Improve sonocatalytic performance using modified semiconductor catalyst SnO\textsubscript{2} and ZrO\textsubscript{2} by magnetite materials

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Abstract. Modifying semiconductor catalysts using magnetic materials could enhance the efficiency of wastewater removal and the separation efficiency demonstrated in our previous studies. The catalytic performance of wide band gap ZrO\textsubscript{2} and SnO\textsubscript{2} semiconductors has not been studied with regard to the ultrasonic radiation catalytic process. Therefore, the ultrasound-assisted sonocatalytic performance of ZrO\textsubscript{2} and SnO\textsubscript{2} semiconductors combined with Fe\textsubscript{3}O\textsubscript{4} (magnetite) nanoparticles has been studied using methylene blue as a model organic pollutant. The nanocomposites were synthesized using sol-gel methods. The structural properties of the samples were characterized using X-ray diffraction (XRD). Sample morphology was obtained by transmission electron microscopy (TEM). The magnetic properties of the samples were characterized using a vibrating sample magnetometer (VSM). The cubic spinel structure of Fe\textsubscript{3}O\textsubscript{4} is successfully identified, as are the tetragonal structures from SnO\textsubscript{2} and ZrO\textsubscript{2}. The samples exhibit ferromagnetic behavior at room temperature. Both ZrO\textsubscript{2} and SnO\textsubscript{2} combined with Fe\textsubscript{3}O\textsubscript{4} show better sonocatalytic efficiency than without Fe\textsubscript{3}O\textsubscript{4} and even better efficiency than the pioneering wide band gap semiconductor TiO\textsubscript{2}. The combination of magnetite nanoparticles with SnO\textsubscript{2} exhibit the highest degradation efficiency. The incorporation of magnetic material into catalysts has been proved to enhance the reusability of catalysts with efficient separation process.

Keywords: SnO\textsubscript{2}, ZrO\textsubscript{2}, Fe\textsubscript{3}O\textsubscript{4}/SnO\textsubscript{2}, Fe\textsubscript{3}O\textsubscript{4}/ZrO\textsubscript{2}, sonocatalytic, methylene blue.

1. Introduction

Environmental pollution is a topic of interest because of its negative impact on society. Dye wastes from industrial processes, including textiles and pharmacies among others, are a particularly large source of environmental pollution. The problem of dye wastes must be overcome by using appropriate methods and technologies [1]. Methods using advanced oxidation processes (AOPs) have been widely used because they have the capacity to degrade organic compounds in solutions [2]. Sonolysis is one of the most effective AOP methods for decomposing pollutants in transparent solutions. Sonolysis uses the formation of hydroxyl radicals (•OH), which result from the splitting of water molecules using an ultrasonic wave. The formation of hydroxyl radicals by acoustic cavitation bubbles consists of three stages, i.e., formation, growth, and implosive collapse [3, 4]. In this process, increased pressure and temperature in the acoustic cavitation bubbles causes thermal dissociation within the solution to form hydroxyl radicals (•OH) and other reactive oxygen species such as •O\textsubscript{2}, •O, and •OOH, which can oxidize the organic pollutant in the solutions [5, 6]. However, the efficiency of pollutant degradation using the sonolysis process is very low due to the limited amount of •OH available upon ultrasonic


radiation. To overcome this issue, catalysts must be added to the sonolysis process, increasing the efficiency of the degradation of dye wastes [7, 8].

Metal-oxide semiconductors have attracted much attention due to their wide application to processes such as water purification, water splitting to produce hydrogen, biological and biomedical sensing, and photovoltaics among others [9]. Wang et al. [10] researched the degradation of hydrogen peroxide solutions by sonocatalyst activity of TiO$_2$, and the results showed that the semiconductor is an efficient catalyst. Zirconium dioxide (ZrO$_2$) and tin oxide (SnO$_2$) are also potentially ideal candidates for semiconductor suitable for use as catalysts due to their high photostability, high thermodynamic stability, lack of toxicity, good adsorption capacity, unique physical and chemical properties, and ease of production [11, 12]. However, the high electron–hole recombination rate of those semiconductors could limit the efficiency of degradation. Combining these semiconductors with other materials is an effective way to inhibit the electron–hole recombination rate and thus increase the efficiency of the catalyst to degrade organic pollutants in solutions [13]. Other shortcomings include the process of separating the catalyst material from the dye waste, which is still difficult, limiting the reusability of catalysts for the sonocatalytic process (recycling). Other shortcomings of ZrO$_2$ and SnO$_2$ semiconductors could be overcome by adding magnetic material such as Fe$_3$O$_4$ (magnetite). Fe$_3$O$_4$ has several advantages such as low cost, good adsorption capacity, and chemical stability in solutions [14, 15]; it also makes it possible to magnetically separate the catalyst from the solutions so it can be reused [16]. Therefore, the combination of Fe$_3$O$_4$ with SnO$_2$ and ZrO$_2$ is expected to increase the efficiency of these catalysts to degrade pollutants.

In this study, Fe$_3$O$_4$/ZrO$_2$ and Fe$_3$O$_4$/SnO$_2$ nanocomposites were prepared using the sol-gel method. The sample was characterized using X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) techniques. Sonocatalytic activity of the two nanocomposites was analyzed using methylene blue (MB) as a model organic pollutant. The sonocatalytic activity of the two nanocomposites is studied by comparing the results to the catalytic activity of other semiconductor catalysts, applied in advance.

2. Experimental

2.1. Materials

All reagents used were analytical grade and were used without further purification. Zirconium (IV) chloride (ZrCl$_4$), anhydrous tin chloride (SnCl$_2$), iron (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O), titanium dioxide (TiO$_2$), sodium hydroxide (NaOH), methylene blue (MB), ethanol, ethylene glycol (EG), ammonium oxalate, sodium sulfate, and tert-butyl alcohol (TBA) were purchased from Merck (Kenilworth, NJ, USA).

2.2. Synthesis of nanomaterials

The Fe$_3$O$_4$ nanoparticles were synthesized using the same method used in our previous study [17]. The ZrO$_2$ nanoparticles was synthesized using the sol-gel method. First, ZrCl$_4$ and NaOH were each dissolved in aqueous solutions using magnetic stirring. Then, the ZrCl$_4$ solution was mixed slowly into the NaOH solution, and the mixture was stirred using magnetic stirring at 80°C for 3 h until a homogenous solution formed. The mixture solutions were centrifuged to separate out the precipitate, which was then washed using aqueous solution and ethanol several times to remove unexpected compounds. The resulting product was heated at 120°C for 12 h. ZrO$_2$ nanoparticles were obtained by calcination for 5 h at 550°C.

The SnO$_2$ nanoparticles were synthesized using a modification of the method reported by Li et al. [18]. First, SnCl$_2$ was dissolved in a mixture of ethanol and aqueous solution, which was then added into the NaOH solutions using magnetic stirring. Then, the mixed solutions were heated at 180°C for 3 h, then chilled to room temperature. The precipitate was obtained by centrifugation and washed using aqueous solutions and ethanol several times. The precipitated particles were dried under vacuum at 80°C, and SnO$_2$ particles were obtained by calcination for 3 h at 700°C.

The Fe$_3$O$_4$/ZrO$_2$ and Fe$_3$O$_4$/SnO$_2$ nanocomposites were synthesized using the sol-gel method. First, ZrO$_2$ and SnO$_2$ nanoparticles were mixed with Fe$_3$O$_4$ in a mixture of ethanol and aqueous solution. Each mixture was ultrasonicated for 2 h and then centrifuged to obtain the precipitate. The resulting product
was then dried under vacuum at 80°C for 12 h to obtain Fe$_3$O$_4$/ZrO$_2$ and Fe$_3$O$_4$/SnO$_2$ nanoparticles. The Fe$_3$O$_4$/TiO$_2$ nanocomposites were synthesized using our previous method [19].

2.3. **Characterization**

The sample was characterized by XRD using a Rigaku Miniflex 600 (Rigaku, Tokyo, Japan) with a Cu K-α radiation source (λ =1.5406 Å), and the magnetic character of the sample was measured with an Oxford Type 1.2T VSM.

2.4. **Sonocatalytic experiments**

The sonocatalytic experiment was done by mixing each sample of SnO$_2$, ZrO$_2$, Fe$_3$O$_4$/SnO$_2$, and Fe$_3$O$_4$/ZrO$_2$ into 100 mL solutions of MB with concentrations of 20 mg/L; pH was adjusted using NaOH. The solutions were allowed to stand until reaching adsorption–desorption equilibrium. The solutions were put in an ultrasonic bath with frequency and tension of 40 kHz and 150 W, respectively, and ultrasonicated for 2 h. After every 15 min, the concentration of the MB solution was analyzed using a UV-Vis spectrometer. Sonocatalytic activity of TiO$_2$ nanoparticles and Fe$_3$O$_4$/TiO$_2$ nanocomposites were tested in the same way.

2.5. **Scavanger experiments**

Different radical-scavengers were used in MB solutions to determine the most influential species in sonocatalytic activity. Ammonium oxalate, sodium sulfate, and TBA were each used for scavenging holes, electrons, and hydroxyl radicals. The measurements were done as described above.

3. **Results and discussion**

3.1. **Structural and optical properties**

Figure 1 shows the XRD spectrum of Fe$_3$O$_4$, ZrO$_2$, and SnO$_2$ nanoparticles and Fe$_3$O$_4$/ZrO$_2$ and Fe$_3$O$_4$/SnO$_2$ nanocomposites. The diffraction pattern of the Fe$_3$O$_4$ sample observed at the values 2θ = 30.14°, 35.49°, 43.28°, 57.20°, 62.83°, and 74.8° shows each area (220), (311), (400), (511), (440), and

![Figure 1](image1.png)

**Figure 1.** XRD patterns of Fe$_3$O$_4$, ZrO$_2$, and SnO$_2$ nanoparticles and Fe$_3$O$_4$/ZrO$_2$, Fe$_3$O$_4$/SnO$_2$ nanocomposites.

![Figure 2](image2.png)

**Figure 2.** VSM spectra of Fe$_3$O$_4$, Fe$_3$O$_4$/TiO$_2$, Fe$_3$O$_4$/ZrO$_2$ and Fe$_3$O$_4$/SnO$_2$ nanocomposites.
Table 1. Lattice parameters and grain size of Fe₃O₄, ZrO₂, SnO₂ nanoparticles and Fe₃O₄/ZrO₂, Fe₃O₄/SnO₂ nanoparticles.

| Sample            | Lattice Parameter | <D> (nm) | M-S (emu/g) |
|-------------------|-------------------|----------|-------------|
|                   | Fe₃O₄             | ZrO₂     | SnO₂        | Fe₃O₄ | ZrO₂ | SnO₂ |
|                   | a=b=c             | a=b     | c          | a=b=c | a=b | c    |       |         |       |
| Fe₃O₄             | 8.36              | -       | -          | 45    | -   | -    | 82     |
| ZrO₂              | -                 | 3.60    | 5.14       | -     | -   | -    | 13     |
| SnO₂              | -                 | -       | -          | -     | -   | 38   | -      |
| Fe₃O₄/ZrO₂        | 8.37              | 3.6     | 5.14       | 25    | 13  | -    | 59     |
| Fe₃O₄/SnO₂        | 8.38              | -       | 4.76       | 28    | -   | 21   | 62     |

Figure 3. Sonocatalytic degradation (a) rate constant of all samples (b) effect of dosage nanocomposites Fe₃O₄/TiO₂, Fe₃O₄/ZrO₂ and Fe₃O₄/SnO₂.

3.2. Magnetic properties

Figure 2 shows the magnetic hysteresis curve of the Fe₃O₄/ZrO₂ and Fe₃O₄/SnO₂ nanocomposites. As a comparison, the magnetic hysteresis curve of Fe₃O₄ nanoparticles is also shown in the picture. Loop (533) of the cubic spinel structure. The diffraction pattern of the ZrO₂ sample observed at the values 2θ = 30.18°, 35.03°, 50.36°, and 59.94° shows the reflection index of each area (111), (200), (220), and (311) of the tetragonal structure of ZrO₂, while the diffraction pattern of the SnO₂ nanoparticle sample observed at the values 2θ = 26.5°, 33.8°, 38°, 39°, 51.8°, 54.8°, 58°, 62°, 64.7°, 65.8°, 71.2°, 78.2°, 81.2°, and 83.7° shows the existence of areas (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202), (321), (400), and (222) of the tetragonal structure of SnO₂ nanoparticles. The XRD patterns of Fe₃O₄/ZrO₂ and Fe₃O₄/SnO₂ nanocomposites show the existence of the cubic spinel phase of Fe₃O₄, followed by the addition of tetragonal SnO₂ and ZrO₂ phases for Fe₃O₄/SnO₂ and Fe₃O₄/ZrO₂ nanocomposites. The grain size was calculated using Scherrer’s equation and lattice parameters were calculated using the Rietveld refinement method. The results are shown in table 1.
Table 2. Rate constants and maximum sonocatalytic degradation of MB in presence of prepared samples.

| Samples          | Rate constant (min⁻¹) | Maximum Degradation (%) |
|------------------|-----------------------|--------------------------|
| TiO₂             | 0.01088               | 72.01                    |
| Fe₃O₄/TiO₂       | 0.01206               | 76.75                    |
| ZrO₂             | 0.01163               | 74.75                    |
| Fe₃O₄/ZrO₂       | 0.01318               | 80.29                    |
| SnO₂             | 0.01205               | 77.19                    |
| Fe₃O₄/SnO₂       | 0.01427               | 83.50                    |

Figure 4. (a) Effect of scavenger, (b) Reusability of Fe₃O₄/ZrO₂ and Fe₃O₄/SnO₂.

hysteresis of the Fe₃O₄ nanoparticle and both nanocomposites shows ferromagnetic behavior at room temperature with magnetization saturation (Mₛ) of 82, 62, and 59 emu g⁻¹ for Fe₃O₄, Fe₃O₄/SnO₂, and Fe₃O₄/ZrO₂, respectively. The magnetization saturation of Fe₃O₄/ZrO₂ and Fe₃O₄/SnO₂ nanocomposites is smaller than that of the Fe₃O₄ nanoparticles. This is due to the addition of non-magnetic materials ZrO₂ and SnO₂ nanoparticles, which decreases the total magnet moment in the sample. If it is compared with the magnetic characteristics of Fe₃O₄/TiO₂ nanocomposite from previous research [20], as shown in figure 2, it can be seen that the magnetization saturation of Fe₃O₄/TiO₂ nanocomposite is higher than that of both Fe₃O₄/ZrO₂ and Fe₃O₄/SnO₂ nanocomposites.

3.3. Sonocatalytic activity

The results of sonocatalytic activity for all samples are shown as degradation rates and %degradation of methylene blue. The degradation rate of methylene blue in the sonocatalytic process was calculated using the kinetics equation ln(Cₜ/C₀) = -kt, where k is the pseudo-first-order rate constant, C₀ is the initial concentration of MB, and Cₜ represents MB concentration at time t. The degradation efficiency of the samples was calculated using the equation %Degradation = 100 × (1 - Cₜ/C₀). Figure 3a shows the degradation rate of methylene blue through the sonocatalytic process. The result obtained shows that ZrO₂ nanoparticles and SnO₂ show a slower degradation rate than do Fe₃O₄/ZrO₂ and Fe₃O₄/SnO₂ nanocomposites; the rate constants and maximum degradation are shown in table 2. The sonocatalytic activity test was also done for TiO₂ nanoparticles and Fe₃O₄/TiO₂, as shown in figure 3a. The Fe₃O₄/ZrO₂ and Fe₃O₄/SnO₂ nanocomposites show better results for MB degradation capacity than do TiO₂ nanoparticles and the Fe₃O₄/TiO₂ nanocomposite. This is because the energy band gap of TiO₂ (~3.2 eV) is smaller than those of SnO₂ (~3.8eV) and ZrO₂ (~5eV), so the lifetime of generated electron–hole
pairs increases and the recombination rate of electrons and holes decreases [21]. The sonocatalytic activity capacity of all nanocomposite samples compared to nanoparticles could be caused by the increased efficiency of separating electron–hole pairs on the nanocomposite [22]. The order of sonocatalytic activity efficiency based on test results is $\text{Fe}_2\text{O}_3/\text{SnO}_2 > \text{Fe}_2\text{O}_3/\text{ZrO}_2 > \text{SnO}_2 > \text{Fe}_2\text{O}_3/\text{TiO}_2 > \text{ZrO}_2 > \text{TiO}_2$.

3.4. Effect of catalyst dosage

Figure 3b shows the effect of catalyst dosage addition, $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ and $\text{Fe}_2\text{O}_3/\text{SnO}_2$ nanocomposites from 0.1 g/L to 0.4 g/L, on the efficiency of degradation of methylene blue through the sonocatalytic process. As seen in figure 3b, after 120 min, the maximum degradation for $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ with dosages of 0.1 g/L, 0.2 g/L, 0.3 g/L, and 0.4 g/L are 68.25%, 76.19%, 80.29%, and 72.19%, respectively, while for $\text{Fe}_2\text{O}_3/\text{SnO}_2$ with dosages of 0.1 g/L, 0.2 g/L, 0.3 g/L, and 0.4 g/L the maximum degradations are 72.19%, 80.04%, 83.5%, and 75.83%, respectively. The maximum degradation for both samples occurred with the addition of a dosage of 0.3 g/L. The catalyst dosage was also varied for the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite (figure 3b), which resulted in maximum degradations for dosages of 0.1 g/L, 0.2 g/L, 0.3 g/L, and 0.4 g/L, respectively, of 61.4%, 73.77%, 76.75%, and 69.72%. The maximum degradation for $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite was similarly produced at a catalytic dosage of 0.3 g/L. The amount of nanocomposite added influences two things: the number of active sites on the sample and the amount of methylene blue adsorbed by the sample [23]. The dosage of the added catalyst will also increase the number of active sites. The results shown in figure 3b indicate that the optimum catalyst dosage for the nanocomposite sample is 0.3 g/L.

3.5. Effect of scavengers

To determine the reactive species most involved in MB degradation in the three samples, scavengers were added to the solutions. Figure 4a shows the results of MB degradation by sonocatalysis with the addition of scavengers. The scavengers serve to bind the reactive species so that they cannot take part in the sonocatalytic process. The obtained results show that the addition of hole scavengers resulted in the greatest decrease in degradation capacity. This indicates that holes are the most influential reactive species for the three samples.

3.6. Reusability

Cycling testing was carried out to analyze catalyst stability. The cycling test was done by reusing the catalyst four times for the sonocatalytic process. After each test, the sample was separated from its solutions using an external magnet as shown in figure 4b and then reused as the catalyst in the next experiment. Figure 4b shows the results of the reusability tests for the three samples. The three samples all showed good cycling capacity, with decreases of only about 6% after three reuses. This proves that sonocatalytic activity for the three nanocomposite samples is stable.

4. Conclusions

The addition of the magnetic material $\text{Fe}_2\text{O}_3$ to ZrO$_2$ and SnO$_2$ catalysts has been successfully carried out using the sol-gel method. The addition of $\text{Fe}_2\text{O}_3$ has been shown to increase the capacity of sonocatalysis to degrade methylene blue. Using magnetic material also aids the separation of catalyst material from the test solution, allowing reuse of the catalysts.

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