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Recent progress in Fenton/Fenton-like reactions for the removal of antibiotics in aqueous environments

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ABSTRACT

The frequent use of antibiotics allows them to enter aqueous environments via wastewater, and many types of antibiotics accumulate in the environment due to difficult degradation, causing a threat to environmental health. It is crucial to adopt effective technical means to remove antibiotics in aqueous environments. The Fenton reaction, as an effective organic pollution treatment technology, is particularly suitable for the treatment of antibiotics, and at present, it is one of the most promising advanced oxidation technologies. Specifically, rapid Fenton oxidation, which features high removal efficiency, thorough reactions, negligible secondary pollution, etc., has led to many studies on using the Fenton reaction to degrade antibiotics. This paper summarizes recent progress on the removal of antibiotics in aqueous environments by Fenton and Fenton-like reactions. First, the applications of various Fenton and Fenton-like oxidation technologies to the removal of antibiotics are summarized; then, the advantages and disadvantages of these technologies are further summarized. Compared with Fenton oxidation, Fenton-like oxidations exhibit milder reaction conditions, wider application ranges, great reduction in economic costs, and great improved cycle times, in addition to simple and easy recycling of the catalyst. Finally, based on the above analysis, we discuss the potential for the removal of antibiotics under different application scenarios. This review will enable the selection of a suitable Fenton system to treat antibiotics according to practical conditions and will also aid the development of more advanced Fenton technologies for removing antibiotics and other organic pollutants.

1. Introduction

Antibiotics are generally produced by bacteria, mould or other microorganisms with disease-resistant pathogens or other active substances and are important drugs that inactivate or stop the growth of pathogenic bacteria; antibiotics exhibit a wide range of types, a wide range of applications, selectivity for microorganisms and other characteristics (Li et al., 2017). The process of stopping bacterial growth is achieved by affecting their structure and function and disabling their ability to grow and reproduce normally. In recent years, with mass production and the extensive use of antibiotics, the issue of antibiotic emissions has attracted increasing attention (Kümmerer, 2009). More than 100,000 tons of antibiotics are released into the environment globally each year (Kümmerer, 2009; Michael et al., 2013; Walters et al., 2010), the majority of which coming from various wastewaters (Affam and Chaudhuri, 2014; Hassani et al., 2018; Uslu and Balcıoğlu, 2009; Verma and Haritash, 2019; Xing and Sun, 2009). Most antibiotics cannot be effectively removed with existing techniques, and untreated antibiotics are discharged into a receiving water body, including surface water and groundwater, causing contamination (Binh et al., 2018; Cardoso et al., 2014; Kümmerer, 2009; Michael et al., 2013; Zhang et al., 2015). Considering the ecosystem as a whole, the accumulation of antibiotics in natural water has a significant negative impact on microbiota (Blaser, 2016). The presence of antibiotics in the environment leads to the growth of antibiotic-resistant microbial communities that promote bacterial resistance, and polluted river and lake waters become reservoirs of antibiotic-resistance genes (ARGs), which pose a high risk to human health and a long-term threat to environmental ecosystems (He et al., 2017; Huang et al., 2019; Levy, 1998; Shen et al., 2019; Xu et al., 2016). The residues of antibiotics in the environment are also influenced

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by their nature, climate, and environmental media. Li et al. found that antibiotics in groundwater ranged from ng/L to μg/L and in sludge and soil from μg/kg to mg/kg (Li and Zhang, 2013; Martínez, 2008). Currently, the persistence of antibiotics as emerging pollutants in environmental media is also increasing with increasing demand for antibiotics, resulting in a series of environmental issues, including the generation of numerous intermediates in the migration process of antibiotics (Li et al., 2019). The presence of antibiotics in the environment is the main reason for the development of microbial resistance. Gao et al. analysed the occurrence and distribution of 22 antibiotics mainly in the Haihe River basin and in surface water, fish products and sediments. Sulfonamides were found to be the main antibiotics in the surface water of this area; sulfadiazine, ofloxacin, sulfamethoxazole, roxithromycin, and erythromycin were found in all surface waters (Gao et al., 2012). Bai et al. investigated the distribution and occurrence of antibiotics in water and sediment samples from the Liao River valley in China, from which most of the antibiotics in water were found to be mainly macrolides, with concentrations up to 3162.22 ng/L. In addition, the main antibiotics in sediment were macrolides and tetracyclines, with concentrations ranging up to 402 μg/kg. Urban discharge and anthropogenic activities along the river basin are the main reasons for the geographical differences in the distribution of antibiotic concentrations (Bai et al., 2014). The distribution characteristics of antibiotics in surface water are closely related to human activities. Liu et al. found that 37 antibiotics were detected in typical lakes in China, including 5 tetracyclines, methotrexate, 14 sulfonamides, 9 quinolones and 2 lincosamides, and the concentration range of antibiotics in lake surface water ranged from nondetectable to 940 ng/L. Overall, the highest concentrations of sulfonamide antibiotics in Chinese lakes compared to concentrations in the surface water of the world are at a high level (Liu et al., 2018). Lyu et al. analysed the spatial distribution of 65 antibiotics in surface water, coastal water, and soil and found that the detection rate of antibiotics in China was relatively high. Bohai Bay is an area with a high level of antibiotics. Quinolones and tetracyclines are the main antibiotics in the soil, which may be caused by the reuse of domestic wastewater and feces. Due to the discharge of domestic sewage and aquaculture, macrolides, tetracyclines, and quinolone antibiotics are found mainly in surface water. The concentrations of tetracyclines, macrolides and quinolones detected in water and soil in China were higher than the concentrations in other countries (Lyu et al., 2020). The analysis of 14 antibiotics in natural water environments in Europe and Asia revealed that the concentrations of these antibiotics in surface water could range from 0 to 4330 ng/L and from 0 to 4500 ng/L in groundwater (Li, 2014). Antibiotics were also tested in surface water in the Yangtze River basin in China, and 20 antibiotics were detected in the concentration range of 0–19 ng/L (Yan et al., 2013). In addition, antibiotic concentrations in drinking water were also detected in the range of 3.6–4200 ng/L (Guerra et al., 2014). Antibiotic residues occur in the ecological environment as a multicomponent mixture, and traces of antibiotics can be detected in seawater, groundwater, surface water, and soil. When an increasing number of antibiotics accumulate in the environment, they will hinder the structure and function of microorganisms. Moreover, because antibiotics have the effect of killing bacteria and inhibiting bacterial growth, they will lead to the loss of ecological functions of some microbial communities (Fekadu et al., 2019; Grenni et al., 2018; Martinez, 2009). Although antibiotic residues concentrations in the environment are low, long-term exposure can still trigger chronic toxic effects in terrestrial and aquatic organisms (Geiger et al., 2016). Therefore, the degradation and treatment aspects of antibiotics are a key concern to reduce the impact of these compounds on the natural water environment and to improve the efficiency of natural microbial transformation.

The abiotic transformation of antibiotics is based mainly on photolysis, hydrolysis and adsorption. When antibiotics flow into the aquatic environment, they can physically adsorb on sediment and particulate matter with a pore-like structure with some carboxyl, amino, aldehyde and other functional groups in the adsorption site and the formation of complexes or chelates (Zhu et al., 2014). Photolysis is one of the main forms of antibiotic degradation in surface water environments, among which direct photolysis is mainly direct photolysis upon photon absorption, followed by indirect photolysis, mainly because irradiated humic acid will produce·OH and O_2 reactive groups under light irradiation when the reactive groups absorb photons and reactive groups that promote the degradation of antibiotics (Nikolaou et al., 2007). Many antibiotics readily undergo hydrolysis reactions in water; thus, hydrolysis is the main pathway for antibiotic degradation in the aquatic environment. The pH of the aqueous environment is an important factor influencing the degradation of antibiotics. Loftin et al. showed that tetracyclines are susceptible to hydrolysis and transformation mediated by different pH values. Macrolide antibiotics are relatively stable in the neutral range, while the ring of β-lactam antibiotics is easily attacked by water molecules in acidic, basic and neutral aqueous environments, and the acyl-oxygen bond is easily broken, causing ring opening and faster degradation (Hou and Poole, 1971; Loftin et al., 2008). Biological transformation is also an effective method of organic degradation. Under aerobic conditions, microorganisms convert large organic compounds into small molecules, which are eventually mineralized into small inorganic molecules such as CO_2 (Sarmah et al., 2006).

The introduction of antibiotics into the aquatic environment leads to the development of resistance in microorganisms, which in turn leads to the production of resistance genes (Wright, 2007). The production and spread of resistance genes are among the greatest environmental pollution risks of antibiotic contamination; therefore, it is important to use appropriate means to efficiently remove antibiotics and eliminate the environmental risk of resistance genes. Usually, easily degradable substrates are important indicators to maintain the normal operation of wastewater treatment plants (Feng et al., 2019; Zhang et al., 2020a). For the degradation of antibiotics such as tetracycline and amoxicillin, the addition of easily degradable substrates greatly improves the degradation efficiency and even enables some antibiotics to reach complete mineralization (Du et al., 2018; Xiong et al., 2018). Among these substrates, easily degradable substrates such as sodium acetate, sucrose, and glucose can promote the degradation of antibiotics by microorganisms (Liu et al., 2020b), and the degradation rate of antibiotics decreases significantly when organic matter is present, thereby decreasing treatment efficiency and reducing the treatment effect on antibiotic wastewater (Ji et al., 2017; Rezaei and Mohseni, 2017). Therefore, there is an urgent need for effective methods to treat antibiotics in aqueous environments (Berman et al., 2009).

In recent years, various physical, biological and chemical methods have been used for antibiotic removal (Daumer et al., 2007). Traditional methods of treating antibiotics include physical, biological and chemical methods (Homem and Santos, 2011; Karoui et al., 2021; Phoon et al., 2020; Wang and Zhuan, 2020). The rationale behind a physical method for treating antibiotics is reducing the level of pollutants by physically or mechanically separating suspended pollutants. Although this method works well for antibiotic treatment, the method only transfers the antibiotic to another phase and does not fundamentally degrade it. Although biological approaches, such as activated sludge processes and biological membrane methods, are commonly used, they have some inevitable defects. For instance, the metabolism of microorganisms takes a long time and releases heat that is not easily gathered and reused. Chemical methods (e.g., disinfection and solid–liquid separation) utilize mainly chemical reactions to separate or remove pollutants present in dissolved or colloidal states and then transform them into nontoxic and nonhazardous substances. In sum, the abovementioned methods focus mainly on the degradation of organic matter, microorganisms, and soluble solids but do not attach importance to mineralizing antibiotics (Azimi and Nezamzadeh-Ejhieh, 2015). In some cases, the presence of certain organic contaminants greatly limits the degradation efficiency of these methods (Yan et al., 2019). In addition, because the composition of antibiotics in aqueous environments is complex and the constituents are difficult to biodegrade, these conventional methods are not ideal selections (Daughton and Ternes, 1999).

As an alternative to conventional strategies, Fenton reaction-based methods have received increasing attention due to their low cost, easy operation, high removal rate and ability to induce complete mineralization. This method achieves the degradation of antibiotics by using·OH as a strong oxidant, since·OH degrades organic pollutants through H-atom extraction reactions, electron transfer or electrophilic addition to π-systems (Barhoumi et al., 2016; Brillas et al., 2009; Ghoneim et al., 2011; Oturan et al., 2011); these processes involve chemical, photochemical or electrochemical techniques, such as the Fenton reaction, ultraviolet (UV)/H_2O_2 or H_2O_2/ozonation, photo-Fenton reaction, multiphase photocatalysis or electro-Fenton reaction, to maximize the mineralization of antibiotics (Loaiza-Ambuludi et al., 2013; Oturan et al., 2011; Özcan et al., 2013; Shu and Chang, 2005; Yang et al., 2010). Under optimal conditions, the Fenton reaction can be used to convert antibiotics into products ranging from organic to small inorganic molecules, thus achieving complete degradation of antibiotics and eliminating environmental pollution.

Based on this information, this paper summarizes recent progress on the removal of antibiotics by the Fenton/Fenton-like reaction and discusses the current application profile for Fenton/Fenton-like oxidation technology. First, we outline the applications of various Fenton oxidation technologies for the removal of antibiotics; the advantages and disadvantages of these Fenton reactions in antibiotic removal are then further compared to demonstrate that Fenton-like oxidation requires less severe reaction conditions than Fenton oxidation, is more applicable to a wider range of processes, and exhibits lower economic costs and much higher cycle times, in addition to simple and easy recycling of the catalyst. Finally, based on detailed comparisons of various Fenton reactions, we discuss the applicability of these Fenton reactions for the removal of antibiotics under different conditions. This study systematically summarizes recent applications of the Fenton reaction in antibiotic removal, which will aid future selection of a suitable Fenton reaction to treat antibiotics according to practical conditions, and this paper is expected to provide useful information for the future development of additional Fenton reaction technology for the removal of antibiotics and other organic pollutants (Scheme 1).

2. Recent progress in Fenton technology for the removal of antibiotics

2.1. Traditional Fenton reaction for the removal of antibiotics

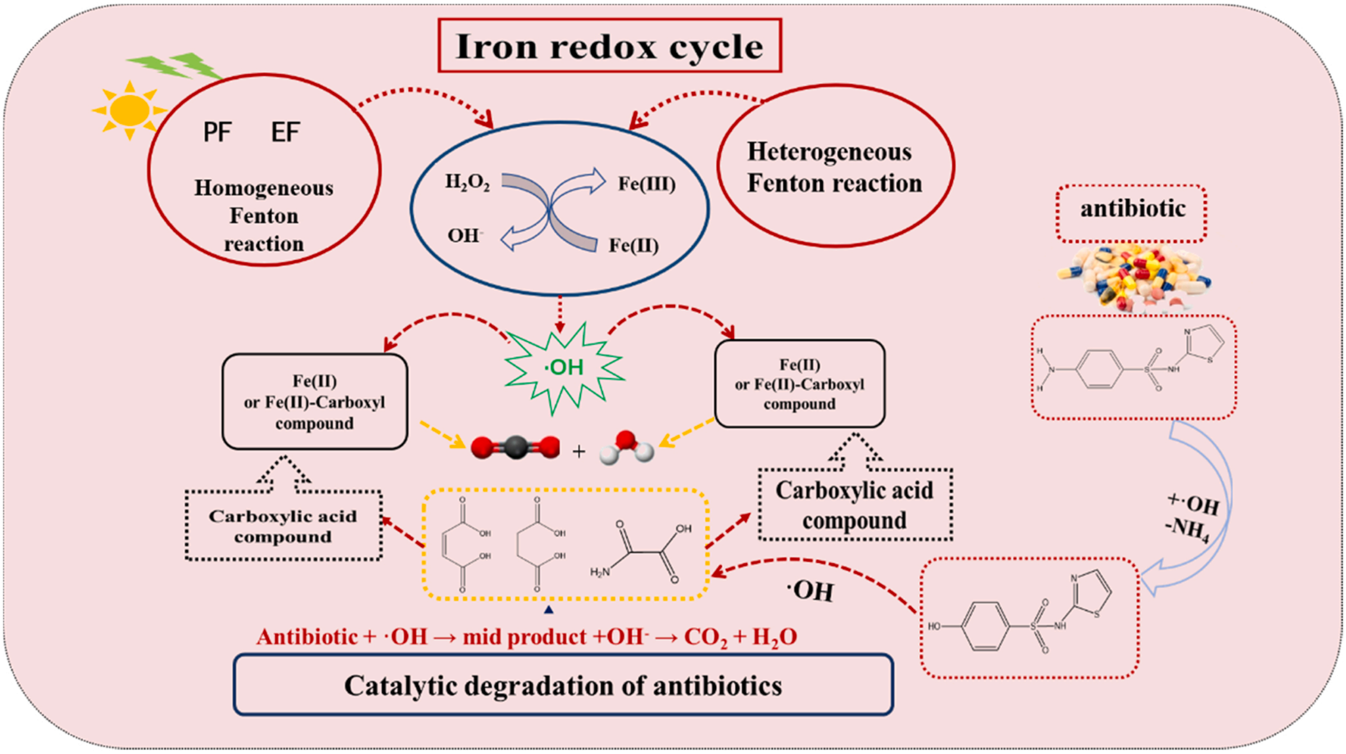
The Fenton reaction was discovered in 1894 by a British chemist named Fenton, who noted that organic substances can be rapidly oxidized to inorganics in a solution containing iron ions and H_2O_2. The mixture of Fe^{2+} and H_2O_2 is a strong oxidizing agent called Fenton's reagent, which can effectively degrade many organic pollutants that are otherwise difficult to degrade in water (e.g., phenols and antibiotics). With its high removal efficiency, complete reaction and limited secondary pollution (Dehghani et al., 2013; Elmolla and Chaudhuri, 2012; Ghasemi et al., 2021; Zhang et al., 2020b), the Fenton reaction has become one of the most effective means for the removal of organic pollutants, especially hard-to-degrade organic pollutants (Cheng et al., 2018; Ren et al., 2019; Rivas-Ortiz et al., 2017; Zou et al., 2014). The specific mechanism is listed as follows: in the first stage, as shown in Eq. (1) under acidic conditions, Fe^{2+} acts as a catalyst and reacts rapidly with the oxidizer H_2O_2 to produce Fe^{3+} and·OH with strong oxidizing properties. When Fe^{3+} is present in the solution, Fe^{3+} reacts with H_2O_2 to produce Fe^{2+}. In the case of sufficient H_2O_2, the cycle of Fe^{2+} can generate more·OH (Chen et al., 1997; De Laat et al., 1999; Liou et al., 2004):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \tag{1}$$

Then, the reaction of·OH and H_2O_2 produces $HO_2\cdot$ and H_2O, as shown in Eq. (2), but the oxidizing power of $HO_2\cdot$ is not as high as the oxidizing power of·OH:

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \tag{2}$$

Fe^{2+} reacts with·OH to give Fe^{3+}, as shown in Eq. (3):



Scheme 1. Schematic diagram of the Fenton reaction used for the treatment of antibiotics in aqueous environments (PF: photo-Fenton; EF: electro-Fenton).

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

Fe^{3+} further reacts with $HO_2\cdot$ to produce Fe^{2+}. Eq. (3) and Eq. (4) show that the production of Fe^{2+} and Fe^{3+} is a cyclic process that occurs continuously as Fe^{2+} reacts again with H_2O_2 to produce$\cdot$OH.

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + O_2 + H^{+} \quad (4)$$

Finally, the strongly oxidizing$\cdot$OH decomposes the organic compounds into H_2O and other intermediates that are eventually degraded to CO_2, as shown in Eq. (5):

$$\text{Organic compounds} + \cdot OH \rightarrow H_2O + \text{mid-product} \rightarrow CO_2 + H_2O \quad (5)$$

The radical$\cdot$OH, which plays a major role in the Fenton system, is present in the solution for a very short time; therefore, even though the yield of$\cdot$OH is high, the utilization rate is low. In addition, in an actual polluted aqueous environment, the composition is complex, and$\cdot$OH is easily scavenged by organic matter and inorganic molecules (Kochany and Lipczynska-Kochany, 1992).

In view of the advantages of the Fenton reaction, the reaction has also been widely studied for the removal of various antibiotics (Ammar, 2016; Arslan-Alaton and Gurses, 2004; Elmolla and Chaudhuri, 2012). For instance, Affam et al. used response surface methodology to optimize the Fenton reaction to degrade the refractory antibiotic pollutants amoxicillin and cloxacillin (Affam and Chaudhuri, 2014). Elmolla et al. used the Fenton method to achieve oxidative degradation of amoxicillin, ampicillin and cloxacillin in aqueous solution (Elmolla and Chaudhuri, 2009). Under the optimal operating conditions, the three antibiotics were completely degraded within 2 min. These results show that the method is effective for treating these three antibiotics (Dehghani et al., 2013). The$\cdot$OH generated in the Fenton oxidation process plays a key role in degrading organic pollutants, and the generation of$\cdot$OH shows flexibility and can be carried out in both homogeneous and heterogeneous phases through free radical chain reactions, which are simple, rapid, inexpensive, easy to run, etc. However, the Fenton reaction also has inevitable drawbacks. First, the reaction process of the Fenton method is complicated; the whole process is triggered by the strong oxidant$\cdot$OH, the optimal pH range for the Fenton method is 2.8–3.0, the reaction mechanism is composed mainly of Eqs. (1) and (4), and the$\cdot$OH generated in Eqs. (1) determines the ability of the Fenton method to degrade organic pollutants. Intermediate$\cdot$OH is continuously generated in the presence of Fe^{2+}, reaction $(1-4)$ constantly produces the Fe^{2+} catalyst, and the production rate of$\cdot$OH is 6000 times higher than the production rate of ferrous ions. Conventional Fenton oxidation is catalyzed mainly by the cycle between Fe^{2+}/Fe^{3+} to generate$\cdot$OH and $HO_2\cdot$ from H_2O_2, so the form of Fe^{2+} and Fe^{3+} present in the solution also affects the reaction cycle (Navalon et al., 2010). Fenton oxidation is also influenced by the initial pH of the solution. When the solution $pH < 3.0$, Fe^{2+}/Fe^{3+} exists mainly in ionic form; therefore, the Fe^{2+}/Fe^{3+} cycle catalyzing H_2O_2 to$\cdot$OH was not affected by pH, and reactions $(1-4)$ could continuously produce Fe^{2+} with catalytic properties. When the pH is approximately 3.0, the highest content of $Fe(OH)^{2+}$ is in the solution, and its chemical activity is also higher; therefore, the Fenton reaction system exists mainly in the form of $Fe(OH)^{2+}$ and Fe^{3+} (Kiyonaga et al., 2009; Naya et al., 2011), and the $Fe(OH)^{2+}$ produced during the reaction can be converted into Fe^{2+} (Munoz et al., 2015). When the pH range is 3–4, Fe^{2+} in solution is converted to $Fe(OH)^{+}$ and $Fe(OH)_2$, and the reaction rate of $Fe(OH)_2$ is 10 times higher than the reaction rate close to Fe^{2+}. The pH increase is accompanied by an increase in $Fe(OH)_2$ content and a simultaneous increase in$\cdot$OH production. When the pH is close to 4.0, the reaction of H_2O_2 and Fe^{2+} increases simultaneously with increasing pH. When $pH > 4.0$, almost all Fe^{3+} exists in the form of $Fe(OH)_3$, and the Fe^{2+}/Fe^{3+} content in the solution decreases rapidly, leading to a decrease in the production rate of$\cdot$OH and $HO_2\cdot$ in the solution and resulting in ineffective Fenton oxidation and the additional problem of iron sludge pollution treatment. In summary, solution pH affects the degradation of antibiotics by the Fenton reaction through influencing the presence of Fe^{2+}/Fe^{3+} in the solution. Therefore, the conventional Fenton reaction is severely influenced by the solution pH. In addition, regarding traditional homogeneous Fenton systems, acidic conditions ($pH=3$) are indispensable for preventing the precipitation of Fe^{2+}/Fe^{3+} ions. Therefore, they require a large amount of acid and alkali to adjust the pH to the desired value before and after the reaction, making the process cumbersome and economically inefficient, and it is difficult to recover the catalyst. In this regard, there is a need to develop catalysts suitable for neutral or weakly basic conditions. Thus, developing far more advanced Fenton systems has become an active research area. To overcome the drawbacks of traditional Fenton oxidation, researchers have done much work to strengthen Fenton/Fenton-like oxidation: (i) introducing physical stimuli (e.g., light, electricity and ultrasound) and (ii) adding complexing agents or redox media to the reaction system. In the following context, we introduce the reaction principles and applications of homogeneous/heterogeneous Fenton reactions. To identify suitable methods for treating antibiotics, we also compare the advantages and disadvantages of these two Fenton methods.

2.2. Homogeneous Fenton-like reaction

In recent years, light, ultrasound and electricity have been introduced into the Fenton reaction to improve its oxidation capacity and degradation efficiency. Commonly, as-developed reaction systems are called homogeneous Fenton-like reactions, which include photo-Fenton, electro-Fenton, solar electro-Fenton, photo-electro-Fenton, solar photo-Fenton, and solar photoelectro-Fenton methods. Compared to conventional Fenton reactions, homogeneous Fenton-like reactions show improved catalytic efficiency, reduced reaction costs, and environmental friendliness. In particular, the photo-Fenton reaction and the electro-Fenton reaction have been successfully utilized for treating organic pollutants. The following sections describe the advances in applications of the homogeneous photo-Fenton reaction, electro-Fenton reaction and other Fenton-like techniques in the degradation of antibiotics.

2.2.1. Homogeneous photo-Fenton reaction

The photo-Fenton reaction combines Fenton reagent and UV or visible light to catalyze the production of$\cdot$OH from H_2O_2, which leads to further degradation of antibiotics. The core of the photo-Fenton reaction is the illumination device. The main mechanism of the photo-Fenton method is described as follows (Lucas et al., 2006; Zepp et al., 1992):

Fe^{2+} reacts with H_2O_2 to form Fe^{3+},$\cdot$OH and OH^{-}, as shown in Eq. (6):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^{-} \quad (6)$$

Under UV light irradiation, H_2O_2 absorbs energy and produces$\cdot$OH, as shown in Eq. (7).

$$H_2O_2 + UV \rightarrow 2\cdot OH \quad (7)$$

During the reaction, H_2O_2 reduces Fe^{3+} to Fe^{2+} and produces$\cdot O_2H$, as shown in Eq. (8):

$$H_2O_2 + Fe^{3+} + UV \rightarrow \cdot O_2H + Fe^{2+} + H^{+} \quad (8)$$

$\cdot$OH affects the degradation of organic antibiotics to inorganic small molecules such as CO_2 and H_2O, as shown in Eq. (9):

$$OH + \text{Antibiotics} \rightarrow \text{Intermediate products} + H_2O \rightarrow CO_2 + H_2O \quad (9)$$

The catalytic capability of the traditional Fenton reaction is limited by the slow regeneration rate of Fe^{2+}, while the photo-Fenton reaction solves this problem. Since Fe^{3+} is the main active species in water and $Fe(OH)^{2+}$ is photosensitive, the irradiation energy accelerates the conversion of Fe^{3+} to Fe^{2+}, therefore forming an iron cycle in the reaction system, which in turn improves the utilization of H_2O_2, promotes the catalytic production of·OH and accelerates the catalytic degradation of pollutants (Ammar et al., 2016; Avetta et al., 2015; Giraldo-Aguirre et al., 2018). Sun et al. applied a photo-Fenton reaction to degrade the antibiotic sulfamonomethoxine sodium (SMMS) (Sun et al., 2012). They found that under the optimal conditions, 98.5% SMMS was consumed. Giraldo-Aguirre et al. developed a near-neutral photo-Fenton method (artificial light and sunlight as the light source) to catalyze the degradation of the β-lactam antibiotic oxacillin (OXA) (Giraldo-Aguirre et al., 2018). Therefore, the catalytic degradation of antibiotics in aqueous solutions by the photo-Fenton method under near-neutral conditions is a promising degradation method, which also enhances the applicability of this method for the treatment of pharmaceutical plant wastewater. Ammar et al. used gradual addition of H_2O_2 over time to limit competition from side reactions and minimize the consumption of H_2O_2 (Ammar et al., 2016). The percentage removal of antibiotics by the photo-Fenton system reached 96%. Compared with the traditional Fenton method, the antibiotic removal percentage was increased by 16% due to the increase in activity of the ferrous catalyst caused by solar irradiation. Table 1 summarizes more antibiotic treatments with photo-Fenton reactions.

Overall, the photo-Fenton reaction is a promising strategy for antibiotic removal because of its short reaction time, high degradation efficiency and easy control of the whole system. The main drawback of photo-Fenton oxidation is that the utilization of light energy is inefficient, which results in high energy consumption. Since only 4% natural light is UV light, UV irradiation increases the reaction efficiency of the photo-Fenton reaction. However, UV irradiation generates considerable heat, which results in deposition of sediments under lamp shade and therefore reduces the utilization of UV light. In addition, fragile instrumentation and high operating costs also limit the widespread use of UV light in photo-Fenton reactions (Brillas, 2020; Wang et al., 2020; Zhu et al., 2021). Moreover, the low solubility and low photoactivity of iron species under neutral conditions also have a negative influence on the reaction. Therefore, new methods must be found to synthesize iron substrates that serve as effective catalysts under neutral conditions.

2.2.2. *Homogeneous electro-Fenton reaction*

The electro-Fenton method is one of the most effective advanced oxidation techniques for degrading antibiotics. During electrolysis under acidic conditions, the anode oxidizes water and generates a small amount of·OH, while the cathode produces H_2O_2 by reducing O_2 without the continuous addition of Fe^{2+} and controls the reaction rate. Herein, both anodic oxidation and electrical absorption (under the action of an electric field, the surface of particulate materials with electrical conductivity or adsorption generates an electric potential difference to form microelectrodes, which increases the surface area of the electrochemical reaction, reduces the migration distance of reactants and improves the degradation effect of target pollutants (Zheng et al., 2016)) can be used to treat organic pollutants effectively. That is, Fe^{2+} and H_2O_2 combine to produce·OH after the in situ electrogeneration of H_2O_2. The electro-Fenton process has obvious advantages, including easy control, high efficiency, and good environmental compatibility (Flox et al., 2006). H_2O_2 can be produced continuously in the electro-Fenton reaction, and Fe^{2+} can be continuously regenerated in situ by electrolysis (Tang et al., 2021). The reaction principle is described below (Hassan et al., 2020; Olvera-Vargas et al., 2021; Oturan et al., 2014; Zhang et al., 2019; Zhou et al., 2018): in the electro-Fenton reaction system with a sacrificial anode, the sacrificial iron anode provides Fe^{2+} for the reaction under the condition of energization by the addition of H_2O_2. In addition, the Fe^{3+} generated during the reaction is reduced to form Fe^{2+} at the cathode, and Fe^{2+} and H_2O_2 undergo the Fenton reaction in the system. and the cathode continuously reduces O_2 to H_2O_2, as shown in Eq. (10):

$$O_2 + 2H^+ + 2\,e^- \rightarrow H_2O_2 \tag{10}$$

Table 1
Photo-Fenton oxidation of antibiotics.

Target	catalyst	Operating conditions	Research result	Ref.
Thiazole Sulfate (STZ)	$UV/H_2O_2/Fe^{2+}$	[sulfathiazole] $_{\text{spiked sample}}$ = 47 μM $[Fe^{2+}]$ = 157 μM $[H_2O_2]$ = 1219 μM 6 × 20 W lamps (365 nm) Irradiance (3.5 mW/cm^2, photon flux 106.6 $\mu mol \cdot m^{-2} \cdot s^{-1}$) pH = 3.0	Degradation efficiency = 90% TOC[a] removal = 75%	(Velásquez et al., 2014)
Tylosin	$UV/H_2O_2/Fe^{2+}$	pH= 2.6 $[H_2O_2]$ = 0.4 g/L $[Fe^{2+}]$ = 6 mg/L [Tylosin] $_{\text{spiked sample}}$ = 15 mg/L UV light lamp (λ_{max} = 350 nm, P = 11 W)	Degradation efficiency = 97.1% TOC removal = 91.5%	(Sarrai et al., 2016)
Ciprofloxacin Hydrochloride	$UV/H_2O_2/Fe^{2+}$	pH= 3.5–5.0 [Ciprofloxacin hydrochloride] $_{\text{spiked sample}}$ = 15 mg/L $[H_2O_2]$ = 5.0 mM $[Fe^{2+}]$ = 0.05 mM pH= 4.0 6 W UV lamp(365 nm)	Degradation efficiency = 71%	(Sun et al., 2009)
Chloramphenicol (CAP)	$UV/H_2O_2/Fe^{2+}$	[CAP] $_{\text{spiked sample}}$ = 200 mg/L $[H_2O_2]$ = 400 mg/L $[Fe^{2+}]$ = 5–10 mg/L UVA= 31.7 kJ/L pH= 2.5–2.8	DOC $_{\text{removal}}$ = 92% COD $_{\text{removal}}$ = 98% Degradation efficiency = 98%	(Trovó et al., 2013)
Amoxicillin Cloxacillin	UV–Vis/Iron oxalate/ H_2O_2	pH= 3.0 [Amoxicillin]$_{\text{spiked sample}}$ = 150 mg/L [Cloxacillin] $_{\text{spiked sample}}$ = 150 mg/L H_2O_2/Fe^{3+} molar ratio = 75 $H_2O_2/C_2H_2O_4$ molar ratio = 37.5 solar intensity = 0.85 kW/m^2	COD removal efficiency = 78.37% TOC removal efficiency = 52.3%	(Chaudhuri et al., 2013)
Tetracycline initial	$UV/H_2O_2/Fe^{2+}$	pH = 2.7 ± 0.1 [Tetracycline initial] $_{\text{spiked sample}}$ = 40 mg/L $[Fe^{2+}]$ = 5 mg/L $[H_2O_2]$ = 71.5 mg/L 230 W mercury lamp (300–550 nm)	Mineralization efficiency = 77%	(Yamal-Turbay et al., 2013)

[a] TOC = total organic carbon

Fe^{2+} reacts with H_2O_2 to generate·OH with an oxidation potential of 2.8 eV, and·OH, with its strong oxidizing capability, can oxidize many hard-to-degrade antibiotics to eventually yield small inorganic molecules such as CO_2 and H_2O, as shown in Eq. (11):

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \tag{11}$$

Fe^{3+} receives electrons from the cathode and is reduced to Fe^{2+}, as shown in Eq. (12):

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{12}$$

Fe^{3+} also reacts with H_2O_2 to form Fe^{2+}, as shown in Eq. (13):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \cdot HO_2 + H^+ \tag{13}$$

Fe^{3+} reacts with·HO_2 to form Fe^{2+} and O_2, as shown in Eq. (14):

$$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + O_2 + H^+ \tag{14}$$

HO_2·reacts with H_2O_2 to form O_2, H_2O and·OH, as shown in Eq. (15):

$$HO_2\cdot + H_2O_2 \rightarrow H_2O + O_2 + \cdot OH \tag{15}$$

In recent years, the electro-Fenton method has been developed rapidly and applied to the removal of antibiotics. In contrast to the photo-Fenton reaction, the electro-Fenton system has an automatic H_2O_2 generation mechanism that is generated by the electrochemical reaction. Tang et al. devised a dual-cathode electrophoresis device for the removal of tetracycline (Tang et al., 2021) (Fig. 1a). One cathode in the system was used to activate graphite felt (AGF) with KOH and produce H_2O_2, and the other cathode was used to activate H_2O_2 by growing FeOCl (FeOCl/carbon cloth (CC)) in situ on CC, thus triggering the Fenton reaction. The advantage of producing Fe^{2+} in situ from CC is that it exposes more Fe active sites, enhances Fe^{2+}/Fe^{3+} cycling stability and lessens iron precipitation. Furthermore, the double-cathode electro-Fenton system achieves efficient degradation of tetracycline. The efficiency for removal of tetracycline was up to 95% within 1.5 h, and the efficiency for mineralization was up to 88% within 4 h. The double-cathode electro-Fenton system is easy to prepare, inexpensive and effective for antibiotic removal, so it may constitute a process for large-scale antibiotic treatments. Dirany et al. used the electro-Fenton method to treat sulfamethoxazole and then reduced the toxicity of cyclic and aromatic products as measured by bioluminescence (Dirany et al., 2011). Ganzenko et al. used a boron-doped diamond anode and a carbon felt cathode as an electrolysis bath (Ganzenko et al., 2018); at an applied current of 300 mA, tetracycline was completely degraded within 5 min with a mineralization rate of 89%, and the biological oxygen demand (BOD)/COD ratio increased from 0.02 to 0.56 after 6 h of electrolysis, thereby illustrating the feasibility of the electro-Fenton pretreatment. In addition, an electro-Fenton reaction (at 300 mA) was used for the complete degradation of 5-fluorouracil; thus, the electro-Fenton reaction is an interesting alternative method for degrading antibiotics. Graphite felt (GF) modified with nitric acid can be oxidized and thermally activated by oxidizing agents and can be used as a cathode to degrade levofloxacin (Liu et al., 2020a). The pretreated GF was immersed in a thermal reactor containing nitric acid and heated at 90 °C for 0, 3, 6, 9 and 12 h, labeled GF-0, GF-3, GF-6, GF-9 and GF-12, respectively. Hours after treatment, the modified GF-9 introduced a large number of oxygen-containing functional groups, had a larger surface area, higher hydrophilicity, significantly higher redox activity, and higher total organic carbon removal rate and mineralization current

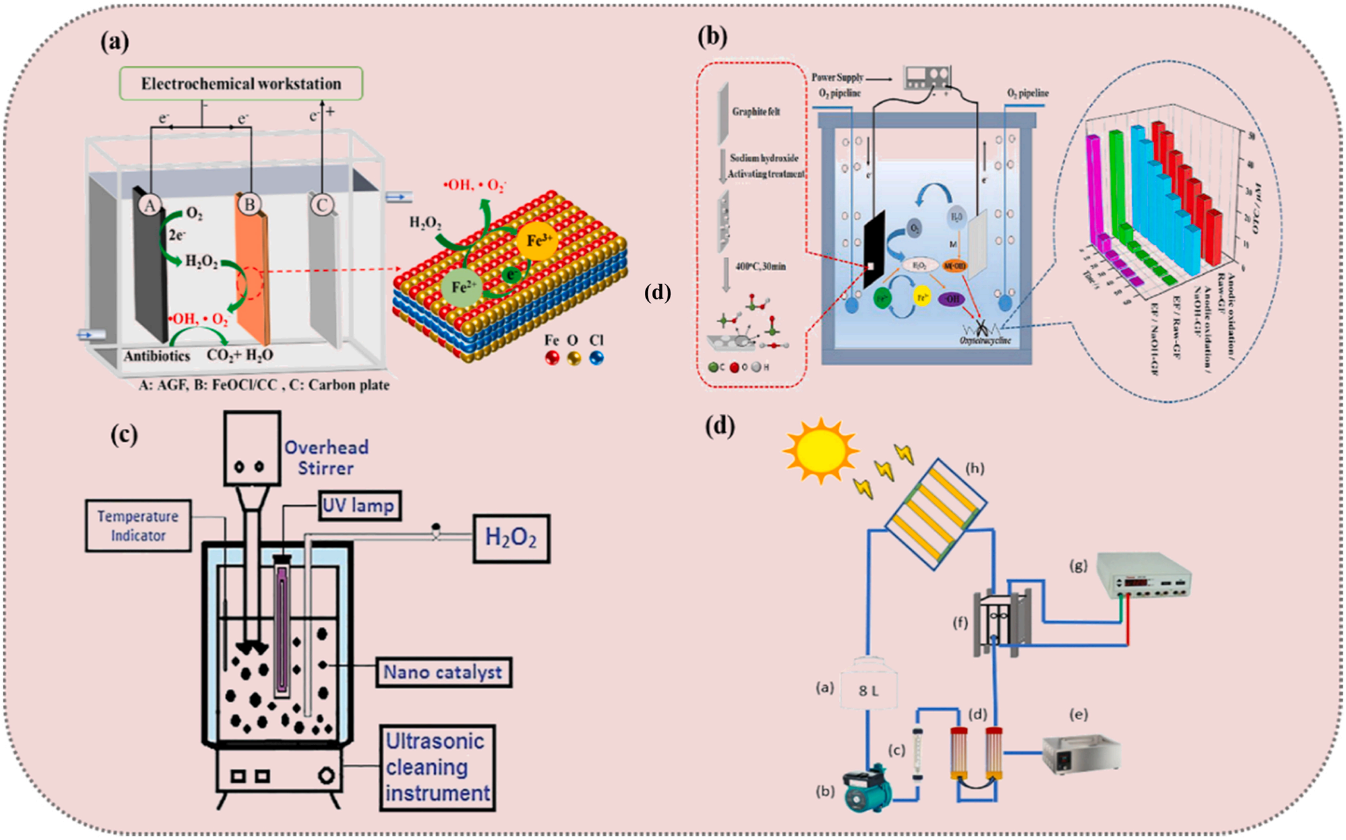


Fig. 1. (a) Double-cathode electro-Fenton (EF) system for the degradation of TC. (b) Kinetics and mechanisms of oxytetracycline degradation in an electro-Fenton system with a modified graphite felt cathode. (c) Experimental setup for application at the scale of real wastewater purification through the photo-Fenton reaction. (d) The system uses solar energy and a photoelectro-Fenton system.
(a) (adapted with permission from ref. (Tang et al., 2021)). (b) (adapted with permission from ref. (Lai et al., 2020)). (c) (adapted with permission from ref. (Hosseini et al., 2018)).

efficiency than the unmodified graphite felt; therefore, GF-9 is a promising cathode material, which is expected to be developed within electro-Fenton in the field of organic pollutant removal. Lai et al. activated graphite felt with NaOH (Lai et al., 2020) (Fig. 1b); the redox capacity and·OH generation rate of the modified graphite felt were significantly increased, and the electro-Fenton method was used for catalytic degradation of antibiotics with NaOH-glass fiber serving as the cathode at pH 3.0. The COD decrease during the removal of oxytetracycline by NaOH-glass fiber reached 83.75% in 30 min. The glass fiber cathode showed high degradation capability and stability to

Table 2
Electro-Fenton oxidations of antibiotics.

Target	Catalyst	Operating conditions	Research result	Ref.
Sulfanilamide	H_2O_2/Fe^{2+}/Current	pH = 3.0 $[\text{Sulfanilamide}]_{\text{spiked sample}} = 0.5$ mM $[Fe^{2+}] = 0.5$ mM $[H_2O_2] = 7$ mg/L $[Na_2SO_4] = 0.05$ M Applied current = 60 mA Conductivity = 0.1 µS/cm	COD removal efficiency =92%	(Ganiyu et al., 2021)
Ciprofloxacin	$H_2O_2/(Fe^{2+}/Fe^{3+})$/Current	pH = 3.0 $[\text{Ciprofloxacin}]_{\text{spiked sample}} = 200$ mg·dm^{-3} $[Fe^{2+}/Fe^{3+}] = 1.50$ mM·dm^{-3} $[Na_2SO_4] = 0.05$ M Constant current intensity = 18 mA·cm^{-2} Conductivity = 0.1 µS/cm	Mineralization yields = 88% TOC removal efficiency = 73%	(Chen et al., 2017)
Tetracycline	H_2O_2/Fe^{2+}/Current	pH = 3.0 $[\text{tetracycline}]_{\text{spiked sample}} = 25$ mg/L $[Fe^{2+}] = 0.1$ mM $[Na_2SO_4] = 0.05$ M Applied current = 300 mA Conductivity = 0.1 µS/cm	Mineralization yields = 83% Degradation efficiency = 100%	(Ferrag-Siagh et al., 2013)
Enoxacin	H_2O_2/Fe^{2+}/Current	pH = 3 $[\text{Enoxacin}]_{\text{spiked sample}} = 50$ mg/L $[Fe^{2+}] = 0.2$ mM $[Na_2SO_4] = 0.05$ M Applied current = 300 mA Conductivity = 0.1 µS/cm	Degradation efficiency = 98% TOC removal efficiency≤ 32%	(Annabi et al., 2016)
Sulfamethazine	O_2/Fe^{2+}/current	pH = 3.0 $[\text{Sulfamethazine}]_{\text{spiked sample}} = 0.2$ mM $[Fe^{2+}] = 0.5$ mM $[Na_2SO_4] = 0.05$ M Applied current= 500 mA Conductivity = 1.2 mS/cm	Mineralization yields = 81.4% Degradation efficiency = 100%	(Mansour et al., 2015a)
Sulfamethazine	H_2O_2/Fe^{2+}/Current	pH = 3.0 $[Fe^{2+}] = 0.1$ mM $[\text{Sulfamethazine}]_{\text{spiked sample}} = 0.36$ mM $[Na_2SO_4] = 0.05$ M Applied current = 200 mA Conductivity = 0.1 µS/cm	Mineralization yields = 93.9% Degradation efficiency = 99.1%	(Mansour et al., 2014)
Sulfamethazine	H_2O_2/Fe^{2+}/Current	pH = 3.0 $[\text{sulfamethazine}]_{\text{spiked sample}} = 0.2$ mM $[Fe^{2+}] = 0.2$ mM $[Na_2SO_4] = 50$ mM Current density = 20.83 mA/cm^2 Conductivity = 0.1 µS/cm	Total mineralization efficiency = 98.5%	(Sopaj et al., 2016)
Tetracycline	H_2O_2/Fe^{2+}/Current	pH = 7 $[\text{Tetracycline}]_{\text{spiked sample}} = 50$ mg/L Fe plate (5 cm × 6 cm ×0.2 cm) $[Na_2SO_4] = 0.05$ M Power supply(1–9 V) Conductivity = 500 µS/cm	Removal efficiency = 97.21% TOC removal efficiency = 82.84%	(Dai et al., 2022)
Ciprofloxacin	$H_2O_2/(Fe^{II}Fe^{III}$ LDH/CF)/Current	pH = 3–9 $[\text{Ciprofloxacin}]_{\text{spiked sample}} = 0.2$ mM $[Fe^{2+}] = 0.2$ mM $[Na_2SO_4] = 0.05$ M Current = 200 mA Conductivity = 0.1 µS/cm	Degradation efficiency = 88.11%	(Yao et al., 2021)
Sulfamethazine	H_2O_2/Fe^{2+}/Current	$[\text{Sulfamethazine}]_{\text{spiked sample}} = 0.2$ mM $[Fe^{2+}] = 0.2$ mM $[Na_2SO_4] = 0.05$ M pH = 3 Current = 300 mA Conductivity = 0.1 µS/cm	TOC removal = 90% Mineralization degree = 95%	(Barhoumi et al., 2016)
Trimethoprim	H_2O_2/Fe^{2+}/Current	$[\text{Trimethoprim}]_{\text{reality}} = 0.2$ mM $[Fe^{2+}] = 0.69$ mM $[Na_2SO_4] = 0.05$ M pH = 3.0 Current = 466 mA Conductivity = 4.36 mS/cm	Removal efficiency = 100%	(Mansour et al., 2015b)

oxytetracycline after activation by NaOH. The advantages of this system are low operating costs, low reagent usage, and much lower labor intensity and safety risks, which would be useful in antibiotic degradation. Zhang et al. prepared a double anode and Pd/CeO_2 catalyst for the removal of the antibiotic sulfadiazine with an electro-Fenton system using photovoltaic energy as the power source (Zhang et al., 2020c). In situ generation of H_2O_2 with regular replacement of catalysts and iron anodes resulted in more than 95% removal of sulfadiazine. Table 2 summarizes more cases of antibiotic treatments with electro-Fenton reactions.

The factors affecting the catalytic degradation of antibiotics with the whole electro-Fenton reaction system include the initial pH of the solution, catalyst concentration, electrolyte type, H_2O_2 concentration, temperature, and dissolved oxygen concentration, which together determine the oxidation efficiency of the electro-Fenton process (Annabi et al., 2016; Barhoumi et al., 2016; Brillas et al., 2009; Kubo and Kawase, 2018; Lai et al., 2021; Poza-Nogueiras et al., 2018; Wang et al., 2014). With the gradual transformation of the energy infrastructure, which is now based mainly on power generation, a greener energy situation has become normal for social life applications. The outstanding advantage of the electro-Fenton reaction is that the reaction automatically generates H_2O_2, which reduces the cost of drug degradation and improves cycling efficiency, so the electro-Fenton reaction is widely used for antibiotic degradation. However, the electro-Fenton method still has certain defects, among which the need to adjust the pH value to achieve acidic conditions is the most demanding. In addition, if the current efficiency of the reaction process is low, the low concentration of H_2O_2 produced leads to a low output of·OH, which in turn affects the operation of the electro-Fenton reaction. Therefore, the consumption of electricity has become a major concern, and it is particularly important to develop catalysts with fewer demands for pH control and less consumption of electrical energy to replace the deficiencies of homogeneous electro-Fenton reactions.

2.2.3. Auxiliary Fenton technology

In traditional Fenton technology, auxiliary Fenton technology refers to the introduction of ultrasound, microwaves, UV light, electrolysis, etc. Such combined processes can enhance the catalytic decomposition of H_2O_2 by strengthening the variable valence of the metal ions or the variable valence electron transfer, thus improving the efficiency of homogeneous Fenton systems or homogeneous Fenton-like oxidation for the catalytic degradation of organic pollutants.

These Fenton reactions are ideal alternative techniques. For example, Hosseini et al. prepared tin dioxide nanosheets modified with zinc sulfide quantum dots by a hydrothermal method and used roxithromycin and clarithromycin antibiotics as target contaminants (Hosseini et al., 2018) (Fig. 1c). The combined ultrasonic (US) irradiation/UV/catalytic treatment produced H_2O_2, which in turn led to the generation of·OH. Compared with the conventional Fenton method, the addition of a catalyst to the UV-irradiated test solution greatly improved the efficiency for the degradation of roxithromycin and clarithromycin, making the coupled sono-photo-Fenton system a promising process for the treatment of macrolide antibiotic-containing wastewater. Serna-Galvis et al. significantly enhanced the removal efficiency of antibiotics by adding citric acid to the photochemical system, forming soluble iron complexes for use with a single stimulus (light, H_2O_2, or Fe (II)) and the whole photochemical system (light/H_2O_2/Fe(II)), thus demonstrating efficient antibiotic removal with the photo-Fenton method in aqueous media containing high concentrations of citric acid (Serna-Galvis et al., 2020).

Considerable effort has been made in recent years to develop solar energy for water treatments (Shah et al., 2020). The combination of solar irradiation with the electro-Fenton reaction constitutes an effective way to remove antibiotics and is therefore gaining attention (Salazar et al., 2012). This combined method can be implemented in two ways: one way involves direct treatment with solar energy (Salazar et al., 2019); the second type involves indirect solar processing, namely, solar energy is used indirectly in electrochemical cells to generate electricity (Zhao et al., 2015). The solar photoelectro-Fenton (SPEF) process of a carbon cathode in water also plays a key role in acidic and alkaline media through redox reactions to promote the generation of H_2O_2 based on cathode electricity and the release of Fe^{2+} from iron anodes, enhancing the generation of·OH and inducing the degradation of antibiotics (Martínez-Huitle and Panizza, 2018). Bugueño-Carrasco et al. equipped an electrochemical pressure filter cell with a solar electrochemical device (Bugueño-Carrasco et al., 2021). The cathode was directly exposed to solar light, and a solar photoreactor was used to degrade antibiotics (tetracycline, sulfamethazine and ampicillin) (Fig. 1d). The degradation of these antibiotics started within 10 min in this system, proving that the SPEF process can treat this type of antibiotic in a short time.

2.3. Heterogeneous Fenton-like reactions

Although the conventional Fenton system exhibits a rapid reaction, easy operation, mild reaction conditions, and high efficiency for oxidative degradation, the reaction also has the following disadvantages: it is only active under strongly acidic conditions, Fe^{2+} is difficult to recover, and the rate for utilization of H_2O_2 is low. When the pH is raised, a large amount of iron sludge is produced due to iron aggregation, resulting in a significant reduction in the catalytic activity and causing secondary pollution to the environment. These deficiencies increase the treatment costs and limit the application of the Fenton reaction. Therefore, in response to the shortcomings mentioned above for homogeneous Fenton reactions, many researchers have conducted extensive research on the immobilization of ferric and ferrous ions to accelerate catalytic oxidation. In this regard, heterogeneous Fenton-like methods have been developed. Similar to the classical Fenton reaction, the heterogeneous Fenton-like reaction refers to the process of reaction between Fe^{2+} and H_2O_2 with a solid catalyst by introducing light, electricity, ultrasound, microwave and other auxiliary means, which can enhance the catalytic decomposition of H_2O_2 to produce·OH, improving the efficiency of catalytic degradation of antibiotics. Compared with the homogeneous Fenton reaction, the heterogeneous version is compatible with a wide range of pH values, generates fewer free iron ions and is simple, practical and easy to operate. This type of catalyst includes a carrier and a main catalyst that can be recycled and reused to reduce costs (Ameta et al., 2018). Therefore, this type of catalyst is also the most attractive alternative to the homogeneous Fenton method and has gained attention in recent years.

To date, there are three types of heterogeneous Fenton systems (Andreozzi et al., 2002; Feng et al., 2006; Neamţu et al., 2004; Wu et al., 2006): (I) iron compounds, mainly Fe_2O_3, Fe_3O_4, and Fe hydroxyl oxides (α-, β-, γ-FeOOH). (II) loaded Fenton catalysts, i.e., Fe^{2+} and Fe^{3+} loaded onto activated carbon, clay, molecular sieves, etc. (III) multiphase Fenton catalysts loaded with other metal ions in addition to iron ions, which can improve the reaction rate and catalytic activity.

Iron exhibits low cost, high natural abundance, environmental friendliness, easy separation and stability, and activity towards heterogeneous Fenton processes. Iron oxide as the active center is often used in water treatment processes. The reactivity of Fenton-like processes using iron ore shows a linear relationship with the Fe^{2+} content in iron minerals, and since nanomaterials are well dispersed and provide a large number of reactive sites, nanomagnetite may be synthesized by various chemical and hydrothermal methods (Affam and Chaudhuri, 2014; Ding et al., 2017; Hou et al., 2016; Luo et al., 2010; Wang et al., 2010a, 2010b). For example, Hassani et al. used nano Fe_3O_4 as a catalyst for antibiotic removal and they selected ciprofloxacin (CIP) as the target pollutant (Hassani et al., 2018) (Fig. 2a). The physical properties of milled nano Fe_3O_4 were improved by a ball milling process, and the catalytic performance in heterogeneous Fenton oxidation for the removal of ciprofloxacin from aqueous solution was greatly enhanced.

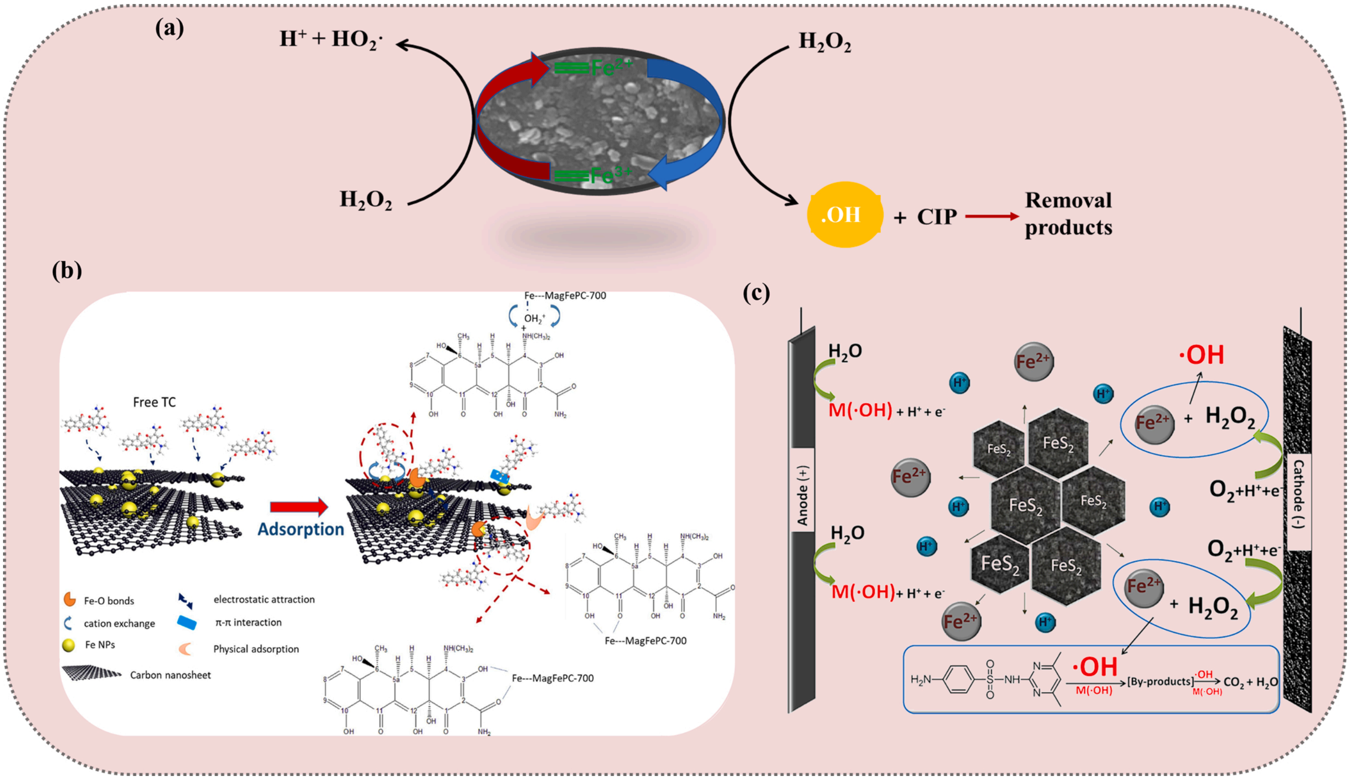


Fig. 2. (a) Schematic mechanism for the removal of CIP with the heterogeneous Fenton process in the presence of ball-milled magnetite. (b) Mechanism for the adsorption of TC by MagFePC-700. (c) Degradation of sulfamethazine with a heterogeneous electro-Fenton process using pyrite as the catalyst.
(a) (adapted with permission from ref. (Hassani et al., 2018)) (b) (adapted with permission from ref. (Gu et al., 2021)) (c) (adapted with permission from ref. (Barhoumi et al., 2016)).

The nano Fe_3O_4 catalyst could be magnetically separated from aqueous solution, so this catalyst is more environmentally friendly because no dissolved or suspended iron is released. Gu et al. achieved efficient removal of tetracycline (TC and good adsorption capacity for TC over a wide pH range by using synergistic adsorption of carbon and iron in an MIL-101 (Fe)-derived magnetic Fe/porous carbon hybrid (MagFePC) that provided pore channels for TC transport and enrichment due to the microporous and mesoporous nature of the carbon in MagFePC (Gu et al., 2021) (Fig. 2b). MagFePC can be regenerated without pH adjustment, which has a high adsorption capacity and can be applied to the adsorption of antibiotics such as tetracycline, oxytetracycline and aureomycin hydrochloride. This material is easily separated in the environment and can be reused. Thus, this complex is a green and recyclable antibiotic adsorbent and catalyst that can be used for the adsorption and treatment of organic pollutants. As the Fenton reactivity of magnetite is related to the surface Fe^{2+} species, when atmospheric oxygen encounters Fe^{2+}, the atmospheric oxygen will oxidize Fe^{2+} to Fe^{3+}. For the surface of magnetite exposed to air with Fe^{3+}, its Fenton reaction is not active. Unfortunately, magnetite is easily oxidized, and its inactivation is indeed inevitable in practice. Therefore, the preservation problem of magnetite still needs to be solved (Bertinetti et al., 2019). Zero-valent iron nanoparticles (n-ZVI) in Fenton-active materials may solve the oxidation problem of magnetite and other materials. Although the zero-valent iron nanoparticles in Fenton's active materials are chemically active, they have poor performance stability and are prone to oxidation reactions with the media present in the environment, so their activity decreases accordingly, which is a problem of zero-valent iron nanoparticles. If the zero-valent iron nanoparticles are loaded on other solid surfaces, it not only makes them stably loaded on the carrier but also plays a role in dispersing and avoiding the oxidation of iron nanoparticles, and if the carrier has adsorption properties, it can accelerate the pollutants to reach the nanoparticle surface and improve the pollutant removal effect. In addition, zero-valent nanoiron has excellent reactivity and high activity over a wide pH range, and the application of zero-valent nanoiron in the Fenton system is also interesting due to the major study. Compared with other materials, such as magnetite, ZVI does not require special attention to its storage conditions, and passivated ZVI still has Fenton reaction applicability. Based on the ZVI-Fenton system, ZVI plays a key role in the ZVI-Fenton system, which is characterized mainly by H_2O_2 reacting at the surface of ZVI, and no dissolved Fe(II) is needed as a catalyst to trigger the reaction. As a result, the dissolved Fe content in ZVI-Fenton is minimal or even undetectable. Another advantage of ZVI is that if it is oxidized to form Fe^{2+}, the classical Fenton system is characterized mainly by the reaction of Fe^{2+} with H_2O_2 so that the Fenton reaction continues even if ZVI is oxidized. Furia et al. used ZVI to degrade residual antibiotics (cefazolin, imipenem and vancomycin) in hospital wastewater. ZVI-Fenton was comparable to the conventional Fenton reaction (pH=2–3) under near-neutral conditions (pH=5), without dissolved iron leaching; Moreover, ZVI is magnetic and has an advantage in recycling (Furia et al., 2021). Therefore, the future application of ZVI-Fenton technology to the treatment of residual antibiotics could significantly reduce the possibility of antibiotics triggering antibiotic resistance and antibiotic-resistance genes. In the presence of reduced sulfur, Cao et al. reduced dissolved iron to Fe^0 or Fe_xS_y and synthesized more stable sulfide-modified nZVI using a one-step method, resulting in Fe^0/Fe-sulfide particles for degradation of the antibiotic florfenicol (Cao et al., 2017). Barhoumi et al. tested the degradation of tetracycline with a heterogeneous Fenton method by using natural pyrite as a Fenton catalyst, boron-doped diamond (BDD) or platinum as the anode and carbon felt as the cathode (Barhoumi et al., 2017). Compared with the traditional electro-Fenton method, the electro-Fenton-pyrite method using boron doping as the anode demonstrates enhanced degradation efficiency for tetracycline and accelerated mineralization. Barhoumi et al. utilized pyrite as the Fe^{2+} source in an integrated electrochemical cell with a Pt or BDD anode and carbon felt as the cathode to mineralize sulfamethoxazole (SMX) with an applied current (Barhoumi et al., 2016) (Fig. 2c). This pyrite-electro flocculation process resulted in 95% TOC removal for the target pollutant. Compared to the traditional electro-Fenton process, the process using BDD as anodes exhibited higher mineralization of pyrite. Xing et al. adopted a combined process involving coagulation of polymeric ferrous sulfate, the Fenton reaction and precipitation to degrade antibiotics (Xing and Sun, 2009). The removal ratios of overall color, COD and suspended matter reached 97.3%, 96.9% and 86.7%, respectively, thus indicating that polymerized ferric sulfate coagulation combined with the Fenton reaction and precipitation processes provided an effective method for antibiotic treatment.

However, the catalytic efficiency was generally low, and the efficiency for the utilization of·OH was also low. Therefore, doping transition metals into iron oxides significantly improves the efficiency of H_2O_2 decomposition to generate·OH and increases the activity and efficiency for the utilization of·OH. Apart from these properties, doping iron oxides with small amounts of transition metals increases the specific surface area and number of active sites. Tavasol et al. developed a novel marine sediment/titanate for use as a photocatalyst in the removal of cefadroxil from aqueous media in the presence of UV light, H_2O_2 and ultrasound (Tavasol et al., 2020) (Fig. 3a). With increased titanium loading on the sediment, which had a high specific surface area and photocatalytic activity, the rate of cephalexin removal was as high as 94.71%. Jain et al. prepared ZnO nanomaterials by a hydrothermal method and catalyzed the oxidation to generate·OH with strong oxidative properties by adding ZnO nanoparticle catalysts to aqueous H_2O_2 solution under daylight irradiation conditions, and the·OH thus generated oxidatively degraded norfloxacin. The recovered catalyst was also able to perform six Fenton cycles with no reduction in activity. ZnO nanoparticles are robust, efficient and reusable photocatalysts. The heterogeneous Fenton method catalyzed by ZnO is a promising approach for the degradation of antibiotics (Jain et al., 2020). Zhong et al. synthesized copper ion-doped Bi_2WO_6 nanomaterials with photoactivity, and the introduction of transition metals improved the photocatalytic activity in redox reactions (Zhong et al., 2020). Visible light had a synergistic effect in the sulfate-containing Fenton reaction, and these nanomaterials catalyzed the degradation of 89.27% of the antibiotic norfloxacin (NOF) and showed a high degradation rate of NOF over five cycles. Tang et al. prepared three-dimensional flower-like FeCu@C composites with a mesoporous carbon matrix encapsulating Fe-Cu bimetallic nanoparticles by pyrolysis of [Fe, Cu]-BDC precursors, and the bimetallic nanoparticles served as active sites to enhance the catalytic degradation of sulfamethazine through synergistic effects (Tang and Wang, 2019) (Fig. 3b). In addition, this flower-like carbon matrix structure facilitated rapid diffusion of reactants to the active sites of bimetallic nanoparticles and prevented the aggregation of iron-based nanoparticles, which would reduce the catalytic efficiency. At pH= 3.0, with 20 mg/L sulfamethazine and 0.25 g/L FeCu@C, the percentage of conversion to TOC by the FeCu@C catalyst reached 72.3% within 4 h. Nguyen et al. synthesized reduced graphene oxide (GO)-loaded bimetallic palladium-zerovalent iron bimetallic (Pd/nZVI/rGO) composites by using sodium borohydride as a reducing agent in a one-step liquid-phase reduction reaction (Nguyen et al., 2021). The advantages of using graphene oxide as a substrate are listed as follows: (1) graphene prevents the aggregation of Pd/nZVI nanoparticles and disperses these nanoparticles uniformly; (2) Pd/nZVI nanoparticles prevent the accumulation of graphene oxide. Therefore, these catalysts were used for catalytic degradation of the antibiotic hygromycin. The introduction of graphene oxide as a substrate for Pd/nZVI nanoparticles was found to significantly improve the efficiency of hygromycin degradation. Studies showed that the addition of 5 wt% graphene oxide to a 0.1 g/L solution of the catalyst resulted in 96.5% removal of 100 mg/L hygromycin after two hours of reaction.

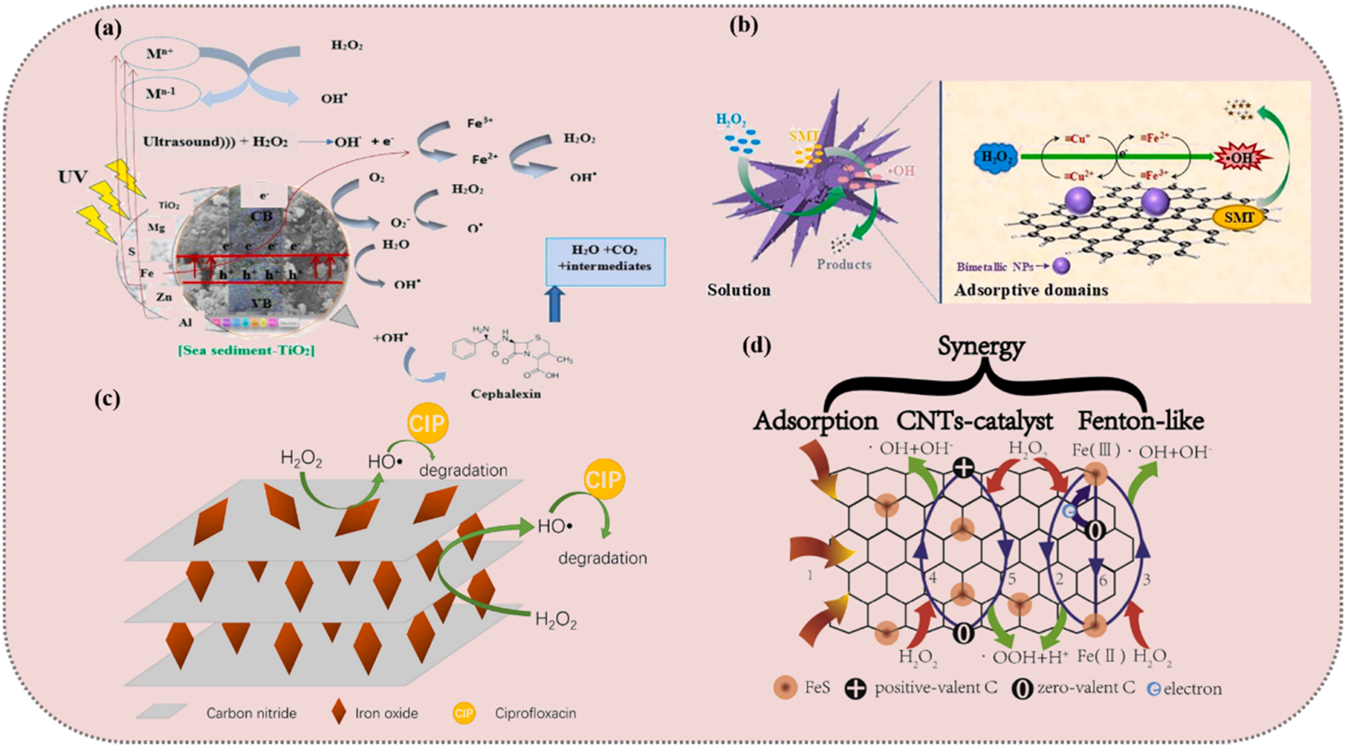


Fig. 3. (a) Proposed mechanism for the removal of cephalexin by the "sea sediment/titanium-H_2O_2-UV-ultrasonic" system; (b) Possible reaction mechanism for SMT degradation in the FeCu@C/H_2O_2 system. (c) Schematic diagram of the process for CN@IO preparation and (d) schematic diagram of the mechanism of ciprofloxacin removal by the CNT/FeS catalyst.
(a) (adapted with permission from ref. (Tavasol et al., 2020)) (b) (adapted with permission from ref. (Tang and Wang, 2019)) (c) (adapted with permission from ref. (Ding et al., 2019)) and (d) (adapted with permission from ref. (Ma et al., 2015)).

Such materials have some reusability and therefore show promise for the removal of antibiotics from aqueous solutions.

In traditional heterogeneous Fenton reactions, the catalytic capacity of the solid catalyst is low due to the low specific surface area and lack of active sites. Therefore, solid catalysts are loaded on carriers with porous structures, thus reducing catalyst particle sizes, which improves the stability of catalysts on carriers, increases the dispersion of catalysts, reduces agglomeration and increases the number of reactive sites. Ding et al. prepared graphite carbon nitride (g-C_3N_4)-supported iron oxide (CN@IO) for the removal of antibiotics by synthesizing g-C_3N_4 in situ with iron oxide (Ding et al., 2019) (Fig. 3c). The g-C_3N_4 doping changed the chemical and structural properties of iron oxide. Iron oxide was embedded in the g-C_3N_4 nanosheets and increased their surface area, thus providing more active sites and increasing the catalytic activity of CN@IO composites in a dark Fenton system. Since iron oxide was embedded in g-C_3N_4, the iron oxide was stabilized, and leaching of iron by the aqueous environment was diminished. Under the optimal dark reaction conditions (pH=3.0, 1 g/L CN@IO-2, 20 mg/L CIP and 0.0056 M H_2O_2), CIP was completely degraded with a mineralization rate of 48.5%. The dark Fenton system is easier to industrialize than the photo-Fenton reaction. Therefore, the prepared CN@IO composite is a promising heterogeneous Fenton catalyst for the degradation of refractory target pollutants.

Ma et al. prepared carbon nanotubes (CNTs) by vapor deposition, and the carbon layer was coated with a layer of iron nanoparticles used to synthesize carbon-based (CNT/FeS) Fenton-like catalysts for the removal of ciprofloxacin from water (Ma et al., 2015) (Fig. 3d). Iron nanoparticles in the carbon layer catalyzed the reaction, and the antibiotics were adsorbed onto the surfaces of carbon nanotubes over a wide pH range. Therefore, CNTs/FeS has high catalytic activity for tetracycline removal and is a reusable catalyst; the synergy with adsorption gave high catalytic activity after four catalytic cycles, which reduced the cost and amount of H_2O_2 needed and improved the efficiency of the Fenton oxidation process.

In contrast to homogeneous Fenton oxidation, heterogeneous Fenton oxidation catalysts occur as solids in the reaction system. The morphology, chemical composition, and surface properties of the solid-phase catalysts affect the efficiency of the catalytic reaction and are influenced by the pH of the reaction system, the amount of catalyst, the amount of H_2O_2, the amount of pollutant treated, and the nature of the intermediate products. The operation of multiple interfacial reactions in heterogeneous Fenton-like catalytic processes has led to greatly reduced reaction rates, poor utilization of H_2O_2, and long catalysis times. Heterogeneous Fenton oxidation solves the problems of maintaining a narrow pH range for homogeneous Fenton oxidation, contamination by iron dissolution, and difficult catalyst recovery, but the preparation of heterogeneous catalysts is complicated, the catalytic activity is low under neutral conditions and the cost is high, so there is an urgent need to develop a new process to solve the problems of heterogeneous Fenton catalysts.

2.3.1. Heterogeneous Fenton reaction

The introduction of light into a heterogeneous Fenton reaction with a solid iron-based catalyst as the active center accelerates the Fe^{3+} and Fe^{2+} redox cycle, promotes the generation of·OH, improves the efficiency of antibiotic degradation, and overcomes the disadvantages of difficult catalyst recovery, narrow pH range, low utilization of H_2O_2 and easy production of large amounts of iron-precipitate in traditional Fenton reactions.

The preparation of magnetic catalysts for heterogeneous reactions also has certain advantages. The easy recovery and prolonged cycling of magnetic materials solve the difficult problem of catalyst recovery from Fenton systems. However, the degradation of antibiotics by magnetic materials alone does not reach the ideal 100% removal level, and the modification of magnetic catalysts is gradually being considered. Wang et al. synthesized magnetic g-C_3N_4/$MnFe_2O_4$/graphene (g-C_3N_4@$MnFe_2O_4$-G) composites with enhanced photocatalytic activity by impregnation and solvothermal methods (Wang et al., 2017) (Fig. 4a); the formation of heterogeneous junctions between g-C_3N_4 and $MnFe_2O_4$, the high carrier migration rate and long separation between electrons and holes improved the optical, adsorption and catalytic properties of the material, and the efficiency for removal of metronidazole reached 94.5%. This unique photocatalyst exhibited magnetic properties, easy separation, good stability and stable catalytic activity, so it can be used as an efficient magnetic catalyst for the photo-Fenton reaction. Cruz et al. synthesized Fe^{3+}/alginate as a catalyst for the degradation of sulfadiazine antibiotics in two matrices, i.e., deionized water and mineral water, and evaluated the performance of the photo-Fenton method over a wide range of pH values (Cruz et al., 2017). Their results showed that the stability of the Fe^{3+}/alginate catalyst was strongly dependent on the pH of the medium, and a large amount of iron was released into the medium at pH values below the pK_a of alginate. In this case, the reaction became a homogeneous process. At pH$\leq$ 5.0 or below,·OH was effectively generated for degradation. These catalysts could be recycled repeatedly, but the overall catalytic efficiency decreased after each use due to reductions in catalyst sizes. Rojas-Mantilla et al. synthesized copper-modified magnetite (Rojas-Mantilla et al., 2020). During the degradation of sulfathiazole, the catalytic activity of copper-modified magnetite was quite different from the catalytic activity of unmodified magnetite. Due to the mesoporous structure of copper-modified magnetite, it exhibited a high adsorption capacity and was highly stable under neutral conditions. Under irradiation, the rapid electron transfer to the surface of the copper-modified magnetite catalyst led to an increase in the rate of the Fe-Cu redox reaction and rapid formation of·OH, which caused rapid degradation of sulfathiazole. In addition, the efficiency for the degradation of sulfathiazole was highest under sunlight and UV light, thus indicating that copper-modified magnetite promoted a heterogeneous photo-Fenton reaction under solar irradiation.

The recovery of magnetic catalysts by using carriers or substrates is also a viable approach. Sun et al. evaluated the effectiveness of SMX removal under UV irradiation by coating ferrite needles (α-FeOOH) on a ceramic membrane (Sun et al., 2020). The rate for removal of SMX from the filtrate under UV irradiation with H_2O_2 was 92%, which was higher than the rate for removal of SMX from the filtrate without H_2O_2 (67%), and this reactive membrane filtration method can be applied to solve contaminant degradation problems. Tian et al. synthesized copper-modified magnetite (Fe-Dis@ Sep) by pyrolysis of ferrocene with chemically modified sepiolite (Tian et al., 2020). The highly dispersed, electron-deficient Fe-Dis@ Sep became an efficient photo-Fenton catalyst for the degradation of ofloxacin (OFX) with visible light (Fig. 4b). The presence of Si-O-C-Fe bonds made FeC_6 highly electron deficient, the Fe(III) to Fe(II) cycle was promoted by Fe-H_2O_2 complexes, and electron-deficient FeC_6 was the active site in Fe-Dis@ Sep; H_2O_2 more easily captured electrons at these sites and produced·OH and O_2^{-}, and the total organic carbon removal percentage for OFX was as high as 89.35%. Such materials also provide a new idea for achieving a high dispersion of active ingredients on the carrier used to degrade antibiotics.

Currently, hydrogels are widely used in biomedical fields due to their unique porous structures, good biocompatibility and high stability. In addition, the unique adsorption properties of hydrogels have been extended to environmental water treatment. Du et al. used boric acid and ferric chloride as crosslinking agents to construct porous poly(vinyl alcohol) (PVA)/sodium alginate (SA) hydrogel microspheres containing iron(III) (Fig. 4c) because the hydrogel is an environmentally friendly material for the degradation of the antibiotic tetracycline; its three-dimensional porous structure hinders photocatalyst aggregation and generates high adsorption capacity, high mechanical strength, and thermal stability (Du et al., 2021). Under optimal conditions, PVA/SA-$FeCl_3$ hydrogel beads degraded tetracycline with an efficiency of 90.5% due to the synergism between the photocatalyst, visible light and

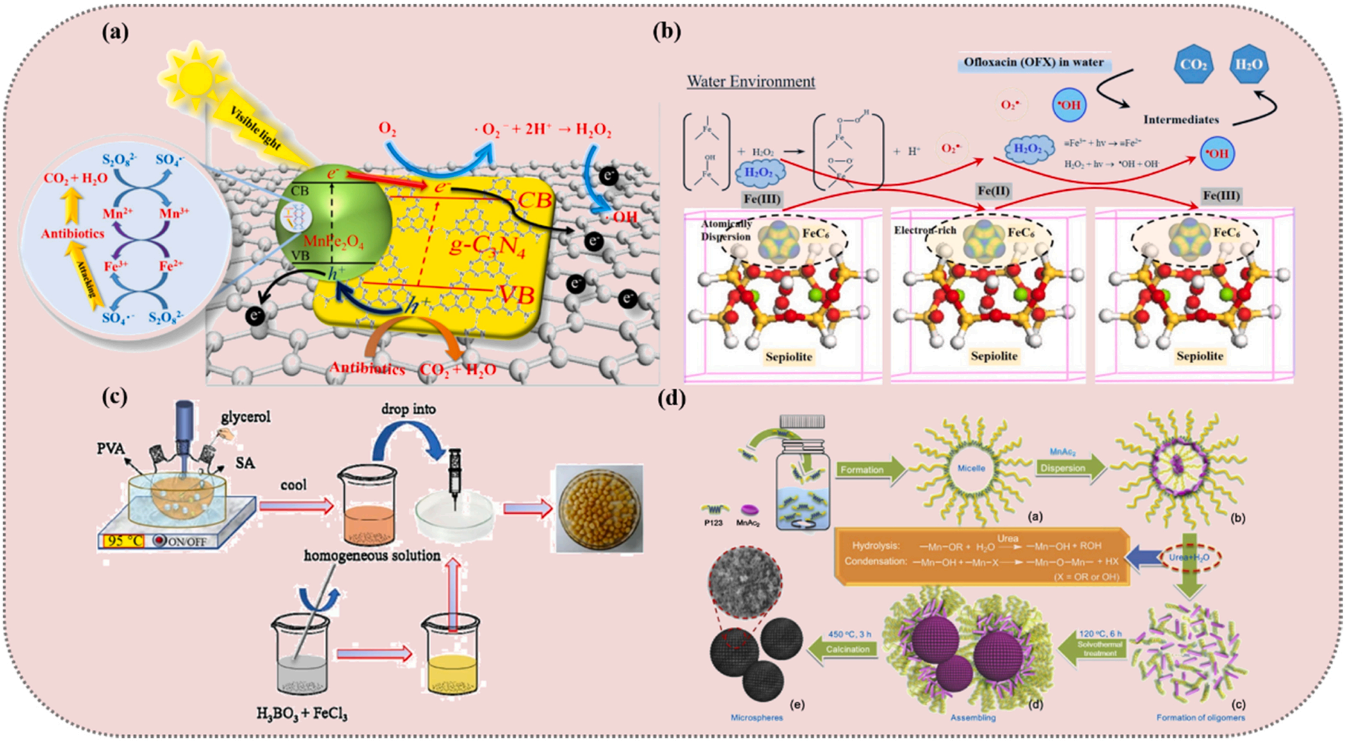


Fig. 4. (a) Mechanism for antibiotic degradation in the C_3N_4@$MnFe_2O_4$-G/PS/vis system; (b) Proposed Fenton-like reaction mechanism in the Fe-Dis@Sep-H_2O_2-Vis system; (c) Schematic illustration of the route for constructing PVA/SA-$FeCl_3$ hydrogel beads; and (d) Schematic illustration of the synthesis of mesoporous MnO microspheres.

(a) (adapted with permission from ref. (Wang et al., 2017)) (b) (adapted with permission from ref. (Tian et al., 2020)); (c) (adapted with permission from ref. (Du et al., 2021)); and (d) (adapted with permission from ref. (Wang et al., 2019a)).

H_2O_2, and the total organic carbon removal rate reached 28.6%. These hydrogel microspheres were easily separated and reusable and could be recycled for up to five times. Wang et al. used photoinduced persulfate (PS)/peroxymonosulfate (PMS) activation for controlled syntheses of mesoporous manganese oxide (MnOx) microsphere materials with a soft-template P123-assisted solvothermal method (Wang et al., 2019a) (Fig. 4d). MnOx has the advantages of a porous structure, low toxicity, and high availability. The catalytic activity of MnOx is related to its surface structure and morphology, and the prepared MnOx microspheres expose more reaction sites and regulate the Fenton-like system to enable the efficient removal of fluoroquinolone antibiotics such as ciprofloxacin and ofloxacin. Mn_3O_4 microspheres containing 2 g of P123 (P2-Mn_3O_4) were prepared under UV irradiation and showed excellent catalytic activity against fluoroquinolone antibiotics and yielded almost complete degradation of antibiotics.

2.3.2. *Heterogeneous electro-Fenton reaction*

The electro-Fenton reaction derived from a homogeneous Fenton system has been widely used in removing antibiotics. Iron ions are the main active centers for the electro-Fenton reaction, but iron precipitation occurs easily with increasing pH of the reaction system, which reduces the catalytic efficiency of the homogeneous electro-Fenton reaction. To overcome this deficiency, solid iron catalysts have been used to replace dissolved iron ions, and these catalysts improve catalytic efficiency and facilitate recycling. Huang et al. used chemically modified graphite felt (MGF) as a cathode (Huang et al., 2020). Unlike raw graphite, the MGF cathode exhibited multiple deposited nitrogen-containing groups and a large gas-liquid contact surface, which is beneficial for improving the electrochemical activity of the cathode. Under the optimal conditions, the percent degradation of CIP reached 95.62% within 30 min, and the TOC removal reached 94.0% within 8 h. The use of Mn^{2+}/Fe^{2+}-rich electro-Fenton catalysts instead of homogeneous catalysts in the electro-Fenton system improved the degradation of antibiotics and might be applied to treat areas containing heavy metals and other organic pollutants. Mi et al. investigated the use of porous nanomaterials modified with carbon mats as electro-Fenton cathodes by using mesoporous $MnxCo_{3-x}O_4$ nanoparticles ($MnxCo_{3-x}O_4$ NPs) with high specific surface areas, in which the synergistic effects of Mn and Co provided active sites for enhanced electron transfer and redox activity; these systems served as efficient and stable electro-Fenton catalysts for the degradation of ciprofloxacin (Mi et al., 2019b). Chen et al. used alkali-assisted activation of carbon felts at different temperatures to prepare electro-Fenton cathodes with different adsorption properties (Chen et al., 2019a). The modified carbon felt (CF-900), unlike the original carbon felt, exposed tetracycline to high concentrations of·OH in a homogeneous catalytic system, and the mineralization efficiency and degradation percentage for antibiotics were significantly higher than those of the original carbon felt and enabled the most efficient removal of tetracycline.

In addition to the modification of the electrode carbon felt to improve the degradation of antibiotics in the electro-Fenton system, maintaining the morphology of the catalyst at nanometer sizes is also a way to improve its catalytic efficiency. Ghasemi et al. used layered double hydroxides containing nanostructures (NLDH) modified by Fe and Cu as heterogeneous catalysts (Fe-Cu-NLDH) in an experimental run of the continuous electro-Fenton process, and the removal efficiency of the Cu-Fe-NLDH process for gentamicin in acidic solution was as high as 91.3% with increasing currents (Ghasemi et al., 2019). Since LDH is a layered structure composed of divalent metal cation hydroxides, the use of Cu/Fe transition metal ions as active sites along with oxygen injection also improved the removal efficiency of the Cu-Fe-NLDH process. Therefore, heterogeneous catalysts modified with Cu and Fe can be applied to the degradation of antibiotics in aqueous phases. Hassan et al. used new M-type strontium hexaferrite nanoparticles (SrM-NPs) as heterogeneous electro-Fenton catalysts for microbial fuel cells designed to induce catalytic removal of tetracycline, tylosin and sulfamethoxazole in an H-type microbial electro-Fenton (MEF) system, and they showed that these antibiotics were completely degraded within 24 h (Hassan et al., 2020).

Avetta et al. used an in situ synthesis of γ-FeOOH by multiphase carbonization to improve electrical conductivity, electrochemically active surface area, and corrosion resistance and to control the pore sizes of aerogels (Avetta et al., 2015). Subsequently, γ-FeOOH was uniformly distributed in the carbonized aerogel skeleton to prepare a γ-FeOOH graphene polyacrylamide carbonized aerogel (γ-FeOOH GPCA) serving as the cathode material and catalyst for an electro-Fenton reaction, and multiphase carbonization was used to improve the conductivity, electrochemically active surface area, and corrosion resistance and to control the pore sizes of the aerogel. The cathode effectively generated H_2O_2 and Fe^{2+} via two-electron reduction. Additionally, γ-FeOOH GPCA exhibited good stability under neutral conditions, and the TOC removal rate reached 89.8 ± 0.8%. Table 3 summarizes more cases of antibiotic treatments with heterogeneous photo/electro-Fenton reactions.

2.3.3. *Other oxidation methods*

In addition to the abovementioned homogeneous Fenton and heterogeneous Fenton-like reactions in the removal of antibiotics, other oxidation methods can also be applied in the removal of antibiotics, including oxidation techniques such as ozonation, ultraviolet oxidation, and ultrasonic oxidation (Norte et al., 2018). For example, due to the high consumption of H_2O_2, narrow pH range and high cost for Fenton oxidation, various studies on Fenton oxidation have been linked with biological methods and other complexation methods in recent years, and this combination has provided new prospects for development and application in Fenton oxidation. Pariyarath et al. reported the bio-Fenton method for the degradation of tetracycline antibiotics (Pariyarath et al., 2021). The addition of different iron particles allowed H_2O_2 produced by aquatic phytoplankton through natural metabolic processes to undergo conversion to·OH. The generated·OH effectively degraded antibiotic-like hard-to-degrade organic pollutants, and the bio-Fenton process was the main removal mechanism. Diatom cells were also used as substrates for iron fixation, and the adsorption of metal ions and the formation of iron complexes also worked with diatoms to achieve effective removal of tetracycline. Titouhi et al. explored the applicability of sodium alginate and cyclohexane dinitrilo tetraacetic acid/Fe (SA/CDTA/Fe) as nonhomogeneous carriers for the catalytic degradation of ofloxacin using SA and CDTA as alginate surface metal-iron complexing agents to prepare composites (Titouhi and Belgaied, 2016). Under the optimal reaction conditions, the efficiency for the degradation of ofloxacin reached 94%. The synthesized material showed good stability and low iron dissolution, so this material could be ideal for water treatment.

2.4. *Antibiotic oxidation byproducts and their associated risks*

Under ideal conditions, it is possible to degrade antibiotics to small molecules by Fenton-catalyzed oxidation, which in turn mineralizes them to inorganic small molecules. However, considering the lack of experimental conditions and facilities, some difficult-to-degrade antibiotics did not reach complete mineralization. Some oxidation byproducts are generated therein. At the same time, these byproducts pose more or less a threat to the environment. Gonçalves et al. showed that sulfamethoxazole produces more toxic intermediates than the parent compound during single ozonation/catalytic oxidation (Gonçalves et al., 2012). Wang et al. investigated the electrocatalytic oxidation of tetracycline at Ti/Ti_4O_7 anodes and experimentally found that the intermediates produced in the tetracycline degradation pathway had different toxicities, and these toxic intermediates delayed the reduction in tetracycline toxicity during the oxidation process (Wang et al., 2018). Zhu et al. used UV-catalyzed degradation of tetracycline and found that NH_4^+ was one of the final products, which also indicated that TC was not completely degraded to nontoxic and harmless inorganic small molecules. (Zhu et al., 2013). Zhu et al. investigated the antibacterial activity and toxicity of quinolone antibiotics (CIP), norfloxacin (NOR), and ofloxacin (OFL)) during degradation, which showed that ciprofloxacin and norfloxacin retained their antibacterial properties but were less active. Second, the toxicity of ofloxacin and norfloxacin to green algae remained unchanged, while the toxicity of ofloxacin increased significantly. Therefore, electrochemical oxidation of ofloxacin has some environmental risks (Zhu et al., 2016). Dirany et al. used BDD as the anode and stainless steel (SS) as the cathode for the electrocatalytic oxidation of SMX. The toxicity evaluation of SMX intermediate byproducts in electrocatalytic oxidation was also tested by *E. coli* experiments. Short-chain carboxylic acids may be generated during the degradation of SMX, which has certain toxicity to some degree (Dirany et al., 2011). After 4 h of electrolysis, the toxicity of the solution was almost zero despite the presence of 60% COD, as analysed by the COD residue representing the oxidation rate of SMX, which also indicates that the toxicity of SMX and intermediates was significantly reduced during the electrolysis process (Hai et al., 2020). Dantas et al. generated toxic cyclic or aromatic intermediate products during the electro-Fenton oxidation of sulfamethoxazole, whose toxicity persists, and the generated intermediates are more toxic and persistent for luminescent bacteria than the parent SMX. Therefore, the application of the electro-Fenton method for antibiotic degradation requires the use of specific experimental conditions, such as current intensity and electrolysis time, to completely mineralize SMX (Dantas et al., 2008). Halling-Sørensen et al. found that the intermediate products obtained from incomplete degradation of tetracycline antibiotics were less active than the parent antibiotics and had some bactericidal effect on soil bacteria and resistant bacteria in the environment, but their toxicity was higher than the toxicity of the parent antibiotics (Halling-Sørensen et al., 2002). Many researchers have focused their efforts in the direction of complete mineralization of antibiotics, and there are relatively few reports on the oxidative byproducts of antibiotics and the associated risk assessment, which cannot be ignored in terms of the toxicity associated with the byproducts of incomplete degradation of antibiotics. Therefore, while exploring the use of emerging technologies to catalyze the degradation of antibiotics, research on incompletely degraded antibiotics should be considered. However, unlike evaluating the degradation of pollutants dissolved in ultrapure water under laboratory conditions, how to check the mineralization of pollutants in the framework of actual wastewater containing "natural" DOC is another issue that needs to be examined. Starting from the investigation of the structure and properties of antibiotic intermediates, we are committed to transforming antibiotic oxidation byproducts into the most central purpose of advanced oxidation technologies, i.e., ultimately into nontoxic and harmless small molecules such as CO_2 and H_2O, which meet the criteria of being green and friendly to the environment. Therefore, further work is needed to more comprehensively investigate how to achieve the goal of complete oxidation.

3. Conclusions, challenges and perspectives

In this paper, we first summarized the basic principles and advantages and shortcomings of homogeneous Fenton and Fenton-like reactions published in recent years. To solve the defects of homogeneous Fenton-like processes, heterogeneous catalysts were introduced for use in the Fenton reaction, and a heterogeneous Fenton reaction occurred by replacing dissolved Fe^{2+} with the solid catalyst. Fenton-like oxidation derived from Fenton oxidation has the advantages of a wide pH range, controllable reaction conditions, high removal efficiency, easy recovery of catalysts, and more available cycles than Fenton oxidation, overcoming the shortcomings of Fenton oxidation and becoming one of the most effective means of wastewater treatment. Additionally, an overview of antibiotic degradation in aqueous environments was presented

Table 3
Heterogeneous photo/electro-Fenton oxidation of antibiotics.

	Target	Catalyst	Operating conditions	Research result	Ref.
Heterogeneous photo -Fenton	Tetracycline	UV/H_2O_2/FeS_2/g-C_3N_4	[Tetracycline] $_{\text{spiked sample}}$ = 0.05 g/L [FeS_2/g-C_3N_4] = 0.05 g [H_2O_2] = 50 mM pH = 7–8 150 W xenon lamp	Degradation efficiency = 93%	(Li et al., 2021)
	Tetracycline	UV/H_2O_2/$ZnFe_2O_4$	[Tetracycline] $_{\text{spiked sample}}$ = 60 mg/L [$ZnFe_2O_4$] = 30 mg pH = 2 LEDa lamp (λ = 420 nm)	Degradation efficiency = 94.2%	
	Sulfamethoxazole	UV/H_2O_2/Fe_3S_4	[Sulfamethoxazole] $_{\text{spiked sample}}$ = 5 mg/L [Fe_3S_4] = 15.0 mg [H_2O_2] = 9.79 mM pH = 5.0 10 W LED (λ = 369 nm)	Degradation efficiency = 100%	(Hang et al., 2022)
	Tetracycline	UV/H_2O_2/g-C_3N_4/Fe_2O_3	[Tetracycline] $_{\text{reality}}$ = 20 mg/L [g-C_3N_4/Fe_2O_3] = 20 mg [H_2O_2] = 50 mM pH = 3–11 300 W Xenon lamp (light intensity = 2500 W·m^{-2})	Degradation efficiency = 95%	(Zhao et al., 2021)
	Sulfamethoxazole	UV-A/H_2O_2/NiFe-CNT	[Sulfamethoxazole] $_{\text{spiked sample}}$ = 5 mg/L [NiFe-CNT] = 0.025 g/L [H_2O_2] = 1 μL/mL pH = 5 Xe arc lamp (150 W)	TOC removal = 68% Degradation efficiency = 100%	(Nawaz et al., 2020)
	Tetracycline hydrochloride	UV/H_2O_2/FePOM/CNNS-Nvac	[Tetracycline hydrochloride] $_{\text{spiked sample}}$ = 20 mg/L [Fe-POM/CNNS-Nvac] = 50 mg/L [H_2O_2] = 30 wt% pH = 4.5 300 W Xenon lamp (λ < 420 nm)	Degradation efficiency = 95.5% TOC Removal efficiency = 78.5%	(Jiang et al., 2020)
	Tetracycline	Vis/H_2O_2/$CuFeO_2$/biochar	[Tetracycline] $_{\text{spiked sample}}$ = 20 mg/L [$CuFeO_2$/biochar] = 200 mg/L [H_2O_2] = 20 mM pH = 5.0 300 W Xe lamp (λ = 357 nm)	Degradation efficiency = 92.5%	(Xin et al., 2021)
	Cefuroxime	UV/H_2O_2/α-Fe_2O_3-TiO_2	[Cefuroxime] $_{\text{spiked sample}}$ = 20 mg/L [α-Fe_2O_3-TiO_2] = 1 g/L [H_2O_2] = 5.3 mM pH = 3.0 UV–vis lamp (365–850 nm)	Degradation efficiency = 73%	(Hernández-Coronado et al., 2021)
	Sulfamethoxazole	UV/H_2O_2/PPyC@Py-MIL (Fe)	[Sulfamethoxazole] $_{\text{spiked sample}}$ = 20 mg/L [MIL-88B (Fe)] = 100 mg/L [H_2O_2] = 1 mM pH = 6.5 300 W Xenon lamp (λ > 420 nm)	TOC removal = 93%	(He et al., 2022)
	Norfloxacin	UV/H_2O_2/Fe_3O_4/MWCNTs	[Norfloxacin] $_{\text{spiked sample}}$ = 0.5 mg/mL [Fe_3O_4/MWCNTs] = 1.2 g/L [H_2O_2] = 0.098 M pH = 2 300 W xenon lamp	Degradation efficiency = 90%	(Shi et al., 2017)
Heterogeneous electro-Fenton	Sulfadiazines	H_2O_2/EEGr-Fe^{2+}/Current	[Sulfadiazines] $_{\text{spiked sample}}$ = 10 mg/L [Fe^{2+}] = 0.4 mM [H_2O_2] = 73.5 mg/L pH = 7.13 [Na_2SO_4] = 0015 M I = 50 mA Conductivity = 2640 μS/cm	Removal efficiency = 100%	(Ren et al., 2019)
	Sulfamethoxazole	H_2O_2/γ-FeOOH GPCA/Current	[Sulfamethoxazole] $_{\text{spiked sample}}$ = 0.1 mM [γ- FeOOH GPCA] = 0.15 g H_2O_2(kappa10^{-1}) = 0.77 min^{-1} pH = 7.0 [Na_2SO_4] = 0.15 M	Percentages of TOC removal = 95.6 ± 0.9%	(Wang et al., 2019b)

(*continued on next page*)

Table 3 (*continued*)

	Target	Catalyst	Operating conditions	Research result	Ref.
	Sulfamethoxazole	H_2O_2/Cu-Fe_2O_3/EGF/Current	I = 50–500 mA Conductivity = 26.37 S/m [Sulfamethoxazole] $_{\text{spiked sample}}$ = 20 mg/L Cu-Fe_2O_3/EGF (2 cm × 5 cm) [Na_2SO_4] = 0.05 M aeration rates (generate H_2O_2) = 0.6 L·min^{-1} pH = 6.0	Removal efficiency = 100.0%	(Qi et al., 2022b)
	Tetracycline	H_2O_2/Fe_2Co_1/NPC/Current	Current density = 6.0 mA·cm^{-2} Conductivity = 0.17 m S/cm [Tetracycline] $_{\text{spiked sample}}$ = 20 mg/L [Fe_2Co_1/NPC] = 0.3 g/L [Na_2SO_4] = 0.025 M pH = 7	Removal efficiency = 91% Mineralization efficiency = 90.3%	(Hu et al., 2021)
	Ciprofloxacin	H_2O_2/RGO-Ce/WO_3/Current	I = 100 mA Conductivity = 0.1 µS/cm [Ciprofloxacin] $_{\text{spiked sample}}$ = 50 mg/L [Fe^{2+}] = 0.1 mM [Na_2SO_4] = 0.05 M pH = 3.0	Degradation efficiency = 94.73%	(Mi et al., 2019a)
	Ciprofloxacin	H_2O_2/FMBO-GF/Current	I = 300 mA Oxygen flow (generate H_2O_2) = 100 mL·min^{-1} Conductivity = 0.08 mS·cm^{-1} [Ciprofloxacin] $_{\text{spiked sample}}$ = 25 mg/L m(FMBO-GF) = 300 mg [Na_2SO_4] = 0.05 M pH = 7.0	Removal efficiency = 95.4%	(Huang et al., 2021)
	Sulfamethoxazole	H_2O_2/Ce/Fe@NPC-GF/Current	Current density = 2 mA/cm^2 Conductivity = 0.1 µS/cm [Sulfamethoxazole] $_{\text{spiked sample}}$ = 20 mg/L [Ce/Fe@NPC-GF] = 5 mM [Na_2SO_4] = 0.05 M pH = 3.0	Degradation efficiency = 100%	(Qiu et al., 2021)
	Sulfathiazole	H_2O_2/ZVI NPs/Current	I = 20 mA Conductivity = 0.1 µS/cm [Sulfathiazole] $_{\text{spiked sample}}$ = 50 mg/L [ZVI NPs] = 1 g/L [Na_2SO_4] = 0.05 M pH = 5	Removal efficiency = 100%	(Chen et al., 2019b)
	Tetracycline	H_2O_2/Cu/CuFe_2O_4/Current	j = 7.5 mA/cm^2 Conductivity = 0.1 µS/cm [Tetracycline] $_{\text{spiked sample}}$ = 50 mg/L [Cu/CuFe_2O_4] = 0.84 ± 0.11 mg/L [Na_2SO_4] = 0.05 M pH = 3.0	Degradation efficiency = 80%	(Cui et al., 2021)
	Amoxicillin	H_2O_2/Cu–Fe–Fe_3C@NDB)/Current	I = 30 mA Conductivity = 0.1 µS/cm [Amoxicillin] $_{\text{spiked sample}}$ = 100 mg/L [Cu–Fe–Fe_3C@NDB] = 2 g/L Current = 120 mA pH = 4.0 [Na_2SO_4] = 0.05 M Conductivity = 0.1 µS/cm	Removal efficiency (%) = 100%	(Qi et al., 2022a)

[a] LED = light-emitting diode

for traditional Fenton reactions and homogeneous/heterogeneous Fenton reactions. The conventional Fenton method suffers from low catalytic efficiency. Light and electricity were incorporated into the Fenton system to improve its catalytic efficiency, but a narrow pH applicability range remained. Finally, solid iron catalysts were used to replace dissolved iron, the pH range was greatly expanded, and the catalyst recovery problem was solved to some extent. The literature indicates that the heterogeneous Fenton reaction is particularly suited for the treatment of antibiotics and exhibits the advantages of high antibiotic degradation efficiency and easy catalyst recovery and reuse. In the future, heterogeneous Fenton reactions may provide solutions for the treatment of environmental wastewater. Various Fenton techniques, such as Fenton-like oxidation derived from traditional Fenton oxidation methods, are effective methods for controlling and removing antibiotics. Although their oxidation mechanisms are different, all of them achieve antibiotic degradation through reactions that generate·OH. Fenton reactions have been widely used in the removal of antibiotics, and many researchers have focused on the experimental operating conditions, the final degradation of antibiotics, and the recovery and recycling of catalysts from Fenton reactions in recent years.

The high efficiency of the catalyst contributes to the generation of free radicals in the reaction system, and the process may eventually be used in antibiotic treatment. The electro-Fenton reaction does not require continuous injection of Fe^{2+}, which reduces secondary pollution of the environment$\cdot H_2O_2$ is continuously generated during the reaction, the use of H_2O_2 is reduced, the degradation efficiency is improved, and the electro-Fenton process costs less than other Fenton reactions. Therefore, electro-Fenton oxidation may be an important method for the future catalytic degradation of antibiotics.

It is also important to consider that the Fenton oxidation process does not achieve complete catalytic degradation, from which the problem of antibiotic oxidation byproducts and phase risks cannot be ignored. More research is needed to consider not only how to mineralize antibiotics into inorganic small molecules but also to tackle the problem of incomplete degradation. From a green perspective, the ultimate research goal should be to truly achieve complete degradation of antibiotics and eliminate their harm to the environment.

Fenton/Fenton-like reactions have proven to be capable of antibiotic degradation under laboratory conditions, but corresponding commercial products have seldom been reported. Although we list many publications about Fenton/Fenton-like reactions for the removal of antibiotics in this paper, most of these cases only gathered works with spiked waters of low complexity. As we know, organic matter and anions in the actual water environment can affect the stability of advanced oxidation techniques. Anions such as chloride ions and nitrate ions, which have been present in the water body for a long time, have different functions of scavenging free radicals and affect the efficiency of antibiotic degradation in wastewater (Kaur et al., 2019; Wang and Chu, 2011). For example, when organic matter is present, the$\cdot$OH/sulfate radicals that can degrade antibiotics are suddenly reduced, and the degradation rate of antibiotics decreases significantly (Liu et al., 2020b). Herein, considering the matrix effect and the actual concentrations of antibiotics in aqueous environments, the effect of the Fenton/Fenton-like reaction on antibiotic degradation in the actual water environment needs to be further verified. Additionally, in actual water environment treatment, sustainability (and thus economic cost) is another important concern that needs to be considered.

Fenton oxidation technology exhibits high reactivity in a wide range of applications and degrades antibiotics using Fe^{2+} as the active center. Fe^{2+} easily leaches out and causes secondary pollution of the environment. The use of solid iron compounds instead of soluble iron sources in the heterogeneous Fenton reaction improves the utilization of metal ions, and the presence of a small amount of soluble iron within the allowed range of certain iron concentrations is negligible. In addition, although many recent studies have combined Fenton reagents with light, electricity and other stimuli to improve the efficiency of catalytic oxidation and reduce costs, catalytic oxidation by the resulting Fenton system cannot achieve industrial wastewater treatment due to imperfections in equipment and technology; the environmental hazards of the reagents must still be eliminated, and physical methods to enhance the reaction rate, economic efficiency, and ease of implementation still require investigation. New materials must be developed to improve catalytic efficiency and reduce costs without causing secondary pollution while solving existing problems.

CRediT authorship contribution statement

Yu Jiang: Conceptualization, Methodology, Software, Data curation, Writing- Original draft preparation. **Jiabing Ran**: Conceptualization, Writing- Reviewing and Editing. **Kang Mao**: Conceptualization, Writing- Reviewing and Editing. **Xuefeng Yang**: Writing- Reviewing and Editing. **Li Zhong**: Writing- Reviewing and Editing. **Xinbin Feng**: Writing- Reviewing and Editing. **Changying Yang**: Supervision, Writing- Reviewing and Editing. **Hua Zhang**: Supervision, Conceptualization, Writing- Reviewing and Editing.

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.

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