Synergistic effect of magnetite and carbonous materials incorporated with iron (III)-doped ZnO on the photodegradation of organic dyes

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Abstract. Fe-doped ZnO (Fe:ZnO) was combined with both magnetite (Fe$_3$O$_4$) and carbonous materials (graphene) using a co-precipitation method to form Fe:ZnO/G/Fe$_3$O$_4$ nanocomposites with various weight ratios (1:0, 1:0.05, 1:0.1, 1:0.3, 1:0.5, and 1:1). These nanocomposites were characterized using different methods of measurements; such as Fourier transform infrared spectroscopy to record the absorption spectra of certain functional groups, X-ray diffraction spectroscopy to identify the structure of the samples, and thermogravimetric analysis to study the loss in samples’ weight under increasing temperature. The magnetite and carbonous materials were used to support Fe:ZnO in the photodegradation of methylene blue dye, as a representation of organic dyes. The photocatalytic activity was examined under ultraviolet (UV) light irradiation. The effects of Fe:ZnO/G/Fe$_3$O$_4$ ratio, scavenger addition, and catalyst dosage on the photocatalytic activity were also studied. Finally, the reusability of the catalyst was examined and proved.

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1. Introduction
Zinc oxide (ZnO) semiconductor is considered as a heterogeneous photocatalyst that can generate electron-hole pairs (or excitons) when subjected to irradiation at certain wavelengths. However, excitons often recombine, which decreases the photocatalytic efficiency of ZnO [1]. Therefore, research should focus on extending the lifetime of excitons using several methods, such as transition metal loading [1–4] and incorporation of supporting materials [5–7]. Both methods can be simultaneously applied in the same semiconductor.

It was found that the doping of ZnO with Fe ions could increase its photocatalytic activity because it causes a decrease in the bandgap energy and formation of electron trap [1–3], which prevents the recombination of the excitons. Carbon materials can be also used to prevent the recombination of the excitons in photocatalysts by acting as an adsorbent and electron transfer bridge between the catalyst and the pollutant molecules [6,8]. Moreover, research has focused on increasing the stability and reusability of the photocatalyst by incorporating magnetic materials, such as Fe$_3$O$_4$, which enables the magnetic separation of the photocatalyst by applying external magnetic field. This is an easier method compared to filtration and centrifugation, especially when used on a large scale [7].
In this study, the characterization and photocatalytic performance of Fe:ZnO/G/FeO nanocomposites were investigated using various FeO loading. The samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) spectrometries. The photocatalytic activity was studied under ultraviolet (UV) light irradiation with methylene blue (MB) as the organic dye pollutant. The effects of the weight ratio of Fe:ZnO/G to FeO, scavenger addition, and catalyst dosage on the photocatalyst performance were observed. The reusability of the photocatalyst was also examined using it in four cycles.

2. Details of experiments

2.1. Sample preparations
Analytical grade materials were used in this study with no further purification. FeSO$_4$.7H$_2$O, ZnSO$_4$.6H$_2$O, ethylene glycol, acetate acid, and NaOH were purchased from Merck, and reduced graphene oxide was purchased from Angstrom Materials. In addition, distilled water was used in all solutions during the experiment.

First, Fe:ZnO and FeO nanoparticles were synthesized using co-precipitation and sol–gel methods, respectively, as described in the authors’ previous work [2]. Second, the Fe:ZnO/5 wt.% G nanocomposite was prepared using a hydrothermal method. In this experiment, the graphene sheet was placed in ultrasonic bath for 2 h, and then mixed with Fe:ZnO and stirred for another 2 h. Furthermore, the solution was heated for 3 h at 120 °C. It was then centrifuged and left to dry for 2 h at 100 °C. Next, the Fe:ZnO/G/FeO nanocomposites were prepared using a co-precipitation method. The Fe:ZnO/G and FeO nanoparticles were mixed in alcohol and water, respectively, and then placed in ultrasonic bath for 2 h. The following Fe:ZnO/G:FeO weight ratios were prepared: 1:0, 1:0.05, 1:0.1, 1:0.3, 1:0.5, and 1:1. The solutions were then stirred for 15 min and centrifuged. Finally, the nanocomposites were dried in an oven for 2 h at 100 °C.

2.2. Characterization
The prepared nanocomposites were characterized using several techniques. Nicolet iS5 FTIR spectrometer was used to confirm the existence of graphene and magnetite. The structure and phase of the nanocomposites were studied using XRD (Rigaku Miniflex 600) operated under 30 kV and 15 mA with CuKα ($\lambda = 1.54$ Å) as a radiation source and monitored at $2\theta = 20^\circ$–80°. The stability of the nanocomposites under elevated temperatures was examined at a temperature ranging from room temperature to 1000 °C using Rigaku Thermo Plus EVO2 TG-8121 thermogravimetric analysis/differential thermal analysis (TGA/DTA) with aluminum reference.

2.3. Photocatalytic experiment
The photocatalytic experiment was conducted at room temperature with MB as the organic pollutant in an aqueous solution at pH = 7. The catalysts were stirred with the MB solution in a beaker until the solution reaches adsorption–desorption equilibrium. Thirty minutes after finishing the stirring process, the samples were irradiated for 2 h using two Xe lamps. The degradation of MB was measured at 15-min intervals using a UV-Vis Hitachi UH5300 spectrophotometer. The effects of Fe:ZnO/F:FeO ratio, scavenger addition, and catalyst dosage were studied in the photocatalytic experiment. The reusability and adsorption process were also examined.

3. Results and discussion
FTIR spectroscopy was used to detect the vibrations of the molecules in the prepared samples. Figure 1 shows the absorption spectra of five different Fe:ZnO/G:FeO weight ratios within a wavenumber range of 500–4000 cm$^{-1}$. The figure indicates that there is an overlapping peak of Zn-O and Fe-O vibrations between 500 and 700 cm$^{-1}$ [9]. The stretching vibration of Fe-O at 590 cm$^{-1}$ [10] confirms the existence of Fe and FeO doping nanoparticles in the nanocomposites. The absorption peaks at 1200 cm$^{-1}$, 1552 cm$^{-1}$, and 1718 cm$^{-1}$, which correspond to the vibrations of C-O-H, C≡C, and C≡O, confirm the existence of carbon materials in the nanocomposites [11]. However, their effect was reduced by the increase in the FeO amount. The absorption peaks at 1728 cm$^{-1}$ and between 3000 and 3600 cm$^{-1}$ correspond to the O-H bonds in the H$_2$O molecules [7].

The structure of the samples was studied using XRD spectroscopy. Figure 2 displays the diffraction patterns of five different weight ratios of Fe:ZnO/G:FeO. The recorded spectra indicated that there were two different phases associated with each sample. The peaks denoted by # correspond to the
hexagonal wurtzite structure of ZnO at $2\theta = 31.85^\circ$, $34.50^\circ$, $36.22^\circ$, $47.57^\circ$, $56.62^\circ$, $62.89^\circ$, $66.49^\circ$, $67.95^\circ$, and $69.15^\circ$ and represent the planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively [3]. The peaks denoted by * correspond to the spinel structure of Fe$_3$O$_4$, which represent the planes (220), (311), (400), (442), (511), and (440) [10]. The amorphous peak of graphene could not be detected in the diffraction spectra because of its low concentration.

Figure 3 shows the relationship between the loss in the sample weight vs temperature of the nanocomposites within the temperature range from room temperature to 1000 °C. The depression in the curves at around 400 °C was caused by the decomposition of carbon materials from the graphene sheet [12], because Fe$_3$O$_4$ nanoparticles are known to be sufficiently stable at high temperatures [13–14]. The figure also shows that the percentage weight loss gradually decreased from 8.77 % to 3.56 % with increasing portion of magnetic material in the Fe:ZnO/G sheets. This demonstrates that magnetic materials could increase the stability of the samples at high temperature.

Figure 4 shows the degradation curves of MB. The initial concentration of MB was 30 mg/L, which was reduced by 79.86% before the addition of any magnetic material. The magnetic material, which was added at a ratio of 1:0.05, caused the MB degradation to increase to 90.10%. The combined effect of Fe$_3$O$_4$, which is known to enhance the transfer of the photogenerated electrons from the surface of
the nanocatalyst to the dye solution, and the graphene sheets, which act as electron bridges, improves the photocatalytic performance. However, increasing the FeO material caused the MB degradation to decrease; when Fe:ZnO/G:FeO ratios of 1:0.1, 1:0.3, 1:0.5, and 1:1 were used, they resulted in 74.71%, 41.21%, 34.86%, and 15.05% degradation, respectively. This can be attributed to the hindrance to light penetration into the surface of the catalyst, which is caused by the increased number of FeO nanoparticles. Therefore, the optimum Fe:ZnO/G:FeO ratio for MB degradation was determined to be 1:0.05. These results agree with those obtained in the authors’ previous work [15,16].

Several active species, such as electrons, holes, and hydroxyl radicals, play important roles in the photocatalytic activity. Sodium hydroxide, di-ammonium oxalate, and tert-butanol were added to the mixture as scavengers for electrons, holes, and hydroxyl radicals, respectively, to determine the most active species (figure 5). The addition of tert-butanol slightly decreased the MB degradation, which was further decreased by the addition of di-ammonium oxalate and sodium hydroxide. This indicates that electrons are the most active species, followed by holes and then hydroxyl radicals. The result is reasonable enough, because Fe-ion dopants act as an electron trap that prevents the recombination of photogenerated electrons and holes. The graphene sheets and magnetic material had a significant

**Figure 5.** Effect of scavenger addition on the photodegradation of methylene blue

**Figure 6.** Degradation of MB under different dosage of Fe:ZnO/G/0.05 FeO nanocomposite

**Figure 7.** Kapp histogram of MB degradation with different dosages of Fe:ZnO/G/0.05 FeO nanocomposite

**Figure 8.** Degradation percentage of MB over four cycles of reuse
synergistic effect caused by the transferring of the electrons from the catalyst surface or dopant to the solution, which proves that they also prohibit the recombination of the excitons. Finally, the electrons were used in the reduction of water molecules into radicals that cause the decomposition of MB into less toxic products.

The effect of catalyst dosage on dye degradation was studied using various catalyst concentrations (0.3, 0.5, 0.7, and 1.0 g/L). Figure 6 illustrates the results of this test, which indicate that increasing the dosage to 0.7 g/L could enhance the photocatalytic efficiency, because of the increase in active sites that interact with light and enable the adsorption of MB molecules by the graphene sheets. However, at 1.0 g/L catalyst dosage, the MB degradation started to decrease, possibly due to the light scattering effect and high solution opacity [17,18]. Therefore, the optimum dosage of the catalyst, where the maximum reduction took place, was observed at 0.7 g/L. The degradation rate/kapp (min⁻¹) was also calculated using first-kinetic order equation (Figure 7). The values obtained were 0.0039, 0.0201, 0.0839, and 0.0718 min⁻¹ with catalyst dosages of 0.3, 0.5, 0.7, 1.0 g/L, respectively.

Figure 8 shows the percentage of MB photodegradation in four cycles of using the Fe:ZnO/G/0.05 FeO catalyst. This test was performed with a catalyst concentration of 0.7 g/L. The figure indicates that the degradation percentage did not significantly decrease after four cycles of reuse, which proves the good stability of the catalyst. However, continuous reuse can reduce magnetic interaction due to weakening of magnetization.

4. Conclusions
Fe:ZnO/G:FeO nanocomposites were successfully synthesized using a co-precipitation method. Different ratios of Fe:ZnO/G:FeO were used. FTIR spectra were used to confirm the existence of FeO, and graphene. The structures of ZnO and FeO were examined using XRD, which showed that they had hexagonal wurtzite and cubic spinel structures, respectively. However, XRD spectroscopy could not detect the graphene peaks, due to its low concentration. The TGA results indicated that incorporating FeO into Fe:ZnO/G could enhance its stability at high temperatures. The photocatalytic activity was studied using UV light irradiation with MB as the organic pollutant. It was also proven that the degradation percentage did not significantly decrease after four cycles of reuse, which proves the good stability of the catalyst. However, continuous reuse can reduce magnetic interaction due to weakening of magnetization.

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