Role of weak magnetic field for enhanced oxidation of orange G by magnetic Fenton

Zhenyu Shi 1,2 · Ruijia Zhang 3 · Jing Zhang 1

Received: 20 January 2021 / Accepted: 9 June 2021 / Published online: 19 June 2021 © The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract
The role of weak magnetic field (WMF) on the degradation of a common textile azo-dye, orange G (OG), by magnetic Fenton system was investigated in detail. The results showed that the presence of WMF can provide better performance of the Fe3O4/H2O2 system for OG degradation. The optimized reaction conditions were contained at 1 mM Fe3O4 as Fe, 20 mT of magnetic field intensity, 20 mM H2O2, and initial pH of 3.0. The removal efficiency of OG by Fe3O4/H2O2 coupling with WMF increased largely from 56.3 to 82.3% compared with Fe3O4/H2O2 process. Both the electron paramagnetic resonance (EPR) analysis and the quenching effect of tert-butyl alcohol (TBA) confirmed that hydroxyl radical (•OH) was the primary reactive oxygen species in WMF-Fe3O4/H2O2 system. The improving effect of WMF was explained by the magnetoconvection theory. The presence of WMF could accelerate the corrosion rate of Fe3O4 and thus promoted the release of Fe(II), which led to the increased production of •OH and enhanced the degradation of OG. Moreover, it was surprising to observe that the WMF induced improvement in OG degradation by heterogeneous Fenton involving the iron sludge, namely FeOOH and Fe2O3, as catalysts. These results indicated that WMF could be utilized as an efficient and cost-effective strategy to improve the removal of organic pollutants by iron oxide-based Fenton process.

Keywords Weak magnetic field · Heterogeneous Fenton · Magnetite · Orange G · Iron sludge

Introduction
Advanced oxidation processes (AOPs) have been intensively studied for the removal of refractory organic pollutants in water and wastewater treatment. Among various AOPs, the Fenton reaction which uses ferrous ions and hydrogen peroxide (H2O2) for the formation of nonselective hydroxyl radicals (•OH) is an especially powerful method due to its ease of implementation and high catalytic efficiency. However, the large-scale application of homogeneous Fenton system is typically restricted by the low operation pH range (pH=2.5–3.5) and the generation of undesirable iron sludge (Brillas et al. 2009). To minimize negative effects of homogeneous Fenton process, various heterogeneous Fenton catalysts have been developed (Nidheesh 2015; Thomas et al. 2020).

Iron oxides, such as goethite (α-FeOOH), magnetite (Fe3O4), and hematite (α-Fe2O3), are often treated as heterogeneous Fenton catalysts because of their abundance in earth’s crust, low cost, negligible toxicity, and environmentally benign (Thomas et al. 2020). Compared with hematite and goethite, magnetite (Fe3O4) has gain much more attention with its outstanding properties. Fe3O4 is usually represented by the formula (Fe(III))4[Fe(II)Fe(III)]16O4 where Fe(II) ions occupy octahedral sites and Fe(III) ions are equally in both octahedral and tetrahedral sites (Avetta et al. 2015). Due to its redox properties, Fe3O4 can provide high catalytic activity in the oxidation processes. It has been applied as a heterogeneous Fenton catalyst for abatement of various organic pollutants, such as p-nitrophenol (Sun and Lemley 2011), aniline (Zhang et al. 2009), phenol (Hou et al. 2014), and polycyclic aromatic hydrocarbons (Usman et al. 2012). It is noteworthy that the catalytic efficiency of Fe3O4 is still unsatisfactory due to the insufficient Fe(III)/Fe(II) cycle which needs further improvement. To date, researchers have developed numerous
countermeasures, including introducing external energy (e.g., ultraviolet irradiation (Minella et al. 2014), ultrasound (Hou et al. 2016), microwave (Vieira et al. 2020), and electricity (Choe et al. 2021)), adding chelating or reducing agents (such as nitritotriacetic acid (Sun et al. 2014), citrate (Xue et al. 2009b), and ascorbic acid (Sun et al. 2020)), and doping other metals (e.g., Cu (Jin et al. 2017), Mn (Zhong et al. 2014), and Ce (Xu and Wang 2012b)) into the magnetite structure, to promote the Fe(III)/Fe(II) cycle of iron oxide in heterogeneous Fenton reactions. Nonetheless, these methods always suffer from operational complexity, being costly, and ecological toxicity. Therefore, it is imperative to explore an efficient, low-cost, and environmentally friendly process to improve the removal efficiency of organic compounds by Fe3O4/H2O2.

Recently, researchers have reported that the irradiation of weak magnetic field (WMF) is an effective and economic strategy to enhance removal efficiency of contaminants by Fe0 activated H2O2 or persulfate (Xiong et al. 2014, 2015). In the combination of WMF with Fe0, the WMF gradient forces cause paramagnetic Fe(II) ions to move in high-gradient field regions, leading to accelerate the dissolution rate of Fe0 and thus accompany the leaching of Fe(II) from Fe0 activated H2O2 or persulfate (Xiong et al. 2014, 2015). As a result, the generation of radicals in the solution is increased, which is conducive to enhance the abatement of contaminants. Because of the presence of Fe(II) in Fe3O4, the superimposed WMF on Fe3O4 might also highly activate H2O2 for treating the contaminants. To our best knowledge, no studies have been done so far to explore the influence of the WMF on Fe3O4/H2O2 process.

Thus, the aim of this work was to investigate the feasibility and mechanism of heterogeneous Fenton process coupling with weak magnetic field (WMF-Fe3O4/H2O2), which can also be named as magnetic Fenton. Orange G (OG), which is a common textile azo-dye, was chosen as a model organic compound. Then, influencing parameters, such as pH, H2O2 and Fe3O4 dosage, and magnetic field intensity, were studied, and reactive species was identified by electron paramagnetic resonance (EPR) spectroscopy and radical scavenger experiments. Additionally, various characterization technologies (e.g., XRD, BET, TEM, and XPS) and Fe leaching experiment were employed to further demonstrate the mechanism of WMF-Fe3O4/H2O2 system. Finally, the suitability and effectiveness of heterogeneous Fenton process based on another two iron sources (FeOOH and Fe2O3) as a catalyst was also evaluated.

**Experimental section**

**Materials**

Fe3O4 was supplied by Nanjing Emperor Nano Material Co., Ltd. OG, sulfuric acid, sodium hydroxide, Fe2O3 (average diameter 300 nm, 98%), tert-butyl alcohol (TBA), and H2O2 (30%) were obtained from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). These chemicals were of analytical grade and used without further purification. The goethite (FeOOH) catalyst was prepared with the method used by Lin et al. (2012). Methanol of HPLC grade was provided by Merck (Darmstadt, Germany). All solutions were prepared with Milli-Q water (18.2 MΩ cm).

**Characterization**

The phase identification of Fe3O4 was performed by X-ray diffraction (XRD, ARL, X’TRA ) with a Bruker D8-Advance using Cu Kα radiation. The morphology and size distribution of Fe3O4 were obtained from a transmission electron microscope (TEM) of H-7500 (Hitachi) operating at 80 kV accelerated voltage. The Brunauer-Emmett-Teller (BET) specific surface area was determined by nitrogen adsorption-desorption measurement on an ASAP 2020 instrument (Micromeritics) with analysis bath temperature 77 K. The metal oxidation states on Fe3O4 surface before and after the Fenton reaction were recorded by the X-ray photoelectron spectroscopy (XPS, Thermal scientific, ESCALAB 250Xi) with monochromatic Al Kα X-ray radiation at 1486.71 eV, and the XPSPEAK 4.1 software was used for data analysis. The binding energy at 284.6 eV of C 1s peak was used to calibrate binding energy of all the spectra.

**Experimental procedures**

All experiments were conducted in a series of borosilicate glass jars continuously mixed by mechanical stirring and maintained at 25 ± 1 °C by a thermostatic water bath. As shown in Fig. S1, two thin cylindrical neodymium-iron-boron permanent magnets were assembled under the reactor to provide magnetic field. The magnetic field intensity was measured with a Teslameter (HT201, Shanghai Hengtong Magnetic & Electric Technology Co., Ltd) at the bottom of the reactor. The tests were initiated by simultaneously adding Fe3O4 and H2O2 into 500-mL unbuffered reaction solution containing OG. The solution of initial pH was adjusted with sulfuric acid and sodium hydroxide. During treatment, the solution was mixing by a mechanical stirrer at 400 rpm to prevent the aggregation of Fe3O4 particles. At the given intervals, water samples were withdrawn and quenched by methanol immediately, and the mixture was filtered through 0.22 μm membranes to remove the suspended solids before OG analysis. All batch experiments were conducted in duplicates, and the average data were obtained as the mean of the two replicates.
Analytical methods

OG concentration was examined with an automatic scanning UV-Vis spectrophotometres (TU-1902, Purkinje) at 478 nm. Dissolved Fe ion concentration was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5900). Electron paramagnetic resonance (EPR) experiments were explored on a Bruker A200 system with 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO) as a spin trapping agent. The mixture of DMPO and sample was mixed for 30s and then transferred to a glass tube, which was inserted into the cavity of EPR. The EPR instrument was operated in the following parameters: center field 353.5 mT, sweep width 7 mT, microwave frequency 9.85 GHz, microwave power 6.1 mW, a sweep time 81.92 s, modulation frequency 100 kHz, and modulation amplitude 0.05 mT.

Results and discussion

Performance of WMF-Fe₃O₄/H₂O₂ process

The degradation efficiency of OG along time under different experimental conditions was assessed as demonstrated in Figs. 1 and S2. It was observed that only 5.0% of OG was removed by only 20 mM H₂O₂ within 360 min of reaction (Fig. S2a), attributed to the weak oxidation potential of H₂O₂. Less than 13% of OG removal was achieved in the control reactions with 1 mM Fe₃O₄ (as Fe) alone, which was mainly expected to surface adsorption (Xue et al. 2009a). As seen in Fig. 1, the addition of Fe₃O₄ to H₂O₂ at pH 3.0 could remove 36.3% OG after 6 h of reaction, suggesting the high catalytic ability of Fe₃O₄ to H₂O₂. Surprisingly, the introduction of WMF greatly enhanced the removal efficiency of OG to 82.3% under the same condition. As either the WMF-H₂O₂ or the WMF-Fe₃O₄ systems had negligible influence on OG degradation (Fig. S2b), the presence of WMF might promote the degradation of OG in the WMF-Fe₃O₄/H₂O₂ system by enhancing the Fenton reaction. Besides, it is still easy to separate the Fe₃O₄ by magnet after reaction. In order to optimize the WMF-Fe₃O₄/H₂O₂ process, the influence of initial solution pH, magnetic field intensity, Fe₃O₄ dosage, and H₂O₂ concentration were examined systematically in the following sections.

Effect of reaction conditions

Effect of initial solution pH

The pH value is one of the most important factors because it determines the route of the Fenton processes. In this study, the decomposition of OG was carried out at pH range from 2.0 to 3.5 in both Fe₃O₄/H₂O₂ and WMF-Fe₃O₄/H₂O₂ systems (Fig. 2a). The degradation efficiency of OG by WMF-Fe₃O₄/H₂O₂ at pH 2.5, 3.0, and 3.5 was increased by 5.6%, 46%, and 7.8%, respectively. The enhancement was likely related to the fact that the amount of leaching of Fe ions from the Fe₃O₄ particle under WMF was higher than that without WMF, which would be shown in the next section. Thus, the more •OH generated in homogeneous reaction can be ascribed to the enhancement of OG removal by the WMF-Fe₃O₄/H₂O₂ process. It was also observed that the rates of OG removal drastically decreased with the pH increasing from 2.5 to 3.5 in both systems, suggesting OG degradation was closely pH-dependent. This phenomenon might be ascribed to the concentration of iron ions in the bulk which is relatively low as pH increases (Li et al. 2016). Moreover, when the initial pH decreased from 2.5 to 2.0, the presence of WMF had negligible effect on the degradation of OG by Fe₃O₄/H₂O₂ process, and the performance of both systems was much less effective. It may be attributed to the generation of complex species [Fe(H₂O)₆]²⁺ at lower acid environment, which reacts more slowly with H₂O₂ to that of [Fe(OH)(H₂O)₅]²⁺ (Li et al. 2016). Additionally, the strong acidity could have a scavenging effect on both H₂O₂ and •OH. Due to the remarkable enhancement of OG by the WMF-Fe₃O₄/H₂O₂ system, the solution pH of 3.0 was chosen in the following studies.

Effect of the magnetic field intensity

As shown in Fig. 2b, the effect of magnetic field (MF) intensity on OG decomposition in WMF-Fe₃O₄/H₂O₂ process was investigated by applying different magnetic field intensities from 0 to 30 mT. The removal of OG by Fe₃O₄/H₂O₂ at pH 3.0 remarkably improved from 33.4 to 82.3% with the MF
intensity increasing from 0 to 20 mT. According to the previous studies (Fan et al. 2019; Sun et al. 2017), two forces, including the magnetic field gradient force \( F_B \) and the Lorentz force \( F_L \), have been proposed to be responsible for the WMF effect. However, it was recently verified that the magnetic field gradient force is the major driving force for the enhancing effect of WMF (Li et al. 2017). The magnetic field gradient force \( F_B \) could drive paramagnetic ions (Fe (II)) along the magnetic field from far away to close to the \( \text{Fe}_3\text{O}_4 \) surfaces. Then, electromagnetic forces and galvanic coupling could promote paramagnetic ion movement and the \( \text{Fe}_3\text{O}_4 \) surface corrosion. Additionally, it was also reported that the additional convection induced by the \( F_L \) in the presence of WMF could increase the mass transport of \( \text{H}^+ \) toward the \( \text{Fe}_3\text{O}_4 \) particle surface, leading to the lower pH at the \( \text{Fe}_3\text{O}_4 \) particle surface than that without WMF (Xiong et al. 2015). These physical processes were conducive to increase the dissolution of Fe ions from particles, responsible for enhancement of OG decomposition in WMF-\( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) process. Besides, with increasing the WMF intensity, the influence of paramagnetic ions transport induced by the \( F_B \) would be further strengthened. The dissolving rate of Fe(II) from \( \text{Fe}_3\text{O}_4 \) surface can be accelerated, resulting in the more yield of \( \cdot \text{OH} \). However, further increasing the WMF intensity to 30 mT leads to a dropped OG removal, which should be resulted from the \( \text{Fe}_3\text{O}_4 \) aggregation with MF intensity greater than 20 mT. The phenomenon about the inhibition of OG removal in the presence of excessive MF intensity was consistent with previous studies (Xiong et al. 2014, 2015). The aggregation might result in the decrease of active sites of \( \text{Fe}_3\text{O}_4 \), which could deteriorate the performance of catalyst for OG removal. Thus, 20 mT is the best for the intensity of WMF on the removal efficiency of OG in the \( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) process.

It was evident that the whole reaction of OG degradation by \( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) process with or without WMF can be divided into three stages. The first stage lasts for 2 min, during which the surface adsorption of a little fraction of OG (7%) on \( \text{Fe}_3\text{O}_4 \) is the dominant procedure. Subsequently, a lag period (second stage) and a followed rapid degradation stage (third stage) which displayed apparent first-order kinetic were observed (Fig. S3), which was also demonstrated by previous studies (Xu and Wang 2012a). As shown in Fig. S3, the kinetic constant \( k \) of the third stage was obviously higher than that of the second stage. The \( k \) of second stage slightly increased from \( 3 \times 10^{-4} \) to \( 7 \times 10^{-4} \) min\(^{-1} \) with the increase of MF intensity from 0 to 20 mT, while the \( k \) of third stage at MF intensity of 20 mT was 5.8 times higher than that without WMF. It was well known that in the \( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) system, the homogeneous reaction dominated under acidic conditions, and the heterogeneous reaction only played the minor role (Sun et al. 2013). The significantly increased oxidation efficiency at the third stage may be attributed to the more dissolved fraction of Fe ions generated under WMF. The leaching of Fe ion during the \( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) reaction superimposed WMF was specifically discussed in Section “Mechanism of WMF-\( \text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2 \) process.”
Effect of catalyst dosage

Figure 2c depicts the influence of different catalyst dosages on the removal of OG at pH 3.0 via the heterogeneous Fenton process containing 0.1 mM of OG, 20 mM of H$_2$O$_2$, and the MF intensity of 20 mT. The superimposed WMF can significantly enhance the removal efficiency of OG by Fenton reaction at different catalyst dosages, compared with that in the absence of WMF. However, the OG removal efficiency by WMF-Fe$_3$O$_4$/H$_2$O$_2$ system has been decreased with the catalyst dosage increasing from 1 to 10 mM. The decrease of OG removal may be ascribed to the agglomeration of nanoparticles under the magnetic field which could reduce active sites on the surface. Besides, the larger amount of Fe$_3$O$_4$ dosage in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ system might lead to more Fe(II) leaching from catalyst, responsible for the scavenging of •OH by excess Fe(II) (Xu and Wang 2012a), according to Eq. (1). Based on the obtained results, 1 mM of Fe$_3$O$_4$ was adequate to be applied in the removal of OG by the WMF-Fe$_3$O$_4$/H$_2$O$_2$ process.

\[
\text{Fe(II)} + \cdot \text{OH} \rightarrow \text{Fe(III)} + \text{HO}^-
\]  

Effect of H$_2$O$_2$ concentration

In the heterogeneous Fenton reaction, the H$_2$O$_2$ concentration can directly affect the formation of active radicals. As can be seen in Fig. 2d, the removal efficiency of OG in the Fe$_3$O$_4$/H$_2$O$_2$ system elevated with the H$_2$O$_2$ dosage increasing from 10 to 15 mM, and a further increase of the H$_2$O$_2$ dosage to 30 mM hardly improved the OG degradation. The similar trend was also observed in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ system. However, with the increase of H$_2$O$_2$ concentration from 20 to 30 mM, the OG removal efficiency significantly decreased by 39.1% in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ system. This was attributed to the fact that the increasing H$_2$O$_2$ dosage enhanced the generation of hydroxyl radicals in Fenton reaction, while the over high H$_2$O$_2$ scavenged •OH (Gao et al. 2018), as described in Eq. (2). Taking into consideration economy and efficiency, H$_2$O$_2$ of 20 mM was selected as the optimal value in the OG removal by the WMF-Fe$_3$O$_4$/H$_2$O$_2$ process.

\[
\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^-
\]  

Identification of reactive radicals

The formation of reactive oxygen species in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ system was firstly investigated with the addition of radical scavenger. TBA is a common •OH scavenger because of its high-rate constant reaction with •OH ($k = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) (Shi et al. 2019). As shown in Fig. 3a, only ~9.0% of OG was removed at pH 3.0 during both Fe$_3$O$_4$/H$_2$O$_2$ and WMF-Fe$_3$O$_4$/H$_2$O$_2$ processes in the presence of 50mM TBA. It should be noted that the degradation efficiency of OG by WMF-Fe$_3$O$_4$/H$_2$O$_2$ system in the presence of TBA was approximately equal to that by Fe$_3$O$_4$ alone. Thus, the removal of OG in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ system with the addition of TBA can be attributed to the surface adsorption of OG onto Fe$_3$O$_4$. It was demonstrated that •OH was the major reactive species for the OG abatement in the Fe$_3$O$_4$/H$_2$O$_2$ system, regardless of with and without the WMF. Subsequently, electron paramagnetic resonance (EPR) spectra were employed to confirm the production of •OH by DMPO as a spin trap. As depicted in Fig. 3b, typical signals of DMPO-•OH spin adduct (quartet peaks with relative intensity ratios of 1:2:2:1) (Xiao et al. 2018) were distinguished from the EPR spectra in Fe$_3$O$_4$/H$_2$O$_2$ system with and without the WMF. Obviously, the signal intensity of DMPO-•OH spin adduct in WMF-Fe$_3$O$_4$/H$_2$O$_2$ system was much stronger than that in Fe$_3$O$_4$/H$_2$O$_2$ system. The dramatic difference between the two systems demonstrated that the introduction of WMF to Fe$_3$O$_4$/H$_2$O$_2$ could not change but rather promote the generation of •OH. This phenomenon was similar to that reported by Guan’s group in the WMF-Fe$^{6+}$/H$_2$O$_2$ system (Xiong et al. 2015). In sum, these results suggested that the superimposed WMF could improve the decomposition of H$_2$O$_2$ to product •OH, while •OH was the primary radical species during the WMF-Fe$_3$O$_4$/H$_2$O$_2$ process.

Mechanism of WMF-Fe$_3$O$_4$/H$_2$O$_2$ process

In order to explore the mechanism of Fe$_3$O$_4$/H$_2$O$_2$ coupling with WMF, various characterization technologies were employed to check the possible change in morphology and composition of Fe$_3$O$_4$. As shown in Fig. 4, the TEM of virgin Fe$_3$O$_4$ and Fe$_3$O$_4$ used after Fenton-like reaction with and without WMF revealed that the catalyst exhibited a spherical morphology with an average particle size of approximately 15 nm. Compared with Fe$_3$O$_4$/H$_2$O$_2$, some Fe$_3$O$_4$ particles were more easily to agglomerate after the WMF-Fe$_3$O$_4$/H$_2$O$_2$ process (Fig. 4), which was mainly attributed to the influence of the external magnetic field. Figure S4 shows that the XRD patterns of virgin Fe$_3$O$_4$ and its counterpart with and without WMF after Fenton-like reaction. Six characteristic peaks for Fe$_3$O$_4$ ($2\theta = 30.2^\circ$, 35.5$^\circ$, 43.2$^\circ$, 53.7$^\circ$, 57.2$^\circ$, and 62.8$^\circ$), marked by their indices (220), (400), (422), (440), and (511), were observed for the catalyst before and after use. Additionally, no other peaks were appeared in the XRD pattern of reused Fe$_3$O$_4$, suggesting that there was no obvious change of structure and component of the catalyst after Fenton reaction in the presence and absence of the WMF. The crystal size obtained from the XRD results was 12.5 nm, which was similar to the TEM result. The BET surface area of virgin Fe$_3$O$_4$ was 37.8 m$^2$ g$^{-1}$. After the Fe$_3$O$_4$/H$_2$O$_2$ and WMF/Fe$_3$O$_4$/H$_2$O$_2$ processes, the BET surface area of Fe$_3$O$_4$
decreased to 35.2 and 33.6 m²·g⁻¹ respectively, due to the aggregation of magnetic nanoparticles resulting in the decrease of their specific surface area. These results show that the introduction of WMF had negligible influence on the morphology stability of Fe₃O₄ during the heterogeneous Fenton reaction.

X-ray photoelectron spectroscopy (XPS) was further performed to confirm the surface compositions and valence state of Fe₃O₄. As demonstrated in Fig. 5, peaks at the binding energies of 284, 530, and 711 eV in the wide-scan XPS spectrum of Fe₃O₄ indexed to C 1s, O 1s, and Fe 2p, respectively. Peaks at 711 and 725 eV in the Fe 2p spectrum can be ascribed to Fe 2p₃/2 and Fe 2p₁/2, respectively. Then, the Fe 2p₃/2 spectrum was deconvoluted into two peaks at 710.7 and 712.4 eV to further quantify the surface Fe(II) and Fe(III) fractions in the sample (Jia et al. 2018). For the Fe₃O₄ sample treated by WMF-Fe₃O₄/H₂O₂ system, the surface Fe(II)/Fe(III) ratio of the Fe 2p₃/2 peak was 0.22 (Table S1), which was much lower than that from virgin Fe₃O₄ (1.00) and Fe₃O₄ used in Fe₃O₄/H₂O₂ process. The reduced ratio of surface Fe(II)/Fe(III) in Fe₃O₄ sample after the Fenton reaction was mainly associated with the following reasons: (1) the release of Fe(II) ion from catalyst at acidic conditions and (2) the H₂O₂ oxidation of surface Fe(II) to Fe(III), according to the classical Haber-Weiss mechanism (Eqs. (3)–(4)) (Hu et al. 2011). Previous studies reported that the introduction of WMF had negligible influence on Fe(III)/Fe(II) cycle either in the solution or on the surface during the Fenton reaction, but significantly accelerated the leaching of Fe(II) (Xiong et al. 2015). This could lead to the lower Fe(II) content in the catalyst after the WMF-Fe₃O₄/H₂O₂ process.

\[
\begin{align*}
\text{Fe}^{II} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{II} \cdot \text{H}_2\text{O}_2 \\
\text{Fe}^{II} \cdot \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{III} + \cdot\text{OH} + \text{OH}^- \\
\end{align*}
\]

We assumed that the significant enhancement in WMF-Fe₃O₄/H₂O₂ system might be caused by the more dissolution of Fe ions into the solution. To clarify this issue, the total Fe ion concentration in solution was determined by ICP-OES during the degradation process (Fig. 6). As expected, the concentration of dissolved Fe ion in both Fe₃O₄/H₂O₂ and WMF-Fe₃O₄/H₂O₂ systems increased steadily. It should be noted that no Fe (II) was detected during Fe₃O₄/H₂O₂ reaction with and without WMF, implying that Fe (II) can be promptly oxidized by H₂O₂ once it was leached from Fe₃O₄. By comparison, the leaching of iron during OG degradation by WMF-Fe₃O₄/H₂O₂ system was much faster than by Fe₃O₄/H₂O₂ system. Thus, the superimposed WMF facilitated the dissolution of Fe₃O₄, resulting in the enhanced Fenton reaction, which performed an important function for OG removal. The concentration of dissolved iron in Fe₃O₄/H₂O₂ and WMF-Fe₃O₄/H₂O₂ systems after 660 min was detected at 3.0 μM and 4.2 μM, respectively, equivalently to only
0.30% and 0.42% of total iron of catalyst used. To evaluate the contribution of Fe ions to the decomposition of OG, the homogeneous Fenton experiments were taken with 4.2 μM and 3 μM Fe(II), respectively, based on the maximal amount of iron leached from the catalyst during the above experiments. As can be seen in Fig. 6, the whole removal of OG in homogeneous Fenton was higher than that in Fe₃O₄/H₂O₂ and WMF/Fe₃O₄/H₂O₂ processes, which indicated the catalytic contribution from the dissolved Fe(II) ions is significant. This result further supported that the homogeneous Fenton reaction in the WMF-Fe₃O₄/H₂O₂ system is expected predominantly in OG degradation.

Based on the above experimental data, a possible mechanism of Fe₃O₄/H₂O₂ coupling with WMF was proposed. The degradation of OG by WMF-Fe₃O₄/H₂O₂ system may be mainly ascribed to the homogeneous Fenton reaction in aqueous solution. Under acidic conditions, the dissolved Fe ion, including Fe(II) and Fe(III), from Fe₃O₄ surface can activate H₂O₂ to generate reactive oxygen species (•OH) in bulk solution. The generated •OH was primarily responsible for the degradation of OG due to their high oxidizing potential. The theory of magnetoconvection could well explain the enhancing effect of WMF in our study (Waskaas and Kharkats 1999). In the presence of WMF, the paramagnetic ions (Fe(II)) pulled by magnetic gradient force could move along magnetic lines to the place with higher MF flux intensity, leading to the uneven distribution of Fe(II) and eventually a gradient of Fe(II) concentration. Moreover, with the introduction of WMF, the additional driving force existing as the same direction of the gradient of the paramagnetic ions could act on the reaction mixture and then induce a redistribution of velocities in the diffusion layer (Li et al. 2017). Consequently, WMF caused an additional convective transfer of all constituents of the mixture, that is, acceleration of releasing iron. Thus, the enhancing effect of WMF can be related to cause the more dissolved fraction of iron species in solution. Hence, more concentration of •OH is generated for oxidizing OG during the homogenous Fenton reaction.

Fig. 5  a XPS survey for virgin Fe₃O₄, spent Fe₃O₄ in Fe₃O₄/H₂O₂, and WMF-Fe₃O₄/H₂O₂, b Fe 2p XPS for virgin Fe₃O₄, c Fe 2p XPS for spent Fe₃O₄ in Fe₃O₄/H₂O₂ process, d Fe 2p XPS for spent Fe₃O₄ in WMF-Fe₃O₄/H₂O₂ process

Fig. 6 Degradation of OG in homogeneous Fe(II)/H₂O₂ process with and without WMF. The dosage of Fe(II) was set according the maximum dissolved Fe ions at the end of reactions. Reaction conditions: [OG]=0.1 mM, [H₂O₂]=20 mM, pH=3.0, and T=25 °C
Wide suitability and regeneration performance of WMF-Fe$_3$O$_4$/H$_2$O$_2$ system

The degradation rate of OG was dramatically enhanced by introducing WMF in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ process, so it would be reasonable to believe that WMF-Fe$_3$O$_4$/H$_2$O$_2$ is also effective in other processes. To check the wide suitability of WMF-Fe$_3$O$_4$/H$_2$O$_2$, we evaluated the performance of the WMF-Fe$_3$O$_4$/H$_2$O$_2$ system toward representative contaminants (e.g., acetaminophen, ofloxacin, tetracyclin, and 2,4-dichlorophenol), as shown in Fig. S5. Compared with Fe$_3$O$_4$/H$_2$O$_2$ process, significant enhanced removal of these contaminants was observed in WMF-Fe$_3$O$_4$/H$_2$O$_2$ process. These results imply that the WMF-Fe$_3$O$_4$/H$_2$O$_2$ process has wide suitability and presents significant improvement than Fe$_3$O$_4$/H$_2$O$_2$ process.

To evaluate the reusability of Fe$_3$O$_4$ as a heterogeneous catalyst in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ system, the Fe$_3$O$_4$ after reaction was collected from the solution and used in the next cycle of test. Figure S6 depicts that the recycled Fe$_3$O$_4$ still exhibited high activity for the removal of OG after five consecutive runs. About 64% OG was decomposed in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ process, and the enhanced effect of WMF was still obvious. The results demonstrate that the Fe$_3$O$_4$ was durable in the WMF-Fe$_3$O$_4$/H$_2$O$_2$ system and could be reused several times, which was of economic significance.

Wide suitability and environmental implication of magnetic Fenton process

It was surprising to observe that the WMF-induced enhancement in OG abatement by heterogeneous Fenton process was also adaptable for another two iron species as a catalyst, including FeOOH and Fe$_2$O$_3$, as demonstrated in Fig. 7. In comparison with the absence of WMF, the degradation efficiency of OG by WMF-Fe$_3$O$_4$/H$_2$O$_2$ and WMF-FeOOH/H$_2$O$_2$ systems obviously increased by 16.5% and 26.3%, respectively, at the end of reactions. It has been reported that surface Fe(II) could be produced on the surface of iron oxide based on the surface complexation mechanism in the heterogeneous Fenton system (Hou et al. 2017), as described by Eqs. (5)–(7). With the introduction of WMF, the dissolution rate of newly generated Fe(II) might be accelerated from Fe$_3$O$_4$ or FeOOH surface to the bulk solution, resulting in the more yield of ·OH. Both FeOOH and Fe$_2$O$_3$ can be seen as the main components of industrial iron sludge. Previous studies have often reused the iron sludge as an iron source for Fenton process. The most widely used way is the addition of regenerated Fe(III) via acidification dissolution of iron sludge to the classic Fenton reactor. In our study, the superimposed WMF to promote removal of organic pollutants by heterogeneous Fenton process could be conducive to the recycling and reuse of iron sludge. This magnetic Fenton process can avoid the utilization of expensive corrosive substances which can increase risk to the environment and humans. Therefore, employing WMF to improve the reactivity of iron oxide-based Fenton process can provide a promising alternative for the abatement of contaminants in water and wastewater treatment.

Conclusions

In this study, the WMF exhibited a high efficiency in facilitating the degradation of OG by Fe$_3$O$_4$/H$_2$O$_2$ system, which was of practical and fundamental importance to the environmental decontamination by the system. The effects of different operational parameters, including pH, MF intensity, Fe$_3$O$_4$ dosage, and H$_2$O$_2$ concentration, on the OG degradation were investigated. Besides, chemical quenching experiments and EPR experiments both proved that WMF did not change reactive oxygen species generated in WMF-Fe$_3$O$_4$/H$_2$O$_2$ system. The ·OH was verified as the primary reactive oxygen species. The role of WMF in WMF-Fe$_3$O$_4$/H$_2$O$_2$ system could be well explained with the theory of magnetoconvection. The enhancement caused by the WMF was due to the fact that the

Fig. 7 Degradation of OG by heterogeneous Fenton process coupling with the WMF for a FeOOH and b Fe$_2$O$_3$ as a catalyst. Reaction conditions: [OG]=0.1 mM, [H$_2$O$_2$]=20 mM, [FeOOH]=[Fe$_2$O$_3$]=1 mM as Fe, and T=25 °C
WMF impacted the mass transfer and thus promoted the release of Fe(II), which was conducive to produce more •OH in bulk solution. Moreover, the introduction of WMF was also suitable for enhancing catalytic reactivity of other two iron sources, such as FeOOH and Fe₃O₄, as a catalyst, which shed a light on the recycling and reuse of iron sludge in heterogeneous Fenton process.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-14887-2.

Author contribution Material preparation and background analysis were performed by ZYS, RJZ, and JZ. The manuscript specific experimental design and operation and experimental data processing were performed by ZYS and RJZ. Data analysis was performed by ZYS, RJZ, and JZ. ZYS and JZ performed writing, review, and editing; JZ supervised the research.

Funding This work was supported by the National Key Research and Development Project (2019YFD1100101) and the National Natural Science Foundations of China (No. 51878095 & 22076016).

Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Avetta P, Pensato A, Minella M, Malandrino M, Maurino V, Minero C, Vione D (2015) Activation of persulfate by irradiated magnetic: implications for the degradation of phenol under heterogeneous photo-Fenton-like conditions. Environ Sci Technol 49: 1043–1050

Brillas E, Sritos I, Otruan MA (2009) Electro-Fenton process and related electrochemical technologies based on Fenton’s reaction chemistry. Chem Rev 109:6570–6631

Choe YJ, Kim J, Byun JY, Kim SH (2021) An electro-Fenton system with magnetite coated stainless steel mesh as cathode. Catal Today 359:16–22

Fan P, Li L, Sun Y, Qiao J, Xu C, Guan X (2019) Selenate removal by Fe₆³⁺ coupled with ferrous iron, hydrogen peroxide, sulfidation, and weak magnetic field: a comparative study. Water Res 159:375–384

Gao J, Liu Y, Xia X, Wang L, Dong W (2018) Feₓ₋₀.₃ZnₓS ternary solid solution as an efficient Fenton-like catalyst for ultrafast degradation of phenol. J Hazard Mater 353:393–400

Hou L, Zhang Q, Jérôme F, Duprez D, Zhang H, Royer S (2014) Shape-controlled nanostructured magnetite-type materials as highly efficient Fenton catalysts. Appl Catal B 144:739–749

Hou L, Wang L, Royer S, Zhang H (2016) Ultrasound-assisted heterogeneous Fenton-like degradation of tetracycline over a magnetite catalyst. J Hazard Mater 302:458–467

Hou X, Huang X, Jia F, Ai Z, Zhao J, Zhang L (2017) Hydroxylamine promoted goethite surface Fenton degradation of organic pollutants. Environ Sci Technol 51:5118–5126

Hu X, Liu B, Deng Y, Chen H, Luo S, Sun C, Yang P, Yang S (2011) Adsorption and heterogeneous Fenton degradation of 17α-methyltestosterone on nano Fe₃O₄/MWCNTs in aqueous solution. Appl Catal B 107:274–283

Jia D, Sun SP, Wu Z, Wang N, Jin Y, Dong W, Chen XD, Ke Q (2018) TCE degradation in groundwater by chelators-assisted Fenton-like reaction of magnetite: sand columns demonstration. J Hazard Mater 346:124–132

Jin H, Tian X, Nie Y, Zhou Z, Yang C, Li Y, Lu L (2017) Oxygen vacancy promoted heterogeneous Fenton-like degradation of ofloxacin at pH 3.2–9.0 by Cu substituted magnetic FeₓOₓ@FeOOH nanocomposite. Environ Sci Technol 51:12699–12706

Li T, Zhao Z, Wang Q, Xie P, Ma J (2016) Strongly enhanced Fenton degradation of organic pollutants by cys teine: an aliphatic amino acid accelerator outweighs hydroquinone analogues. Water Res 105:479–486

Li J, Qin H, W-x Z, Shi Z, Zhao D, Guan X (2017) Enhanced Cr (VI) removal by zero-valent iron coupled with weak magnetic field: role of magnetic gradient force. Sep Purif Technol 176:40–47

Lin K, Ding J, Wang H, Huang X, Gan JCC (2012) Goethite-mediated transformation of bisphenol A. Chemosphere 89:789–795

Minella M, Marchetti G, De Laurentiis E, Malandrino M, Maurino V, Minero C, Vione D, Hanna K (2014) Photo-Fenton oxidation of phenol with magnetite as iron source. Appl Catal B 154–155:102–109

Nidheesh PV (2015) Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review. RSC Adv 5:40552–40577

Shi Z, Jin C, Zhang J, Zhu L (2019) Insight into mechanism ofarsenic acid degradation in permanganate-sulfite system: role of reactive species. Chem Eng J 359:1463–1471

Sun SP, Lemley AT (2011) p-Nitrophenol degradation by a heterogeneous Fenton-like reaction on nano-magnetic: process optimization, kinetics, and degradation pathways. J Mol Catal A Chem 349:71–79

Sun S-P, Zeng X, Lemley AT (2013) Nano-magnetite catalyzed heterogeneous Fenton-like degradation of emerging contaminants carbamazepine and ibuprofen in aqueous suspensions and montmorillonite clay slurries at neutral pH. J Mol Catal A Chem 371:94–103

Sun S-P, Zeng X, Li C, Lemley AT (2014) Enhanced heterogeneous and homogeneous Fenton-like degradation of carbamazepine by nano-Fe₃O₄/H₂O₂ with nitritrotiacetic acid. Chem Eng J 244:44–49

Sun Y, Hu Y, Huang T, Li J, Qin H, Guan X (2017) Combined effect of weak magnetic fields and anions on arsenite sequestration by zerovalent iron: kinetics and mechanisms. Environ Sci Technol 51:3742–3750

Sun H, Xie G, He D, Zhang L (2020) Ascorbic acid promoted magnetite Fenton degradation of alachlor: mechanistic insights and kinetic modeling. Appl Catal B 267:118383–118392

Thomas N, Dionysiou DD, Pillai SC (2020) Heterogeneous Fenton catalysts: a review of recent advances. J Hazard Mater 404:124082–124104

Usman M, Faure P, Ruby C, Hanna K (2012) Remediation of PAH-contaminated soils by magnetite catalyzed Fenton-like oxidation. Appl Catal B 117–118:10–17

Vieira Y, Silvestri S, Leichtweis J, Jahn SL, de Moraes Flores EM, Dotto GL, Folletto EL (2020) New insights into the mechanism of heterogeneous activation of nano-magnetite by microwave irradiation for use as Fenton catalyst. J Environ Chem Eng 8:103787–103795

Waskaa M, Kharkats YI (1999) Magnetoeconvection phenomena: a mechanism for influence of magnetic fields on electrochemical processes. J Phys Chem B 103:4876–4883

Hou L, Zhang Q, Jérôme F, Duprez D, Zhang H, Royer S (2014) Shape-controlled nanostructured magnetite-type materials as highly efficient Fenton catalysts. Appl Catal B 144:739–749

Hou L, Wang L, Royer S, Zhang H (2016) Ultrasound-assisted heterogeneous Fenton-like degradation of tetracycline over a magnetite catalyst. J Hazard Mater 302:458–467

Hou X, Huang X, Jia F, Ai Z, Zhao J, Zhang L (2017) Hydroxylamine promoted goethite surface Fenton degradation of organic pollutants. Environ Sci Technol 51:5118–5126

Hu X, Liu B, Deng Y, Chen H, Luo S, Sun C, Yang P, Yang S (2011) Adsorption and heterogeneous Fenton degradation of 17α-methyltestosterone on nano Fe₃O₄/MWCNTs in aqueous solution. Appl Catal B 107:274–283

Jia D, Sun SP, Wu Z, Wang N, Jin Y, Dong W, Chen XD, Ke Q (2018) TCE degradation in groundwater by chelators-assisted Fenton-like reaction of magnetite: sand columns demonstration. J Hazard Mater 346:124–132

Jin H, Tian X, Nie Y, Zhou Z, Yang C, Li Y, Lu L (2017) Oxygen vacancy promoted heterogeneous Fenton-like degradation of ofloxacin at pH 3.2–9.0 by Cu substituted magnetic FeₓOₓ@FeOOH nanocomposite. Environ Sci Technol 51:12699–12706
Xiao K, Pei K, Wang H, Yu W, Liang S, Hu J, Hou H, Liu B, Yang J (2018) Citric acid assisted Fenton-like process for enhanced dewaterability of waste activated sludge with in-situ generation of hydrogen peroxide. Water Res 140:232–242

Xiong X, Sun B, Zhang J, Gao N, Shen J, Li J, Guan X (2014) Activating persulfate by Fe⁰ coupling with weak magnetic field: performance and mechanism. Water Res 62:53–62

Xiong X, Sun Y, Sun B, Song W, Sun J, Gao N, Qiao J, Guan X (2015) Enhancement of the advanced Fenton process by weak magnetic field for the degradation of 4-nitrophenol. RSC Adv 5:13357–13365

Xu L, Wang J (2012a) Fenton-like degradation of 2,4-dichlorophenol using Fe₃O₄ magnetic nanoparticles. Appl Catal B 123-124:117–126

Xu L, Wang J (2012b) Magnetic nanoscaled Fe₃O₄/CeO₂ composite as an efficient Fenton-like heterogeneous catalyst for degradation of 4-chlorophenol. Environ Sci Technol 46:10145–10153

Xue X, Hanna K, Abdelmoula M, Deng N (2009a) Adsorption and oxidation of PCP on the surface of magnetite: kinetic experiments and spectroscopic investigations. Appl Catal B 89:432–440

Xue X, Hanna K, Despas C, Wu F, Deng N (2009b) Effect of chelating agent on the oxidation rate of PCP in the magnetite/H₂O₂ system at neutral pH. J Mol Catal A Chem 311:29–35

Zhang S, Zhao X, Niu H, Shi Y, Cai Y, Jiang G (2009) Superparamagnetic Fe₃O₄ nanoparticles as catalysts for the catalytic oxidation of phenolic and aniline compounds. J Hazard Mater 167:560–566

Zhong Y, Liang X, He Z, Tan W, Zhu J, Yuan P, Zhu R, He H (2014) The constraints of transition metal substitutions (Ti, Cr, Mn, Co and Ni) in magnetite on its catalytic activity in heterogeneous Fenton and UV/Fenton reaction: from the perspective of hydroxyl radical generation. Appl Catal B 150-151:612–618

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.