The Structural and Morphology Properties of Fe$_3$O$_4$/Ppy Nanocomposite

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Abstract. Fe$_3$O$_4$ nanoparticles based on natural iron sand from Buaya river in DeliSer dang had been synthesized by co-precipitation and ultrasonic method. The HCl and NH$_3$ were used as solvent and precipitation agent, respectively. The Fe$_3$O$_4$/Ppy nanocomposite was synthesized at a low temperature of 70$^\circ$C with 10gPpy. The structural and morphology of the Fe$_3$O$_4$/Ppy were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FT-IR), and Thermo Gravimetric Analysis (TGA). XRD analysis confirmed that the crystal structure of the sample was cubic spinel with lattice parameter $a=8.3656$ Å and the highest $d_{hkl}$ field at the millier index (311). This indicated the reduction in agglomeration of the sample. The results of FTIR analysis showed that PPy was successfully well correlated with Fe$_3$O$_4$ nanocomposites. TGA analysis showed a mass reduction of about 20% at 800$^\circ$C this is due to the interaction between Fe$_3$O$_4$/Ppy and the addition of polymer PEG 6000.

Keywords: Nanoparticles, Fe$_3$O$_4$, PPy, Morphology

1. Introduction

Synthesis and characterization of nanomaterials have been intensively carried out by researchers. Fe$_3$O$_4$ nanoparticles attracted the attention of people due to its excellent properties such as magnetism, optical and catalytic properties. It has been widely used in various applications such as Drug Delivery System (DDS) [1], Magnetic Resonance Imaging (MRI) [2], a heavy metal separator for water purification [3] and Hyperthermia Therapy System [4]. Magnetic nanoparticles have been widely studied because they have unique properties in nano-size for environmental processing. Among of them are superparamagnetic iron oxide nanoparticles, referred to as Fe$_3$O$_4$ nanoparticles [5]. Fe$_3$O$_4$ nanoparticles have unique properties including magnetic properties, large surface area, and low toxicity. Natural iron sand is a natural resource that has iron oxide compounds [6]. The process of natural sand to nanometers in size can be done by several methods such as hydrothermal, ultrasonic, and co-precipitation[7]. Materials in nanometer size have a very large surface area. This characteristic is the advantage of Fe$_3$O$_4$ nanoparticles which have a lot of applications in various fields such as Li-ion batteries, microwave absorption, magnetically separable photocatalysts, absorption and separable, biosensors, and heavy metal absorption [8, 9]. Unfortunately, Fe$_3$O$_4$ nanoparticles have agglomeration problems, because Fe$_3$O$_4$ nanoparticles are susceptible to oxidation. Agglomeration prevention has been carried out using polymeric materials such as PEG 6000 and PPy [9]. PEG 6000 has been used as a template in synthesis nanoparticles to control particle size, surface modification and to control interactions between particles [10]. Recently, conductive polymers have been developed as electronic device components. Polypyrrole (PPy) as a conductive polymer has been widely studied and attracted
the attention of researchers. The reasons are because polypyrrole has good redox properties, easy to
electro synthesis in aqueous solutions and high conductivity [11, 12], non-toxic and good stability.
The low cost and facile of preparation are advantageous in some applications [13, 14]. In addition,
there is the fact that the pyrrole monomer is easily oxidized and soluble in water. We choose this
conductive polymer due to it is naturally easy decomposed compared to inorganic materials such as Li,
Ni and Ni-Cd [15]. With these properties, magnetite Fe₃O₄ nanoparticles are composited with
polypyrrole to achieve excellent absorption. PPy / Fe₃O₄ nanocomposites were used as adsorbents and
effectively reduced the levels of Cr (VI) heavy metals carried out by Ansari in 2010 [16]. In this
paper, the authors discuss the synthesis of Fe₃O₄ nanoparticles from the natural iron sand with the
effect of adding the Ppy by an ultrasonic method.

2. Methodology
2.1. Materials
In this study, iron oxide (Fe₃O₄) was naturally obtained after purification treatment of black natural iron
sand from Buaya river, Deli Serdang. The purification was done using a pull of the permanent magnet.
HCl (Merck 37%) was used as a molarity (12 M), NH₃ (Merck 37%) is used as a precipitator with
molarity (6.5 M), PPy polymer (Aldrich) and PEG 6000 (Merck) were used as templates to reduce
agglomeration and as a binder.

2.2. Instrumentation
Structural analysis was performed using X-ray diffractometer (XRD Shimadzu) with the light source
Cu-Kα with a wavelength of 1.54000 Å and scan rate of 2.0000 deg/min. Infrared absorption analysis
was performed using Fourier Transform Infrared (FT-IR) Alpha Platinum ATR A220 / D-01 with range
wave number of 500-4000 cm⁻¹. Thermal analysis with TGAQ500 from TA Instrument.
Morphology and particle size were observed by Field Emission Scanning Electron Microscope (FE-SEM JSM 6500F).

2.3. Synthesis of Fe₃O₄/PPy nanocomposite
Fe₃O₄ was coupled with PEG 6000 by using co-precipitation method. Then, Fe₃O₄ nanoparticles were
composited with 10.0 g PPy and addition of 66 g FeCl₃. The temperature process was kept at 0-5°C to
assist the polymerization process by ultrasonic method.

3. Results and Discussion
3.1. XRD Analysis
The synthesized nanoparticles from natural iron sand from Buaya river in Deliserdang, the structures
characterization by using XRD are shown in Fig.1 bellow:

Figure 1. XRD pattern of Fe₃O₄, Fe₃O₄ / PEG, and Fe₃O₄ / PEG / PPy 10 g.

Figure 1 shows XRD pattern of Fe₃O₄, Fe₃O₄ / PEG, and Fe₃O₄ / PEG / PPy 10 g. It can be seen
that intensity of Fe₃O₄ increases after synthesis and formation of composite with PPy. The XRD
pattern of Fe₃O₄ and Fe₃O₄/PEG confirm their single phase of Fe₃O₄ (magnetite). Those peaks with index (202), (311), (400), (422), (511) and (440) are the typical index of Fe₃O₄ cubic spinel structure which always appears in the XRD diffractogram of Fe₃O₄ material [9], [17, 18]. The XRD result of Fe₃O₄ / PEG / PPy show that at 2θ = 20-30° there is another diffraction peak of Ppy with Miller index (220) [19]. The XRD results show that peak intensity increases with the addition of Ppy and it indicates that the addition of polymer to the sample do not affect the crystal structure of Fe₃O₄ nanoparticles. The average particles size are estimated using Scherrer equation.

\[ D = \frac{k \cdot \lambda}{\beta \cos \theta} \]

Where \( d \) is crystalline size, \( k \) is a Scherrer constant, \( \lambda \) is the wavelength of the x-ray and \( B \) is full width at half maximum (FWHM). The calculated particle size of Fe₃O₄/PEG/Ppy nanocomposite at \( 2\theta = 35, 57\ ) (311) is 27.24 nm.

3.2. SEM Analysis

The information obtained from SEM are surface morphology of sample and particle size. We also can obtain information of particle distribution with helping of ImageJ software. Figure 2 shows the SEM image of Fe₃O₄/PPy 10 gr with magnification of 30,000 X.

![SEM Image](image)

Figure 2. The result of SEM morphology Fe₃O₄ / PEG / PPy 10 g.

The results of the analysis using SEM show a variety of particle size patterns. From the figure 2 can be seen nanoparticles tend to be roughly round. Each test sample using SEM will produce the output in the form of composition and morphology of the material. In the synthesis of Fe₃O₄ which is comosited with PPy using the ultrasonic method, the particle size has reached the nanometer (nm) in size. The particles that have formed tend to form bonds with other particles which often called as agglomeration. This is because the iron sand has magnetic properties and electrical properties which in each particle will tend to pull each other and form lumps like particles. The analysis results show that particle size diameter of Fe₃O₄/PPy is about 38.6-40 nm.

3.3. FT-IR Analysis

FTIR results give the information of Transmittance and wave numbers in the form of peak to find out the functional group. FTIR result of Fe₃O₄ material after forming composite with PPy is shown in Figure 3 below:
The results above show that PEG 6000 and PPy have interacted with Fe3O4 that marked by the appearance of new peaks or deeper and sharper of peaks. The peak at 550-600 cm⁻¹ is the peak absorption of Ppy spectrum [20] with Stretching and Bending vibration. The peak at 401 and 570 cm⁻¹ is the absorption peak of the Fe-O group. Another peak at 1627.9 and 3402.43 cm⁻¹ show the O-H bond which is a vibration of Stretching and Bending. Those peak show a decrease in the sharpness of the absorption peak, which indicates that PPy has been successfully composited with Fe3O4 nanoparticles. The peak at 1072.2 cm⁻¹ shows the C-O-C absorption function of stretching vibrations shifting when PPy is added due to changes in energy and the interaction between PPy and Fe3O4 [5].

3.4. TGA Analysis

Analysis of thermal properties and weight loss of Fe3O4 / PEG 6000 after being composited with the addition of 10 g PPy by using ultrasonic method was characterized and analyzed using TGAQ500 from TA Instrument. The results is shown in Figure 4.

TGA is used to find out the thermal properties of the material and the point of weight loss. Figure 4 shows a low mass loss at a temperature (30-180 °C) caused by removing water molecules. While for Fe3O4 / Ppy 10 g composites decomposes at 220-270 °C. The final mass reduction is around 20% at 800°C, this is due to the interaction between Fe3O4 / Ppy and the addition of polymer PEG 6000. It
can be explained that the changes of total mass of nanocomposite are affected by thermal treatment [22]

4. Conclusions
Iron oxide (Fe3O4) nanoparticles had been successfully combined with PPy to achieve excellent absorption. The XRD measurement result confirmed that the structure of cubic spinel crystal and parameter a=8.3656 Å with the highest dhkl miller index (311). The nanocomposite Fe3O4/PPy tends to form rough spherical in the shape and distribution particles around 38.6 nm, the wave number of innate pure Ppy spetrum absorption is at wave number 550-600 cm⁻¹. The thermal properties of Fe3O4/PEG/PPy nanocomposites show the low mass loss at temperatures (30-180 °C) and decompose at 220-270 °C with a mass reduction of about 20% at 800 °C this is due to the interaction between Fe3O4/PPy and the addition of polymer PEG 6000.

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