

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

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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 $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system for OG degradation. The optimized reaction conditions were contained at 1 mM Fe_3O_4 as Fe, 20 mT of magnetic field intensity, 20 mM H_2O_2 and initial pH of 3.0. The removal efficiency of OG by $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ coupling with WMF increased largely from 56.3–82.3% compared with $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process. Both the electron paramagnetic resonance (EPR) analysis and the quenching effect of tert-butyl alcohol (TBA) confirmed that hydroxyl radical ($\cdot\text{OH}$) was the primary reactive oxygen species in WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system. The improving effect of WMF was explained by the magnetoconvection theory. The presence of WMF could accelerate the corrosion rate of Fe_3O_4 and thus promoted the release of Fe(II), which led to the increased production of $\cdot\text{OH}$ 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 Fe_2O_3 , 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.

1. 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 (H_2O_2) for the formation of nonselective hydroxyl radicals ($\cdot\text{OH}$) 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 ($\alpha\text{-FeOOH}$), magnetite (Fe_3O_4), and hematite ($\alpha\text{-Fe}_2\text{O}_3$), are often treated as heterogeneous Fenton catalysts because of their abundance in earth crust, low cost, negligible toxicity, and environmentally benign (Thomas et al. 2020). Compared with hematite and goethite, magnetite (Fe_3O_4) has gain much more attention with its outstanding properties. Fe_3O_4 is usually represented by the formula $(\text{Fe(III)})_{\text{tet}}[\text{Fe(II)Fe(III)}]_{\text{oct}}\text{O}_4$ where Fe(II) ions occupy in octahedral sites and Fe(III) ions are equally in both octahedral and tetrahedral sites (Avetta et al. 2015). Due to its redox properties, Fe_3O_4 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 & 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 Fe_3O_4 is still unsatisfactory due to the insufficient Fe(III)/Fe(II) cycle and need 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 nitrilotriacetic acid (Sun et al. 2014), citrate (Xue et al. 2009b), and ascorbic acid (Sun et al. 2020)), and doping other metal (e.g., Cu (Jin et al. 2017), Mn (Zhong et al. 2014), and Ce (Xu & 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 complex, costly, and ecologically toxic. Therefore, it is imperative to explore an efficient, low-cost, and environmentally friendly process to improve the removal efficiency of organic compounds by $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$.

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 Fe^0 activated H_2O_2 or persulfate (Xiong et al. 2014, 2015). In the combination of WMF with Fe^0 , the WMF gradient forces causes paramagnetic Fe(II) ions to move in high-gradient field regions, leading to accelerate the dissolution rate of Fe^0 and thus accompany the leaching of Fe(II) from Fe^0 particles (Xiong et al. 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 Fe_3O_4 , the superimposed WMF on Fe_3O_4 might also highly activate H_2O_2 for treating the contaminants. To our best knowledge, no studies have been done so far to explore the influence of the WMF on $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process.

Thus, the aim of this work was to investigate the feasibility and mechanism of heterogeneous Fenton process coupling with weak magnetic field (WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$), 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, H_2O_2 and Fe_3O_4 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- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system. Finally, the suitability and effectiveness of heterogeneous Fenton process based on another two iron sources (FeOOH and Fe_2O_3) as a catalyst was also evaluated.

2. Experimental Section

2.1. Materials

Fe_3O_4 was supplied by Nanjing Emperor Nano Material Co., Ltd. OG, sulfuric acid, sodium hydroxide, Fe_2O_3 (average diameter 300 nm, 98%), tert-butyl alcohol (TBA), and H_2O_2 (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 M Ω cm).

2.2. Characterization

The phase identification of Fe_3O_4 was performed by X-ray diffraction (XRD, ARL, X'TRA) with a Bruker D8-Advance using Cu K α radiation. The morphology and size distribution of Fe_3O_4 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 Fe_3O_4 surface before and after the Fenton reaction were recorded by the X-ray photoelectron spectroscopy (XPS, Thermal scientific, ESCALAB 250Xi) with monochromatic Al K α 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.

2.3. Experimental procedures

All experiments were conducted in a series of borosilicate glass jars continuously mixed by mechanical stirring and maintained at $25 \pm 1^\circ\text{C}$ 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 Fe_3O_4 and H_2O_2 into 500 mL unbuffered reaction solution containing OG. The solution of initial pH were 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 Fe_3O_4 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.

2.4 Analytical methods

OG concentration was examined with an automatic scanning UV-Vis spectrophotometers (TU-1902, Purkinje) at 478 nm. Dissolved Fe ions 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.

3. Results And Discussion

3.1 Performance of WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ 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 H_2O_2 within 360 min reaction (Fig. S2a), attributed to the weak oxidation potential of H_2O_2 . Less than 13% of

OG removal was achieved in the control reactions with 1 mM Fe_3O_4 (as Fe) alone, which was mainly expected to surface adsorption (Xue et al. 2009a). As seen in Fig. 1, the addition of Fe_3O_4 to H_2O_2 at pH 3.0 could remove 36.3% OG after 6 h reaction, suggesting the high catalytic ability of Fe_3O_4 to H_2O_2 . Surprisingly, the introduction of WMF greatly enhanced the removal efficiency of OG to 82.3% under the same condition. As either the WMF- H_2O_2 or the WMF- Fe_3O_4 systems had negligible influence on OG degradation (Fig. S2b), the presence of WMF might promote the degradation of OG in the WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system by enhancing the Fenton reaction. Besides, it is still easy to separate the Fe_3O_4 by magnet after reaction. In order to optimize the WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process, the influence of initial solution pH, magnetic field intensity, Fe_3O_4 dosage, and H_2O_2 concentration were examined systematically in the following sections.

3.2 Effect of reaction conditions

3.2.1 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 $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ and WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ systems (Fig. 2a). The degradation efficiency of OG by WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ 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 Fe_3O_4 particle under WMF was higher than that without WMF, which would be shown in later section. Thus, the more $\cdot\text{OH}$ generated in homogeneous reaction can be ascribed to the enhancement of OG removal during the WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ 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 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 $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process, and the performance of both systems was much less effective. It may be attributed to the generation of complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ at lower acid environment, which reacts more slowly with H_2O_2 to that of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ (Li et al. 2016). Additionally, the strong acidity could have a scavenging effect on both H_2O_2 and $\cdot\text{OH}$. Due to the remarkable enhancement of OG by the WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system, the solution pH of 3.0 was chosen in the following studies.

3.2.2 Effect of the magnetic field intensity

As shown in Fig. 2b, the effect of magnetic field (MF) intensity on OG decomposition in WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process was investigated by applying different magnetic field intensity from 0 to 30 mT. The removal of OG by $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ at pH 3.0 remarkably improved from 33.4–82.3% 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 Fe_3O_4 surfaces. Then, electromagnetic forces and galvanic coupling could promote paramagnetic ions movement and the Fe_3O_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 H^+ towards the Fe_3O_4 particle surface, leading to the lower pH at the Fe_3O_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 intensify, the influence of paramagnetic ions transport induced by the F_B would be further strengthened. The dissolving rate of Fe(II) from Fe_3O_4 surface can be accelerated, resulting in the more yield of $\cdot\text{OH}$. However, further increasing the WMF intensity to 30 mT lead to a dropped OG removal, which should be resulted from the Fe_3O_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 Fe_3O_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 Fe_3O_4 is the dominant procedure. Subsequently, a lag period (second-stage) and a followed rapid degradation stage (third-stage) displayed apparent first-order kinetic was observed (Fig. S3), which was also demonstrated by previous studies (Xu & Wang 2012a). As shown in Fig. S3, the kinetic constant (k , min^{-1}) of the third stage was obviously higher than that of the second stage. The k of second stage slightly increased from 3×10^{-4} to $7 \times 10^{-4} \text{ min}^{-1}$ 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 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 the Sect. 3.4.

3.2.3 Effect of catalyst dosage

Figure 2c depicts the influence of different catalyst dosage on the removal of OG at pH 3.0 via the heterogeneous Fenton process containing 0.1 mM of OG, 20 mM of H_2O_2 , and the MF intensity of 20 mT. The superimposed WMF can significantly enhanced 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- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system has been decreased with the catalyst dosage increasing from 1 mM 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_3O_4

dosage in the WMF-Fe₃O₄/H₂O₂ system might lead to more Fe(II) leaching from catalyst, responsible for the scavenging of •OH by excess Fe(II) (Xu & Wang 2012a), according to the Eq. (1). Based on the obtained results, 1 mM of Fe₃O₄ was adequate to be applied the removal of OG by the WMF-Fe₃O₄/H₂O₂ process.



3.2.4 Effect of H₂O₂ concentration

In the heterogeneous Fenton reaction, the H₂O₂ concentration can directly affect the formation of active radicals. As can be seen in Fig. 2d, the removal efficiency of OG in the Fe₃O₄/H₂O₂ system elevated with the H₂O₂ dosage increasing from 10 to 15 mM, and a further increase of the H₂O₂ dosage to 30 mM hardly improved the OG degradation. The similar trend was also observed in the WMF-Fe₃O₄/H₂O₂ system. However, with the increase of H₂O₂ concentration from 20 to 30 mM, the OG removal efficiency significantly decreased by 39.1% in the WMF-Fe₃O₄/H₂O₂ system. This was attributed to that the increasing H₂O₂ dosage enhanced the generation of hydroxyl radicals in Fenton reaction, while the over high H₂O₂ scavenged •OH (Gao et al. 2018), as described in Eq. (2). Taking into consideration economy and efficiency, H₂O₂ of 20 mM was selected as the optimal value in the OG removal by the WMF-Fe₃O₄/H₂O₂ process.



3.3 Identification of reactive radicals

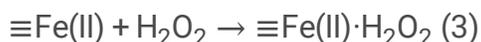
The formation of reactive oxygen species in the WMF-Fe₃O₄/H₂O₂ system was firstly investigated with the addition of radical scavenger. TBA is a common •OH scavenger because of its high-rate constant reaction with •OH ($k = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) (Shi et al. 2019). As shown in Fig. 3a, only ~ 9.0% of OG was removed at pH 3.0 during both Fe₃O₄/H₂O₂ and WMF-Fe₃O₄/H₂O₂ processes in the presence of 50mM TBA. It should be noted that the degradation efficiency of OG by WMF-Fe₃O₄/H₂O₂ system in the presence of TBA was approximately equal to that by Fe₃O₄ alone. Thus, the removal of OG in the WMF-Fe₃O₄/H₂O₂ system with the addition of TBA can be attributed to the surface adsorption of OG onto Fe₃O₄. It was demonstrated that •OH was the major reactive species for the OG abatement in the Fe₃O₄/H₂O₂ 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 trapper. 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 Fe₃O₄/H₂O₂ system with and without the WMF. Obviously, the signal intensity of DMPO-•OH spin adduct in WMF-Fe₃O₄/H₂O₂ system was much stronger than that in Fe₃O₄/H₂O₂ system. The dramatic difference between the two systems demonstrated that the introduction of WMF to Fe₃O₄/H₂O₂ could does not change but rather promote the generation of •OH. This phenomenon was similar to that reported by Guan's group in the WMF-Fe⁰/H₂O₂ system (Xiong et al. 2015). In sum, these results suggested that the superimposed WFM could improve

the decomposition of H_2O_2 to product $\cdot\text{OH}$, while $\cdot\text{OH}$ was the primary radical species during the WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process.

3.4 Mechanism of WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process

In order to explore the mechanism of $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ coupling with WMF, various characterization technologies were employed to check the possible change in morphology and composition of Fe_3O_4 . As shown in Fig. 4, the TEM of virgin Fe_3O_4 and Fe_3O_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 $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$, some Fe_3O_4 particles were more easily to agglomerate after the WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process (Fig. 4), which was mainly attributed to the influence of the external magnetic field. Fig. S4 shows that the XRD patterns of virgin Fe_3O_4 and its counterpart used after Fenton-like reaction with and without WMF. Six characteristic peaks for Fe_3O_4 ($2\theta = 30.2^\circ, 35.5^\circ, 43.2^\circ, 53.7^\circ, 57.2^\circ, \text{ and } 62.8^\circ$), 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_3O_4 , suggested 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_3O_4 was $37.8 \text{ m}^2\cdot\text{g}^{-1}$. After the $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ and WMF/ $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ processes, the BET surface area of Fe_3O_4 decreased to 35.2 and $33.6 \text{ m}^2\cdot\text{g}^{-1}$ 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 Fe_3O_4 during the heterogeneous Fenton reaction.

X-ray photoelectron spectroscopy (XPS) was further performed to confirm the surface compositions and valence state of Fe_3O_4 . As demonstrated in Fig. 5, peaks at the binding energies of 284, 530 and 711 eV in the wide-scan XPS spectrum of Fe_3O_4 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 $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. Then, the Fe $2p_{3/2}$ 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 Fe_3O_4 sample treated by WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system, the surface Fe(II)/Fe(III) ratio of the Fe $2p_{3/2}$ peak was 0.22 (Table S1), which was much lower than that from virgin Fe_3O_4 (1.00) and Fe_3O_4 (0.76) used in $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process. The reduced ratio of surface Fe(II)/Fe(III) in Fe_3O_4 sample after the Fenton reaction was mainly associated with the following reasons: 1) the release of Fe(II) ion from catalyst at acidic conditions; 2) the H_2O_2 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 accelerate the leaching of Fe(II) (Xiong et al. 2015). This could lead to the lower Fe(II) content in the catalyst after the WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process.





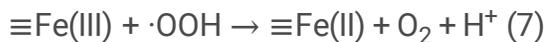
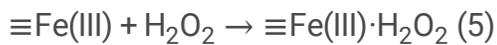
We assumed that the significant enhancement in WMF-Fe₃O₄/H₂O₂ system might be caused by the more dissolution of Fe ions into the solution. To clarify this issue, the total Fe ions concentration in solution was determined by ICP-OES during the degradation process (Fig. S5). As expected, the concentration 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 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. S5, 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 homogenous 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 ($\cdot\text{OH}$) in bulk solution. The generated $\cdot\text{OH}$ 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 & 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 $\cdot\text{OH}$ is generated for oxidizing OG during the homogenous Fenton reaction.

3.5 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

Fe₂O₃, as demonstrated in Fig. 6. In comparison with the absence of WMF, the degradation efficiency of OG by WMF-Fe₂O₃/H₂O₂ and WMF-FeOOH/H₂O₂ 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 Fe₂O₃ or FeOOH surface to the bulk solution, resulting in the more yield of •OH. Both FeOOH and Fe₂O₃ 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 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 increased risk to the environment and human. Therefore, employing WMF to improve the reactivity of iron oxides-based Fenton process can provide a promising alternative for the abatement of contaminants in water and wastewater treatment.



4. Conclusions

In this study, the WMF exhibited a high efficiency in facilitating the degradation of OG by Fe₃O₄/H₂O₂ 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, Fe₃O₄ dosage, and H₂O₂ 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-Fe₃O₄/H₂O₂ system. The •OH was verified as the primary reactive oxygen species. The role of WMF in WMF-Fe₃O₄/H₂O₂ system could be well explained with the theory of magnetoconvection. The enhancement caused by the WMF was due to that the WMF impacted the mass transfer and thus promoted the releasing 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 another two iron sources, such as FeOOH and Fe₂O₃, as a catalyst, which shed a light on the recycling and reuse of iron sludge in heterogeneous Fenton process.

Declarations

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

Author contributions 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 RJZ and RJZ. Data analysis was performed by ZYS, RJZ, and JZ. ZYS and JZ performed writing, review, and editing; JZ supervised the research.

Compliance with ethical standards

Ethical approval Not applicable.

Consent to participate All the authors declare that they participate in this work.

Consent to publish Not applicable.

Competing interest The authors declare that there is no conflict of interest.

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Figures

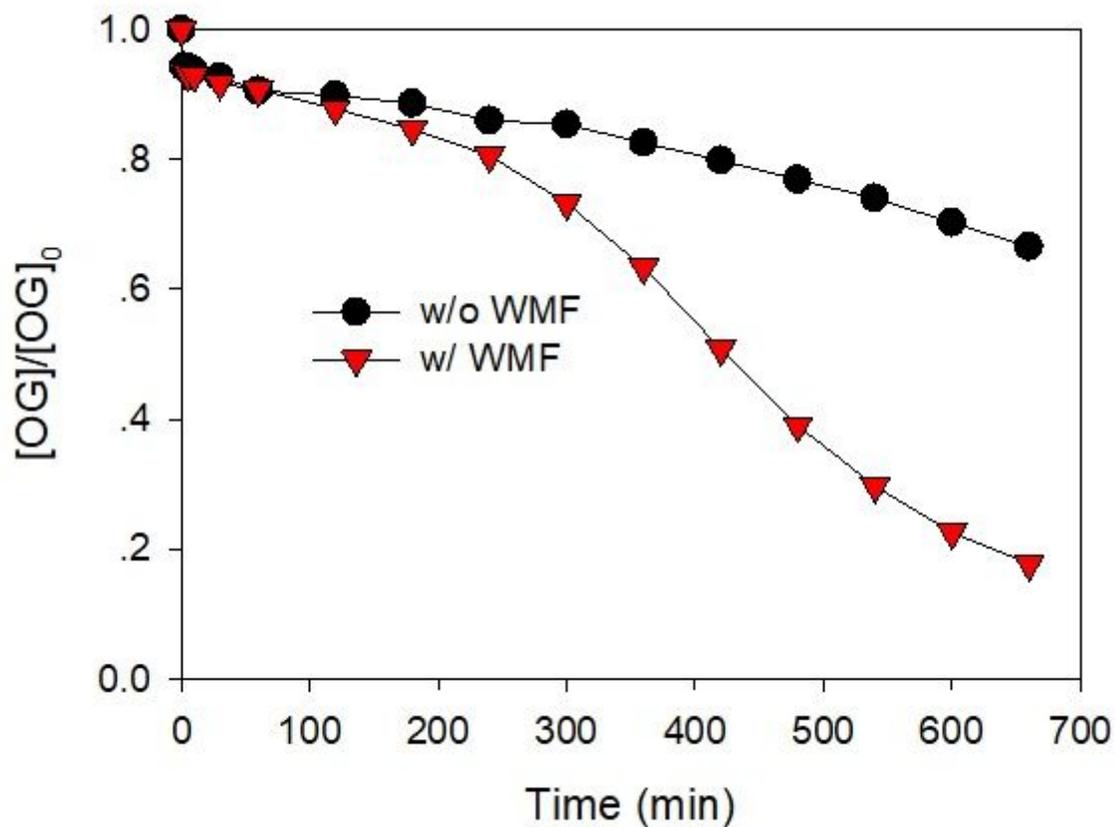


Figure 1

Degradation efficiency of OG in Fe₃O₄/H₂O₂ with or without the WMF. Reaction conditions: [OG]=0.1 mM, [H₂O₂]=20 mM, [Fe₃O₄]=1 mM as Fe, pH=3.0, T=25 oC.

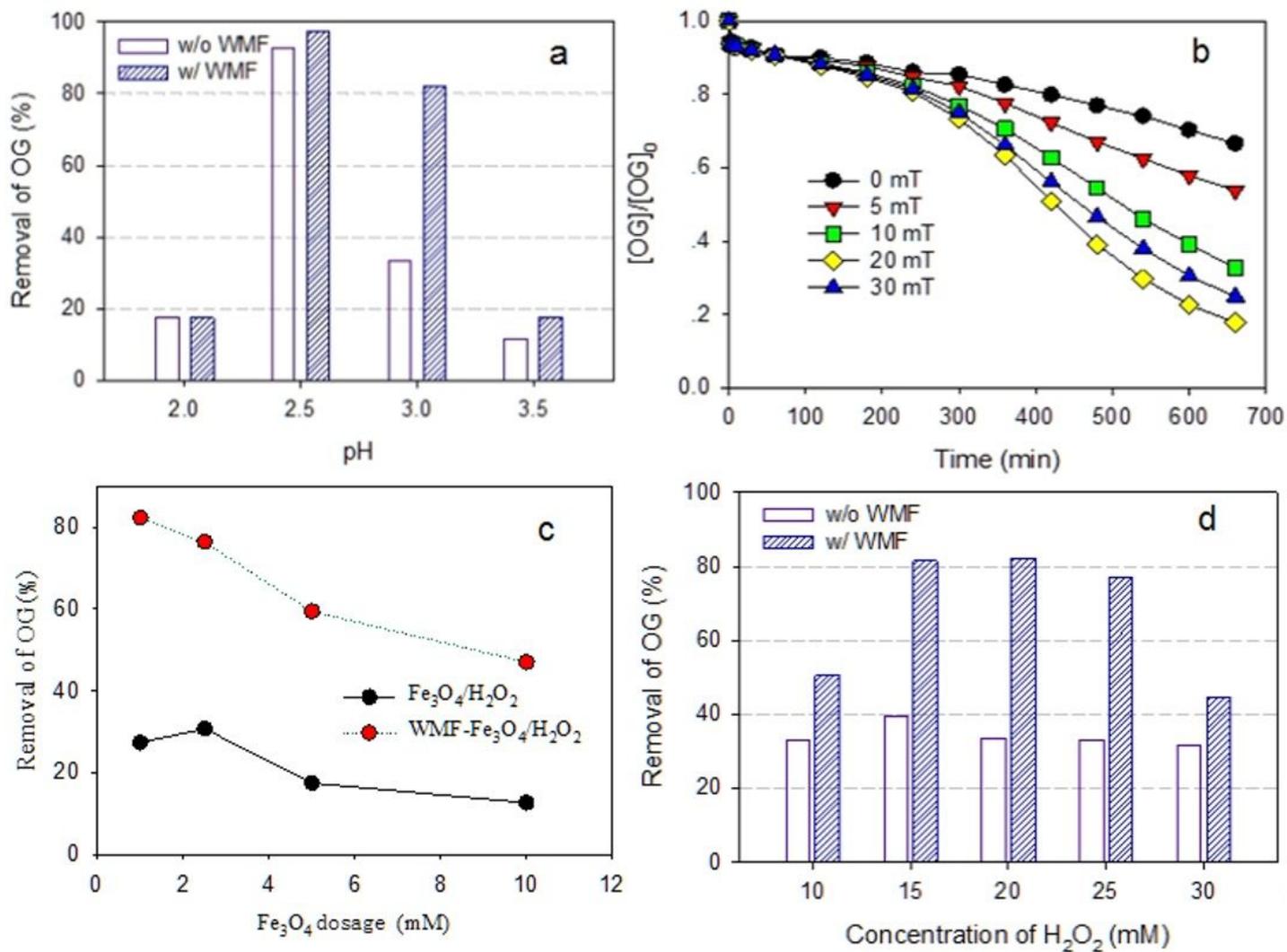


Figure 2

Effect of (a) initial pH, (b) magnetic field intensity, (c) Fe_3O_4 dosage and (d) H_2O_2 concentration on the removal of OG by Fe_3O_4/H_2O_2 system with or without the WMF. Reaction conditions: $[OG]=0.1$ mM, $[H_2O_2]=20$ mM, $[Fe_3O_4]=1$ mM as Fe, $pH=3.0$, $T=25$ oC.

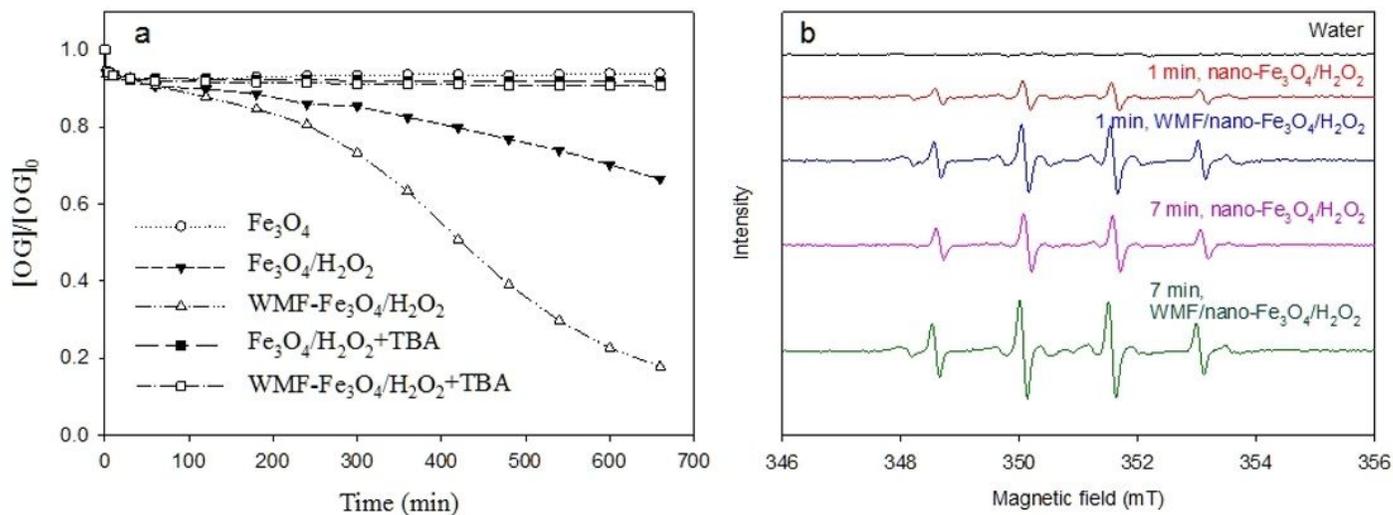


Figure 3

(a) Inhibition effect of TBA on OG degradation in $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process with and without the WMF. Conditions: $[\text{OG}] = 0.1 \text{ mM}$, $[\text{H}_2\text{O}_2] = 20 \text{ mM}$, $[\text{Fe}_3\text{O}_4] = 1 \text{ mM}$ as Fe, $[\text{TBA}] = 20 \text{ mM}$, $\text{pH} = 3.0$, $T = 25 \text{ }^\circ\text{C}$. (b) EPR spectra obtained from ultrapure water, $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process, and WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process with the existence of DMPO. Reaction conditions: $[\text{H}_2\text{O}_2] = 40 \text{ mM}$, $[\text{Fe}_3\text{O}_4] = 20 \text{ mM}$ as Fe, $[\text{DMPO}] \approx 0.1 \text{ M}$, $\text{pH} = 3.0$, $T = 25 \text{ }^\circ\text{C}$.

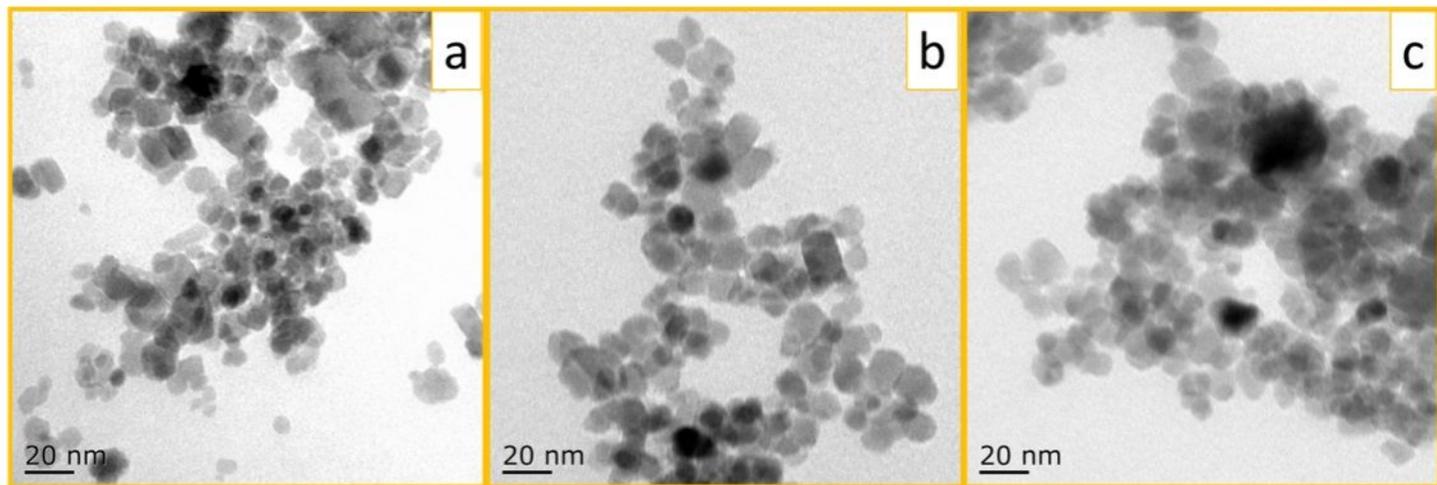


Figure 4

TEM for virgin Fe_3O_4 (a), spent Fe_3O_4 in $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process (b) and in WMF- $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ process (c).

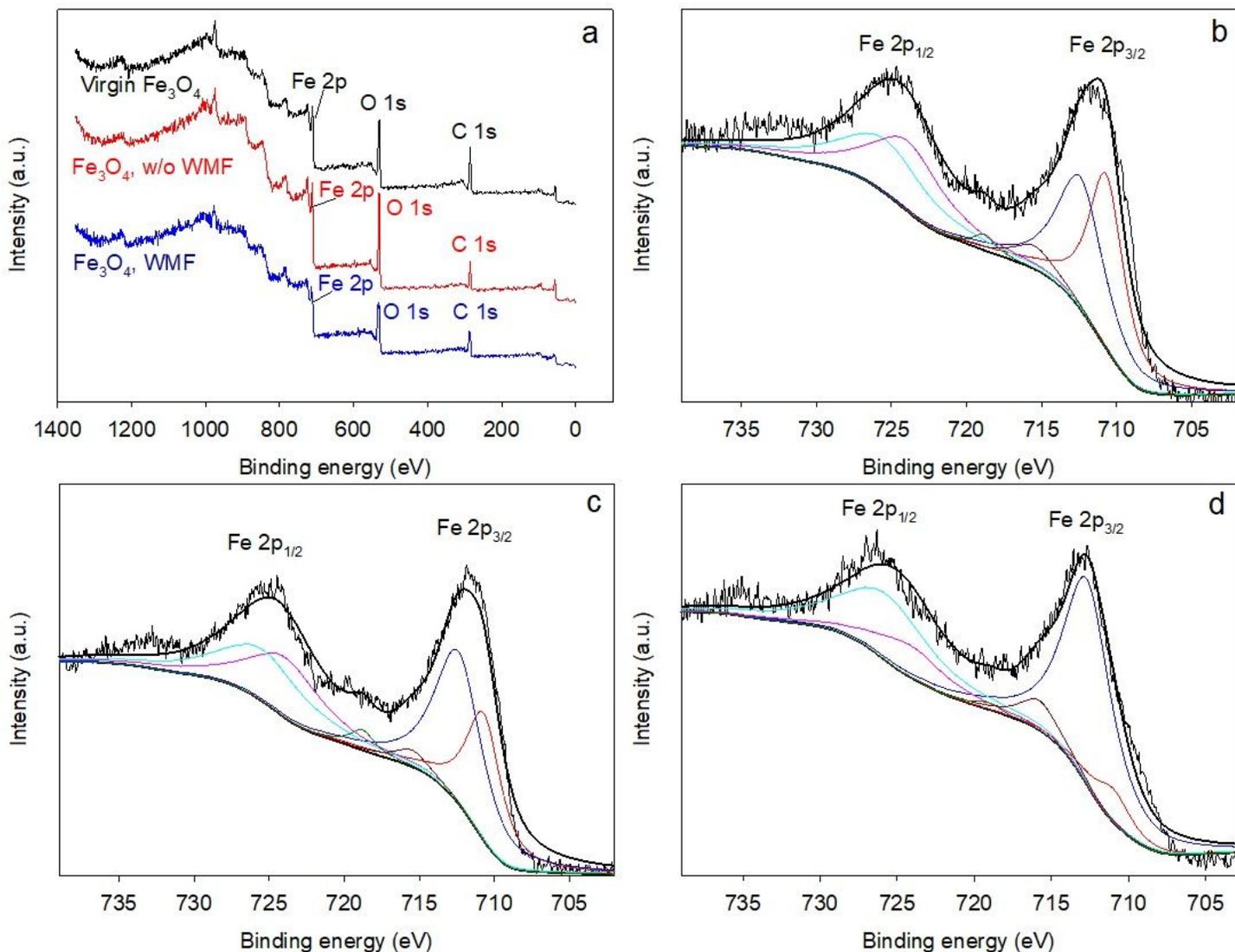


Figure 5

(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.

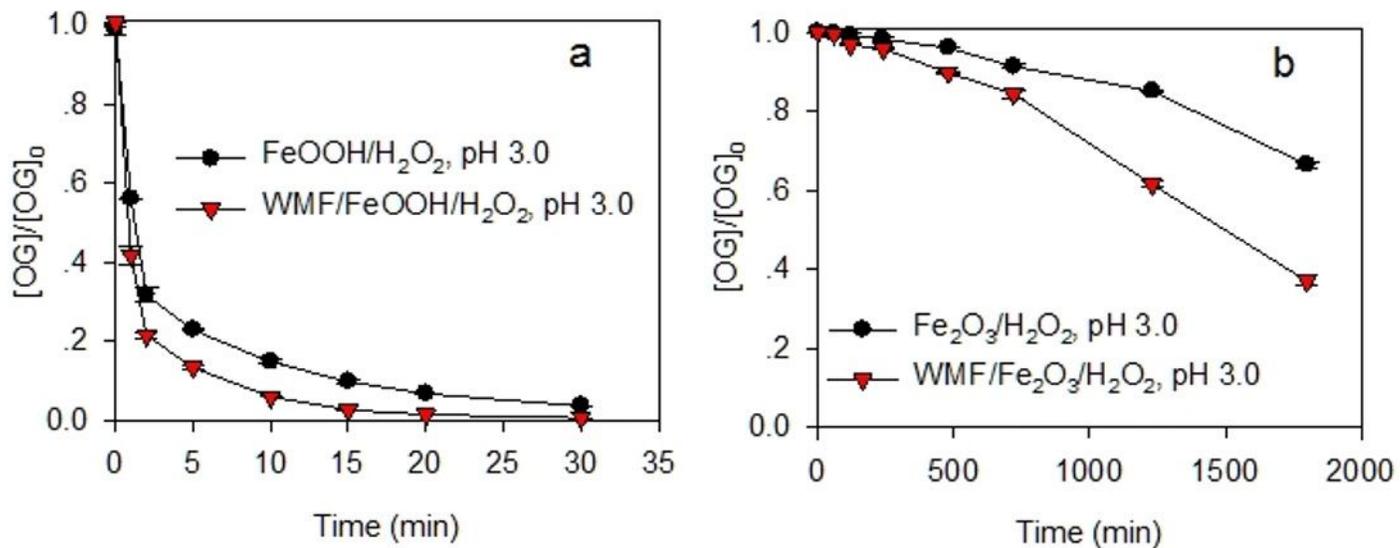


Figure 6

Degradation of OG by heterogeneous Fenton process coupling with the WMF for (a) FeOOH and (b) Fe₂O₃ as a catalyst. Reaction conditions: [OG]=0.1 mM, [H₂O₂]=20 mM, [FeOOH]=[Fe₂O₃]=1 mM as Fe, T=25 oC.

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