Preparation and Characterization of Magnetite Nanoparticles Combined with Polyaniline and Activated Carbon

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Abstract. In this paper, we report the preparation of magnetite nanoparticles combined with polyaniline and activated carbon. The results of the X-Ray diffraction data analysis showed that the samples had a magnetite crystal phase without other phases. The existence of polyaniline and activated carbon was confirmed using Fourier transform infrared spectroscopy characterization shown by the presence of S=O, C-N, and C-C. The sample of synthesis results in this work had the band gap of 3.23 eV. Moreover, the results of data analysis using vector network analyzer revealed the maximum reflection loss value of -14 with the absorbance of 50%. Thereby, the synthesis optimization needs to be done to increase the sample absorbance to the radar wave.

Keywords: Magnetite, nanoparticle, polyaniline, activated carbon, radar absorbing material.

1. Introduction
Magnetite nanoparticles, nowadays, become one of the materials highly studied by many researchers, especially for the application as a radar absorbing material (RAM). In general, magnetite nanoparticles have some high properties regarding permeability [1], flexibility [2], and magnetization. Due to such characteristics, magnetite can be used for RAM that can be functioned to enhance the defense of a country [3,4]. However, to make the application performance maximum, the magnetite should be core-shelled or composited with the other materials [4]. This case is significant since magnetite has a high-density property, while maximum RAM application needs a material with low-density [5].

Commonly, radar consists of dielectric and magnetic components which are perpendicular to each other [6]. Therefore, to make RAM, a high dielectric loss and magnetic loss materials are necessary. Besides, the material that will be applied as RAM should have a wide bandwidth [7]. In the defense field, RAM works by reducing radar cross-section of a particular defense like combat ships, fighter planes [8], and the other war needs [9]. Thereby, the number of radar wave reflection will reduce or diminish that will make the enemy difficult in detecting such war tools [6,10].
One of the dielectric materials that have good performance to be RAM is polyaniline. In more detail, this material has controllable dielectric property, good environmental stability [11], high conductivity, and low density [12]. Therefore, polyaniline can function as a material that results in a good dielectric loss. Regarding this case, the previous research showed that magnetite/polyaniline nanocomposites could yield the reflection loss value of -6.5 dB [13]. However, such performance should be increased to make the reflection loss value better. One of the ways is by combining the magnetite nanocomposites with the other materials having great absorbance in the form of nanocomposites. In this research, we propose an addition of activated carbon material having good absorbance to enhance the reflection loss of the magnetite combined with polyaniline. Besides, the primary material used to synthesize the magnetite in magnetite nanocomposites combined with polyaniline and activated carbon is Indonesian iron sand to reduce the cost of material production.

2. Methods
Magnetite was synthesized using the coprecipitation method with the same steps as our previous works [14,15]. The activated carbon was entered to iron sand and HCl solution and titrated using NH₄OH continued by washing and drying processes to obtain a sample in the form of powder. The powder as the synthesis result was then composited with polyaniline powder through dissolution reaction with distilled water stirred using magnetic stirrer. The sample was then heated to obtain a composite powder of magnetite combined with polyaniline and activated carbon. In characterizing the sample, X-ray diffractometer was used to study the phase, particle size, and lattice parameter. Scanning electron microscopy was employed to investigate the morphology of the sample. Fourier transform infrared spectrometer was utilized to identify the functional group of the sample. UV-Vis characterization was conducted to determine the optical properties of the sample. Meanwhile, by using a vector network analyzer, we could know the reflection loss value and the absorbance of the sample to the radar wave.

3. Results and Discussion
The X-ray diffraction (XRD) pattern of the magnetite composite combined with polyaniline and activated carbon is shown in Figure 1. The phase purity was then analyzed by matching the XRD data with ICSD-30860 data which resulted in some main peaks in 2θ = 30.1°, 35.5°, 43.2°, 47.3°, 53.6°, 57.1°, and 62.7° with the Bragg plane namely (0 0 2), (1 1 3), (0 0 4), (1 3 3), (2 2 4), (1 1 5), and (0 4 4). Based on Figure 1, the peaks confirm that there is a Fe₃O₄ phase with the inverse cubic spinel structure [11]. The results of refinement using the Rietveld method yield the lattice parameter value of a = b = c = 8.374 Å with the particle size of 20 nm. The peak of polyaniline and activated carbon in the diffraction pattern of magnetite composites combined with polyaniline and activated carbon does not appear since both materials tended to have amorphous phases.

The highest diffraction peak of the composite was detected on 2θ = 35.5° on the hkl plane (1 1 3). The particle size of magnetite was also found using Scherer equation shown by Equation 1.

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

where \( K \) is constant with the value of 0.94, \( \lambda \) is the wavelength 1.5443 Å, \( \beta \) is broadening in the half-maximum intensity (FWHM), and \( \theta \) is the Bragg angle of the highest peak [16]. The \( \beta \) value was obtained by fitting the highest peak using the Lorentzian model, and the fitting result is presented in Figure 2.
Figure 1. XRD pattern of magnetite composites combined with polyaniline and activated carbon

Figure 2. FWHM fitting for magnetite composites combined with polyaniline and activated carbon

The fitting result showed the $\beta$ value of 0.448 radians so that based on the calculation result using Equation 1, the particle size of Fe$_3$O$_4$ was 19 nm. Such amount was not far different from particle size obtained using the Rietveld method. Subsequently, to confirm the particle size distribution of magnetite composites combined with polyaniline and activated carbon, we also characterized the sample using scanning electron microscopy (SEM) as shown in Figure 3. Qualitatively, it can be seen that in Figure 3 (a), there are spherical and irregular shaped particles. Such form described magnetite nanoparticles activated carbon [17,18], and polyaniline [19].

The particles size distribution of magnetite composites combined with polyaniline and activated carbon resulted in the average value of 22 nm. Such amount approached the particle size result based on X-ray diffraction data analysis. The difference in particle size between SEM and XRD results gained using Rietveld, and Lorentzian methods were because SEM only did scanning on the sample surface so that the diameter caught was just based on the particle in the sample surface. Another research reported the forming of magnetite combined with polyaniline had the particle size of 60 nm [11], and the forming of magnetite/activated carbon had the particle size of 30-80 nm [17].
Figure 3. (a) SEM image and (b) the distribution of particle size of magnetite composites combined with polyaniline and activated carbon

Fourier transform infrared (FTIR) spectrum of the magnetite combined with polyaniline and activated carbon is shown in Figure 4. The functional groups of Fe-O were detected on the wavelength of 417 and 589 cm$^{-1}$ that indicated the octahedral and tetrahedral vibration of magnetite, respectively. Based on the previous works, the vibration of Fe-O was also detected on the wavelength of about 417 [20], 580-590 [21], and 590 cm$^{-1}$ [22]. Both vibrations of Fe-O in the nanocomposites as the synthesis results in this research were confirmed by the X-ray diffraction pattern showing that the structure of magnetite is cubic inverse spinel.

Figure 4. FTIR spectrum of magnetite composites combined with polyaniline and activated carbon

In general, the existence of polyaniline in the sample was detected by the presence of vibration in the wavelength of 1040 cm$^{-1}$ showing the stretching band S=O or sulfonate and C-H as out of plane bending detected on the wavelength of 823 and 1147 cm$^{-1}$. Such thing was also confirmed by some previous works revealing S=O bond on the wavelength of 1040 [23] and 1040 cm$^{-1}$ [24]. Meanwhile, the functional group of out of plane blending C-H was detected on the wavelength of 866-899 [25].
Moreover, the functional group of C-N from benzoid ring was detected on the wavelength of 1496 cm$^{-1}$. Theoretically, such bonds are the unique properties of polyaniline material in the form of emeraldine salt. Finally, the existence of activated carbon in the sample was indicated by the presence of stretching C-C functional group on the wavelength of 1309 cm$^{-1}$ with a relatively high peak.

In this research, some vibrations were also detected like O-H on the wavelength of 1577 cm$^{-1}$ from the carbolic acid structure and 3298 cm$^{-1}$ from the air. Such thing was also confirmed by some previous researches showing the presence of O-H bond on the wavelength of 1578 [27] and 3200-3600 cm$^{-1}$ [28]. Furthermore, the C=O bond in the area of 2299 cm$^{-1}$ showed the forming of CO$_2$. This result was also in line with the study conducted by the previous researcher reporting the existence of C=O in the same area [29].

Optical properties of magnetite nanocomposites combined with polyaniline and activated carbon were determined based on the value of band gap energy as the result of UV-Vis characterization. Mathematically, the value of band gap was determined using the Kubelka Munk Equation written in Equation 2.

\[
\left( \frac{ \alpha h \nu }{ A( h \nu - E_g ) } \right)^2 = \frac{2}{h} A \nu \sin^2 \theta
\]

where $E_g$ is the band gap energy, $A$ shows an effective mass of the electron, $h$ is Planck constant with the value of 6.55×10$^{-34}$ Js, $\alpha$ is absorbance coefficient, and $\nu$ shows frequency [30]. To determine the value of band gap energy was carried out by fitting analysis using Tauc Plot method of the pattern of the relationship between $(\alpha h \nu)^2$ and $h \nu$; where the value of $h \nu$ as the $x$-axis and the value of $(\alpha h \nu)^2$ as the $y$-axis. Such analysis result is presented in Figure 5.

Figure 5. Band gap energy of magnetite composite combined with polyaniline and activated carbon

Based on Figure 5, the band gap energy of the sample as the synthesis result in this research was 3.23 eV. If this result was compared to the pure magnetite nanoparticles, it would be a little bit higher. Based on the previous study, the value of the band gap energy of magnetite nanoparticles was 2.3 eV [30]. The dissimilarity of this difference is believed as a contribution to the presence of activated carbon and polyaniline that unites in the sample as a nanocomposite. Theoretically, two or more materials combined in the form of composite results in absorbance shift to a different wavelength of each composer.
Figure 6. The reflection loss of magnetite composite combined with polyaniline and activated carbon

To investigate the absorption of the sample to the radar wave was undertaken using vector network analyzer at room temperature and the result is shown in Figure 6. The reflection loss value was obtained based on the calculation using Equation 3.

\[ RL = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \]  

(3)

where \( RL \) is the reflection loss (dB), \( Z_{in} \) is the input impedance, and \( Z_0 \) is the characteristic impedance of free space [31]. The results of sample characterization showed the relationship between the reflection loss and frequency. The calculation result showed the reflection loss value of the sample was -14 dB. The calculation resulted in absorbance of the material to the radar wave of 50%. The negative reflection loss indicated the absorbance to the radar wave by the sample [16]. Conceptually, the lower the reflection loss value, the radar wave absorbed is getting higher indicating that the material has a good absorbance. In order to be applied for advanced RAM, the sample resulted in this work needs to be developed to obtain excellent performance.

4. Conclusion
Magnetite nanoparticles combined with polyaniline and activated carbon as a nanocomposite has been successfully synthesized using the precipitation method. The results of the analysis of X-ray diffraction data showed that the sample had a magnetite material crystal phase. Meanwhile, polyaniline and activated carbon were identified by characterizing the functional groups of S=O, C-N, and C-C. The value of the band gap energy of the nanocomposite was 3.23 eV. Furthermore, the absorbance of the composite to the radar wave was of 50% with the reflection loss of -14 dB. Thereby, this material has a significant opportunity to be developed further as an antiradar material.

Acknowledgments
This work was financially supported by the research grant from KEMENRISTEKDIKTI RI for AT.

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