


 Cite this: *RSC Adv.*, 2020, 10, 32671

Removal of reactive brilliant red X-3B by a weak magnetic field enhanced Fenton-like system with zero-valent iron†

 Liping Liang,^{ab} Yuting Zhang,^a Liubiao Cheng,^a Qian Wu,^a Yuanyuan Xue,^a Qian Wang^a and Xu Meng^{*cd}

The effect of a weak magnetic field (WMF) on the removal of reactive brilliant red X-3B (X-3B) by zero-valent iron (ZVI)/H₂O₂ was studied. The optimum conditions for the removal of X-3B by the ZVI/H₂O₂/WMF system were as follows: pH = 4.0, X-3B was 50 mg L⁻¹, H₂O₂ was 8 mM, and ZVI with particle size of 20 μm was 0.5 g L⁻¹. The X-3B decolorization rate could reach 99.41% in 10 minutes. The superposed WMF increased the working pH of ZVI from 3.0 to 4.0. The main part of ZVI/H₂O₂ removal kinetics of X-3B followed the zero order rate law. In this study, the removal effect of X-3B by pre-magnetization ZVI was not as good as that of real-time magnetization, but it was better than the removal of X-3B by the ZVI/H₂O₂ system. The ZVI/H₂O₂/WMF system still had the ability to remove X-3B after 4 consecutive cycles. The use of WMF improved the removal of X-3B by ZVI/H₂O₂ mainly due to the corrosion of ZVI. Under acidic conditions, WMF enhanced the activity of ZVI, which promoted the efficiency of the Fenton reaction. The use of WMF to enhance the ZVI/H₂O₂ removal X-3B was a promising and environmental friendly process because it did not require additional energy and expensive reagents and did not cause secondary pollution.

 Received 18th April 2020
 Accepted 23rd August 2020

DOI: 10.1039/d0ra03480k

rsc.li/rsc-advances

Introduction

Dye wastewater from the textile, dyeing, and printing industries has been a serious environmental problem in China. Discharge wastewater from the manufacture of textiles, clothing, and apparel reached 2.0 billion tons which exceeded 10% of the total industrial wastewater in China.¹ About 2–12% of synthetic dyes were directly released into the water environment in the process of production and use. Of all dyes, azo dyes accounting for about 70% of the total synthetic dye production² are the most widely used dyes in the world.³ Azo dyes with one or more azo groups (–N=N–) connected to aromatic rings exhibited an excellent water-solubility, and relative stability during usage.⁴ Azo dyes not only lead to high color in water,⁵ but also induced serious human and animal health problems due to their potential mutagenicity, carcinogenicity, and toxicity.⁶ Besides, azo dyes in water were very stable for their commercial requirement⁷ which induced their resistance to traditional

biodegradation and gentle photodegradation. So it's necessary to develop new strategies to treat azo dyes in wastewater.

Common chemical treatments such as coagulation,⁸ filtration,⁹ adsorption,¹⁰ and ion exchange¹¹ have been used to treat azo dye wastewater, but these methods have some disadvantages such as high cost, secondary pollution, low efficiency, and the inability to destroy complex structures of dyes. Compared to other chemical technologies, chemical oxidation method especially for advanced oxidation processes (AOPs) have become an excellent strategy to rapidly degrade dyes in water. Generally, AOPs requires the addition of additional energy (such as light, ultrasound, and microwave) or different catalysts into oxidants such as H₂O₂, persulfate (PDS), and peroxymonosulfate (PMS). ZVI was considered as a readily available, inexpensive, nontoxic and moderately strong reductant¹² which has been widely used in activating H₂O₂ and PDS.¹³ Generally, ZVI possessed a high reactivity exhibited an excellent performance in AOPs. So, many methods have been developed to improve the reactivity of ZVI samples such as acid washing,¹⁴ hydrogen reduction,¹⁵ the synthesis of nano-scale ZVI (nZVI)¹⁶ or bimetallic.¹⁷ However, these enhancing technologies on ZVI reactivity have some barriers of high cost,¹² hard handling, and potential ecotoxicity.^{18,19} Besides, the high reactivity of ZVI might also induce the formation of iron oxides or hydroxides on the surface of ZVI which inhibited the reactions between ZVI and oxidants.^{20,21} Therefore, it is very important to explore an environmental friendly method which can improve the reactivity of ZVI and hinder the formation of passivation layer on the surface of ZVI.

^aSchool of Civil Engineering, Shaoxing University, Shaoxing 312000, P. R. China

^bCollege of Life Science, Shaoxing University, Shaoxing 312000, P. R. China

^cCollege of Textile and Garment, Shaoxing University, Shaoxing 312000, P. R. China. E-mail: mengxu0@163.com

^dKey Laboratory of Clean Dyeing and Finishing Technology of Zhejiang Province, Shaoxing University, Shaoxing, 312000, P. R. China

 † Electronic supplementary information (ESI) available: Complete XRD and SEM data, supplementary data of WMF on ZVI/H₂O₂ removal of X-3B under different PH conditions. See DOI: 10.1039/d0ra03480k


Recently, WMF of low cost, easy handling, and no secondary pollution has become a new technology to improve the reactivity of ZVI which can enhance contaminants removal efficiency. Guan's group^{22–27} carried out a lot of researches on heavy metals and dyes removal by microscale ZVI (mZVI) coupled with WMF. Their results indicated that WMF accelerated ferrous release from ZVI and promoted the corrosion of ZVI. Besides, WMF can also recover the reactivity of aged ZVI²² and depassivate the passive film on ZVI samples.²⁵ Li *et al.*²³ proved that the magnetic gradient force was the major driving force for the enhancing effect of WMF by driving the paramagnetic Fe^{2+} to the place with higher MF flux intensity with magnetic lines. The movement of the paramagnetic Fe^{2+} could expose more reactive sites on the ZVI samples. These advantages of enhancing ZVI reactivity induced by WMF might be also applied in AOPs. Xiong *et al.*^{28,29} firstly studied various organics removal performances in ZVI/ H_2O_2 /WMF and ZVI/PDS/WMF systems, WMF exhibited a significant enhancement on organics removal rate by ZVI/ H_2O_2 and ZVI/PDS, and the accelerating effect of WMF on 4-nitrophenol degradation by ZVI/ H_2O_2 /WMF was increased with the intensity of WMF from 5 mT to 20 mT. When the magnetic field intensity was greater than 20 mT, ZVI particles were easy to aggregate. Therefore, the optimum intensity of WMF was determined to be 20 mT. Then Zhou *et al.*^{30–33} and Du *et al.*¹³ also investigated WMF enhanced organic contaminants removal by ZVI/ H_2O_2 and ZVI/PDS. And WMF accelerated the generation of reactive radicals by promoting the release of ferrous. Therefore, WMF could be considered as an excellent technology to enhance azo dyes removal in ZVI/ H_2O_2 system.

In this study, a typical azo dye reactive brilliant red X-3B (X-3B) was selected as the target dye. And the optimal reaction conditions and removal kinetics of X-3B removal by ZVI/ H_2O_2 coupled with WMF were investigated. Finally, mechanisms of X-3B removal in ZVI/ H_2O_2 /WMF systems were proposed.

Materials and methods

Materials

The ZVI used in the experiment was purchased from Haotian Nano Technology Co., Ltd (Shanghai). All chemicals were at the analytical level and were used without other treatment. The raw solution was prepared by dissolving the corresponding salt in the ultra-pure water produced in the Milli-Q reference water purification system.

Batch experiments procedure

The laboratory-scale experimental device used in this experiment was shown in Fig. S1 (in the ESI).[†] The non-uniform weak magnetic field in this experiment was generated by two permanent magnets. The experiment was carried out in A (with WMF) exposed to air (as shown in Fig. S1A[†]). During the experiment, the permanent magnet was always placed at the bottom of the reactor and it was determined that the maximum magnetic field strength was 20 mT. This experimental method was called “real-time magnetization”. The solution was mixed by continuous mechanical stirring at 400 rpm to uniformly

disperse ZVI particles in the solution. At this stirring intensity, the aggregation of ZVI caused by WMF could be avoided. All experiments were carried out at 25 °C which controlled by a cryostat. A certain amount of ZVI and H_2O_2 were added into a reactor to initial experiments. The specific experimental conditions were: pH = 4.0, H_2O_2 was 8 mM, X-3B was 50 mg L⁻¹. Before all experiments, NaOH and HCl were used to adjust the pH of solution. At a fixed time-interval, 5 mL of water sample was taken with a syringe, filtered through a 0.45 μm filter. The ZVI samples after reactions were collected by filtering through the 0.45 μm membrane, then washed with distilled water and freeze-dried. The pre-magnetization meant to place 0.5 g L⁻¹ ZVI on permanent magnet, magnetize it for different time (0.5, 1, 3, 5, 7, 10 min), immediately added it to B (without WMF) for experiment (as shown in Fig. S1B[†]).

Chemical analysis

X-3B was determined at 538 nm by using a spectrophotometer (UV 752N, JinShiSu). ZVI samples were characterized by X-ray diffraction (XRD) (X'Pert Powder, Malvern Analytical) and scanning electron microscope (SEM) (JSM-6360LV, JEOL).

Results and discussion

Effect of WMF on the removal of X-3B by ZVI/ H_2O_2 at different pH

The effect of WMF on ZVI removal X-3B at pH 4.0 was shown in Fig. S2 (in the ESI),[†] 10.79% and 3.28% of X-3B were removed by ZVI in 60 min in the presence and absence of WMF, respectively. WMF could slightly increase the removal rate of X-3B by ZVI. The effect of WMF on the removal of X-3B by ZVI/ H_2O_2 in the range of pH 3.0–5.0 was investigated. As shown in Fig. 1, in the absence of WMF, 93.2%, 24.6%, and 1.3% of X-3B were removed by the ZVI/ H_2O_2 system in 20 min at pH 3.0, 4.0, and 5.0, respectively. With the increase of pH from 3.0 to 5.0, the removal rate of X-3B was significantly inhibited. Obviously, ZVI/

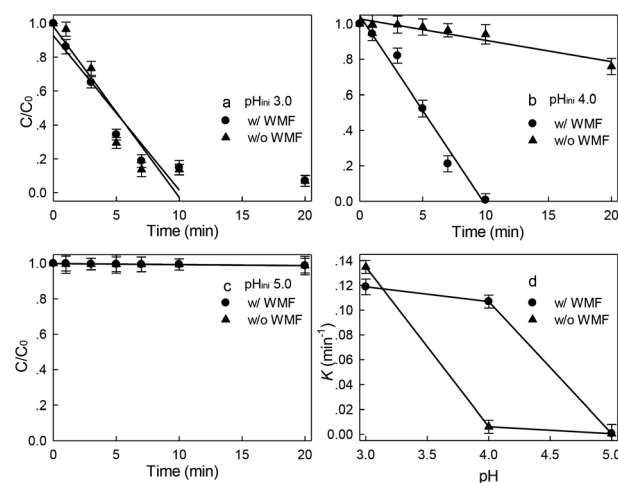
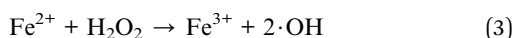
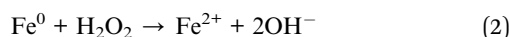
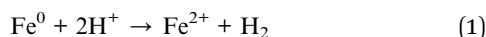


Fig. 1 Effect of WMF on ZVI/ H_2O_2 removal of X-3B under different initial pH reaction conditions (8 mM H_2O_2 , 50 mg L⁻¹ X-3B, 0.5 g L⁻¹ Fe^0 , and $T = 25\text{ }^\circ\text{C}$).



H₂O₂ system removal of X-3B was strongly dependent on pH,³⁴ it was probably due to the corrosion of ZVI under strong acidic conditions (eqn (1)) (at pH 3.0), which produced more Fe²⁺. But with the increase of pH from 3.0 to 5.0, the removal rate of X-3B was significantly inhibited. Only 1.3% of X-3B was observed to be degraded by ZVI/H₂O₂ at pH 5.0. The XRD pattern of ZVI samples was shown in Fig. S3 (in the ESI),† and no lepidocrocite was found in ZVI samples at pH 5.0. In the presence of WMF, the removal rate of X-3B at pH 3.0 did not increase. After the reaction, the ZVI samples in the ZVI/H₂O₂ and ZVI/H₂O₂/WMF systems showed abundant lepidocrocite at pH 3.0, indicating that WMF under strong acidic conditions did not enhance the reactivity of ZVI. However, about 99.4% X-3B was removed within 10 min at pH 4.0 which was much higher than that without WMF (only about 10% in 10 min), the corrosion degree of ZVI was also greatly improved, and abundant lepidocrocite were found in ZVI samples. SEM images of ZVI removal of X-3B under different pH conditions (as shown in Fig. S4†) showed that the corrosion degree of ZVI with WMF was higher than that of ZVI without WMF. Generally, X-3B degradation in ZVI/H₂O₂ system depended on the generation of ·OH via eqn (2) and (3). In a ZVI/H₂O₂ reaction, the release rate of Fe²⁺ from ZVI particles (eqn (1) and (2)) determined the production of ·OH. Other researchers^{23,26} reported that WMF accelerated the release rate of Fe²⁺. So WMF could enhance X-3B removal by ZVI/H₂O₂. But the removal of X-3B by ZVI/H₂O₂/WMF was inhibited at pH 5.0. Although the corrosion of ZVI was depended on pH, Liang *et al.*²⁴ proved that WMF could enhance the release rate of Fe²⁺ during the reduction of Se(IV) to Se(0) by ZVI at the range of 4.0–7.0. So WMF could enhance the release of Fe²⁺ from ZVI at pH 5.0. But WMF did not exhibit any enhancement of X-3B removal at pH 5.0 which might be ascribed to the limitation of Fenton reactions depending on the narrow effective pH range (2.5–3.0).³⁵ But WMF could still extend the effective reaction pH from 3.0 to 4.0 in ZVI/H₂O₂ system. In addition, ZVI/H₂O₂ could remove neglected X-3B in 60 min at pH 4.0 in the presence of WMF (data shown in Fig. S5†). So, the removal of X-3B was ascribed to ·OH generated by eqn (3).



Most studies^{13,28} reported that contaminants removal by AOPs based on ZVI follows pseudo first-order kinetics. However, the pseudo first-order kinetics could not well simulate the main stages of X-3B removal. The zero-order kinetic model was used to describe the main part of each data set in the initial rapid removal phase, and the removal rate of X-3B by ZVI/H₂O₂ within 10 min in the pH range of 3.0–5.0 was described, as shown by eqn (4).

$$C_0 - C_t \rightarrow -kt \quad (4)$$

where k is the X-3B zero-order rate constant (min⁻¹), C_0 is the initial X-3B concentration, and C_t is the X-3B concentration at the fixed time. The fitting results were shown in Fig. 1(d). WMF increased the reaction rate constant of X-3B decolorization by 17.8 times at pH 4.0, and WMF exhibited a strong enhancement to X-3B removal at pH 4.0 in ZVI/H₂O₂ systems.

Effects of initial ZVI dosages on the removal of X-3B by ZVI/H₂O₂ and ZVI/H₂O₂/WMF

Effects of ZVI dosages on X-3B removal rate by ZVI/H₂O₂ system were investigated with the initial X-3B concentration of 50 mg L⁻¹ at pH 4.0 in the presence of WMF. As shown in Fig. 2, the removal rate of X-3B was increased with the increased of ZVI dosages in the absence of WMF. Only 4.5% X-3B was removed by H₂O₂ coupled with 0.25 g L⁻¹ ZVI in 20 min. When the ZVI dosage increased to 0.5 and 1.0 g L⁻¹, about 24.1% and 95.1% X-3B were removed during 20 min, respectively. In the presence of WMF, the removal rate of X-3B increased at first and then decreased with the increase of ZVI dosage. About 50.0 mg L⁻¹ X-3B was completely removed by ZVI/H₂O₂/WMF at 0.5 g L⁻¹ ZVI in 10 min. The Lorentz force generated by WMF and the magnetic field gradient force generated by the induced magnetic field generated on the surface of ZVI promoted the corrosion of ZVI and generated more Fe²⁺,²³ which promoted the Fenton system to degraded the dye. However, with the increase of ZVI dosages from 0.5 to 1.0 g L⁻¹, the removal rate of X-3B was seriously inhibited, it might be due to the excessive amount of ZVI that consumed the ·OH in the solution. In summary, WMF could significantly increase the removal rate of X-3B at lower ZVI dosage. The promoting effect of WMF was not obvious when the ZVI dose was 0.25 g L⁻¹. This might be due to the limited number of active sites on the surface of ZVI, the generation of Fe²⁺ by 0.25 g L⁻¹ ZVI was much lower, so it was

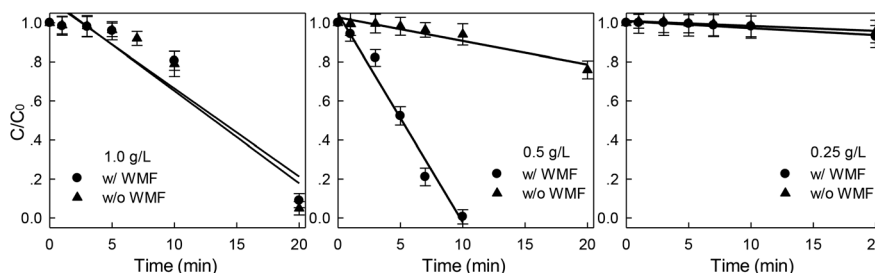


Fig. 2 Effect of WMF on ZVI/H₂O₂ removal of X-3B under different ZVI dosages (pH 4.0, 8 mM H₂O₂, 50 mg L⁻¹ X-3B, and $T = 25$ °C).



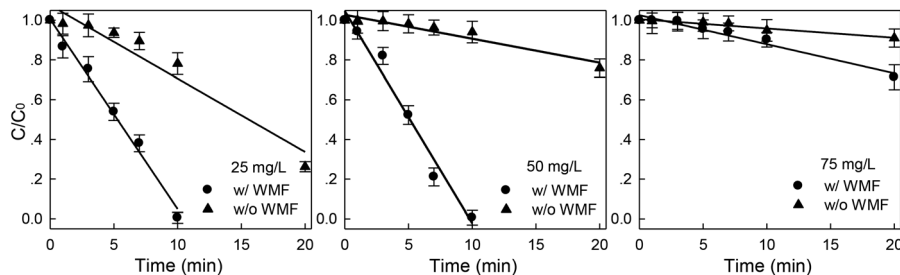


Fig. 3 Effect of WMF on ZVI/H₂O₂ removal of X-3B under different concentrations (pH 4.0, 8 mM H₂O₂, 0.5 g L⁻¹ Fe⁰, and T = 25 °C).

Table 1 Removal kinetic constants of different X-3B concentrations

Without WMF			With WMF		
X-3B (mg L ⁻¹)	<i>k</i> _{obs} min ⁻¹	<i>R</i> ²	X-3B (mg L ⁻¹)	<i>k</i> _{obs} min ⁻¹	<i>R</i> ²
25	0.037	0.918	25	0.108	0.986
50	0.012	0.903	50	0.107	0.971
75	0.005	0.937	75	0.015	0.957

difficult to catalyze the decomposition of H₂O₂ to produce more ·OH in the presence of WMF.

Effects of initial X-3B concentrations on the removal of X-3B by ZVI/H₂O₂ and ZVI/H₂O₂/WMF

Dye concentration was another factor affecting X-3B removal rate. Fig. 3 showed the effect of WMF on X-3B removal by ZVI/H₂O₂ at different initial X-3B concentrations. The removal rate of X-3B by ZVI/H₂O₂ decreased significantly with the increase of X-3B concentration. In the presence of WMF, the removal rates reached 99.5%, 99.4% and 9.8% in 10 min at the initial X-3B concentrations of 25, 50 and 75 mg L⁻¹, respectively. The superimposed WMF obviously improved the removal rate of X-3B by ZVI/H₂O₂. Furthermore, X-3B was completely removed by ZVI/H₂O₂/WMF in 20 minutes in the initial X-3B concentration range of 25.0–50.0 mg L⁻¹. The main part of each data set in Fig. 3 could be well described by zero-order dynamics, and the fitting results were shown in Table 1. Zero-order rate constants (*k*_{obs}) were found to be in the range of 0.005–0.108 min⁻¹, which was significantly dependent on the initial concentration of X-3B. In the presence of WMF, *k*_{obs} reduced linearly from 0.108 to 0.015 min⁻¹ with the increase of X-3B concentrations from 25.0 to 75.0 mg L⁻¹. This was due to non-availability of

sufficient number of hydroxyl radicals. The presumed reason was that when the initial concentration of X-3B was increased, the ·OH concentration was not increased correspondingly. At the concentration of 25 mg L⁻¹, the generated ·OH was not exhausted. And at 75 mg L⁻¹, ·OH became exhausted. The application of WMF improved the removal rate of X-3B at the different initial X-3B concentrations.

Effects of initial H₂O₂ concentrations on the removal of X-3B by ZVI/H₂O₂ and ZVI/H₂O₂/WMF

Effects of WMF on the removal of X-3B by ZVI at different H₂O₂ concentrations (4, 8, 12 mM) were investigated in Fig. 4. The removal rate of X-3B increased first and then decreased with the increase of H₂O₂ concentrations. More than 99.4% of X-3B could be removed when the concentration of H₂O₂ reached 8 mM at 10 min. But when H₂O₂ concentration were 4 or 12 mM, the removal of X-3B was negligible at 20 min. This was similar to the corrosion situation of ZVI shown in Fig. S6.† Only when the H₂O₂ concentration was 8 mM in the presence of WMF, ZVI particles were observed to break. In other cases, the degree of ZVI corrosion was slight. The ·OH generated by H₂O₂ and Fe²⁺ in the solution was not enough to attack the chromophores and the color-assisting groups in X-3B at a low H₂O₂ concentration of 4 mM. The ·OH produced by the Fenton-like reaction would react with excess H₂O₂ in the solution to form a weak oxidizing HO₂·, which consumed the ·OH in the solution, as shown in eqn (5). The oxidation capacity of HO₂· was far weaker than that of ·OH, and X-3B could not be removed effectively. Besides, Fe³⁺ could be reduced to Fe²⁺ by excessive H₂O₂, which was an unfavorable reaction to remove X-3B (eqn (6) and (7)). And the optimal H₂O₂ concentration in this study was 8 mM.

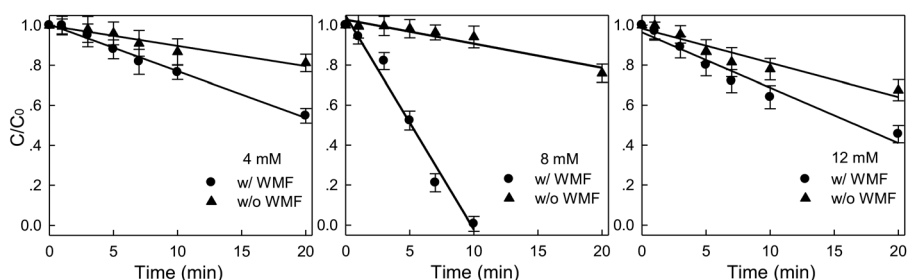


Fig. 4 Effect of WMF on ZVI/H₂O₂ removal of X-3B under different H₂O₂ concentrations (pH 4.0, 50 mg L⁻¹ X-3B, 0.5 g L⁻¹ Fe⁰, and T = 25 °C).



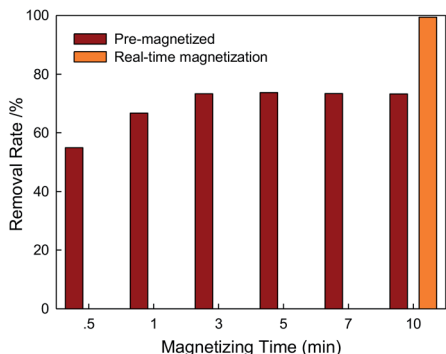


Fig. 5 Effects of magnetizing time on X-3B removal by ZVI/H₂O₂/WMF (pH 4.0, 8 mM H₂O₂, 50 mg L⁻¹ X-3B, 0.5 g L⁻¹ Fe⁰, and T = 25 °C).

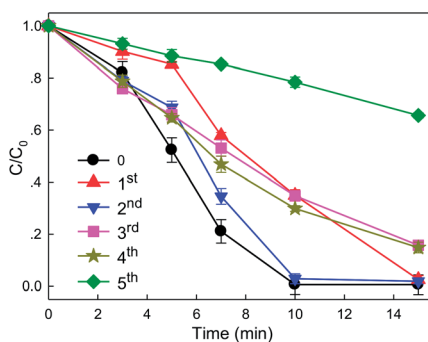
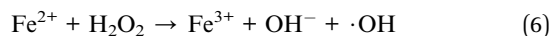
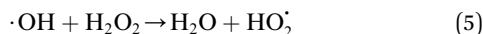


Fig. 6 Reuse efficiency of ZVI for X-3B removal by ZVI/H₂O₂/WMF (pH 4.0, 8 mM H₂O₂, 50 mg L⁻¹ X-3B, 0.5 g L⁻¹ Fe⁰, and T = 25 °C).



Effects of magnetization time on X-3B removal by ZVI/H₂O₂/WMF

Previous experiments proved that WMF exhibited an enhancement on X-3B removal by ZVI/H₂O₂. Generally, ZVI possessed the magnetic memory after magnetization treatment by WMF.

Herein, effects of magnetization time on X-3B were illustrated in Fig. 5. The removal rate of X-3B by ZVI/H₂O₂/WMF increased with the increase of magnetizing time. Without the presence of WMF, the removal rate of X-3B only reached 5.9% within 10 min. The magnetizing time of 30 s could also increase the removal rate of X-3B from 5.9% to 54.88%. So the effect of pre-magnetization ZVI removing X-3B was better than that of ZVI/H₂O₂ system. The removal rate of X-3B was very stable when the magnetizing time increased to 3 min. Although the WMF was discharged after the magnetizing of the solution, the removal rate of ZVI was not depressed because of the magnetic memory of ZVI. Besides, the magnetization of ZVI over the reaction time did not improve the removal rate of X-3B more. So the optimizing magnetizing time in this study was 3 min. The real-time magnetization of 10 min ZVI/H₂O₂/WMF system could remove 99.4% of X-3B, while the pre-magnetization of 10 min ZVI/H₂O₂/WMF could only remove 73.2% of X-3B. Therefore, the effect of pre-magnetization was far less than that of real-time magnetization, but this advantage of magnetic memory could shorten the magnetizing time during the reaction which was very important to the application of WMF technology by reducing magnetizing time and the reactors volume.

Effects of ZVI reuse times on X-3B removal by ZVI/H₂O₂/WMF

WMF improved the reactivity of ZVI towards H₂O₂ by accelerating the release of ferrous. Liang *et al.*²² found that WMF could increase the removal rate of Se(IV) by aged ZVI, and concluded that WMF induced nonuniform depassivation and eventually localized corrosion of the ZVI surface by the coefficients of the Lorentz force and the field gradient force. Then Xu *et al.*²⁵ also proved that the presence of WMF could restore the reactivity of the aged ZVI samples with Fe₃O₄, α-Fe₂O₃, γ-FeOOH as the passive film. So, the reusability of ZVI in the presence of WMF could also be improved. As shown in Fig. 6, the reuse experiments of ZVI for X-3B removal kinetics coupled with H₂O₂ was studied. The removal rate of X-3B by ZVI/H₂O₂/WMF was inhibited in the 1st reuse experiment especially in the initial 5 min. The generation of iron oxides on the surface of ZVI after the first run reaction limited the reaction between ZVI and H₂O₂. But the presence of WMF could recover the reactivity of ZVI after 5 min. And the final removal rate at 15 min reached almost 100%. And the removal rate of X-3B by ZVI/H₂O₂/WMF was promoted after ZVI reused 1 times, but still was lower than the initial run reaction. The removal rate of X-3B during the 2nd

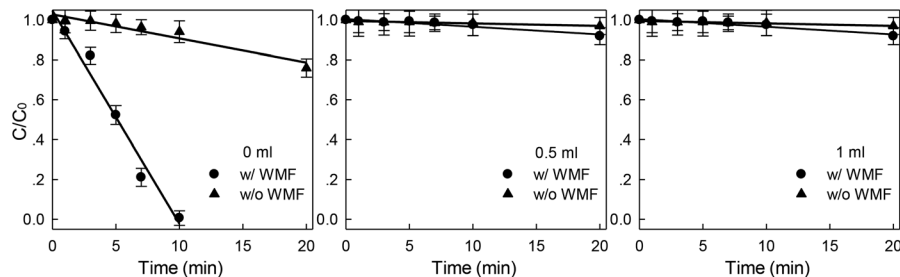


Fig. 7 Effect of WMF on ZVI/H₂O₂ removal of X-3B under different methanol dosages (pH 4.0, 8 mM H₂O₂, 50 mg L⁻¹ X-3B, 0.5 g L⁻¹ Fe⁰, and T = 25 °C).



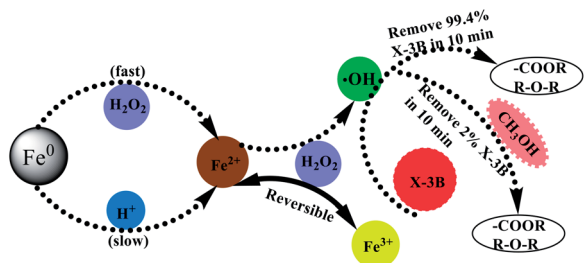


Fig. 8 Mechanism diagram of ZVI/H₂O₂ removal of X-3B (pH 4.0, 8 mM H₂O₂, 50 mg L⁻¹ X-3B, 0.5 g L⁻¹ Fe⁰, and T = 25 °C).

reuse reaction was always higher than that after ZVI reused 1 time. And the removal rate of X-3B by ZVI/H₂O₂/WMF at 15 min also reached 85% during the 3rd and 4th reuse reactions. But the removal rate of X-3B by ZVI/H₂O₂/WMF at 15 min decreased to 34% during the 5th reuse test due to the serious loss of ZVI after 5 recycle reactions.

Mechanism of WMF enhancing X-3B removal by ZVI/H₂O₂

The degradation of X-3B by ZVI/H₂O₂ system mainly depended on ·OH, and the methanol (CH₃OH) as the quencher of ·OH was added to the solution to further investigated the effect of ·OH on the system and confirmed the role of ·OH in the reaction process. As shown in Fig. 7, the removal rate of X-3B by ZVI/H₂O₂ decreased rapidly after methanol was added into the solution. In the presence of methanol with different concentrations, the removal of X-3B by ZVI/H₂O₂/WMF and ZVI/H₂O₂ was negligible. So ·OH could be considered as the main reactive oxidation species in ZVI/H₂O₂/WMF system, and the mechanism diagram was shown in Fig. 8.

In order to further investigate the effect of WMF on ZVI/H₂O₂ removal of X-3B, samples of UV-Vis were taken at different time during the reaction, and the scanning range was 200–800 nm. The decolorization of the dye was observed from the UV spectrum, and the degree of destruction of the molecular structure of the dye was analyzed. As shown in Fig. 9, X-3B had five characteristic absorption peaks. The absorption peaks at 538 nm and 512 nm in the visible region were caused by the conjugated structure of X-3B molecule, which made the dye unique red.³⁶ The absorption peaks at 330 nm, 284 nm, and 238 nm in the ultraviolet region correspond to the benzene ring and the naphthalene ring in the molecular structure of the dye.

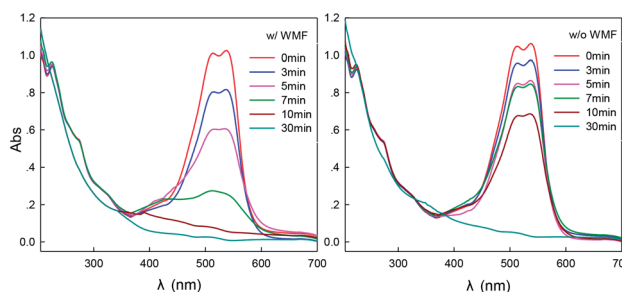


Fig. 9 UV-Vis absorption spectrum of ZVI removal of X-3B with or without WMF (pH 4.0, 8 mM H₂O₂, 50 mg L⁻¹ X-3B, 0.5 g L⁻¹ Fe⁰, and T = 25 °C).

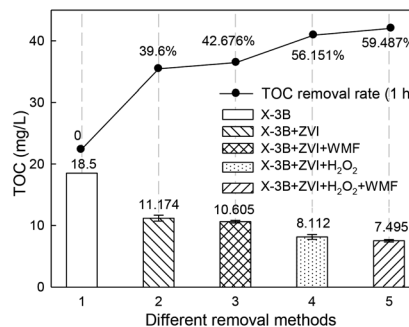


Fig. 10 TOC removal rate of X-3B under different removal methods (pH 4.0, 8 mM H₂O₂, 50 mg L⁻¹ X-3B, 0.5 g L⁻¹ Fe⁰, and T = 25 °C).

The azo bond in X-3B and the linked naphthalene ring and amino group are unstable, and the reaction is easily destroyed.³⁵ The two absorption peaks at 538 nm and 512 nm disappeared within 10 min in the presence of WMF which because of ·OH first attacked the azo bond of the dye, broke the conjugated system of X-3B. The absorption peaks at 238, 284 and 330 nm disappeared after 30 min, indicating that both the naphthalene rings and the triazinyl groups were destroyed and the dye had completely faded. The absorption peak only decreased within 30 min and the dye was not completely decolorized in the absence of WMF. As shown in Fig. 10, the TOC removal rate of dye wastewater under different removal methods showed that the TOC removal rate of X-3B in the ZVI/H₂O₂/WMF system was as high as 59.49% in 1 h, which was significantly higher than that of ZVI, ZVI/WMF and ZVI/H₂O₂ systems. Obviously, the ZVI/H₂O₂/WMF system not only promoted the decolorization rate of X-3B, but also increased the degree of mineralization of X-3B wastewater.

The removal of X-3B by ZVI/H₂O₂ was a process in which ZVI was corroded as the main part, and could be described by eqn (1)–(3). ZVI was corroded, releasing Fe²⁺ and H₂O₂ to react quickly to form ·OH to destroy the molecular structure of the dye and make it fade. Guan *et al.*¹² found that under aerobic conditions, H₂O₂ reacts with ZVI or Fe²⁺ under acidic conditions. Fe²⁺ could accelerate the Fenton reaction and allow a greater proportion of oxidants to be produced. When WMF was superimposed, the fading rate of dye molecules was accelerated, and the discoloration of X-3B mainly occurs in the first 10 min of WMF. The Lorentz force generated by the applied weak magnetic field and the magnetic field gradient force generated by the induced magnetic field generated on the surface of the ZVI act on Fe²⁺, promoted the corrosion of ZVI, increased the release rate of Fe²⁺, and generated more ·OH, promoted the dye molecules fade. WMF promoted the formation of Fe²⁺ and accelerated the degradation rate of X-3B.

Conclusions

On the basis of many experiments, the optimum conditions of Fenton-like reaction were obtained as follows: the concentration of reactive brilliant red X-3B was 50 mg L⁻¹, pH = 4.0, the dosage of ZVI with particle size of 20 μm was 0.5 g L⁻¹, and the dosage of H₂O₂ was 8 mM, the decolorization rate of X-3B could



reach 99.41% within 10 min. WMF extended the reaction pH range from 3.0 to 4.0. The initial main reaction process of removal of X-3B by ZVI/H₂O₂/WMF or ZVI/H₂O₂ was basically consistent with the zero-order reaction kinetics, but there was a large increase in the reaction rate when there was with WMF than when there was without WMF. The optimized magnetization time of ZVI pre-magnetization was 3 min. The effect of ZVI pre-magnetization was not as good as real-time magnetization, but ZVI pre-magnetization could shorten the magnetization time in the reaction process and reduce the reactor volume. ZVI reuse experiments clearly showed that the ZVI/H₂O₂/WMF system still had the ability to remove X-3B after 4 consecutive cycles, but the removal efficiency of ZVI would decrease. The decolorization of X-3B was mainly a hydroxyl radical attacked dye conjugate structure. Superimposed WMF greatly accelerated the degradation of X-3B by ZVI and shortens the reaction time. The WMF used in this study was produced by permanent magnets and did not require energy input. WMF applications were efficient, energy-efficient, free of harsh chemicals and environmental friendly, superimposed WMF to promote the removal of X-3B by ZVI/H₂O₂ was a promising and environmental friendly approach.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (Grant No. 41807468), Zhejiang Provincial Natural Science Foundation of China (Grant No. LY18E080018), State Key Laboratory of Pollution Control and Resource Reuse Foundation, (Grant No. PCRRF18021).

Notes and references

- N. B. o. Statistics and M. o. E. Protection, *China Statistical yearbook on environment 2016*, Beijing, 2016.
- L. Labiadh, A. Barbucci, G. Cerisola, A. Gadri, S. Ammar and M. Panizza, *J. Solid State Electrochem.*, 2015, **19**, 3177–3183.
- K. Sathishkumar, M. S. AlSalhi, E. Sanganyado, S. Devanesan, A. Arulprakash and A. Rajasekar, *J. Photochem. Photobiol., B*, 2019, **200**, 111655.
- A. J. dos Santos, I. Sirés, C. A. Martínez-Huitle and E. Brillas, *Chemosphere*, 2018, **210**, 1137–1144.
- E. Brillas and C. A. Martínez-Huitle, *Appl. Catal., B*, 2015, **166**, 603–643.
- M. M. Ghoneim, H. S. El-Desoky and N. M. Zidan, *Desalination*, 2011, **274**, 22–30.
- E. Forgacs, T. Cserhati and G. Oros, *Environ. Int.*, 2004, **30**(1), 953–971.
- C. Z. Liang, S. P. Sun, F. Y. Li, Y. K. Ong and T. S. Chung, *J. Membr. Sci.*, 2014, **469**, 306–315.
- A. Y. Zahrim and N. Hilal, *Water Resour. Ind.*, 2014, **3**, 23–34.

- Z. H. Huang, Y. Z. Li, W. J. Chen, J. H. Shi, N. Zhang, X. J. Wang, Z. Li, L. Z. Gao and Y. X. Zhang, *Mater. Chem. Phys.*, 2017, **202**, 266–276.
- C. Grégorio, E. Lichtfous, L. D. Wilson and N. Morin-Crini, *Environ. Chem. Lett.*, 2018, 195–213.
- X. H. Guan, Y. K. Sun, H. Qin, J. X. Li, I. M. C. Lo, D. He and H. R. Dong, *Water Res.*, 2015, **75**, 224–248.
- J. S. Du, W. Q. Guo, D. Che and N. Ren, *Chem. Eng. J.*, 2018, **351**, 532–539.
- L. J. Matheson and P. G. Tratnyek, *Environ. Sci. Technol.*, 1994, **28**, 2045–2053.
- Y. H. Liou, S. L. Lo, C. J. Lin, W. H. Kuan and S. C. Weng, *J. Hazard. Mater.*, 2005, **126**, 189–194.
- C. B. Wang and W. X. Zhang, *Environ. Sci. Technol.*, 1997, **31**, 2154–2156.
- S. Harendra and C. Vipulanandan, *Colloids Surf., A*, 2008, **322**, 6–13.
- C. Lee, J. Y. Kim, W. I. Lee, K. L. Nelson, J. Yoon and D. L. Sedlak, *Environ. Sci. Technol.*, 2008, **42**, 4927–4933.
- L. J. Zhou, W. Q. Zhuang, X. Wang, K. Yu, S. F. Yang and S. Q. Xia, *Water Res.*, 2017, **111**, 140–146.
- D. H. Phillips, B. Gu and D. B. Watson, *Environ. Sci. Technol.*, 2000, **34**, 4169–4176.
- Y. Roh, S. Y. Lee and M. P. Elless, *Environ. Geol.*, 2000, **40**, 184–194.
- L. P. Liang, X. H. Guan, Z. Shi, J. L. Li, Y. Wu and P. G. Tratnyek, *Environ. Sci. Technol.*, 2014, **48**, 6326–6334.
- J. X. Li, H. J. Qin, W. X. Zhang, Z. Shi, D. Y. Zhao and X. H. Guan, *Sep. Purif. Technol.*, 2017, **176**, 40–47.
- L. P. Liang, W. Sun, X. H. Guan, Y. Y. Huang, W. Choi, H. L. Bao, L. Li and Z. Jiang, *Water Res.*, 2014, **49**, 371–380.
- H. Y. Xu, Y. K. Sun, J. X. Li, F. M. Li and X. H. Guan, *Environ. Sci. Technol.*, 2016, **50**, 8214–8222.
- J. X. Li, H. J. Qin and X. H. Guan, *Environ. Sci. Technol.*, 2015, **49**, 14401–14408.
- Y. K. Sun, Y. H. Hu, T. L. Huang, J. X. Li and X. H. Guan, *Environ. Sci. Technol.*, 2017, **51**, 3742–3750.
- X. M. Xiong, Y. K. Sun, B. Sun, W. H. Song, J. Y. Sun, N. Y. Gao, J. L. Qiao and X. H. Guan, *RSC Adv.*, 2015, **5**, 13357–13365.
- X. M. Xiong, B. Sun, J. Zhang, N. Y. Gao, J. M. Shen, J. L. Li and X. H. Guan, *Water Res.*, 2014, **62**, 53–62.
- X. Li, M. H. Zhou, Y. W. Pan and L. T. Xu, *Chem. Eng. J.*, 2017, **307**, 1092–1104.
- Y. W. Pan, M. H. Zhou, X. Li, L. T. Xu, Z. X. Tang, X. J. Sheng and B. Li, *Chem. Eng. J.*, 2017, **318**, 50–56.
- X. Li, M. H. Zhou, Y. W. Pan, L. T. Xu and Z. X. Tang, *Sep. Purif. Technol.*, 2017, **178**, 49–55.
- Y. W. Pan, M. H. Zhou, X. Li, L. T. Xu, Z. X. Tang and M. M. Liu, *Sep. Purif. Technol.*, 2016, **169**, 83–92.
- A. Ghauch, H. Baydoun and P. Dermesropian, *Chem. Eng. J.*, 2011, **172**, 18–27.
- A. Goi and M. Trapido, *Chemosphere*, 2002, **46**, 913–922.
- Y. P. Mao, Y. Tao, Z. M. Shen, Y. M. Lei and W. H. Wang, *Environ. Sci. Technol.*, 2009, **32**(19), 67–70.

