Synthesis of Fe3O4 Nanoparticles Using the Electrolysis Method Capped with *Clitoria Ternatea* Extract

Ruzain Rafie Sukma Putra1, Kartika A. Madurani2, Heru Suryanto3,Daimon Syukri4, Fredy Kurniawan5,a)

1, 2, 5Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia

3Center of Excellence for Cellulose Composite, Department of Mechanical Engineering, Universitas Negeri Malang, Jl. Semarang 5, Malang, 65145, Indonesia

4Department of Food and Agricultural Product Technology, Andalas University, Limaum Manis, Padang, 25163, West Sumatera, Indonesia

Author Emails  
a)fredy@chem.its.ac.id

**Abstract.** The application of nanoparticles of magnetite (Fe3O4 NPs) has been widespread in various sectors. It is due to the NPs unique properties, including superparamagnetism, a high ratio of surface to volume, a large surface area, and easy separation. Various methods are used to obtain the NPs. One of them is using an extract of the plant to reduce the use of reagents and as a capping agent for stabilising NPs**.** In this study, the NPs were successfully synthesised using the electrolysis method. Fe3O4 NPs were fabricated by the electrolysis method using iron (Fe) metal as anode and cathode electrodes in a 0.1 M Na2SO4 solution. The synthesis was applied at various voltages, i.e., 10, 20, 30, 40, and 50 volts. The NPs obtained were capped using the extract of *Clitoria ternatea* after the electrolysis process*.* The best results for theNPs were obtained after the characterization process using ultraviolet-visible (UV-Vis) spectrometry, X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), and particle size analyzers (PSA).

# INTRODUCTION

Nanoparticle (NPs) can be defined as a material that has a size of less than 1 micrometer, typically, the accepted size range for NPs is between 10-500 nm [1]. Metal Nanoparticles (MNPs) have been widely used in many sectors, such as sensors catalysts, and adsorption. The use of MNPs is caused by their unique properties, such as their high surface area, catalytic properties, high selectivity, and adsorption ability [2]. MNPs that have been known to be used are gold (Au), Silver (Ag), Platinum (Pt), Copper (Cu), Zinc (Zn), Nickel (Ni), Aluminium (Al), Cobalt (Co), and Iron (Fe) [3]. In recent years, many scientists have use MNPs in various research, especially Fe3O4 nanoparticles (Fe3O4 NPs) for its economic value and characteristics [4].Fe3O4 also known as magnetite are spinel’s ferromagnetic material consisting of ferrous (Fe2+) and ferric (Fe2+) ion that binds with oxygen (O) [5]. Fe3O4 NPs have been used in many applications for its properties and characteristics such as magnetic, biocompatibility, high surface area, low cost [6]. The synthesis of Fe3O4 NPs can be carried out through various methods, such as coprecipitation, thermal decomposition, hydrothermal, and microemulsion. Some of these methods have some drawbacks, such as time it takes to synthesize, a high cost, and relatively require more material. Therefore, other methods are needed to produce the Fe3O4 nanoparticles (NPs) as an alternative. One method that has been used as an alternative to these problems the electrochemical method [7].

Electrochemical methods for synthesis of Fe3O4 have been reported using an iron plate or needle as the iron source of Fe2+ and Fe3+. This method utilizes electrical energy to create a chemical reaction, in this case, the nanoparticles. The advantages of this method are that it requires relatively fewer materials, making it cheaper and more environmentally friendly. Additionally, the electrochemical method in nanoparticles synthesis can be used to control the size of the Fe3O4 NPs by adjusting the potential (Voltage) during the synthesis process [7,8]. One of the drawback of Fe3O4 NPs is that they are prone to agglomeration due to magnetic properties and high surface area possessed by Fe3O4 nanoparticles [4,9]. The size and stability of Fe3O4 NPs can be maintained through surface modification with additional compounds, such as adding a capping agent or surfactant during synthesis [8,10,11].

Capping agents have been widely used for maintaining the size and stability of NPs, one of the examples of capping agents is Polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), Ethylene diamine tetra acetic (EDTA), Chitosan, and plant extract [12]. From various capping agent, plant extract has several advantages, including being environmentally friendly, easy to use, non-toxic, and cheap [13]. *Clitoria ternatea* (CT) has been reported to be used in various metal nanoparticles, such as PtNPs [14], AuNPs [15], and AgNPs [16]. The extract of CT has been found to be rich in antioxidants caused by flavonoid content, such as anthocyanin contained within the flower. This compound can be used for the synthesis of NPs as a reducing agent and a capping agent [15–17]. This study focuses on utilizing CT extract as a capping agent in Fe3O4 synthesis through the electrochemical method. So far, no research has been conducted using CT flower extract in Fe3O4 synthesis.

# EXPERIMENT

## Materials

The iron plate with a dimension of 10 cm x 2 cm x 0,2 cm was obtained from EELIC China. Sodium Sulfate Anhydrous (Na2SO4, 99%) was obtained from SAP CHEMICALS, Indonesia. Demineralized water and ethanol (CH3OH, 98%) were purchased from PT. Brataco Chemicals, Indonesia. Dried CT flower was bought from local market.

## Preparation *Clitoria ternatea* Extract

CT flower extract was prepared as in a previous study, with modification (15). Dried CT flower was ground into a powder. A 10 g portion of flower powder was extracted using 200 mL of heated demineralized water at 80°C. The extraction was conducted for 1 hour at a constant temperature in stirring conditions (250 rpm). After the extraction process, the CT flower extract was filtered using filter paper. The CT flower extract is a purple-colored solution and then stored at 4°C prior to use.

## Synthesis of Fe3O­4 Nanoparticles

Synthesis of Fe3O4 NPs was adopted and modified from previous work [7,18]. The experimental setup was shown in Figure 1. The iron plate was abraded using emery paper. The iron plate was washed using demineralized water and ethanol, respectively. The synthesis of Fe3O4 NPs was carried out using the electrolysis method. The iron plate as both the anode and cathode, was connected to a power supply. The electrodes were immersed in a 0.01 M Na2SO4 solution with a depth of 2 cm. The distance between the electrodes was kept at 2 cm. The potential effect was carried out at variations of 10, 20, 30, 40, and 50 V for 30 minutes. After the electrolysis process, the Fe3O4 NPs were formed as a colloid that dispersed in the solution. The colloid was mixed with 5 mL of CT flower extract and then stirred at 250 rpm for 30 minutes. During the electrolysis process at 10 V, pH is measured using MQuant pH indicator at 0, 5, 10, 15, 20, 25, and 30 minutes. The Fe3O4 NPs obtained were characterized using ultraviolet-visible (UV-Vis) spectrometry (Thermo Genesys 10), Particle size analyzers (PSA) (Melvern Zetasizer), X-ray diffraction (XRD) (X’Pert Pro MPD), and Field emission scanning electron microscopy-dispersive X-Ray spectroscopy (FESEM/EDX) (Hitachi Regulus 8220).

A diagram of a test tube

Description automatically generated

**Figure 1** Experimental setup of electrolysis for Fe3O4 NPs synthesis.

# RESULT AND DISCUSSION

## Synthesis Result

Figure 2 shows the solution color change during the electrolysis process. In the first 10 minutes, the solution was yellow-brown (Figure 2a), which indicates of Fe ions in the solution [8]. Subsequently, the solution changes into red brown (Figure 2b). After 30 minutes of the electrolysis process, the Fe3O4 NPs were formed (Figure 2c). Figure 3 shows the increase in pH value in the solution during the electrolysis process. Increasing pH indicates the presence of hydroxide ions (OH-) that formed during the electrolysis process. This condition is suitable for the formation of Fe3O4 NPs [8]. The Fe3O4 NPs obtained were capped with CT flower extract for 30 minutes and then filtered and dried. The dried Fe­3O4 NPs were obtained as shown in Figure 5. The formation of Fe3O4 NPs was confirmed by an external magnet field (Figure 6) [19].

|  |  |  |
| --- | --- | --- |
| A measuring cup with yellow liquid  Description automatically generated  **(a)** | A measuring cup with a yellow liquid  Description automatically generated  **(b)** | A beaker with a brown liquid in it  Description automatically generated  **(c)** |

**Figure 2** Color changes in the solution at 10 V in (a) 10 minutes, (b) 20 minutes, and (c) 30 minutes



**Figure 3** The change of pH in solution during the process of electrolysis at 10 V

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| (a) | A black substance in a circle  Description automatically generated  (b) | A round glass plate with black specks  Description automatically generated  (c) | A black substance on a clear circle  Description automatically generated  (d) | A round glass plate with a black substance in it  Description automatically generated  (e) |

**Figure 4** Images of Fe3O4 NPs with CT extract at (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V, and (e)50 V.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| (a) | (b) | (c) | (d) | (e) |

**Figure 5** Images of magnetic separation of Fe3O4 NPs at (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V, and (e) 50V.

## Characterization

UV-Vis spectral analysis of Fe3O4 NPs is shown in Figure 6. The synthesized Fe3O4 at a variation of voltage reveals continuous absorption in the visible range of 300-900 nm, with the peak shown at 361 nm. Similar results of green synthesis of Fe3O4 NPs from previous work conducted by Yen Pin Yew and Buafia have identical UV-Vis Spectra for Fe3O4 NPs using *Kappaphycus alvarezii* and *artemisia* extract [20,21].



**Figure 6** UV-Vis absorption spectra of Fe3O4 NPs

PSA analysis of Fe3O4 NPs is done not less than 1 hour after synthesis and is shown in Table 1. The synthesized Fe3O4 NPs are shown to have a decrease in particle size with an increase in voltage. The smallest Fe3O4 NPs size by Z-Average was obtained at 50 V, with the size of NPs reaching 352.8 nm. Fe3O4 NPs have also been shown to have smaller particles reaching 21.44 nm in size. By this, electrolysis can be used to control the size of nanoparticles by applying higher voltages during the synthesis process [8]. Fe3O4 NPs synthesized with CT extract also show a smaller size and dispersity compared to Fe3O4 NPs without using CT extract. This confirms the ability of the CT extract to control the Fe3O4 NPs size.

**Table 1** PSA analysis of Fe2O4 NPs

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Variation** | | **Fe3O4 NPs without CT Extract** | | | | | | **Fe3O4 NPs with CT Extract** | | | | |
| **Z-Average (nm)** | | **Polydispersity Index (PDI)** | | **Ordered by Size** | | **Z-Average (nm)** | | **Polydispersity Index (PDI)** | | **Ordered by Size** |
| 10 Volt | 1825 | | 0,6909 | | 366,2 nm (14,77%)  1272 nm (85,23%) | | 2278 | | 1 | | 2674 nm (100%) | |
| 20 Volt | 2869 | | 0,8405 | | 915,7 nm (100%) | | 677,6 | | 0,5046 | | 210,1 nm (24,83 %)  754,8 nm (57,54 %)  4830 nm (17,63 %) | |
| 30 Volt | 1296 | | 0,7941 | | 181,6 nm (22,24 %)  1029 (77,76%) | | 552,8 | | 0,4259 | | 514,4 nm (79,04%)  3914 nm (20,96%) | |
| 40 Volt | 3487 | | 0,9024 | | 886,8 nm (100%) | | 482,1 | | 0,4429 | | 981,9 nm (100%) | |
| 50 Volt | 3208 | | 0,8214 | | 938,4 nm (100%) | | 352,8 | | 0,7541 | | 21,44 nm (5,30%)  125,9 nm (32,99%)  687,9 (42,65%) | |

Figure 8 shows peaks at 30,1087o; 35,5064o; 43,0933o; 57,0473o; and 62,6455ocorresponded to (220), (311), (400), (511), and (440) respectively. The spinel structure of Fe3O4 NPs has been confirmed by the standard JCPDS card no. 19-0629 (7). The crystalline size (D) of Fe3O4 NPs is estimated by using the full width half maximum (FWMH) values obtained from the predominant peak at 2θ = 35,5064o.

The crystalline size of Fe3O4 NPs is calculated to be about 13.30 nm for 10 V; 14.82 nm for 20 V; 15.10 for both 30 V and 40 V; and lastly 15.10 nm for 50 V, this result indicates Fe3O4 has small crystallite sizes.



**Figure 7** XRD patterns of synthesize Fe3O4 NPs

FESEM Analysis was shown in Figure 9(a-b). The analysis shows the morphology Fe3O­4 NPs using CT extract. Fe3O4 NPs display at magnification of 50.000x and 70.000x show the nanoscale of Fe3O4 with the shape of plate-like with various sizes. The size of Fe3O4 was analyzed in the most optimum states (50 V). The histogram of Fe3O4 NPs (figure 3(d)) shows that the average size of Fe3O4 NPs was 60,16 nm. Figures 9c confirms the presence of Fe and O content in Fe3O4 NPs, with percentages of each atom present within NPs being 59,7% and 40,3%.

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| --- | --- |
| A close-up of a grey object  Description automatically generated  (a) | A close-up of a grey surface  Description automatically generated  (b) |
| A graph of a yellow line  Description automatically generated with medium confidence  (c) | (d) |

**Figure 8** SEM images of Fe3O4 NPs at (a) magnification of 50.000x and (b) magnification of 70.000x. (c) EDX image of Fe3O4 NPs. (d) Particle Size Histogram

**Mechanism of Particle Formation**

The proposed mechanism of reaction that occurred during the electrolysis process is shown in reactions 1 to 6. The reaction occurred in the anode and cathode as the voltages were applied. At the beginning of the reaction, the iron anode is oxidized into ferrous iron (reaction 1). Figure 3(a) shows a yellow-brown color of precipitates that appeared, indicating the formation of Fe(OH)2 (reaction 4). The formation of Fe(OH)2 was caused by the presence of OH- ions (8). The ion OH- may come from the reduction of water molecules (H2O) in the cathode, creating hydrogen gas (H2) and OH- ions (reaction 3) [7)]. Another reaction of H2O molecule also occur in anode where H2O is turned into O2 (reaction 5) [22]. The O2 oxidizes Fe(OH)2, resulting in FeOOH, as shown in Figure 3(b) (reaction 6), which is indicated by the appearance of redish-brown precipitate in the solution. The results are Fe2+ and Fe3+, which are present in the solution, and are creating Fe3O4 NPs (reaction 6) [8] .

(1)

(2)

(3)

(4)

(5)

(6)

(7)

The mechanism of Fe3O4 NPs capped with CT extract can be studied based on research by Dauthal (2015), Khwannimit (2020), and Yoga (2023). The studies were conducted to find the effects of plant extract used in the synthesis of PtNPs, AgNPs, and Fe3O4 NPs using the coprecipitation method. The synthesis of NPs involves the flavonoid content found in the plant extracts. This flavonoid compound acts as a reducing agent and capping agent for the NPs. The mechanism involves the -OH group and carboxyl group that are reducing the metal ion via ionic bonds. As the reduction process continued, the new NPs were formed, also known as the nucleation process. During the growth phase, NPs combine to form various morphologies. Subsequently, NPs reach the termination phase, at which point they have a stable form, and the final NPs shape is formed [11,14,16].

A glass beaker filled with dark liquid

Description automatically generated

**Figure 9** CT extracted in aquous solution

# CONCLUSION

Fe3O4 NPs were successfully synthesized through electrochemical method with various voltages applied and employing Clitoria Ternatea extract as the capping agent. The UV-Vis spectra show the constant absorption in visible area of 300-900 nm with a peak at 361 nm. PSA analysis has found the smallest size for Fe3O4 NPs was reaching the Z-Average of 352,8 nm. XRD analysis showed the spinel’s Fe3O4 NPs were successfully synthesized with a crystal size between 13-15 nm. FESEM/EDX analysis found the morphology of Fe3O4 NPs was plate-like shape with average particle size reaching 60,16 nm.

# Acknowledgments

The authors gratefully acknowledge the support of a research grant from the DIKTI with scheme Riset Kolaborasi Indonesia [1672/PKS/ITS/2023].

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