The Role of Annealing Temperature in Photocatalytic Performance of Fe₃O₄/SnO₂ nanocomposites

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Abstract. In this work, SnO₂ nanoparticles with the variation of annealing temperature (400°C-800°C) were used as photocatalyst for remove organic dye from the aqueous solution. SnO₂ nanoparticles were synthesized using sol-gel method. For enhancing the stability and the photocatalytic activity of the samples, magnetite materials (Fe₃O₄) were combined with SnO₂ nanoparticles. The prepared samples characterized by X-ray Diffraction (XRD). The X-ray diffraction shows tetragonal structure of SnO₂ and cubic spinel of Fe₃O₄ as the components of the prepared nanocomposites. The photocatalytic activity of the samples was studied using Methylene Blue (MB) as a model organic pollutant. The photocatalytic degradation of MB by SnO₂ and Fe₃O₄ nanocomposites under UV light irradiation was examined by varying the operational parameters such as catalyst dosage and scavengers. Among the variation annealing temperature of SnO₂ nanoparticles, the 700°C annealing temperature of SnO₂ showed the highest photocatalytic activity. The repeatability of photocatalytic activity was also tested.

1. Introduction
Dyes widely used in many industries often create severe environmental pollutions in the form of colored wastewater discharged into environmental water bodies [1]. Therefore, in recent years, the treatment of various organic dye effluents has become an important topic in the research field on environmental pollution and control [2]. Of all various method, advance oxidation processes (AOPs) such as photocatalysis has attracted remarkable interest because it offers a sustainable pathway to drive chemical reactions such as water splitting carbon fixation, and degradation of organic pollutants [3-5].

Among various semiconductors, SnO₂ is an n-type semiconductor that has been applied in many applications and potentially to be ideal catalyst due to their several advantages [6-8]. But, high rate recombination electron holes pairs and reusability limitation of those semiconductor could limit the efficiency as a catalyst. Therefore, by adding with other material such as Fe₃O₄ could resolve the problem. So the material is possible to do the magnetic separation from the solutions for reusing and could inhibit the recombination of electron holes pairs [9,10]. Besides of recombination rate of the sample, still, have many things that could be affected by the catalytic activity of the sample. Many studies have reported a correlation between catalytic activity and annealing temperature, crystallinity and charge recombination rate, which significantly affects the properties of the sample [11].

In this study, Fe₃O₄/SnO₂ nanocomposite with the various of annealing temperature (400°C, 500°C, 600°C, 700°C, 800°C) were prepared using ultrasonic assisted method. The sample was characterized
using X-ray Diffraction (XRD). The catalytic activity of the Fe$_3$O$_4$/SnO$_2$ nanocomposites with various annealing temperature was analyzed using methylene blue as organic pollutant model. The catalytic activity of the Fe$_3$O$_4$/SnO$_2$ with 700°C annealing temperature showed best photocatalytic performance under UV-light irradiation.

2. Experimental

2.1. Materials
All reagents used were analytical grade and without further purification. Tin chloride anhydrous (SnCl$_2$), Iron (II) sulfate heptahydrate (FeSO$_4$.7H$_2$O), sodium hydroxide (NaOH), methylene blue (MB), ethanol, ethylene glycol (EG), ammonium oxalate, sodium sulfate, and tertbutyl alcohol (TBA) were purchased from Merck.

2.2. Synthesis of nanomaterials
The Fe$_3$O$_4$ nanoparticles were synthesized using the same method of our previous study [12]. The SnO$_2$ nanoparticles were synthesized using modification method reported by Yue li and friends [13]. First, SnCl$_2$ was dissolved into ethanol and the aqueous mixture then added into the NaOH solutions using magnetic stirring. Then, the mixture solutions were heated 180°C temperature for 3 hours and chilled in room temperature. The precipitated obtained was centrifuged and washed using aqueous and ethanol several times. The precipitated particles were dried in vacuum condition at 80°C temperature. The SnO$_2$ particles obtained after calcination process for 3 hours at various temperature (400°C, 500°C, 600°C, 700°C and 800°C).

Fe$_3$O$_4$/SnO$_2$ nanocomposites were synthesized using the sol-gel method. First, SnO$_2$ nanoparticles were mixed with Fe$_3$O$_4$ in aqueous and ethanol mixture. Each mixture was given ultrasonic for 2 hours then was centrifuged to obtain product on its precipitated. The product result obtained was dried in vacuum condition at 80°C temperature for 12 hours to obtain Fe$_3$O$_4$/SnO$_2$ nanoparticles.

2.3. Characterization
The sample was characterized using X-Ray Diffraction (XRD) measurement by using Rigaku Miniflex 600 with radiation source Cu K-α (λ =1,5406 Å).

2.4. Photocatalytic experiments
The photocatalytic experiment was done by mixing the sample Fe$_3$O$_4$/SnO$_2$ (400°C,500°C,600°C,700°C,800°C) into 100mL methylene blue (MB) solutions used as pollutant model with concentrations 20mg/L respectively, and pH solutions adjusted NaOH. The solution was allowed to stand in stirring state for adsorption and desorption balance. The photocatalytic test, the solution was given UV light irradiation with power 40W and wavelength of 320-400 nm. The solution was given UV light irradiation for 2 hours. Every 15 minutes span the concentration of MB solution was analyzed using UV-vis spectrometer.

3. Result and Discussion
Figure 1 shows the XRD spectrum of SnO$_2$ nanoparticles and Fe$_3$O$_4$/SnO$_2$ nanocomposites with various annealing temperature. The diffraction pattern of Fe$_3$O$_4$ sample observed at the value 2θ = 30.14°, 35.49°, 43.28°, 57.20°, 62.83° and 74.8° which shows each area (220), (311), (400), (511), (440) and (533) of the cubic spinel structure. Diffraction pattern of SnO$_2$ nanoparticle sample observed at value 2θ = 26.5°, 33.8°, 38°, 39°, 51.8°, 54.8°, 58°, 62°, 64.7°, 65.8°, 71.2°, 78.2°, 81.2°, 83.7° which shows the existence of areas (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202), (321), (400), (222) of tetragonal structure of SnO$_2$ nanoparticle. The XRD pattern of Fe$_3$O$_4$/SnO$_2$ nanocomposites shows the existence of cubic spinel phase of Fe$_3$O$_4$, followed by the addition of tetragonal SnO$_2$ nanocomposites. As it is clear from this figure, there is no any impurity in the nanoparticle sample.
Strong and sharp peaks can indicate that the prepared samples are highly crystalline [14]. The grain size measurement was calculated using Scherrer’s equation and lattice parameter was calculated using Rietveld refinement method. The analysis result of grain size and lattice parameter is shown in Table 1.

Fe$_3$O$_4$/SnO$_2$ nanocomposites with various annealing temperature were subjected to methylene blue (MB) degradation process in the condition of UV at 320-400 nm. The catalytic degradation of methylene blue was observed (Fig. 2). The maximum degradation of photocatalytic activity is 43.5%, 53.2%, 60.6%, 68.1%, and 65% for Fe$_3$O$_4$/SnO$_2$ 400°C, Fe$_3$O$_4$/SnO$_2$ 500°C, Fe$_3$O$_4$/SnO$_2$ 600°C, Fe$_3$O$_4$/SnO$_2$ 700°C, and Fe$_3$O$_4$/SnO$_2$ 800°C, respectively. As can be seen from the Fig. 2, the degradation rate of MB is increased with increasing calcination temperature until 700°C. But the photocatalytic activity of Fe$_3$O$_4$/SnO$_2$ calcined at 800°C is slightly lower than that of the photocatalyst calcinated 700°C. It may be due to the crystallite size of Fe$_3$O$_4$/SnO$_2$ are bigger than the other (Table. 1.), which resulting in a reduction of quantum size effect [15]. Fe$_3$O$_4$/SnO$_2$ 700°C nanocomposite exhibits the best photocatalytic performance under UV light irradiation.

Figure 3 shows the effect of catalyst dosage addition, Fe$_3$O$_4$/SnO$_2$ calcinated at 700°C nanocomposites from 0.1 g/L until 0.4 g/L, to the efficiency of methylene blue degradation through a

![Figure 1. XRD patterns of (a) SnO$_2$ nanoparticles and (b) Fe$_3$O$_4$/SnO$_2$ nanocomposites with various annealing temperature](image)

Table 1. Lattice parameters and grain size of Fe$_3$O$_4$/SnO$_2$ nanoparticles with various annealing temperature

| Sample       | Lattice Parameter |  <D>   |
|--------------|-------------------|--------|
|              | Fe$_3$O$_4$ a=b=c | SnO$_2$ a=b | c | Fe$_3$O$_4$ | SnO$_2$ |
| Fe$_3$O$_4$/SnO$_2$ 400°C | 8.384 | 4.738 | 3.193 | 24 | 24 |
| Fe$_3$O$_4$/SnO$_2$ 500°C | 8.391 | 4.739 | 3.190 | 27 | 22 |
| Fe$_3$O$_4$/SnO$_2$ 600°C | 8.388 | 4.740 | 3.196 | 29 | 23 |
| Fe$_3$O$_4$/SnO$_2$ 700°C | 8.380 | 4.760 | 3.190 | 28 | 21 |
| Fe$_3$O$_4$/SnO$_2$ 800°C | 8.387 | 4.741 | 3.193 | 30 | 28 |
Figure 2. Photocatalytic activity of Fe₃O₄/SnO₂ nanocomposites with different annealing temperature.

Figure 3. Effect of dosage on photocatalytic activity of Fe₃O₄/SnO₂ 700°C nanocomposite.

Figure 4. Effect of scavengers on photocatalytic activity of Fe₃O₄/SnO₂ 700°C nanocomposite.

Figure 5. Reusability of Fe₃O₄/SnO₂ 700°C nanocomposites.

photocatalytic process. As seen in Fig. 3, after 120 minutes, maximum degradation for Fe₃O₄/SnO₂ calcinated at 700°C with dosage 0.1 g/L, 0.2 g/L, 0.3 g/L and 0.4 g/L each are 58.6%, 61.8%, 68.1%, and 65%. The amount of sample will influence two things; the amount of active site on the sample and the amount of dyes adsorbed by the sample [16]. Catalyst dosage addition will also increase the amount of active site. The result in Fig. 3 indicates that the optimum catalyst dosage for Fe₃O₄/SnO₂ calcinated at 700°C nanocomposite sample is 0.3 g/L.

To know the most involved reactive species MB degradation to the all samples, the addition scavenger was done. In Fig. 4 shows the result of MB degradation in the photocatalytic process with scavenger addition influence. The scavenger addition serves to bind the reactive species to not take role in the photocatalytic process. The result obtained shows that the addition of hole scavenger shows the lowest degradation capacity. This indicates that the most influential reactive species for the samples is hole.
To analyze the catalyst stability, the cycling test was done. The cycling test was done by reusing catalyst four times for photocatalytic process. After photocatalytic process test, the sample was separated from its solutions using magnetic external as seen in Figure 5 to be reused as catalyst in next experiment. In figure 5 shows the result of reusing data of Fe$_2$O$_3$/SnO$_2$ calcinated at 700°C nanocomposites. It is shown that the sample showed good cycling capacity result with the decrease only about 5% after reusing three times. It proves that photocatalytic activity for the Fe$_2$O$_3$/SnO$_2$ of nanocomposite is stable.

4. Conclusion
The Fe$_2$O$_3$/SnO$_2$ nanocomposites with different annealing (400°C, 500°C, 600°C, 700°C, 800°C) temperature have been successfully synthesized via sol-gel method. The maximum degradation of photocatalytic activity is 43.5%, 53.2%, 60.6%, 68.1%, and 65% for Fe$_2$O$_3$/SnO$_2$ 400°C, Fe$_2$O$_3$/SnO$_2$ 500°C, Fe$_2$O$_3$/SnO$_2$ 600°C, Fe$_2$O$_3$/SnO$_2$ 700°C, and Fe$_2$O$_3$/SnO$_2$ 800°C, respectively. Fe$_2$O$_3$/SnO$_2$ 700°C nanocomposite exhibits the best photocatalytic performance under UV light irradiation. The optimum catalyst dosage for Fe$_2$O$_3$/SnO$_2$ calcinated at 700°C nanocomposite sample is 0.3 g/L. Scavengers experiment shows that the most influential reactive species for the samples is hole. Sample showed good cycling capacity result with the decrease only about 5% after reuse three times.

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