The effects of adding Ag and graphene to Fe₃O₄/TiO₂ nanocomposites on adsorptive and sonophotocatalytic capabilities

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Abstract. Fe₃O₄/TiO₂ was synthesized using the sol-gel method both with and without the addition of Ag. Fe₃O₄/TiO₂ and Fe₃O₄/TiO₂/Ag were also synthesized with added graphene by using the co-precipitation method. All the prepared samples were characterized using X-ray Diffraction (XRD), UV-Vis Absorbance, and Thermogravimetric Analysis (TGA). Furthermore, adsorptive and sonophotocatalytic capabilities were tested using a degradation of Methylene Blue (MB) as an organic dye. Sonophotocatalytic activity was measured using UV or visible light and ultrasound. It was found that Ag/Fe₃O₄/TiO₂/NGP composites have better adsorption and sonophotocatalytic capabilities than other samples. The adsorption process followed a pseudo-second-order kinetic model, with the maximum adsorption capacity being 76 mg/g. The catalyst can go through the sonophotocatalytic process for four cycles. In addition, the hole is the main active species in sonophotocatalytic activity.

1. Introduction
In recent years, the degradation of organic pollutants has received significant research attention. Organic dyes that cause damage to the environment are found often in industry—for example, Methylene Blue (MB). Several methods can be utilized to degrade organic dyes, such as the adsorption [1] and sonophotocatalytic [2] processes. The adsorption process tends to be used most often because it is cost effective, easy to administer, and relatively environmentally friendly. The method is not effective, however, if the dye has a high concentration. In such cases, the sonophotocatalytic process can be used effectively to degrade organic dye into harmless molecules.

Several metal oxides can be utilized in the sonophotocatalytic process, including TiO₂, ZnO, ZrO₂, and SnO₂. In this study, TiO₂ nanoparticles (NPs) were used due to them being cheap, environmentally friendly, and the first choice of material for photocatalytic experiments [3]. The TiO₂ NP has limitations, however, such as a wide band gap, a high recombination electron hole, and a resistance to separation from dye solutions [4]. This limitation can be overcome by utilizing methods such as incorporation with Fe₂O₃ NPs [5] or Ag NPs [6], or graphene [7]. Incorporation of Fe₂O₃ NPs enhances the magnetization of the samples, thus improving the separation process [8]. Meanwhile, the addition of Ag [9] can be used to inhibit recombination electron holes, thus rendering the material active under visible light irradiation. Ag NPs also have surface plasmons resonance (SPR), which can accelerate the separation of electron holes under visible light irradiation [9] and UV light irradiation. Here, Ag acts as an electron trap that inhibits the recombination-electron-hole rate. Coupling TiO₂ with graphene gives the material a larger surface area, which is an advantage in the adsorption process.

In this study, samples of Fe₂O₃/TiO₂ were characterized using the sol-gel method both with and without Ag. In addition, samples of Fe₂O₃/TiO₂/Ag were synthesized with the addition of graphene via
the co-precipitation method. All the prepared samples were characterized using X-ray Diffraction (XRD), UV-Vis Absorbance, Transmission electron microscopy (TEM) and Thermogravimetric analysis (TGA). Moreover, all the samples underwent the adsorption and sonophotocatalytic processes for degrading MB under UV or visible light and ultrasound irradiation. Tests for the influence of the dosage catalyst were carried out, as was the scavenger test. Lastly, in order to determine the reusability of samples in the sonophotocatalytic process, that samples underwent the cycling process four times.

2. Methods

All the chemicals and reagents used, including Iron (II) sulfate heptahydrate (FeSO₄, 7H₂O, 99%), titanium dioxide (TiO₂, 99%), silver nitrate (AgNO₃), sodium hydroxide (NaOH), ethanol, and ethylene glycol (EG), were highly pure and were purchased from Merck. The graphene (N002-PDE) was purchased from Angstron Materials.

Nanocomposites of Fe₃O₄/TiO₂ were synthesized with and without Ag using the sol-gel method. In the first step, Fe₃O₄ NPs were synthesized using the sol-gel method utilized in a previous study [10] and Ag NPs was synthesized using the microwave-assisted approach. In the next step, TiO₂ NPs were dissolved in distilled water via magnetic stirring, then Fe₃O₄ was dissolved in ethanol (with or without Ag NPs) and subsequently added to the solution at 80 °C for 2 h. Next, the solution was centrifuged and washed using distilled water and ethanol. The precipitate was dried for 24 h and then heated at 120 °C for 12 h under vacuum conditions. Finally, Fe₃O₄/TiO₂ (with and without Ag) was synthesized successfully, with a Fe₃O₄/TiO₂ molar-ratio of 1:1 and an Ag weight percentage of 25 wt.%.

Afterwards, graphene was added to the nanocomposites via the co-precipitation method in order to achieve Fe₃O₄/TiO₂/graphene and Ag/Fe₃O₄/TiO₂/graphene composites. The first step was to dissolve the graphene in ethanol and distilled water. Next, sonication of the solution took place for 2 h. The NaOH and Fe₃O₄/TiO₂ or Ag/Fe₃O₄/TiO₂ nanocomposites were dissolved in the solution via magnetic stirring for 1 h, before the solution was heated at 125 °C for 3 h. Subsequently, the solution was centrifuged and washed using ethanol and distilled water. Finally, Fe₃O₄/TiO₂/graphene and Ag/Fe₃O₄/TiO₂/graphene nanocomposites were synthesized successfully, with a weight percentage of graphene to nanocomposites of 10 wt.%.

All the samples were characterized using X-ray Diffraction (XRD Rigaku Miniflex 600), UV-Vis Absorbance (Hitachi UH-5300), and Thermogravimetric Analysis (Rigaku TG/TGA 8121) in order to determine the phases, structures, optical properties, and thermal stability of the samples.

The adsorption experiment was conducted by adding 0.3 g/L of the various samples to an MB solution with an initial concentration of 20 mg/L (via magnetic stirring in dark conditions for 4 h). Sonophotocatalytic activity was tested by degrading MB in the presence of the various samples, which were mixed in solutions under combination of UV (2 lamps, 40 W UV-C) or visible light (2 lamps, 40 W Xe-lamps), plus irradiation and ultrasound (40 kHz, power 150 W). Again, 0.3 g/L was added to an MB solution with an initial concentration of 20 mg/L, and the solutions underwent magnetic stirring in dark conditions for 30 min in order to reach adsorption-desorption equilibrium. Then, the solutions were irradiated with a combination of UV or visible light and ultrasound irradiation for 2 h. Every 15 min, a sample of the solution was collected and analyzed via UV-Vis spectrometer in the wavelength region 450-750 nm (as maximum MB intensity is observed at 644 nm).

3. Results and discussion

The structures and phases of the samples were studied using XRD. Figure 1 shows the variations in the XRD patterns for all the samples. In every case, there is a series of peaks characteristic of crystalline cubic spinel Fe₂O₄ and anatase TiO₂. In the samples with added Ag, there are also peaks characteristic of the cubic structure of Ag. In the samples with the addition of graphene, however, there is no peaks characteristic of graphene recorded. They were probably not detected by XRD due to low graphene content and weak diffraction intensity. As a result, no additional phases were detected in the samples with added graphene.

Figure 2 presents the optical absorption spectrum for all of the samples. For the samples without added Ag, there is a typical absorption peak at 200 nm. The samples with added Ag have a remarkably enhanced light-absorbance capability in the whole visible range, when compared with the samples without added Ag. The absorbance peaks at 310-600 nm in samples with added Ag can be attributed to the surface plasmon resonance (SPR) of Ag. Under visible light irradiation, SPR can enhance the process of electron-hole separation. From this figure, we can conclude that visible light responses are significantly improved with the addition of Ag.
The relative amounts of Fe$_3$O$_4$/TiO$_2$ and Ag/Fe$_3$O$_4$/TiO$_2$ NPs on graphene were determined through TGA, as were the thermal-stability properties of the samples. Figure 3 gives the TGA patterns for all of the samples. The results show that, in the samples without added graphene, the weights did not decrease. It can be concluded, therefore, that the samples are sufficiently stable at up to 1000 °C. In the samples with the addition of graphene, the thermal stability decreased after 600 °C. This can be attributed to the combustion of carbon material from graphene. The residual weight of the samples can be identified by determining the total amount of Fe$_3$O$_4$/TiO$_2$ and Ag/Fe$_3$O$_4$/TiO$_2$ in the samples.

The TEM image for the Ag/Fe$_3$O$_4$/TiO$_2$/graphene composites is given in figure 4. As the figure shows, there are fine particles dispersed in a layer. The three particles seem to be a clear indication of the existence of Ag, TiO$_2$, and Fe$_3$O$_4$ NPs. The existence of the layer form can be attributed to the presence of graphene.

Before investigating the sonophotocatalytic activity, the adsorption ability of the samples was evaluated. Figure 5 gives the adsorption capacities in relation to time. The equation for the amount of dye adsorbed at different time intervals was calculated as follows:

$$ q_t = \frac{(C_0 - C_t)V}{m} $$

where the amount of dye adsorbed per unit mass of adsorbent (mg/g) at time t is $q_t$, the concentration of dye (mg/L) at time t is $C_t$, the amount of adsorbent (g) is $m$, and the amount of dye solution is (L) $V$. 

Figure 1. XRD patterns for all the variations of composites.

Figure 2. UV-Vis Absorbance spectra for all the variations of composites.

Figure 3. TGA spectra for all the variations of composites.

Figure 4. TEM image Ag/Fe$_3$O$_4$/TiO$_2$/graphene
As early as 30 min, all the samples were significantly adsorbed. After 30 min, in all the samples, the adsorption capacity reached the equilibrium stage. The adsorption capacity in the samples with added graphene increased more gradually than in the samples without added graphene. It was found that the Ag/FeO/ TiO2/graphene samples have the best adsorption capacity of all the samples, at 63 mg/g. In adsorption, kinetic studies are necessary in order to determine the adsorption mechanism. In order to evaluate and further interpret the adsorption kinetics of MB in the composites in this study, the pseudo-first-order, pseudo-second-order, and intra-particle-diffusion models described by equation (2) and equation (3) were applied [11]. The pseudo-first-order kinetic model can be described as follows:

\[ \ln(q_e - q_t) = \ln q_e - K_1 t \]  

(2)

while the pseudo-second-order kinetic model is described as below:

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  

(3)

In these equations, \( q_e \) and \( q_t \) represent the adsorption capacity at equilibrium and time \( t \), respectively, while \( K_1 \) is the pseudo-first-order rate constant (min\(^{-1}\)) and \( K_2 \) is the pseudo-second-order rate constant (g mg\(^{-1}\) min\(^{-1}\)). Figure 6 and figure 7 show the plot of pseudo of first and second order rate constant for
Figure 8. Sonophotocatalytic activity for all the variations of composites using a combination of UV/Visible and ultrasound irradiation.

Figure 9. Effects of the addition of different scavengers on the sonophotocatalytic activity of Ag/Fe_3O_4/TiO_2/graphene.

Figure 10. The effects of reusing Ag/Fe_3O_4/TiO_2/graphene on sonophotocatalytic activity.

From the data, it is clear that all samples follow the pseudo-second-order kinetic reaction, with an R^2 of about 0.99. This suggests that the adsorption of MB occurs through surface exchange until active sites are occupied. When using the pseudo-first-order kinetic reaction, the R^2 is only about 0.87.

Figure 8 depicts the sonophotocatalytic activity for all the samples, as prepared under UV or visible light and ultrasound (US) irradiation and through the degradation of MB for 2 h. From the figure, we can see that, with the addition of Ag, sonophotocatalytic performance can be enhanced via visible light and US irradiation. This can be attributed to the SPR of Ag in composites active under visible light irradiation. In UV light irradiation, the role of Ag in the samples is electron trapping. It was also found that the incorporation of graphene in Fe_3O_4/TiO_2 and Ag/Fe_3O_4/TiO_2 could enhance sonophotocatalytic performance because graphene acts as an electron trapper, inhibiting recombination electron holes. Ag/Fe_3O_4/TiO_2/graphene composites display better sonophotocatalytic performance than the non-graphene samples, with 100% degradation of MB at 75 min. Based on these findings, the Ag/Fe_3O_4/TiO_2/graphene composites were used for the scavenger and sample-reusability tests.

In order to determine the mechanism behind sonophotocatalytic activity, the effect of the addition of scavengers was evaluated. The degradation of MB in the presence of tert-butyl alcohol, Na_2S_2O_8, and ammonium oxalate (which are scavengers for hydroxyl radical, electrons, and holes, respectively), is plotted in figure 9. The data indicates that the addition of the hole-scavenger ammonium oxalate
inhibits the sonophotocatalytic degradation of MB. It can be suggested here that the hole is the main active species in sonophotocatalytic activity.

The reusability of catalysts in sonophotocatalytic activity was measured via a four–time cycling process. For each cycle, fresh MB with same concentration was used. The reusability results are shown in figure 10. After four cycles, the catalyst still demonstrated good sonophotocatalytic performance, with just a slight decline in the MB degradation rate (about 3–4 %). It is concluded that the catalyst remains stable after being re-used in a four-time cycling process.

4. Conclusions

This study has reported on the influence of adding Ag and graphene to FeO/TiO2 nanocomposites on adsorption and sonophotocatalytic activity when degrading MB. Samples with and without Ag were synthesized by using the sol-gel method, while samples with added graphene were synthesized via the co-precipitation method. All the prepared samples were characterized using XRD, UV-Vis Absorbance, and TGA. An analysis of the results of the adsorption and sonophotocatalytic activity experiments indicates that the addition of Ag and graphene can enhance both adsorption capacity and sonophotocatalytic activity. It was determined that Ag/FeO/TiO2/graphene composites have the best adsorption capacity and sonophotocatalytic performance. The main active species in sonophotocatalytic activity is the hole. After a four-time sonophotocatalytic-activity cycling process, the sample remained stable.

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