Synthesis of Magnetic Iron Oxide Nanoparticle from Logas Natural Sand and Its Application for the Catalytic Degradation of Methylene Blue

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Abstract. Structural properties, morphology, and the catalytic activity of hematite (α-Fe2O3) nanoparticles for degradation of methylene blue have been studied. For this purpose, the hematite particles were synthesised from Logas natural sand by 2 steps ball milling method. X-ray diffraction (XRD) confirmed the presence of a hematite (α-Fe2O3) phase. However, other phases such as SiO2 and FeTiO3 are also confirmed by XRD. Scanning electron microscopy (SEM) showed a wide distribution of particle sizes. Moreover, the shape of the grains is irregular form. The effect of reaction time and hematite nanoparticles dosage which affect the efficiency of catalytic reaction was investigated. Catalytic activity of hematite nanoparticles in the degradation of methylene blue (MB) was studied through ultraviolet visible spectroscopy (UV-Vis).

1. Introduction
Magnetic iron oxide particles such as hematite (α-Fe2O3), maghemite (γ-Fe2O3) and magnetite (Fe3O4) with controllable size and structure have attracted wide attention during the past few decades due to their catalytic and magnetic properties [1]. Among these oxides, hematite nanoparticles have broad applications including catalytic purposes [2], magnetic data storage [3], magnetic sensor [4], inks for photocopy machines [5], magnetic resonance imaging [6], and drug delivery target [7]. Magnetic iron oxide nanoparticles can be obtained by a variety of methods, including hydrothermal reaction [8], microwave [9], sol–gel method [10], micro emulsion method [11], forced hydrolysis [12], and physical methods [13,14]. In physical methods, one of well-known methods is ball milling [14-16]. The main advantage of this method is simple, efficient, high yield and low cost compared to other methods. Previous researchers [17,18] have used ball milling method to produce magnetic iron oxide nanoparticles. Controlling the particle size and morphology of as synthesized particles is very important, since their properties depend on the morphology and particle size [19]. Nowadays, researchers have focused on the investigation of the factors influencing the particle shape and size of the synthesized magnetic iron oxide nanoparticles. For example, previous researchers [20, 21] found that magnetic properties, phase and morphology of the obtained particles are depended on time, speed and types of milled balls.

Methylene blue is one of the dyes used in dyeing and painting textiles [22] and the release of this dye into the body of water or rivers can generate carcinogenic effects that may be harmful against human health and environment [23,24]. Therefore, removing the dyes from wastewater without
secondary pollution is very important for the safety environment. However, removal dyes from wastewater is very difficult process, since its chemical structure is stable and hard-degradation [23]. Various techniques have been developed to improve the efficiency to remove methylene blue from waste water, including adsorption [26], coagulation [27], and others [28]. However, advanced oxidation processes are promising technologies which aim at the decolourization and mineralization of a wide range of dyes and transform dyes into biodegradable or harmless products [29]. It is well known that advanced oxidation processes (AOPs) [30] has become a powerful oxidation technology that results the decomposition of methylene blue as organic contaminants in wastewater [31]. Therefore, Methylene blue is well known anionic dye which is popularly used as representative of contaminated wastewater in several experimental work [32, 33]. The objective of this study is to use magnetic iron oxide particles doped with cobalt ions prepared using ball milling method as a catalyst for decolourization of Methylene Blue.

2. Experimental procedure
The starting material was natural sand from Logas, Kuansing District Riau Province. In the first stage, the natural sand was dried prior to be processed by iron sand separator. The product of iron sand separator called ISS-1. In the second stage, the ISS-1 was mechanically milled for 60 h and 120 h. Hematite nanoparticles of 120 h of ball milling process were selected for further investigation. The structural and morphological properties of the hematite nanoparticles have been studied by X-Ray Diffractometer (XRD) and scanning electron microscope (SEM) respectively.

3. Catalytic degradation of Methylene blue
The catalytic performance of samples was studied based on degradation of methylene blue in an aqueous solution. 15 mL aqueous solution of methylene blue with a concentration of 25 was placed into the reaction glass, and hematite nanoparticles powder as much as 0.15 mg/L was added. The concentration of oxidizing agent (H₂O₂) was 15 ml. The aqueous solutions of methylene blue were mechanically stirred for 2 hours to establish the equilibrium. At every 2 hours time intervals, 1 mL of solution was removed and then analysed using the UV-Vis spectrophotometer. The degradation rate of MB was calculated using $C_0/C_t$ where, $C_0$ and $C_t$ are the initial and at given time concentration of methylene blue respectively.

4. Results and Discussion
Figure 1 shows the powder XRD patterns of magnetic iron oxide particles synthesized from Logas natural sand in Kuansing District Riau Province using ball milling for 60 hours and two step ball milling for (60+60) hours. The as synthesised iron oxide particles for both times are highly crystalline with diffraction peaks corresponding hematite ($\alpha$-Fe₂O₃) phase. The XRD pattern for magnetic oxide particles synthesized for 60 hours revealed eight intense peaks in the whole spectrum of 2θ values ranging from 10° to 90°. The diffraction peaks are clearly shown at 20 values of 23.993°, 32.761°, 35,372°, 40,465°, 48,956°, 53,385°, 61,822° and 63, 469°. Which are well corresponding to the (102), (104), (110), (113), (024), (116), (018), and (214) planes of hematite ($\alpha$-Fe₂O₃). It also can be seen from Fig. 2 that some other diffraction peaks from other crystalline forms such as silicon (Si) and ilminate phase (FeTiO₃) were detected, which demonstrates that these magnetic iron oxide particles ($\alpha$-Fe₂O₃) samples are not purely hematite as confirmed by X-Ray Fluorescence Spectroscopy (XRF) results [21]. The intensity of (1 0 4) reflection is stronger for magnetic iron oxide synthesized for 60 hours than that of 2 step ball milling. This indicates the product grown along (1 0 4) direction. Average crystallite size is calculated using Scherrer’s formula $D = k \lambda / \beta \cos \theta$, where D is the crystalline size, k is the Scherrer’s constant (k = 0.9), $\lambda$ is the wavelength of the X-ray used, $\beta$ is the (FWHM) intensity and $\theta$ is the diffraction angle of the peak. Average crystallite size is determined for flections (104) for first step ball milling (60 hours) and second step ball milling (60+60) hours are 44.9 nm and 39.2 nm respectively. The average crystallite size decreases with increase in milling time.
A comparison of SEM images shows a reduced particle size in the ball-milled magnetic iron oxide particles as milling time increases from 60 to 120 hours are shown in Figure 2. It can be clearly observed from low-resolution SEM images (1000x magnifications) that the 60 hours and 120 hours of the synthesized hematite nanoparticles show an irregular morphology. In the case of 60 hours milling time, particles size decreases after 120 h of ball milling with irregular sizes and shapes. As ball milling time increases the size of the particles becomes smaller compared to those for 60 hours milled time.

Figure 2. Scanning electron microscope (SEM) images for magnetic iron oxide particles (a) milled for 60 hours and (b) 120 hours milling time
Figure 3a shows the effect reaction time on methylene blue degradation for H$_2$O$_2$, α-Fe$_2$O$_3$ and H$_2$O$_2$+ α-Fe$_2$O$_3$ while the remaining parameters such as pH, concentration of solution and magnetic iron oxide amount were kept constant. From Figure 3(a), it can be seen that when only H$_2$O$_2$ was added into the solution, then methylene blue was nearly not degraded. Moreover, the degradation of methylene blue could not be observed when magnetic iron oxide particles were added into the solution. However, as mentioned in Fig. 3, the degradation efficiency of methylene blue was very high when H$_2$O$_2$ combined with hematite nanoparticles (H$_2$O$_2$+ α-Fe$_2$O$_3$). Higher degradation efficiency of methylene blue is due to the combination effect (H$_2$O$_2$+ α-Fe$_2$O$_3$). This result is agree well with other researcher [34]. Within 14 hours, the methylene blue was removed about 84.89 % and 88.90 % for 0.1 g and 0.15 g hematite nanoparticles respectively. This was due to the efficient peroxidise activity of α-Fe$_2$O$_3$ particles. This result clearly showed that there is a strong combination effect between the H$_2$O$_2$ and α-Fe$_2$O$_3$ hematite nanoparticles on degradation efficiency of methylene blue. The removal of methylene blue from the solution for 14 hours reaction time was about 88.90%. The corresponding plot of methylene blue removal as function of reaction time in the presence of hematite (α-Fe$_2$O$_3$) nanoparticles is shown in Figure 3(b). Accordingly, the degradation efficiency of MB was found to be much larger for catalyst mass of 0.1 and 0.15 g compared to that of 0.05 g. The degradation efficiency or MB removal is not change after 8 hours for mass of hematite nanoparticles of 0.10 and 0.15g. Figure 3c shows the effect of the amount hematite (α-Fe$_2$O$_3$) nanoparticles on the degradation efficiency of methylene blue. In this experiment, the amount of H$_2$O$_2$ was chosen to be 15 ml. Variation of amount of hematite nanoparticles is to obtain the information about how much magnetic iron oxide particles is needed in order to remove methylene blue from aqueous solution. It can be seen from Fig.3c that the degradation efficiency of methylene blue increases as the amount of magnetic iron oxide increases from 0.05 mg to 0.10 mg for degradation time of 14 hours. Increasing the amount of magnetic iron oxide particles to 0.15 g, the trend of degradation efficiency seems to be independent of the amount of magnetic iron oxide particles.

![Figure 3](image_url)

**Figure 3.** (a) Trend of degradation of methylene blue in presence of H$_2$O$_2$, α-Fe$_2$O$_3$ and H$_2$O$_2$+ α-Fe$_2$O$_3$, (b) influence of amount of hematite nanoparticles on the MB removal and (c) Effect of reaction time on methylene blue removal as a function of hematite nanoparticle amount.
The optimum weight of magnetic iron oxide particles in the removal of methylene blue is shown in Fig. 3c. The weight of the magnetic iron oxide particles that used were 0.05, 0.10, and 0.15mg. Magnetic iron oxide particles were tested for optimum weight in a reaction time of 14 hours. It was found that trend of degradation depends on the amount of magnetic iron oxide particles and rising of the catalyst loading to 0.10 g/L improves the degradation very significantly, while afterward the trend of methylene removal shows to be independent of the magnetic iron oxide particles mass.

5. Conclusion
From the above studies, it may be concluded that the hematite nanoparticle size can be modified by ball milling method as confirmed by SEM. The XRD patterns demonstrate that the product of ball milling is not purely hematite, however, there are other diffraction peaks from other crystalline forms such as silicon (Si) and titanium (Ti). Therefore, further experiments are needed to obtain particles in nanometer size and purely hematite phase. The ball milled hematite nanoparticles for 120 hours showed high catalytic activity in methylene blue removal. The methylene blue removal percentage arrived at above 88% for reaction time of 14 hours. The results showed that hematite nanoparticles dosage affects the degradation efficiency of methylene blue.

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