Effect of Single-Walled Carbon Nanotubes (SWCNTs) on Structural and Morphology Properties of Fe$_3$O$_4$ Nanoparticle

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Abstract. Synthesis and characterization of Fe$_3$O$_4$/Ppy / CNTs nanocomposite magnetic materials have been prepared. Iron sand obtained from the Buaya river was processed using Planetary Ball Mill for 16 hours and sifted 200 mesh and synthesized with the coprecipitation method by using acids and bases reaction to obtain magnetic nanoparticles (Fe$_3$O$_4$). Fe$_3$O$_4$ particles were synthesized with 10 gr of Polypyrrole and 1.0 gr of Carbon nanotubes (CNTs) on nanocomposites. Structure and morphology of the prepared nanocomposite were characterized by X-ray diffraction (XRD) where the highest d$_{hkl}$ field is on the millier index (311) with 2$\theta$ is 35.50 and the crystal system is cubic. Functional group sited of each nanocomposite material was detected by Fourier transform infrared (FTIR). Thermo-gravimetric analysis (TGA) was used to characterize the iron oxide content in the as-obtained composites. SEM was used to characterize the morphology of the nanocomposite.

Keyword : Nanocomposite, Carbon nanotubes, Fe$_3$O$_4$

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention since they were first discovered in 1991, due to their unique structural, electrical, thermal, gas and mechanical absorption properties[1-4]. To improve the function and ability of a nanomaterial, CNTS is supported by other materials or modified to expand its application in the field of technology such as magnetism and electricity from CNTs[2, 3, 5]. Among the many CNTs-based nanocomposites, magnetic CNT composites attract more attention because of their potential in magnetic data storage, xerography, biosensors, wastewater treatment[5]. In the latest research, CNTs have been widely composited with magnetite Fe$_3$O$_4$[1, 3, 5-7], polypyrrole[8], magnetite Fe$_3$O$_4$ / Ag[9], magnetite Fe$_3$O$_4$ / polypyrrole[10, 11].

Nanoscale materials have unique advantages, especially in their chemical and physical properties, size, surface structure, good interaction between particles and broad application potential[12]. Among the many nanomaterials, Fe$_3$O$_4$ nanoparticles are more widely used in research. Fe$_3$O$_4$ nanoparticles which have super magnetic and ferromagnetic properties are more developed because they are widely
applied in various fields such as photonic crystals, magnetic recording media, magnetoresistive sensors, heavy metal absorption and others[13].

In the process of synthesizing Fe$_3$O$_4$ nanoparticles, the agglomeration may appear that can cause unevenly particles. Agglomeration can be prevented by adding polymers, such as PEG and PPy. PEG is widely used because of non-toxic nature, easily soluble in water[14] and good thermal ability[15]. In this paper, Fe$_3$O$_4$ will be coated with PEG 6000 because PEG can be used to control the size of crystalline size of particles to be smaller and not react to Fe$_3$O$_4$ and act as a template[16]. The use of polymers in nanoparticles can improve absorption, particle size control and the interaction between particles[17]. In polymer materials, Ppy is more widely used because of its properties, namely good environmental stability[18, 19], high conductivity[18], potentially used as an excellent ion exchange material that selectively removes ions from the water so that the environment becomes stable[20]. The presence of a conductive polymer layer on the surface of the Fe$_3$O$_4$ nanoparticles greatly influences the complex permittivity and thus can control absorption efficiency[11]. In previous studies, Magnetic Fe$_3$O$_4$ with Ppy was composited and has been used to adsorb toxic metals Cr[20, 21]. Besides Magnetic nanoparticles (Fe$_3$O$_4$), nanotubes are also attractive candidates for the absorption of metal compounds because of their large surface area. Its large surface area makes it a promising adsorbent[10] with remarkable stabilization[1]. The previous study that composites Fe$_3$O$_4$ with nanotubes has worked out to test their adsorption properties[3, 11] and were applied to adsorb mercury from coal-derived fuel gas[22], acid pollutant extraction[10], removing contaminant materials such as phthalic ester acid (PAEs) in carbonated soft drinks[9]. Nanocomposites CNTs / Ppy without Fe$_3$O$_4$ were also successfully carried out which were applied as supercapacitors[8] and with Fe$_3$O$_4$ which was applied as an adsorbent[10].

In this paper, Fe$_3$O$_4$ nanocomposites are made. They have been coated with PEG with polypyrrole and also carbon nanotubes which are expected to increase the structural and morphology properties and absorption.

2. Experimental

2.1. Materials

Iron sand was taken from the Buaya River in Deli Serdang which was separated from the impurities with a magnet. Chemicals such as 12M HCl, 13.7 M NH$_3$, PEG 6000 are supplied from Merck. Polypyrrole polymers are supplied from Sigma Aldrich. Carbon nanotubes (CNTs) with a diameter ± 25 nm.

2.2. Instrumentation

Structural analysis was carried out by XRD Shimadzu type with a Cu-Kα wavelength of 1.540600Å with a scan speed of 2.0000 deg/min. Infrared absorption analysis with Fourier transform infrared (FT-IR) Alpha Platinum ATR A220 / D-01 with the wave number is in the range 4000-450 cm$^{-1}$. Thermal analysis with TGAQ500 from TA Instrument with a maximum temperature of 800$^\circ$C. Morphological analysis use emission scanning electron microscope field (JSM 6500F FE-SEM).

2.3. Synthesis of Nanocomposite Fe$_3$O$_4$/Ppy/CNTs

Natural pure iron sand was mashed with the ball mill method then sieved with a 200 Mesh sieve to obtain an iron sand powder. Iron sand was synthesized by coprecipitation method to obtain Fe$_3$O$_4$ nanoparticles. In the nanoparticle synthesis process, PEG 6000 is used as a template to control particle size. The obtained Fe$_3$O$_4$ nanoparticles from the coprecipitation method were synthesized with Ppy (Polypyrrole) and FeCl$_3$, with the polymerization process before being composited with Carbon nanotubes by ultrasonic method.
3. Results and Discussion

3.1 XRD Analysis
In the process of nanocomposite synthesis, Fe3O4 is needed as much as 5 grams, Ppy as much as 10 grams, CNTs as much as 1 gram and FeCl3 as much as 66 grams which are useful to help the polymerization process. The results of XRD characterization of nanocomposite Fe3O4/Ppy/CNTs can be seen in Figure 1.

![Figure 1. XRD graphs from a nanocomposite sample](image)

From Figure 1 can be seen that the main peak is found in the index (311) with an estimated angle of 35.55° and with the Fe3O4 phase. In addition, it is reinforced by the appearance of other peaks with the Miller index (111), (202), (400), (422), (333), (404). The emergence of a new peak in XRD nanocomposite diffraction with a miller index (002) with an estimated angle of 26.22° refers to the appearance of carbon nanotubes in nanocomposite samples[9, 23]. The crystalline structure for the nanocomposites is cubic with a crystalline particle size were 15.4 nm.

3.2 FTIR Analysis
To find out the functional groups of Fe3O4 material which have been composited with Ppy and CNTs, FTIR test is performed as shown in Figure 2.

![Figure 2. FTIR spectrum of nanocomposites Fe3O4/Ppy/CNTs](image)

In the FTIR test Figure 2, show that there are various absorption peaks from the test sample. The peaks show the sample absorption groups indicating the characters of the molecular vibrations of the sample. From the FTIR test results show that there is a Fe-O absorption group with a wave number of 532.25 cm⁻¹ representing a characteristic absorption group of Fe3O4. For wavenumbers 790 cm⁻¹ shows the characteristic absorption groups of Ppy[24]. The C-O-C bond at a peak of 1071.58 cm⁻¹ which is a functional group of PEG 6000, indicating that PEG has completely coated Fe3O4 nanoparticles[25].

In absorption groups, 3404.44 cm⁻¹ and 1627.90 cm⁻¹ show the O-H bond representing the bond of water in nanocomposites. At peak absorption of 1580 cm⁻¹ reveals the characteristic peak of
CNTs[1]. The results of this FTIR show that Fe₃O₄ / Ppy / CNTs nanocomposites have been well composted indicating by the appearance of each absorption group from each material used.

3.3 TGA Analysis
TGA was used to characterize the iron oxide content in the as-obtained composites. TGA curve of nanocomposites shows in figure 3.

![Figure 3. TGA curves of nanocomposite Fe₃O₄/Ppy/CNTs](image)

From the TGA characterization can be shown that nanocomposite samples begin to change weight at low temperatures in the range 30°C-165°C. At this temperature, the sample experiences a mass loss of about 4.1% which indicates the loss of water bonds in nanocomposites. Nanocomposite experienced significant mass weight loss in the temperature range of 520°C-680°C at 15.5%. There is a significant loss of mass weight due to the oxidation of the carbon nanotubes in the nanocomposite [26].

3.4 SEM Analysis
SEM characterization show the particle size and particle distribution with the help of ImageJ software as shown in Figure 4. Figure 4 describes the shape of particle are not completely rounded, there are already formed cylindrical particles which indicate that the nanotubes cover magnetite. The size of particle in Figure 4 was 20 nm.

![Figure 4. SEM image of nanocomposite Fe₃O₄/Ppy/CNTs](image)
4. Conclusion
The nanocomposites $\text{Fe}_3\text{O}_4/\text{Ppy}/\text{CNTs}$ have been successfully synthesized. The presence of CNTs was confirmed via XRD, FTIR, TGA, and SEM analyses. The crystalline size of $\text{Fe}_3\text{O}_4/\text{Ppy}/\text{CNTs}$ nanocomposite particles was 15.4 nm and the CNTs in the nanocomposites give a new peak. The FTIR results show that $\text{Fe}_3\text{O}_4/\text{Ppy}/\text{CNTs}$ nanocomposites have been composited well, this is figure out with the emergence of each absorption group from each material used. Accordingly, Carbon nanotubes have affected the morphology of nanocomposites.

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