Magnetic Properties of $\text{Fe}_3\text{O}_4@\text{Graphene}$: Preparation from Natural Material

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Abstract. This work presents a study of structure and the magnetic behavior of $\text{Fe}_3\text{O}_4$ nanoparticles produced in the extraction process and Magnetic Nanoparticle of $\text{Fe}_3\text{O}_4$ coated by graphene oxide (GO) from natural materials of coconut shells (graphite). Preparation of the core-shell composite $\text{Fe}_3\text{O}_4@\text{Graphene}$ was carried out with ex-situ process. Superparamagnetic analysis of $\text{Fe}_3\text{O}_4$, and $\text{Fe}_3\text{O}_4@\text{Graphene}$ using VSM (vibrating sample magnetometer), structure analysis using HRPD, TEM and adsorption of dyes solution in the drink water. Obtained results, along with the thickening of the skin (Graphene that encloses the core particles ($\text{Fe}_3\text{O}_4$), the saturation of the magnetization ($M_s$) decreases. And the amount of GO composition affects the coating decorated (shell); $\text{Fe}_3\text{O}_4$/Graphene absorptivity increases when walls are thinner.

Key words: Magnetite, Graphene, Superparamagnetic

1. Introduction

Nanoparticles (NP) currently lead the way in sophisticated developments in the field of nanotechnology. Iron is the most recent transition metal in the earth's crust, iron stands as the backbone of today's infrastructure technology. However, compared to group elements such as cobalt, nickel, gold and platinum, iron oxide is somewhat neglected.

The main compositions of iron oxide possessed by iron sand are magnetite ($\text{Fe}_3\text{O}_4$), hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) and maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$) and silicon oxide ($\text{SiO}_2$) and other compounds which contain lower content [1]. Magnetite ($\text{Fe}_3\text{O}_4$) has a cubic phase, while $\gamma$-$\text{Fe}_2\text{O}_3$ and $\alpha$-$\text{Fe}_2\text{O}_3$ although they have the same chemical composition, the two materials have different phases. $\gamma$-$\text{Fe}_2\text{O}_3$ is cuboidal while $\alpha$-$\text{Fe}_2\text{O}_3$ is hexagonal. Researchers typically use hematite as a base material in the process of ferrite magnet powder synthesis because hematite has a single phase that is believed to have strong magnetic properties when compared to mixed phases [2]. The three phases can be obtained through oxidation at different temperatures. Initially the material is magnetite and when heating reaches 250°C maghemites begin to form and dominate at 350°C. At 450°C the composition of the maghemite phase begins to decrease and the phase transformation becomes maghemite in the form of a tetragonal structure. Whereas hematite starts to appear at a temperature of 550°C in single phase and dominates at a temperature of 700-800°C [3]. Utilization of iron ore in the form of iron oxide is $\gamma$-$\text{Fe}_2\text{O}_3$ has various applications such as recording.
memory devices, magnetic resonance imaging and α-Fe₂O₃ showing high resistance to corrosion applications such as gas sensors, catalysts, lithium ion batteries, pigment. Magnetic Fe₃O₄ nanoparticles and silica nanoparticles in a core-shell structure can be applied as a drug delivery system (DDS) material, and water treatment [4-5].

Graphene is a sheet of carbon atoms as thick as one atom arranged in a honeycomb-like pattern. Graphene is the thinnest, strongest material, has good electrical and thermal properties. Many studies prove: (1) graphene can increase the strength of other materials such as plastic, metal or other materials; (2) graphene has good thermal conductive properties that can be applied to the field of microelectronics (LED lighting is more durable) and thermal foil on cellular devices; (3) graphene has the highest surface area and volume ratio, so it is very prospective to be applied to batteries and supercapacitors, because graphene is capable of storing a lot of energy, faster charging, prospects for efficient solar cell panels, also for superconducting materials, and many again [6].

Composite material of Fe₃O₄@Graphen is currently being studied, in addition to the advantages of its constituent particles, namely magnetite and graphene; this material can be applied to DDS systems and water treatment materials [Munasir, 2019]. The superparamenetic nature of Fe₃O₄ is possible to be controlled, and at the same time can be applied for special purposes. Core-shell formation is a design as well as a fabrication method for controlling the magnetic properties of Fe₃O₄ as a Core, and GO as an outer shell. This study will report the results of the study of the magnetic properties of Fe₃O₄@Graphen, by controlling the composition of its nanoparticles.

2. Materials and Method

2.1. Materials

The materials used for the preparation of Fe₃O₄ nanoparticles are Iron Sand, 12.063 M HCL Solution, 6.5 M NH₄OH Solution, and Aquades. The materials used in the preparation of rGO are the Old Coconut shell, 2 M HCL solution and Aquades. And for the fabrication of Fe₃O₄ @ rGO composites, the main ingredient of Fe₃O₄ nanoparticles and rGO nanoparticles has been prepared through previous synthesis, based on natural materials.

2.2. Preparations and Analysis Method

For the preparation of Fe₃O₄ nanoparticles from iron sand, a co-precipitation method is used, referring to the method used in previous studies. [2-6]. Iron sand is stirred in a HCl solution (37%, PA), to form a dark yellow solution. Then separated with the precipitate, to the filtrate (FeCl₃, FeCl₂) as precursors, add NH₄OH (6M) solution gradually and while stirring, until the solution is black. The equation for the reaction is as follows:

\[
\text{Fe₃O₄(s)} + 8\text{HCl(l)} \rightarrow 2\text{FeCl₃(l)} + \text{FeCl₂(l)} + 4\text{H₂O(l)} \]

\[
\text{filtrate} + 8\text{NH₄OH(l)} \rightarrow \text{Fe₃O₄(s)} + 8\text{NH₄Cl(l)} + 5\text{H₂O(l)}
\]

The final step is washing to remove NH₄Cl, and dried in the oven to obtain Fe₃O₄ in powder form.

Preparation of graphene, done from burning the old coconut shell into charcoal with a temperature of 400°C for 5 hours. Activated carbon from combustion, then mashed up to 200 mesh size (homogeneous). Carbon powder is immersed and stirred in a HCl solution (37%, PA) conditioned at a temperature of around 70°C. The next stage is the ultrasonic cutting process with 500 watts of power for 2 hours [6,7].

Fe₃O₄@Grafen composites were prepared by the wet mixing method [5]. Using polar solvents, namely butanol. The first step to take is to mix all components, namely Fe₃O₄, rGO and Alcohol using a magnetic stirrer hot plate. After going through the stirring process a slurry will form and a drying process will be carried out at room temperature and will produce a powder, Fe₃O₄@Grafen.
characterization and sample analysis using Diffraction patterns collected in the backscattering detectors of HRPD (High Resolution Powder Diffractometer), TEM (Transmission electron microscopy), and VSM (Vibrating sample magnetometer).

3. Result and Discussion

3.1. Structure and Magnetic Properties

The crystalline structure of Fe₃O₄/Graphene was observed as shown in Figure 1, it appears that graphene covers Fe₃O₄ NPs, so that the peaks of the magnetite plane are not visible at a glance, and tend to be amorphous; because graphene structure tends to be amorphous, it is rather difficult to observe by diffraction method.

![Figure 1](image1.png)

**Figure 1.** Diffraction pattern collected in the backscattering detectors of HRPD of Fe₃O₄ Nanoparticle

![Figure 2](image2.png)

**Figure 2.** Magnetic properties of (a) Fe₃O₄, (b) Fe₃O₄@Graphene
From the diffraction peak analysis (Figure 1), the Fe$_3$O$_4$ structure is cubic, the spinel family structure, classification by properties ferrimagnet, ferromagnetic, half metal, intermediate valence, and ionic conduction; the name of the mineral is magnetite; with crystal fields: (220), (311), (440), (422), (511), (440), (620), (533). The results obtained from the XRD data matching the results of experiments with reference data (PDF- 01-088-0866) [2,5,8].

Figure 3. Magnetic behavior of Fe$_3$O$_4$@Graphene

Shown in Figure 2 of M-H hysteresis curves of samples of Fe$_3$O$_4$ and Fe$_3$O$_4$/Graphene nanoparticles; The magnetic behavior reveals that the modification can decrease the saturation magnetization of Fe$_3$O$_4$ MNPs due to the surface effect, by coating Graphene as a wrapper on the surface of Fe$_3$O$_4$ (as core). There was a decrease in magnetization of $\Delta M$ around 5 emu/g for 1: 1 composition for Fe$_3$O$_4$and graphene. It can be seen in Figure 3, the absorption of Fe$_3$O$_4$/Graphene to the Methylene-Blue dyes dissolved in water, and is attracted by a magnetic bar. This shows that magnetic behavior is still quite strong. When observing the width of the hysterical curve of each sample (Figure 2), it appears that the two are superparamagnetic, the area of the curve is very narrow [3-4,9]. Superparamagnetic properties of Fe$_3$O$_4$ with a maximum magnetization value of about 20 emu/g when applied to the external magnetic field a maximum of 23,500 oersted; and magnetization when the external magnetic field is removed, there are still around 3-5 emu/g.

This phenomenon can be attributed to the effect of small particle size because the non-collinear rotation arrangement occurs mainly at or near the surface, which results in a reduction in the magnetic moment of Fe$_3$O$_4$ NPs.

3.2. Morphology

The morphologies of Fe$_3$O$_4$/Graphene were observed as shown in Figure 4, the test results using SEM; with a magnification scale of 100 nm, then by taking one spot, then enlarged it appears that the particle shape tends to be spherical with a particle size of Fe$_3$O$_4$ NPs $\sim$ 5-16 nm (see Figure 4, below). And it can be shown that graphene particles cover the surface of Fe$_3$O$_4$, a very thin coating.
3.3. Discussion

From previous research, studies on Superparamagnetic Iron Oxide Nanoparticles (SPIONs) of Fe$_3$O$_4$, the results of synthesis with variations in temperature and types of chemical solvents NH$_4$OH, obtained particle size of Fe$_3$O$_4$ varies with larger sizes. Then each particle was coated with PEG, the results of the measurement of vibrating sample magnetometer showed that the smaller the grain size (diameter) of Fe$_3$O$_4$ nanoparticles, the higher the magnetic response, and the coercivity also decreased. Magnetic behavior Magnetite is naturally built by its crystalline structure in the form of an inverse spinel cubic and has the general formula Fe$^{3+}$ (A) [Fe$^{2+}$ Fe$^{3+}$] (B) O$_4$. Side A is the tetrahedral side occupied by Fe$^{3+}$

![Image of Fe$_3$O$_4$ particles](image)

**Figure 4.** Morphology of Fe$_3$O$_4$@Graphen
ions and surrounded by four oxygen atoms (O), while B is the octahedral side occupied by Fe$^{2+}$/Fe$^{3+}$ ions surrounded by six O atoms [3,9].

The superparamagnetic of Fe$_3$O$_4$ and Fe$_3$O$_4$/graphene, thus the argument is strengthened, both of the crystal structures of Fe$_3$O$_4$ are magnetite, and the majority of particle sizes are very small (5-16 nm), particles tend to form agglomeration formations [6].

4. Conclusion
Magnetic nanoparticles (MNPs) Fe$_3$O$_4$ and Fe$_3$O$_4$/Graphene have been fabricated from iron sand and coconut shell materials; MNPs Fe$_3$O$_4$ as nuclei have particle sizes below 20 nm (~5-16 nm), and are superparamagnetic. The presence of graphene acts as an MNPs shell covering Fe$_3$O$_4$, has a very thin thickness, also plays a role in controlling the magnetic behavior of Fe$_3$O$_4$.

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