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

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Abstract
This study focused on the feasibility of using Fe₃O₄/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 coprecipitating iron salts onto GO sheets in basic solution. The characterization of the resulting material structures and functionalities was performed using a range of analytical techniques. A low GO loading afforded a good Fe₃O₄ nanoparticle dispersibility and resulted in a higher Brunauer–Emmett–Teller surface area and pore volume. The FGO nanocomposites and pure Fe₃O₄ 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 Fe₃O₄. 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.

Keywords Graphene oxide/magnetite composite (GO/Fe₃O₄) · Papermaking wastewater · Catalytic degradation · Advanced treatment · Photo-Fenton catalyst · Heterogeneous catalyst

Introduction
Pulp and paper production requires enormous amounts of fresh water and generates large quantities of heavily polluted effluents (Svensson and Berntsson 2014). The water used in pulp and paper mills ranges from 5 to 100 m³ per ton of the 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 pulp and paper 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 pulp and paper 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 nonbiodegradable and toxic substances from industrial wastewater (Abedinzadeh et al. 2018; Wang et al. 2012).

Advanced oxidation processes (AOPs) exhibit competitive potential for the nonselective 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 posttreatment 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 H2O2 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 Fe3O4 has been widely used in heterogeneous Fenton/photo-Fenton catalysts to degrade organic pollutants (Hu et al. 2011). The octahedral structure of Fe3O4 can easily accommodate both Fe2+ and Fe3+, which implies that Fe2+ can be reversibly oxidized while maintaining the structure of Fe3O4 unchanged (Costa et al. 2006). The Fe2+ present in Fe3O4 plays an important role in the initiation of the Fenton reaction. In addition, Fe3O4 can be easily separated from the reaction medium by an external magnetic field. However, several drawbacks exist in heterogeneous Fenton systems based on Fe3O4 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 Fe3O4 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). 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). Fe3O4 NPs fixed on GO can prevent aggregation and consequently maintain a high surface area. The catalytic activity of GO/Fe3O4 nanocomposites can also be improved through the synergistic interaction between the two components. In this context, Yu et al. (2016) used Fe3O4/GO nanocomposites as catalysts, achieving phenol and total organic content (TOC) removal rates of approximately 98.8 and 81.3%, respectively. In addition, Fe3O4/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 Fe3O4/GO nanocomposites in catalysis for the reduction of chlorpheniramine from aqueous solution (Li et al. 2017; Lin et al. 2019). Fe3O4/RGO nanocomposites possessed excellent photocatalytic performance for Cr(VI) removal and showed 97 and 76% of Cr(VI) reduction and phenol degradation, respectively (Padhi et al. 2017).

Although Fe3O4/GO displayed excellent photocatalytic activity in the degradation of pollutants, their practical application for the treatment of real industrial wastewater has rarely been reported, particularly for the treatment of complex wastewater containing complex recalcitrant organics. Herein, our work was aimed at investigating the efficiency and feasibility of Fe3O4/GO catalysts in the advanced treatment of papermaking effluents. Magnetic nanocomposites were used to characterize the morphological, textural, and magnetic properties of Fe3O4/GO with different GO loadings. The catalytic reactivity of Fe3O4/GO was compared with that of other catalysts. Some important factors, including iron leaching from the support and the magnetic properties after successive reuse, were also studied. The organic components in the wastewater before and after treatment were compared by gas chromatography–mass spectrometry (GC–MS) and 3D excitation–emission-matrix (3D-EEM) analysis.

**Experimental**

**Materials**

Graphite powder (≥ 325 mesh) was purchased from Shanghai Aladdin Chemical Co. Ltd. (China). FeCl3·6H2O was obtained from Guangdong Guanghua Sci-Tech Co., Ltd. H2SO4 (95–98%), H3PO4, 85%, and CH3CH2OH (≥ 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 MΩ 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 pulp and paper mill (Guangxi Guitang Sugar Group Co., Ltd (Guigang, China)), with an initial pH and CODCr of 6.58 and 282 ± 2 mg·L−1, respectively.
Preparation of the Fe₃O₄/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. Subsequently, FeCl₃·6H₂O (4 mM), (NH₂)₂CO (20 mM), and C₆H₅Na₃O₇·2H₂O (12 mM) were added to the above exfoliated GO solution, and the mixture was stirred for 12 h at room temperature (25 °C). Subsequently, 0.75 mL of poly(acrylic acid) (solid content 30%) was added to the resulting dispersion. The experimental parameters for the synthesis of FGO nanocomposites were shown in Table S1. 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 Fe₃O₄ nanocomposites were also prepared via an analogous method without the addition of GO.

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 setup. The light source was a 200 W high-pressure mercury lamp (wavelength range, 350–450 nm), and the reaction temperature was adjusted to 25 ± 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 (C₀) and measured COD when sampling (Cₜ), as follows:

\[
\alpha = \frac{C₀ - Cₜ}{C₀} \times 100\% \tag{1}
\]

Characterizations and chemical analysis

The X-ray diffraction (XRD) patterns of the FGO nanocomposites were acquired using a Rigaku MiniFlex600 X-ray diffractometer with Cu Kα radiation, operated at 40 kV × 15 mA with 2θ ranging from 5° to 80°. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo ESCALAB 250XI spectrometer with Al Kα 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 N\textsubscript{2} 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 μL 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 the 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 ± 2 °C.

Results and discussion

Characterization of the different materials

To explore the dispersion of Fe\textsubscript{3}O\textsubscript{4} particles on the GO sheets, the morphologies of GO, Fe\textsubscript{3}O\textsubscript{4}, FGO1, FGO2, and FGO3 were investigated by SEM, as shown in Fig. 1 a–e. Figure 1 a shows SEM images of the pure Fe\textsubscript{3}O\textsubscript{4} NPs, which reveal spherical nanostructures with an average diameter of ~260 nm. The Fe\textsubscript{3}O\textsubscript{4} NPs agglomerate in large clusters. The edges of the Fe\textsubscript{3}O\textsubscript{4} NPs are black, and the central region is grayish-white, indicating that they are hollow (Fig. 1 a). Figure 1 c–f shows micrographs of the GO-loaded nanocomposites. Compared with pure Fe\textsubscript{3}O\textsubscript{4} NPs, it is clearly observed that Fe\textsubscript{3}O\textsubscript{4} NPs were deposited onto the surfaces of GO with the GO sheet as a support, and no distinct large or aggregated Fe\textsubscript{3}O\textsubscript{4} NPs were observed. The Fe\textsubscript{3}O\textsubscript{4} NPs fixed on GO can eliminate aggregation and exhibit an improved dispersibility compared to the pure Fe\textsubscript{3}O\textsubscript{4} particles. The Fe\textsubscript{3}O\textsubscript{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\textsubscript{2} adsorption/desorption isotherms for Fe\textsubscript{3}O\textsubscript{4} and FGO are shown in Fig. S2 (a). The N\textsubscript{2} adsorption/desorption isotherms of Fe\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{4} and FGO (Fig. S2 (b)) 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\textsubscript{3}O\textsubscript{4} was determined to be 26.8 m\textsuperscript{2} g\textsuperscript{−1}, which is significantly lower than those of FGO1, FGO2, and FGO3 (80.4, 87.4, and 41.6 m\textsuperscript{2} g\textsuperscript{−1}, respectively). The pore volume and pore size values of Fe\textsubscript{3}O\textsubscript{4}, FGO1, FGO2, and FGO3 were 0.07, 0.43, 0.10, and 0.11 cm\textsuperscript{3} g\textsuperscript{−1} and 3.82, 3.83, 3.41, and 3.41 nm, respectively. FGO displayed a higher adsorption quantity than pure Fe\textsubscript{3}O\textsubscript{4}, because GO loading helped to prevent severe aggregation in Fe\textsubscript{3}O\textsubscript{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\textsubscript{3}O\textsubscript{4} NPs, which is consistent with the reduction in pore volume. Similar observations have been reported by other researchers (Zubir et al. 2014).

The XRD patterns were then measured to study the crystal phases and components of the GO, Fe\textsubscript{3}O\textsubscript{4}, and FGO nanocomposites, as shown in Fig. 2 a. The diffraction peak of GO was located at 2θ = 10.3°, which is a characteristic XRD peak for synthesized GO powder (Moon et al. 2010). The diffraction peaks (2θ) of Fe\textsubscript{3}O\textsubscript{4} 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 Fe\textsubscript{3}O\textsubscript{4} (JCPDS card, file No. 76-1849) (Lei et al. 2017).

Compared with pure Fe\textsubscript{3}O\textsubscript{4} NPs, the (111), (220), (311), (400), (422), (511), and (440) reflections for both FGO samples were identical to those of the pure Fe\textsubscript{3}O\textsubscript{4} NPs. These results suggest that Fe\textsubscript{3}O\textsubscript{4} nanocrystals were successfully deposited onto the surface of GO (Yu et al. 2016).

The magnetization curves of Fe\textsubscript{3}O\textsubscript{4}, FGO1, FGO2, and FGO3 are shown in Fig. 2 b. There was no remanence or coercivity at room temperature, indicating all exhibit superparamagnetic characteristics. The saturation magnetization of Fe\textsubscript{3}O\textsubscript{4} was 60.68 emu g\textsuperscript{−1}, and the saturation

| Catalysts | BET (m\textsuperscript{2} g\textsuperscript{−1}) | Pore Volume (cm\textsuperscript{3} g\textsuperscript{−1}) | Pore size (nm) |
|-----------|---------------------------------|---------------------------------|----------------|
| Fe\textsubscript{3}O\textsubscript{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 |
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 (Fig. 2 b).

The surface compositions of the GO, Fe3O4, and FGO1 nanocomposites were then analyzed by XPS. The results are shown in Fig. 3, and the summarized data deduced from the respective peaks of GO, Fe3O4, and FGO1 are listed in Table S2. The binding energies of 284, 530, and 711 eV correspond to C 1s, O 1s, and Fe 2p, respectively.

The C 1s 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=O 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=O) was 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 1s 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 S2, 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 coprecipitation.

Figure 3 g and h shows the high-resolution Fe 2p spectra of Fe3O4 and FGO1. The binding energies at 711 and 725 eV can be ascribed to Fe 2p3/2 and Fe 2p1/2, respectively, according to the reported literature for magnetite (Wan and Wang 2017). The Fe 2p1/2 spectrum could be deconvoluted into two components corresponding to Fe$^{2+}$ (709.7 eV) and Fe$^{3+}$ (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 (Lin et al. 2014; Wang and Lo 2014; Yang et al. 2004).

**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 pulp and paper mill as the substrate for photocatalytic degradation. 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. 4 a).

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 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 irradiation. This finding indicates the importance of UV 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 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. These results showed that the generation of hydroxyl radical (OH) in H2O2 could degrade the pollutant, but the synergistic effect of H2O2, Fe3O4, GO, and UV irradiation enhanced the treatment efficiency. The introduction of GO
can increase the surface area of the catalyst, enhance the catalyst stability, and create new micropores at the interface of Fe$_3$O$_4$ and GO sheets facilitating the mass transfer of reactants and products during the reaction (Geraldino et al. 2020). The conjugated bonds (Fe–O–C) formed in FGO could effectively facilitate the electron transfer, accelerate the redox cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$, and further decompose H$_2$O$_2$ into OH (Chen et al. 2020). According to the Haber–Weiss mechanism, under light irradiation, the surface Fe$^{3+}$ is recovered to Fe$^{2+}$ by light-induced electron transfer, thereby initiating the Fenton reaction. Light irradiation can rapidly decompose H$_2$O$_2$ into hydroxyl radicals, prevent the self-recombination of hydroxyl radicals, and improve the utilization efficiency of H$_2$O$_2$ and Fe$^{2+}$ (Wan and Wang 2017; Zubir et al. 2015).

Figure 4 a 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 H$_2$O$_2$ activation by FGO may therefore involve (1) the initial formation of Fe(II)-H$_2$O$_2$ by ligand displacement between the hydrous surface of Fe(II)-H$_2$O and H$_2$O$_2$ (Eq. 2) or (2) Fe(II)-H$_2$O$_2$ 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$_3$O$_4$ nanospheres and H$_2$O$_2$ (Guo et al. 2015; Yue et al. 2016).

$$\text{Fe(II) \cdot H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(II) \cdot H}_2\text{O}_2$$  \hspace{1cm} (2)

$$\text{Fe(II) \cdot H}_2\text{O}_2 \rightarrow \text{Fe(III) + OH + OH}^-$$  \hspace{1cm} (3)

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 4b 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 obtained herein (Arnold et al. 1995). According to the Haber–Weiss circle, the formation of OH from H$_2$O$_2$ is a key step in the degradation process. In this context, the generation of OH on the surface of Fe$_3$O$_4$/GO is gradually mitigated with increasing pH, thereby resulting in a low degradation rate of COD (Hua et al. 2014).

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 5 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 2 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 second, fourth, and sixth 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 2). This indicates that FGO1 is particularly stable under neutral conditions.

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. 6a) and the wastewater sample after heterogeneous Fenton photocatalytic treatment (Fig. 6b). The y-axis represents the abundance, and the x-axis denotes the retention time. Each chromatogram shows the overlaid GC–MS chromatograms of the untreated wastewater (Fig. 6a) and the wastewater sample after heterogeneous Fenton photocatalytic treatment (Fig. 6b). 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 pulp and paper 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-pentamethylheptane and 2,2-dimethyldecane.

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 7 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. 7 a), 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 $3.88 \times 10^5$ (a.u.), while that of peak B was $2.55 \times 10^5$ (a.u.). After the heterogeneous photo-Fenton reaction under optimized conditions, as can be seen in Fig. 7 b, the intensity of peak A decreased to $2.83 \times 10^4$ (a.u.), while that of peak B decreased to $8.5 \times 10^3$ (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.

**Conclusions**

In this study, the applicability of the heterogeneous photo-Fenton process in the advanced treatment of pulp and paper wastewater with Fe$_3$O$_4$/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$_3$O$_4$. 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 3D 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.

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

**Author’s contribution** Yecan Peng: Conceptualization, data curation, formal analysis, and writing—original draft preparation. Guirong Ye: Conceptualization and data curation. Yangliu Du: Investigation and reviewing. Lingyu Zeng: Investigation. Jiawen Hao: Software. Jinghong Zhou: Conceptualization, methodology, reviewing and editing, and writing—review and editing. Shuangfei Wang: Supervision, methodology, and reviewing.

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**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Conflict of interests** The authors declare no competing interests.

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