Study of Iron Oxide Nanoparticles Doped with Manganese for Catalytic Degradation of Methylene Blue

Erwin Amiruddin, Amir Awaluddin, Salomo Sinuraya, Heri Hadianto, Muhammad Deri Noferdi and Ainun Syarifatul Fitri

1 Physics Department Faculty of Mathematics and Natural Sciences Riau University, 2 Chemistry Department Faculty of Mathematics and Natural Sciences Riau University 3 Magnetic Laboratory, Physics Department Faculty of Mathematics and Natural Sciences Riau University, Indonesia 28293.

Abstract. Modification of iron oxide nanoparticles by doping with transition metals has been intensively reported and many applications have been proven. Magnetic and structural properties, and the catalytic activity of undoped and manganese doped iron oxide nanoparticles for degradation of methylene blue have been studied. Preparation of undoped and manganese doped iron oxide nanoparticles was done by ball milling method using Logas natural sand as raw materials. The magnetic properties of the samples were determined using vibration sample magnetometer (VSM). A detailed analysis of the loop hysteresis reveals a reduction of saturation magnetization of the samples towards higher manganese-doping concentration (wt.%). The reduction in magnetization from 13.25 to 11.67 emu/g and enhanced the coercivity on manganese-doped samples from 224.35 to 352.18 Oe are observed to produce an improvement in the catalytic activity for manganese doped iron oxide nanoparticles compared to undoped samples. Catalytic activity of undoped and manganese doped iron oxide nanoparticles in the degradation of methylene blue was studied through ultraviolet visible spectroscopy (UV-Vis). Manganese doped iron oxide nanoparticles exhibit better catalytic activity for degrading methylene blue (88.880%) compared to that for undoped iron oxide nanoparticles (81.805%) for 300 minutes reaction time.

1. Introduction
In recent years, research on iron oxide nanoparticles have received increasing attention due to their potential applications in ranging from environmental remedy include catalysts [1,2] to biomedical applications[3,4]. Iron oxides exist in natural environment in many different forms, however, the most common forms are hematite $\alpha$-Fe$_2$O$_3$, maghemite $\gamma$-Fe$_2$O$_3$ and magnetite Fe$_3$O$_4$[5]. In nanometer size, these particles exhibit superparamagnetic behaviour and therefore they have wide range applications[6]. Iron oxide nanoparticles can be prepared by various methods including solvo thermal[7], laser pyrolysis[8], thermal oxidation[9], hydrothermal [10] techniques. However, the simplest way to prepare iron oxide nanoparticles is ball milling method [11]. Physical properties such as magnetic, electrical, optical and structural of iron oxide nanoparticles can be modify by doping them using different materials such as transition metal elements[12]. Choice of doping elements and
method of doping determines the extent of modification in properties. For example, some researchers [13] prepared iron oxide/hematite doped with 1% of Sn, Nb, Pt, Zr, Ti, Zn and Ni cations as well as with Si and Ge. They employed ball milling method to prepare iron oxide mixed with some dopants in the form of oxide. Similar modifications have been reported for iron oxide nanomaterials when doped by other transition metals [14]. Modification of magnetic properties of iron oxide nanoparticles using some dopants has also been carried out by some researchers [15,16]. Doping of transition metal such as manganese in magnetic nanoparticles may have the ability to control Mn/Fe ratio and thus may change the structural and magnetic properties of iron oxide nanoparticles and therefore can optimize them for catalyst application.

Methylene blue is one of the organic dyes used in dyeing and painting textiles [17] and the release of this dye into the body of water can generate carcinogenic effects that may be harmful against human health and environment [18,19]. Therefore, removing the dyes from wastewater is very important for the safety environment. However, removal dyes from wastewater is a difficult process, since its chemical structure is stable and hard-degradation [20]. Various techniques have been developed to improve the efficiency to remove methylene blue from waste water, including adsorption [21], coagulation, [22] and others [23]. 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 [24]. Therefore, Methylene blue is well known anionic dye which is used as representative of contaminated wastewater in several experimental work [27,28]. The objective of this study is to modify iron oxide nanoparticles by doping them with manganese using ball milling method and uses them as a catalyst for degradation of methylene blue in aqueous solution.

2. Methodology

Raw Material
The starting material to prepare the iron oxide particles was natural sand from Logas district- Kuansing Regency- Riau Province, Indonesia. Manganese powder (99.97%) was bought from Toko Pedia (www.tokopedia.com).

Preparation of undoped and manganese doped iron oxide particles
Iron oxide nanoparticles were prepared from Logas natural sand, Kuansing Regency Riau Province using ball milling method. First, sample of natural sand were dried prior to iron sand separator (ISS) process. The iron oxide and non iron oxide nanoparticles of ISS product was separated again using NdFeB magnet. This product was milled for 120 hours and the product was process again using NdFeB for separating between iron oxide and non iron oxide. The ball milling product was divided into 4 parts with the same amount. Iron oxide particles were doped with manganese in concentration of 0, 5, 10 and 15%. The powder of manganese and iron oxide particles were mixed and milled for 20 hours. These compounds were studied for their magnetic properties and for particle size and particles size distribution using X-Ray Diffractometer (XRD) and Particles Size Analyzer (PSA). The hysteresis loop was used to confirm the presence of weak magnetic behaviour in each sample.

3. Results and Discussion
Loop hysteresis measurements of undoped and manganese doped iron oxide samples were carried out using vibration sample magnetometer (VSM). As shown in Fig. 1, the applied magnetic field used was ranging from +20.000 Oe to -20.000 Oe. The magnetic nanoparticles reveal weak ferromagnetic behaviour. These results are in agreement with those described by other researchers [29] for evidence of weak ferromagnetic behaviour due to manganese dopant. The detailed values of magnetic
parameters ($M_s$, $M_r$, $H_c$ and loop squareness) the three samples are listed in table 1. The saturation magnetization for the undoped magnetic nanoparticles is 13.25 emu/g and it decreases for the manganese doped 5 wt.% and 10wt.% to about 12.18 emu/g and 11.67 emu/g, respectively. It is obvious that the saturation magnetization value decreases as the concentration of manganese increases which might be because of the presence of more manganese atoms at the grain boundaries as revealed in the X-Ray Diffraction (XRD) results[30]. Similar results of decreased magnetizations after doping the magnetic particles with manganese have also been reported [31,32]. The coercivity of the undoped magnetic particles is found to be 224.35 Oe and it increases for the manganese doped nanoparticles to 352.18 Oe as indicates in Table 1. Moreover, the undoped magnetic particles show the remanent magnetization ($M_r$) value of 2.54 emu/g and it decreases for the manganese doped magnetic nanoparticles to about 2.50 and 2.34 emu/g for manganese concentration of 5 and 10 wt. %, respectively as sown in Table 1. In addition, As could be seen in Table 1, the loop squareness increased from 0.166 to 0.213 with the increase of manganese concentration of 0 to 10 wt.%.

Figure 1. Hysteresis loop of manganese doped (a) 0% (b) 5%, and (c) 10% iron oxide nanoparticles
Table 1. Magnetic parameters of hysteresis loop

| Concentration of Mn (wt.%) | Ms (emu/g) | Mr (emu/g) | Hc (Oe) | S  (Loop Squareness) |
|---------------------------|------------|------------|--------|----------------------|
| 0                         | 13.250     | 2.540      | 224.350| 0.166                |
| 5                         | 12.180     | 2.500      | 341.160| 0.205                |
| 10                        | 11.670     | 2.340      | 352.180| 0.213                |

The catalytic activities of undoped and manganese doped iron oxide nanoparticles were investigated. Fig. 3 shows the changes of manganese concentrations as a function of reaction time. The degradation of the methylene blue was examined under three different conditions namely using only H₂O₂, only iron oxide nanoparticles and H₂O₂ + undoped and manganese doped iron oxide nanoparticles. In this experiment, the parameters of experiment such as concentration of solution and iron oxide nanoparticles amount were kept constant. The result showed that when only H₂O₂ was used, degradation efficiency of methylene blue was relatively slow as shown in Fig.2. The degradation efficiency increases from 2.28 % to 4.35 % of the initial within 300 minutes reaction time. In the presence of iron oxide nanoparticles without H₂O₂, degradation efficiency of methylene blue was also slow and increase to 7.57 within 300 minutes reaction time. This result is clearly shown that degradation efficiency of the methylene blue in the presence of the iron oxide nanoparticles without H₂O₂ is very slow. The degradation of methylene blue as a function of reaction time under H₂O₂ without iron oxide nanoparticles and iron oxide without H₂O₂ are shown in Fig. 2. The degradation efficiency of methylene blue using H₂O₂ + iron oxide nanoparticles is found to be much larger than the degradation efficiency as compare to that for H₂O₂ and iron oxide nanoparticles treatment. The degradation efficiency of methylene blue using iron oxide nanoparticles + H₂O₂ was achieved about 69.609% and 81.805 for 60 and 300 minutes reaction time, respectively. However, degradation efficiency of methylene blue using iron oxide nanoparticle 5 wt.% and 10 wt.% Mn + H₂O₂ increases from 76.247% to 86.627 % and 80.060% to 88.88%, respectively as reaction time increases from 0 to 300 minutes. It is believed that based on the catalytic activity of manganese doped iron oxide nanoparticles and the simple preparation method (ball milling method), manganese doped iron oxide nanoparticles have potential application in environmental remedy.

Table 2. Methylene blue degradation efficiency

| No | Reaction Time (minutes) | H₂O₂ | α-Fe₅O₃ | α-Fe₃O₄ + H₂O₂ | α-Fe₅O₃ + Mn 5% wt. + H₂O₂ | α-Fe₅O₃ + Mn 10 wt.% + H₂O₂ |
|----|-------------------------|------|--------|----------------|-----------------------------|-----------------------------|
| 1  | 0                       | 0    | 0      | 69.609        | 76.247                      | 80.060                      |
| 2  | 60                      | 2.28 | 4.42   | 81.223        | 86.207                      | 88.226                      |
| 3  | 120                     | 3.32 | 5.42   | 81.550        | 86.253                      | 88.460                      |
| 4  | 180                     | 3.58 | 5.96   | 81.636        | 86.440                      | 88.740                      |
| 5  | 240                     | 4.02 | 6.75   | 81.805        | 86.627                      | 88.880                      |
| 6  | 300                     | 4.35 | 7.57   | 81.805        | 86.627                      | 88.880                      |
Figure 2. Trend of degradation efficiency of methylene blue in presence of H$_2$O$_2$ and iron oxide nanoparticles

Figure 3. Effect of manganese doped iron oxide (IO) nanoparticles on degradation efficiency of methylene blue.

4. Conclusion

From the above studies, undoped and manganese doped iron oxide nanoparticles have been prepared with manganese concentration of 0, 5 and 10 wt.% using ball milling method and then we investigated the magnetic properties of the compounds. The results of magnetic measurements show a weak ferromagnetic behaviour. Manganese doped iron oxide nanoparticles were observed to have lower magnetization value compared to that for undoped iron oxide nanoparticles. Our study showed that the catalytic activity of manganese doped iron oxide nanoparticles increases as concentration of manganese increases from 0 to 10 wt.% . It is also found that around 88.88% of the methylene blue in aqueous solution was removed using manganese doped iron oxide nanoparticles (10 wt. %) within 300 minutes.
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