REVIEW

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The synergistic effect of adsorption and Fenton oxidation for organic pollutants in water remediation: an overview

Junzhe Song,†[ab] Linan Zhu,†[c] Sheng Yu,*[c] Guobiao Li [ID] [b] and Dong Wang [ID] *[ab]

Water pollution from industrial sources presents a significant environmental challenge due to the presence of recalcitrant organic contaminants. These pollutants threaten human health and necessitate effective remediation strategies. This article reviewed the synergistic application of adsorption and Fenton oxidation for water treatment. Adsorption, a common technique, concentrates pollutants onto a solid surface, but offers limited degradation. Fenton oxidation, an advanced oxidation process (AOP), utilizes hydroxyl radicals for efficient organic compound breakdown. When adsorption and Fenton oxidation combine, adsorption pre-concentrates pollutants, boosting Fenton oxidation effectiveness. This review delves into the mechanisms and advantages of this integrated approach, highlighting its potential for enhanced removal of organic contaminants. The discussion encompasses the mechanisms of Fenton oxidation and the synergistic effects it has with adsorption. Additionally, various support materials employed in this combined process are explored, including carbon-based supports (activated carbon, graphene, carbon nanotubes and biochar), metal–organic frameworks (MOFs), and clays. Finally, the applicability of this approach to diverse wastewater streams, such as medical and industrial wastewater, is addressed. The review contains 105 references and summarizes the key findings and future perspectives for this promising water remediation technology.

1 Introduction

Nowadays, with the fast growth of industries including the chemical industry, agriculture and animal husbandry, food processing and manufacturing industry, textile waste treatment and pharmaceutical manufacturing, the large number of organic contaminants in wastewater that are related to these industries have caused severe environmental problems.[1–3] Indeed, most of these organic pollutants are not only toxic but also difficult to be degraded in natural conditions. Thus, these organic pollutants could always penetrate the barrier of the human body through breathing or the food chain, resulting in health problems such as cardiovascular system disease, nervous system disease, immune system diseases, and respiratory system diseases. Therefore, the removal of toxic organic pollutants is still a major challenge in upcoming years.[4–6] In the recent decade, various methods have been developed for the

removal of toxic organic pollutants, and adsorption stands out among them because of its ease of use, low cost, speed of pollution removal, and minimal sludge creation.[7,8] Adsorption is basically a separation-based technique (a phase-changing technology) that just redirects the pollutants from water to another phase, producing sorbents that are contaminated and need to be disposed of in the side stream or subjected to additional treatment to prevent the possibility of secondary contamination.

Particularly, the advanced oxidation processes (AOPs) constitute a promising technique for the treatment of toxic organic pollutants due to its highly oxidizing ability. Indeed, AOPs is a technology to effectively oxidize toxic and non-degradable compounds based on intermediary of hydroxyl and other radicals. AOPs are very commonly used to treat pharmaceutical wastewater within last decade. AOPs contains different approaches such as Fenton, ozonation, sonolysis, photocatalysis and wet air oxidation. The Fenton reaction is a kind of advanced oxidation process (AOPs). It combines H_2O_2 with Fe^{2+}, which has a strong oxidation ability in acidic solutions and can effectively degrade organic pollutants in the wastewater field.[9] Compared with other AOP, the Fenton reaction has the following advantages, making it one of the most promising strategies:[10]

[a]Key Laboratory of Green Process and Engineering, National Engineering Research Center of Green Recycling for Strategic Metal Resources, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China. E-mail: wangdong@ipe.ac.cn

[b]Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou, 341007, China

[c]School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA. E-mail: shengyuacdemic@163.com

† These two authors contribute equally to this work.

(i) Easy to operate: the Fenton reaction is simple to operate and does not require complex equipment or conditions. This makes it more convenient for practical applications.

(ii) Fast and non-polluting: the Fenton reaction has a fast reaction rate and does not produce harmful by-products. This helps efficiently treat organic pollutants in water bodies.

(iii) High degradation efficiency: the Fenton reaction can effectively degrade organic pollutants, including refractory compounds. Its strong oxidation ability makes it perform well in water purification.

Therefore, Fenton reaction has broad potential in the removal of environmental pollutants, for example, it can be used to treat the removal of pollutants in soil: Fenton reaction can effectively degrade organic pollutants by generating hydroxyl radicals (˙OH). Secondly, Fenton reaction can also convert organic dyes and other pollutants in industrial waste into harmless products. In addition, the Fenton reaction can also degrade antibiotic residues in wastewater: by reacting with hydrogen peroxide, the hydroxyl radicals generated by the Fenton reaction can effectively decompose antibiotic molecules.

As Fenton reaction is of great significance in pollutant treatment, and recent studies have shown that the synergistic effect of adsorption and Fenton reaction can greatly improve the efficiency of pollutant interpretation. However, there have been no review articles on the synergistic effects of adsorption and Fenton reaction in recent years. Therefore, as a review paper, this article reviews the recent research on the synergistic effect of adsorption and Fenton reaction in the field of water pollutant treatment. It is of great importance for researchers in related fields and practitioners in the field of wastewater treatment.
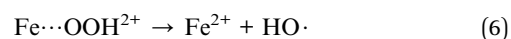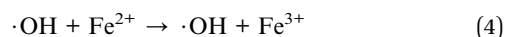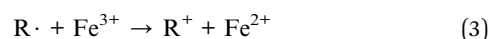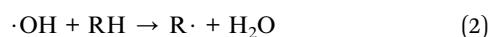
Even though adsorption is an effective method of treating waste water, it could be limited by adsorbent material which would cause more cost and the properties of adsorbents would also affect the whole process. Combining different water treatment techniques would help enhance the treatment performance and lower the cost and treatment time. Due to the significant chemical input, Fenton oxidation when used alone can be costly and damaging to the environment.[11] Dual-functional materials are being researched more and more as heterogeneous catalysts and adsorbents to address these issues.[7,8,11] These substances have the capacity to simultaneously remove contaminants through Fenton oxidation (degradation-based removal) and adsorption (separation-based removal). These composites' dual activity allows for the coupling of Fenton oxidation and adsorption for enhanced treatment effectiveness while lowering the costs and restrictions of separate procedures (*via* material renewal and more pollutant removal). Additional light input (photo-Fenton), which has also been investigated, has the potential to improve heterogeneous Fenton processes even more. By utilizing the same components, these integrated treatments can be applied both *in situ* (without separating the adsorbent) and *ex situ* (after separating the adsorbent). This can be done by combining or impregnating multiple materials to create a hybrid material that has the dual functionality, or by employing a single material that serves both purposes.

Also, the limitations of both processes can be addressed by the integration. Adsorption requires huge amount of absorbent and regeneration of spent absorbents. AOPs are designed to degrade adsorbed organic pollutants which also regenerating adsorbent. Thus, AOPs can occur with adsorption simultaneously which can ensure continuous supply of adsorbent.

It should be noted that in addition to toxic organic pollutants, heavy metals such as Cr, Hg, Cu, Pb, *etc.*[12] are also typical pollutants in water. However, due to limited space and the existing recent review article in this field, this paper only introduced the combination of Fenton oxidation process and adsorption in removal of non-biodegradable organic compounds, and different materials could be used in the support of combination of adsorption and Fenton process, such as carbon-based material, graphitic carbon nitride and MOFs are discussed. Furthermore, the applications are involved such as medical wastewater, industrial wastewater and other types of wastewaters.

2 Mechanism of Fenton oxidation and the synergistic effects of adsorption

For the mechanism of the Fenton reaction, researchers have put forward many theories, but there are still some disputes. However, the strong oxidation of ·OH in the Fenton reaction process is supported by most scholars. Fenton reaction is mainly formed by two reactions. Firstly, Fe^{2+} and H_2O_2 react to produce ·OH, which degrades organic pollutants, as shown in eqn (1)–(4). Secondly, Fe^{3+} generated by oxidation will undergo a series of reactions with H_2O_2 and can be reduced to Fe^{2+} as shown in eqn (5) and (6). Specific reactions are as follows:[13]

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

$$\cdot OH + RH \rightarrow R\cdot + H_2O \tag{2}$$

$$R\cdot + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{3}$$

$$\cdot OH + Fe^{2+} \rightarrow \cdot OH + Fe^{3+} \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\cdots OOH^{2+} + H^+ \tag{5}$$

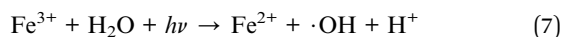$$Fe\cdots OOH^{2+} \rightarrow Fe^{2+} + HO\cdot \tag{6}$$

Due to the limitations of Fenton process, Fenton could be modified with different conditions such as photo-Fenton, electro-Fenton and photo-electro-Fenton. The combination of photo/electro with tradition Fenton greatly improved the reaction efficiency, and their pathways of promotion are illustrated in the following.

2.1 Photo-Fenton

Since the 1990s, photo heterogeneous Fenton reactions have been used for the degradation of structured compounds.[14] The photo Fenton reaction can be briefly summarized as follows. Iron acts as a catalyst and cycles through oxidation and reduction, and Fe^{2+} reacts with H_2O_2 in a very rapid reaction to
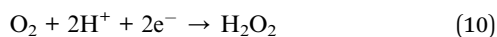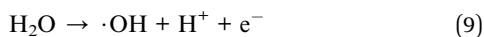
produce $\cdot OH$, which is oxidized to Fe^{3+}. The Fe^{3+} can absorb light in the range of ultraviolet light–visible light while producing $\cdot OH$, which is reduced again to Fe^{2+}, as shown in the reaction formula (7). The iron reduction can also occur in the dark, as shown in eqn (8). Since eqn (7) is much faster than eqn (8), light can increase the reaction rate. Thus, the process depends largely on the concentration of iron and the wavelength of the light.[15,16]

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + \cdot OH + H^+ \tag{7}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \tag{8}$$

2.2 Electro-Fenton

Electrochemical advanced oxidation processes (EAOPs) are considered to be one of the most promising advanced oxidation technologies, among which the high efficiency and cleanliness of the electric-Fenton process have been extensively studied.[17] The reaction mechanism can be interpreted as that H_2O is oxidized at the anode to produce $\cdot OH$ (see eqn (9)), and O_2 is reduced at the cathode to produce H_2O_2 (see eqn (10)). At the same time, Fe^{2+} consumed in the Fenton reaction can be reduced to Fe^{2+} at the cathode through Fe^{3+} (see eqn (11)).[18]

$$H_2O \rightarrow \cdot OH + H^+ + e^- \tag{9}$$

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

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{11}$$

A large amount of iron(II) salt is required in traditional Fenton compared to electro-Fenton. Due to the regeneration of Fe^{2+} in electro-Fenton, the electro-Fenton process overcomes the shortcomings of the classical Fenton process, including avoiding the use of large amounts of Fe^{2+} and the formation of large amounts of ferric hydroxide sludge.[19]
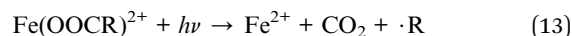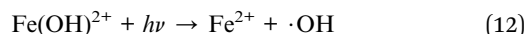
2.3 Photo-electro-Fenton

Photo-electro-Fenton technology irradiates artificial UV-visible light or natural sunlight into the electric Fenton system based on the electric Fenton technology. Compared with the electric Fenton technology, the photoelectric Fenton technology can improve the mineralization efficiency of organic pollutants and has increasingly prominent advantages in the treatment of organic wastewater. Moreover, the solar light resource is cheap and renewable, so they can greatly save the treatment cost of organic pollutants.

Photo-electro-Fenton (PEF) process is based on photochemical/photocatalytic actions assisted by UV irradiation. The intensity and wavelength of incident light affects the destruction rate of organic pollutants. The photo-electro-Fenton contains simultaneous support of electrogenerated H_2O_2, Fe^{2+} and UV illumination of the solution to destruct organic pollutants. In PEF process, photoreduction of $Fe(OH)^{2+}$ and the predominant Fe^{3+} species in acid medium and/or the photolysis

of complexes of $Fe(III)$ with generated carboxylic acids would increase the amount of hydroxyl radical produced. The UV irradiation enhance the process of electro-Fenton which helps produce Fe^{2+} according to eqn (9)–(11). The synergistic effect of photo and electro Fenton provides better efficiency of decomposing organic pollutants.

It is known that cathodic two-electron reduction:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH \tag{12}$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + \cdot R \tag{13}$$

$$H_2O_2 + h\nu \rightarrow 2\cdot OH \tag{14}$$

However, the application of artificial ultraviolet light for the homogeneous photo-Fenton reaction also has disadvantages. In addition to the system's restriction on the acidity and alkalinity of solution, the use of the artificial ultraviolet light requires an external power supply and the electrical cost is relatively high, which hinders the application of homogeneous photo-Fenton technology in the industrial processing.[20] The solar photovoltaic Fenton technology overcomes this shortcoming well. Solar Fenton technology refers to the use of sunlight irradiation solution (usually $\lambda > 300$ nm), greatly saving the application cost. In addition, this solar-assisted electro-Fenton technology has better degradation and mineralization effects on organic pollutants than the original photo-Fenton technology, because the combination of powerful ultraviolet input from sunlight and photolysis with $\lambda > 400$ nm enhances decarboxylation of Fe^{3+} carboxylate species.[21] This solar-assisted electro Fenton technology also has fatal shortcomings, because the daily sunshine duration varies in different regions and climates, and the intensity of solar sunlight is greatly affected by the weather and the cycle of four seasons, so the practical application of this method is also limited.

2.4 Synergistic effect of Fenton and adsorption

Generally, Fenton reactions can be classified into homogeneous and heterogeneous Fenton reactions. Homogeneous Fenton reactions include classical, modified Fenton reactions (sono-Fenton, photo-Fenton, electro-Fenton, sono-electro-Fenton, photo-electro-Fenton, sono-photo-Fenton, and solar photoelectron-Fenton), Heterogeneous Fenton reactions use recyclable solid catalysts instead of Fe^{2+} which helps overcome the disadvantages of homogeneous Fenton such as narrowed pH range.[5] The homogeneous system can only produce a good reaction in pH = 2.5–3.5. When pH > 4, a large amount of $Fe(OH)$, commonly known as iron mud, will be produced.[22] A relatively narrow pH range not only limits the application of the Fenton reaction but also produces a large amount of iron mud which forms secondary pollution and increases the treatment cost.[4] Therefore, the homogeneous Fenton reaction has not been applied to industrial wastewater treatment on a large scale due to the cost and reaction conditions. On the contrary, the heterogeneous Fenton catalyst provides an advantage of long lifetime which effectively reduces the concentration of iron bivalent. Iron ions are slowly leached, so the working pH range

will be expanded, which will not cause secondary pollution to the environment.

Besides, various functional materials or support can also provide more active sites for the Fenton catalyst, thus showing higher catalytic activity and accelerating $Fe(III)/Fe(II)$ redox cycle. While this can be ascribed to the synergistic effect of between Fenton and adsorption. The synergistic effect come from the effective adsorption of pollutants onto heterogeneous Fenton catalysis *via* ion exchange, electrostatic interactions, hydrophobic attractions, π–π stacking, hydrogen bonding, and/or van der Waals forces interactions, as well as the acceleration of electron transfer during the Fenton reaction, thus enhancing the whole process efficiency.

The synergistic effect of Fenton and adsorption can be studied through its improvement and limitations. Some research vividly shows that the combination of Fenton and adsorption can improve the removal percentage. In Gvoic's research, the decolorization percentage for homogeneous and heterogeneous Fenton process was 79% and 54% respectively with 59% and 33% COD removal. With the addition of adsorption, a huge enhance of the process is discovered. The toxicity reduction reached 95% and decolorization achieved 90%. Thus, it would be extremely beneficial to combine Fenton and adsorption (Fig. 1).[23]

In the future, the performance and life of new Fenton catalysts and catalyst support will be the focus of the research. The new Fenton technology is expected to be more efficient and environmentally friendly in the application of large-scale industrial wastewater.

3 Supports used in the combination of adsorption and Fenton oxidation process

The integration of adsorption with the Fenton oxidation paradigm is chiefly evident in the heterogeneous Fenton process.[24]
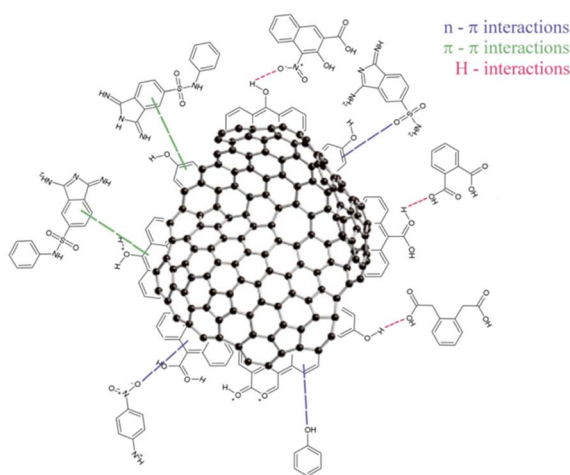

Fig. 1 Proposed adsorption mechanism of yellow dye degradation products on biochar (this figure has been reproduced with permission from Gvoic *et al.*[23] from Springer, copyright 2024).

The foundational premise of this combined methodology lies in the adsorptive capture of pollutants onto specific substrates, facilitated by a spectrum of mechanisms such as ion exchange, electrostatic interactions, hydrophobic attractions, π–π stacking, hydrogen bonding, and van der Waals forces interactions.[25] Substrates that undergo functionalization to increase their adsorptive sites can foster accelerated electron transfer during the Fenton reaction, culminating in an enhanced process efficiency.[26] This synergistic mechanism obviates the need for excessive dosages and mitigates the production of iron-rich sludge, a residual byproduct typically linked with the traditional homogeneous Fenton process.[27] Furthermore, this approach adeptly navigates the limitations inherent to the conventional homogeneous Fenton process, particularly those related to aquatic environmental parameters such as pH.[28] Owing to the advantages conferred by these combined interactions, support materials have emerged as a focal point of scholarly exploration. A comprehensive analysis of contemporary research indicates that the primary substrates utilized as supports include carbon-based materials,[29] MOFs,[30] and minerals/clay.[31] Ensuing discussions will delve into these material classifications and synthesize the avant-garde design philosophies that characterize them.

3.1 Carbon based materials

3.1.1 Activated carbon. Carbon-based materials, including activated carbon,[29] graphene,[32] graphitic carbon nitride (g-C_3N_4),[33] biochar,[34] and others, boast a wide range of applications.

Activated carbon (AC) is widely used for pollutant adsorption due to its economic efficiency, large specific surface area per unit volume, significant surface reactivity, and strong affinity for various types of dissolved organic compounds.[35] It can also serve as a substrate for simultaneous adsorption and Fenton oxidation processes. In this context, activated carbon assumes a dual function: it serves as an adsorbent and plays a crucial role in facilitating the Fenton reaction, which is typically conducted in sequential stages.[29] By acting as a support matrix for essential Fenton reaction elements such as iron, activated carbon increases the reaction's effectiveness while preserving its inherent adsorption capabilities. AC is used extensively across various Fenton reactions, including traditional Fenton processes, electro-Fenton, photo-Fenton, and sono-Fenton methodologies. This versatility underscores its adaptability and effectiveness in various advanced oxidation processes. The Fenton reaction involves the interaction between hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) to generate hydroxyl radicals (˙OH) for the degradation of organic pollutants. This reaction results in the oxidation of Fe^{2+} to ferric ions (Fe^{3+}), which are subsequently reduced back to Fe^{2+}, thus perpetuating the cycle.[12] Contemporary research has focused on integrating the Fenton oxidation process with activated carbon (AC) adsorption for the remediation of various pollutants. For instance, Cui J. *et al.* concentrated on the removal of residual organic compounds in manganese (Mn) electrochemical solutions.[36] Their findings revealed that employing a dose of 3.75 g

L^{-1} of AC at a temperature of 70 °C for 120 minutes significantly enhanced the Chemical Oxygen Demand (COD) removal rate to 93.1% during the activated carbon stage (see Fig. 2).

Indeed, several studies explored modifying activated carbon (AC) with magnetic properties for improved water treatment. Duan introduced an innovative method for producing magnetic activated carbon (MAC) by immersing porous activated carbon in iron oxide, followed by the co-precipitation of ferrous and ferric iron onto the carbon's surface.[29] This modification led to the degradation of over 90% of a 4-chlorophenol solution within an hour, with a consistent removal efficiency above 80% over five regeneration cycles. This enhancement indicates a significant improvement in AC's adsorption capacity for iron following magnetic modification, thereby maintaining high efficiency over multiple cycles. Amir' group developed a nanocomposite, Fe_3O_4 magnetic activated carbon (Fe_3O_4@AC), using a co-precipitation method. Characterized by its pseudospherical shape, strong magnetic field, and large surface area, Fe_3O_4@AC demonstrated high reusability and chemical stability. It showed efficient oxidation performance over a wide pH range.[37]

In addition, activated carbon can be used in traditional Fenton reactions in combination with a fluidized bed reactor. Bello et al. explored the effectiveness of granular activated carbon (GAC) in a fluidized bed Fenton process for removing COD and color from wastewater.[28] In conjunction with a fluidized bed reactor, GAC expanded the surface area, promoting iron oxide crystallization and enhanced pollutant adsorption. When compared to the SiO_2 fluidized carrier, the GAC process exhibited a 20% improvement in removal efficiency and was efficient in removing COD within a pH range of 3 to 7, potentially obviating the need for conventional acidification and neutralization stages. Lyu et al. designed an integrated system that combined adsorption with Fenton oxidation in a fluidized bed reactor for dye removal.[38] Activated carbon not only facilitated dye adsorption but also served as a site for iron

precipitation and crystallization, acting as a heterogeneous catalyst. Fe^{3+} produced during the Fenton reaction precipitated on the activated carbon surface as FeO(OH) or $Fe(OH)_3$, which could be recovered and reused as a catalyst. The remaining Fe^{3+} was adsorbed on the activated carbon as organic iron complexes, minimizing iron hydroxide sludge production in the reactor. The above studies illustrate the key role of activated carbon as an adsorbent and carrier in enhancing Fenton reaction efficiency. Its synergistic effect in the Fenton process helps improve the overall efficiency of the reaction. Thus, the optimization of the Fenton reaction can be achieved by combining it with other catalytic methods. One particularly straightforward and promising approach is to combine the Fenton reaction with electrical energy, often called the electro-Fenton process. The Fenton reaction's core is the electron transfer cycle, which is driven by the redox cycling of iron ions between the Fe^{2+} and Fe^{3+} states, facilitated by hydrogen peroxide. In the electro-Fenton process, introducing an external electric field can directly affect the electron transfer cycle, and the rate of electron gain and loss can be controlled through it. This new approach conforms to the basic principles of redox chemistry and provides a promising way to optimize the degradation of organic pollutants in various environmental remediation applications. The integration of activated carbon with the electro-Fenton reaction has led to significant advancements in the field, as evidenced by recent works. Researchers are developing improved Electro-Fenton (EF) technologies for wastewater treatment. One key advancement is the ACSS cathode, a cost-effective design that combines activated carbon (for H_2O_2 generation and adsorption) with stainless steel mesh (for current distribution). This approach proved efficient in dye removal over multiple cycles.[39] Another promising direction is integrating EF with adsorption, as demonstrated by Godínez et al.'s reactor design. This setup combines porous carbon electrodes, granular activated carbon, and Fe(II) ions for

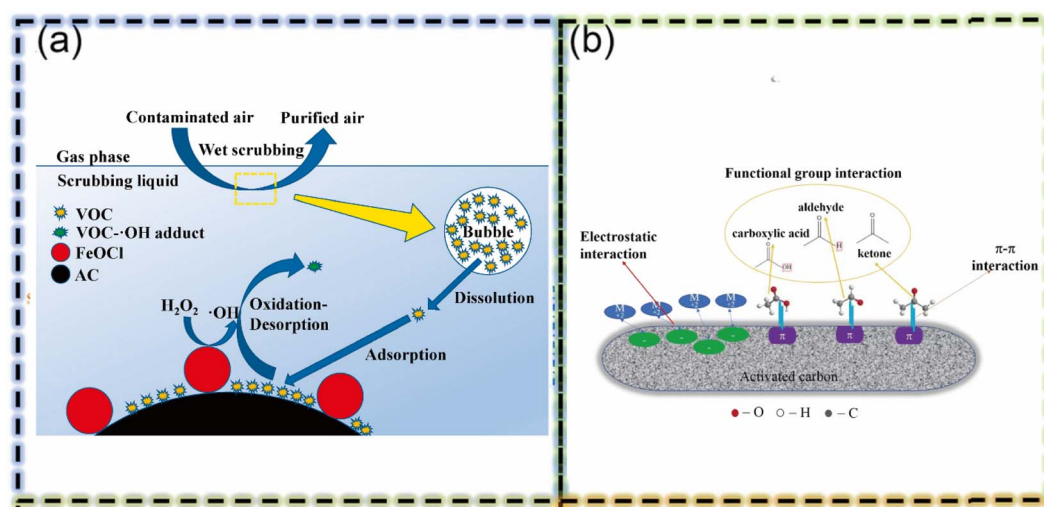Fig. 2 (a) Schematic illustration of DCE removal by wet scrubbing using FeOCl/AC.[36] (b) The possible mechanism of Mn^{2+} adsorption over AC[36] (this figure has been reproduced with permission from Najm et al.[35] from Elsevier, copyright 2020).

enhanced H_2O_2, hydroxyl radical generation, and organic pollutant removal (Fig. 3).[40]

This innovative setup utilized a cation-exchange resin to supply Fe(II) ions to an activated carbon adsorption bed positioned between two porous carbon electrodes. This configuration synergistically combined activated carbon adsorption with the electro-Fenton process, leading to effective H_2O_2 and hydroxyl radical (OH) generation and the removal of model dyes from both synthetic and real aqueous solutions. The system demonstrated that the introduction of pure oxygen could enhance OH formation. Furthermore, the compaction level of activated carbon within the reactor significantly affected its adsorption and electrochemical performance, with denser packing leading to increased surface area and electrical conductivity. Song et al. developed an innovative flow-through heterogeneous electro-Fenton (FHEF) reactor to improve mass transfer for the efficient and stable degradation of trimethoprim (TMP).[41]

These studies illustrated above collectively highlight the versatility and efficacy of activated carbon in enhancing electro-Fenton processes, offering promising avenues for the efficient removal of pollutants and advancing environmental remediation technologies. The exploration of combining activated carbon with optical Fenton processes, such as photo-Fenton, represents another promising direction for enhancing reaction efficiency in environmental remediation. Given its ability to utilize natural sunlight as an energy source, photo-Fenton offers an economical and environmentally friendly alternative to the electro-Fenton process. The work of Babaei et al. serves as a notable example in this context.[42] They employed a direct chemical co-precipitation method to embed magnetic nanoparticles (MNPs) onto powdered activated carbon, creating magnetically recyclable composites (MNPs@C) specifically designed for the eradication of Direct Red 16 (DR16) in water-based systems. These MNPs@C composites, characterized by a mesoporous structure and a zero-point charge (pHzpc) of approximately 6.2, demonstrated a catalytic efficiency of 47% during the UV-Fenton process. This efficiency indicates that MNPs@C effectively collaborates with UV radiation and hydrogen peroxide (H_2O_2) to enhance catalytic activity for DR16 degradation. In a related study, Jiang Z.-Y. and his team developed composites of activated carbon fiber and cobalt ferrite (ACF/CoFe$_2O_4$) using a hydrothermal method.[43] The CoFe$_2O_4$ nanoparticles were uniformly deposited onto activated carbon fibers, leading to a synergistic interaction between the components. This integration resulted in a reduction of the bandgap of

CoFe$_2O_4$ nanoparticles from 1.82 eV to 1.62 eV, enhancing the photocatalytic activity. The effective collaboration of CoFe$_2O_4$ and ACF within the composite boosted the catalytic potential of the photo-Fenton agents. The observed changes in the valence states of Co and Fe in the composite suggest that both Co^{3+}/Co^{2+} and Fe^{3+}/Fe^{2+} redox cycles contribute to the Fenton-like reactions. This composite was found to be efficient in producing hydroxyl radicals in the photo-Fenton system, thereby facilitating the oxidative degradation of atrazine (ATZ), a commonly used herbicide.

3.1.2 Graphene and carbon nanotubes. In comparison to activated carbon, both graphene and carbon nanotubes exhibit distinct advantages in terms of their physical and chemical properties. A significant contrast lies in their specific surface area.[26] Notably, the surface areas of graphene and carbon nanotubes substantially exceed that of activated carbon, indicating an enhanced adsorption capacity. Examining their molecular structures, graphene and carbon nanotubes are abundant in π bonds.[44] These bonds play a pivotal role in facilitating interactions with other entities rich in π bonds. Such interactions give rise to a unique mechanism known as π–π bond stacking, which amplifies their adsorption capabilities. Simultaneously, particles laden with metals display an affinity towards graphene and carbon nanotubes, driven by inherent electrostatic forces.[45] This affinity not only simplifies the material synthesis process but also holds promise for scalable manufacturing. Beyond their adsorptive prowess, graphene and carbon nanotubes are renowned for their exceptional electrical conductivity.[46] This characteristic proves invaluable in scenarios necessitating rapid electron transfer, as exemplified by the Fenton reaction. The intrinsic conductivity of these materials ensures swift electron transit within the medium, thereby enhancing reaction efficiency, as observed in the Fenton process.

This review will now focus on studying graphene and carbon nanotubes in the context of ordinary Fenton reactions, following an exploration of activated carbon materials. Like activated carbon, these advanced materials are of significant interest for their potential to enhance the efficiency of Fenton-based processes.

As illustrated in Table 1, several graphene and carbon nanotube based supports are investigated in recent years.

Sajab et al. created a highly effective porous cellulose nanofibrils (CNF) aerogels amalgamated with graphene oxide-iron (III) nano-composites (CNF-GO-Fe aerogel) for removing methylene blue from water.[47] It combines superior adsorption with Fenton oxidation (adding iron significantly boosts efficiency), achieving double the removal rate compared to adsorption alone. This innovative material shows promise for industrial wastewater treatment due to its reusability. Another recent work introduced a promising method for cleaning water by combining adsorption with a built-in Fenton-like reaction.[45] Their design uses iron nanoparticles trapped within a 3D graphene network (3D-GN@nZVI). This material effectively removes sulfadiazine (SDZ) from water through a combination of adsorption and degradation, since the 3D-GN matrix's exemplary electronic conductivity precipitated the formation of
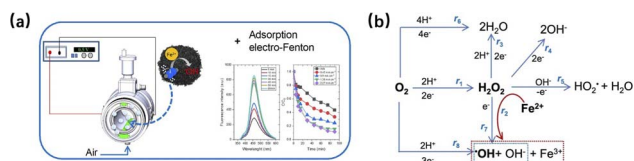

Fig. 3 (a) Side view of the electrochemical reactor air vent valve, (b) equations describing the chemical and electrochemical reactivity of H_2O_2.[40]

Table 1 The reported graphene and carbon nanotube based supports in this review

Pollutants	Supports	Ref.
Methylene blue	CNF-GO-Fe aerogel	47
Sulfadiazine	3D-GN@nZVI	45
Methylene blue	Fe_3O_4/RGO-2	48
Mitoxantrone	rGO/Fe NPs	49
Phenol	GO@Fe_3O_4	32
αE2	FeNPs/rGO	50
Tetracycline	Fe_3O_4/3D-PU-G	51
Sulfadiazine	Pt1-FeOX/G	52
Phenol	OCNT-Fe	53
Acyclovir	MMT/rGO/Fe_3O_4	54
Rhodamine B	GF@CuS–Fe_3O_4	55

multiple micro-electrolytic cells encircling the nZVI particles. This research shows promise for future water treatment technologies prehensive adsorption and reaction with SDZ and its derivatives.

Zhang *et al.* synthesized colloidal Fe_3O_4 nanoparticles through a hydrothermal process and subsequently immobilized them on a three-dimensional graphene aerogel framework.[48] This process of adherence, driven by electrostatic interactions, was facilitate entirely through colloidal coagulation effects (CCE), obviating the need for auxiliary bonding agents. The Fe_3O_4/RGO-2 composite exhibited an impressive adsorption capacity, with its adsorption isotherms and kinetics analysis for Methylene Blue (MB) revealing a maximum adsorption capacity of 163.83 mg g^{-1}. The catalytic activity in the heterogeneous Fenton reaction was predominantly surface-centric, with minimal iron leaching, attributable to the synergistic interplay between zero-dimensional Fe_3O_4 nanoparticles and graphene nano-sheets. This amalgamation rendered Fe_3O_4/RGO-2 a highly efficacious adsorbent and heterogeneous Fenton catalyst. The composite's enhanced performance under alkaline conditions, leading to complete MB degradation within 60 minutes, is particularly noteworthy. Besides, a highly effective system with reduced graphene oxide and iron nanoparticles (rGO/Fe NPs) for removing mitoxantrone (MTX) from water, was also developed.[49] This combination of reduced graphene oxide and iron nanoparticles achieves a remarkable 99.8% MTX removal rate at neutral pH. The secret lies in its ability to generate hydroxyl radicals, which effectively target MTX over other contaminants. Additionally, Wang *et al.* addressed the challenge of phenol contamination by synthesizing Fe_3O_4 nanocrystals onto graphene oxide (GO) nanosheets, thereby creating a GO@Fe_3O_4 composite.[32] This novel composite emerged as a potent catalyst in phenol degradation, with a key mechanism involving the adsorption of phenol molecules at the Fe_3O_4-GO interface through coordination and hydrogen bonds, pivotal for facilitating non-radical degradation pathways. In the Fenton reaction, the presence of H_2O_2 significantly enhanced the GO@Fe_3O_4 composite's catalytic efficiency, underscoring its potential in diverse environmental remediation applications. Another interesting work explored a method for removing αE2 from water using FeNPs/rGO.[50] Their findings suggest that π–π

bonds form between αE2 and rGO, while the oxidation process alters the FeNPs, promoting the generation of hydroxyl radicals. This dual mechanism-adsorption and Fenton-like oxidation-significantly improves αE2 removal efficiency. In 2023, Hong *et al.* addressed the challenges associated with traditional Fenton-like catalysts like Fe_3O_4, particularly its limited operational pH range, metal leaching, and suboptimal catalytic efficiency.[51] The proposed Fe_3O_4/three-dimensional (3D) graphene composite, Fe_3O_4/3D-PU-G (H), synthesized through a solvothermal process followed by mild post-heating, exhibited an exceptional performance. This was largely attributed to the formation of a stable, compact 3D porous conductive network, enhancing electron transfer between Fe species and H_2O_2 and thereby facilitating the generation of hydroxyl radicals (˙OH). This advancement in the Fe_3O_4/3D-PU-G composite technology marks a pivotal step in environmental remediation, enabling rapid degradation of tetracycline without the need for external energy inputs.

Graphene and carbon nanotubes not only play the traditional role of adsorbents and carriers in the field of Fenton reactions. These nanomaterials manifest exceptional adaptability and efficiency when integrated into specialized Fenton methodologies, namely electro-Fenton and photo-Fenton reactions. The electro-Fenton process harnesses electrical energy to amplify the production of hydroxyl radicals, while the photo-Fenton reaction exploits light, often of solar origin, to activate the catalyst. The unique electrical and optical properties inherent to graphene and carbon nanotubes significantly augment the efficacy of these processes. Their integration not only enhances the degradation efficiency of organic pollutants but also paves the way for more energy-efficient and environmentally sustainable remediation techniques. As a result, these nanomaterials represent a seminal advancement in the field of environmental remediation, particularly in scenarios where conventional Fenton reactions may encounter limitations.

For instance, Song *et al.* demonstrated this by creating Pt-FeOX single atoms on graphene (Pt1-FeOX/G).[52] This catalyst efficiently generates H_2O_2, crucial for the degradation process. The study highlights the role of material structure in performance (Fig. 4). Notably, using single atoms reduces material consumption and enhances efficiency. Additionally, the excellent conductivity of graphene and carbon nanotubes benefits the electro-Fenton process. Similarly, iron-doped oxidized carbon nanotubes (OCNT-Fe) as a catalyst for electro-Fenton applications also developed.[53] Oxygen groups on the OCNT surface aid in Fe(II) regeneration, improving efficiency. Notably, using a Fe catalyst avoids the need for dissolved iron (Fe^{2+}), expanding the operational pH range and reducing sludge formation compared to traditional Fenton processes. This method generates hydroxyl radicals (˙OH) *via* a continuous oxygen reduction reaction (ORR), forming H_2O_2 as an intermediate that decomposes into ˙OH. The process relies solely on environmentally friendly O_2 and H_2O, eliminating the need for additional H_2O_2. Also, the combination of iron oxide nanoparticles with reduced graphene oxide and montmorillonite (MMT/rGO/Fe_3O_4) could for the catalyst for 3D electro-Fenton systems.[54] This approach leverages the strengths of each
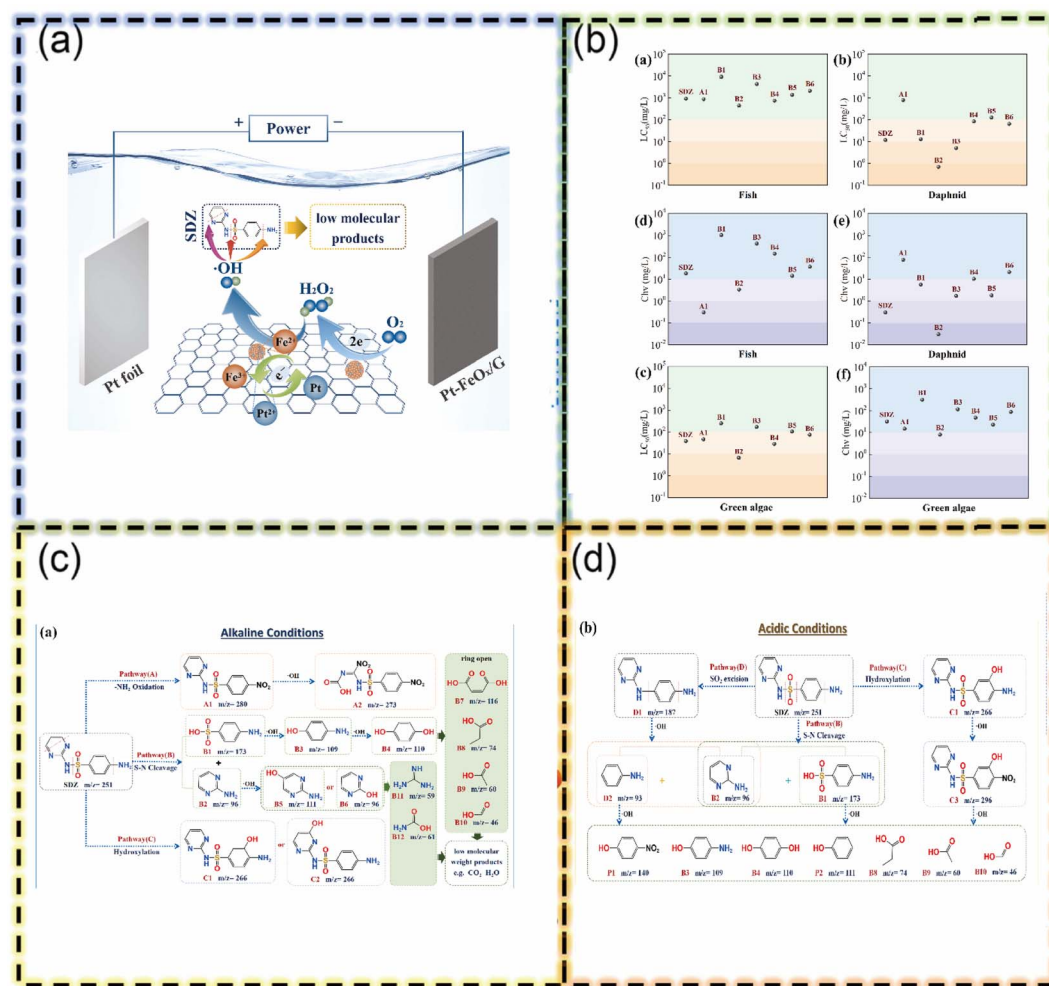
Fig. 4 (a) Schematic diagram of SDZ degradation in the heterogeneous EF system with Pt1-FeOX/G cathode. (b) Acute toxicity (a–c) and chronic toxicity (d–f) of SDZ and its generated products established *via* ECOSAR in conjunction with trophic aquatic organisms (fish, daphnids, and green algae) (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article). Proposed degradation pathways for SDZ in the heterogeneous EF system with Pt1-FeOX/G cathode under alkaline condition (c) and acidic condition (d) (this figure has been reproduced with permission from Song *et al.*[52] from Elsevier, copyright 2024).

material for efficient acyclovir (ACV) degradation. Since it produces more hydroxyl radicals and facilitates Fe(II) regeneration compared to traditional Fenton methods. However, limitations like corrosion and stability require further solution. A recent work reported by Matos and colleagues, synthesized nanocomposites comprising graphene sheets (GF) combined with CuS, Fe_3O_4, and $CuS–Fe_3O_4$ (GF@CuS–Fe_3O_4).[55] These nanocomposites, specifically GF@Fe_3O_4, GF@CuS, and GF@CuS–Fe_3O_4, were fabricated through the amalgamation of two or three different components, each possessing complementary effects, aimed at enhancing the efficiency and stability of the photocatalyst. Within this ensemble, Fe_3O_4 assumes the role of a Fenton-type catalyst, CuS functions as a visible light photocatalyst, and GF serves as a charge carrier. Fe_3O_4 and/or CuS nanoparticles were directly anchored to GF without the need for additional chemical treatments. The adsorption and photocatalytic properties of these GF-based nanocomposites were meticulously investigated for the removal of rhodamine B

(RhB) contaminants at room temperature. This research comprehensively demonstrates the synergistic effect arising from the combination of graphene and carbon nanotubes in the photo-Fenton reaction, ultimately leading to a marked improvement in catalytic efficiency.

3.1.3 Graphitic carbon nitride (g-C_3N_4). Graphitic carbon nitride (g-C_3N_4) has emerged as a prominent carbon-based material due to its exceptional activity and superior adsorption properties. Constructed exclusively from earth-abundant elements, carbon and nitrogen, g-C_3N_4 demonstrates significant chemical and thermal resilience, attributable to the robust covalent bonds within its conjugated layered structure. Furthermore, g-C_3N_4 is characterized by a unique delocalized conjugation structure, comprising graphitic stacks of C_3N_4 layers linked by tertiary amines. Such a configuration imparts it with unparalleled electronic conductivity. The facile synthesis of g-C_3N_4, combined with the affordability of its raw materials,

has led to its widespread utilization in various synergistic Fenton reactions.

Recent work of g-C$_3$N$_4$ based support material in Fenton reactions actively participates through several mechanisms: g-C$_3$N$_4$'s unique structure makes it effective in electro-Fenton and photo-Fenton processes as well. Its rich nitrogen atoms readily capture transition metals for catalysis. Also, the double C=C bonds in g-C$_3$N$_4$ improve current efficiency compared to graphene under electrical stimulation. This allows for *in situ* H$_2$O$_2$ generation at the cathode, crucial for electro-Fenton degradation. For instance the g-C$_3$N$_4$ could form Fe–N coordination complex: Wang *et al.* showed g-C$_3$N$_4$'s π bonds form a complex with Fe(III) ions, creating oxygen vacancy (OV) oxides.[33] These oxides enhance electron transfer between Fe and nearby H$_2$O$_2$, leading to O$_2$ evolution. Further research explored co-doping g-C$_3$N$_4$ with metals like Na and Fe can improve catalytic activity[56,57] by (i) increased active sites: co-doping creates more sites for Fe and enhances electron transfer; (ii) metal synergy: copper, for example, accelerates the rate-limiting step and boosts H$_2$O$^\bullet$ generation.[58–60]

3.1.4 Biochar.

Biochar, a carbonaceous sorbent of notable richness, is derived from the thermochemical conversion of various biomasses employing methodologies such as pyrolysis, gasification, torrefaction, and hydrothermal carbonization.[61] This conversion predominantly transpires under hypoxic or anoxic environments.[62] Several factors, encompassing the selection of biomass precursors, the pyrolytic temperature, and the reaction duration, critically influence the elemental constitution and surface characteristics—like specific surface area and functional groups—of the resultant biochar.[62] Owing to its intricate porous architecture and a plethora of surface functional groups, biochar emerges as an exemplary material for efficient sequestration and adsorption.[63] Biochar has emerged as a sustainable and promising alternative for the synthesis of functional materials, particularly in the development of heterogeneous catalysts for Fenton reactions. Diverging from the realm of purely chemically synthesized materials, such as graphene, carbon nanotubes, and graphitic carbon nitride (g-C$_3$N$_4$), biochar offers a diverse and abundant source of raw materials. This spectrum of materials encompasses a wide array of biomass, including wood waste, agricultural residues, and other plant-derived biomass, predominantly composed of cellulose, lignin, and hemicellulose. Moreover, animal-derived biomass, such as feces and food waste, which chiefly contain elements like chitin, glycogen, alginate, gelatin, and various industrial by-products, further enriches the raw material base for biochar production.[64] Significantly, certain methodologies capitalize on waste biomass, thereby providing an abundant and cost-effective resource for biochar manufacturing. The process of converting waste biomass into biochar not only enables the effective utilization of solid waste as a raw material but also addresses the challenges associated with managing other forms of waste. This approach effectively meets the dual objectives of waste management.[65] Such a strategy aligns with sustainable practices for managing organic pollutants and resonates with the contemporary global emphasis on environmental protection and waste reduction initiatives.[66–73]

Biochar derived from plant biomass is gaining traction in Fenton reactions due to its ability to combine adsorption and catalysis. Alizadeh *et al.* created a biochar-based nanocomposite (MC@nano-Fe$_3$O$_4$) by incorporating magnetic nanoparticles into microbial cellulose.[34] This material effectively removes tetracycline (TC) through adsorption onto its high surface area and subsequent degradation *via* electron transfer between metal ions in the biochar, mimicking a Fenton-like process. The composite's impressive performance and reusability make it a promising candidate for water treatment. In a study of similar import, Wang *et al.* exemplify this through the use of corncob biochar as a precursor to synthesize a cost-effective magnetic iron–copper bimetallic nanomaterial (MBC), targeted for the removal of ciprofloxacin (CIP) from aqueous solutions.[66] The innovative synthesis of MBC involves a combination of coprecipitation and pyrolysis techniques. Crucially, the presence of H$_2$O$_2$ in the aqueous solution activates MBC, resulting in a significant enhancement of its adsorption capacity for CIP in the MBC/H$_2$O$_2$ system during the Fenton reaction. This leads to a comprehensive interaction between CIP and the magnetic iron–copper bimetallic components on the MBC material through direct adsorption. Subsequently, the degradation of CIP is achieved *via* electron transfer and redox cycles among the metal ions. This process epitomizes a typical synergistic effect, where catalytic degradation is seamlessly coupled with adsorption, thereby illustrating the potential of biochar-based materials in advanced environmental remediation techniques (Fig. 5).

Inspired by algae-based biochar, Yu *et al.* created biochar/iron oxide composites from *Aegagropila linnaei* algae (AL) for BPA removal.[67] The cost-effective AL is activated with KOH to form a biochar with a high surface area, then functionalized with ferrous sulfate to introduce Fe$_3$O$_4$ nanoparticles. This composite effectively removes BPA through a combination of adsorption and Fenton-like reactions triggered by the iron oxide. This approach highlights the potential of biochar/iron oxide composites for efficient BPA removal.

While biochar is derived from a variety of sources, its modification bestows it with advantageous electrochemical properties, notably improved conductivity and reduced impedance, which are essential for its integration into the electro-Fenton process For instance, Deng *et al.* created a nitrogen-doped biochar cathode (B@Ni-F) from waste giant trees.[68] This cathode effectively degrades sulfadiazine (SMR) by combining adsorption and Fenton-like reactions. This research highlights the potential of biochar for sustainable wastewater treatment (Fig. 6).

Biochar derived from waste materials like bamboo and agricultural residue shows promise for wastewater treatment *via* electro-Fenton processes.[69,70] These biochar electrodes effectively remove pollutants through a combination of adsorption and Fenton-like reactions. For example, bamboo waste as a source of biochar with composed of zero-valent iron nanoparticle hybrids (NZVIeBC) could efficiently removes clothianidin (CLO) by first adsorbing it and then degrading it through an electro-Fenton reaction with zero-valent iron nanoparticles.[69] Meanwhile, utilizing Fe/N co-doped biochar (Fe-g-C$_3$N$_4$/biochar)
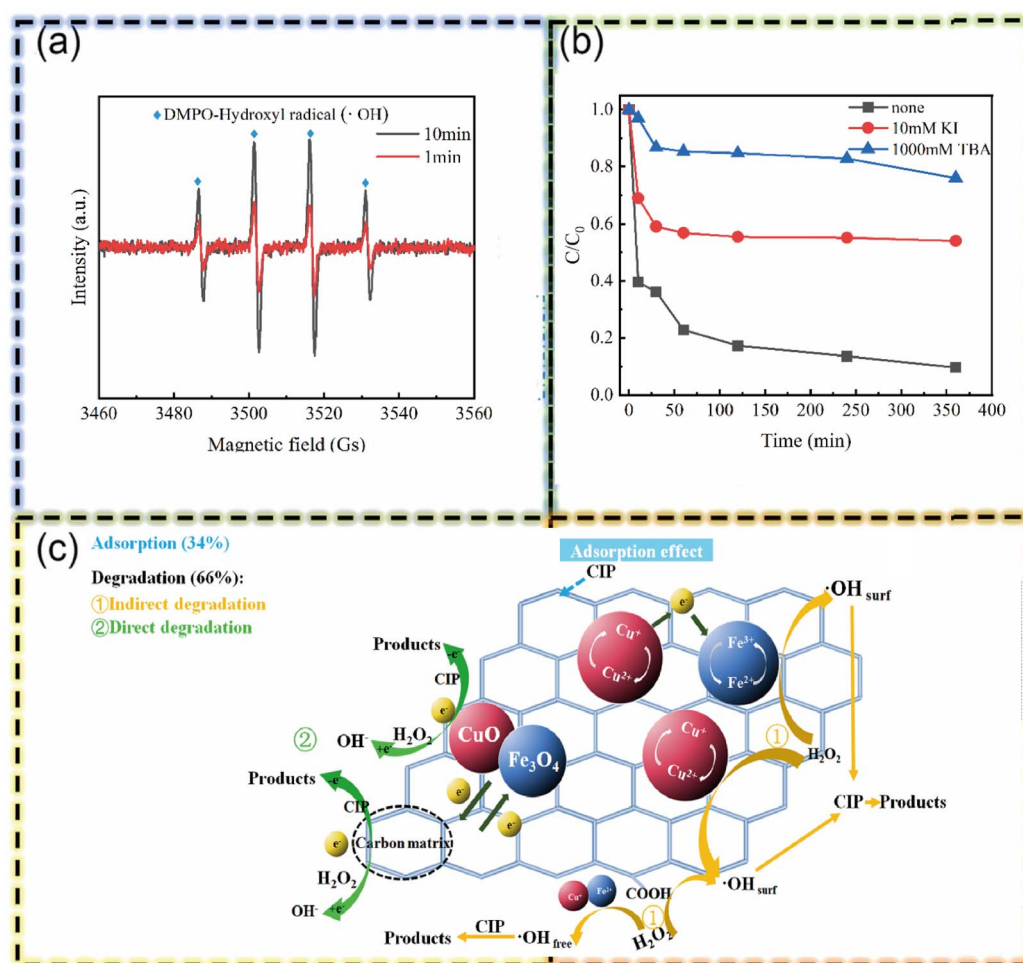
Fig. 5 (a) Comparison of EPR spectra at 1 min and 10 min in the MBC/H$_2$O$_2$. (b) Effect of TBA or KI scavengers on the removal of CIP in the MBC/H$_2$O$_2$. (c) Mechanisms of CIP removal in the MBC/H$_2$O$_2$ (this figure has been reproduced with permission from Wang H. *et al.*[66] from Elsevier, copyright 2020).

membrane degrades tetracyclines while minimizing membrane fouling.[70] Its high activity stems from abundant functional groups and nitrogen species, promoting efficient hydroxyl radical generation. These studies highlight biochar's potential for sustainable and adaptable electro-Fenton treatment of organic pollutants in wastewater.

While biochar-enhanced electro-Fenton processes effectively treat pollutants, integrating biochar with renewable energy sources like light offers a more promising path towards even more sustainable water treatment. Exploring biochar in photo-Fenton remediation could unlock new avenues for degradation using clean and abundant solar energy. This approach aligns with sustainability goals and potentially offers greater efficiency and lower environmental impact than traditional methods.

Other biochar supports such as starch and red mud also plays importance roles in Fenton reaction. Cai *et al.* designed a novel starch-derived carbon (SC)-modified and copper-doped (Fe, Cu)S/CuFe$_2$O$_4$ (CFS/CFO@SC) composite for efficient 17α-ethinylestradiol (EE2) removal. The unique structure of CFS/CFO@SC facilitates high EE2 adsorption and promotes efficient charge transfer for photogenerated electron–hole

separation. This synergistic effect, combining adsorption and photo-Fenton mechanisms, enables efficient EE2 degradation. Their work highlights the potential of integrating adsorption and photocatalysis for organic pollutant treatment.[71] Lin *et al.* leverage biochar's adsorption and photocatalysis for efficient dye removal.[73] Their iron-containing red mud biochar (RMBC) effectively adsorbs Acid Orange 7 (AO7) dye. Upon light irradiation, Fe in RMBC undergoes redox cycling, generating hydroxyl radicals (˙OH) that degrade AO7 *via* photo-Fenton reactions. This study highlights the potential of biochar for integrating adsorption and photocatalysis in wastewater treatment. The integration of biochar with various Fenton reactions, employing a synergistic approach of initial adsorption followed by Fenton processing, is pivotal in enhancing the overall reaction efficiency. This principle holds across different applications of biochar, whether in traditional Fenton, electro-Fenton, or photo-Fenton reactions. A critical aspect of this synergy is the enhancement of the material's adsorption capacity. The ability of biochar to effectively adsorb pollutants sets the stage for the subsequent Fenton reaction. Equally crucial is the promotion of the redox cycle of Fe^{2+}/Fe^{3+} within the system, which is the core
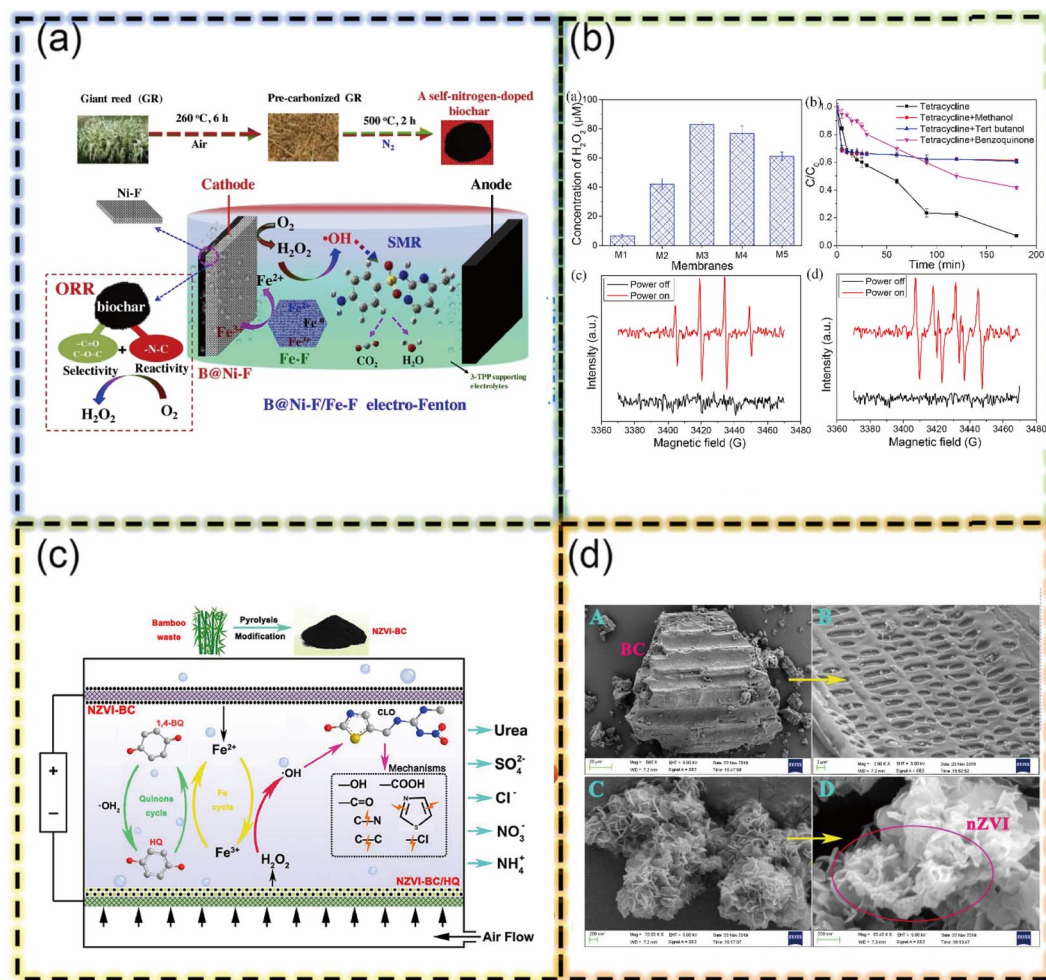
Fig. 6 (a) B@Ni–F cathode in electro-Fenton for sulfamerazine degradation (b) concentration of electro-generated H_2O_2 by EF catalytic membranes (c) the ecotoxicity evaluation of degradation products indicated that CLO degradation in 3D–ICE–EF system (d) FE-SEM characterizations of BC and NZVI–BC (this figure has been reproduced with permission from Deng F. *et al.*[68] from Elsevier, copyright 2019).

of the Fenton process, generating reactive species that are essential for pollutant degradation.

Carbon materials exhibit high adsorption capacity, effectively removing pollutants from water, and can anchor Fenton catalytic ions, such as iron, thereby enhancing Fenton reaction efficiency. This dual functionality allows carbon materials to serve both as exceptional adsorbents and optimal matrices for integrating catalysts, including iron ions. Additionally, their inherent electrical conductivity facilitates the integration with electrical and photonic energies, thereby improving electron mobility and the overall efficiency of Fenton processes.

3.2 MOFs

In developing new materials for adsorption and Fenton catalysis, four factors are crucial: a strong intrinsic adsorption capacity for initial pollutant capture, the ability to bind or support catalytic metals like iron, high electrical conductivity for efficient electron transfer, and an abundance of functional groups to chelate metals, thereby enhancing catalytic activity. These functional groups not only stabilize metal ions but also

position them optimally for enhanced catalytic activity, leading to the formation of robust and active catalytic sites. Such considerations ensure efficient pollutant degradation and robust Fenton catalysis, making carbon materials highly valuable in environmental decontamination efforts. Drawing from the aforementioned insights, it is apparent that Metal–Organic Frameworks (MOFs) thereby eliciting considerable interest within the scientific fraternity. Several types of MOFs have been investigated in Fenton reactions, and the relevant literature in this review are listed in the followed table. (See Table 2).

At their core, MOFs consist of two fundamental components: metallic ions or their clusters, and organic segments, often referred to as linkers. These organic segments predominantly manifest as bi-, tri-, or tetradentate ligands.[80,81] A notable aspect of MOF synthesis is the utilization of homogeneous ligands, albeit with varying metallic constituents.[82] Such versatility facilitates the precise modulation of MOF pore dimensions, extending from microporous to mesoporous frameworks, through the strategic selection of diverse metallic elements.[83] This attribute of tunability bestows upon MOFs the capacity to

Table 2 The reported MOFs based supports for Fenton reactions

MOF-based adsorbent/catalyst	Target pollutants	Operational conditions	Mechanism		Ref.
			Adsorption	Fenton	
NH₂-MIL-88B	Pefloxacin	pH: 6, C_0: 0.5 g L^{-1} and T: 30 °C, adsorbent/catalyst dosage: 0.5 g L^{-1}, H₂O₂: 8 mM	π–π stacking/electrostatic/functional group interaction	˙OH	74
MFC@Mn–NH₂-UiO-66@IL	Methylene blue	pH: 6, C_0: 50 mg L^{-1}, T: 25 °C, adsorbent/catalyst dosage: 0.5 g L^{-1}, time: 250 min, H₂O₂: 30 mM	π–π stacking/electrostatic/hydrogen bonds interaction	˙OH	75
Fe/Ni@ZIF-8	Ofloxacin	pH: 6.32, C_0: 10 mg L^{-1}, T: 25 °C, adsorbent/catalyst dosage: 0.5 g L^{-1}, time: 210 min, H₂O₂: 10 mM	π–π stacking/electrostatic interaction	˙OH	76
Mn$_x$Co$_{3-x}$@C	Ciprofloxacin	pH: 3, C_0: 20 mg L^{-1}, T: 25 °C, I: 20 mA, time: 60 min, Fe²⁺: 0.02 mm, Na₂SO₄: 0.05 M	π–π stacking/electrostatic/hydrogen bonds interaction	Electron transfer/HO₂˙/O₂˙⁻/˙OH	77
xFe-N/C	Carbamazepine	pH: 7, C_0: 5 mg L^{-1}, T: 25 °C, I: 15 mA, catalyst dosage: 50 mg L^{-1}, time: 100 min	π–π stacking/electrostatic/hydrogen bonds interaction	Electron transfer ¹O₂/O₂˙⁻/˙OH	78
FeNi1/15-BDC	Methylene blue/methyl orange	pH (methylene blue): 6.5, pH (methyl orange): 6.9, C_0: 40 mg L^{-1}, T: 30 °C, adsorbent/catalyst dosage: 0.1 g L^{-1}, time: 40 min, H₂O₂: 10 mM	π–π stacking/electrostatic/interaction	˙OH/¹O₂/h⁺	44
Co0.8Fe0.2N-NC	Methylene blue/methyl orange	pH (methylene blue): natural pH, pH (methyl orange): natural pH, C_0: 20 mg L^{-1}, T: 25 °C, adsorbent/catalyst dosage: 0.1 g L^{-1}, time: 40 min, H₂O₂: 0.75 mL, 300 W fluorescent lamp	π–π stacking/electrostatic/hydrogen bonds interaction	˙OH/˙O₂⁻/h⁺	17
MOFs (2Fe/Co)/CNF	Methylene blue/erythromycin	pH (methylene blue): 3, pH (erythromycin): 3, C_0 (methylene blue): 50 mg L^{-1}, C_0 (erythromycin): 20 mg L^{-1}, T: 25 °C, adsorbent/catalyst dosage: 0.1 g L^{-1}, time: 30 min, 500 W Xe lamp	π–π stacking/electrostatic/interaction	˙OH	79

meticulously customize their pore size and architecture. Their adaptable pore interfaces confer a distinct advantage to MOFs, particularly in applications centered around adsorption, enabling the selective entrapment of various guest molecules distinguished by their unique functional groups. Recent studies highlight MOFs' ability to adsorb and neutralize environmental pollutants, emphasizing their extensive porosity. Iron-based MOFs, for example, have intrinsic Fenton catalytic capabilities, eliminating the need for additional metals. Organic ligands enhance catalytic sites by chelating supported metals, opening new research avenues in doping MOFs with diverse elements for efficient catalysts. These properties make MOFs promising for adsorption and Fenton reactions.[84] In the realm of environmental remediation, Fe-based Metal–Organic Frameworks (MOFs) have emerged as promising catalysts due to the widely recognized efficacy of iron as a catalyst in the Fenton reaction. In their notable study, Ma H *et al.* explored the use of functional NH_2-MIL-88B MOFs, which exhibit both adsorption and Fenton oxidation capabilities, for the degradation of pefloxacin in aqueous solutions.[74] This integrated approach marries the benefits of adsorption with those of advanced oxidation processes. The intrinsically strong adsorption capacity of the MOF material plays a crucial role in this methodology. It facilitates the mass transfer of organic pollutants to the surface of the material designed for advanced oxidation. Once on the surface, the advanced oxidation process, leveraging the Fenton reaction, effectively degrades the adsorbed organic pollutants. The synergy between adsorption and Fenton oxidation in the Fe-based MOF (NH_2-MIL-88B) framework leads to the successful removal of organic pollutants, either through adsorption or through Fenton-based oxidative degradation. This study by Ma H. *et al.* underscores the potential of MOFs, particularly Fe-based variants, in environmental cleanup strategies. The dual functionality of these MOFs, enabling both adsorption and catalytic degradation, presents a compelling case for their application in the efficient and effective removal of contaminants from aqueous environments.

Metal–organic frameworks (MOFs) inherently contain Fenton catalytic metals, providing them with natural Fenton catalytic capabilities. The functional groups on MOFs facilitate efficient loading of catalytic metals, increasing active sites and enhancing effectiveness. Interaction mechanisms such as electrostatic interactions, hydrogen bonding, and π–π stacking significantly boost the adsorption efficiency for organic pollutants. These interactions between MOF functional groups and pollutants lead to more effective capture and degradation of contaminants. Simple modifications can enhance both adsorption capacity and Fenton catalytic efficiency in MOFs, creating a synergistic effect. This synergy results in a combined impact that exceeds the sum of individual processes, making the dual enhancement more effective than separate applications of adsorption and Fenton catalysis.

In their groundbreaking research, Lu R. *et al.* utilized UiO-66 series metal–organic frameworks (MOFs) as the foundational substrate, leveraging their renowned chemical and hydrothermal stability. These MOFs underwent a sophisticated functionalization process with Mn(II)-doped ionic liquids (ILs),

culminating in the formation of Fe_3O_4@Zr-MOFs featuring core–shell structures. This innovative approach was adeptly applied to the removal of methylene blue (MB) from wastewater.[75] The enhanced adsorptive capacity of this MOF material in aqueous environments can be attributed not merely to its layered and porous structure, which provides a high surface area and porosity, but also to the electrostatic interactions between the MOF's functional groups and MB. The adsorption capacity is further augmented by hydrogen bonding and π–π stacking interactions. Additionally, the Fe_3O_4 supported by the MOF plays a pivotal role in catalyzing the Fenton reaction. The incorporation of zirconium (Zr) within the MOF framework is instrumental in facilitating electron transfer between Fe and Zr, leading to the creation of dual active sites for Fenton-like reactions. This synergy results in the rapid decomposition of H_2O_2 in the Zr-MOF and Fe_3O_4 systems, producing hydroxyl radicals for the oxidative breakdown of MB. This study exemplifies a prototypical synergistic interaction between adsorption and Fenton reactions.

The MOF material, characterized by its multi-layered porous structure and the presence of specialized functional groups, exhibits a remarkable pollutant adsorption capacity. This is further enhanced by electrostatic interactions, hydrogen bonding, and π–π stacking, surpassing the adsorption efficiencies of previously discussed carbonaceous materials.

Moreover, the inclusion of Zr in the MOF establishes dual active centers with Fe_3O_4, significantly enhancing the Fenton reaction. This research underscores the inherent Fenton catalytic potential of the metals contained within the MOF material. Diverging from the carbon-based materials earlier mentioned, MOFs serve not only as supports for adsorbents and catalysts but also as active catalysts in their own right. Furthermore, MOFs can be utilized as catalyst supports to develop multiple catalytic cores, thus enhancing catalytic efficiency. The dual functionality of MOFs as both adsorbents and catalysts, coupled with their ability to house multiple catalytic sites, markedly improves the synergistic efficacy of adsorption and Fenton reactions. In pursuit of augmenting Fenton efficiency, the approach of bimetal doping emerges as a promising strategy. In this context, Zhang T. *et al.* conducted a groundbreaking study by doping Ni and Fe bimetals into a Zn-containing Zeolitic imidazolate frameworks (ZIFs) material, ZIF-8. This innovative endeavor led to the creation of the Fe/Ni@ZIF-8 composite material, which demonstrated remarkable efficacy in the oxygen Fenton oxidation of ofloxacin (OFX).[76] The mechanism underlying the removal of OFX *via* Fe/Ni@ZIF-8 involves a two-pronged approach: initially, OFX is adsorbed onto the Fe/Ni@ZIF-8 composite through a combination of π–π bond intercalation and electrostatic interactions. Following this adsorption, the adsorbed OFX undergoes oxidative degradation, mediated by hydroxyl radicals (˙OH) generated through the Fenton reaction, catalyzed by the Fe/Ni bimetallic nanoparticles supported on ZIF-8 in the presence of H_2O_2. This process of OFX removal using the Fe/Ni@ZIF-8 composite exemplifies a typical outcome of the synergistic effect combining ZIF-8 adsorption and Fe/Ni Fenton-like oxidation. The study not only highlights the enhanced catalytic efficiency achieved through bimetal
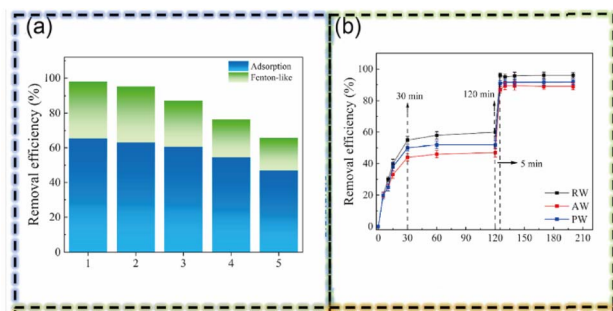
Fig. 7 Reusability of Fe/Ni@ZIF-8 in adsorption and Fenton-like oxidation (a); practical removal efficiency of OFX from three wastewater by Fe/Ni@ZIF-8 under non-Fenton (0–120 min) and Fenton-like (>120 min) conditions (b) (this figure has been reproduced with permission from Zhang T. et al.[76] from Elsevier, copyright 2022).

doping in MOFs but also underscores the potential of these composite materials in advanced oxidation processes (Fig. 7).

Metal–organic frameworks (MOFs) excel in integrating adsorption and Fenton reactions. Their large surface area, porous structure, and functionalizable groups enhance adsorption efficiency through mechanisms like electrostatic interactions, hydrogen bonding, and π–π stacking. MOFs with Fenton-active metals like iron possess inherent catalytic abilities. Their functional groups chelate metal ions, enabling efficient loading of Fenton-active metals and creating multiple active centers that boost Fenton efficiency. MOFs demonstrate superior Fenton activity compared to other carbon materials. This synergy of strong adsorption and robust Fenton catalysis makes MOFs highly effective for pollutant removal, simplifying and enhancing environmental cleanup. Furthermore, MOFs are compatible with other catalytic modalities, notably electro-Fenton catalysis. Their conductive framework, porous structure, and high surface area make them suitable as electrode materials or supports for electrocatalysts, facilitating electron transfer processes crucial in electrocatalysis. In electro-Fenton systems, MOFs enhance the electrochemical generation of Fenton reagents, boosting hydroxyl radical production for efficient pollutant degradation. In the context of advanced Fenton processes, the electro-Fenton system presents a significant advancement, particularly in terms of operational efficiency and cost-effectiveness. A key feature of this system is its ability to generate hydrogen peroxide (H_2O_2) in situ via the two-electron oxygen reduction reaction (ORR) on the cathode. This capability circumvents the need for continuous addition of H_2O_2 to the reaction mixture, thereby reducing operational expenses.[19] An additional noteworthy feature of metal–organic frameworks (MOFs) that further augments their utility in Fenton processes is their excellent electrical conductivity. When MOFs are subjected to an electric field, the conductivity of the material facilitates an accelerated movement of electrons within the framework. Metal–organic frameworks (MOFs) enhance Fenton processes due to their excellent electrical conductivity, which accelerates electron movement under an electric field. This increased electron mobility boosts the generation of reactive species like hydroxyl radicals ($^{\bullet}OH$), which are central to the

Fenton reaction, thereby improving pollutant degradation rates. This is particularly beneficial in electro-Fenton systems, where MOFs' rapid electron transfer processes synergize with electrochemical aspects, enhancing overall efficiency. In a notable study, Huang S. et al. developed Mn/Co MOF derivatives (Mn_x-Co_{3-x}@C-GF) for ciprofloxacin (CIP) treatment. By adjusting the Mn/Co ratio in the MOF-74 precursor, they achieved a hierarchical porous structure, which enhanced adsorption and electrochemical activity. This structure facilitated rapid CIP adsorption and faster electron transfer, improving $Mn^{2+/3+/4+}$ and $Co^{3+/2+}$ Fenton-like reactions, generating more active radicals ($^{\bullet}OH$) and thus enhancing degradation performance. This study highlights MOFs' potential in electro-Fenton processes, creating efficient, cost-effective, and environmentally sustainable pollutant degradation solutions.[77] Similarly, Guo J. et al. encapsulated an iron precursor in a ZIF-8 cage, forming a single-atom Fe-N/C structure after calcination. This MOF efficiently adsorbs carbamazepine (CBZ) and rapidly degrades it via hydroxyl radicals ($^{\bullet}OH$) and oxygen (O_2) generated from H_2O_2 reacting with single-atom iron sites. This study demonstrates the use of MOFs for single-atom catalysts, showcasing the synergistic effects of adsorption and electro-Fenton processes. The material effectively activates H_2O_2 over a wide pH range, offering new insights into MOFs' potential for environmental remediation and advanced pollutant degradation. Both studies exemplify the innovative use of MOFs in enhancing electro-Fenton processes and creating multifunctional catalysts for environmental cleanup (Fig. 8).[78]

Beyond their significant role in electro-Fenton reactions, Metal–Organic Frameworks (MOFs) have also garnered
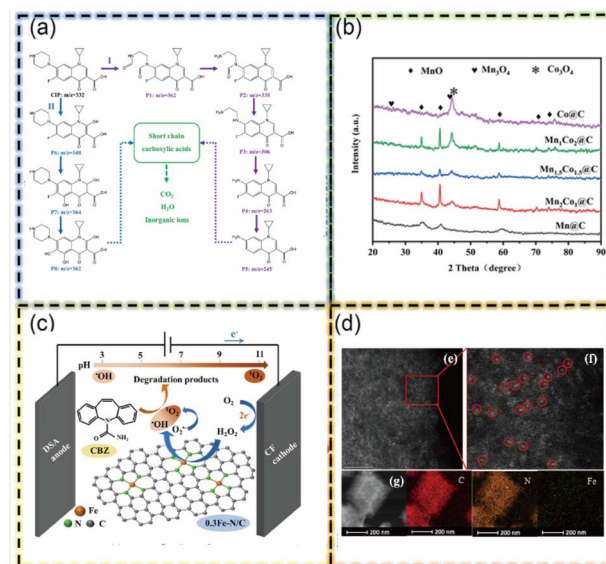

Fig. 8 (a) Proposed pathways for degradation of CIP. (b) XRD patterns of Mn_xCo_{3-x}@C (this figure has been reproduced with permission from Huang S. et al.[77] from Elsevier, copyright 2022). (c) Schematic diagram of possible CBZ degradation mechanism by 0.3Fe-N/C/hetero-EF. (d) HAADF-STEM and corresponding element maps of 0.3Fe-N/C (this figure has been reproduced with permission from Guo J. et al.[78] from Elsevier, copyright 2022).

widespread interest in the realm of photo-Fenton processes. In photo-Fenton reactions, MOFs can act as both catalysts and supports for catalysts, leveraging light energy to enhance the generation of hydroxyl radicals ($\cdot$OH) through the Fenton reaction. The versatility of MOFs allows for the tuning of their optical properties, making them responsive to different wavelengths of light. This adaptability is crucial in photo-Fenton processes, as it enables the activation of the Fenton reaction under light irradiation, potentially expanding the range of operational conditions and enhancing the efficiency of pollutant degradation. Moreover, the structural diversity and modifiability of MOFs offer opportunities for designing materials that can effectively harness solar energy, thereby contributing to the development of more sustainable and energy-efficient photo-Fenton systems.

In a notable advancement in pollutant remediation, Wu Q. *et al.* engineered an iron–nickel bimetallic organic framework (FeNiX-BDC) targeting the adsorption and photo-Fenton degradation of methylene blue (MB) and methyl orange (MO). The specific ratio of Ni and Fe optimized the MOF's surface area, pore volume, and surface charge, enhancing its adsorption capacity and photocatalytic properties. This synergy significantly improved the removal rate of these pollutants, demonstrating FeNiX-BDC's potential in environmental cleanup.[30] Aligning with evolving research trends, Miao S. *et al.* synthesized magnetic MOF-derived nitrogen-doped cobalt–iron bimetallic carbon composite nanomaterials (Co0.8Fe0.2N-NC). Created through self-assembly and annealing, this material features nitrogen doping into a Co–Fe MOF structure, enhancing adsorption and Fenton activity. The interplay between cobalt–iron centers and H_2O_2 amplified active species generation, expediting MB degradation. Co0.8Fe0.2N-NC demonstrated superior performance, being 2.9 times more effective than traditional Fenton systems and 25.2 times more than conventional photocatalytic systems. This study highlights significant advances in pollutant degradation and the stability of nitrogen-doped bimetallic MOFs.[44] (see Fig. 9). In 2023, Li B. *et al.* innovatively prepared an electrospun cathode (MOFs (2Fe/Co)/CNF) with photocatalytic and electrocatalytic functionalities. Utilizing graphene templates, carbonization, and *in situ* growth, this material effectively degraded dyes like methylene blue and antibiotics like erythromycin. The flexible electrospun cathode's unique heterostructure, facilitated by carbon nanofibers (CNF), promoted efficient electron transport and suppressed electron–hole recombination, enhancing catalytic performance. This system, combining adsorption and photo-electro-Fenton processes, represents a significant leap in pollutant degradation technologies' efficiency and effectiveness.[79] The array of research discussed above clearly illustrates the extensive utilization of metal–organic frameworks (MOFs) in systems that harness both adsorption and Fenton synergistic processes. MOFs inherently possess a strong adsorption force, and when they contain Fenton catalytic metals, they also function as effective catalysts. This dual functionality is a cornerstone of their utility in environmental remediation. A key aspect of MOFs is the array of functional groups present on their surface, which not only contribute to the structural advantages
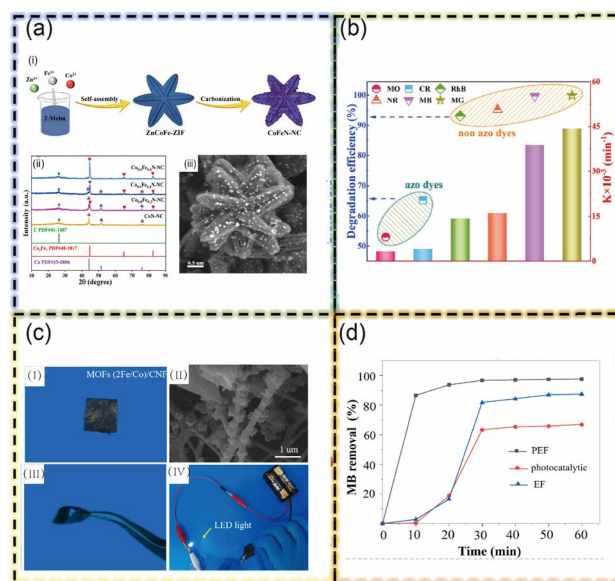

Fig. 9 (a) (i) Schematic diagram of $Co_xFe_{1-x}N$-NC prepared by self-assembly and annealing. (ii) XRD patterns of $Co_xFe_{1-x}N$-NC materials with various molar ratios of Co and Fe after carbonization. (iii) SEM, (b) Relationship between degradation efficiency and degradation rate constant of six organic dyes ($T = 30 \pm 1$ °C; $Co_{0.8}Fe_{0.2}N$-NC = 0.1 g L^{-1}; $C_0 = 40$ mg L^{-1}; natural pH; $H_2O_2 = 0.75$ mL; 300 W fluorescent lamp). (c) (I) MOFs (2Fe/Co)/CNF, (II) SEM diagrams, (III) the flexibility, (IV) the conductivity (this figure has been reproduced with permission from Miao S. *et al.*[44] from Elsevier, copyright 2022). (d) The MB removal efficiency with different treatments (with PEF, EF and photocatalyst, respectively).

of the material in adsorption but also facilitate various interactions. These interactions include electrostatic attractions, hydrogen bonding, and π–π stacking, all of which collectively enhance the adsorptive force of the MOFs. Furthermore, these functional groups can chelate with Fenton metals, thereby improving the efficiency of Fenton-based reactions. In addition to these properties, the high conductivity and photosensitivity of MOF materials expand their applicability. These characteristics enable MOFs to participate not only in adsorption and traditional Fenton processes but also in more complex systems involving electro-Fenton and photo-Fenton reactions. The culmination of these capabilities is the ability of MOFs to engage in adsorption and photo-electro-Fenton processes, thereby offering a multifaceted approach to the synergistic degradation of organic pollutants. This versatility positions MOFs as a pivotal material in the field of environmental science, particularly in the efficient and sustainable removal of a wide range of contaminants.

3.3 Minerals/clay

In addressing the challenges of organic pollutant treatment, especially in the context of adsorption and Fenton reactions, the practical limitations of metal–organic frameworks (MOFs), such as high material costs and difficulties in mass production, necessitate the exploration of alternative materials. Consequently, attention has shifted towards mineral/clay matrix

materials, which are increasingly recognized for their potential in large-scale industrial applications due to their cost-effectiveness and scalability. Mineral/clay matrices, characterized by their inherent porous structure and expansive specific surface area, demonstrate exceptional adsorption capabilities. These properties render them comparable to carbonaceous matrices and MOFs in terms of effectiveness as adsorbents. The primary mechanisms underpinning the adsorption capabilities of these materials include capillary action, surface tension dynamics, hydrogen bond formation, and van der Waals forces. Notable among the spectrum of mineral/clay matrices are substances such as kaolin, diatomaceous earth, sepiolite, bentonite, perlite, SiO_2, attapulgite, vermiculite, fly ash, and opal. Montmorillonite, in particular, stands out for its immense specific surface area and substantial cation exchange capacity.[85] The inherent qualities of mineral/clay matrices, including their abundance, economic viability, chemical stability, and thermal consistency, position them as ideal candidates for adsorbents and precursor materials. Moreover, the ease of modification of these materials facilitates the loading of metal substances with Fenton catalytic effects, thereby enabling their application in Fenton reactions. This capacity for modification enhances the suitability of mineral/clay matrix materials for adsorption and Fenton synergy. Consequently, mineral/clay matrix materials emerge as exceptionally viable materials for the treatment of organic pollutants, particularly in contexts where large-scale production and cost-effectiveness are paramount (Fig. 10).

It is note that the clay-based supports are also efficient in heterogeneous Fenton catalyst function for PFAS decomposition. Indeed, the per- and polyfluoroalkyl substances (PFAS) are manufactured chemicals that have been widely used in industry, and continuously exposed in water in the form of perfluorooctanoic acid (PFOA). It is reported that an iron–clay(montmorillonite)-cyclodextrin(β-CD)-DFB (decafluorobiphenyl) with the iron-clay segment containing a heterogeneous Fenton catalyst function, could adsorbed and oxidized more than 65% of long-chain PFAS within 10 min.[86]

In the realm of environmental remediation, similar to other materials previously discussed, mineral/clay matrix materials have been explored for their potential in synergistic applications combining adsorption with various Fenton processes. This exploration encompasses integrating these materials in traditional Fenton reactions, electro-Fenton systems, and photo-Fenton processes.

3.3.1 Metal oxides. In the realm of mineral materials, metal oxides stand out as direct and fundamental components, especially for catalytic applications involving adsorption and Fenton-like reactions. Emphasizing this, Liu and colleagues employed the impregnation-calcination method to create a magnetic Fe_3O_4/CeO_2 composite material. This material is characterized by a highly ordered mesoporous structure and a substantial specific surface area, making it particularly effective for the removal of methylene blue (MB).[87] The remarkable adsorption capacity of the mesoporous Fe_3O_4/CeO_2 is largely attributed to its abundant oxygen vacancies, extensive specific surface area, and well-organized mesoporous channels on the CeO_2 surface.

3.3.2 Silica and bentonite. Besides, the utilization of silica, a mineral material well-regarded for its porous architecture, has been effectively harnessed in environmental remediation, particularly due to its exceptional adsorption properties. Beyond metal oxides and silica, a variety of natural stones, including clay minerals like bentonite, play a significant role in facilitating the synergistic effects of adsorption and Fenton reactions in environmental remediation. For instance, by utilizing ozone as a base material and impregnating it with Fe_3O_4 nanoparticles can effectively degrade PFAS.[88]

3.3.3 Zeolites. In addition to the above minerals and clay materials, the most commonly used mineral materials in adsorption and Fenton reactions are zeolites. Zeolite, a natural stone, has garnered significant attention in the research community due to its unique properties, which make it an exceptional adsorbent and catalyst. Characterized by its microporous structure, uniform cage-like configuration, high specific surface area, finely tunable acid–base sites, and hydrophobic characteristics, zeolite offers an ideal platform for adsorption processes.[89] Additionally, its diverse and stable framework structures, coupled with excellent ionic exchange capabilities, render it a promising carrier or host material for stabilizing metal particles. This trait facilitates the easy loading of various metals onto zeolites. Zhu and colleagues have harnessed these properties to synthesize a novel iron-doped, nanorod-shaped zeolite catalyst, Fe-ZSM-5 microsphere, with a hierarchical pore structure. This catalyst has been effectively applied in the adsorption and degradation of chlorobenzene (CB) in the presence of hydrogen peroxide (H_2O_2).[90] The unique porous structure of the zeolite plays a pivotal role in adsorbing CB into its micropores. Within these pores, the highly dispersed and valence-controlled framework of Fe^{3+}/Fe^{2+} species functions as a catalyst, initiating the Fenton oxidation of CB. The Fe-ZSM-5 microsphere also referred to as FZ-CA-5EG, exhibits an adsorption capacity comparable to that of carbon black. In the presence of H_2O_2, the Fe^{3+}/Fe^{2+} ions in the material catalyze the formation of hydroxyl radicals, which are the primary active oxygen species responsible for the oxidative degradation of CB. This demonstrates the dual functionality of the Fe-ZSM-5 microsphere, combining adsorption and oxidative
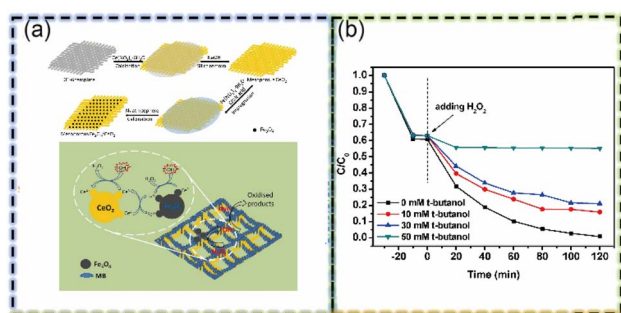

Fig. 10 (a) Schematic diagram for the preparation of mesoporous Fe_3O_4/CeO_2 and MB removal mechanism by mesoporous Fe_3O_4/CeO_2 composite. (b) Effect of t-butanol on removal of MB in Fe_3O_4/CeO_2 (Fe : Ce = 1 : 1) catalyzed system (this figure has been reproduced with permission from Li *et al.*[85] from Elsevier, copyright 2017).

degradation pathways, which underscores its potential as a highly effective material for environmental remediation, particularly in the treatment of pollutants like chlorobenzene.

In each of these scenarios, the inherent properties of mineral/clay materials, such as their wide specific surface area, porosity, and chemical stability, contribute significantly to the overall efficiency of the combined processes. The versatility of these materials, coupled with their cost-effectiveness and abundance, makes them a promising area of research in the development of advanced environmental remediation technologies. Their integration into various Fenton-based systems exemplifies a sustainable approach to addressing the complex challenge of organic pollutant degradation.

3.4 The art of material design

To maximize the combined benefits of adsorption and Fenton oxidation for water purification, it is imperative to enhance the adsorption capacity and improve the Fenton reaction's efficiency.

Firstly, the selected substrate must exhibit robust adsorption characteristics, which are primarily driven by factors such as an extensive specific surface area and a porous structure. Leading strategies to boost adsorption capacity emphasize the use of materials with inherent porous structures, particularly activated carbon. Upon establishing the fundamental properties of the adsorption medium, enhancing its adsorption capacity may require introducing additional components. For example, materials rich in π bonds can leverage the π–π bond stacking mechanism to fortify their adsorption capabilities. Prominent materials in this context include graphene, carbon nanotubes, and g-C_3N_4. The choice of these materials is not merely based on their intrinsic π bonds; their ability to host hydrophilic functional groups is also crucial.[82] These groups, naturally efficient at adsorption, further heighten the overall adsorptive potential of the substrate. Moreover, electrostatic interactions present a vital tool for enhancing adsorption. The synergistic combination of electrostatic interactions, π–π stacking, and hydrogen bonding underpins many Metal–Organic Frameworks (MOFs), signaling a renewed perspective in materials science.

Secondly, to achieving the Fenton reaction's efficiency, the increasing active sites and enhancing electron transfer in the architectures of supports are called for.

However, within applied research, particularly in environmental engineering and conservation, the dual concerns of cost-effectiveness and sustainability frequently emerge. This shows that utilizing cost-effective mineral or clay-based materials provides practical solutions. When these substrates undergo specific scientific alterations, they significantly improve their inherent capacities, facilitating a robust synergy between adsorption processes and Fenton oxidation in multifaceted aquatic environments. This methodology elevates contaminant removal efficiency and promotes prudent resource allocation. From an environmental and sustainable materials science perspective, biochar stands out. As a carbon-dense, renewable material derived from biomass, biochar exhibits a range of physicochemical attributes, making it apt for water

treatment applications and a substrate of considerable research relevance. Its untapped potential presents opportunities for innovative strides in sustainable water treatment techniques.

4 Application

The synergistic prowess of combining adsorption with Fenton oxidation, showcasing its efficacy in mitigating water pollution. Indeed, these applications span several domains, including medical wastewater treatment,[91] industrial wastewater treatment,[32] and urban wastewater treatment.[92] This broad array of applications not only demonstrates the versatility of these methods but also highlights their potential to contribute significantly to environmental conservation efforts.

4.1 Medical wastewater

The domain of medical wastewater represents one of the most critically affected areas in terms of organic pollutant contamination. The effective degradation of organic pollutants in medical wastewater emerges as a paramount application field. Medical wastewater is predominantly characterized by trace concentrations of soluble drugs[91] and antibiotics.[25] These contaminants, due to their minuscule concentrations, often elude the efficacy of traditional water treatment methods like precipitation and neutralization, which are typically insufficient in such scenarios.[25] Considering these challenges, the synergistic employment of adsorption and Fenton oxidation has emerged as a highly effective strategy for treating such contaminated water systems.

In practical scenarios, especially for large-scale treatment of diverse organic pollutants in medical waste liquids, the selection of Fenton catalytic materials predominantly focuses on carbonaceous and mineral materials.[93] As a typical carbonaceous material, biochar materials are of particular interest due to their high specific surface area, akin to other adsorbents, and their effective absorption of harmful substances found in medical waste liquids. The production of biochar involves the pyrolysis of biomass materials under low-oxygen conditions, a process that transforms waste materials into beneficial products, thereby reducing waste accumulation and environmental pollution.[62] Biochar's relatively low production and application costs render it a better way for real water treatment than other advanced materials like graphene, carbon nanotubes, and Metal–Organic Frameworks (MOFs).[25,91–94]

For instance, Zhou and colleagues have innovatively developed biochar-based adsorptive catalysts derived from waste leather (WLBC) by chemically modifying waste leather. This modification is designed for the dual purpose of adsorption and Fenton co-processing of sulfamethoxazole (SMX), an antibiotic frequently present in large-scale medical waste liquids.[25] The chemically modified WLBC demonstrates exceptional efficiency in adsorbing trace quantities of SMX, utilizing mechanisms such as electrostatic attraction, hydrophobic interaction, and π–π interactions. Additionally, the surface functional groups of WLBC are adept at chelating chromium ions, thereby facilitating their incorporation into the WLBC. In an environment

containing hydrogen peroxide (H_2O_2), these chromium ions catalyze the $Cr(VI)/Cr(III)$ redox cycle, resulting in the prolific generation of hydroxyl radicals ($^{\cdot}OH$). These radicals play a crucial role in the Fenton degradation of SMX that is absorbed on the WLBC. This study proposes a feasible strategy for the large-scale treatment of antibiotic-laden medical waste. Particularly laudable is the utilization of waste leather as the raw material, effectively embodying a waste-to-treatment approach for the control of organic pollutants. This innovative method not only addresses the pressing issue of waste management but also significantly contributes to the sustainable handling of environmental contaminants.

Similarly employing biochar materials, the research team led by Della-Flora A. has demonstrated the effective use of avocado seed activated carbon (ASAC) in medical wastewater treatment.[91] In 2020, the team led by Della-Flora A. implemented a novel approach combining adsorption with solar-driven Fenton reactions (SPF) using avocado seed activated carbon (ASAC) to address the presence of the anticancer drug flutamide (FLUT) in medical waste. This method involved the use of ASAC as an adsorbent in conjunction with SPF to effectively treat FLUT. The primary step in this process is the adsorption of FLUT onto the ASAC surface, facilitated primarily by π–π interactions. Additionally, the surface activated ASAC, characterized by its abundance of functional groups, allows for the even distribution of iron ions on its surface. In the presence of the Fenton reagent hydrogen peroxide (H_2O_2), the iron laden ASAC catalyzes the generation of hydroxyl radicals ($^{\cdot}HO$) through the Fe^{2+}/Fe^{3+} redox cycle, enhanced by sunlight. These hydroxyl radicals are instrumental in the rapid Fenton degradation of FLUT absorbed on the ASAC surface. This process exemplifies the effective synergy.

4.2 Industrial wastewater treatment

Industrial wastewater represents a significant challenge in the realm of organic pollution, characterized by a diverse array of organic contaminants. This complexity is due to the variety of industries contributing to wastewater, each with its specific type of organic pollutants. The predominant contaminants encapsulate Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), salicylic acid (SA), phenol, and related compounds. The primary culprits, as identified, are wastewater from textiles, refineries, dairies, and pharmaceutical sectors.[32] Additionally, the industrial environment's complexity and the diversity of wastewater characteristics, such as varying pH values, necessitate a broad range of materials for effective treatment using adsorption and Fenton synergies between adsorption and photo-Fenton mechanisms. Following this, in 2021, the same team progressed to degrading a mixture of nine drugs, including fluconazole, using the identical material (ASAC) in combination with Solar Fenton (SPF).[91] The mechanisms of adsorption and Fenton reactions in this instance were analogous to those previously described. The integration of adsorption and photo-Fenton processes resulted in remarkably high degradation rates for the target pharmaceuticals. Specifically, fluconazole experienced a degradation rate of up to 80%, while the remaining eight drugs in the mixture were degraded by up to 99%. This research not only presents an advanced methodology for wastewater treatment but also underscores the efficacy of utilizing natural materials like avocado seed carbon in environmental remediation, offering sustainable and efficient solutions for managing pharmaceutical pollutants (Fig. 11).

In the treatment of industrial wastewater, the materials employed to exploit the synergy between adsorption and Fenton
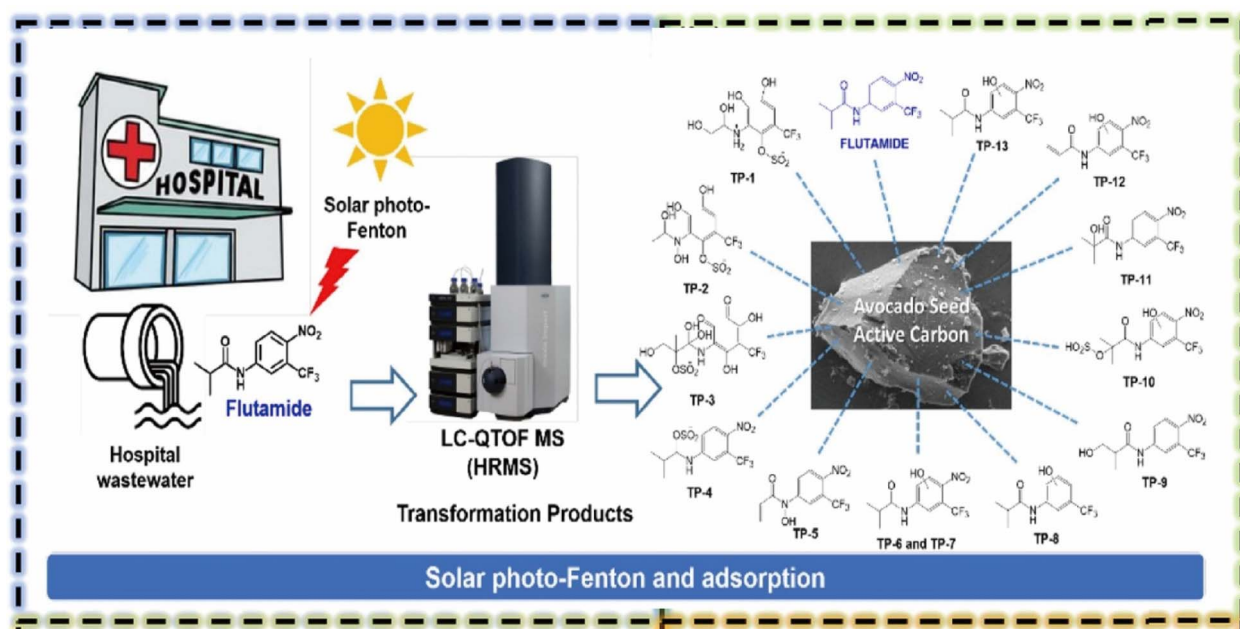

Fig. 11 Scanning electron microscopy of ASAC and proposed adsorption mechanisms and interaction of FLUT and TPs present after solar photo-Fenton treatment in a competitive and of HWW matrix (this figure has been reproduced with permission from Della-Flora A. *et al.*[91] from Elsevier, copyright 2021).

processes are diverse.[95–103] These include: (i) activated carbon: widely used due to its high surface area and porous structure, making it effective for absorbing a wide range of organic pollutants; (ii) graphene and carbon nanotubes: known for their exceptional adsorption capacities and ability to enhance catalytic processes, these materials are effective in removing complex organic compounds; (iii) graphitic carbon nitride (g-C_3N_4): this material is notable for its stability and photocatalytic properties, making it suitable for photo-Fenton applications; (iv) biochar: a sustainable option, biochar is effective in absorbing various organic pollutants and is often used in conjunction with Fenton reactions; (v) Metal–Organic Frameworks (MOFs): MOFs are known for their high porosity and customizable structure, which can be tailored for specific pollutants; (vi) minerals/clay materials: these materials are valued for their natural abundance, adsorption capabilities, and stability, making them suitable for a range of applications. When treating industrial wastewater, the combination of adsorption with various Fenton processes is applied, including traditional Fenton, electro-Fenton, and photo-Fenton. Each combination offers unique advantages and is selected based on the specific requirements of the wastewater being treated.

4.3   Urban wastewater treatment

The final realm of application for the synergy of adsorption and Fenton processes holds significant relevance to everyday life, particularly in urban sewage treatment. Given the unique characteristics of urban sewage, the selection of materials for practical applications is crucial. Predominantly, activated carbon, biochar, and minerals/clay are employed extensively in actual urban sewage treatment due to their efficacy and safety.[92,104–108]

For instance, impregnating granular activated carbon (GAC) with Fe ions has been proved to be an efficient method for the degradation of the antibiotics for urban wastewater.[92] Meanwhile the biochar also utilized for organic pollutant degradation.[107] Particularly, the innovative work by Zeng et al., explored the direct application of iron-containing minerals, specifically pyrite (FeS_2), goethite (α-FeOOH), and magnetite (Fe_3O_4), in the restoration of groundwater.[108] These minerals, characterized by their affordability and abundant availability, are intrinsically valuable in wastewater treatment due to their inherent composition. Each of these minerals naturally contains Fe ions, which serve as Fenton catalysts. Additionally, the ore materials themselves exhibit notable adsorption properties. Their utility is further enhanced by their electrical conductivity and magnetic properties, which allow them to function dually as both adsorbents and catalysts, that is particularly advantageous in the treatment process.

5   Conclusion and perspectives

This review provides an overview of the application of the combined action of adsorption and Fenton oxidation in water remediation. In conclusion, the combined action of adsorption and Fenton oxidation is an effective water remediation

technology that can effectively remove organic pollutants from water. The mechanisms of this combined action mainly include: the enrichment effect of the adsorbent on pollutants, the catalytic effect of the adsorbent on the Fenton oxidation reaction, and the protective effect of the adsorbent on hydroxyl radicals. This combined action has been used to remove a variety of organic pollutants from water, including aromatics, phenols, and pesticides. However, there are still rooms for future improvement for Fenton oxidations:

(i) New adsorbent/catalyst composite materials to improve the efficiency and stability of the combined action are required for future study. The adsorbent not only adsorbs pollutants but also catalyzes the Fenton oxidation process. This dual function accelerates the degradation of organic compounds. Therefore, the investigating the optimal conditions for this catalytic effect such as pH, temperature, and adsorbent dosage remains an important avenue for research.

(ii) The application effect of the combined action in complex water bodies are still need to be investigated. It is needed to conduct a more in-depth study on the application effects of combined action in complex water bodies. This includes considering the interactions between different components of wastewater, environmental factors, and possible synergistic effects. Research in this field will help optimize the treatment strategies for complex water bodies based on the Fenton reaction.

(iii) Develop economic and large-scale application technologies of the combined action are also called for. For instance, the utilization of mineral or clay-based materials or other cost-effective materials in Fenton reaction may provide practical solutions.

In conclusion the combined action of adsorption and Fenton oxidation holds promise for sustainable water remediation. Addressing the above outlined research gaps will contribute to its future success.

Data availability

No new data were collected or analyzed in this study.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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