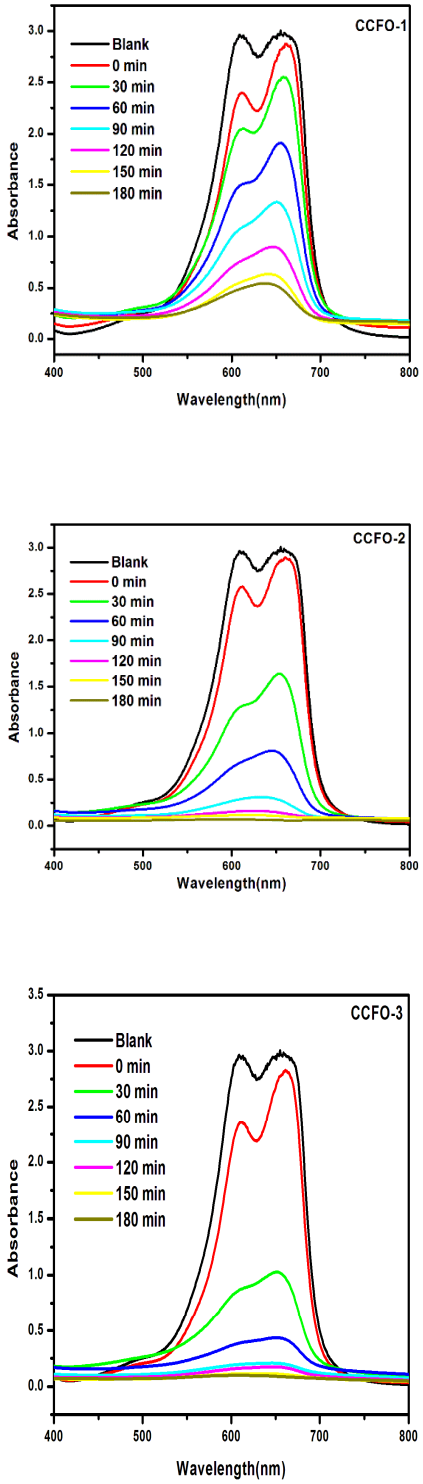

Fig. 7 Photocatalytic degradation of a) CCFO-1 b) CCFO-2 c) CCFO-3 nanoparticles under UV lamp irradiation

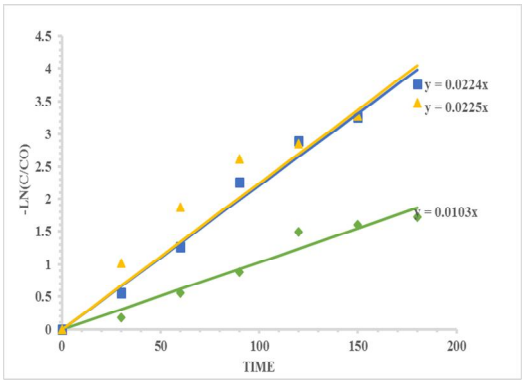

Fig. 7.1 Kinetic plot for CCFO nanocomposites

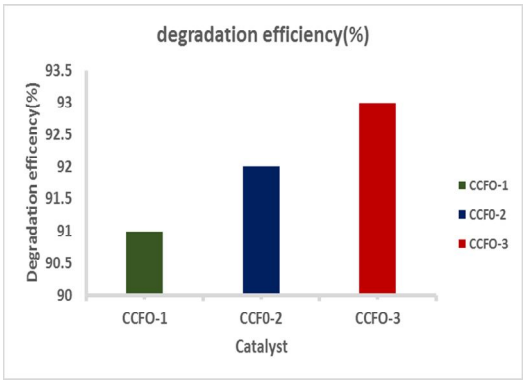

Fig.7.2 Degradation efficiency graph for CCFO nanocomposites

IV. CONCLUSION

Calcium Copper ferrite nanomaterials were prepared by co-precipitation method. The FT-IR spectrum show characteristic absorption bands at 579and 480 cm^{-1} corresponding to the stretching vibration modes of tetrahedral and octahedral sites responsible for the spinel compounds. The diffraction pattern revealed that the synthesized ferrites are nano crystalline with the crystallite size of about 12-40 nm. TEM images showed the surface morphology a distribution of spherical and irregular morphology. VSM analysis indicated that the as synthesized nano materials are magnetically soft ferrites. The reduction in absorption maximum of the degradation study with methylene blue dye indicated that $CaCuFe_2O_4$ nanocatalysts exhibited 92% degradation in 180 minutes due to the combination of several factors such as crystallite size and its semiconducting nature.

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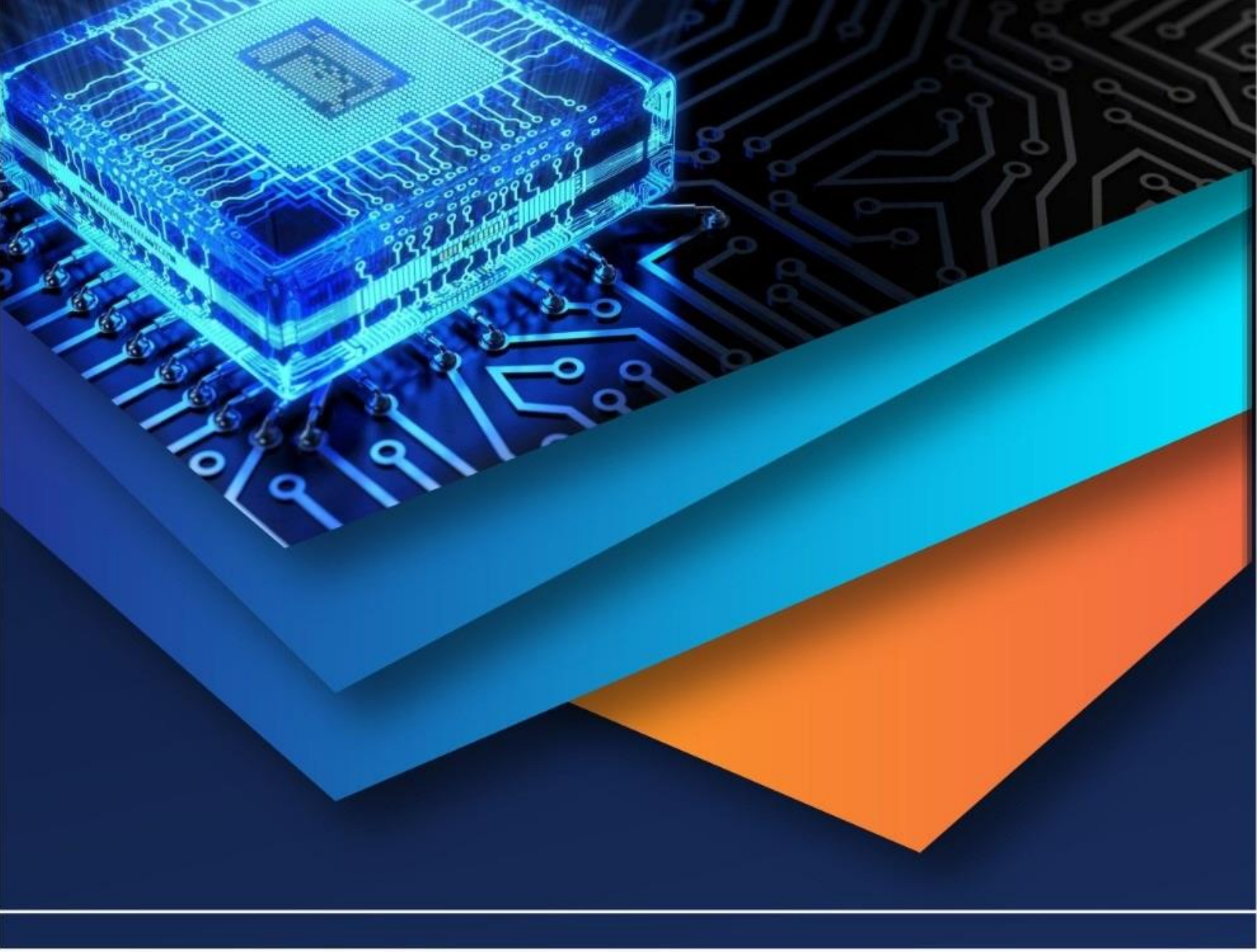

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