

Co-Precipitation Synthesis of $MnFe_2O_4$ and $CoFe_2O_4$ Nanoparticles

Beril Ozcelik
Department of Mechanical Engineering, Faculty of Engineering and Architecture,
Kahramanmaras Sutcu Imam University, Onikisubat, Kahramanmaras, 46050, Turkiye
* E-mail of the corresponding author: bozcelik@ksu.edu.tr

Abstract
Nano-sized magnetic manganese ferrite, cobalt ferrite particles were produced by a co-precipitation method at room temperature. The effects of pH value of solutions, where the particles were synthesized, on the morphology and crystal structure of the $MnFe_2O_4$ and $CoFe_2O_4$ particles were investigated. The particles were pure and nearly spherical shaped. The sizes of synthesized magnetic nanoparticles had between 55 nm and 84 nm, with uniform morphologies. As the pH value increased, the diameter of the synthesized particles decreased and agglomeration of the nanoparticles increased.
Keywords: cobalt ferrite, co-precipitation, manganese ferrite, nanoparticle
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1. Introduction

Magnetic nanoparticles, which are used in a wide variety of fields such as optics, electronics, chemicals, mechanics, biotechnology and biomedicine, are materials of interest for researchers, scientists and engineers due to their unique properties (Zhou *et al*. 2016; Gnanaprakash 2007). Magnetic nanoparticles can be divided 4 main groups: iron oxides (magnetite and maghemite), metal ferrites (MFe_2O_4: manganese ferrite, cobalt ferrite, magnesium ferrite…), powder metals (Fe and Co) and alloys ($CoPt_3$ and FePt) (Bayrak 2012). Ferrites can be classified as hexagonal, cubic and orthorhombic ferrites based on their crystallographic structure. Both cubic MFe_2O_4 (M = Mg, Mn, Ni or Co) and orthorhombic MFe_2O_4 (M = Ba or Ca) are promising magnetic materials for microelectronic applications (Pereira 2012; Wang 2016).

Many methods can be used for magnetic nanoparticle synthesis. Co-precipitation method, which is one of them, is low cost, less time consuming and easily scalable for industrial applications. In addition, it is an environmentally friendly method. There is no need for high reaction temperature, pressure and the use of hazardous solvents and reagents. However, control of particle size and magnetic properties is still limited in the co-precipitation method (Pereira 2012; Sun *et al*. 2006). The process and parameters must be carefully controlled to obtain particles of the desired size, shape and composition. If process parameters such as solution pH, reaction temperature, mixing rate, solute concentration, and surfactant concentration are carefully controlled, particles of desired shapes and sizes can be synthesized (Sun *et al*. 2006).

In this study, well-known spinel (with cubic lattice) magnetic nanoparticles manganese ferrite ($MnFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$) were synthesized by co-precipitation method at room temperature. The pH of the solution was adjusted by varying the amount of NaOH used as the catalyst. Structural and morphological changes in the synthesized particles were investigated depending on the pH value of the solution. They were coated with oleic acid to prevent the particles from contacting with the air and oxidation and to ensure biocompatibility. The phase structures of the synthesized particles were characterized by X-ray diffraction (XRD), their morphology and dimensions were characterized by scanning electron microscopy (SEM).

2. Materials Methods

2.1 Synthesis of Nanoparticles

All of the chemical used in the experiments were purchased from E-Merck and used without purification. 0,016 mol of iron salts, $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$, was dissolved in 40 ml distilled water until a homogeneous mixture was obtained. Depending on the cubic ferrite type, 0.016 mol of $Mn(NO_3)_2.4H_2O$ or $Co(NO_3)_2.6H_2O$ was dissolved in 40 ml of distilled water. After these 3 aqueous solutions were mixed together at least 15 minutes, coating agent, oleic acid ($C_{18}H_{34}O_2$) at concentration 0.2% ,v/v and various aqueous NaOH concentrations were added into the solution to give various pH values. The final pH of the solution was adjusted to values given in Table 1 by adding NaOH solution. The sample names (as seen Table 1) indicated the synthesis solution type and pH value of the solutions from which the particles were obtained. The alkaline oleic acid added solution was mixed approximately 3 hours with mechanical stirrer (MS 3040, MTOPS, Korea) at certain speed until the crystallization of the particles completed. The precipitate was collected, washed at least ten times in distilled water to remove excess chemicals on the surface of the particles, and then dried in an oven at 60^{o}C.

Table 1. Composition and pH Value of Mn and Co Based Solutions

Sample	*NaOH	pH
Mn-4	3.2 gr	3.9
Mn-8.5	4.5 gr	8.5
Mn-12	5 gr	12.0
Mn-12.8	5.5 gr	12.8
Mn-13.3	6.5 gr	13.3
Mn-13.5	6.75 gr	13.5
Co-5	3.2 gr	5
Co-13	5.5 gr	13.09
Co-13.3	6 gr	13.3
Co-13.5	6.5 gr	13.5
Co-13.7	7.5 gr	13.7
Co-13.8	8 gr	13.8

*The given amounts of NaOH was dissolved in 15 ml of distilled water

2.2 Characterization of Nanoparticles

In XRD analysis, Panalytical X'pert Powder type PW3040 diffractometer was used to determine the phases of the particles. It operated with Cu-Kα radiation (λ=0.154 nm) produced at 40 kV and 35 mA. Scanning was worked at diffraction angles (2θ) between 20^o and 80 ^{o} in increments of 0.01 for 1 s. The diffraction signal intensity was monitored throughout the scan and was processed using the X'Pert High Score Plus 2.2b software. The size and surface morphology of the synthesized particles was investigated using a Scanning Electron Microscope (Zeiss EVO/LS10).

3. Results and Discussion

The colours of the synthesized particles from Mn-based solutions and their magnetic properties determined with the help of magnets are given in Table 2. The characteristic colour of $MnFe_2O_4$ particles is brown to black (Americanelements 2022). It has been observed that the particles obtained from acidic solutions (Mn-4) were light brown and they were not magnetic. As the pH value of the solution was increased, the colour of the synthesized particle darkened and changed to black. The magnetic properties of the particles improved with increasing pH of the solutions. Therefore, particle syntheses were carried out in alkaline solutions.

Table 2. Properties of the Synthesized Particles from Mn-Based Solutions

Sample	Color	Magnetic properties
Mn-4	Light brown	not magnetic
Mn-8.5	brown	poor magnetic
Mn-12	black	magnetic
Mn-12.8	dark brown	magnetic
Mn-13.3	black	magnetic
Mn-13.5	black	magnetic

The XRD patterns of the particles synthesized from Mn-based solutions with a pH value higher than 12 are presented in Figure 1.

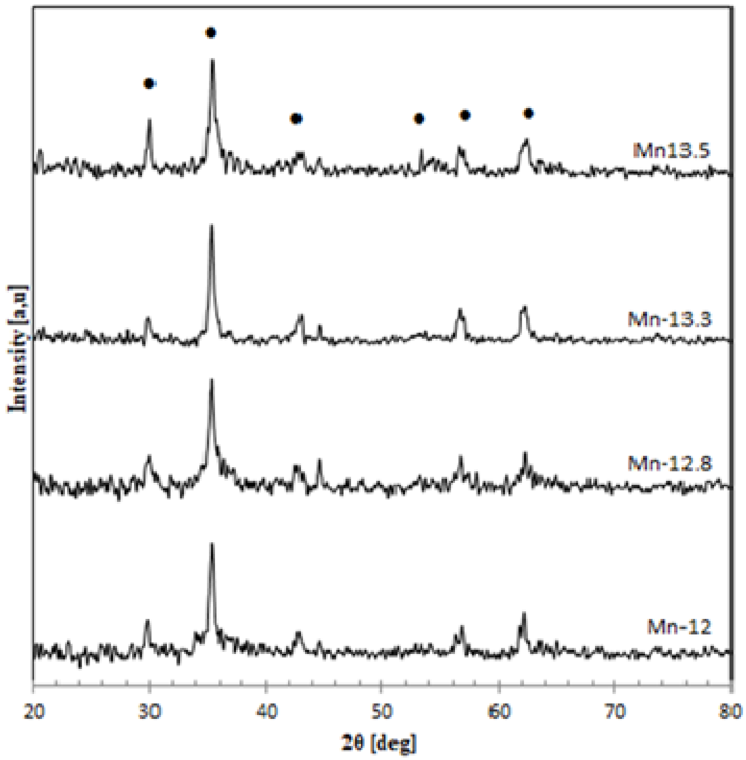

Figure 1. XRD Patterns of Particles Synthesized from Mn-Based Solutions (●)$MnFe_2O_4$

The particles showed magnetic properties and all the peaks in the graph were indexed as $MnFe_2O_4$. There was no other peak belonging to any impurity compound. This indicated the purity of the particles.

The colours of the particles synthesized from Co-based solutions and their magnetic properties determined with the help of magnets are given in Table 3. The characteristic colour of CoFe2O4 particles is gray to black (Americanelements 2022). It has been observed that the particles obtained from acidic solutions (Co-5) were light gray and they were not magnetic, while the particles obtained from alkaline solutions (over pH 13) were magnetic. It was observed that the magnetic properties of the particles improved with increasing pH of the solutions.

Table 3. Properties of the Synthesized Particles from Co-Based Solutions

Sample	Color	Magnetic properties
Co-5	Light gray	not magnetic
Co-13	dark gray	magnetic
Co-13.3	black	magnetic
Co-13.5	black	magnetic
Co-13.7	black	magnetic
Co-13.8	black	magnetic

The XRD patterns of the particles, synthesized from Co-based solutions with a pH value higher than 13, are presented in Fig. 2.

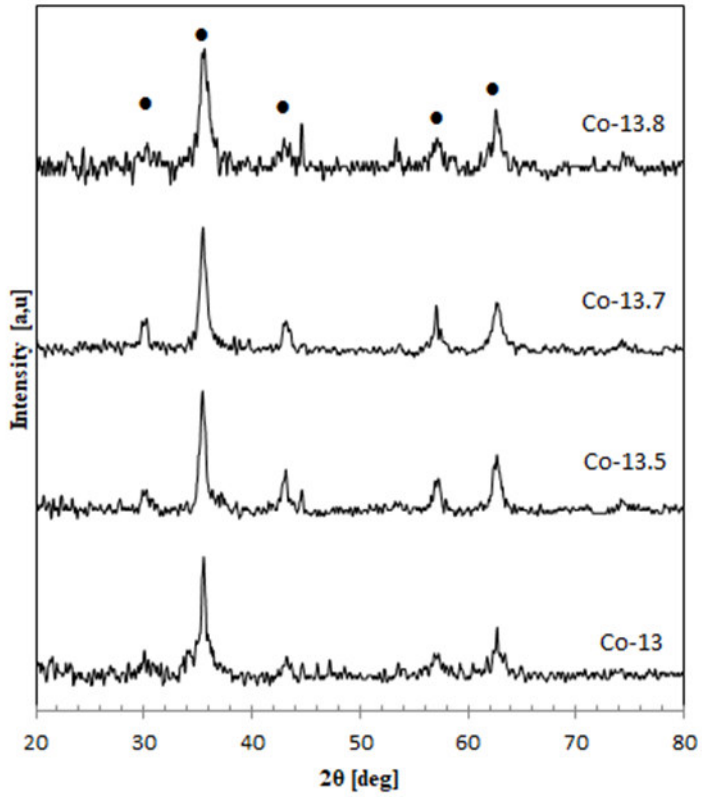

Figure 2 .XRD Patterns of Particles Synthesized from Co-Based Solutions (●) $CoFe_2O_4$

$CoFe_2O_4$ was the only stable phase in the particles synthesized from Co-based solutions with the pH value upper than 13. Fig. 3 shows the SEM images of $MnFe_2O_4$ particles were synthesized from Mn-based solutions of pH 12, 12.8, 13.3, 13.5, respectively. The average diameter of the particles obtained at all pH values was less than 100 nm. The average diameter of the Mn-12 and Mn-13.5 particles was 84 nm and 65 nm, respectively. As the pH value increased, the diameter of the synthesized particles decreased and agglomeration of the particles increased. The particles are nearly spherical shape.

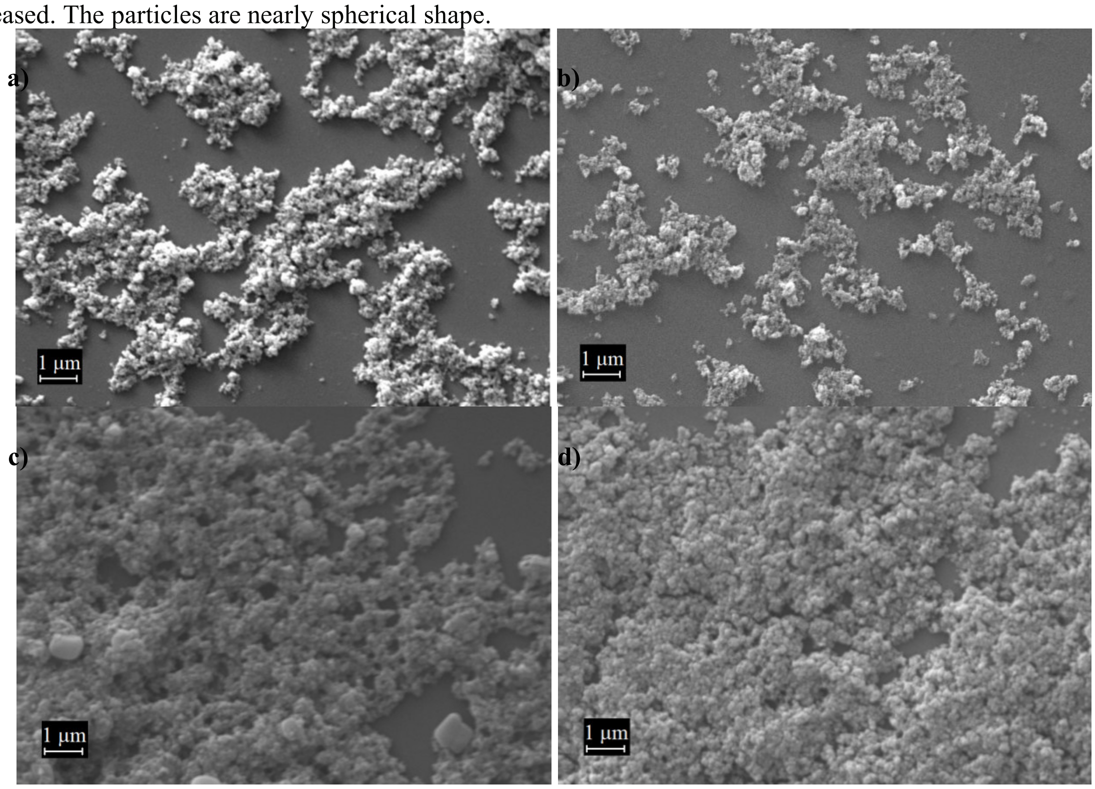

Figure 3. SEM Images of the $MnFe_2O_4$ Particles; a) Mn-12, b) Mn-12.8, c) Mn-13.3 d) Mn-13.5

Figure 4 shows the SEM images of $CoFe_2O_4$ particles were synthesized from Co-based solutions of pH 13, 13.5, 13.7, 13.8, respectively. As with $MnFe_2O_4$ particles, the average diameter of the synthesized particles was less than 100 nm. The average diameter of the Co-13, Co 13.5, Co-13.7 particles was 75 nm, 68 nm and 55 nm, respectively.

The particles had homogeneous sizes but agglomeration increased with decreasing particle size. As the pH value increased, the average diameter of the synthesized particles decreased and agglomeration of the particles increased. Small particles especially in nanometer size tend to agglomerate together because they have a larger surface area (Ozcelik 2014). The agglomerated smaller particles were found to form aggregates with an average diameter of approximately 156 nm for Co-13.5, 190 nm for Co-13.7. The morphology of the $CoFe_2O_4$ particles was nearly spherical.

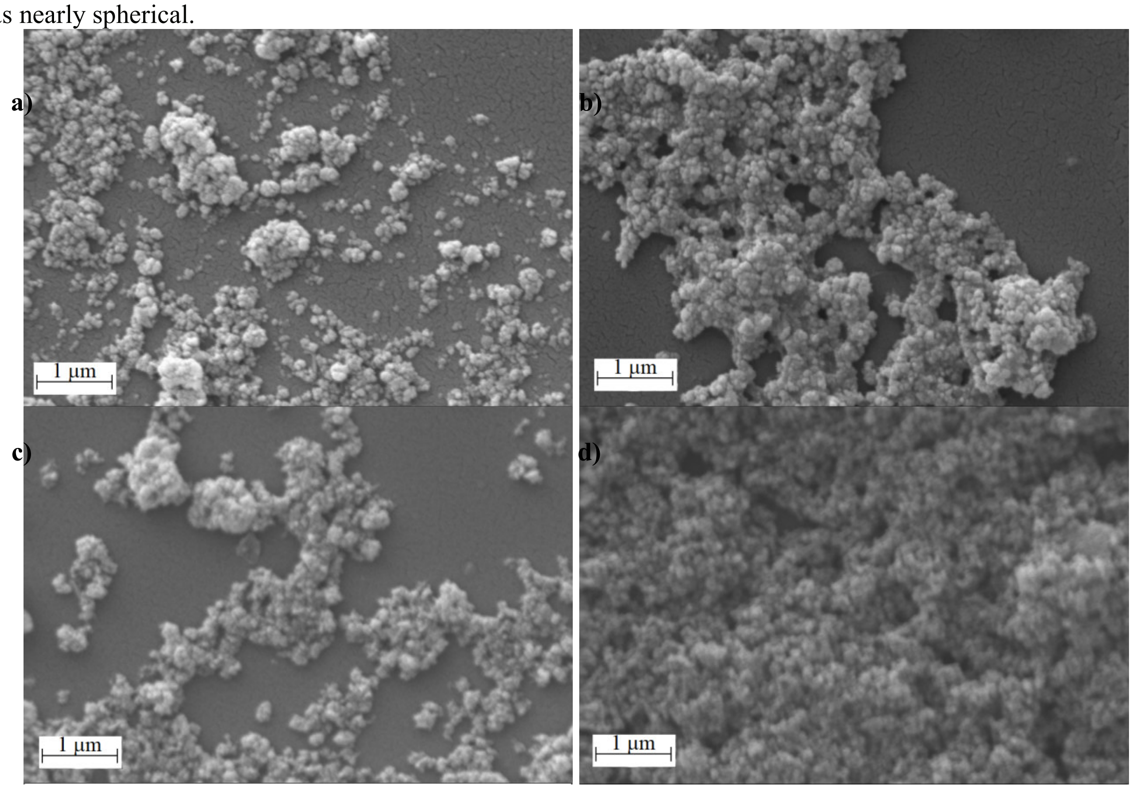

Figure 4. SEM Images of the CoFe2O4 Particles; a) Co-13, b) Co-13.5, c) Co-13.7, d) Co-13.8

4. Conclusion

Magnetic nanoparticles were synthesized using the co-precipitation method, which is low cost, takes less time than other synthesis methods, and is easily scalable for industrial applications. Pure $MnFe_2O_4$ and $CoFe_2O_4$, were synthesized at room temperature by using oleic acid as the coating agent and NaOH as the precipitation agent. The effect of solution pH value on the microstructure and size of the synthesized particles were investigated. As the pH value increased, the diameter of the synthesized particles decreased. The diameter of $MnFe_2O_4$ nanoparticles varied between 84-65 nm, and the diameter of $CoFe_2O_4$ nanoparticles varied between 75-55 nm depending on the pH of the solutions. As the pH value increased, agglomeration of the nanoparticles increased. $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles were nearly spherical shape.

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Beril OZCELIK received her B.Sc., M.Sc. and Ph.D degree in Mechanical Engineering from Istanbul Technical University, Turkey in 2005, 2007 and 2014, respectively. She is currently working at the Faculty of Enginering and Architecture in Kahramanmaras Sutcu Imam University as an assistant professor.