Fe₃O₄ hollow nanospheres on graphene oxide as an efficient heterogeneous photo-Fenton catalyst for advanced treatment of biotreated papermaking effluent

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9.

Abstract

This study focused on the feasibility of using Fe_3O_4 /graphene oxide (FGO) nanocomposites as heterogeneous catalysts for the advanced treatment of real industrial wastewater. FGO nanocomposites with different graphene oxide (GO) ratios were synthesized by co-precipitating iron salts onto GO sheets in basic solution. Characterization of the resulting material structures and functionalities was performed using a range of analytical techniques. A low GO loading afforded a good Fe_3O_4 nanoparticle dispersibility and resulted in a higher Brunauer–Emmett–Teller surface area and pore volume. The FGO nanocomposites and pure Fe_3O_4 were used to treat papermaking wastewater in a heterogeneous photo-Fenton process. The results suggested that the nanocomposite designated FGO1 (GO loading of 25 mg) exhibits a higher photocatalytic efficiency than other FGO nanocomposites and pure Fe_3O_4 . A maximum chemical oxygen demand degradation efficiency of 89.6% was achieved in 80 min with 1.5 g.L^{-1} FGO1 at pH 3. The degradation of different pollutants present in wastewater was evaluated with the aid of gas chromatography–mass spectrometry and 3D excitation–emission-matrix analysis. Inductively coupled plasma atomic emission spectroscopy and magnetic measurements confirmed that the FGO1 nanocomposites possess a low iron leachability and a high reusability. Thus, a comprehensive advanced treatment of real industrial wastewater using a magnetic FGO catalyst is demonstrated.

1. Introduction

Pulp and paper (P&P) production requires enormous amounts of fresh water and generates large quantities of heavily polluted effluents (Svensson and Berntsson 2014). The water used in P&P mills ranges from 5 to 100 m^3 per ton of paper produced, and the water consumption depends on factors such as the raw materials used, the production processes employed, and the extent of water reuse (Buyukkamaci and Koken 2010). Conventional P&P treatment processes (biological and physiochemical methods), including activated sludge processes, aerated lagoons, and biological reactors, have limited application in the case of refractory organic pollutants. Therefore, these biologically treated effluents still contain many complex structural compounds, such as lignin and its derivatives (Elnakar and Buchanan 2019; Grotzner et al. 2018; Toczylowska-Maminska 2017). To satisfy harsher environmental regulations and to avoid secondary wastewater pollution, it is necessary to search for environmentally friendly and efficient techniques for P&P industry wastewater treatment (Marques et al. 2017; Sridhar et al. 2011). In this context, the combination of biological and chemical treatment is an effective method to remove non-biodegradable and toxic substances from industrial wastewater (Abedinzadeh et al. 2018; Wang et al. 2012).

Advanced oxidation processes (AOPs) exhibit competitive potential for the non-selective degradation of pollutants (Catalkaya and Kargi 2007; Hermosilla et al. 2012; Lucas et al. 2012; Perez et al. 2002). AOPs have been introduced as pre- or post-treatment steps to eliminate bio-recalcitrant and harmful organic compounds before or after further biological treatment. The Fenton process is one of the most common AOPs used in wastewater treatment, and has the dual functions of oxidation and coagulation, which can

efficiently degrade many different compounds (Alver et al. 2015; Bianco et al. 2011). However, the homogeneous Fenton process is limited by substantial iron sludge production, a high H_2O_2 consumption, and difficult catalyst regeneration (Catalkaya and Kargi 2007; Hermosilla et al. 2012; Lucas et al. 2012). Another drawback is that the Fenton reaction is strongly dependent on pH, wherein the optimum pH is usually around 3 (Perez et al. 2002). This implies that the homogeneous Fenton process is rather inefficient within the pH range of most natural water systems (pH 5–9). Heterogeneous Fenton processes have therefore attracted widespread attention owing to their efficient elimination of recalcitrant pollutants within a wider pH range, reduced sludge formation, and significantly lower iron loss (Gonzalez-Olmos et al. 2012; Guo et al. 2013). The inverse spinel magnetite of Fe_3O_4 has been widely used in heterogeneous Fenton/photo-Fenton catalysts to degrade organic pollutants (Hu et al. 2011). The octahedral structure of Fe_3O_4 can easily accommodate both Fe^{2+} and Fe^{3+} , which implies that Fe^{2+} can be reversibly oxidized, while maintaining the structure of Fe_3O_4 unchanged (Costa et al. 2006). The Fe^{2+} present in Fe_3O_4 plays an important role in the initiation of the Fenton reaction. In addition, Fe_3O_4 can be easily separated from the reaction medium by an external magnetic field. However, several drawbacks exist in heterogeneous Fenton systems based on Fe_3O_4 nanoparticles (NPs), such as the tendency to aggregate and form large particles, specifically in the aqueous phase; this leads to the loss of dispersion and specificity, resulting in a decrease in catalyst activity and a poor adsorption (Prakash et al. 2012; Song et al. 2010; Thi Dung et al. 2011). The immobilization of Fe_3O_4 NPs on solid supports is therefore a potential method to preserve its unique catalyst properties.

Among the many available materials, graphene oxide (GO) has proved to be a suitable support material for the immobilization of NPs (Zubir et al. 2014; Zubir et al. 2015). GO has unique properties, such as a high specific surface area, a high chemical stability, and a superior mechanical strength. In particular, it disperses well in water, which can facilitate pollutant adsorption in water (Chen et al. 2020). GO has multiple oxygen-containing functional groups (epoxides, carboxyl groups, alcohols, and ketones), which can serve as activation sites for GO and metal ions to form metal oxide/graphene oxide (MO/GO) nanocomposites (Wu et al. 2014; Zubir et al. 2014). Fe_3O_4 NPs fixed on GO can prevent aggregation and consequently maintain a high surface area. The catalytic activity of GO/ Fe_3O_4 nanocomposites can also be improved through the synergistic interaction between the two components. In this context, Yu et al. (2016) used Fe_3O_4 /GO nanocomposites as catalysts, achieving phenol and total organic content (TOC) removal rates of approximately 98.8 and 81.3%, respectively. In addition, Fe_3O_4 /GO was found to cause significant degradation and adsorption of the trace BPA present in an aqueous solution through a heterogeneous Fenton reaction (Hua et al. 2014). In this case, the maximum TOC removal was 64.7% and the BPA removal reached almost 85%. Several studies have also reported the use of Fe_3O_4 /GO nanocomposites in catalysis for the reduction of Acid Orange 7 (AO7) (Zubir et al. 2014) and nitrobenzene (He et al. 2013).

Although Fe_3O_4 /GO is frequently reported for the photo-Fenton treatment of various organic pollutants, investigations of the effect of Fe_3O_4 /GO as a photo-Fenton-like catalyst for the treatment of real

industrial wastewater have rarely been reported, particularly for the treatment of complex wastewater containing complex recalcitrant organics. Herein, our work is aimed at investigating the efficiency and feasibility of $\text{Fe}_3\text{O}_4/\text{GO}$ catalysts in the advanced treatment of papermaking effluents. Magnetic nanocomposites are used to characterize the morphological, textural, and magnetic properties of $\text{Fe}_3\text{O}_4/\text{GO}$ with different GO loadings. The catalytic reactivity of $\text{Fe}_3\text{O}_4/\text{GO}$ is compared with that of other catalysts. Some important factors, including iron leaching from the support and the magnetic properties after successive reuse, are also studied. The organic components in the wastewater before and after treatment are compared by gas chromatography–mass spectrometry (GC–MS) and 3D excitation–emission-matrix (3D-EEM) analysis.

2. Experimental

2.1 Materials

Graphite powder (≥ 325 mesh) was purchased from Shanghai Aladdin Chemical Co. Ltd. (China). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was obtained from Guangdong Guanghua Sci-Tech Co. Ltd. H_2SO_4 (95–98%), H_3PO_4 , 85%, and $\text{CH}_3\text{CH}_2\text{OH}$ ($\geq 99.7\%$) were purchased from Tianjin Zhiyuan Chemical Co. Ltd. The other reagents were of analytical grade. Deionized water with a resistivity of $18.0 \text{ M}\Omega \text{ cm}^{-1}$ was obtained from a Milli-Q apparatus (Millipore, Bedford, MA, USA). The wastewater sample used for the purpose of this study was acquired from the biotreated effluent of a P&P mill (Guangxi Guitang Sugar Group Co., Ltd (Guigang, China)), with an initial pH and COD_{Cr} of 6.58 and $282 \pm 2 \text{ mg} \cdot \text{L}^{-1}$, respectively.

2.2 Preparation of the Fe_3O_4 /graphene oxide nanocomposites

GO was prepared using a modified Hummers method, following a previously reported procedure (Marcano et al. 2010). The FGO nanocomposites were synthesized via a one-pot hydrothermal process. Three different amounts (25, 75, and 125 mg) of GO were added to the flasks, and the GO mixture (60 mL) was sonicated for 2 h (Table S1). Subsequently, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (4 mmol), $(\text{NH}_2)_2\text{CO}$ (20 mmol), and $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ (12 mmol) were added to the above exfoliated GO solution, and the mixture was stirred for 12 h at room temperature (25 °C). Subsequently, of poly(acrylic acid) (0.75 mL, solid content 30%) was added to the resulting dispersion. After stirring for 30 min, the mixture was transferred to a 100 mL Teflon-lined autoclave and maintained at 200 °C for 12 h. After cooling the autoclave to room temperature, the products were washed three times with deionized water and ethanol and then dried at 60 °C in a vacuum oven. According to the GO loadings—25, 75, and 125 mg—the obtained FGO nanocomposites were designated as FGO1, FGO2, and FGO3, respectively. For comparison, pure Fe_3O_4 NPs were also prepared via an analogous method without the addition of GO.

2.3 Characterization

The X-ray diffraction (XRD) patterns of the FGO nanocomposites were acquired using a Rigaku MiniFlex600 X-ray diffractometer with Cu K α radiation, operated at 40 kV $\times$ 15 mA with 2 θ ranging from 5 to 80°. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo ESCALAB 250XI spectrometer with Al K α radiation, and C1s peaks were used as an internal reference standard calibration peak at 284.6 eV. The morphologies of the sample surfaces were characterized using field-emission scanning electron microscopy (FESEM; ZEISS SIGMA HD). Transmission electron microscopy (TEM) images were acquired on a JEOL 2010 high-resolution transmission electron microscope at an acceleration voltage of 200 kV. The magnetic hysteresis loops of the magnetic catalyst were measured using vibrating sample magnetometry (VSM, LDJ9600). The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were measured by N₂ adsorption and sorption at 77 K using a Micromeritics TriStar II 3flex automatic specific surface and porosity analyzer. The 3D-excitation-emission-matrix (3D-EEM) spectra of the experimental water samples were acquired using a Horiba FluoroMax-4 fluorescence spectrophotometer. All samples were scanned over an excitation wavelength between 220 and 440 nm and an emission wavelength between 300 and 600 nm. The COD of the water samples was measured using an ultraviolet–visible (UV–vis) spectrophotometer (Analytik Jena SPECORD 50 PLUS). GC–MS was performed using an Agilent 7890 gas chromatograph directly coupled to the mass spectrometry system of an Agilent 5977A inert MSD with a triple-axis detector. The injector temperature was 280 °C. We injected 1 μ L of the sample into the gas chromatograph and performed the analysis at a split rate of 10:1. The temperature program was as follows: 40 °C for 4 min, 10 °C/min, 180 °C for 4 min, 5 °C/min, 210 °C for 4 min, 10 °C/min, and 280 °C for 5 min. MS analysis was performed with ionization of electronic impact at 1200 V, and the spectra were recorded at intervals of 33–500 amu. Identification was performed with the aid of the NIST database library (130,000 spectra). The iron leaching concentration was measured using inductively coupled plasma atomic emission spectroscopy (ICP–AES) analysis (Thermo ICAP 6300). Magnetic measurements were made using VSM (Quantum Design MPMS-5S) at 25 °C $\pm$ 2 °C.

2.4 The heterogeneous photo-Fenton reaction

The heterogeneous photo-Fenton reaction of the biotreated papermaking effluent was carried out in a GHX-V photochemical reactor (Shanghai Jiapeng Technology Co., Ltd.). Figure 1 shows a schematic representation of the reactor set-up. The light source was a 200 W high-pressure mercury lamp (wavelength range: 350–450 nm), and the reaction temperature was adjusted to 25 $\pm$ 2 °C. In each run, wastewater (250 mL) was added to the reactor, and the initial pH of the reaction was adjusted using either a 0.1 M NaOH or a 0.1 M H₂SO₄ solution. Subsequently, the desired amount of the FGO nanocomposite and the desired volume of H₂O₂ were added to the solution (Fig. 1). The suspension was continuously stirred and exposed to light irradiation. The COD was determined by taking water samples at regular intervals. All the experiments were conducted for 180 min to investigate the effects of photocatalytic treatment. Each group of samples was run in triplicate, and the average COD was analyzed. The COD removal rate from wastewater sample (α) can be expressed in terms of the initial COD (C_0) and measured COD when sampling (C_t), as follows:

$$\alpha = (C_0 - C_t) / C_0 \times 100\% \quad (1)$$

3. Results And Discussion

3.1 Characterization of the different materials

To explore the dispersion of Fe_3O_4 particles on the GO sheets, the morphologies of GO, Fe_3O_4 , FGO1, FGO2, and FGO3 were investigated by SEM, as shown in Figs. 2a–2e. Figure 2a shows SEM images of the pure Fe_3O_4 NPs, which reveal spherical nanostructures with an average diameter of ~ 260 nm. The Fe_3O_4 NPs agglomerate in large clusters. The edges of the Fe_3O_4 NPs are black, and the central region is grayish-white, indicating that they are hollow (Fig. 2b). Figures 4c–4f show micrographs of the GO-loaded nanocomposites. Compared with pure Fe_3O_4 NPs, it is clearly observed that Fe_3O_4 NPs were deposited onto the surfaces of GO with the GO sheet as a support, and no distinct large or aggregated Fe_3O_4 NPs were observed. The Fe_3O_4 NPs fixed on GO can eliminate aggregation and exhibit an improved dispersibility compared to the pure Fe_3O_4 particles. The Fe_3O_4 nanospheres were largely wrapped by the GO sheets, revealing the tight bond between the components and the adequate flexibility of the GO sheets.

The N_2 adsorption/desorption isotherms for Fe_3O_4 and FGO are shown in Fig. 3a. The N_2 adsorption/desorption isotherms of Fe_3O_4 and FGO exhibit wide hysteresis, indicating the wide distribution of pores in these materials (Wang et al. 2013). The pore size distributions for Fe_3O_4 and FGO (Fig. 3b) were calculated from the adsorption branch using the Barrett–Joyner–Halenda (BJH) method, and the detailed texture parameters of samples are listed in Table 1. The BET surface area of Fe_3O_4 was determined to be $26.8 \text{ m}^2\text{g}^{-1}$, which is significantly lower than those of FGO1, FGO2, and FGO3 (80.4 , 87.4 , and $41.6 \text{ m}^2\text{g}^{-1}$, respectively). The pore volume and pore size values of Fe_3O_4 , FGO1, FGO2, and FGO3 were 0.07 , 0.43 , 0.10 , and $0.11 \text{ cm}^3\text{g}^{-1}$, and 3.82 , 3.83 , 3.41 , and 3.41 nm, respectively. FGO displayed a higher adsorption quantity than pure Fe_3O_4 , because GO loading helped to prevent severe aggregation in Fe_3O_4 , which is beneficial for the distribution of NPs over the GO sheets. Compared to higher GO loadings (FGO2 and FGO3), a low GO loading is more conducive to the dispersion of Fe_3O_4 NPs, which is consistent with the reduction in pore volume. Similar observations have been reported by other researchers (Zubir et al. 2014; Zubir et al. 2015).

Table 1
Texture parameters of synthetic materials

Catalysts	BET (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Pore size (nm)
Fe ₃ O ₄	26.8	0.07	3.82
FGO1	85.4	0.43	3.83
FGO2	87.4	0.10	3.41
FGO3	41.6	0.11	3.41

The XRD patterns were then measured to study the crystal phases and components of the GO, Fe₃O₄, and FGO nanocomposites, as shown in Fig. 4a. The diffraction peak of GO was located at $2\theta = 10.3^\circ$, which is a characteristic XRD peak for synthesized GO powder (Moon et al. 2010). The diffraction peaks (2θ) of Fe₃O₄ at 18.1° (111), 30.0° (220), 35.4° (311), 43.0° (400), 53.4° (422), 57.0° (511), and 62.5° (440) are consistent with the standard XRD data for cubic-phase Fe₃O₄ (JCPDS card, file No. 76-1849) (Lei et al. 2017). Compared with pure Fe₃O₄ NPs, the (111), (220), (311), (400), (422), (511), and (440) reflections for both FGO samples were identical to those of the pure Fe₃O₄ NPs. These results suggest that Fe₃O₄ nanocrystals were successfully deposited onto the surface of GO (Yu et al. 2016).

The magnetization curves of Fe₃O₄, FGO1, FGO2, and FGO3 are shown in Fig. 4b. There was no remanence or coercivity at room temperature, indicating that all exhibit superparamagnetic characteristics. The saturation magnetization of Fe₃O₄ was 60.68 emu g⁻¹, and the saturation magnetizations of FGO1, FGO2, and FGO3 were 57.73, 56.18, and 50.79 emu g⁻¹, respectively. It was therefore apparent that higher GO contents resulted in lower saturation magnetizations for the magnetic nanocomposites. This could be because of the presence of a diamagnetic GO coating on the surface of FGO and the lower content of Fe₃O₄ in FGO. Although the saturation magnetization decreased, it could guarantee the easy separation of FGO from an aqueous solution with a low magnetic field gradient (insert in Fig. 4b).

The surface compositions of the GO, Fe₃O₄, and FGO1 nanocomposites were then analyzed by XPS. The results are shown in Fig. 5, and the summarized data deduced from the respective peaks of GO, Fe₃O₄, and FGO1 are listed in Table 2. The binding energies of 284, 530, and 711 eV correspond to C 1s, O 1s, and Fe 2p, respectively.

Table 2
Contributions of individual chemical moieties in the high-resolution C 1 s, O 1 s, and Fe 2p spectra of GO, Fe₃O₄, and FGO1.

	B.E. (eV)	Moiety	GO (%)	Fe ₃ O ₄ (%)	FGO1 (%)
C 1 s	284.8	C–C	13.70	32.64	24.17
	286.28–286.54	C–O–C; C–OH	15.13	7.19	6.53
	288.29–288.6	C=O	8.42	6.00	4.82
O 1 s	529.80–529.94	Fe–O	— ^a	17.01	17.02
	531.71–531.77	Fe–O–C	— ^a	12.01	28.23
	532.58	C=O	36.26	— ^a	— ^a
	532.99–533.38	C = O; COO	26.49	5.40	11.60
Fe 2p	709.84–709.97	Fe(III) 2p _{3/2}	— ^a	3.42	1.06
	710.75–710.93	Fe(III) 2p _{3/2}	— ^a	5.63	2.44
	722.64–722.77	Fe(III) 2p _{1/2}	— ^a	4.09	1.28
	724.55–724.73	Fe(III) 2p _{1/2}	— ^a	6.61	2.85
^a Value was below the detection limit of XPS analysis.					

The C 1 s spectra of GO exhibited two main peaks at 284.8 ± 0.1 and 286.5 ± 0.3 eV, corresponding to the C–C/C=C and C–O–C/C–OH moieties, respectively. There was also a small peak at 288.8 ± 0.2 eV, which was attributed to the C=O group (Ederer et al. 2017). Compared with GO, the strength of the peak of the C–C bond increased in the case of FGO1, which was owing to the deposition of Fe₃O₄ in the GO sheet, while the intensity of the peaks corresponding to the oxygenated functional groups (C–O–C/C–OH) were reduced. These results were attributed to the deoxygenation of GO under alkaline conditions during the preparation of the FGO nanocomposites (Zubir et al. 2014).

The O 1 s spectra of Fe₃O₄ could be deconvoluted into three bands around 529.9, 531.7, and 533 eV, corresponding to the Fe–O and Fe–O–C moieties in the metal oxide and the C=O/COO groups on the surface, respectively (Qian et al. 2018). Compared with Fe₃O₄, as shown in Table 2, the C=O/COO and Fe–O–C contents of FGO1 increased from 5.40 to 11.60% and from 12.01 to 28.23%, respectively. These results indicated that GO sheets support the FGO, which was partially reduced by gradually removing oxygen-containing functional groups on the surface and edges during co-precipitation.

Figures 5(g) and 5(h) show the high-resolution Fe 2p spectra of Fe₃O₄ and FGO1. The binding energies at 711 and 725 eV can be ascribed to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively, according to the reported

literature for magnetite (Wan and Wang 2017). The Fe 2p_{1/2} spectrum could be deconvoluted into two components corresponding to Fe²⁺ (709.7 eV) and Fe³⁺ (711.1 eV), indicating two oxidation states on the surface iron species and magnetite in the materials, which further confirmed that the oxide in the sample was Fe₃O₄ (Qin et al. 2014). These results are consistent with previous studies regarding the characteristics of the Fe₃O₄ structure (Wang and Lo 2014; Yang et al. 2004).

3.2 Effect of the FGO nanocomposites on the advanced treatment of wastewater by heterogeneous Fenton-like photocatalysis

With the aim of investigating the photocatalytic activities of the FGO nanocomposites for organic pollutant degradation, we selected the biotreated effluent of a P&P mill as the substrate for photocatalytic degradation (Fig. 6a). Different catalyst types, including H₂O₂, Fe₃O₄/H₂O₂, FGO1, FGO1/H₂O₂, FGO2/H₂O₂, and FGO3/H₂O₂ systems, were employed in the dark and under UV irradiation at pH 3 (Fig. 6a).

The absorptions of the FGO1, Fe₃O₄/H₂O₂, FGO1/H₂O₂, FGO2/H₂O₂, and FGO3/H₂O₂ systems in the dark were 20.3, 5.6, 11.3, 18.5, and 19.5%, respectively, and after UV–vis irradiation for 80 min, the removal efficiencies of COD reached 34.1, 69.8, 89.6, 68.2, and 65.4%, respectively. The highest degradation rate (89.6%) was achieved by FGO1/H₂O₂ after UV–vis irradiation. This finding indicates the importance of UV–vis light irradiation in heterogeneous Fenton systems. Without H₂O₂, the absorption of FGO1 in the dark was only 20.3%, and the degradation rate of COD reached 34.1% after UV–vis light irradiation. If H₂O₂ was used alone, only 56.7% of COD was degraded. Combining UV–vis irradiation, H₂O₂, and the FGO catalysts together, the removal efficiency of COD was significantly improved. Therefore, the degradation of COD can be attributed to the synergistic effect of H₂O₂, Fe₃O₄, GO, and UV–vis irradiation. According to the Haber–Weiss mechanism, under light irradiation, the surface Fe³⁺ is recovered to Fe²⁺ by light-induced electron transfer, thereby initiating the Fenton reaction. Light irradiation can rapidly decompose H₂O₂ into hydroxyl radicals, prevent the self-recombination of hydroxyl radicals, and improve the utilization efficiency of H₂O₂ and Fe²⁺ (Wan and Wang 2017).

Figure 6a shows the effect of the GO content in the FGO nanocomposite on COD removal. When the GO content in the FGO nanocomposite was 25 mg (FGO1), the highest COD removal efficiency was achieved. With a further increase in the GO content (FGO2 and FGO3), the removal efficiency of COD decreased compared to that of FGO1. As shown in Table 1, the pore volume, pore size, and surface area of FGO1 were higher than those of the other catalysts. This indicates that the structures of the nanocomposites can affect their catalytic activities. The mechanism underlying H₂O₂ activation by FGO may therefore involve: (1) the initial formation of Fe(II)·H₂O₂ by ligand displacement between the hydrous surface of Fe(II)·H₂O and H₂O₂ (Eq. 2), or (2) Fe(II)·H₂O₂ species producing ·OH by intramolecular electron transfer; ·OH can readily degrade and mineralize organic pollution (Eq. 3) (Hua et al. 2014; Lin and Gurol 1998). In addition, a high GO loading may cause stacking of the GO sheets through π–π interactions, and an

excess of GO sheets may cover the active sites on the surface of the FGO and block the contact between the Fe_3O_4 nanospheres and H_2O_2 (Guo et al. 2015; Yu et al. 2016).

The solution pH is also known to have a significant influence on the Fenton reaction. To investigate the degradation capacity of FGO under acidic, alkaline, and neutral conditions, pH values of 3, 5, 7, and 9 were selected to evaluate the effect of pH on organic pollutant degradation. Figure 6b shows that the maximum removal efficiency of COD was achieved at pH = 3, wherein approximately 89.6% of COD removal was obtained after 80 min of photo-Fenton treatment. The removal efficiencies at pH 5, 7, and 9 were 41.3, 37.6, and 38.9%, respectively. These results indicated that the FGO catalyst could be used under neutral conditions, and so can be employed in the advanced treatment of actual industrial wastewater containing organic pollutants. Indeed, a pH of approximately 3 is known to be an optimum value for the treatment of organic pollutants in homogeneous systems, which is a similar result that obtained herein (Arnold et al. 1995). According to the Haber–Weiss circle, the formation of $\cdot\text{OH}$ from H_2O_2 is a key step in the degradation process. In this context, the generation of $\cdot\text{OH}$ on the surface of $\text{Fe}_3\text{O}_4/\text{GO}$ is gradually mitigated with increasing pH, thereby resulting in a low degradation rate of COD (Hua et al. 2014).

3.3 Recyclability and stability of the FGO nanocomposites

In heterogeneous Fenton photocatalytic reactions, the recyclability and reusability of the catalyst are important parameters for evaluating its industrial applicability. The reusability of FGO1 was examined for the degradation of organic pollutants during six-cycle experiments. Figure 7a shows that the degradation rate of COD was 90.77% in the first use, and that the degradation rate remained relatively high at 60.57% after six cycles. Compared with the fresh catalyst, the activity of the catalyst decreased slightly after six reuse cycles. Table 3 shows the saturation magnetization and iron leaching of FGO1 after the cyclic experiment. The concentrations of dissolved Fe at pH 3 were 1.14, 1.65, 1.85, and 1.95 mg L^{-1} for the fresh catalyst, and after the 2nd, 4th, and 6th reuse experiments, respectively. The magnetic power decreased slightly after successive reuses, i.e., the saturation magnetizations were 57.73, 49.74, 47.66, and 46.04 emu g^{-1} , respectively, which were sufficient to maintain the magnetic performances of the catalysts. It should also be noted here that the pH of the solution affects the dissolution of iron. More specifically, iron leaching at pH 6.8 was significantly lower than that observed under acidic conditions (pH 3; Table 3). This indicates that FGO1 is particularly stable under neutral conditions.

Table 3
Saturation magnetization and iron leaching concentration in cycle experiment (COD = 282.8 mg L⁻¹, FGO1 = 1.5 g L⁻¹, T = 25 °C, and H₂O₂ = 2.5 mL L⁻¹, time = 100 min).

Cycle number	MS (emu g ⁻¹)		Fe leaching (mg L ⁻¹)	
	pH = 3.0	pH = 6.8	pH = 3.0	pH = 6.8
0	57.73	57.73	1.14	0.01
2nd	49.74	57.68	1.65	0.05
4th	47.66	57.45	1.85	0.11
6th	46.04	57.25	1.95	0.21

3.4 Degradation of organic pollutants

GC–MS analysis can indicate changes in the organic components present in wastewater. Figure 8 shows the overlaid GC–MS chromatograms of the untreated wastewater (Fig. 8a) and the wastewater sample after heterogeneous Fenton photocatalytic treatment (Fig. 8b). The y-axis represents the abundance and the x-axis denotes the retention time. Each chromatogram peak represents an organic compound in the wastewater. It can be observed that the peak abundance of the treated wastewater is significantly lower than that of the untreated wastewater. These results indicate that there was a considerable reduction, both in the concentration of organic compounds, and in the types of compounds. Eight types of main organic compounds (confidence interval of 90%) were detected in the untreated P&P wastewater sample: butylated hydroxytoluene, o-xylene, p-xylene, 2,2,4,6,6-pentamethylheptane, 2,2-dimethyldecane, 1-iodododecane, eicosane, and 1-iodotetradecane. Six of these compounds were absent following heterogeneous Fenton photocatalytic treatment, and the remaining two substances were 2,2,4,6,6-pentamethyl-heptane and 2,2-dimethyl-decane. In addition, no new organic matter was produced during the photo-Fenton reaction.

3D-EEM analysis was then applied to analyze the organic compounds present in the wastewater. The compounds were evaluated based on the position, shift, and intensity of each fluorescence peak present in the obtained spectrum (Li et al. 2016; Meng et al. 2016). Figure 9 shows the 3D-EEM spectra of the untreated wastewater and wastewater samples after photo-Fenton treatment. Two fluorescence peaks, A and B, could be detected for the untreated wastewater sample (shown in Fig. 9a), where peak A was centered at Ex/Em = 322 nm/435 nm and is related to humic acid-like substances (Ou et al. 2014; Zhao et al. 2005), while peak B was centered at Ex/Em = 246 nm/425 nm and can be ascribed to fulvic acid-like substances (Gone et al. 2009; Matthews et al. 1996). The intensity of peak A in the untreated sample was 3.88×10^5 (a.u.), while that of peak B was 2.55×10^5 (a.u.). After the heterogeneous photo-Fenton reaction under the optimized conditions, as can be seen in Fig. 9b, the intensity of peak A decreased to 2.83×10^4 (a.u.), while that of peak B decreased to 8.5×10^3 (a.u.), indicating that the removal rate of the humic-like substance was 92.17%, while that of the fulvic-like substance was 96.67%. Hence, both humic-

like and fulvic-like substances can be effectively removed through the heterogeneous photo-Fenton reaction.

4. Conclusions

In this study, the applicability of the heterogeneous photo-Fenton process in the advanced treatment of pulp and paper wastewater with Fe_3O_4 /graphene oxide (FGO) nanocomposites was successfully evaluated. Using graphene oxide (GO) sheets as a support, a series of FGO nanocomposites with different GO contents were synthesized. FGO1, with a lower content of GO, exhibited a significantly higher photocatalytic activity than the other FGO nanocomposites and pure Fe_3O_4 . A maximum COD degradation efficiency of 89.6% was achieved after 80 min with 1.5 g.L^{-1} FGO1 at pH 3. The results of gas chromatography–mass spectrometry and three-dimensional excitation–emission matrix analysis showed that the heterogeneous photo-Fenton reaction using FGO can effectively degrade the majority of organic pollutants present in wastewater, such as humus-like substances and fulvic acids. The results of the reuse test showed that the remaining capacity of the catalyst to degrade organic pollutants after six usage cycles remained relatively high at 60%, and the catalyst maintained a high saturation magnetization after six cycles. This study demonstrates that these FGO nanocomposites exhibit outstanding catalytic performances and promising potential for the removal of organic pollutants from industrial wastewater.

Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Availability of data and materials: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests: The authors have no conflicts of interest to declare that are relevant to the content of this article.

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Figures

Figure 1

Schematic of reactor applied for heterogeneous photo-Fenton reaction

Figure 2

SEM images of Fe₃O₄ (a), GO (b), FGO1 (d), FGO2 (e), FGO3 (f), and TEM image of FGO1 (c)

Figure 3

N₂ adsorption/desorption isotherms (a) and pore size distribution (b) of Fe₃O₄ NPs and FGO

Figure 4

(a) XRD patterns of the as-prepared sample (b) magnetization hysteresis curves of the as-prepared samples (bottom inset, photographs showing sample FGO1 magnetic re-dispersion and separation).

Figure 5

Deconvoluted C 1s of GO (a), Fe₃O₄ (b) and FGO1 (c); deconvoluted O 1s of GO (d), Fe 2p (f); deconvoluted Fe 2p of Fe₃O₄ (g), FGO1 (h); Wide-scan XPS of GO, Fe₃O₄ and FGO1 (i).

Figure 6

(a) COD degradation under different reaction conditions (COD = 282.8 mg L⁻¹, catalyst = 1.5 g L⁻¹, pH 3.0, T = 25 °C, and H₂O₂ = 2.5 mL L⁻¹) (b) COD degradation with FGO1 at different pH values (COD = 282.8 mg L⁻¹, catalyst = 1.5 g L⁻¹, T = 25 °C, and H₂O₂ = 2.5 mL L⁻¹). Before initiation of the reaction, the mixture was stirred in the dark for 30 min to reach the adsorption/desorption equilibrium between the catalyst and pollutants.

Figure 7

Six cycles of degradation of COD using FGO1 (Reaction conditions: COD = 282.8 mg L⁻¹, FGO1 = 1.5 g L⁻¹, pH 3.0, T = 25 °C, and H₂O₂ = 2.5 mL L⁻¹, time = 100 min).

Figure 8

GC–MS spectra of (a) untreated wastewater and (b) wastewater after photo-Fenton treatment (COD = 282.8 mg L⁻¹, FGO1 = 1.5 g L⁻¹, pH 3.0, T = 25 °C, and H₂O₂ = 2.5 mL L⁻¹, time = 100 min).

Figure 9

3D-excitation-emission-matrix (3D-EEM) spectra of (a) untreated wastewater and (b) wastewater after photo-Fenton treatment (COD = 282.8 mg L⁻¹, FGO1 = 1.5 g L⁻¹, pH 3.0, T = 25 °C, and H₂O₂ = 2.5 mL L⁻¹, time = 100 min).

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