The Influence of Milling Ball Size on the Structural, Morphological and Catalytic Properties of Magnetite (Fe₃O₄) Nanoparticles toward Methylene Blue Degradation

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Abstract. Structural, morphological properties and the catalytic activity of magnetite (Fe₃O₄) nanoparticles for degradation of methylene blue have been studied. The magnetite nanoparticles were synthesised from Padang beach sand West Sumatera by 2 steps ball milling method. Structures and morphologies of the synthesized magnetite nanoparticles were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was shown that the particle size of the magnetite nanoparticles can be controlled by milling ball size. The average grain size of magnetite particles milled for milling ball size of 0.7 cm and 1.5 cm was found to be 81.25 nm and 30.75 nm, respectively. Scanning electron microscopy (SEM) images show that the particle size of samples decreases as milling ball size increases and the grains exhibit irregular form. The effect of milling ball size on the degradation efficiency of catalytic reaction exhibited a good ability to degrade methylene blue from aqueous solutions with a maximum methylene blue removal rate of 86.79% for 10 hours reaction time.

1. Introduction

Iron oxide in nanometer scale with controllable properties are very important technologically [1], and therefore, they are the subject of current research. There are three most common forms of iron oxide such as magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and hematite (α-Fe₂O₃) [2]. When magnetite is prepared into well-defined nanoscale structures, it may be applied in a wide range of fields, including catalysis [3,4], biomedicine [5], magnetic data recording devices [6], toners and inks for electro photography [7]. In order to obtain these particles, various methods have been developed including hydrothermal reaction[8], microwave[9], sol–gel method[10], micro emulsion method[11], forced hydrolysis[12] and physical methods[13,14,15]. Although several methods have been developed in the synthesis of magnetite nanoparticles, a simple, efficient, low cost and high yield fabrication still remains a challenge. Therefore, ball-milling method has become a successful method for the large scale in which both nanostructures size and structures of magnetite nanoparticles can be controlled. Meanwhile, the properties of nanoparticles obtained by the ball-milling method are affected by milling parameters such as the milling-time, number, diameter and mass of balls etc [16].

Methylene blue is one of organic dyes that are used in textile industry to colour the products. [17]. The release of coloured wastewater from this industry to the water body such as rivers and lakes can cause serious water pollutions. The removal of methylene blue from wastewater released by textile
industries is quite difficult. Hence, it is necessary to remove methylene blue from wastewater to prevent the tremendous threat of methylene blue on ecosystem and public health. Several methods have been developed for the removal of methylene blue from wastewater such as reverse osmosis, ion exchange, precipitation, adsorption, ultrasonic decomposition, advanced chemical oxidation and nano filtration, etc. [19]. However, Advanced oxidation processes (AOPs) are widely utilized for degradation of methylene blue due to its simplicity, low cost and green treatment technology. [20] Among the various AOPs, Fenton reaction has high impact in degradation of methylene blue due to the ability of it to decompose of methylene blue into safer product such as CO$_2$, H$_2$O, and mineral acids. [21] Several works have been carried out regarding the application of the Fenton’s process to remove organic dyes from textile industry [22] and methylene blue [23].

In this paper, magnetite nanoparticles (Fe$_3$O$_4$) obtained by synthesizing natural sand from Padang beach West Sumatera using 2 steps ball milling method were used as catalyst for degradation of methylene blue in aqueous solution and investigates the effects of catalyst loading.

2. Methodology

2.1. Preparation of magnetite nanoparticles.
Magnetite (Fe$_3$O$_4$) nanoparticles were obtained from Padang beach sand West Sumatera using 2 steps ball milling method. The sand was dried prior to iron sand separator process. The product of iron sand separator is called ISS-1. In the second stage, the ISS-1 was mechanically milled for 60 h with milling ball size of 1.5 cm. In the third stage, the ball milling product was divided into 2 samples, the first sample was mechanically milled using milling ball size of 0.7 cm for 40 h and the second sample was milled using milling ball size of 1.5 cm for 40 h. The structural and morphological properties of the powder have been studied by X-Ray Diffractometer (XRD) and Scanning Electron Microscope (SEM) respectively.

2.2. Characterization
The as synthesised samples were characterized by the following techniques: X-ray diffraction (XRD) and scanning electron microscopy (SEM). The diffraction pattern of the samples were obtained using a diffractometer equipped with a Cu target X-ray tube and Cu-Kα radiation producing x-ray wavelength of 1.5406 Angstroms. The X-ray profile was collected from 10-90 degree in scattering angle using a 0.01° step. The morphology of the magnetite nanoparticles was observed by using SEM.

2.3. Procedure for degradation of methylene blue.
Catalytic activity of magnetite nanoparticles was studied by degradation of methylene blue in aqueous solution. Methylene blue was selected as a model organic pollutant and its degradation was studied in the presence of magnetite nanoparticles. Several key factors such as the methylene blue concentration, concentration of oxidizing agent (H$_2$O$_2$), loading of magnetite nanoparticles were investigated to provide a better knowledge of this chemical reaction. Magnetite nanoparticles as much as 0.10 mg were added to a solution of methylene blue in distilled water (100 mL, 15 mg/L) at pH of 4.8, and the suspension stirred using hand stirrer for 2.5 hours. 15 mL of hydrogen peroxide was injected into the reaction mixture. The reaction mixture was sampled at 2 hours intervals.

3. Results and Discussion

3.1. X-Ray Diffraction Results
Figure 1 shows two XRD patterns for as synthesized magnetite nanoparticles for difference milling ball size that is 0.7 cm and 1.5 cm for 40 h milling time. It can be seen that the diffraction peaks of magnetite nanoparticles at 20 value of 30.0742°, 35.4547°, 43.0350°, 53.4098°, 56.9228°, 62.3834° and 74.4201° were completely matched the reflections of (220), (311), (400), (422), (511), (440), and (533) respectively indicates the formation of magnetite (Fe$_3$O$_4$) phase. Moreover, It seems that the (3 1 1 ) peak in the case of 1.5 cm ball milling size magnetic iron oxide particles has higher intensity than that of 0.7 cm ball size milled magnetic iron oxide particles. This indicates that the particles size is
smaller when milled with bigger size of milling ball with constant time. However, some other diffraction peaks from other crystalline forms such as silicon (Si) and titanium (Ti) were detected especially for the as synthesize magnetite nanoparticles, which demonstrates that these magnetite nanoparticles (Fe₃O₄) samples are not high purity. The average magnetite crystalline size of the as synthesized samples is calculated using Debye-Scherrer equation [24].

\[ d = \frac{0.9\lambda}{\beta \cos \theta} \] ........................................... (1)

where \( d \) is size of crystallite, \( k \) is the shape factor, \( \lambda \) is the wavelength of X-ray, \( \beta \) is the full width at half maximum (FWHH) of the diffraction peak, and \( \theta \) is the peak position. The crystallite size of the as synthesized sample calculated based on diffraction pattern peak of (3 1 1) with milling ball size of 0.7 cm and 1.5 cm is 49 nm and 24 nm respectively.

**Figure 1.** X-ray diffraction patterns for magnetite (Fe₃O₄) nanoparticles prepared with different milling ball sizes (a) 0.7 cm and (b) 1.5 cm.
3.2. Morphology of Magnetite Nanoparticles

The morphology of the synthesized magnetite (Fe$_3$O$_4$) nanoparticles milled for (60+40) hours with different milling ball diameters of 0.7 cm and 1.5 cm are shown in Fig. 2. SEM analysis shows that, in all the samples, the particles are irregular in shape, randomly organized, and tend to form agglomerates especially for the as synthesized sample prepared using ball size diameter of 1.5 cm. In addition, particle's shape and size (between 5 and 200 $\mu$m) are clearly shown in Fig. 2(a). Particle’s size did significantly reduce after milling with milling ball size of 1.5 cm and consisted of a narrower particle size distribution compared to that for the sample synthesized using milling ball size of 0.7 cm as revealed in Fig. 2(a). Moreover, the irregular particle size from a few to ten micrometers of magnetite nanoparticles can be seen very clearly in Fig. 2b. Some of them are the agglomeration of micro size magnetite nanoparticles.

3.3. Degradation of Methylene Blue from Aqueous Solution

The catalytic activity of as-synthesized magnetic iron oxide particles was evaluated by the degradation of methylene blue in aqueous solution. The decolourization of the methylene blue was examined under three different conditions namely H$_2$O$_2$ without Fe$_3$O$_4$, Fe$_3$O$_4$ without H$_2$O$_2$ and H$_2$O$_2$ + Fe$_3$O$_4$. The parameters of experiment such as concentration of solution and magnetite nanoparticles amount were kept constant. The result showed that when only H$_2$O$_2$ was used, methylene blue was not degraded. In the presence magnetite (Fe$_3$O$_4$) nanoparticles without H$_2$O$_2$, degradation of methylne blue was not observed throughout in the 10 hours. This result confirms that degradation of the methylene blue in the presence of the magnetite nanoparticles without H$_2$O$_2$ is insignificant. The corresponding plots of percent degradation as a function of reaction time under H$_2$O$_2$ without Fe$_3$O$_4$ and Fe$_3$O$_4$ without H$_2$O$_2$ are shown in Figure 3(a). As shown in Figure 4(a), the degradation of methylene blue was significantly occurred when the system consisted of H$_2$O$_2$–magnetite (Fe$_3$O$_4$) nanoparticles. The degradation of methylene blue was achieved about 86.89% for 2 hours reaction time. However, for longer reaction time methylene removal was achieved higher than that for 2 hours reaction time as mention in Fig. 3b. The degradation of methylene blue using catalytic system of H$_2$O$_2$ + Fe$_3$O$_4$ was found to be much larger than the degradation efficiency as compare to H$_2$O$_2$ and Fe$_3$O$_4$ treatment.
In order to determine the effect of magnetite nanoparticle amount for removal of methylene blue through Fenton process, three experiments were conducted with magnetite nanoparticles amount of 0.10, 0.15 and 0.20 g as shown in Fig. 4(a). The figure shows that trend of degradation efficiency depends on the amount of magnetite nanoparticles and increasing of the magnetite nanoparticles amount to 0.10 g/L improves the degradation efficiency very significantly. However, higher magnetite nanoparticles amount namely 0.15 g resulted decrease in degradation efficiency, while increasing the amount of magnetite nanoparticles to 0.20 g, the trend of degradation efficiency seems to be independent of the amount of magnetite nanoparticles. The effect of magnetite nanoparticles prepared by different milling ball size namely 0.7 cm and 1.5 cm is shown in Fig. 4(b). It is clear that the degradation efficiency of methylene blue is greater for magnetite nanoparticles prepared by milling ball size of 1.5 cm compared to that of 0.7 cm. The main reasons for this difference were smaller particle sizes of the magnetite nanoparticles as confirmed by SEM results Fig. 2(b).
4. Conclusion

The findings of this study show that the magnetite (Fe₃O₄) nanoparticles have been prepared using 2 steps ball milling method. XRD results indicated the formation of magnetite phase in magnetic iron oxide particles. The particle size decreases as milling ball size increases. SEM confirmed irregular morphology of magnetite nanoparticles with agglomeration and non-homogenous distribution. Our study showed that the combination of magnetite nanoparticles and is essential for the decomposition of methylene blue from aqueous solution and showed a good degradation efficiency. The catalytic activity of magnetite nanoparticles increased as milling ball size increased from 0.7 cm to 1.5 cm. Moreover, it was found that around 86.79% of the methylene blue in aqueous solution was removed within 10 hours.

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