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Preparation of Ag/Fe_3O_4/graphene composites for wastewater removal via the photo-Fenton reaction

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Preparation of Ag/Fe_3O_4/graphene composites for wastewater removal via the photo-Fenton reaction

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Abstract. In this study, Ag/Fe_3O_4/graphene composites were used as catalysts for the removal of wastewater via the photo-Fenton reaction. The Ag/Fe_3O_4/graphene composites were successfully synthesized by the hydrothermal method. The Ag content was varied from 15 and 25 wt%. The structural properties of the samples were investigated by X-ray diffraction and Raman spectroscopy, and their magnetic properties were examined using a vibrating sample magnetometer. Structural analysis revealed the presence of an inverse-cubic spinel structure corresponding to Fe_3O_4 and a cubic structure corresponding to Ag. The presence of graphene was confirmed by the presence of the D- and G-bands at 1300 and 1500 cm^{-1} in the Raman spectra, respectively, and the magnetic properties of the samples indicated that Ag/Fe_3O_4/graphene exhibits a ferromagnetic behavior at room temperature. The photo-Fenton reaction was examined in terms of the degradation of methylene blue from an aqueous solution. Control experiments were carried out to investigate the effects of the H_2O_2 content and solution pH. The maximum degradation of methylene blue was observed with 4 mL of H_2O_2 and at pH 13, reflecting that Ag/Fe_3O_4/graphene composites demonstrate promise for wastewater removal via the photo-Fenton process.

Keywords: surface phenomena, thermal analysis, composites, X-ray analysis

1. Introduction

Organic pollutants in wastewater are not only toxic but also recalcitrant [1]. Thus, these pollutants adversely affect the environment, mainly aquatic life and human health [1]. Therefore, it is imperative to develop an effective method to minimize and even remove organic pollutants from the environment. In this regard, advanced oxidation processes (AOPs) have been reported as technologies that appears to the efficiently eliminate organic pollutants, has high chemical stability and low biodegradability [2]. Among different AOPs, the photo-Fenton-like reaction has been emphasized because it can produce a high number of oxidative species such as hydroxyl radicals (OH) to accelerate the reaction [3].

Typically, iron oxides are used as Fenton-like catalysts because of their cost-effectiveness and relatively high activity [4]. Among iron oxides, magnetite (Fe_3O_4) has attracted the maximum attention [5]. Fe_3O_4 includes Fe^{2+} in its crystal structure (octahedral sites), which is crucial in Fenton reactions [6]. Moreover, Fe_3O_4 can be easily recovered from solution because of its magnetism, which is crucial for practical applications. However, Fe_3O_4 nanoparticles are limited because of rapid aggregation,

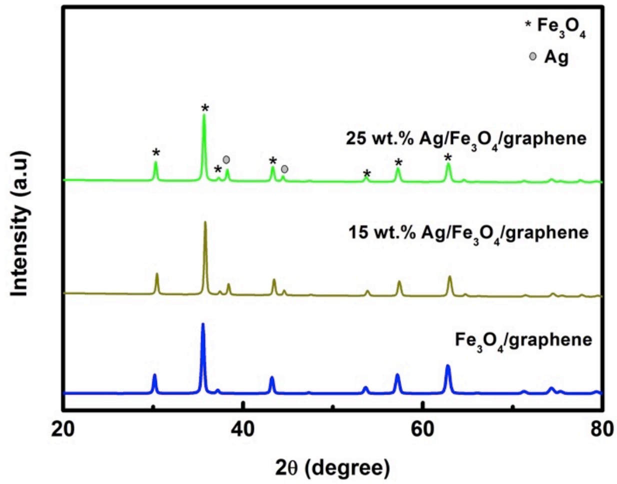

Figure 1. XRD spectra of Ag/Fe_3O_4/graphene composites with different weight percentages of Ag.

which hinders the efficiency of the photo-Fenton reaction. An effective strategy to improve the catalytic activity of Fe_3O_4 involves the formation of composites with metals [7], metal oxides [8], and carbon materials [9].

Therefore, in this study, Fe_3O_4 decorated with Ag and graphene materials was prepared to improve the catalytic activity of Fe_3O_4 materials, and the efficiency as a catalyst for the photo-Fenton reaction was investigated using model organic pollutant, methylene blue. In addition, the effects of the Ag and H_2O_2 contents were investigated.

2. Materials and methods

In the synthesis, $Fe(SO)_4 \cdot 7H_2O$ (iron sulfate heptahydrate), $AgNO_3$ (silver nitrate), NaOH (sodium hydroxide), and CH_3COOH (acetic acid) were purchased from Merck Chemicals and graphene was purchased from Angstron Materials. These materials were used without further purification.

Fe_3O_4 and Fe_3O_4/graphene composites were prepared according to a method reported previously by our group [10]. Ag nanoparticles were synthesized by the microwave-assisted method, and Ag/Fe_3O_4/graphene was synthesized by the hydrothermal method, as well as Fe_3O_4/graphene. First, graphene powder was dispersed into a solution, which is a mixture of alcohol and water. Second, graphene that has been dispersed is then sonicated using ultrasonic bath (frequency of 40 kHz) for 2 h. Third, the graphene dispersion added with nanoparticles Ag and Fe_3O_4 then stirred for 30 minutes. The mixture was heated for 30 min at a temperature of 120 °C, so that Ag and Fe_3O_4 can be deposited on graphene sheets.

All of the prepared samples were characterized by X-ray diffraction (Rigaku MiniFlex 600) operating at 30 kV and 15 mA with Cu-ka as the irradiation source. Thermogravimetric and differential thermal analysis was carried out on a Rigaku Thermo-Plus Evo TG8120, which was operated from room temperature to 100 °C under Ar. Vibrating Sample Magnetometer Oxford Type 1.2 T was used for measuring the magnetic hysteresis of the samples. UV–Vis measurement was carried out using a UV–Vis Hitachi UH5300 system.

The Fenton and photo-Fenton reactions were investigated by the degradation of methylene blue, serving as the model pollutant, from an aqueous solution. Typically, 100 mL of 20 mg/L of methylene blue was first stirred then kept for 30 min in the dark until equilibrium of adsorption–desorption was reached. Second, H_2O_2 was added into the solution, and the 40-W UV-C lamp was turned on. Degradation was monitored every 15 min and analyzed by UV–Vis spectroscopy. In this experiment, the effects of pH and H_2O_2 content were investigated.

3. Results and discussion

Figure 1 shows the X-Ray Difrraction (XRD) spectra of Ag/Fe_3O_4/graphene composites with different weight percentages of Ag. For comparison, the XRD pattern of Ag, Fe_3O_4, and graphene were also

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Table 1. Lattice parameters and grain size of Ag/Fe_3O_4/graphene composites

Samples	Lattice parameters		Grain size	
	Ag	Fe_3O_4	Ag	Fe_3O_4
	a = b = c	a = b = c		
Fe_3O_4/graphene	-	8.332		39
15 wt% Ag/Fe_3O_4/graphene	4.0771	8.334	20	38
25 wt% Ag/Fe_3O_4/graphene	4.0777	8.346	22	38

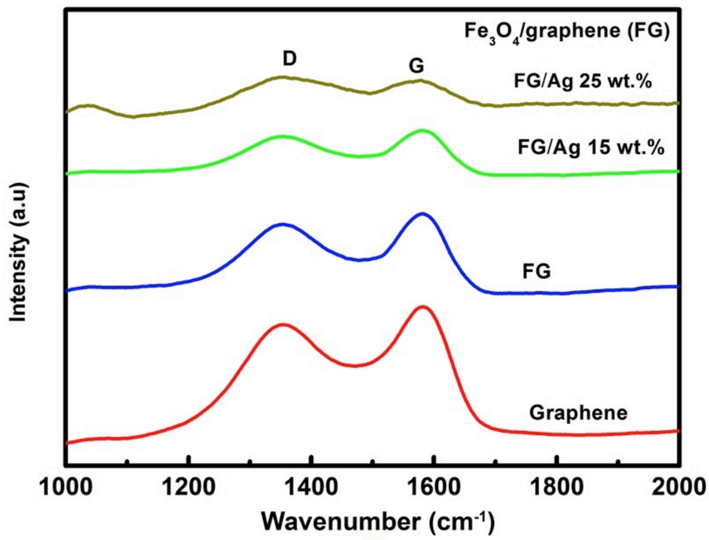

Figure 2. Raman spectra of the Ag/Fe_3O_4/graphene composites with different weight percentages of Ag.

recorded. The XRD pattern of Ag/Fe_3O_4/graphene composites revealed several diffraction peaks at 2θ ≈ 30.14°, 35.49°, 43.28°, 53.76°, 57.20°, and 62.83°, corresponding to the (220), (311), (400), (442), (511), and (440) planes of the cubic spinel structures related to Fe_3O_4 nanoparticles. An additional peak was observed at 2θ ≈ 44.10°, corresponding to the presence of Ag nanoparticles. Peaks corresponding to graphene were not detected, probably related to the low amount of graphene in the samples. Table 1 summarizes the results of the grain size of the samples and also lattice parameters obtained from the Rietveld refinement and Debye–Scherrer equation. The lattice parameters of Ag in the Ag/Fe_3O_4/graphene composites were not significantly different from those of pure Ag nanoparticles (table 1). Moreover, the lattice parameters of the Fe_3O_4 nanoparticles in Ag/Fe_3O_4/graphene composites were constant, indicating that the formation of Ag/Fe_3O_4/graphene composites does not change the structural properties of single-component materials. In addition, the calculated grain sizes for the samples revealed that the grain sizes of Ag and Fe_3O_4 in Ag/Fe_3O_4/graphene do not change significantly.

The presence of graphene in the sample was identified by using Raman spectroscopy. The measurement results are shown in figure 2. The Raman spectra of Ag/Fe_3O_4/graphene showed signals at 1300 and 1500 cm^{-1}, corresponding to the vibration modes of the D- and G-bands, respectively. The D-band involves the two zones of boundary phonons, which is a second-order double resonance between nonequivalent K points of the graphene Brillouin zone (it derived from transverse optical (TO) mode) for the D-band that are related to the out-of-plane breathing mode of sp^2 atoms. The G-band was the only Raman mode observed for graphene that is related to conventional first-order Raman scattering, and was associated with doubly degenerate phonon, in-plane and zone center modes (i.e., transverse optical and longitudinal optical modes, respectively) with E_2g symmetry atoms [11]. Raman measurements confirmed the presence of graphene in the samples.

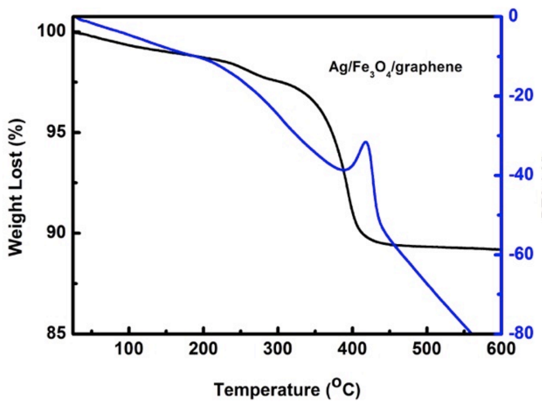

Figure 3. DTA/TGA analysis of Ag/Fe_3O_4/graphene composites.

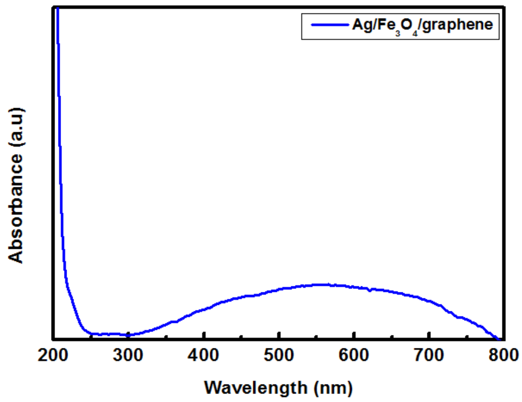

Figure 4. UV–Vis absorption spectrum of Ag/Fe_3O_4/graphene composites.

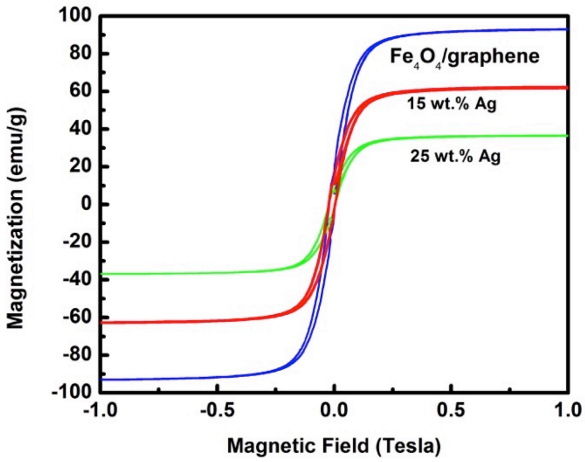

Figure 5. VSM measurement of Ag/Fe_3O_4/graphene composites.

Figure 3 plots the TGA curves of Ag/Fe_3O_4/graphene materials with two Ag concentrations. Ag/Fe_3O_4/graphene composites exhibited good thermal stability from room temperature until 400 °C. However, after 400 °C, a significant weight loss was observed, corresponding to the combustion of graphene materials. Notably, the combustion of graphene materials at 400 °C was an exothermic process. The UV–Vis absorption spectrum was recorded to identify the effect of silver nanoparticles on the optical characteristic of the samples. The UV–Vis spectrum of the Ag/Fe_3O_4/graphene composites is shown in figure 4. The UV–Vis spectrum of the Ag/Fe_3O_4/graphene composites exhibited broad absorption around the visible-light region (350–800 nm), corresponding to the presence of surface plasmon resonance (SPR) related to the silver nanoparticles [12]. Noble metal nanoparticles such as Au, Ag, and Cu show the phenomenon of SPR in the presence of electromagnetic radiation. This interesting optical property is related to the collective oscillations of conduction electrons that interact with the radiation.

Figure 5 shows the magnetic properties of the samples investigated using a VSM. All of the prepared samples exhibited ferromagnetic behavior at room temperature, with a coercive field of ~0.00136 T. With increasing Ag content, the magnetization strength gradually decreased, possibly related to the decrease in the net magnetic dipole moment of the samples in the presence of nonmagnetic materials. The high magnetization of the Ag/Fe_3O_4/graphene composites was suitable for the separation of Ag/Fe_3O_4/graphene composites from the aqueous solution by utilizing magnetic separation.

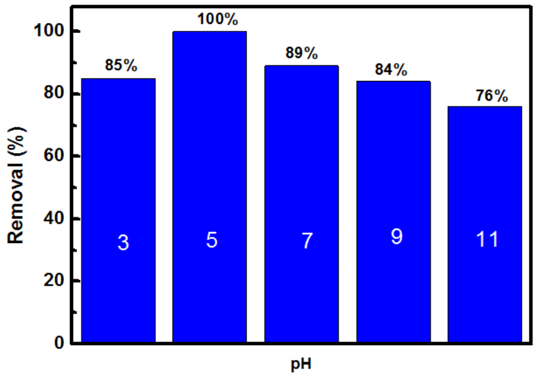

Figure 6. Effect of pH on the photo-Fenton process of Ag/Fe_3O_4/graphene.

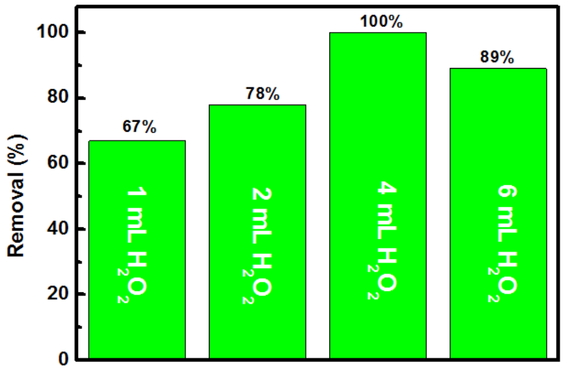

Figure 7. Effect of the H_2O_2 content on the photo-Fenton process of Ag/Fe_3O_4/graphene.

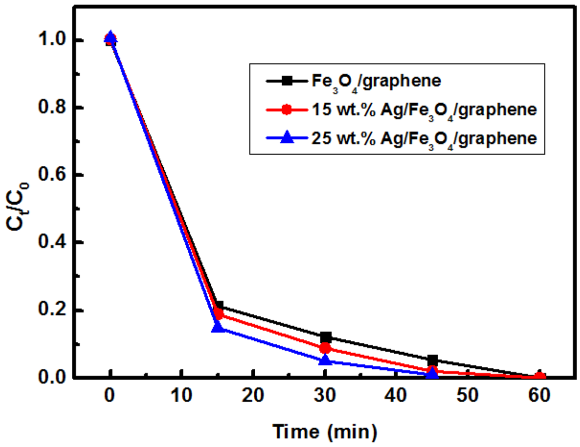

Figure 8. Effect of Ag loading on the photo-Fenton process of Ag/Fe_3O_4/graphene.

The photo-Fenton reaction was investigated at different solution pH values. The solution pH was varied from 3 to 13. Figure 6 shows the results obtained from the photo-Fenton reactions. The photo-Fenton reaction in the presence of Ag/Fe_3O_4/graphene composites was gradually enhanced with pH. From pH 3 to 5, the degradation percentages increased from 85% to 100% and then decreased thereafter. The decrease in the photo-Fenton reaction under alkaline conditions was related to the low degradation rate at high pH, which was caused by the precipitation of Fe^{3+} and the adsorption of iron hydroxides [13].

In addition, the effect of the H_2O_2 content was investigated to estimate the maximum H_2O_2 content for efficiency purposes. The H_2O_2 content was varied (1, 2, 4, and 6 mL). Figure 7 shows the results obtained for the effect of H_2O_2 on the photo-Fenton process. With the increase in the H_2O_2 content from 0 to 4 mL, the degradation ability increased.

The increased degradation ability with the increase in the H_2O_2 content from 0 to 4 mL was probably related to the increased generation of OH radicals with the increase in the H_2O_2 content. However, with the further increase in the H_2O_2 content up to 6 mL, the degradation ability decreased. The decreased degradation ability with the excessive H_2O_2 content was related to the excess H_2O_2, possibly related to the formation of undesirable hydroperoxyl radicals, but the decreased generation of hydroxyl radicals. Moreover, excess H_2O_2 also generated exuberant OH radicals, which is capable of dimerizing to form H_2O_2; which can inhibit the degradation rate of the dye due to the cumulative effects of H_2O_2.

In addition, the effect of the Ag content on the photo-Fenton reaction was investigated. Figure 8 shows the results. The addition of silver nanoparticles possibly improved the photo-Fenton reactions of Fe_3O_4/graphene, probably related to the presence of silver nanoparticles that can induce SPR, which can aid in the degradation of methylene blue from an aqueous solution. The photo-Fenton reaction mechanism of Ag/Fe_3O_4/graphene can be described as follows:

$$Ag/Fe_3O_4/graphene + h\nu \rightarrow Fe_3O_4\ (h^+) + graphene\ (e^-) + Ag\ (e^-)$$
$$O_2 + e^- \rightarrow O_2^-$$
$$H_2O_2 + O_2^- \rightarrow HO + OH^- + O_2$$
$$H_2O_2 + e^- \rightarrow HO + OH^- + O_2$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO + OH^-$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+} + HO_2 + H^+$$
$$HO + MB \rightarrow Degraded\ product$$

4. Conclusions

In this study, Ag/Fe_3O_4/graphene was successfully synthesized by the hydrothermal method. Structural properties revealed the presence of the cubic phase of Ag and the cubic spinel structure of Fe_3O_4. Raman spectra confirmed the presence of graphene, related to the detection of the D- and G-bands. The magnetic properties of the samples decreased with the incorporation of Ag nanoparticles, which was related to the decrease in the net magnetic moment of the samples. The optimum photo-Fenton process was observed under alkaline conditions with H_2O_2 content of 4 mL. The incorporation of Ag nanoparticles possibly enhanced the photo-Fenton reaction, related to the formation of surface plasmon resonance from Ag nanoparticles.

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