Synthesis and Characterization of Fe₃O₄ Nanoparticles Using Different Experimental Methods

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Abstract. This paper reports a comparative study on the synthesis of Fe₃O₄ nanoparticles using three different methods, namely; Co-precipitation, Sonochemical and Solvothermal methods. Ferric chloride hexahydrate (FeCl₃.6H₂O) and Ferrous chloride tetrahydrate (FeCl₂.4H₂O) were used as the iron precursor for the Co-precipitation method; while, Ferrous sulphate Heptahydrate (FeCl₂.7H₂O) and Ferric chloride hexahydrate (FeCl₃.6H₂O) were used as the iron precursor for sonochemical and solvothermal synthesis methods, respectively. The effect of the experimental methods and the precursors used on the shape and size of the Fe₃O₄ nanoparticles were investigated using different characterization techniques. The chemical characterization of the samples were carried out using EDX. The size of the nanoparticles were determined using particle size analyzer. The SEM and TEM images were used study to the surface morphology of the produced nanoparticles. Finally, TGA was used to study the thermal stability of the prepared iron oxide nanoparticles.

Keywords. Synthesis, Fe₃O₄ nanoparticles, Co-precipitation, Sonochemical, Solvothermal, Characterization

1. Introduction

In recent years, Fe₃O₄ nanoparticles have garnered a widespread interest due to their biocompatibility, unique magnetic properties, high electrical resistivity and high chemical stability [1, 2]. The activity of the Fe₃O₄ nanoparticles strongly depends on their size, shape and crystal phase and several studies have shown that the shape has a great impact on the resulting properties of Fe₃O₄ nanoparticles and their potential applications [3-9]. The potential applications of Fe₃O₄ nanoparticles have encouraged the rapid development of several synthesis techniques such as co-precipitation, hydrothermal treatment, spray pyrolysis, ultrasound irradiation, microwave-assisted method and solvothermal method.
However, it still remains challenging for the researchers to know the exact method required to synthesis the desired \( \text{Fe}_3\text{O}_4 \) nanoparticles that will be suitable for different applications. In this work, we demonstrate the synthesis of nanoparticles using Co-precipitation, Sonochemical and Solvothermal methods and perform rigorous analysis techniques to study the characteristics of the nanoparticles produced via each individual methods.

2. Experimental

2.1 Chemicals
Ferric chloride hexahydrate (FeCl\(_3\).6H\(_2\)O), Ferrous chloride tetrahydrate (FeCl\(_2\).4H\(_2\)O), Ferrous sulphate Heptahydrate (FeCl\(_2\).7H\(_2\)O), sodium hydroxide, anhydrous sodium acetate, ethylene glycol all of purity greater than 98% and ammonium hydroxide (25%) were purchased from ResearchLab, India and were used without further purification.

2.2 Co-precipitation Method
The \( \text{Fe}_3\text{O}_4 \) nanoparticles was prepared using co-precipitation method as reported by the work of Bayat et al. [10]. Firstly, 4.8 grams and 1.8 grams of FeCl\(_3\).6H\(_2\)O and FeCl\(_2\).4H\(_2\)O, respectively, were added to 100 mL deionized water under N\(_2\) atmosphere. The solution was stirred at 500 rpm for about 15 minutes. Once the salts were completely dissolved, 10 mL of 28% \( \text{NH}_4\text{OH} \) was added at once, which immediately resulted in formation of a black precipitate. The solution was further stirred for one hour. Finally, the black precipitate were separated by an external magnet and cleaned with water and ethanol and dried vacuum oven at 65 °C overnight.

2.3 Sonochemical Method
The \( \text{Fe}_3\text{O}_4 \) nanoparticles were prepared using sonochemical method following the work of Abbas et al. [11]. For this method, 2.31 gm of FeSO\(_4\).7H\(_2\)O was dissolvd in distilled water (90 mL) and stirred for 15 minutes to obtain a greenish solution. The solution was then transferred to an ultrasonic homogenizer (Xian Toption, TU-1200) equipped with a horn having a diameter of 10 mm to sonicate the solution at 25 kHz. After 15 minutes of sonication, 9 mL of 3 M NaOH was added the solution following which the solution was further sonicated for 60 minutes. At the end of the sonication process, black precipitate of iron oxide nanoparticles were obtained which were separated by an external magnet and cleaned with ethanol and water and then dried in a vacuum oven at 65 °C for 6 hours.

2.4 Solvothermal Method
The preparation of the iron oxide samples via the solvothermal route was accomplished via the method reported by the work of Deng et al. [12]. Firstly, around 2.70 g of FeCl\(_3\).6H\(_2\)O and 7.20 g of anhydrous sodium acetate were dissolved in 100 mL of ethylene glycol. The solution was stirred vigorously for 30 mins resulting in formation of a yellow homogenous solution. The solution was then transferred to a Teflon-lined stainless-steel autoclave which was then sealed and heated for 8 hours at a temperature of 200 °C [13]. The autoclave was then cooled to room temperature to obtain black magnetite particles. These particles were then separated using an external magnet and washed with ethanol and water for several times. The cleaned nanoparticles were then transferred to a vacuum oven at 65 °C for 6 hours.

2.5 Characterization
The particle size of the prepared \( \text{Fe}_3\text{O}_4 \) samples using three different methods were determined using a Malvern ZEN3600 instrument. The X-ray diffraction (XRD) patterns of the \( \text{Fe}_3\text{O}_4 \) samples were examined on a Rigaku MiniFlex II diffractometer that uses Cu-K\(_\alpha\) radiation corresponding to a wavelength \( \lambda = 1.5406 \text{ Å} \) in the range 20–80°. The chemical composition and surface morphologies of the nanoparticles were observed by the Scanning electron microscope combined energy dispersive X-ray (FEI Nova Nano SEM 450). While the details of the internal composition of the nanoparticles were observed using a transmission electron microscope (TEM, FEI, TALOS F200X). Finally, the thermal stability of the samples were analysed by performing a thermogravimetric analysis within a temperature range of 25 – 900 °C at heating rate of 5 °C/min under N\(_2\) atmosphere using a PerkinElmer Pyris 1 TGA.


3. Results and Discussion

3.1 Particle Size Analysis

Particle size analysis of the Fe₃O₄ nanoparticles prepared using three different methods was conducted by Malvern ZEN3600 instrument and obtained results are given in Table 1. The sonochemical method produced the largest iron oxide nanoparticle with average particle size of 370.9 nm. The nanoparticles produced using the co-precipitation were the smallest of the three with an average particle size of around 178.4 nm; while, the nanoparticle produced using solvothermal method had an average particle size of 217.6 nm.

| Synthesis Method     | Average Particle Size, nm |
|----------------------|---------------------------|
| Solvothermal         | 217.6                     |
| Co-precipitation     | 178.4                     |
| Sonochemical         | 370.9                     |

3.2 XRD

The crystallinity of the produced Fe₃O₄ samples were studied using XRD and are shown in Figure 1. The XRD patterns of all three of the Fe₃O₄ samples showed six characteristic peaks at 2θ values of 30, 35, 43, 55, 57 and 62 were corresponding to the (220), (311), (400), (422), (511) and (440) crystal planes. This characteristics were synonymous to that of Fe₃O₄ with inverse cubic spinel structure (JCPDS file PDF no.65-3107) [14, 15]. Figure 1 further revealed that Fe₃O₄ nanoparticles produced using the solvothermal method had very high crystallinity compared to the ones produced via sonochemical and co-precipitation methods. The XRD patterns of all three samples detected no characteristic peak for impurities.
Figure 1. XRD patterns of as-synthesized $\text{Fe}_3\text{O}_4$ nanoparticles

3.3 EDX

The EDX data of the as-synthesized $\text{Fe}_3\text{O}_4$ nanoparticles are summarized in Table 2. The data affirms the presence of only Iron (Fe) and Oxygen (O) elements without any other impurities. The average weight % of iron and oxygen was approximately around 75.91 and 24.09, respectively, for all three of the samples which confirms that the synthesized $\text{Fe}_3\text{O}_4$ are in excellent stoichiometry. The sample area of the SEM image from which EDX data has been generated has been indicated in Figure 2.

| Elements | Co-precipitation | Sonochemical | Solvothermal |
|---------|------------------|--------------|--------------|
| Fe      | 78.14            | 73.06        | 76.54        |
| O       | 21.86            | 26.94        | 23.46        |

3.4 SEM

The SEM images of the as-synthesized $\text{Fe}_3\text{O}_4$ nanoparticles are shown in Figure 2. The SEM image of iron oxide nanoparticles obtained via co-precipitation method shows an agglomeration of uniform nano-spheres with a mean diameter of 10 nm. The nanoparticles synthesized via sonochemical methods reveals the formation of iron oxide with nearly uniform cubic shape with their size varying from 50 – 200 nm. Finally, $\text{Fe}_3\text{O}_4$ nanoparticles produced via solvothermal method formation of nanoparticles that agglomerated into relatively larger spheres with an mean diameter of around 150 nm.
3.5 TEM

The TEM images of the as-synthesized nanoparticles are shown in Figure 3. The findings of SEM images were reaffirmed by the TEM images. The images revealed that the Fe₃O₄ nanoparticles obtained via co-precipitation method showed that the nanoparticles are very well distributed with uniformly narrow size distribution. Fe₃O₄ nanoparticles with nearly cubic shapes were formed via the sonochemical method. Furthermore, the images showed that solvothermal method lead to the formation large spherical Fe₃O₄ nanoparticles with an average diameter of around 150 nm.

3.6 TGA

The thermogravimetric analysis of the iron oxide nanoparticles were carried out at a temperature range of 25 – 900 °C at heating rate of 5 °C/min under N₂ atmosphere and results are shown in Figure 4. From the figure, it is evident that the nanoparticles produced via sonochemical method showed the least weight
loss (1%) followed by the co-precipitation (4%) and solvothermal method (7.8%). Which is justifiable since the sonochemical method requires the least number of reagents of the three. The curve representing the co-precipitation method shows a steep weight loss of 4% up to 250 °C. This can be attributed to the presence of residual physisorbed water and other organic solvents. Almost similar case is observed for the nanoparticles produced via solvothermal method, in this case the weight loss is resulted by the presence of physisorbed ethylene glycol. Further weight loss of about 2% was noticed for nanoparticles produced by this method at around 700 °C. This shows the presence of unreacted sodium acetate within the nanoparticle. Therefore, based on the thermal stability, the nanoparticles can be ordered as follow: sonochemical > co-precipitation > solvothermal method.

![TGA curves](image)

**Figure 4.** TGA curves of as-synthesized Fe₃O₄ nanoparticles

### 4. Conclusion

Iron oxide (Fe₃O₄) nanoparticles were successfully produced via co-precipitation, sonochemical and solvothermal methods and analyzed using various characterization techniques. Analysis on the particle size analyzer revealed that the nanoparticles produced via the co-precipitation had the lowest size, while the nanoparticles produced via sonochemical methods had the highest particle size. The XRD patterns revealed the all three nanoparticles were conforming to the pure standard Fe₃O₄ nanoparticle. Further analysis of the XRD pattern revealed that the nanoparticles via solvothermal methods showed the highest crystallinity. The EDX results confirmed that synthesized Fe₃O₄ are in excellent stoichiometry. The SEM and TEM images both reveal that nanoparticles produced via sonochemical method had cubic shape. The images further revealed that Fe₃O₄ particles produced via co-precipitation and solvothermal methods were spherical in shape. The images also showed that the particles produced via solvothermal methods were relatively larger in size. Finally, TGA curves showed that the Fe₃O₄ nanoparticles produced by sonochemical method had the highest thermal stability followed by the ones produced via co-precipitation and solvothermal methods.
5. References

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