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RESEARCH ARTICLE

Highly active Fenton-like catalyst derived from solid waste-iron ore tailings using wheat straw pyrolysis

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Abstract

The pollutants degradation rate of iron ore tailings–based heterogeneous catalysts is the main factor limiting its application. Herein, an iron ore tailings–based Fenton-like catalyst (I/W(3:1)-900-60) with a relatively fast catalysis rate was constructed by co-pyrolysis (900°C, 60 min holding time) of iron ore tailings and wheat straw with a mass ratio of 3:1. With wheat straw blending, the generated I/W(3:1)-900-60 presented a larger surface area (24.53 m^2/g), smaller pore size (3.76 nm), reduced iron species (Fe^{2+} from magnetic), and a higher catalytic activity (0.0229 min^{-1}) than I-900-60 (1.32 m^2/g, 12.87 nm, 0.012 min^{-1}) pyrolyzed using single iron ore tailing under the same pyrolysis conditions. In addition, biochar and iron ore tailings in I/W(3:1)-900-60 were tightly combined through chemical bonding. The optimal catalyst remains active after three cycles, indicating its catalytic stability and recyclability. The good Fenton-like methylene blue degradation efficiency of I/W(3:1)-900-60 was ascribed to the sacrificial role of biochar, as well as the electron transfer between biochar and iron active sites or the redox cycles of $\equiv Fe^{3+}/Fe^{2+}$. This finding provides a facile construction strategy for highly active iron ore tailings–based Fenton-like catalyst and thereby had a great potential application in wastewater treatment.

Keywords Iron ore tailings · Wheat straw · Heterogeneous catalyst · Biochar · Decomposition rate

Introduction

The mining industry is an important activity to extract mineral products around the world. Nevertheless, the mining process always brings a certain degree of pollution. Tailings are solid waste remaining after mining valuable minerals, which are usually disposed of at waste dams or landfills that present potential environmental damage (Rico et al. 2008; Kossoff et al. 2014). In March 2020, a miserable accident involving a waste dam occurred when the Yichun waste dam (Harbin, China) for the storage of iron ore tailings collapsed. This accident caused 60,000 m^3 of mining tailings disclosing and 3 million m^3 of wastewater releasing, leading to 70 km of river pollution and serious economic loss. A number of other tailings dam accidents have occurred in different countries (Batista et al. 2020). According to statistics (Yi et al. 2020), the accumulated tailings were about 207 billion tons in China, of which the total amount of tailings produced in 2018 was about 12.11 billion tons. Among all types of tailings, iron ore tailings have the largest amount of production, about 4.76 billion tons, accounting for about 39.31% of the total tailings production (Huang et al. 2020).

Therefore, it is imperative to explore new technologies for reducing iron ore tailings and their reuse as raw materials to produce value-added products. Recently, a promising application of iron ore tailings has been utilized as adsorbents or catalysts to remove dye compounds (Silva et al. 2011; Augusto et al. 2018), e.g., as raw/regenerated efficient Fenton and Fenton-like catalysts for wastewater treatment. Given the high-iron contents observed in iron ore tailing, it is reasonable to assume that these wastes are good catalysts

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for Fenton or Fenton-like processes (Augusto et al. 2018). However, Fe^{2+} is the effective state for activating the oxidant, while the most common state in iron waste is Fe^{3+} (dos Santos et al. 2016), and the presence of Fe^{3+} modifies the degradation rate (reaction time as long as 24 h) of substance. Some researchers got significant progress in trying to enhance the pollutant oxidation rate through reducing Fe^{3+} to Fe^{2+} (Augusto et al. 2018; de Freitas et al. 2019). Freitas *et al.* achieved good results (80% dye decomposed with 3 h reaction) for the oxidation of methylene blue when iron ore tailing pretreated in a CH_4 atmosphere at 550°C for 2 h.

Better degradation results could be achieved in the case of iron waste pretreatment under a reducing atmosphere (H_2, CO, CH_4). Biomass could produce reducing gases and compounds during pyrolysis (Williams and Besler 1996; Wang et al. 2010). In our previous paper, we found that a unite mass wheat straw could produce about 5 mg/g H_2 and 18 mg/g CH_4 (Gao and Goldfarb 2019). Therefore, if iron tailings and wheat straw blends were pretreated through pyrolysis to realize the conversion of ferric iron to a low-valent state, it would not only improve the catalytic oxidation efficiency of organic matter but also realize the resource utilization of wheat straw, which is of great significance. Therefore, this paper applies methylene blue (MB) as a model pollutant to investigate the influence of pyrolysis conditions on the catalyzed degradation rate of pollutants. The pyrolyzed products' morphology, physical–chemical properties, stability, and catalytic mechanism were discussed. The research in this article aims to provide a theoretical basis for iron ore tailing catalysts with high degradation rates.

Materials and methods

Materials

Iron ore tailings were kindly provided by the "Hainan's mining" industry, located in Hainan, China. The sample was hematite tailings (I) and ground to 74 μm prior to use. Wheat straw was selected as biomass because of the high production in China, which was ground in a coffee mill and sieved to a particle size between 100 and 300 μm (Gao and Goldfarb 2019). Supplementary Table S1 showed the characteristics of wheat straw and hematite tailings. MB was purchased from Aladdin Chemical Reagent Co., Ltd., China.

Synthesis of the catalysts

Hematite tailings and wheat straw mixed with mass ratio 1:1, 2:1, 3:1, 4:1, and 5:1. Then, these mixtures were treated in a tube furnace using a heating rate of 10°C/min (Wang *et al.* found feedstock pyrolyzed at this heating rate could produce more reducing gas, such as CO and H_2) (Wang et al. 2018) until different temperatures (while we do not have the ability to pyrolyze biochar at a temperature above 1000°C due to the furnace, so we selected the pyrolysis temperature as 500°C, 600°C, 700°C, 800°C, and 900) for different holding times (30 min, 45 min, 60 min, 90 min, and 120 min). The obtained catalyst was denoted as I/W(a:b)-T-t, where I is iron ore tailings, W is wheat straw, a:b is the mass ratio (w/w), T is the final temperature, and t is the holding time.

MB decomposition experiments

To evaluate the decomposition rate of the catalyst produced from iron ore tailings, the bath catalytic experiments were carried out using 0.3 g of pyrolyzed product in contact with 100 mL dye solution with initial concentrations of 60 mg/L and 16 mmol H_2O_2 under a shaker; 1.5 mL of solution was pipetted at given time intervals, centrifuged for 1 min, and the dye concentration (C) was detected by a UV-vis spectrophotometer (Unico UV-2800) at 664 nm. A CTL-12 COD analyzer was applied for measuring the chemical demand oxygen (COD) of the sample catalyzed by I/W(3:1)-900-60 in the optimal pH value Fenton system. All tests were performed in triplicate, the degradation rate (k_i) and the C/C_0 at different degradation times for each sample were calculated, and then the results were expressed as mean ± standard deviation.

To investigate the stability and reusability of catalyst, the optimal pyrolyzed product was reused/recycled four times for the MB decomposition under the same Fenton-like condition.

Analytical method

The phase transformation of the ferrochemical group in pyrolyzed solid was analyzed by X-ray diffraction (XRD; Bruker D8 Advance, Germany). The morphology and composition were characterized by scanning electron microscopy and energy dispersive X-ray spectrometer (SEM-EDX; FEI QuantaTM 250, USA). The textural properties were tested by Brunauer–Emmett–Teller measurement (BET; BELSORP-max, Japan). The functional groups of catalysts were investigated by Fourier transform infrared spectroscopy (FTIR; Bruker Vertex 80v, Germany). Electron paramagnetic resonance (EPR; Bruker 300E spectrometer, Germany) was applied to test the main reactive oxidative species (ROS) generated in the system. Fe valence and carbon functional group variation of catalysts were characterized by X-ray photoelectron spectroscopy (XPS; Thermo Fisher Escalab 250 Xi, USA), and the C1s1/2(284.6 eV) was used as the binding energy calibration standard.

Results and discussion

Determination of optimal pyrolysis based on degradation rate

The pyrolysis preparation mass ratio (iron ore tailings to wheat straw), reaction time, and heating rate were fixed at 3:1, 60 min, and 10°C/min, respectively, and catalysts were obtained under different pyrolysis temperatures. Figure 1(a) showed the comparison of MB removal efficiency versus time and pseudo-second-order kinetic constant (k_2, $R^2 > 0.994$) under different catalysts, in which −5 min means that the H_2O_2 was added after 5-min adsorption. Only approximately 20% of MB was removed after 1 h

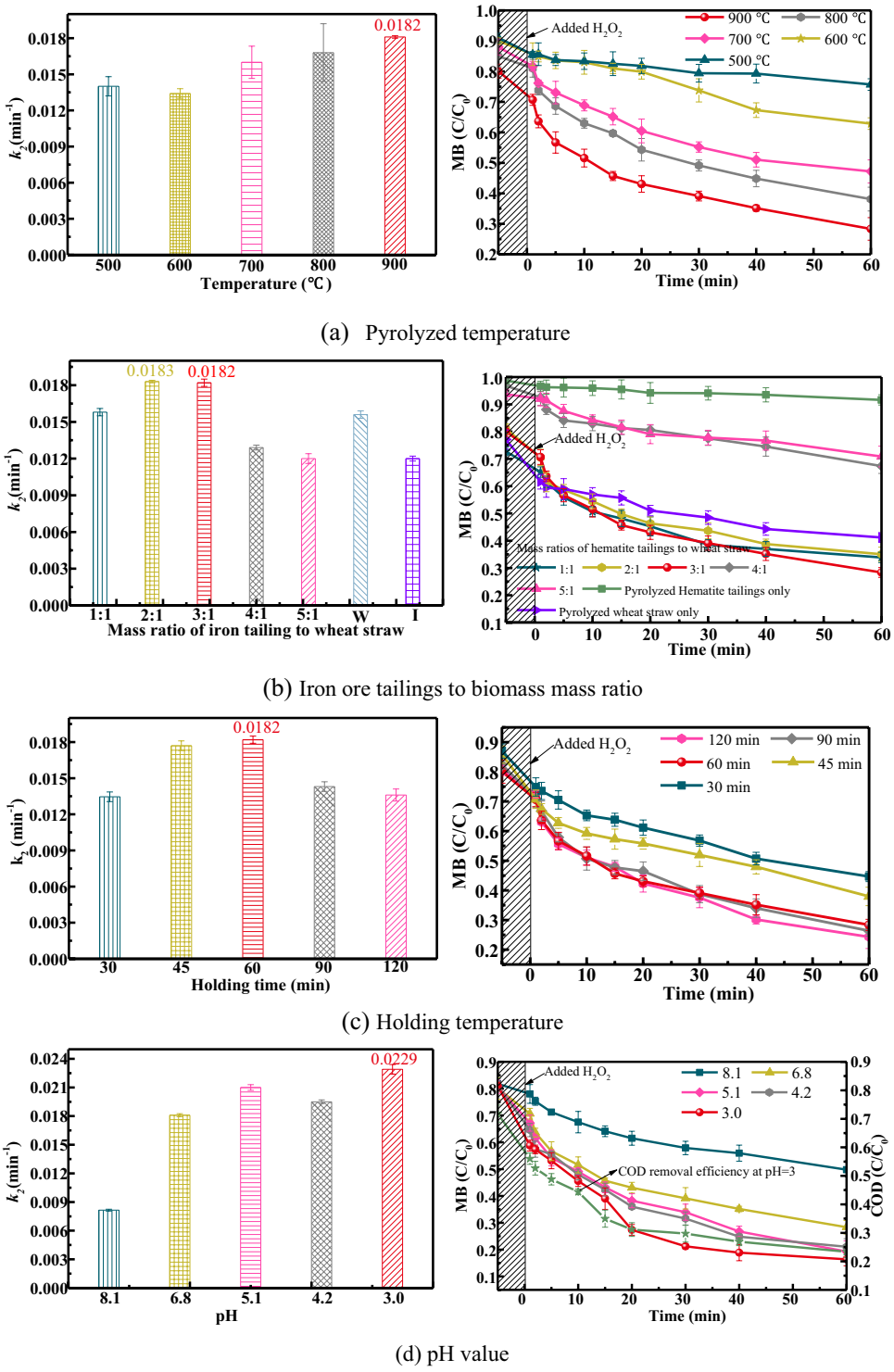

Fig. 1 Degradation of MB by pyrolyzed product prepared under different conditions

with a kinetic rate of 0.0139 min^{-1} when the product prepared at 500°C was used. However, the removal rate and efficiency were substantially improved as the pyrolyzed temperature increased. The best decomposition rate (0.0182 min^{-1}) and efficiency (74%) were reached using a catalyst prepared at 900°C, which was much higher than the generated iron ore tailings catalyst reported by Augusto *et al.* (7.4×10^{-4} min^{-1}, 63%) (Augusto et al. 2018). Considering the dye decomposition rate and efficiency, the optimal pyrolysis temperature for synthesizing catalyst was determined to be 900°C.

Setting the pyrolysis temperature at 900°C, the final holding time at 60 min, and the heating rate at 10°C/min, the removal efficiency and rate of MB were investigated by pyrolysis products at different mass ratios. As shown in Fig. 1(b), only 10% MB was removed with a removal rate k_2 of 0.0120 min^{-1} when the catalyst was prepared by hematite tailings only, indicating that the pyrolyzed product synthesized from iron ore tailings might not be active for dye degradation. While the decomposition efficiency of MB (k_2 increased from 0.0120 to 0.0182/0.0183 min^{-1}) gradually increased when the products made from hematite tailings and wheat straw blends were used as a catalyst. This may be due to biomass blends that helped to reduce the $\equiv Fe^{3+}$ to $\equiv Fe^{2+}$ or low-valent iron (Ellison and Boldor 2021). The mechanism of H_2O_2 activation by iron ore tailings–based catalyst with $\equiv Fe^{2+}$ may involve the following reaction processes (Luo et al. 2010). Firstly, a complex assigned as $\equiv Fe^{2+}\cdot H_2O_2$ may form between the hydrous surface of $\equiv Fe^{2+}\cdot H_2O$ and H_2O_2 (*Eq.*(1)), where $\equiv Fe^{2+}\cdot H_2O$ represents the reduced sites on the iron ore tailings catalyst surface. The formed $\equiv Fe^{2+}\cdot H_2O_2$ can produce ·OH by H_2O_2 activation, which is ready to decompose and oxidize MB (Eqs. (2) and (3)).

$$\equiv Fe^{2+}\cdot H_2O + H_2O_2 \rightarrow \equiv Fe^{2+}\cdot H_2O_2 \quad (1)$$

$$\equiv Fe^{2+}\cdot H_2O_2 \rightarrow \equiv Fe^{3+} + \cdot OH + OH^- \quad (2)$$

$$\cdot OH + MB \rightarrow \cdots CO_2 + H_2O \quad (3)$$

However, the radical formation mechanism by $\equiv Fe^{3+}$ and H_2O_2 is proposed as follows:

$$\equiv Fe^{3+} + H_2O_2 \rightarrow Fe^{3+}\cdot H_2O_2 \quad (4)$$

$$\equiv Fe^{3+}\cdot H_2O_2 \rightarrow \equiv Fe^{2+} + \cdot OOH + H^+ \quad (5)$$

$$\equiv Fe^{3+} + \cdot OOH \rightarrow \equiv Fe^{2+} + O_2 + H^+ \quad (6)$$

The formed $\equiv Fe^{2+}$ subsequently produces ·OH (Eqs. (1)–(3)). Although ·OH can be generated from H_2O_2 when either $\equiv Fe^{2+}$ or $\equiv Fe^{3+}$ is present, the generation rates are much faster between $\equiv Fe^{2+}$ and oxidant (Kwan and Voelker 2002). Although the degradation efficiency for catalysts produced from mass ratio 1:1, 2:1, and 3:1 was equivalent, degradation rate k_2 values of mass ratio 3:1 (0.0182 min^{-1}) and 2:1 (0.0183 min^{-1}) were higher than 1:1 (0.0158 min^{-1}). In order to realize the iron ore tailings bulk utilization and construct a catalyst with a higher degradation rate, we determined that the optimal mass ratio of iron ore tailings to wheat straw was 3:1.

Fixing the pyrolysis temperature at 900°C, the ratio of iron ore tailings to wheat straw at 3:1, and the heating rate at 10°C/min, the optimum holding time was investigated in Fig. 1(c). The dye decomposition efficiency of the pyrolyzed product was enhanced when the holding time for the synthesis catalyst stretched from 30 to 60 min. However, the degradation efficiency of MB was not significantly improved when the holding time was further extended to 90 min and 120 min. Interestingly, k_2 showed a first increasing then decreasing trend as the holding time extended and reached the maximum (0.0182 min^{-1}) when the holding time was 60 min. Thus, 60 min was the optimal catalyst holding time among those investigated parameters.

To sum up, the relative optimal pyrolysis condition was a blends ratio of 3:1, a pyrolysis temperature of 900°C, and a holding time of 45 min. pH as an important factor for the efficiency of Fenton-like reaction, the effect of pH was investigated in Fig. 1(d). We could see that pH could significantly affect the degradation of MB in iron ore tailings–catalyzed Fenton-like process. As shown in Fig. 1(d), the degradation efficiency was relatively low and the k_2 values were 0.0104 min^{-1} and 0.0182 min^{-1} at pH 8.1 and 6.8 (did not adjust). While the decomposition of MB gradually increased as the pH value decreased and got the highest/fastest degradation efficiency (84% MB removal, 0.0229 min^{-1}) at around pH 3, which was consistent with previous studies (Hu et al. 2011). The generation of ·OH from H_2O_2 is the key step in the entire Fenton-like process, and ·OH catalyzed by iron ore tailings are gradually limited with pH increasing. The higher pH with more OH^- will cause the reaction (Eq. (7)) to shift back and reduce the activity of the Fenton reagent (Zheng et al. 2016), which resulted in a slow decomposition rate of I/W(3:1)-900-60. Meanwhile, the COD removal efficiency of I/W(3:1)-900-60 at pH = 3 was shown in Fig. 1(d), and the COD removal efficiency was 76.6% after 60 min (from 141.2 to 32.3 mg/L). Therefore, the heterogeneous reaction with I/W(3:1)-900-60 as the catalyst can not only attack the MB chromophore group but also realize the degradation and mineralization of organic matter.

$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + OH^- + \cdot OH \quad (7)$$

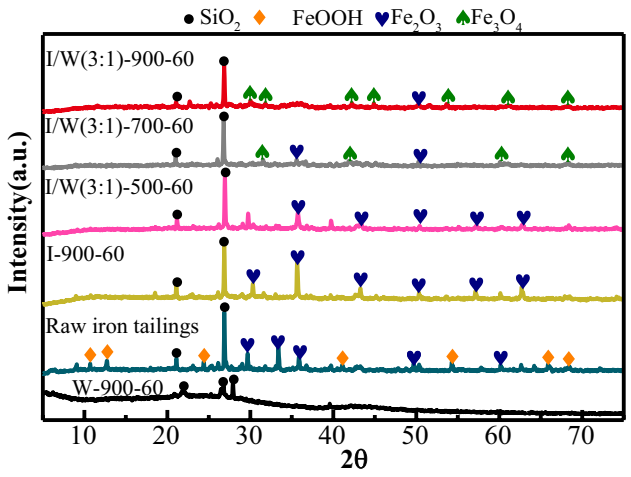

Fig. 2 XRD patterns of the raw and prepared samples

Catalyst characterization

Since the catalytic efficiency was apparently different by I-900-60, W-900-60, and I/W(3:1)-900-60, XRD patterns were collected to indicate the phase information of these samples shown in Fig. 2. The XRD pattern of I/W(3:1)-900-60 showed diffraction peaks at 2θ=30.3°, 43.3°, 53.8°, 57.5°, 68.2° corresponded to Fe_3O_4, which exhibits magnetic characteristics. The peaks of W-900-60 were noted at 2θ = 21.8°, 26.5°, 28.0°, corresponding to SiO_2 crystallites. The diffraction peaks of raw iron ore tailings were attributed to α-FeOOH, and α-FeOOH was converted to Fe_2O_3 when heated to 900°C under N_2 atmosphere (Zhang et al. 2018). Therefore, only the pyrolysis of iron ore tailings or wheat straw cannot produce a composite with low-valent iron.

Significant transformation of Fe_2O_3 to Fe_3O_4 was observed at 700–900°C. When the temperature reached above 700°C, most of the Fe_2O_3 peaks disappeared and the diffraction peaks of magnetite appeared. It can be concluded that Fe_2O_3 with trivalent could be reduced to Fe_3O_4 during high-temperature pyrolysis. More Fe_2O_3 spindles were converted to Fe_3O_4 as the temperature increased. This is due to that there were organic matters such as cellulose, hemicellulose, and lignin in wheat straw, and these organic matters could be cracked and devolatilized into reducing gas or liquid, such as H_2, CH_4. In our previous study, we noted that wheat straw could devolatilize 2.1 mg/g_{ws} H_2 and 15.7 mg/g_{ws} CH_4 at a temperature of 650°C. Meanwhile, the rate of devolatilization and the amount of thermal creaking gas increase as the temperature increases (Gao and Goldfarb 2019). In addition, some literature reported that pyrolyzed gases could lead to a ferric iron reduction (Gong et al. 2012; Sharma et al. 2015; Pang et al. 2019; Xun et al. 2019). In summary, in the process of co-pyrolysis of wheat straw and iron ore tailings, the reducing substances such as H_2 or CH_4 produced from wheat straw exhibited strong reducibility to reduce iron ore tailings to magnetite. Furthermore, the reduction degree increased as the pyrolysis temperature increased.

To illustrate the effect of biomass/wheat straw on the high degradation efficiency catalyst formation, the morphologies of I-900-60 and I/W(3:1)-900-60 were further compared. The surface morphologies of I-900-60 and I/W(3:1)-900-60 were shown in Supplementary Fig.S1. The I-900-60 presented a large flaky structure with a flat and non-porous surface after pyrolysis, mainly because of the natural structure of iron ore tailings. In the case of I/W(3:1)-900-60, SEM images showed that most particles had a smaller flake structure with porous surfaces. This result indicated that mixing wheat straw promotes the formation of a porous and smaller flake structure.

As observed from SEM images, I/W(3:1)-900-60 had a smaller particle than I-900-60. N_2 adsorption–desorption isotherm was applied to calculate the surface area, pore volume, and pore size distribution. As shown in Table 1 and Supplementary Fig. S2, the average pore sizes of I-900-60 and I/W(3:1)-900-60 were 12.87 nm and 3.76 nm. However, the total pore volumes were 0.00387 cm^3/g and 0.0225 cm^3/g, respectively. Thus, we can conclude that wheat straw addition increased the pore volume and decreased the average pore size. Additionally, although I/W(3:1)-900-60 had a much larger specific surface area (24.53 m^2/g) than I-900-60 (1.32 m^2/g), its surface area was smaller than those reported iron-load-activated carbon adsorbent (300–600 m^2/g) (Park et al. 2015; He et al. 2016; Saleh et al. 2017). This result further verified that prepared catalysts from iron ore tailings had weak adsorption ability. Therefore, we speculated that MB degradation by I/W(3:1)-900-60 was due to catalysis instead of adsorption. I/W(3:1)-900-60, with relatively larger surface area and richer pore volume, could provide greater active catalysis sites and increase catalysis performance (Neamţu et al. 2004; Duarte et al. 2012), agreed with the improved MB degradation efficiency catalyzed by I/W(3:1)-900-60.

There is an important question to further discuss that whether composites (wheat straw biochar and iron ore tailings) were simply mixed and exist alone or integrated

Table 1 BET and BJH results of prepared catalysts

Samples	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
I-900-60	1.32	0.00387	12.87
I/W(3:1)-900-60	24.53	0.0225	3.76

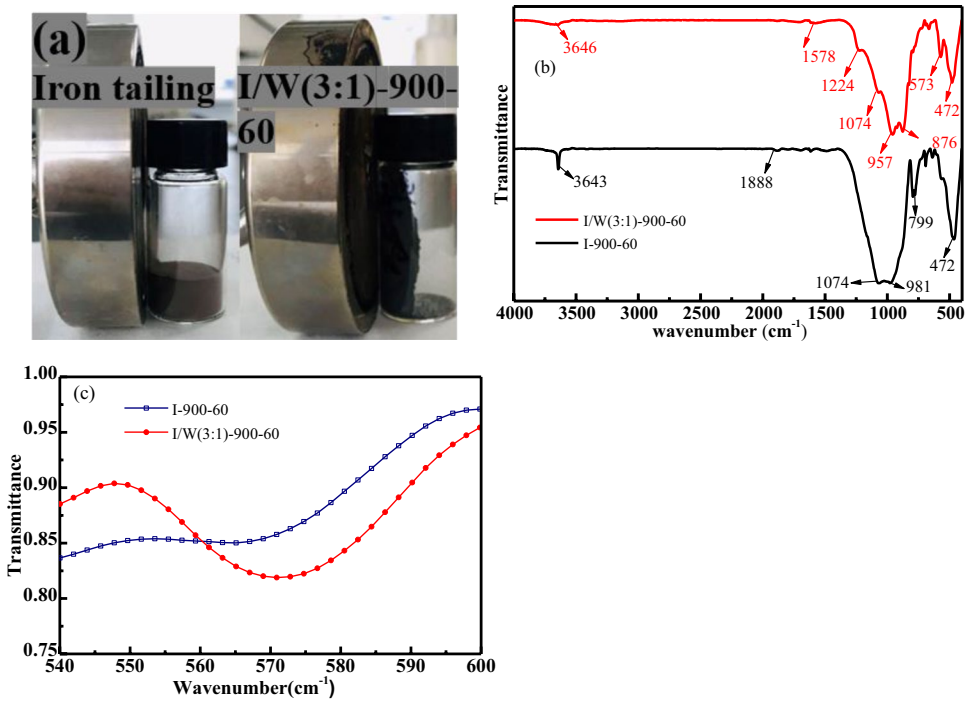

Fig. 3 (**a**) The photos of the products attraction to a magnetic device; (**b**) FTIR spectra of I-900-60 and I/W(3:1)-900-60 in the wavenumber range between 4000 and 400 cm^{-1}; (**c**) zoomed FTIR spectra in the wavenumber range between 540 and 600 cm^{-1}

together. Figure 3(a) showed that the catalysts were attracted as a whole by a magnetic device, indicating iron ore tailings and biochar combined as a whole. This binding form is beneficial to remove the catalyst from wastewater after the reaction. In addition, FTIR spectra in the wavenumber range between 4000 and 400 cm^{-1} were shown in Fig. 3(b). The peak at 3643/3646 cm^{-1} was attributed to O-H stretching and bending vibrations (Zhang et al. 2018). Similar peaks were observed in the spectra of both I-900-60 and I/W(3:1)-900-60, including Si-O stretching vibrations of the Si-O-Si, Si-O-Al, and Si-O-Fe groups (1074 cm^{-1}, 957/981 cm^{-1}, 472 cm^{-1}), although their intensities varied (Doelsch et al. 2003). The silicon content in iron ore tailings was much higher than that in wheat straw (Supplementary Table S1). Therefore, the intensity of Si-O stretching vibration in I-900-60 was stronger than in the spectrum of I/W(3:1)-900-60. Meanwhile, new peaks associated with the -C=O and -C-H stretching vibration at 1224 cm^{-1} and 876 cm^{-1} were observed in the spectrum of I/W(3:1)-900-60; these peaks were assigned mainly to the formed biochar that has the corresponding groups, such as carboxyl and ester groups. In addition, as shown in Fig. 3(c), a new peak at 573 cm^{-1} attributed to an asymmetric Fe-O stretching vibration was observed. It might be caused by loading iron into biochar or Fe_3O_4 itself (Yuan and Dai 2014). Therefore, the new bond Fe-O on I/W(3:1)-900-60 may indicate the combination of iron and biochar that occurred through chemical bonds.

The catalyst's stability and reusability analysis

It is important to evaluate the stability of a heterogeneous catalyst. As illustrated in Supplementary Fig. S3, I/W(3:1)-900-60 was stable in the first three runs and remained high MB degradation efficiency. At the 4th run, the activity of I/W(3:1)-900-60 reduced slightly, but the degradation efficiency is still higher than 80%, showing that the iron ore tailings–based catalyst can be reused for at least 4 Fenton-like cycles without significant activity loss. This slight activity loss is probably due to the small molecules produced during MB degradation occupying part of the active sites, leading to a decrease in catalytic efficiency (Zhang et al. 2018). In addition, the concentration of leaching iron ions after the first three runs was measured. As shown in Supplementary Table S2, the concentrations of leached iron were 0.089 mg/L, 0.085 mg/L, and 0.093 mg/L, which were only 0.8% of the iron content in I/W(3:1)-900-60. Low-leached iron concentration also indicated that heterogeneous Fenton catalysis was the dominant reaction for MB removal (Gao et al. 2017). Meanwhile, XRD and SEM were applied to examine the structural stability of I/W(3:1)-900-60. As illustrated in Supplementary Fig. S4, compared with fresh catalyst, the crystalline nature and morphology of used I/W(3:1)-900-60 did not change significantly. These results indicated that the cost-effective I/W(3:1)-900-60 was a promising heterogeneous catalyst in Fenton-like catalytic degradation of organic wastewater due to its significant stability and reusability.

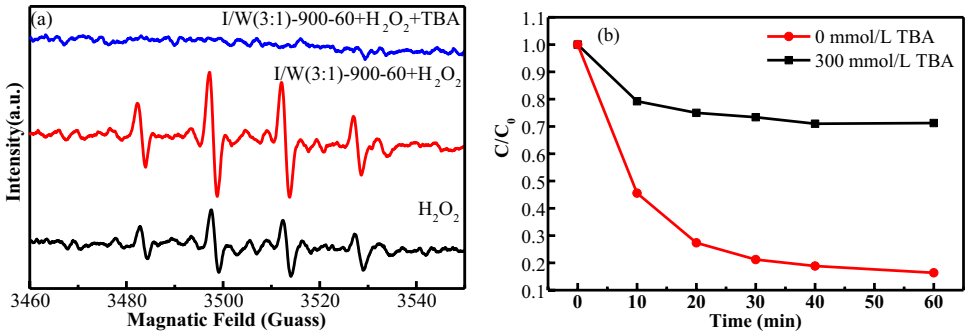

Fig. 4 (**a**) DMPO-ROS adducts generated from I/W(3:1)-900-60 Fenton catalysis reactions at 10 min. (**b**) Influence of radical scavenger (TBA) on the catalytic degradation of MB

Reactive oxidative species and catalysis mechanism

ROS produced in I/W(3:1)-900-60 was detected by an EPR spin-trap technique with DMPO. Figure 4(a) showed the EPR spectrum of the generated adducts during the 10-min reaction. On the EPR spectrum, there was observed a four-fold peak with an intensity of 1:2:2:1, which was labeled to the DMPO-OH (Yang et al. 2013). However, the four-fold peak has not appeared in the presence of 300 mmol/L T-Butyl alcohol (TBA, OH scavenger). Therefore, OH was the key ROS produced in I/W(3:1)-900-60 catalyzed Fenton-like reactions. Figure 4(b) showed the effect of ·OH on MB degradation. We can see the removal efficiency of MB significantly decreased from 84 to 29% in the presence of 300 mmol/L. This result indicated that ·OH played a dominant role in MB degradation in I/W(3:1)-900-60 catalyzed Fenton-like reactions.

The electron exchange between Fe(II)/Fe(III) and H_2O_2 can induce the formation of ·OH in the heterogeneous Fenton-like reaction. XPS was applied to analyze the chemical state of iron species on I/W(3:1)-900-60 before and after the catalysis reaction. Figure 5 shows XPS results of Fe2*p* in fresh and used I/W(3:1)-900-60. The peaks located at 724.8 eV and 710.9 eV were attributed to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ states of Fe2*p* orbits, respectively (Gao et al. 2017; Li et al. 2018). Furthermore, the Gaussian-Lorentzian was applied to decompose these two peaks into 6 different fitting peaks (Ding et al. 2016). Among them, the fitting peaks located at 719.1 eV and 729.9 eV attribute to satellite peaks, as well as at 712.0 eV and 725.3 eV assign to Fe^{3+}, and at 710.6 eV and 723.8 eV correspond to Fe^{2+}, respectively (Li et al. 2018). A summary of deconvoluted peaks' area and the Fe^{2+}/Fe^{3+} ratio was presented in Fig. 5(a). Apparently, the ratio value of Fe^{2+}/Fe^{3+} decreased from 2.18 to 2.17 after the reaction, demonstrating only a small amount of $\equiv Fe^{2+}$ lost electrons and oxidized to $\equiv Fe^{3+}$ during the catalysis reaction. These XPS results are in accordance with the good recyclability and stability of I/W(3:1)-900-60 catalyst, which may attribute to the protective effects of the biochar (Li et al. 2018).

To further verify the protective role of biochar during Fenton-like reaction. XPS analysis was conducted to investigate the functional groups' changes of I/W(3:1)-900-60 catalyst. As illustrated in Fig. 5(b), the C1s spectra can be decomposed into three fitting peaks with C=C sp^2/C-Csp^3 (284.7 eV), C-O (286.1 eV), and C=O (288.8 eV) (Li et al. 2017b). Apparently, compared with the fresh I/W(3:1)-900-60, the relative content of C=C sp^2/C-Csp^3 carbon was reduced by 5.8% and C-O and C=O increased by 4.4% and 1.4% after catalysis reaction. This indicates that biochar was oxidized during the Fenton-like process with turning C=C sp^2/C-Csp^3 carbon to C-O or C=O. Therefore, the recyclability and stability of the I/W(3:1)-900-60 catalyst may owe to the existence of biochar which acted as a sacrificial role and limited the oxidation of iron active sites in the catalyst. Actually, the biochar can act as a catalyst with electron donor-accepter for the induction of H_2O_2 into ·OH or ·OOH. The persistent free radicals (PFRs) on the surface of biochar formed by the thermal decomposition of organic compounds can be the reduced and oxidized active sites through electron

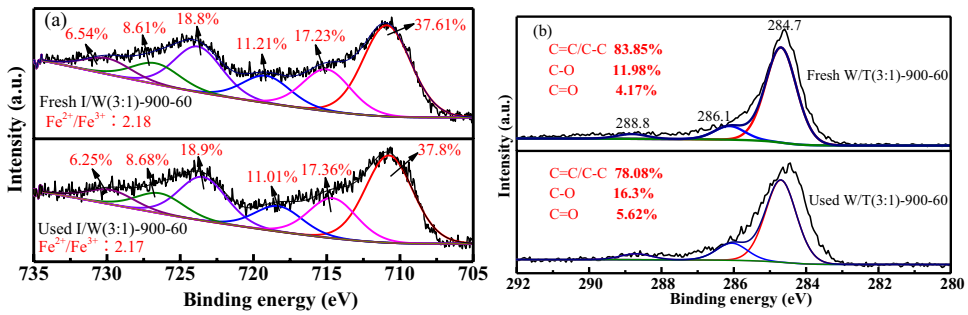

Fig. 5 XPS spectra of Fe 2p (**a**) and C1s (**b**) on I/W(3:1)-900-60 before and after catalysis reaction

transfer to form radical species ((Khachatryan and Dellinger 2011; Zhu et al. 2018). Fang *et al.* found that PFRs on the surface of biochar have an important influence on the production of •OH by H_2O_2 activation (Fang et al. 2014). In addition, the PFRs on the biochar surface lead to the existence of unpaired electrons, which can exchange electrons directly with organic matter, accelerating the MB degradation efficiency (Fang et al. 2013; Yang et al. 2016).

According to the above analysis results and discussion, the possible Fenton-like reaction mechanism was illustrated in Fig. 6. In the beginning, the MB molecules were adsorbed onto biochar of I/W(3:1)-900-60 from aqueous solution through surface action and pore diffusion. Then, the iron active sites of $\equiv Fe^{2+}$ and PFRs in biochar simultaneously transfer an electron to H_2O_2 to generate ·OH for MB degradation. According to the previous research (Zhang et al. 2018), the degradation process of MB can be described as that under the bombardment of ·OH, the N-C_5H_5, and S-C_5H_5 on the MB molecule is first broken and formed 4-(N,N-dimethylamino) phenyl isothiocyanate. Secondly, ·OH radicals combined with aromatic rings to form monocyclic aromatic intermediates through hydroxylation and oxidation reactions. Finally, ring-opening products, such as methyl methacrylate and isopropyl methyl ketone, were produced and then mineralized into CO_2 and H_2O. Moreover, the electron transfer between PFRs and iron active sites or the redox cycles of $\equiv Fe^{3+}/Fe^{2+}$ combined results in the enhanced degradation efficiency and rate of heterogeneous Fenton-like reaction. Significantly, the stable performance of I/W(3:1)-900-60 with good reusability is due to the sacrificial effect of biochar for limiting the oxidation of iron active sites. In addition, the presence of unpaired electrons in PFRs contributes to a certain extent to improve the degradation efficiency of pollutants.

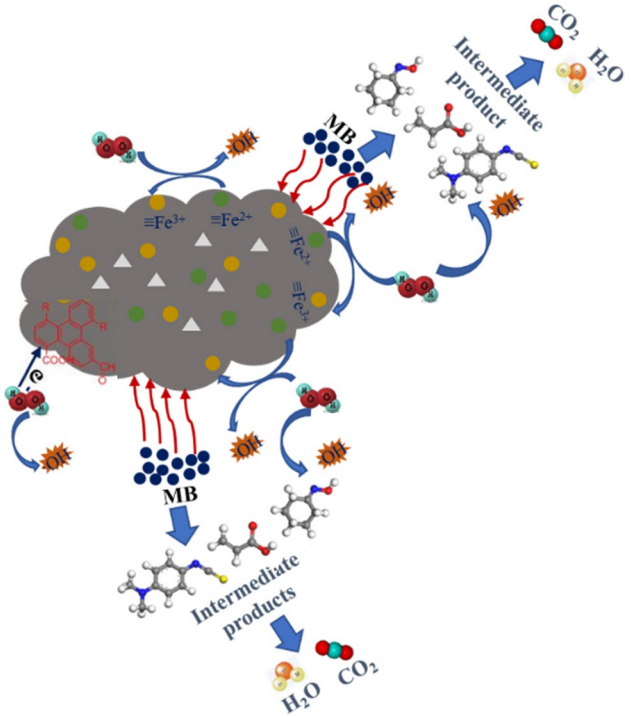

Fig. 6 Proposed mechanism for Fenton catalysis reaction of I/W(3:1)-900-60

Table 2 showed the MB decompose rate k_2 for various Fenton-like catalysts. We can see that I/W(3:1)-900-60 (0.0229 min^{-1}) exhibited a higher k_2 than or comparable to most reported kinetic rate data, which indicates that the co-pyrolysis of iron ore tailings and biomass waste is an effective way to improve the degradation rate/efficiency of iron ore tailings–based heterogeneous catalysts. Meanwhile, it is of great significance to realize the resource utilization of iron ore tailings. However, these kinetic rate dates are far less than the degradation rate of homogeneous Fenton catalysis (Gou et al. 2021). Thus, the performance optimization of iron ore tailings–based heterogeneous catalysts based on porous and low-valent iron still needs further study.

Table 2 Comparison of MB removal by Fenton-like methods with different catalysts

Catalyst	MB (mg/L)	Catalyst dosage (g/L)	Time (min)	k (min^{-1})	Reference
I/W(3:1)-900-60	60	3	60	2.29×10^{-2}	This study
Fe_3O_4	100	3	30	1×10^{-3}	Costa et al. 2008
Fe_3O_4/H_2/300/1h	100	3	30	4×10^{-3}	Costa et al. 2008
Fe_3O_4/H_2/400/1h	100	3	30	2×10^{-2}	Costa et al. 2008
Ferrocene	10	0.372	120	6.17×10^{-3}	Wang et al. 2014
Fe_3O_4/rGO	10	0.3	120	2.6×10^{-3}	Liu et al. 2013
Fe_3O_4/SiO_2/C	50	1	140	3.6×10^{-2}	Liu et al. 2013
Fe_3O_4/CeO_2	100	1	120	2×10^{-2}	Li et al. 2017a
Fe_3O_4/galic acid/GO	64	1	200	1.2×10^{-2}	Hua et al. 2017
N,C/CuO-Fe_2O_3	75	0.1	180	1.08×10^{-2}	Ren et al. 2019
FeNi/C-300	30	1	30	1.05×10^{-2}	Li et al. 2020

Conclusions

An iron ore tailings–based Fenton-like catalyst (I/W(3:1)-900-60) with a relatively fast catalysis rate was constructed by co-pyrolysis (900°C, 60 min holding time) of iron ore tailings and wheat straw with a mass ratio of 3:1. Compared with single pyrolyzed iron ore tailing, the catalytic efficiency and rate of I/W(3:1)-900-60 (0.0229 min^{-1}, 84%) were considerably enhanced for the decomposition of MB due to the electron transfer between biochar and iron active sites or the redox cycles of $\equiv Fe^{3+}/Fe^{2+}$. As a result of the sacrificial effect of biochar, oxidizing $C{=}Csp^2$ bonds and limiting the deactivation of iron active sites ($\equiv Fe^{2+}$), I/W(3:1)-900-60 showed good reusability and stability. Moreover, the presence of unpaired electrons in persistent free radicals (PFRs) of biochar accelerated the electron exchange and further enhanced the MB decomposition rate. This work opens up a way to synthesize an iron ore tailings–based Fenton-like catalyst with a higher degradation rate as well as realize the utilization of solid wastes.

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Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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