

**Research Article**

## **Study on Magnetic Properties of CoFe<sub>2</sub>O<sub>4</sub> Nanocomposites through Surfactant Mediated Synthesis Technique for Biomedical Application**

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### **ABSTRACT:**

Magnetic nanocomposites of cobalt ferrite have been synthesized by wet chemical method using stable ferric and cobalt salts with Tween 80 as the surfactant. X-ray Diffraction (XRD) and Transmission Electron Microscope (TEM) confirmed the formation of single phase cobalt ferrite nanocomposite in the range 43-60nm depending on the annealing temperature and time. The functional groups of the magnetic materials were determined by FTIR spectrum. Energy dispersive X-ray results confirmed the ratio of the transition metal atoms in each material according to the nominal stoichiometry. The VSM studies showed that the coercivity and saturation magnetization of CoFe<sub>2</sub>O<sub>4</sub> were found to be maximum for the reported samples. The size of the particles increases with annealing temperature and time while the coercivity goes through a maximum, peaking at around 37nm. The high field moment is observed to be small for smaller particles and approaches the bulk value for large particles. In future obtained nanocomposites will be used for biomedical application.

**Keywords:** Magnetic nanocomposite; Ferrite Nanoparticles; SEM; VSM; CoFe<sub>2</sub>O<sub>4</sub>; Coercivity.

### **[I] INTRODUCTION**

Overall, Magnetic properties of nanoparticles are still a subject of great interest research activity driven by a fundamental interest in the novel physical properties of the nanoscale system [1]. Below a critical diameter the particles become single domain and have interesting properties such as superparamagnetism, large uniaxial anisotropy, even for bcc particles [2] and strong surface effects. These properties depend, on the

size and shape of particles, on the interaction among them, and on the effects of finite size and super paramagnetic relaxation. In particular, cobalt ferrite is known as a hard magnetic material with high coercivity and moderate magnetization, making it very suitable for applications [3] in high density magnetic recording, ferrofluids, and magnetic refrigeration, among others. Fine particles of cobalt ferrite have

been prepared by various techniques [4–8] such as coprecipitation, hydrothermal synthesis, microemulsion, the sol-gel technique and the sonochemical reaction method. The use of surfactant as a self-assembled nano template enables to synthesize magnetic nanoparticles at room temperature. Comparable inorganic methods for the synthesis of nanoscale mixed-metal oxides require heating to high temperatures in order to produce the desired oxide composition and microstructure. In many such techniques, control of the size and size distribution of the nanoparticles is not possible.

Complex Magnetic oxide nanoparticles have been actively studied due to their having different physical and chemical properties compared to their bulk material counterparts. In particular, spinel ferrites ( $\text{MFe}_2\text{O}_4$ ;  $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$ ) are among the most important magnetic materials because of which they have been widely used in different areas such as electronic devices and information storage, and also in biomedical areas, such as magnetic resonance imaging (MRI) and drug-delivery technology [9-18]. For many applications, the synthesis of uniformly sized nanoparticles is of key importance, because the electrical, optical and magnetic properties depend strongly on the size of the nanoparticles.

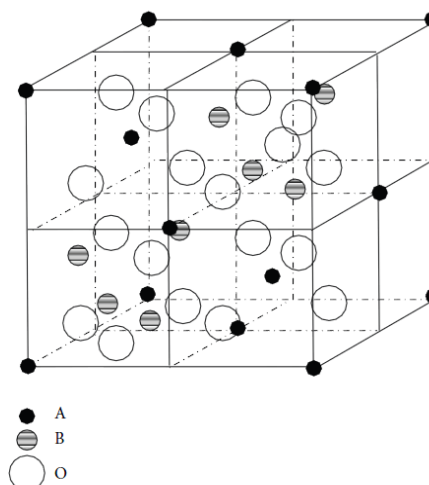
Cobalt ferrite,  $\text{CoFe}_2\text{O}_4$ , is especially interesting because of its high coercivity, moderate saturation magnetization, large anisotropy and unique light-induced coercivity change [19]. This is why, in spite of its possible toxicity, this material is under study for use in many interesting biomedical applications, e.g. drug delivery, DNA separation, magnetic resonance image (MRI) contrast and hyperthermia [20].

Of special interest are their magnetic properties in which the differences between a massive or bulk material and nanoscaled ones are especially pronounced. The magnetic properties are particularly sensitive to the particle size, which is determined by the finite size effects (related to the reduced number of spins cooperatively linked

within the particle), and by surface effects (greater as the particle size decreases) [21–23]. The water solubility of MNPs is necessary for medical applications, and their aggregation, caused by the huge specific surface area and magnetic interactions must be avoided. It is thus necessary to adopt methods to stabilize the MNPs, either by using surfactants or by changing their surface potential.

In the present investigation, the nanocomposite  $\text{CoFe}_2\text{O}_4$  synthesized with surfactant mediated method has been studied and characterized using x-ray diffraction (XRD), Scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), Vibrating sample magnetometer (VSM). Properties are measured on sintered composite samples and results obtained are discussed in this paper.

A schematic description of spinel  $\text{CoFe}_2\text{O}_4$ , where A and B represent tetrahedral and octahedral coordination for cation occupancy, respectively is shown in figure 1.



**Figure 1:** A schematic description of spinel  $\text{CoFe}_2\text{O}_4$ , where A and B represent tetrahedral and octahedral coordination for cation occupancy, respectively.

The general chemical formula of spinel ferrite is  $\text{CoFe}_2\text{O}_4$ . It has a face-centered cubic (FCC) structure with a large unit cell including eight formula units. There are two kinds of lattices for cation occupancy: tetrahedral and octahedral,

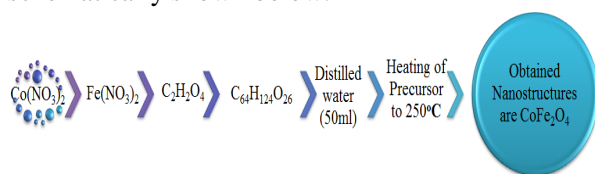
which are denoted as A and B sites, respectively (see Figure 1). Spinel's with only M<sup>2+</sup> ions occupying A or B sites are called direct (or called normal) or inverse, respectively [24].

### [II] MATERIALS AND METHODS

All reagents were analytical grade and used as raw materials without further purification.

#### 2.1 Synthesis of Nanocomposites

Synthesis of CoFe<sub>2</sub>O<sub>4</sub> Spherical Nanoparticles is carried out by surfactant mediated method. All the reagents used were of an analytical grade and used as received without further purifications. Equal quantities of Oxalic acid C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> and Iron nitrate Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in deionized water and after 5 minutes of magnetic stirring, stoichiometric amount of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added into the mixture and stirred for 10 minutes. The solution mixture was placed in an ultrasonic water bath at room temperature for 15 minutes. 0.01 M of Tween 80 was added to the above solution. The black precipitates were then filtered out and washed several times. The precipitates were then dried at 80 °C over night to obtain the CoFe<sub>2</sub>O<sub>4</sub> nanocomposite. Four more samples are prepared using the same procedure varying the concentration of Tween 80 (0.02M – 0.05M). The prepared samples are ground finally, and used for further characterization, without subsequent sintering at high temperatures. The process is schematically shown below.



**Figure 2:** Synthesis of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles assisted by Tween 80 (0.01M – 0.05M)

#### 2.2 Characterization Techniques

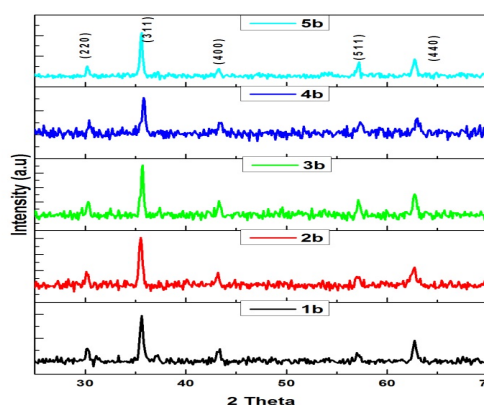
X-ray powder diffraction (D8-Advanced XRD-Bruker) using Cu-K $\alpha$  radiation is carried out for measuring the phase structure of nanocomposites. Scanning Electron Microscopy (SEM) equipped

with an energy dispersive X-ray analyzer (EDX) (S- 3400 N) was used in this study. EDX analysis is an analytical technique used for the elemental analysis or chemical characterization of a sample. The JEOL JEM-2100 was used for TEM analysis. Magnetic properties of samples are obtained by using Lake Shore's Vibrating Sample Magnetometer (model 7410). Perkin Elmer FT-IR spectrometer was used to identify types of chemical bonds, i.e. functional groups in a molecule.

### [III] RESULTS

#### 3.1 X-Ray Diffraction

XRD can be used to characterize the crystallinity of nanoparticle, and it gives average diameters of all the nanoparticles. The XRD patterns of the CoFe<sub>2</sub>O<sub>4</sub> nanoparticle samples are shown in Figure 3. The discernible peaks in Figure 3 are indexed to (220), (311), (400), (511), and (440) planes of a cubic unit cell, which corresponds to that of magnetite structure (JCPDS card no. 22-1086) with Fd3m as space group. The average crystal sizes calculated from Debye-Scherrer equation and Williamson-hall equation from XRD data have been found to be 22..5 nm and 26nm for CoFe<sub>2</sub>O<sub>4</sub> respectively, where in the particle sizes calculated from TEM images showing 28.6 nm for CoFe<sub>2</sub>O<sub>4</sub>. This indicates that the synthesized CoFe<sub>2</sub>O<sub>4</sub> are all nanocrystalline in nature.



**Figure 3:** XRD Pattern of CoFe<sub>2</sub>O<sub>4</sub> Nanocrystals with change in tween 80 (0.01M-0.05M)

### 3.2 Scanning Electron Microscopic Analysis

The magnified FESEM images shown in Figure 3a-3e which are indicative of the detailed morphology of pure  $\text{CoFe}_2\text{O}_4$  nanocomposites with varying Tween 80 concentration. The amorphous nature of the particles was confirmed by various techniques, such as scanning and transmission electron microscopy (SEM and TEM). The magnification was varied from  $5\mu\text{m}$  to  $30\mu\text{m}$  scale. It is clearly observed that the porosity of the sample is increasing with increase in quantity of surfactant.

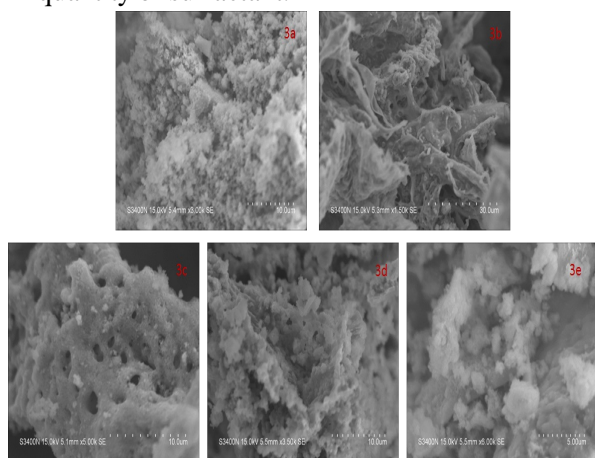


Figure 3a-e showing  $\text{CoFe}_2\text{O}_4$  nanocomposite with varying Tween 80 concentration

### 3.3 Energy Dispersive X-Ray Diffraction Analysis

EDAS results support the formation of nanocomposite. From Figure 4a-4e it is predicted that the more the concentration of Tween 80, the less the impurity, Figure 4e shows the EDAS of the  $\text{CoFe}_2\text{O}_4$  nanocomposite, the particles contain elements of Fe, O, Co and traces of Carbon.

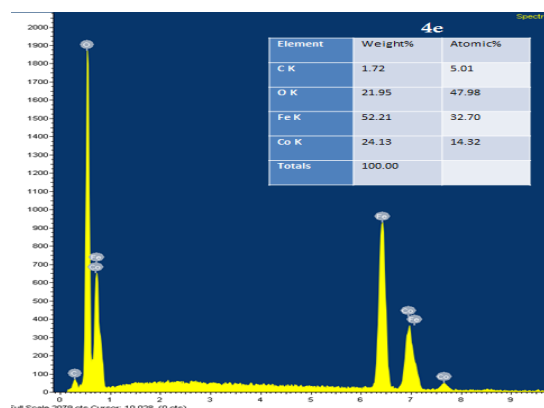
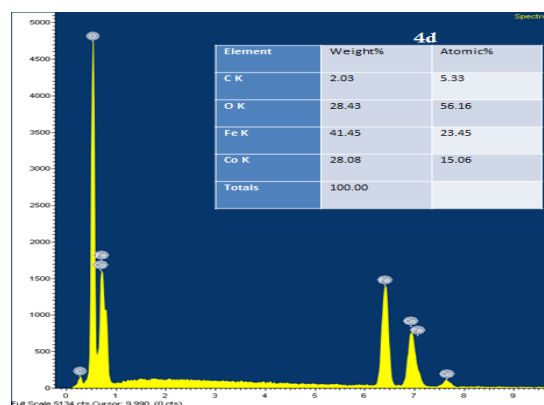
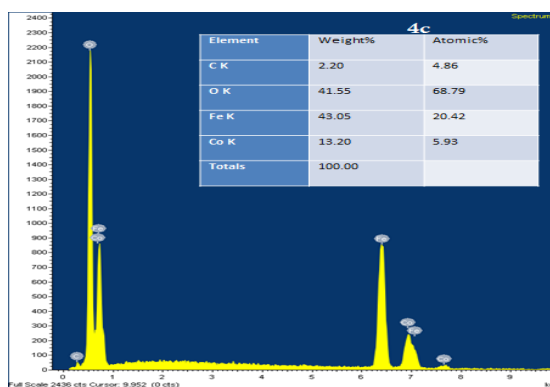
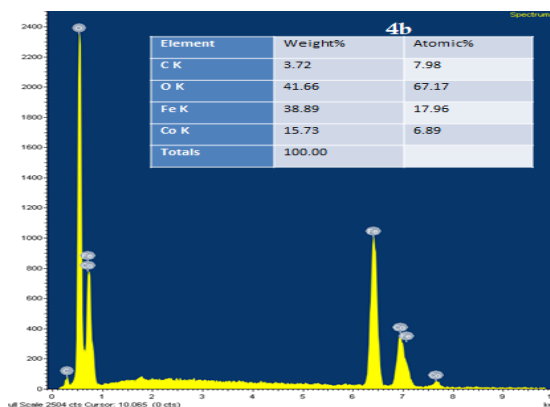
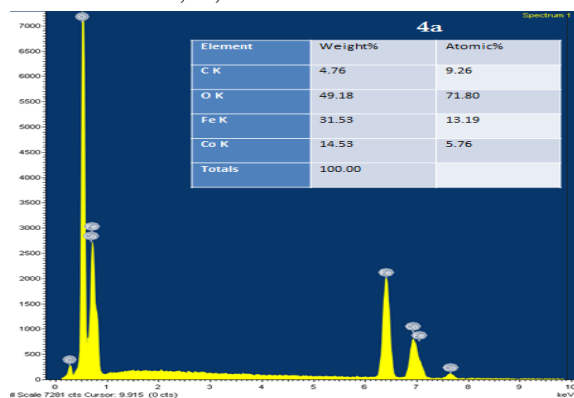
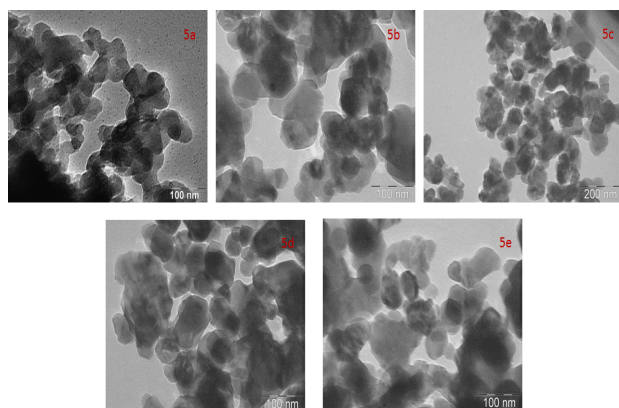


Figure 4 a-e : EDAS Spectra's of nanocomposite with varying surfactant

### 3.4 Transmission Electron Microscopic Analysis

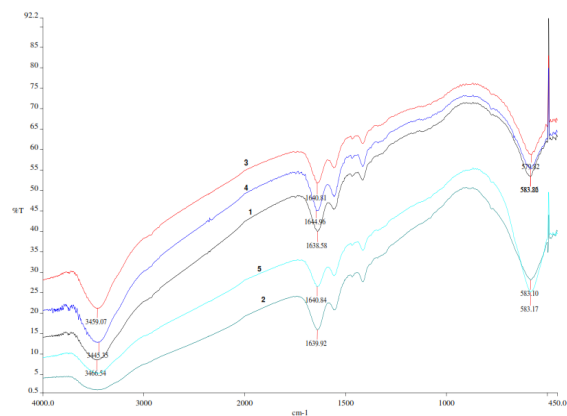
TEM images of the samples confirm their spherical structure. Figure 5a-5e shows the TEM of CoFe<sub>2</sub>O<sub>4</sub> nanocomposite formed by varying the ratio of surfactant i.e Tween 80 and it is observed that most of the CoFe<sub>2</sub>O<sub>4</sub> particles are irregular spherical in structure with an average size of 40nm. The images show there is uniform distribution of particles and no agglomerations formed.



**Figure 5** a-e TEM of CoFe<sub>2</sub>O<sub>4</sub> nanocomposite formed by varying the ratio of surfactant

### 3.5 Fourier Transform Infra Red Spectrophotometer Analysis

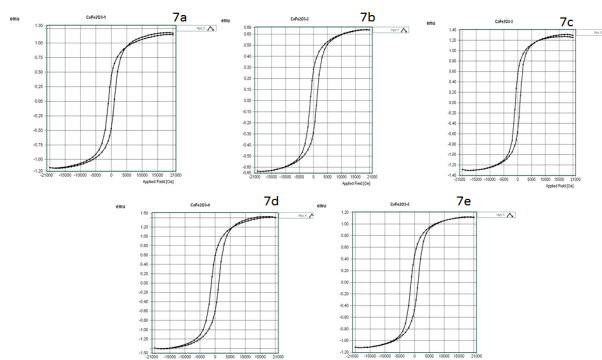
Figure 6 shows FT-IR spectra's which shows the broad band's from 3445 to 3470 cm<sup>-1</sup> belong to high concentrations of O-H stretching. The peak around 1640 cm<sup>-1</sup> still exists meaning that some free N-H in the CoFe<sub>2</sub>O<sub>4</sub> nanoparticle sample have been trapped and these are eliminated by slightly increasing temperature.



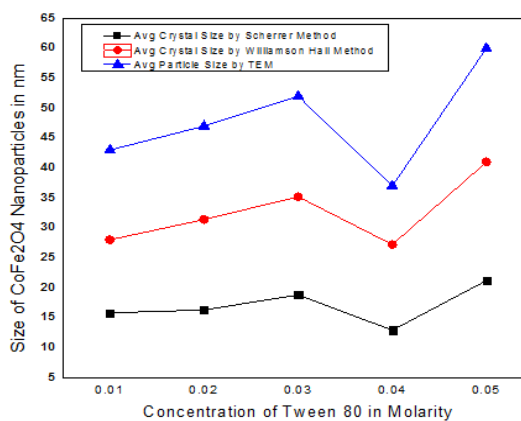
**Figure 6:** FTIR spectra of CoFe<sub>2</sub>O<sub>4</sub> nanocomposite

### 3.6 Vibrating Sample Magnetometer

The magnetization curve of CoFe<sub>2</sub>O<sub>4</sub> nanocomposite spheres tested at 300 K is shown in Figure 5. A hysteresis loop can be observed, indicating that cobalt ferrite spheres are ferromagnetic. With an increase in the external magnetic field to 21000 Oe, the best saturation magnetization of 52 emu/g is achieved for with 0.4M quantity of surfactant which is shown in Figure 7d.



**Figure 7a-7e:** Vibrating sample magnetometer showing varying cohecity of nanocomposite



**Figure 8:** Size distribution curve varying Tween 80

Figure 8 shows the size distribution of CoFe<sub>2</sub>O<sub>4</sub> Nanoparticles with varying concentrations of Tween 80. It has been observed that the 0.4M concentration of Tween 80 is resulting in lower particle size. The comparisons are made with crystal size obtained by scherrer method, Williamson hall method and particle size obtained from TEM and these are brought in the table 1.

Samples	Avg. Crystalline Size (Scherrer Method)	Avg. Crystalline Size (Williamson Hall Method)	Avg. Particle Size (TEM)
CoFe <sub>2</sub> O <sub>4</sub> - 1	15.8nm	28nm	43nm
CoFe <sub>2</sub> O <sub>4</sub> - 2	16.3nm	31.4nm	47nm
CoFe <sub>2</sub> O <sub>4</sub> - 3	18.8nm	35.2nm	52nm
CoFe <sub>2</sub> O <sub>4</sub> - 4	12.9nm	27.2nm	37nm
CoFe <sub>2</sub> O <sub>4</sub> - 5	21.2nm	41 nm	60nm

**Table 1:** Size comparisons of CoFe<sub>2</sub>O<sub>4</sub> Nanoparticles varying Tween 80(surfactant)

## [V] CONCLUSION

In summary, it may be mentioned that CoFe<sub>2</sub>O<sub>4</sub> nanoparticles have been successfully synthesized by a surfactant mediated treatment and it is a simple process. The size of the nanoparticles measured both by XRD and TEM was in very good agreement with each other indicating that there was no agglomeration and that the size distribution of the prepared nanoparticles was small. It has also been found that for smaller size particles the saturation magnetization has a value that was significantly lower than the bulk value while the larger size particles have values approaching those of the bulk. Further research is under progress in our laboratory.

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