Efficient photo-, sono-, and sonophoto-fenton-like degradation of the organic pollutant methylene blue using a BiFeO$_3$/graphene composite

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Abstract. In this study, we investigated the degradation of the organic pollutant methylene blue (MB) using photo-, sono-, and sonophoto-fenton processes under visible light, ultrasonic irradiation, and a combination of the two, respectively, in the presence of an iron-containing perovskite catalyst BiFeO$_3$/graphene composite. The sample structure was characterized using X-ray diffraction; thermal analyses were performed using thermogravimetric analysis and differential thermal analysis; and the BiFeO$_3$/graphene composite was prepared using a hydrothermal method. We observed better MB degradation via the BiFeO$_3$/graphene composite using the sonophoto-fenton method relative to either the photo- or sono-fenton methods, with increased MB degradation occurring through the synergistic effects of both the photo- and sono-fenton techniques. Furthermore, addition of a chelating agent, such as ascorbic acid, to the photo- and sono-fenton reactions enhanced MB degradation.

1. Introduction

Advance oxidation processes (AOPs) capable of generating strongly oxidizing hydroxyl free radicals are among the most important processes necessary for decomposing organic pollutants such as methylene blue (MB). AOPs offer several advantages in terms of degrading organic pollutants into a final mineralized form through the production of a hydroxyl free radical (OH). Among the available AOPs, fenton-like degradation is based on the electron transfer between H$_2$O and a transition metal ion acting as a catalyst and is capable of generating strongly oxidizing OH in the presence of H$_2$O [1,2].

However, fenton-like degradation has several limitations owing to the limited pH range of the reaction, ion sludge, and difficulty in regenerating the catalyst [3,4]. The classic fenton process requires a low pH (3.0) because of the presence of ion sludge at higher pH levels. The limitations of using fenton-like degradation to decompose organic pollutants can be overcome using heterogeneous catalysts. Furthermore, chelating agents such as ascorbic acid can be used to prevent the formation of ion sludge at higher pH levels [5].

H$_2$O in the fenton reaction is activated under ultraviolet light and ultrasonic irradiation; therefore, initiation of the fenton reaction in the presence of visible light irradiation requires a new catalyst with a narrow band gap [6]. Recently, increasing attention has focused on the perovskite catalyst BiFeO$_3$ because of its narrow band gap. BiFeO$_3$ is a multiferroic material that exhibits ferroelectric (Tc = 1103) ordering and antiferromagnetic (TN = 643 K) ordering in the bulk form and has been applied in several catalytic processes owing to its good catalytic performance. However, limitations to its wider application include its rapid electron–hole recombination. Graphene material is two-dimensional and includes a carbon atom with a large surface area, high electron mobility, and good electrical
conductivity. There is great interest in graphene material because it can be used as an electron trap, which promotes MB degradation. In this study, we investigated the fenton-like degradation of MB using BiFeO/graphene under visible light, ultrasonic irradiation, and a combination of the two.

2. Experimental details

2.1. Chemicals

All reagents were analytical grade and commercially available from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO). The reagents used to synthesize the BiFeO/graphene composite were bismuth(III) nitrate (Bi(NO$_3$)$_3$×5H$_2$O; 99% purity; Sigma-Aldrich), iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$×9H$_2$O; 99% purity; Merck), and potassium hydroxide (KOH; 99% purity; Merck).

2.2. Characterization

The crystallite structure of the sample was investigated using X-ray diffraction (XRD; Rigaku Miniflex 600; Rigaku, Tokyo, Japan), and the thermal stability of the sample was characterized using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using a Rigaku TGA8121 device (Rigaku). The sample was heated from room temperature to 1000 °C at a rate of 2 °C/min, with a flow of argon maintained during analysis.

2.3. Catalyst preparation

The BiFeO nanoparticle was synthesized using a hydrothermal method. Equimolar amounts of Bi(NO$_3$)$_3$×5H$_2$O and Fe(NO$_3$)$_3$×9H$_2$O were stirred using a magnetic stirrer, and KOH solution was added dropwise. The mixed solution was transferred to a 25-mL stainless steel autoclave, and hydrothermal treatment was performed at a reaction temperature of 180 °C for 6 h, after which the product was centrifuged and dried at 120 °C for 3 h. The BiFeO/graphene composite was also synthesized using a hydrothermal method by adding a specific weight percentage of graphene during the process, with the reaction temperature maintained at 120 °C for 12 h in a 100-mL stainless steel autoclave.

2.4. Photo- and sono-fenton degradation

The photo-fenton reaction was conducted using a 100-mL glass vessel equipped with a magnetic stirrer and a 40-W Xe lamp used as the light source. The sono-fenton reaction was performed in an ultrasonic bath operated at a fixed frequency and power of 40 kHz and 150 W, respectively. The sonophoto-fenton reaction used a combination of the 40-W Xe lamp and the ultrasound source. All three fenton reactions were initiated by the addition of hydrogen peroxide (H$_2$O$_2$; 1–4 mL), prior to which the pH of the solution was adjusted from 3 to 11 by adding NaOH and CH$_3$COOH. The catalyst was added to the dye solution at a range of 0.1–0.4 g/L, with the initial dye concentration at 20 mg/L.

3. Results and discussion

The XRD patterns of the BiFeO, nanoparticle and the BiFeO/graphene composite harboring different weight percentages of graphene are shown in figure 1. The BiFeO/graphene composite displayed a rhombohedral structure representing the BiFeO nanoparticle, whereas the peak designating the graphene in the BiFeO/graphene composite could not be identified by XRD. To identify and characterize the crystal parameters of the BiFeO nanoparticle and the BiFeO/graphene composite, we used a Williamson–Hall plot. The average size of the BiFeO crystal was 40 nm. The addition of graphene resulted in a smaller BiFeO crystal size (table 1, column 3), which agreed with a previous study reporting that the addition of graphene inhibits the growth of a BiFeO-nanoparticle crystal [7].

We used TGA to characterize sample stability following heating from room temperature to 1000 °C and to confirm the presence of graphene material in the BiFeO/graphene composite, given that its presence could not be confirmed by XRD. TGA, as shown in figure 2a, indicated that the weight loss in the BiFeO/graphene composite occurring from room temperature to 150 °C was associated with the removal of adsorbed water, whereas the weight loss occurring at 400 °C was associated with the combustive effect of the graphene material in the BiFeO/graphene composite [8]. Additionally, DTA, as shown in figure 2b, indicated that the BiFeO/graphene composite exhibited exothermic properties at ~380 °C, with the total heat flow of the graphene material during the exothermic process on the quality of the graphene material on the BiFeO/graphene composite by calculating the I:D:L ratio, as presented in table 1.

| Table 1. Lattice parameter, crystallite structure, and heat flow |
of the BiFeO₃ nanoparticle and BiFeO₃/graphene composite

| Sample                          | Lattice parameter, BiFeO₃ | <D> BiFeO₃ | Heat flow (µV/s/mg) |
|--------------------------------|---------------------------|------------|--------------------|
| BiFeO₃                          | a (Å); b (Å); c (Å)        | 5.58; 13.88; 40 | —                  |
| BiFeO₃/1 wt% graphene           | a (Å); b (Å); c (Å)        | 5.58; 13.88; 39 | 123                |
| BiFeO₃/3 wt% graphene           | a (Å); b (Å); c (Å)        | 5.58; 13.88; 37 | 520                |
| BiFeO₃/5 wt% graphene           | a (Å); b (Å); c (Å)        | 5.58; 13.88; 35 | 988                |

**Figure 1.** XRD pattern of the BiFeO₃/graphene composite.

**Figure 2.** (a) TGA and (b) DTA of the BiFeO₃/graphene composite.

We then used Raman spectroscopy to identify graphene material on the BiFeO₃/graphene composite according to the presence of a D band (1352 cm⁻¹) and a G band (1595 cm⁻¹). We also used this technique to analyze the quality of the graphene material on the BiFeO₃/graphene composite by calculating the I_D/I_G ratio, as presented in table 1.
Figure 3. Raman spectra of the BiFeO/graphene composite.

Figure 4. Effects of (a) different H$_2$O$_2$ concentrations and (b) catalyst doses on MB degradation using the BiFeO/graphene composite.

We then evaluated the effect of pH on each respective fenton reaction (sono-, photo-, and sonophoto-fenton), because this parameter is among the most important influencers of fenton degradation. MB degradation using the BiFeO/graphene composite was performed at a pH range of 3–11, indicating good results at pH 3 and a decreased degradation efficiency as the pH increased, as shown in figure 3. We attributed this result and our observation of bubbles during the reaction to the elevated O$_2$ production from the self-decomposition of H$_2$O$_2$[9,10]. Additionally, the higher oxidative capacity might be attributable to the higher concentration of OH produced under acidic conditions. Furthermore, our assessment of the initial dye concentration showed that a higher dye concentration decreased MB degradation.

Fenton degradation using the BiFeO/graphene composite at a catalyst dose of 0.3 g/L, a pH of 3, and an initial MB concentration of 20 mg/L showed accelerated degradation at higher H$_2$O$_2$ concentrations, as shown in figure 4 [10]. Moreover, figure 5 shows that MB degradation using the BiFeO/graphene composite under both visible and ultrasonic irradiation increased during increases in H$_2$O$_2$ concentrations from 1 to 3 mL; however, further increases in H$_2$O$_2$ from 3 mL decreased MB degradation. We attributed this to the reaction of excess H$_2$O$_2$ with OH to produce HO$_2$, which has a weaker oxidation capacity than OH [10], thereby explaining the decreased oxidation efficiency in the presence of excess H$_2$O$_2$. 

Figure 5. Effects of (a) pH and (b) initial MB concentration on MB degradation using the BiFeO$_3$/graphene composite.

We then evaluated the effects of catalyst dose (BiFeO$_3$/graphene composite; 0.1–0.4 g/L) on the fenton degradation of MB under visible light and ultrasonic irradiation. As shown in figure 4b, MB-degradation efficiency increased according to increases in the catalyst dose from 0.1 to 0.3 g/L; however, at 0.4 g/L, MB-degradation efficiency decreased, possibly due to increased turbidity at higher levels of BiFeO$_3$/graphene, which can inhibit light penetration [11]. These results suggest an optimal dose of catalyst of 0.3 g/L for subsequent experiments.

Figure 5 shows MB degradation using the BiFeO$_3$/graphene composite via fenton processes in terms of the weight percentage of graphene. In the presence of increasing amounts of graphene, we observed an increased MB-degradation efficiency based on the role of graphene as an electron trapper capable of inhibiting electron–hole recombination. Furthermore, the observed increases in MB degradation occurred up to 3 wt.% graphene, with 5 wt.% resulting in decreased MB degradation. We attributed this to excess graphene inhibiting light/ultrasound penetration [11]. On the basis of these results, we chose 3 wt.% graphene as the optimal amount.

We then investigated the effect of the chelating agent ascorbic acid on MB degradation in the presence of the catalysts, finding that the addition of ascorbic acid increased MB degradation for all the three fenton reactions using the BiFeO$_3$/graphene composite. We attributed this to the prevention of ion-sludge formation that can occur during fenton reactions. The data fitting shown in figure 6
Figure 7. Rate constants for the BiFeO/graphene composite catalyst for the photo-, sono-, and sonophoto-fenton reactions.

Figure 8. BiFeO/graphene (a) scavenging and (b) reusability.

shows that the apparent rate constant ($K_{app}$) of the different mechanisms increased in the order blank < BiFeO/graphene without $\text{H}_2\text{O}_2$ < BiFeO+$\text{H}_2\text{O}_2$ < BiFeO/3 wt% graphene < BiFeO/10 wt% graphene < BiFeO/5 wt% graphene < BiFeO/graphene+ascorbic acid. Furthermore, figure 7 shows that MB degradation increased in the order photo-fenton < sono-fenton < sonophoto-fenton, with sonophoto-fenton showing the highest rate of MB degradation due to the synergistic effect of the photo- and sono-fenton reactions.

To determine the contribution of several active species to the fenton reaction, we performed radical trapping by adding an electron scavenger (sodium sulfate), a hole scavenger (diammonium oxalate), a hydroxyl radical scavenger (tert-butyl alcohol), and a superoxide radical scavenger (benzoquinone). Figure 8a shows that the addition of various scavengers decreased MB degradation, with the hydroxyl radical scavenger being the most active species at attenuating MB degradation. Additionally, we assessed sample reusability, with figure 8b showing that MB-degradation efficiency decreased during each subsequent cycle.

4. Conclusions

The sonophoto-fenton reaction using a BiFeO/graphene composite showed the highest rate of MB degradation at pH 3, a catalyst dose of 0.3 g/L, and an initial concentration of 20 mg/L, with the addition of graphene failing to alter the crystal structure of BiFeO while also increasing the overall catalytic efficiency because of its role as an electron trapper. Furthermore, the sonophoto-fenton
reaction exhibited the highest degradation efficiency because of the synergistic effect between the photo- and sono-fenton reactions.

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