

Synthesis and Control of Cadmium Ferrite Nanoparticles via a Facile Co-precipitation Route

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Abstract

The Cd.Fe₂ SO₄ nanocrystalline synthesized by the Co-precipitation techniques based on different in initial molar concentration (pH suspension). The structural and magnetic properties of the products were determined and characterized in detail by X-ray diffraction (XRD), High Resolution scanning Electron Microscope (HR-SEM), Fourier Transform Infrared (FTIR) and vibrating sample magnetometer (VSM). The results suggest the grain size in the range of 7.8:22.4 nm as the calcination temperature increases from 405 to 650°C respectively with different in initial molar concentration (pH suspension) for all techniques. X-ray analysis showed that the samples were cubic spinel structural (kind of inverse spinel oxide). The crystallinity is improved with the increases calcination temperature for all techniques and that proved by the FT-IR and XRD results and compound purity fabricated. HR-SEM analysis showed that nanoparticles size and the shape based on the initial molar concentration (pH suspension) and the calcination temperatures and also indicates that degree of agglomeration for all samples. VSM analysis showed that all the coercivity values were low enough to emphasize that the ferrite was a soft ferrite or super-paramagnetic behavior for most samples. Magnetic nanoparticles with smaller particle size (14 nm), compared to those prepared (22 nm) using sodium hydroxide precipitating agent. In addition, we found that the saturation magnetite nanoparticles was influenced by the obtained particle size. The determined saturation magnetization of the generated magnetite nanoparticles was found to be ca. 61.3, 65.1 emu/g for those prepared using NaOH precipitating agents respectively. AFM showed surface roughness of the nanoparticles.

Keywords: Magnetite nanoparticles; Calcination process; Co-precipitation method; Cd Fe₂SO₄ Nanoparticles; Ferrite; Magnetic properties.

1.Introduction

Ferrite types with chemical composition variance and the spinal crystal structure are magnetic ceramics (such as Co ferrite, Zn ferrite and Co Zn ferrite) of great importance in the manufacturing of insulators and electronic industrials. The physical, chemical and magnetic properties of ferrite are depends on various parameters such as processing conditions, calcination temperature and time as well as on their chemical composition [1,2]. The properties of these materials mainly depend on their shape, size, and structure, which are strongly determined by the fabrication processes [3,4].

There are several different fabrication techniques used to produce ferrites such as sol–gel, combustion methods, hydrothermal, mechano-chemical and refluxing, However most of them cannot be economically applied on a large scale because they required high vacuum system, complicated experimental steps and high reaction temperatures, but co-precipitation method is considered to be economical technique for ferrite production [5-13].

The aim of the present work is to the synthesis of Cd Fe₂SO₄ Nanoparticles are prepared by Co-precipitation method for its manufactured. The structural and magnetic properties of nano-crystalline cobalt zinc ferrite can be controlled by adjusting the synthesis route in the initial mixtures. The synthesized nano- crystals have been characterized by XRD, HR-SEM, AFM, vibrating sample magnetometer (VSM) and FT-IR, provided below are the investigation details.

The cubic inverse spinel structure of Cd Fe₂SO₄ is unique. It might be an N or P type semiconductor. It has the minimum resistivity between iron oxides because its tiny band gap (0.1eV) [3]. Because of the alternating Fe²⁺ and Fe³⁺ lattice interrupted by oxygen atoms that allow for electrical interaction, magnetite is ferromagnetic [4]. Furthermore, surface alteration of magnetite nanoparticles can raise not only their solvent stability, but also their interfacial features and avoid particle aggregation [5]. Magnetite nanoparticles have exclusive properties, including decent magnetic, electric, great surface area, broad surface-to-volume ratio, and simple separation

under an external magnetic field, catalytic, respectable chemical activity and susceptibility to oxidation, bio compatibility and low toxicity properties [6].

2.Experimental Materials

Ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$) and Cadmium sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Alpha Chemika, India. Sodium hydroxide were acquired from pharmaceutical chemicals company, In a typical co-precipitation method: 2.02 g of ferric sulfate and 1.45 g of ferrous sulfate were dissolved in 75 mL distilled water under magnetic stirring at temperature 40°C until complete dissolution. To this, sodium hydroxide solution was added dropwise under magnetic stirring until reaching a value of pH from 7 to 10. The mixture was then cooled to room temperature. The black precipitate (magnetite) was collected through centrifuging at rotation 3000 rpm. The product was washed times with deionized water till reaching a value of pH 7 and then dried for 8 hours in an electric oven at temperature 80°C . At the same circumstance, this procedure was repeated using ammonium hydroxide solution (25 %) as a precipitation agent instead of sodium hydroxide.

3. Results and Discussion

3.1. X-ray diffraction

Figure 3.1,3.2&3.3 displays the XRD patterns of the Cd Fe_2SO_4 nanoparticles synthesized by solutions of sodium hydroxide. The characteristic reflections of the synthesized nanoparticles appeared at 2θ values of 30° , 35° , 43° , 53° , 57° , and 62° , crystalline lattice planes of (220), (311), (400), (422), (511), and (440), respectively, which are in accordance to the JCPDS card No. 88–315 (14-16). The crystal phase structure of the Cd Fe_2SO_4 is cubic and no characteristic peak of impurities are detected. The average of the prepared magnetite nanoparticles; was estimated by using Scherer's equation and it was found to be 22 and 14 nm, respectively Where: D is the mean size of the crystallite (nm), K is the shape factor of the crystallite (dimensionless), λ is the x wavelength (nm), β is the line broadening at half the maximum intensity (FWHM) (radians), and diffraction angle (degrees). Interestingly, the results revealed that both precipitating agents generated pure magnetite nanoparticles; however, sodium hydroxide precipitating agent gave magnetite nanoparticles with smaller crystallite size.

$$D = \frac{K * \lambda}{\beta * \cos \theta}$$

Figure 3.1,2,3 XRD patterns of magnetite nanoparticle samples prepared by using sodium hydroxide precipitating agents. The surface morphological structure of the as magnetite nanoparticles were examined using the scanning electron microscopy technique images of the magnetite products exhibited that both samples are composed of spherical particles. However, the magnetite nanostructure product prepared using sodium hydroxide precipitating agent was more homogenous and regular sphere particles.

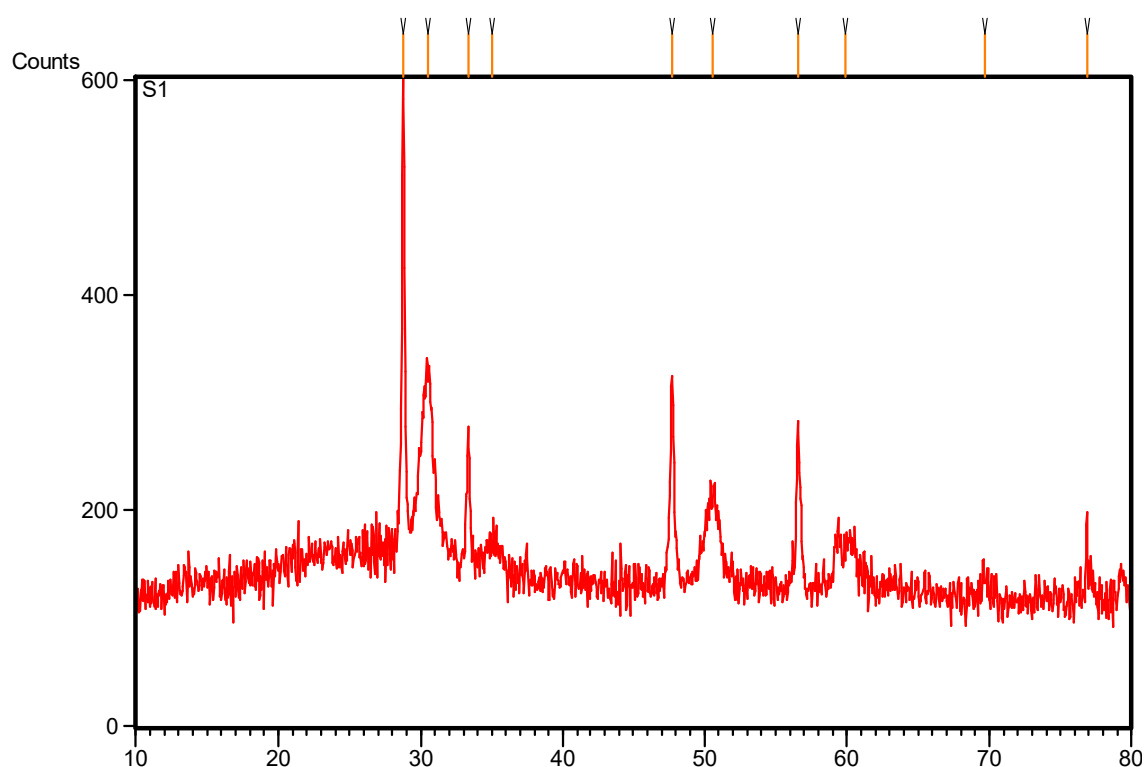


Fig3.1 450⁰c

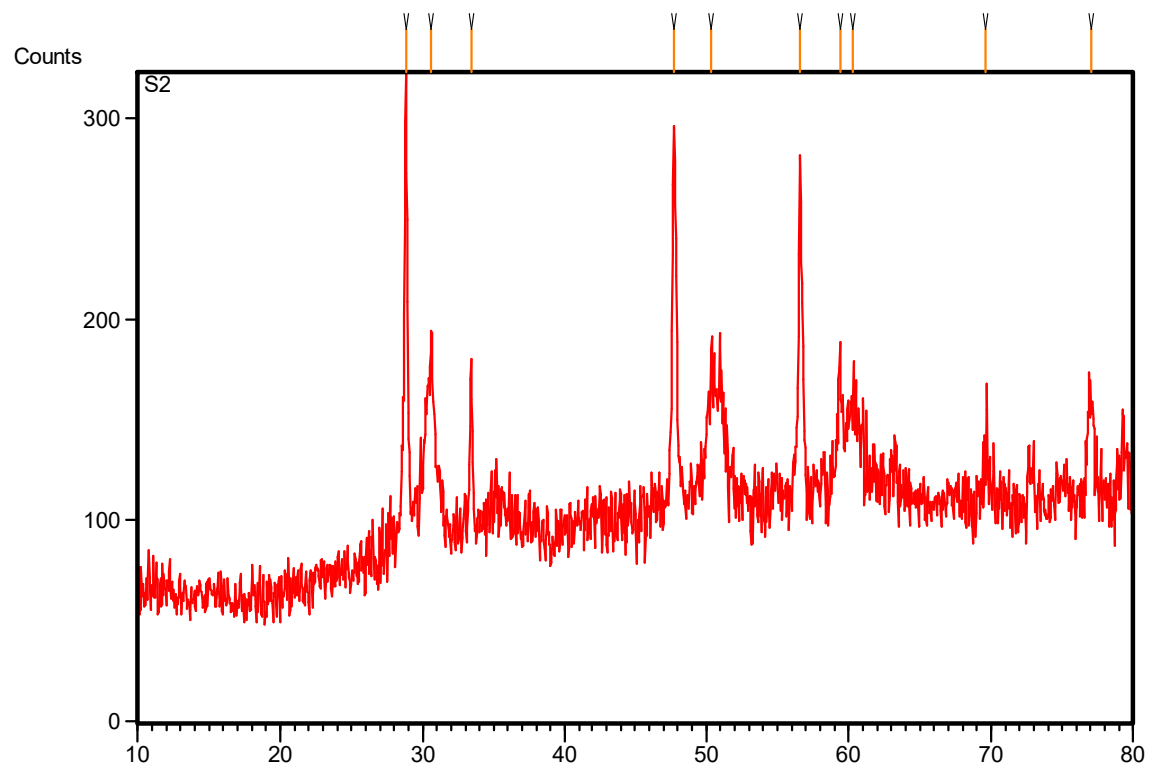


Fig3.2 550⁰c

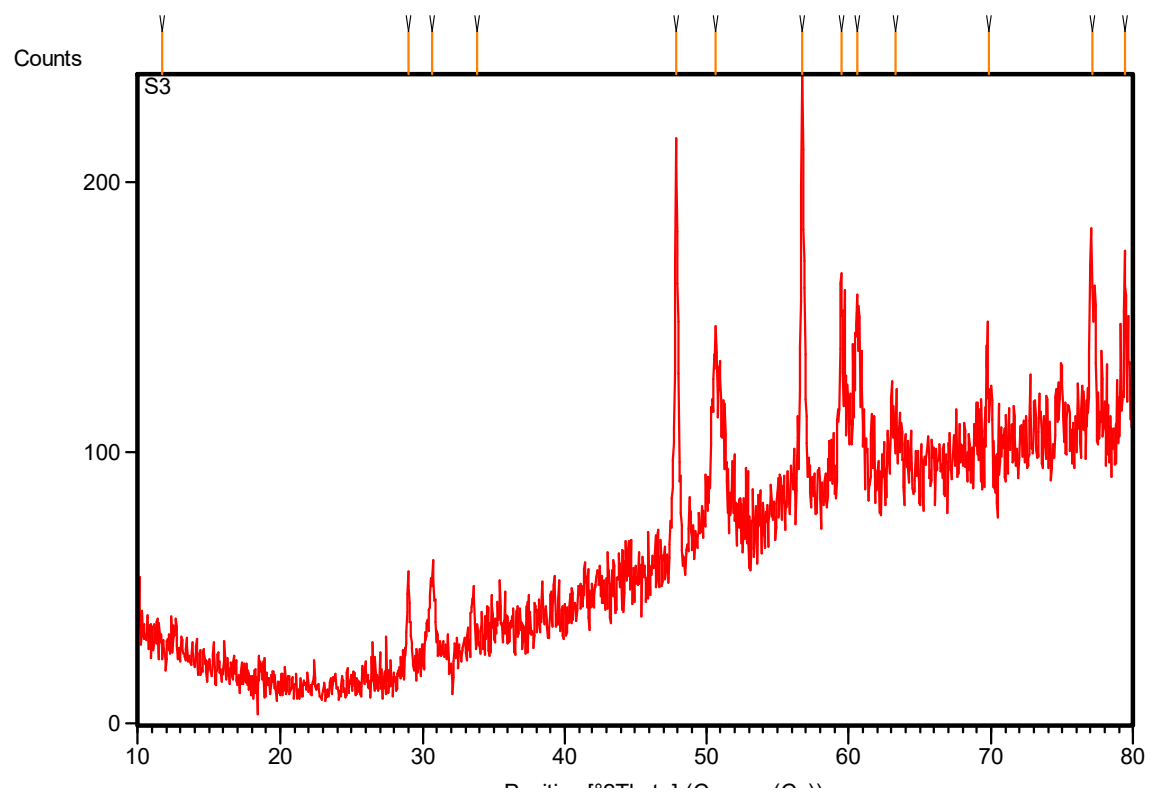
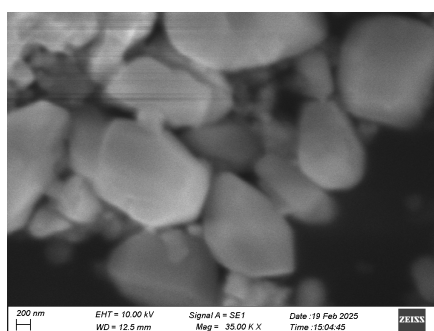
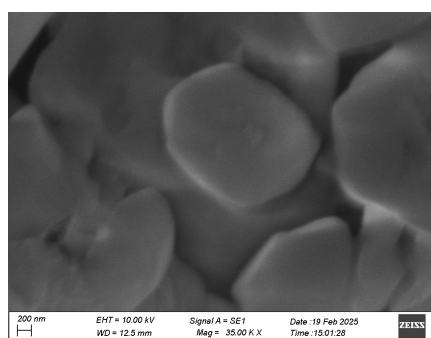
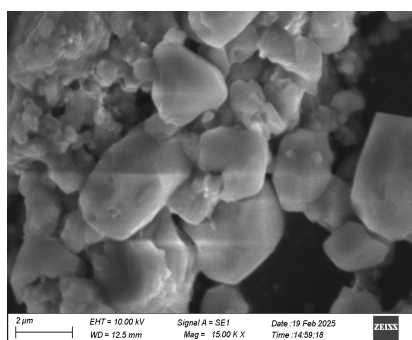


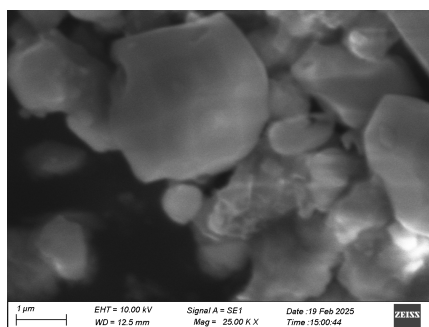
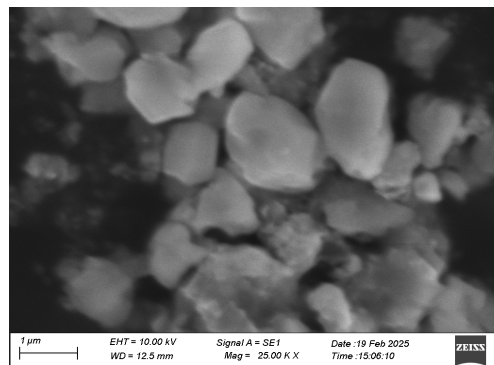
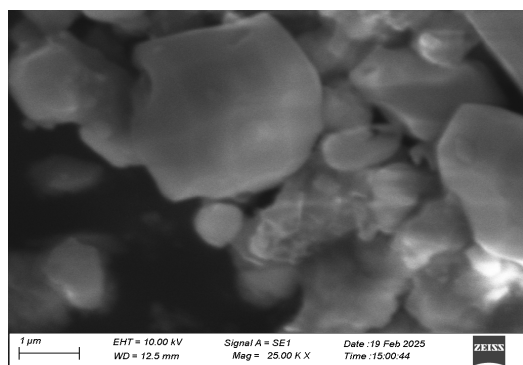
Fig3.3 650⁰c

3.2 Morphological studies of prepared sample

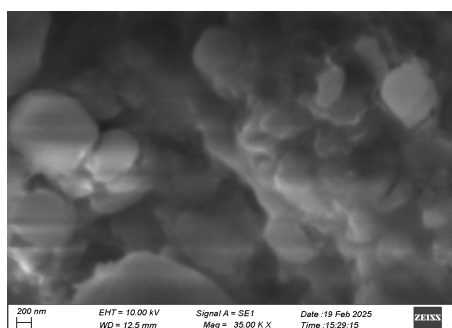
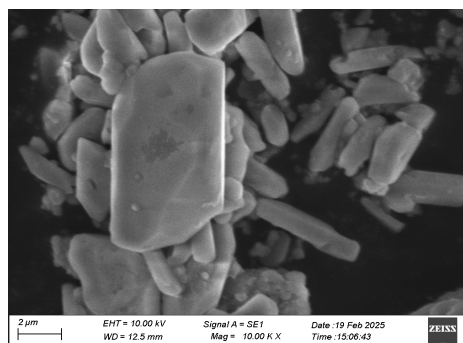
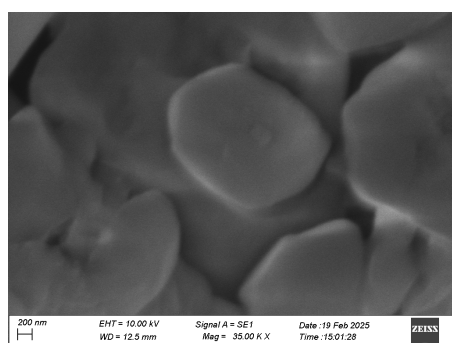
The surface morphological structure of the Cadmium ferrite nanoparticles were examined using the scanning electron microscopy technique. Images of the magnetite products exhibited that both samples are composed of spherical, cubic, and irregular particles with an average particle size of 20 nm. However, the magnetite nanostructure product prepared using sodium hydroxide precipitating agent was more homogenous and regular sphere particles. While the magnetite is notable that the magnetite nanoparticles synthesized using sodium hydroxide was more homogenous and dispersed compared to those prepared using sodium hydroxide precipitating agent. Consequently, NaOH opted as the optimum precipitating agent for our current preparation method for magnetic ferrite nanoparticles.



3.2.1 450⁰c



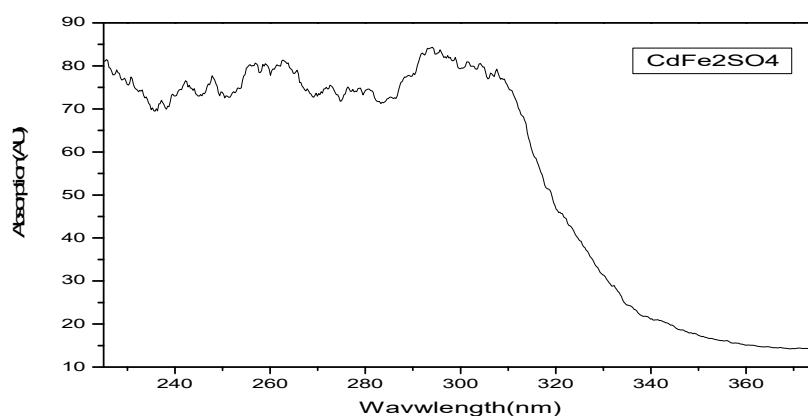
3.2.2 550⁰c



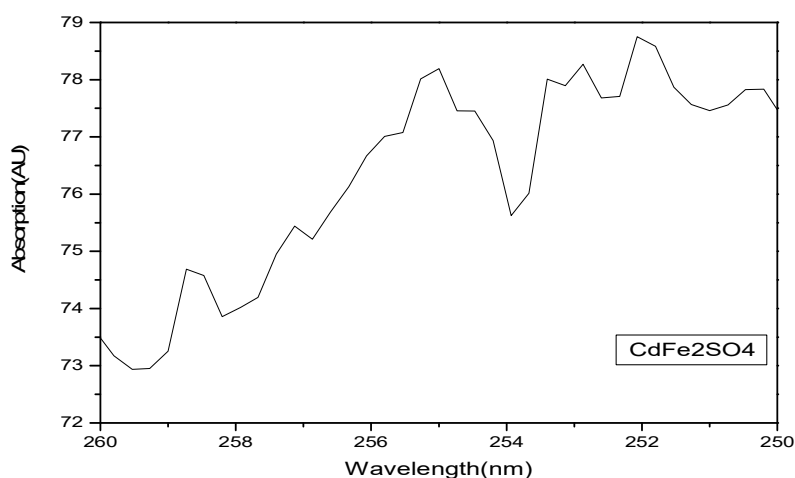
3.2.3. 650⁰c

3.3. Optical studies

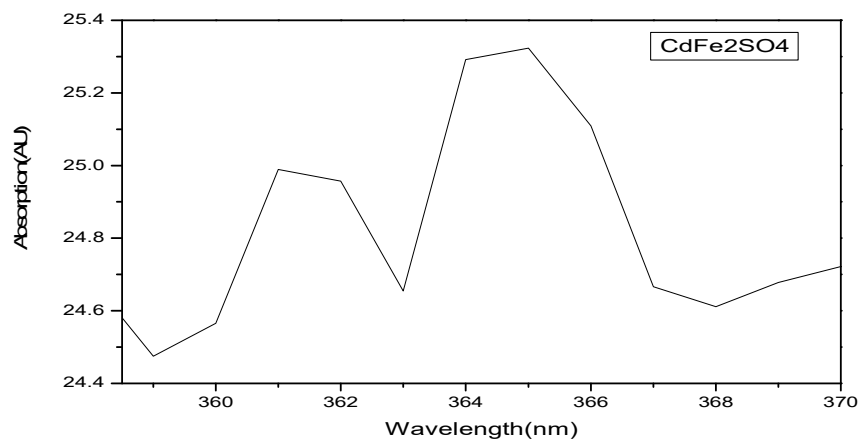
prepared samples with variable concentration of Cadmium ferrite nanoparticles prepared samples with variable concentration of was studied by uv analysis and it is found that the excitation spectra of prepared and shows broad excitation centred at 280 nm (near UV-blue region). The emission spectra with variable concentration of show strong peaks at 380 nm (blue region). Spectrophotometric determinations of peaks are evaluated . Using this absorption throughout the violet (302 nm) and intense blue (300 nm) of the spectra were achieved. Efficient blue light emitting diodes (LEDs) were fabricated using on near ultraviolet excited LED lights. Also useful for sensing application such as biological and chemical sensing.



3.3.1 450⁰c

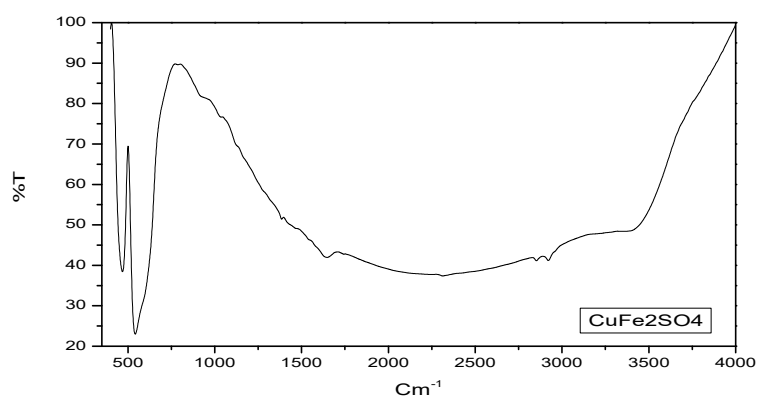


3.3.2 550⁰c

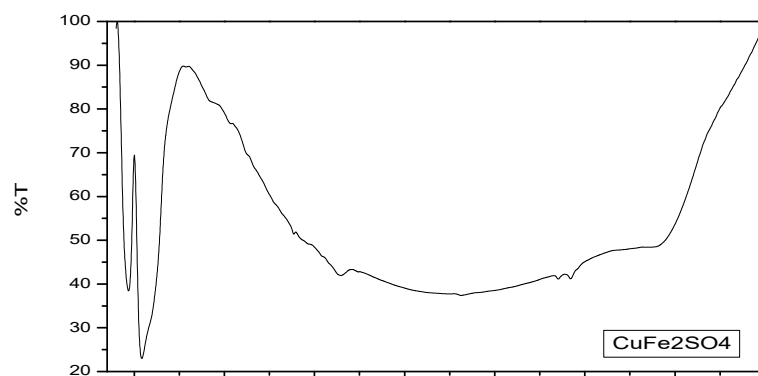


3.3.3 650⁰c

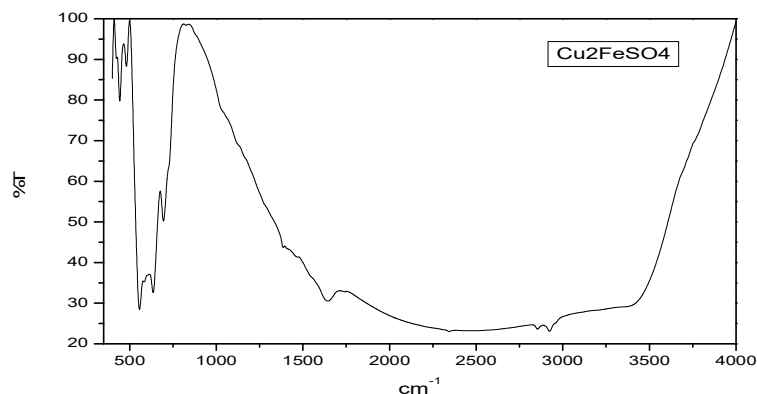
3.4 FTIR Studies



3.4.1 450⁰c



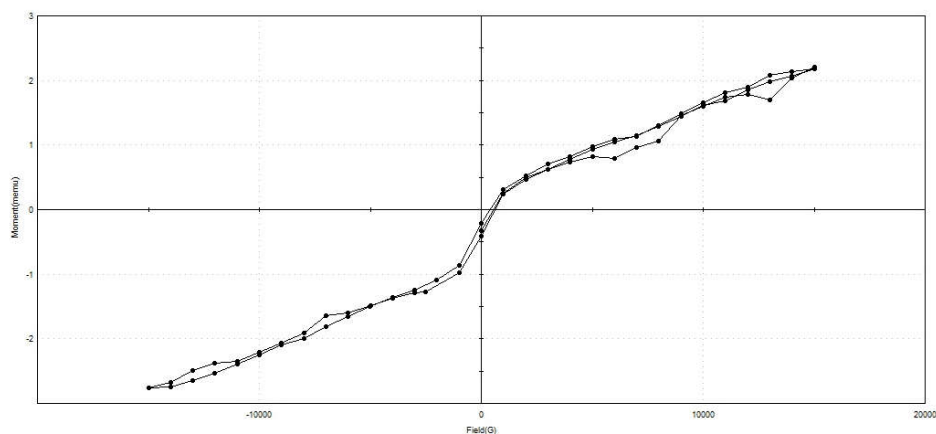
3.4.2 450⁰c

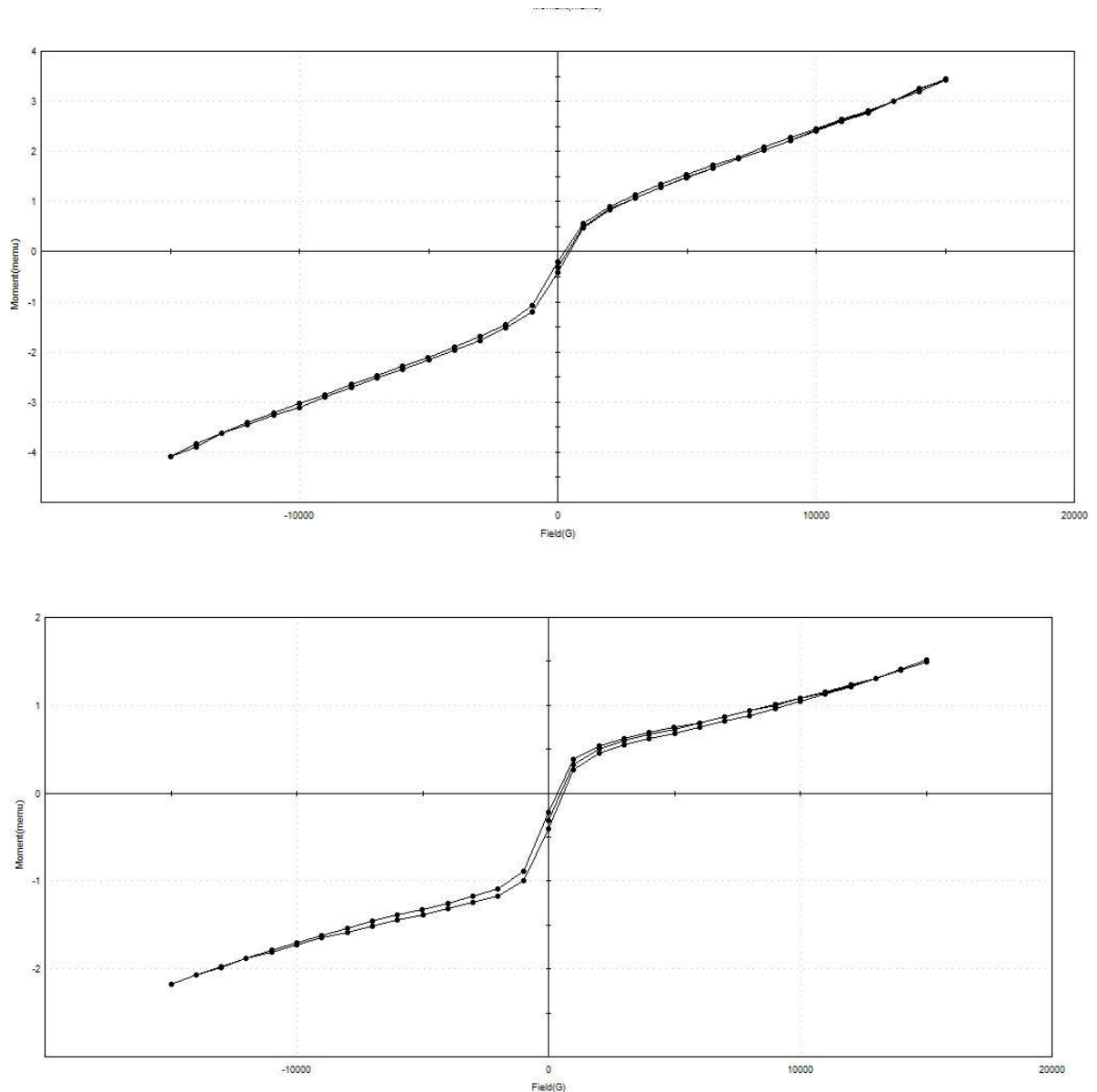


3.4.3 650⁰c FTIR spectra

The chemical structures of the as samples were identified by using FTIR range 4000 to 400 cm^{-1} . The FTIR magnetite products are presented in Figure samples, it can be seen that the broad characteristic at 3340 cm^{-1} could be assigned to O of physically adsorbed hydrogen bonded water molecule. Moreover, the spectra also revealed an band at 1521 cm^{-1} , which can also be correlated to the bending vibration of bonded water molecules, the iron oxide lattice. The vibrational absorption bands 535 cm^{-1} and 656 cm^{-1} , are attributed to the stretching vibration modes of the Cd Fe-O bonds in tetrahedral and respectively. The stretching band in ferrites with the frequency bands near 554-568 cm^{-1} and 415-432 cm^{-1} which refer to the tetrahedral and octahedral clusters in ferrites form, FT-IR spectra of magnetite nanoparticle samples vibrational absorption bands at 538, are attributed to the stretching vibration O bonds in tetrahedral and octahedral sites.

3.5 Magnetic properties





3.5 VSM for 450,550,650°C.

Figure 3.5 shows the hysteresis loop for all samples. Table 1 lists different parameters such as saturation magnetization (M_s), remanent magnetization (M_r), the ratio of remanent magnetization to saturation magnetization (M_r/M_s) and coercivity. The saturation magnetization for all samples by two techniques produced at 450 C, 550 and 650 C where show that the saturation magnetization increases from 7.6503:155592 emu/g to 3.8978 :16.539 emu/g.

This may due to replace ion on the tetrahedral A-sites, causing the decrease of magnetic moment in the sublattice MA, resulting in the increase of total magnetic moment according to Neel's equation two sublattice model of ferrimagnetism, the magnetic moment per formula unit in μ_B , $n_{BN}(x)$ is expressed as:

$$n_{BN}(x) = M_B(X) - M_A(X)$$

Where M_B and M_A are the B- and A-sublattice magnetic moment in μ_B respectively. Therefore, increase of calcination temperature for samples the saturation magnetization increases. This may be because increase in the lattice parameter, the exchange interaction between A and B sites gets higher resulting in strengthening of A-B interaction and weakening of B-B interaction, which leads to increase of saturation magnetization. There is positive relationship between grain size and coercivity H_c in the single domain region according to equation:

$$H_c = -h/D^2$$

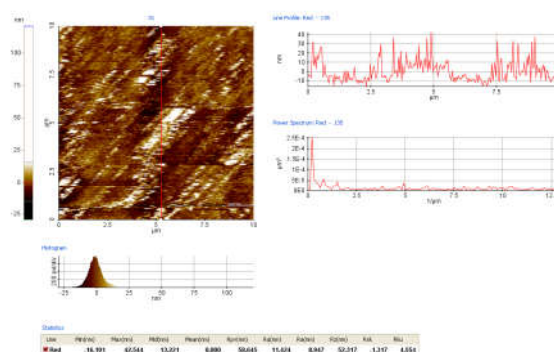
where g and h are constants and ' D ' is the diameter of the particle, this may be because the thermal effects. But the multi domain region there is inverse relationship between grain size and coercivity H_c according to equation:

$$H_c = +b/D,$$

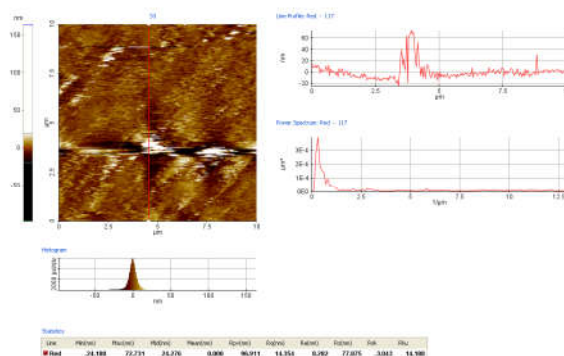
where a and b are constants [22-24].

So, the coercivity reduction with increase in the initial molar concentration (pH suspension) and the calcination temperature, which can be attributed to the reduce in anisotropy field for all techniques, which in turn reduces the domain energy. These refer to results which the coercivity values reached in first technique from 166.09 to 9.992G.

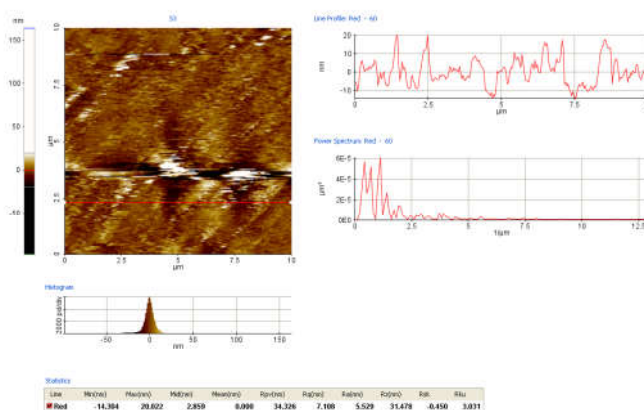
3.6 AFM analysis



3.6.1 450⁰c



3.6.2 550⁰c



3.6.3 650⁰c

AFM images of CdFe₂SO₄ are presented in [Figure 3.6. 1,2,3](#). Based on these images, nanoparticles below 100 nm were verified for these materials. Looking closer CdFe₂SO₄ presents smaller nanoparticles in a range of 20 to 50 nm, while the consisted of domains higher than 50 nm. The smaller particles observed for the particles could be due to the size-modulator effect of CDs .which could act as a nanoreactor for ferrite synthesis, preventing the particles growing during the ferrite synthesis (nucleation process).

4. Conclusions

In the current work, CdFe₂SO₄ nanoparticles were controllably prepared in great yield by co-precipitation at relatively lower temperature using two precipitating Agents NaOH. The results revealed that sodium hydroxide precipitating agent was the optimum precipitating agent for obtaining magnetite nanoparticles with smaller particle size and greater saturation magnetization value.

This preparation approach could shed light on synthesis of cadmium ferrite nanoparticles with different particle sizes for different applications.

The conclusions can be drawn from study of Cd Fe₂SO₄ using precipitation techniques as following:

- The crystallite size depends on the initial molar concentration (pH suspension) and the calcination temperature, where the grain size for first technique is in the range of 8 nm to 22 nm when the calcination temperature increases from 450 to 650°C respectively.
- The crystallinity of Cd Fe₂SO₄ nanoparticles might be improved by increasing calcination temperature but, the crystallinity is better than at 650°C.
- HRSEM indicates a reliance of particle size and the shape on the initial molar concentration (pH suspension) and the calcination temperatures. The particle size increases but a nanoparticle has a higher agglomeration with the calcination temperature increase.
- Hysteresis loop shows a reduction in coercivity with the initial molar concentration (pH suspension) and the calcination temperature for all techniques to approximate superparamagnetic behavior.
- All the coercivity values were low enough to emphasize that the ferrite was a soft ferrite or super-paramagnetic behavior.
- All laboratory results reveal that the initial molar concentration (pH suspension) and the calcination temperature play a major role to change its structural and magnetic properties.

5. References

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