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Use of limonite as a Fenton fluidized bed stretcher to treat tetracycline wastewater with over 90% removal rate

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Abstract: Antibiotics are frequently detected in the aquatic environment but are difficult to remove. In this study, tetracycline, a typical representative of antibiotics, was screened as a natural iron ore, limonite, as a fluidized bed stretcher to investigate the efficacy of its catalytic hydrogen peroxide (H2O2) for the degradation of tetracycline, and the effects of the reaction time, the reaction pH, the stretcher dosage, the tetracycline The effects of reaction time, reaction pH, stretcher dosage, initial concentration of tetracycline solution, H2O2 dosage, number of dosages and stretcher expansion on the degradation of tetracycline in the limonite/Fenton fluidized bed system were investigated, and the repeatability of the stretcher was also studied. The results showed that the removal rate of tetracycline could reach about 90% when the reaction pH, stretcher dosage, initial concentration of tetracycline solution, H2O2 dosage, number of dosages, and stretcher expansion rate were 3, 30 g/L, 40 mg/L, 0.6 mmol/L, 1 time, and 100%, respectively. The removal rate remained around 50% after six batches when in the multi-batch influent experiment. Through SEM, XRD, XPS and EPR characterization of limonite, the rough surface was found by SEM, and the main crystalline phase on the surface was hydroxyl iron oxide analyzed by XRD, and a decrease in the proportion of divalent iron and an increase in the number of organic functional group species on the surface of the stretcher were detected by XPS, and the reactive oxygen species playing a major role in the system was identified as OH by EPR, and the heterogeneous Fenton reaction was assumed to have taken place. reaction was identified as OH, and it was hypothesized that heterophasic Fenton reaction occurred to degrade the tetracycline.

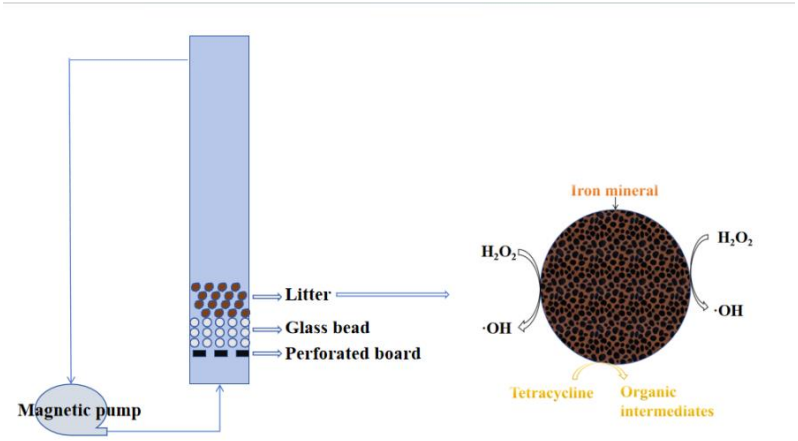

Figure 1. Graphical Abstract

1 Introduction

Antibiotics, as a common medication for the treatment of diseases, are widely present in aquatic environments, among which tetracycline, as a representative of broad-spectrum antibiotics, is often highly detected in different typical regional environments: landfills (63.8 ± 37.7 μg/kg) [1], mariculture (0.2-259.1 ng/L) [2], sediments (126.1 μg/kg) [3], drinking water sources (11.16 ng/L) [4] and groundwater (0.4 μg/L) [5]. Residual low concentration levels of tetracycline in the environment not only affect the growth and metabolism of microorganisms, but also the microbial community structure of the ecosystem [6]. If not effectively controlled for a long period of time, tetracycline antibiotics in the water body will gradually accumulate, which in turn will inevitably lead to the breeding and proliferation of superbugs, resistant genes and other harmful biological factors. The emergence of these biological factors will greatly increase the difficulty of management and pose a serious threat to the living environment of animals and human beings, and may even cause far-reaching ecological and health problems.

In the current academic research, a diversified system of strategies has been developed for the degradation of tetracycline antibiotics in water bodies, and these strategies mainly cover three major directions: physical, chemical and biological [7-10]. It is worth noting that although biological methods are widely used as a means of environmental management, they are not the first choice or the main method for the degradation of tetracycline antibiotics. This is mainly due to the antibacterial and potential ecotoxicity of antibiotics, which not only complicate the removal of conventional pollutants, but also exacerbate the difficulty of tetracycline antibiotic degradation.

The core of the Fenton method lies in inducing a chain reaction between divalent iron ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) to generate hydroxyl radicals (·OH) with extremely strong oxidizing properties. Hydroxyl radicals are capable of efficiently oxidizing and degrading organic pollutants due to their high oxidation potential of up to 2.80 V (second only to fluorine). The Fenton method, because of its wide adaptability and efficient oxidizing ability, excels in treating organic wastewater that is difficult to degrade biologically and difficult to oxidize by conventional chemical oxidation methods. This method has unique advantages in treating organic wastewater oxidation and provides a proven technical way to solve water pollution problems. Worldwide, natural iron ore reserves are extremely large with high iron content and can be used as a catalyst for the Fenton reaction, a green and low-cost fluidized bed stretcher material. As an important industrial contact reaction equipment, the working principle of fluidized bed reactor is based on fluidization technology. A well-designed piping layout in concert with a pump allows the filler within the bed to

dynamically expand upward or downward driven by the fluid [11]. The Fenton fluidized bed technology is the combination of the Fenton method with a fluidized bed reactor, whereby a non-homogeneous Fenton reaction can take place in the reactor through the catalytic action of an active filler (also known as a stretcher) for the removal of contaminants from aqueous solution, and this technology is considered to be promising for engineering applications.

Based on the above, this paper intends to select limonite as the stretcher material of Fenton fluidized bed, and investigate the treatment effect of Fenton fluidized bed system on tetracycline wastewater through multifactorial screening experiments and characterization analyses while decreasing the cost-responsive application orientation.

2 Materials and Methods

2.1 Materials and reagents

Materials: limonite was purchased from a natural iron ore area in a province in China; quartz sand, purchased from Shanghai McLean Biochemical Technology Co.

Reagents: ferrous sulfate heptahydrate, 30% hydrogen peroxide, concentrated sulfuric acid, methanol, p-benzoquinone and other reagents were analytically pure and purchased from Sinopharm Chemical Reagent Co. Furfuryl alcohol, tetracycline, o-phenanthroline and sodium acetate were analytically pure and purchased from Shanghai McLean Biochemistry Technology Co.

Instruments: UV UV-visible spectrophotometer (T6 New Century, Beijing General Instrument Co., Ltd.), water dispenser (ANSHI), weighing scale (Sartorius Scientific Instruments (Beijing) Co. ASAP2460), XRD (Japan Rigaku Smart Lab SE), XPS (U.S. Thermo Scientific K-Alpha), EPR (Germany Bruker EMXplus-6/1), SEM (Germany ZEISS Sigma 300), pH meter (Lei magnetic PHS-3C), magnetic pump (MP-6RZ) of Wenzhou Haoyuan Pump Industry Co.

2.2 Experimental Methods

The stretcher was washed by immersion using sulfuric acid solution at pH=3 and rinsed with deionized water until the pH of the rinse water was 7 and there was no obvious color change. Each time, 0.4 g of tetracycline was taken, and ultrapure water was added to a volumetric flask to 1 L. The tetracycline solution with a concentration of 400 mg/L was prepared as the mother liquor, and the mother liquor was diluted 10-fold each time water was dispensed to obtain a 40 mg/L initial solution. After adding the stretcher and assembling the magnetic circulation pump in the fluidized bed reactor, a certain amount of tetracycline solution was added from the top, the magnetic circulation pump was turned on to fluidize the stretcher, and a certain amount of hydrogen peroxide was added to start the reaction. At 5 min, 15 min, 30 min, 45 min and 60 min after the start of the experiment, a certain amount of solution was taken out using a syringe and filtered using a 0.45 μm filter membrane, and the residual tetracycline concentration in the taken solution was determined by UV spectrophotometry. At least 2 parallels were done for each set of experiments and the results were averaged, and the schematic diagram of the small-scale Fenton fluidized bed is shown in Fig. 2.

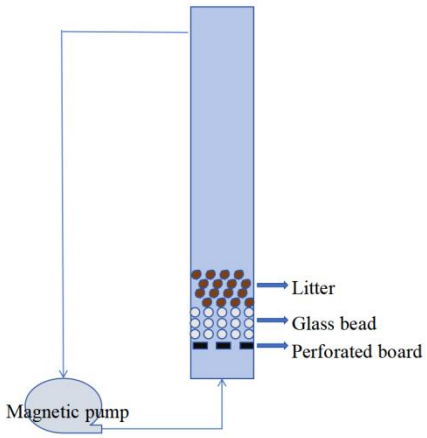

Figure 2. Schematic diagram of a small pilot scale Fenton fluidized bed

3. Results and Discussion

3.1 Study of influencing factors

In this experiment, limonite was selected as the fluidized bed stretcher, and the controlled experimental conditions were pH=3, tetracycline concentration of 40 mg/L, c(H2O2)= 0.6 mM, stretcher dosage of 30 g/L, stretcher expansion of 100%, and retention time of 60 min. Except for a particular parameter under investigation, which was varied within a certain range, all other parameters were maintained at the above conditions during the parametric experiment. The parameters were maintained at the above values during the parametric experiments, except for a certain range of changes in one particular parameter under investigation.

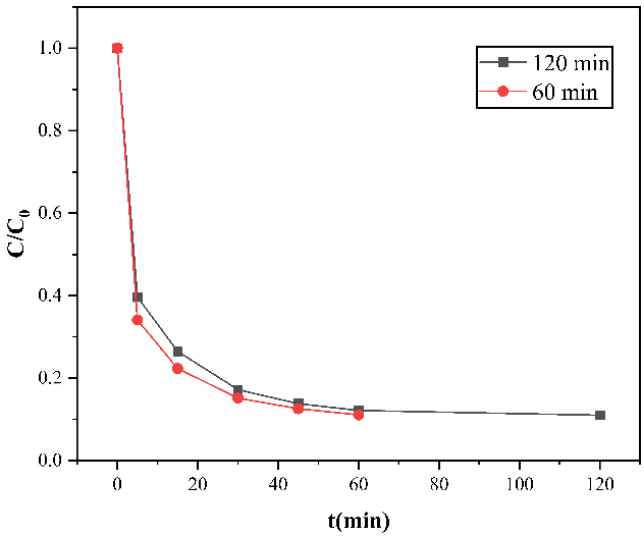

Figure 3. Tetracycline removal at different retention times

In order to investigate the effect of residence time (HRT) on the removal rate of tetracycline in a Fenton fluidized bed, batch experiments were carried out with HRT = 60 min and 120 min, respectively, and the experimental results are shown in Fig. 3. As can be seen in Fig. 3, the removal

rate of tetracycline has reached 89% at 60 min, and in the time period of 60 min-120 min the There was no significant increase in tetracycline degradation, presumably due to the basic depletion of free radicals in the first 60 min. Therefore, the HRT of the subsequent batch experiments was set at 60 min.

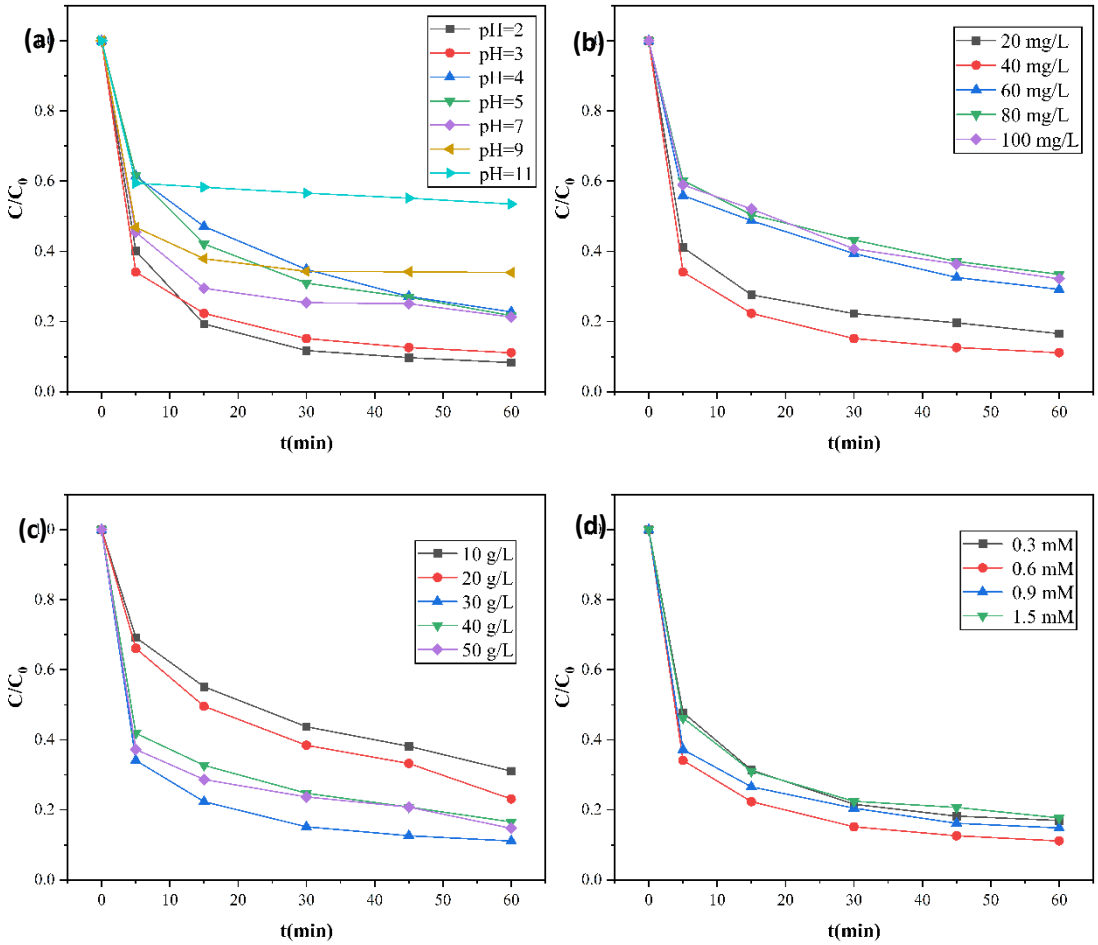

Figure 4. Tetracycline removal under different (a) pH; (b) tetracycline concentration; (c) tandem dosing; (d) hydrogen peroxide dosing conditions

The effect of different pH on the removal process of tetracycline is shown in Fig. 4(a), from which it can be seen that the removal rate of tetracycline will show a more obvious decreasing trend with the increase of pH. When pH=2, the removal rate of tetracycline reached 91.7%. When a certain amount of alkali was added to increase the overall pH of the solution, the removal rate of tetracycline was inhibited to a certain extent, and the removal rates were reduced to 78.7%, 66.0% and 46.5% at pH=7, 9 and 11, respectively, which indicated that the Fenton fluidized bed system was not conducive to the oxidative degradation of tetracycline in alkaline conditions, and this may be related to the decrease in the activity of free radicals under alkaline conditions. However, as a whole, the Fenton fluidized bed system still achieved a high efficiency (≥70%) of tetracycline removal over a wide pH range (2-7).

The effect of different initial tetracycline concentrations on the tetracycline removal process is shown in Figure 4(b). The tetracycline removal rate decreased from 88.9% to 70.8% when the tetracycline concentration was increased from 40 mg/L to 60 mg/L, which could be attributed to the

fact that excessive tetracycline adsorbed on the surface of limonite, which produced some site competition with hydrogen peroxide and affected the generation of free radicals. When the concentration of tetracycline continued to increase, the overall change in the removal rate was not significant, probably due to the fact that the dominant removal mechanism at this time was the surface adsorption of limonite on tetracycline.

The effect of different stretcher dosage on the tetracycline removal process is shown in Fig. 4(c). The tetracycline removal rate reached the maximum value of 88.9% when the stretcher dosage was 30 g/L. The tetracycline removal rate was 69% when the stretcher dosage was 10 g/L and 20 g/L, respectively. When the stretcher dosage was 10 g/L and 20 g/L, the tetracycline removal rate was 69.0% and 77.1%, respectively, which was attributed to the fact that the small amount of stretcher limited the number of contact sites and catalytic sites on the surface of the stretcher, and thus affected the tetracycline removal rate. The tetracycline removal rates were 83.5% and 85.3% when the stretcher dosage was 40 g/L and 50 g/L, respectively, which can be attributed to the increase in the number of collisions of the stretcher particles with each other in the fluidized bed reactor, and this inter-particle collision effect affects the tetracycline degradation process, and may lead to the re-release of tetracycline adsorbed on the surface of the stretcher.

The effect of different hydrogen peroxide dosage on the tetracycline removal process is shown in Fig. 4(d). When the concentration of hydrogen peroxide was 0.6 mM, the tetracycline removal was 88.9%. Excessive amount (0.3 mM) of hydrogen peroxide causes a decrease in the production of free radicals, which affects the oxidative degradation process of tetracycline and ultimately leads to a decrease in the removal rate. The negative effect of excess (0.9 mM and 1.5 mM) hydrogen peroxide on the removal rate of tetracycline can be attributed to the depleting effect of hydrogen peroxide on free radicals.

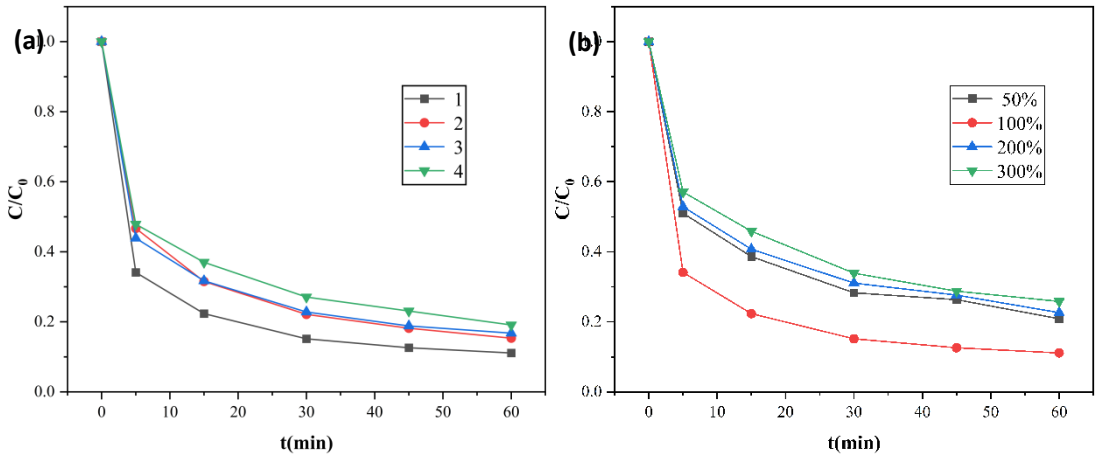

Figure 5. Tetracycline removal under different (a) number of dosing; (b) stretcher expansion rate conditions

The effect of different dosing times on the tetracycline removal process is shown in Fig. 5(a). From the figure, it can be seen that the split dosing of the same concentration of hydrogen peroxide is unfavorable to the removal of tetracycline, and this unfavorable effect will be slightly enhanced with the increase in the number of dosing times. The tetracycline removal was 88.9% and 80.1% when the number of dosing was 1 and 4 times, respectively. Since the presence of hydrogen peroxide is related to the production of free radicals, this phenomenon can be attributed to the fact that batch dosing results in insufficient amount of free radicals generated and a decrease in the reaction time between free radicals and tetracycline.

The effect of different stretcher expansion rates on the tetracycline removal process is shown in Fig. 5(b). The stretcher expansion rate can indirectly reflect the flow rate of the magnetic circulation pump, which mainly affects the contact between tetracycline and stretcher in the solution. As can be seen from the figure, the tetracycline removal rate was 90.2% when the expansion rate was 100%, while the tetracycline removal rates were 79.2%, 77.4% and 74.2% when the stretcher expansion rate was 50%, 200% and 300%, respectively. From the experimental results, it can be seen that both too small (50%) and too large (200% and 300%) stretcher expansion rates are unfavorable for tetracycline removal. When the stretcher expansion rate was too small, the stretcher was not sufficiently fluidized and the contact area exposed on the stretcher surface was limited, thus affecting the catalytic oxidation process and the removal of tetracycline; when the stretcher expansion rate was too large, the solution flow rate was too fast resulting in a shorter contact time between the hydrogen peroxide and tetracycline and the surface of stretcher, which suppressed the extent of the removal process.

3.2 Stretcher reusability study

In order to study the stability of the stretcher over multiple batches of use, a multi-batch influent experiment was conducted. The experimental parameters were pH=3, tetracycline concentration of 40 mg/L, c(H2O2)= 0.6 mM, stretcher dosage of 30 g/L, stretcher expansion of 100%, and retention time of 60 min. As shown in Fig. 6, the Fenton Fluidized Bed System with limonite as the stretcher showed good tetracycline removal and some stability in six batches (six hours), and the removal rate was 43.7% at the time of the final batch. The removal rate at the time was 43.7%. The tetracycline removal rate decreased somewhat with batch experiments, probably due to the decrease of catalytic sites on the surface of limonite. However, considering the engineering properties of the fluidized bed reactor and the cost advantage of natural limonite, the system constructed in this paper still has certain application prospects and economic advantages.

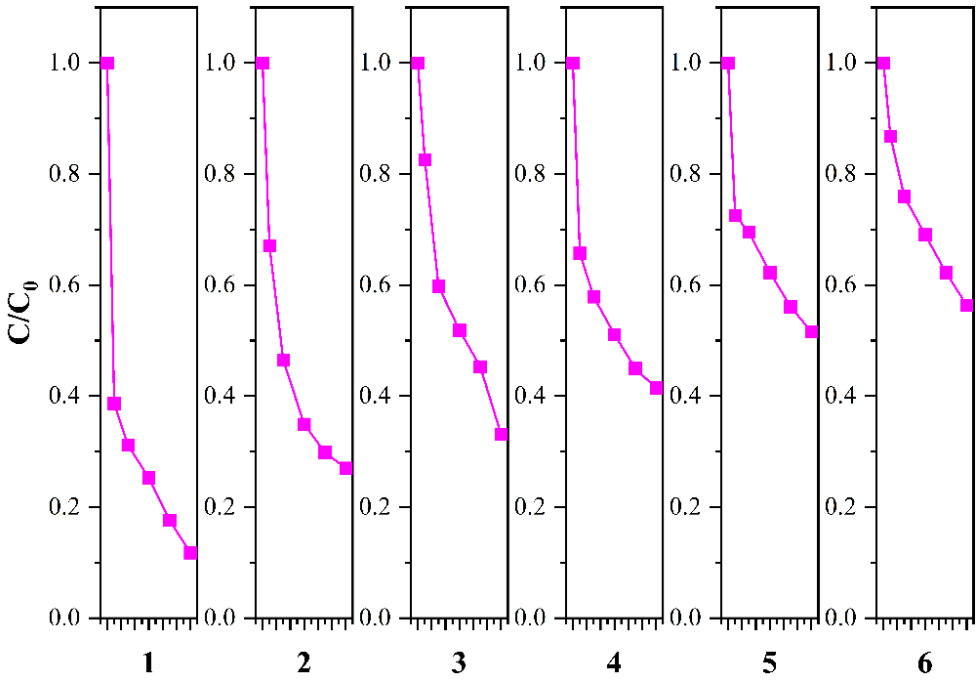

Figure 6. Tetracycline removal rate in multi-batch influent experiments

3.3 Characterization of limonite

3.3.1 SEM characterization

The surface morphology of limonite was characterized by SEM (scanning electron microscope) and the results are shown in Fig. 7. It can be seen that the surface of limonite shows irregular overlapping of lamellar crystals, and there are obvious depressions and protrusions on the surface, which is more in line with the surface irregularity of natural iron minerals under the physicochemical effects in nature.

At the same time, it can be found that the surface of limonite does not have a lot of holes, but there are a lot of crack holes and laminated holes formed by structural fracture and lamellar overlap.

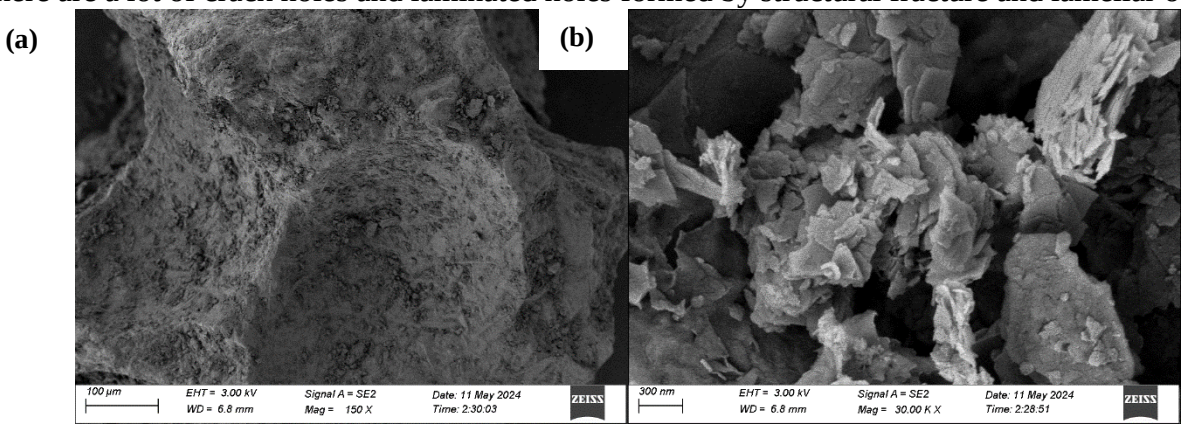

Figure 7. SEM images at (a) 100 µm and (b) 300 nm resolution

3.3.2 XRD characterization

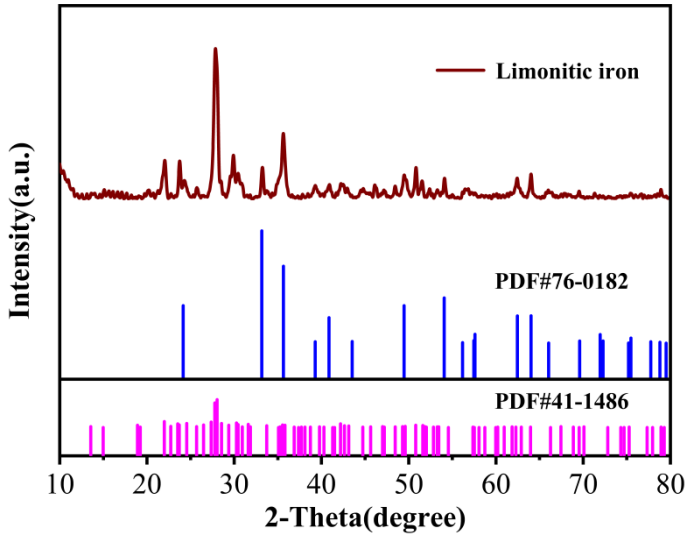

Figure 8. XRD diffraction pattern of limonitic iron ore

The crystalline phase composition of limonite was characterized using XRD, and the results are shown in Fig. 8. Natural minerals present in nature are often a mixture of multiple crystalline phases, so many characteristic peaks can be found in the diffraction pattern of limonite in the analysis of

XRD. The diffraction pattern was fitted and compared using MDI Jade 6 software, and it was concluded that the crystalline phase composition of limonite may be mainly composed of two parts. One is the hydroxyl iron oxide crystalline phase with standard card PDF#76-0182; and the other is the calcium feldspar crystalline phase with standard card PDF#41-1486.

3.3.1 XPS characterization

The XPS characterization of pristine limonite and limonite after multi-batch treatment is shown in Figures9, 10and 11. As can be seen from Fig. 9, the overall signal intensity of the C 1s spectra of limonite before the reaction is low, and the intensity of the main signal segment at 280 ev-290 ev is almost always contributed by C-C bonds, and the signal can be detected in the higher signal segments, which may be due to the metal-carbon binding products in the stretcher minerals. The changes in the C 1s spectra after multiple batch treatment are obvious, with the signals in the 280 ev-290 ev major signal segments attributed to C-C, C-O, and C=O in that order, and the changes in the signals may be due to the bonding of organic matter on the surface of the tensides.

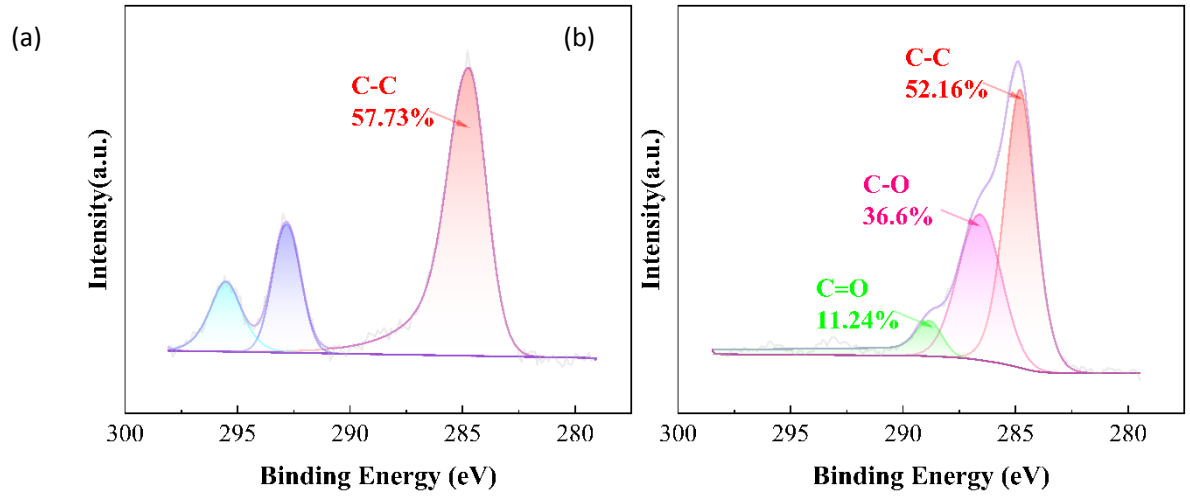

Figure 9. C 1s spectra of (a) limonite and (b) limonite after multi-batch treatment

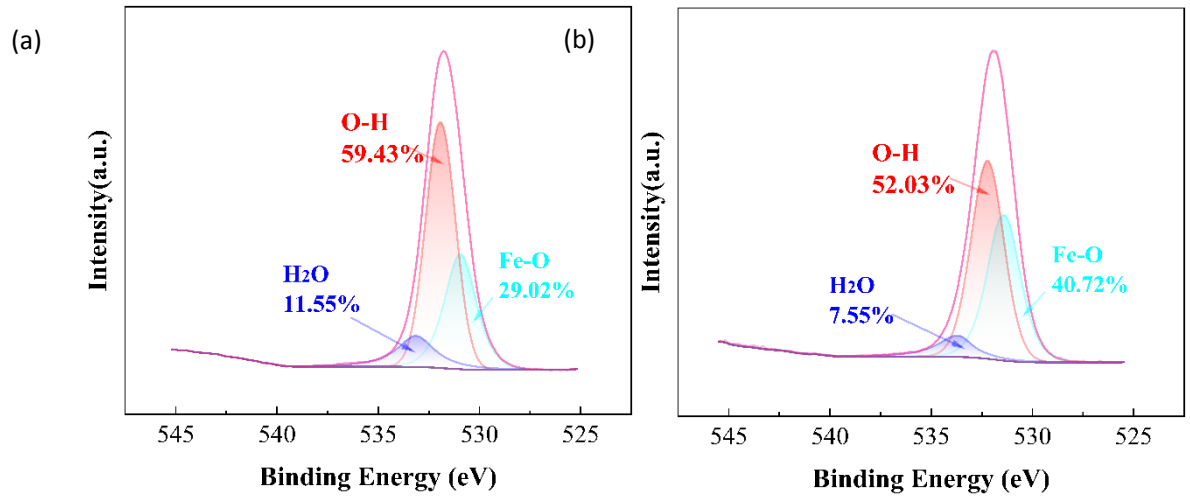

Figure 10. O 1s spectra of (a) limonite and (b) limonite after multi-batch treatment

As can be seen in Fig. 10, the percentage of surface hydroxyl groups of limonite decreased from 59.43% to 52.03% before and after the reaction, while the percentage of bound oxygen (the main form of which is Fe-O) increased from 29.02% to 40.72%, which may be attributed to the catalytic process of the surface iron sites. Figure 11, on the other hand, demonstrates the Fe 2p spectra of limonite before and after multiple batch treatments, and a decrease in the percentage of Fe(II) and an increase in the percentage of Fe(III) on the limonite surface can be observed, which can be attributed to the heterogeneous Fenton reaction of the divalent iron sites on the limonite surface in response to hydrogen peroxide.

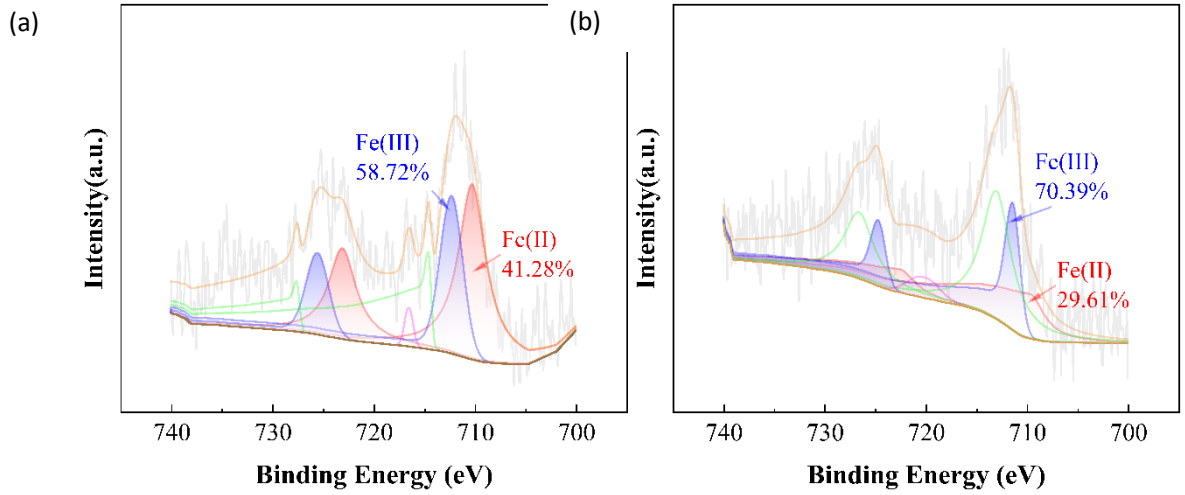

Figure 11. Fe 2p spectra of (a) limonite and (b) limonite after multi-batch treatment

3.3.4 EPR analysis

The results of free radical detection of the reaction system are shown in Fig. 12, through the EPR detection and analysis, it can be found that the free radical that plays a major role within the reaction system is -OH, which indicates that limonite is used as a stretcher catalyst within the system, and its heterogeneous Fenton reaction to hydrogen peroxide.

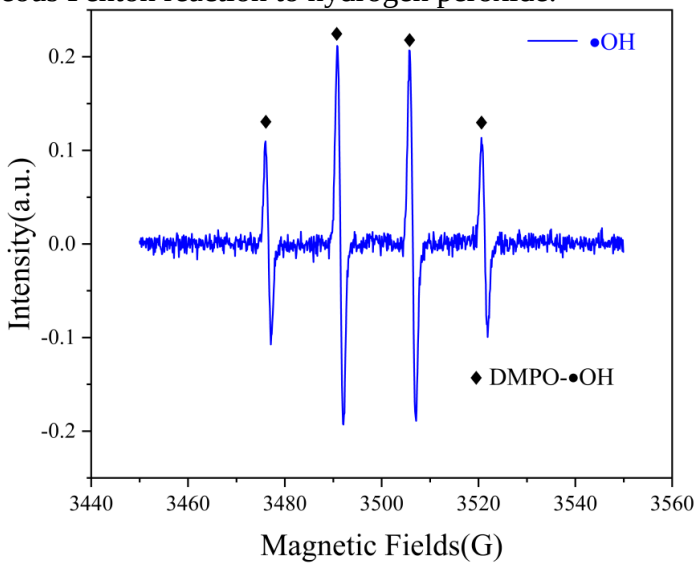

Figure 12. EPR detection analysis

4. Conclusion

(1) The fluidized bed system of limonite/Fenton has a good performance in the treatment of tetracycline, and it is assumed that the removal process mainly relies on the catalytic effect of the divalent iron sites on the surface of limonite rather than the dissolved metal ions on H2O2, and it is a heterogeneous catalytic reaction system dominated by the non-homogeneous catalytic reaction.

(2) The removal rate of tetracycline can reach about 90% when the reaction pH, stretcher dosage, initial concentration of tetracycline solution, H2O2 dosage, number of dosages, and stretcher expansion are 3, 30 g/L, 40 mg/L, 0.6 mmol/L, 1 time, and 100%, respectively.

(3) Multiple batch reactions were carried out for the limonite/Fenton fluidized bed system, and the tetracycline removal rate decreased somewhat with the batch experiments, probably due to the reduction of the catalytic sites on the surface of limonite. However, when the sixth batch was carried out, the reaction system had a removal rate of about 50%. Considering the engineering application properties of the fluidized bed reactor itself and the cost advantage of natural iron ore, the system constructed in this paper still has some application prospects and economic advantages.

(4) Through the characterization of limonite, its main crystalline phases are hydroxyl iron oxide and calcium feldspar, and the surface has fewer holes but more lamellar structure stacking phenomenon. XPS analysis of the stretcher before and after multiple batches revealed a decrease in the proportion of divalent iron as well as a significant increase in the variety of organic functional groups on the surface, and EPR detection of the system revealed that the free radicals within the system that it mainly acted on were -OH, and it was hypothesized that the divalent iron sites on the surface of the stretcher took part in a heterophasic Fenton reaction, producing -OH and thus causing the oxidative degradation of the tetracycline.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Song L, Li L, Yang S, et al. Sulfamethoxazole, tetracycline and oxytetracycline and related antibiotic resistance genes in a large-scale landfill, China[J]. Science of the Total Environment, 2016, 551: 9-15.

[2] Chen C Q, Zheng L, Zhou J L, et al. Persistence and risk of antibiotic residues and antibiotic resistance genes in major mariculture sites in Southeast China[J]. Science of the Total Environment, 2017, 580: 1175-1184.

[3] Liu X, Zhang H, Li L, et al. Levels, distributions and sources of veterinary antibiotics in the sediments of the Bohai Sea in China and surrounding estuaries[J]. Marine Pollution Bulletin, 2016, 109(1): 597-602.

[4] Wang Z, Chen Q, Zhang J, et al. Characterization and source identification of tetracycline antibiotics in the drinking water sources of the lower Yangtze River[J]. Journal of environmental management, 2019, 244: 13-22.

[5] Daghrir R, Drogui P. Tetracycline antibiotics in the environment: a review[J]. Environmental chemistry letters, 2013, 11: 209-227.

[6] Liu H, Yang Y, Sun H, et al. Effect of tetracycline on microbial community structure associated with enhanced biological N&P removal in sequencing batch reactor[J]. Bioresource technology, 2018, 256: 414-420.

[7] Zhang Wen bo,HE Dandan,WANG Jiuling,ZHANG Yupeng,CHU Ling,ZHANG Hong. Adsorption of tetracycline by chitosan/magnetic iron bumpstone[J]. Industrial Water Treatment,2023,43(07):128-134.

[8] LIU Jialu,ZHU Yu,LIU Zhaoyu,HU Boeyin,XIAO Zhaibing.Application of PDS/CoFe2O4 activation system in tetracycline wastewater treatment[J]. Industrial Water Treatment,2023,43(04):139-143.

[9] ZHANG Xiao,ZHANG Jing,YAN Chunhui,HUANG Xue,WU Qingping.CuO@C-catalyzed degradation of tetracycline hydrochloride by peroxodisulfate[J]. Water Treatment Technology,2019,45(04):17-20+26.

[10] Oberoi A S, Jia Y, Zhang H, et al. Insights into the fate and removal of antibiotics in engineered biological treatment systems: a critical review[J]. Environmental science & technology, 2019, 53(13): 7234-7264.

[11] Cai Q Q, Lee B C Y, Ong S L, et al. Fluidized-bed Fenton technologies for recalcitrant industrial wastewater treatment–Recent advances, challenges and perspective[J]. Water Research, 2021, 190: 116692.