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Sludge-derived biochar: A review on the influence of synthesis conditions on environmental risk reduction and removal mechanism of wastewater pollutants

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Abstract: In the context of resource utilization, the applications of waste biomass have attracted increasing attention. Previous studies have shown that forming biochar by heat treatment of sludge could replace the traditional sludge disposal methods, and sludge biochar is proved to be efficient in wastewater treatment. In this work, the pyrolysis, hydrothermal carbonization and microwave pyrolysis methods for preparing sludge biochar were reviewed, and the effects of different modification methods on the performance of sludge biochar in the synthesis process were comprehensively analyzed. This review also summarized the risk control of heavy metal leaching in sludge biochar, increasing the pyrolysis temperature and use of the fractional pyrolysis or co-pyrolysis were usually effectively meathods to reduce the leaching risk of heavy metal in the system, which is crucial for the wide application of sludge biochar in sewage treatment. At the same time, the adsorption mechanism of sludge biochar and the catalytic mechanism as the catalytic material in AOPs reaction, the process of radical and non-radical pathway and the possible impacts in the sludge biochar catalytic process were also analyzed in this paper

Introduction

With the increasing development of industrialization, wastewater treatment is facing a formidable challenge in China. Many organic contaminants such as dyes, antibiotics, petroleum hydrocarbons and emulsified oils from industrial wastewater with stable chemical properties are difficult to be removed via traditional treatment methods (e.g., biological, sedimentation, membrane filtration, and physicochemical methods) to reach environmental requirements. Therefore, it is extremely urgent to develop efficiently methods for the various types of hard-to-degrade pollutants treatment in wastewater.

Advanced oxidation processes (AOPs), have been highly recommended in wastewater treatment to degrade refractory pollutants. This is owing to AOPs are characterized by the generation of hydroxyl free radicals and other active species with strong oxidation capacity (Bogacki and Al-Hazmi 2017). Recently studies showed that, carbon-based materials oxidation as non-homogeneous catalysts, could degrade pollutants without secondary pollution, through radical and non radical pathways and exhibit significant performance in AOPs.

Biochar (BC) is a kind of carbon material prepared from agricultural waste, food waste, sludge and other biomass as raw material. It can avoid the toxicity and leaching problems of metal catalysts, and show good catalytic activity and excellent stability in a wide pH range (Qiu et al. 2022), and has been widely used in wastewater treatment. Sludge is a major by-product of sewage treatment, which is complex in composition and contains various harmful substances such as organic pollutants, trace elements and heavy metals (Borgulat et al. 2022). Therefore, sewage sludge has the dual characteristics of recyclability and environmental pollution risk. However, incineration produces a mass of secondary pollutants (e.g., exhaust gases, soot, dioxins, etc.) while landfills would take up land resources and introduce toxic and harmful pollutants into soil, groundwater and food chain, endangering the environment and human safety. As a result, this makes it challenging to dispose of sewage sludge. Pyrolysis is a kind of efficient and environmental friendly sludge treatment method. Under inert protective gas filling, sludge was converted into biochar by high temperature via this thermal treatment technology. Not only the harmful substances from sludge can be removed, but also sludge can be converted into fuels such as bio-oil and bio-gas in this process (Pulka et al. 2016) (Fig. 1). Figure 1 summarizes the various sludge treatment methods and the concept of sustainable value technology. After pyrolysis, the ash is removed from the sludge biochar, meanwhile, some organic components in the sludge are converted into gases, which then escape to the external, leaving a large number of pore structures on the surface. In addition, the leaching of heavy metals and other inorganic substances are greatly reduced after heat treatment, preventing secondary pollutions (Szarek 2020), so sludge biochar is now widely reported as a value-added product. In previous studies, many applications of sludge biochar and its modified composites as adsorbents are used in wastewater treatment had been reported (Piekarski et al. 2021). Zhang et al. used the adsorbent prepared by carbonization of sludge, the removal efficiency of Cr by was 97.5%, 95.1% and 84.5% respectively at the initial concentration of 20 mg/L, 50 mg/L and 100 mg/L (Zhang et al. 2019). The sludge biochar also plays an effective role in decolorization for printing and dyeing wastewater. Streit et al. Had been used activated carbon from beverage sludge, The maximum values for adsorption capacities were 287.1 mg g^{1} for Allura Red and 640.7 mg g^{1} for Crystal Violet (Streit et al. 2019).

Sludge comes from a wide range of sources, and the pyrolysis products have a wide variety of surface functional groups, large specific surface area, porous layered structure and high porosity. Hence, sludge biochar can be used not only as an adsorbent but also as a catalytic material in AOPs to remove a wide range of pollutants from wastewater. Good pollutants removal scores arose when sludge biochar was used in AOPs technology, which has been reported extensively, including catalysis of persulfate (PS), hydrogen peroxide (H_2O_2), and non-homogeneous Fenton. For instance, sludge--derived biochar-activated PMS was utilized by Wang et al. to remove triclosan from wastewater, with the removal efficiency of 98.9% under optimal conditions (Wang and Wang 2019). Zhang et al. prepared magnetic sludge biochar-activated H_2O_2 degradation for the degradation of methylene blue (MB), achieving a removal efficiency of 98% in 12 min (Zhang et al. 2018). These suggested that sludge biochar is an ideal material for catalytic oxidation.

Co-pyrolysis is a process in which two or more raw materials are treated in the same pyrolysis operating system. Two materials with vastly different compositions will interact under high temperature. This interaction can induce a synergistic effect in the process of co-pyrolysis, therefore, the co-pyrolysis technology can effectively combine the good properties of raw materials to improve the characteristics of biochar. In the process of co-pyrolysis, temperature, raw material, doping ratio and other factors will affect the characteristics of biochar. It is most likely to improve the adsorption capacity of sludge biochar by optimizing co-pyrolysis reaction parameters.

In this study, the preparation and modification of sludge biochar were introduced, the relationship between pyrolysis temperature, pyrolysis rate and sludge biochar performance and the effect of temperature on heavy metal leaching efficiency were explored. Both the mechanism of fixing heavy metals by co-pyrolysis sludge biochar, and the mechanism of elaborating sludge biochar activate AOPs as adsorbent material and catalyst in the system were discussed. The selection of raw material and preparation methods of sludge biochar could be provided this study. Additionally, this research obtained from new ideas for the disposal of urban sludge and industrial sludge to achieve better resource utilization.

Preparation and modification methods of sludge biochar

Carbonation method

The common sludge carbonization methods include pyrolysis, hydrothermal methods, microwave and gasification method. The physical and chemical properties of carbon materials often vary with different the heating time, heating rate and temperature. Although the sludge from sewage plants is and dried by centrifugation, But the water content is still high. For reducing the loss of energy in the subsequent pyrolysis process, the sludge should be dried firstly under the temperature of 55–75°C. In addition, there are differences in the selection of sludge sources. Industrial sludge contains flammable substances occasionally, so the drying temperature should not be too high.

Pyrolysis method

Pyrolysis, as the most common method for biochar carbonization, can blow off or degrade the chemical components under inert gas. The pyrolysis method is divided into slow

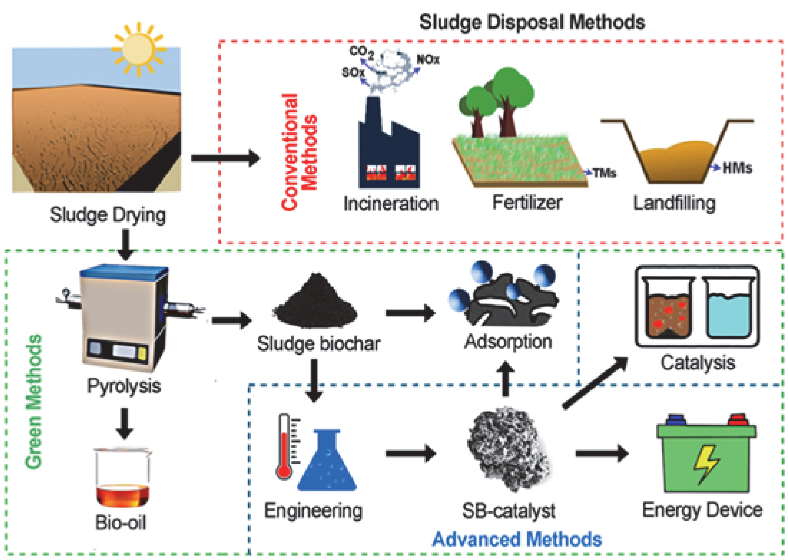

Fig. 1. Schematic illustration of the sludge disposal methods and the concept of sustainable valorization techniques. Reprinted with permission of Ref. Mian et al. (2021b).

pyrolysis and fast pyrolysis. In the slow pyrolysis process, the heating rate, constant temperature, the carbonization temperature were set at 3–25°C/min, 4 ± 2 h and 350–1000°C, respectively. The fast pyrolysis is performed under the heating rate of 10–200°C/min, and the constant temperature of 20 min, Under 450–850°C, (Wang et al. 2022). Due to insufficient reaction time of charring, the organic matter was converted into ash prematurely in fast pyrolysis, leading to the decrease the yield of carbon material, The productive efficiency of slow pyrolysis was higher than fast pyrolysis. However, on the surface of biochar, more -OH and -COOH were produced in fast pyrolysis. This was beneficial to the activation of PMS. At the same time, the carbon material produced had smaller particle size and was prone less to agglomerate in fast pyrolysis. These characteristics provided the generated sludge biochar a better adsorption capability and increased its contact area with oxidants and pollutants.

Hydrothermal method

Hydrothermal method is a mild and low-energy heat treatment method. In this process, water is added to the pressure vessel to heat the sludge biochar. This technology is economical and energy-saving due to the absence of pretreatment of dehydration and drying. The hydrothermal reaction temperature is generally below 250°C, and the heating time would be controlled within 24 hours. while there are rich functional groups on the surface of the sludge biochar prepared by hydrothermal method, its internal aromatization structure and graphitization structure are so minimal that electrostatic attraction and mediated electron transfer ability are weak. To improve this shortcoming, transition metals, (e.g., iron, zinc) are usually added in the hydrothermal process to accelerate the electron transfer capacity.

Microwave method

Microwave heating method is different from the traditional pyrolysis method. since Water has excellent microwave absorption capacity, Microwave was performed by using microwave to induce the internal structure and organization of sludge to make the sludge heated from the inside out, the efficiency of pyrolysis for the biomass with higher water content could be improved. On the other hand, this heating method is more uniform, fast and easy to operate and can be applied to prepare bio-oil, bio-gas and biochar using sludge as raw material. The product of microwave pyrolysis has a more developed microporous structure. With the increase of microwave temperature, the specific surface area of the product increases, while the leaching of heavy metals decreases. It was found that by microwave pyrolysis, the leaching efficiency of heavy metals from sludge biochar was about (60–70%), which was lower than that of conventional pyrolysis (70–80%) (Wallace et al. 2019). This stemmed from that the effect of reduction of heating time and the high-energy center effect (Wang et al. 2022).

Gasification method

Sludge gasification technology refers to that, under 700–900°C, inert gas is added continuously into a pressure reactor and react with gasifiers (oxygen, nitrogen, water vapor, carbon dioxide) to generate biomass fuel. The carbonaceous organic matter in sludge is converted to fuel gas at high temperatures and pathogens and bacteria are killed simultaneously. In addition, gasification is also widely used in the preparation of biochar. For example, Supercritical water gasification (when the temperature and pressure are greater than the critical point of the fluid without liquefaction, this fluid is called supercritical fluid) is the main means of gasification for biochar. H_2 can be generated by adding the composite catalytic materials, and the heavy metals with the prepared biochar are stable in nature (Wei et al. 2021). The ash produced during the sludge pyrolysis can be used to conduct the recovery for phosphorus (Marzena et al. 2020).

Modification methods

Sludge biochar shows excellent potential in the field of adsorption and catalysis, but there are still problems such as underdeveloped pore structure and few active sites. The modification methods commonly used are physical activation techniques and chemical activation techniques, such as changing the reaction temperature, medium, or adding some additives to the precursors, In order to improve the performance.

Physical activation

Physical activation is an environmentally friendly and safely technology, that is atomic crosslinking is destroyed by increasing pyrolysis temperature, so as to form pore structure of sludge biochar. In this process, the macroporous structure of sludge biochar to gradual collapse and creation of microporous structure over 800°C, selection and flow velocity of inert gas became the key steps to improve the performance due to delaying the oxidation, and the specific surface area and porosity of biochar can also be increased by increasing gas flow rate and temperature (Duan et al. 2021).

Table 1. Modification methods advantages/disadvantages

Carbonation method		Advantage	Disadvantage
pyrolysis	fast pyrolysis	More -OH and -COOH groups Increase indicated size	Low yield of carbon materials High energy consumption.
	slow pyrolysis	High yield of carbon materials Low energy loss	Few functional groups Easy agglomerate.
Microwave method		More developed microporous structure Stability of heavy metals asy operation	High energy consumption
Hydrothermal method		Low energy consumption Rich functional groups	Carbonization incompletely minimal internal aromatization structure and graphitization structure
Gasification method		Stability of heavy metals	Complex operation

Chemical activation

Chemical activation is usually by pretreating the sludge with a number of inorganic reagents, including pickling before pyrolysising, alkali washing and impregnation of metal oxides. The pore structure can be enriched by dissolving organic matter and ash in the process of acid washing. By promoting polymerization and dehydration, converts fatty carbon into aromatic carbon, protects the carbon skeleton, inhibits volatile biomass loss, and prevents the rupture and collapse of the pore structure. Alkali washing the infiltration of through leads to crystalline phases expansion to increase the surface area of sludge biochar. The most widely used activation methods are doping and impregnation of transition metals, which provide Lewis acidic sites for carbon materials, promoting chemical bond breaking, and improving ion exchange and electrostatic attraction capacity (Shi et al. 2021). As a frequently-used activator, zinc chloride had been increase the surface area of sludge biochar, increase pore volume, shorten degradation reaction time. At the same time with the increasing of zinc chloride concentration, the adsorption capacity of biochar will also increase (Zhang et al. 2020). The number of surface functional groups (C=O) increased when manganese oxide and biochar were impregnated and pyrolyzed. More defects were generated on the surface of biochar loading with Mn, resulting in smaller electron transfer resistance. This improved the catalytic activity, stability and high performance for recycling (Fang et al. 2022). During pyrolysis process, heavy metals in the sludge biocharcould be interact with iron oxides and reduced to different valence states, leading to the appearance of vast active sites on the surface, improving the adsorption performance. Sludge loaded with iron oxides can be prepared for magnetic sludge biochar, which can be recycled using the external magnetic field and thus achieve reutilization.

Influence of temperature on the properties of sludge biochar and immobilization of heavy metals in sludge

The heavy metal content is the main factor that limits the use of sludge biochar. Controlling the migration ability and leaching efficiency of heavy metals is the critical factor for promoting the usage of sludge biochar. Generally speaking, under high temperature, heavy metals possess more thermal stability and tend to form a stable part inside the sludge biochar (Devi et al. 2014). The source is another crucial factor determining the sludge biochar performance and its risk of heavy metal leaching. The pollutants in sludge vary greatly for the different wastewater origins, such as petrochemical wastewater containing oil, benzene and hydrocarbons, smelting and electroplating industry wastewater with high heavy metal content, and urban domestic wastewater with detergent, chemical products and antibiotics.

Effect of pyrolysis temperature on properties

Pyrolysis temperature has an effect on the properties of sludge biochar and the fixation of heavy metals. Generally, the aromatic structure gradually emerges at about 300°C, and the N (mainly amino) and O groups in the aromatic structure (mainly C=O) gradually enrich the aromatic structure with the increase of temperature. At about 500°C, the graphitized structure appears, and the C=O group disappeared, the aromatization degree continued to increase and tended to be stable at 700°C, and graphite N and pyridine N appeared. This is beneficial for electron transport and plays a positive role in catalytic reactions. At the same time, aryl rings can provide π-electrons and form strong bonds with heavy metal ions, which also improves the stability of heavy metals. Mian et al. showed by FTIR that the strength between 600 and 800 cm^{-1} was attributed to the presence of aryl components, which were basically unchanged, indicating that the aryl C group was quite stable during the pyrolysis process (Xin et al. 2022). Li et al. found that at about 700°C, the aromatics in the sludge can decompose and form C=C structure at high temperature, and C−C and C−O bonds can be formed by thermal poly-condensation, which provides the active site for heavy metal adsorption. It was proved that biochar could prevent heavy metal leaching by chemisorption (Li et al. 2022). The presence of -COOH, -NH2, -OH and -CH groups in the organic components could be another reason for the stabilization of Heavy metals in sludge. The characteristic peak of -conh – shifted from 1660 cm^{-1} at 300°C to 1630 cm^{-1} at 500°C and 1620 cm^{-1} at 700°C, possibly due to complexation between acyl amino groups and heavy metals in pyrolysis (Xin et al. 2022). With the increase of heating time, they form oxides and sulfides with metals, and the types of functional groups gradually decrease, which reduces the activity of heavy metals (Li et al. 2022).

Effect of stepwise pyrolysis on heavy metal immobilization

Because of the long reaction time and high heating temperature, the traditional pyrolysis method of fixing heavy metals will bring high operating costs and risk of harmful gas escape. In order to shorten the heating time and reduce the leaching of heavy metals, fractional pyrolysis has become a new way of pyrolysis and fixation of heavy metals. Fractional pyrolysis could be achieved by microwave heating with fast operation. During this process, heavy metals would be fixed through the vitrification process. The fractional pyrolysis could be divided into three steps including pre-pyrolysis, cooling and re-pyrolysis. The role of pre-pyrolysis is to enhance the heating performance of sludge under microwave radiation. Both the conventional heating and microwave heating could be pre-pyrolysis methods. When conventional heating is used as the pre-pyrolysis method, it is difficult to obtain vitrified sludge biochar, thus the fixing effect of heavy metals could not as expectation (Antunes et al. 2018). If the 10-minute microwave heating is used as the pre-pyrolysis method, due to the excellent microwave absorption capacity of sludge biochar, a large number of fixed carbon points are formed during the period. When the microwave heating is repeated after cooling step, the temperature would rise rapidly, reaching more than 1400°C in a very short time, based on the high-energy site effect, the vitrification structure is rapidly generated in the biochar, and the ability of heavy metal fixing would be significantly enhanced (Chandrasekaran et al. 2013). In addition, due to the high temperature condition (1400°C) of microwave heating, part of the pores of sludge biochar would become collapsed, and some functional groups may generate solidification effects (such as complexation and cation exchange), which are also conducive to the fixation of heavy metals (Li et al. 2017).

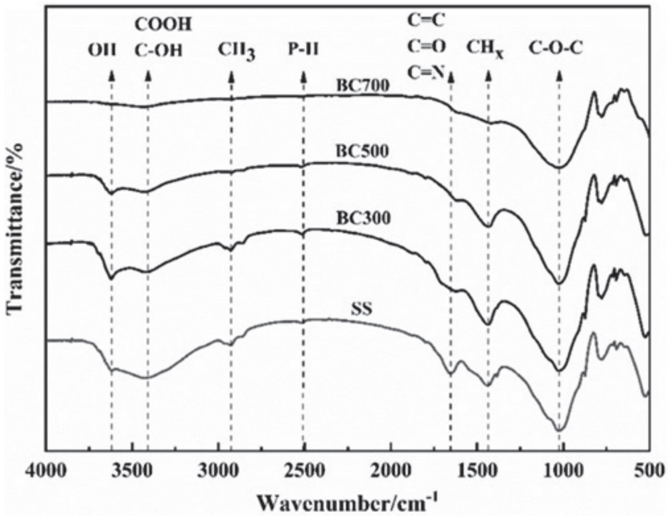

Fig. 2. 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). Reprinted with permission of Ref. Keiluweit et al. (2010)

Effect of sludge co-pyrolysis on heavy metal immobilization

Co-pyrolysis of solid wastes and sludge

Co-pyrolysis is another common method of preparing sludge biochar. During the heating process, various types of solid wastes with high biomass could be added in, which would significantly improve the performance of sludge biochar and reduce the content of heavy metals through dilution effect. Many kinds of agricultural and forestry wastes, food wastes, plastic and waste soil could become adulterated materials for sludge co-pyrolysis.

Co-pyrolysis with agricultural and forestry wastes

For example, when straw is added to the industrial sludge co-pyrolysis system, the surface functional groups of the biochar would be more abundant, the O-H bond, C-H bond, C=O bond and C-C bond are greatly increased, and the structure of carbon skeleton is enhanced (Zhang et al. 2019). The increment of lignin cellulose could reduce the enrichment of heavy metals in the biochar (Peng et al. 2022). Jindo et al. found that in the co-pyrolysis of rice husk and sludge, the inorganic and organic components were combined to produce carbon biomass containing Si-O groups (96% of rice husk ash is silicon dioxide), forming carbon encapsulation, the metals could be encapsulated within the configuration forming metal-organic framework composites in the sewage sludge-rice husk biochar (Jindo et al. 2020). When most agricultural and forestry wastes, such as rice straw, straw, sawdust, etc., are mixed with sludge for pyrolysis, the ash content decreases, and the fixed carbon content increases, which means the promotion of carbonization degree. The biochar with highly carbonization degree showed a high level of internal graphitization, as well as excellent electron transfer performance and its electron-rich domain could provide π bonds combined with metal cations for fixing heavy metals, too (Harvey et al. 2011). At the same time, due to the high calorific value of agricultural and forestry wastes, the co-pyrolysis process with sludge showed a lower energy demand (Dong et al. 2019), which also increased the porosity and the amount of functional groups, thus improving the adsorption and catalytic performance of sludge biochar.

Co-pyrolysis with food waste

Food waste, such as kitchen garbage, is a kind of solid waste rich in biomass, which containing a lot of lignin and cellulose. The biochar prepared by co-pyrolysis of sludge and food waste is also rich in organic functional groups which could fix heavy metals, and the heavy metals and inorganic components inside showed a good synergistic effect, which could be converted into metal oxides, eutectic compounds, etc. at high temperature, leading a decrease of heavy metal leaching risk. Li et al. pretreated lead-containing biomass with phosphate to prepare biochar under the pyrolysis condition of 350–450°C, in which 95% of lead has converted into lead phosphate and remained stable (Li et al. 2018). Some food residues contain animal bones, which contain a certain amount of phosphate and calcium salt Metals could react with the minerals to form stable inorganic or co-crystalline compounds such as Cu_3 $(PO4)_2$ and $Zn_2P_2O_7$, which is conducive for the fixation of heavy metals in biochar (Wang et al. 2022).

Co-pyrolysis with other solid wastes (plastics, waste residue)

Co-pyrolysis of biomass and plastics can improve the performance of sludge biochar by lowering the activation energy of the reaction to accelerate the reaction process. Common plastic wastes, such as PVC (polyvinyl chloride), are stable and hard to degrade, usually containing the additives such as $CaCO_3$, $Mg(OH)_2$, which are used to improve the performance and prolong the service life (Cherif et al. 2013). Li et al. used the co-pyrolysis of sludge and PVC (containing metal additives inside) to prepare biochar, which represented not only an increase of yield, but also an enrichment of Ca in sludge biochar due to the presence of additives (Li et al. 2022). The CaO could facilitate the formation of stable metal oxides or crystal compounds during co-pyrolysis, by forming $CaCrO_4$ or $CaCr_2O_4$, the heavy metals in the pyrolysis products were fixed.

The interior of the landfill soil contains complex pollutants, some contained organic substances inside, which could also be used as adulterants for sludge co-pyrolysis (Jia et al. 2017). This kind of co-pyrolysis biochar preparation had been reported by using hydrothermal method, which could not only save the energy during sludge dewatering, but also made the heavy metals adsorbing into the pores of sludge residue biochar after hydrothermal carbonization of sludge and residue. Additionally, in the hydrothermal process, metals with high electronegativity (Cu, Zn, Cr, Ni and Pb>1.5) could form complexes with organic ligands to prevent the leaching of heavy metals (Chen et al. 2020).

Additionally, in the hydrothermal process, metals with high electronegativity (Cu, Zn, Cr, Ni and Pb>1.5) could form complexes with organic ligands to prevent the leaching of heavy metals.The content of heavy metals in sludge and biochar were shown in Table 1, in which the content of Zn was much higher than other metals, with the maximum value of 2649.6 mg/kg. This was probably attributed to the use of galvanized steel pipes in China's municipal sewage network system. The content of heavy metals in biochar was higher than that in sludge, indicating that the heavy metals were immobilized after co-pyrolysis. The organic matter was transformed into gas or ash under high temperatures and was separated from the biochar while the heavy metals lost less mass after being heated and were concentrated inside the biochar. The heavy metals in the form of mineral salts were converted into sulfides or oxides with higher thermal stability under the high temperature. In addition, the organic matter and metal-bound parts were released due to the heat, and the metal parts formed new precipitates inside the biochar and increased with the degree of pyrolysis. The mechanisms of heavy metal immobilization were as follows: metal organic compounds being embedded in the carbon matrix or being adsorbed in the pore size of the biochar. Metals can react with the crystalline phases and minerals in the sludge to generate stable inorganic and eutectic compounds. On the other hand, metal salts were decomposed into metal oxides or silicates at high temperatures.

The mechanisms of adsorption by sludge biochar and the degradation via AOPs

The main factors affecting the adsorption mechanism of sludge biochar include surface functional groups, pore size and porosity, and pollutant properties. The adsorption process includes physical adsorption and chemical adsorption. Generally, Fourier infrared spectroscopy (FTIR), X-ray spectroscopy (XPS), adsorption kinetics, isothermal adsorption and other characteristics can be used to determine the effectiveness of adsorption and adsorption mechanism.

The porous structure of sludge biochar is the main factor of physical adsorption. The porous structure of sludge biochar is the main factor for physical adsorption. The specific surface area and the number of microporous structures are both positively correlated with the adsorption efficiency. The microporous structure and high specific surface area promote the diffusion of pollutants and ensure the uniform distribution of pollutant molecules on the surface of biochar (Kim et al. 2016). Yan et al. used zinc chloride to soak the pyrolytic carbon material of sludge. Zn atoms with larger particle size can replace H and O atoms in the sludge, increasing the specific surface area from 6.3482 m^2g^{-1} to 852.41 m^2g^{-1}, significantly improving TC adsorption efficiency (Yan et al. 2020).

Table. 2. Heavy metal concentration in co-pyrolysis sludge biochar

SB's Name	Cu [mg/kg]	Zn [mg/kg]	Pb [mg/kg]	Cr [mg/kg]	Cd [mg/kg]	Ni [mg/kg]
sludge (SB1)	111.8	1729.1	50.08	94.25	1.22	30.92
SB1 – Wood chips	149.38	2308.2	70.82	130.95	1.71	42.91
SB1 – Rice husk	155.06	2354.7	68.82	134.24	1.72	74.27
SB1 – Tea leaves	153.41	2351.62	71.60	131.51	1.68	41.5
SB1-PVC	153.93	2264.28	69.38	132.45	1.64	40.65
SB1 – Kitchen waste	153.07	2308.05	70.67	141.35	1.79	42.76
sludge (SB2)	571.05	2649.6	26.77	444.62	\	115.02
SB2 – waste residue soil	902.79	3021.63	39.62	473.75	\	128.68
sludge (SB3)	595.18	4524.9	\	79.8	\	88.42
SB3 – Coconut shell	581.4	2810	\	34.1	\	91.4
sludge (SB4)	400.28	\	27.39	87.22	2.05	30.11
SB4 – Camellia shell	305.01	\	30.82	100.07	1.28	30.21
A Permissible limits for SS	500		300	500	3	100
B Permissible limits for SS	1500		1000	1000	15	200
Permissible limits for biochar	63–1500		70–500	64–1200	1.4–3.9	47–600

SB1 was from Xiamen Municipal Sewage Treatment Plant. SB2 was from Changsha Industrial Sewage Treatment Plant. SB3 was from Tianjin Industrial Sewage Treatment Plant. SB4 was from Hefei Municipal Sewage Treatment Plant. Standard for Control of Pollutants in Agricultural Sludge (GB 4284-2018). Class A sewage sludge can be used in farmland, garden and grassland, while Class B sewage sludge can be used in garden and grassland, but cannot be used in agricultural land for crop production. The maximum allowable threshold was recommended by the International Biocarbon Initiative according to the toxicity standard of biochar.

π-π bond interaction, electrostatic attraction, ion exchange and functional group complexation are the main mechanisms of sludge biochar chemical adsorption. When sludge biochar is used as adsorbent to treat wastewater containing pollutants with aromatic ring structure (such as chemical and pharmaceutical wastewater), the chemical adsorption mainly depends on π-π interaction between sludge biochar and aromatic ring structure of pollutants. Tang et al. prepared sludge biochar for TBBPA treatment, which has the structure of benzene ring, and found that the tensile vibration peak of C=C shifted by FTIR analysis, indicating that the interaction between the π-electron-poor region of TBBPA and the π-electron-rich region on the surface of biochar is the main mechanism of adsorption of TBBPA by sludge biochar (Tang et al. 2015). Generally, the surface charge of biochar is low and the electrostatic force is poor (Oh SY et al. 2016). In the sludge biochar/phosphate system, Oh SY found that the efficiency of pollutant adsorption was closely related to its electrification, and described the process of improving the electrification and adsorption capacity of sludge biochar through the heavy metals contained. Ma's reported the adsorption of tetracycline on sludge biochar with Fe/S modification, which confirmed that electrostatic attraction, ion exchange and complexation are also important processes for the sludge biochar adsorption systems (Ma et al. 2020).

The flocculation structure of sludge and rich organic carbon make biochar have developed pore structure, large specific surface area and rich oxygen-containing functional groups. Developed pore structure and oxygen-rich functional groups provide reaction sites for pollutants and oxidants (Yu et al. 2020). The defect structure on the surface of biochar can easily form the electron transfer between oxidants and catalysts. As a catalyst, sludge biochar could produce a marked effect in the process of AOPs degradation of pollutants through two ways: radical pathway and non-radical pathway. The radical pathway is achieved by increasing the production of oxidative radicals ($\cdot OH$, $SO_4^{\cdot-}$ and $O_2^{\cdot-}$) in the AOPs system, and the non-radical pathway is achieved by catalyzing the electronic transfer between pollutants and oxidants (Mian et al. 2019) (Figure 4). Table 3 lists the AOPs system based on sludge biochar and its performance.

Radical pathway

In AOPs system, sludge biochar can improve the efficiency of oxidants (such as H_2O_2, PS, ozone, etc.) to generate $\cdot OH$, $SO_4^{\cdot-}$ and $O_2^{\cdot-}$through catalysis. In the sludge biochar/H_2O_2 system, the carbon structure doped with heteroatoms and quinone group on the sludge biochar surface could act as electronic mediums to transfer electrons to H_2O_2, producing $\cdot OH$ to achieve the purpose of degrading organic pollutants (Figure 5) (Gan et al. 2020). In sludge biochar/PS system, carbon materials are easy to activate PS decomposition through single electron transfer and release $SO_4^{\cdot-}$. Electrons from the surface of biochar can be transferred to the reaction medium for PS decomposition through free radical process, and electrons can be transferred to PMS to produce various free radicals. For example, $SO_4^{\cdot-}$ and $\cdot OH$, the electron transport rate affects the number of free radicals produced Figure 6 (Wang et al. 2018). In the sludge biochar/O_3 system, the quinone group and carbonyl group on the surface of sludge biochar could promote the decomposition of O_3 to generate $\cdot OH$ and $O_2^{\cdot-}$. The catalytic efficiency of such reactions is mainly depending on the number of quinone and carbonyl functional groups in the sludge biochar (Issaka et al. 2021).

Ye et al. prepared heterogeneous Fenton biochar with Fenton iron sludge (contained Fe $(OH)_3$) from sugar factory to degrade methylene blue. Sugar (such as glucose) contains enough $\cdot OH$ itself for reducing Fe_3O_4 and Fe_2O_3 to FeO, while Fe^{2+} has strong reducibility, and its reduction performance could accelerate the system electron transfer process and the production of $\cdot OH$ (Ye et al. 2022). Generally, metal loading is used to increase the production of $SO_4^{\cdot-}$ and $\cdot OH$ for improving the oxidative degradation effect of PS. The sludge in the water supply plant contains iron and aluminum ions of various valence states due to the process of flocculation and sedimentation. Among these ions, Fe^{2+} and Al^{3+} could accelerate the redox reaction rate and promote the production of $SO_4^{\cdot-}$ and $\cdot OH$. In addition, graphitized carbon produced by pyrolysis could be used as a non-metallic catalyst because of the electron-rich mechanism, and thevsynergistic effect between graphitized carbon and zero-valent iron in sludge biochar would promote more $SO_4^{\cdot-}$ and $\cdot OH$ production for pollutants degradation

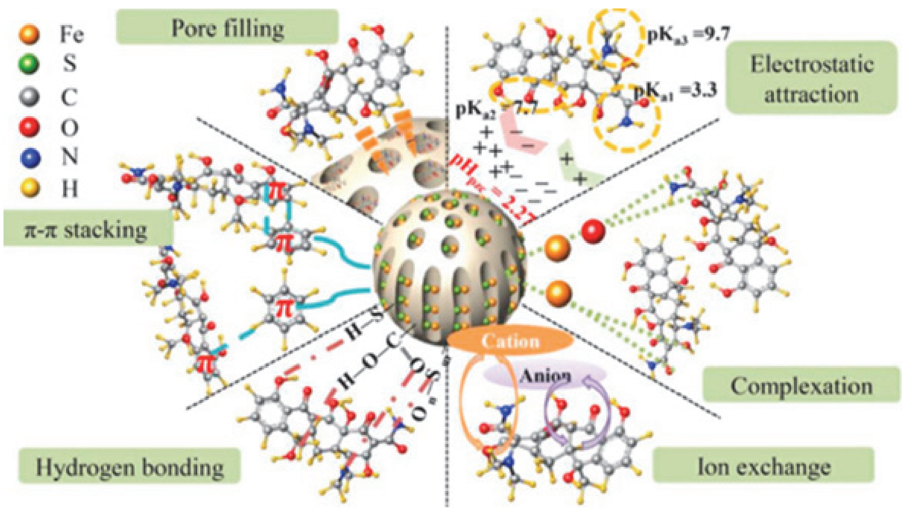

Fig. 3. Proposed mechanism of TC removal by Fe/S modified activated wasted sludge biochar (AWSB/Fe/S-4). Reprinted with permission of Ref. (Ma et al. 2020a).

Table 3. Active sites and performance of SB catalysts in various AOPs

SB's Name	Active cite	Pollutants (Pol.)	AOPs	Reactants/ (Mechanisms)	References
sewage sludge biochar	Pyridinic N, and Graphitic N	Bisphenol A	PMS	SBC→PMS (e^- transfer)	Fan et al. (2021)
Sludge biochar	Fe surface groups	Triclosan	PMS	$SO_4^{\bullet-}$, •OH, $^1O_2$	Wang and Wang (2019)
sewage sludge biochar	Fe^{2+}	Trichloroethylene	H_2O_2	•OH	Y.-F. Huang et al. (2020)
Ferric sludge – biosolid	Fe^{2+}	Aniline	H_2O_2	•OH· O^{2-}	Zhang et al. (2019)
sludge biochar/Fenton like	Fe^{2+}	Ciprofloxacin	H_2O_2	•OH· O^{2-}	Li et al. (2019)
Hydrothermal sludge biochar	C=O	Bisphenol A	PMS	$^1O_2$· non-radical process	Hu et al. (2020b)
wet sewage sludge	C=O	Sulfamethoxazole	PMS	$^1O_2$	Hu et al. (2020a)
Iron sludge/Fe_3C	Fe^{2+}, Fe^0, C=O	Ciprofloxacin	PMS	$SO_4^{\bullet-}$, •OH, $^1O_2$, O^{2-}	Zhu et al. (2019)
Red mud modified sludge biochar	Fe^{2+}, C=O, C=C	Sulfamethoxazole	PMS	$^1O_2$ Minor: $SO_4^{\bullet-}$, •OH,	Wang et al. (2020b)
nitrogen-doped sludge biochar	Fe^{2+}, Pyridinic N, Graphitic N, C=C	Tetracycline Hydrochloride	PDS	$SO_4^{\bullet-}$, •OH	Yu et al. (2019)
Valorization of plastics and paper mill sludge	Fe^{2+}	Methyl orange	PDS	$SO_4^{\bullet-}$, •OH	Kwon et al. (2020)
heterogeneous ultrasound--enhanced sludge biochar	Fe^{2+}, Fe^0	Bisphenol A	PDS	$SO_4^{\bullet-}$, •OH	Diao et al. (2020)
Fenton sludge	Fe^{2+}, Fe^0	Methylene blue	H_2O_2	•OH, $^1O_2$, O^{2-}	Guirong et al. (2022)
oily sludge	Fe^{3+}, Fe^{2+}, Fe^0	Methylene blue Sunset yellow	H_2O_2	•OH, O^{2-}	Yang et al. (2022)
Activated petroleum waste sludge biochar	Mn^{2+}, Fe^{2+}, Al^{3+}	TOC, COD, PRW	O_3	•OH	Chunmao et al. (2019)

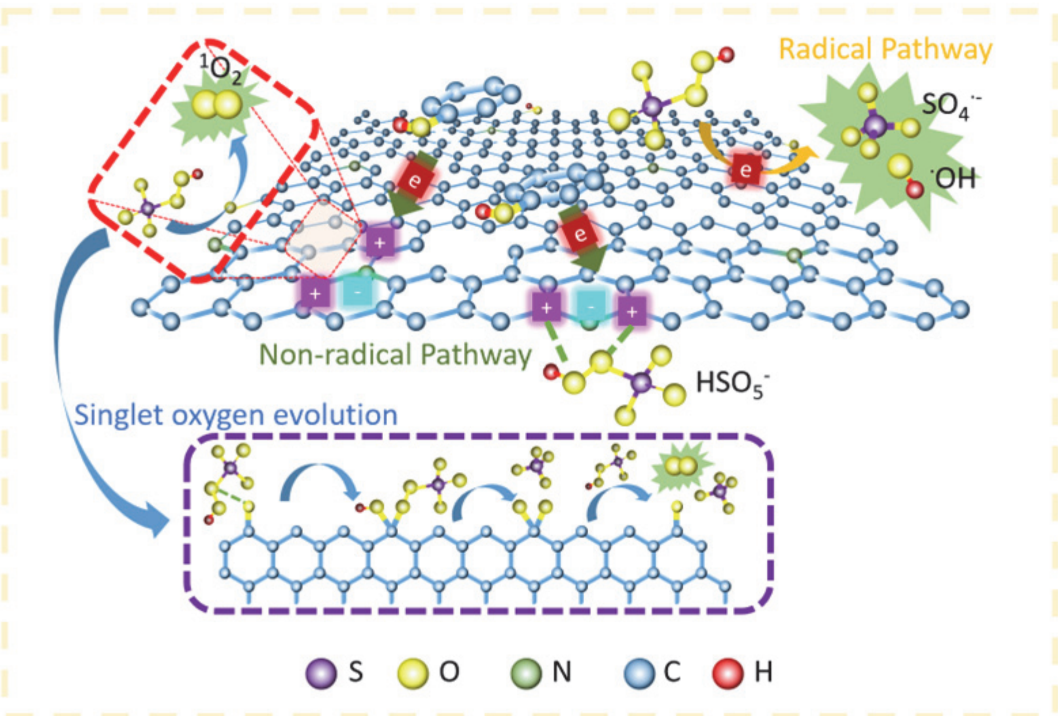

Fig. 4. Mechanism of radical and non-radical processes for phenol degradation and the evolution of singlet oxygen. Reprinted with permission from Ref. Duan et al. (2018a).

(Zeng et al. 2022). $O_2^{\cdot-}$ is also an important kind of radical in AOPs system. In previous studies, superoxide radicals have been proved to be very useful for the degradation of drugs and phenols (Zhang et al. 2022). Wu analyzed the transformation of persistent free radicals (PFRs) generated during sludge pyrolysis to form ROS, which promoted the degradation of phenol. As the redox and reduction sites for electron transfer, PFRs promoted the decomposition of PS into $SO_4^{\cdot-}$, ·OH and $O_2^{\cdot-}$, and $O_2^{\cdot-}$ was not only an intermediate produced in the formation of ·OH, but also played an important role as oxidative degradation through quenching experiments verification (Wu et al. 2020).

Non radical pathways

Pollutants Pollutants can also be degraded by non-free radical pathways. Current studies mainly focus on the biochar/PS system, where pollutants are degraded by the non-free radical mechanism of $^1O_2$ and electron transfer. $^1O_2$ is generated by the activation of PS by the oxygen vacancy on the surface of sludge biochar (Wang et al. 2020). Xu found that graphitized nitrogen can attract electrons from surrounding carbon atoms, and the positive charge of C=O bond reacts with PS more easily to generate $^1O_2$. The activation mechanism of $^1O_2$ is due to the oxygen-containing functional groups, metal ions and hemiquinones on its surface (Xu et al. 2020). Wang et al.

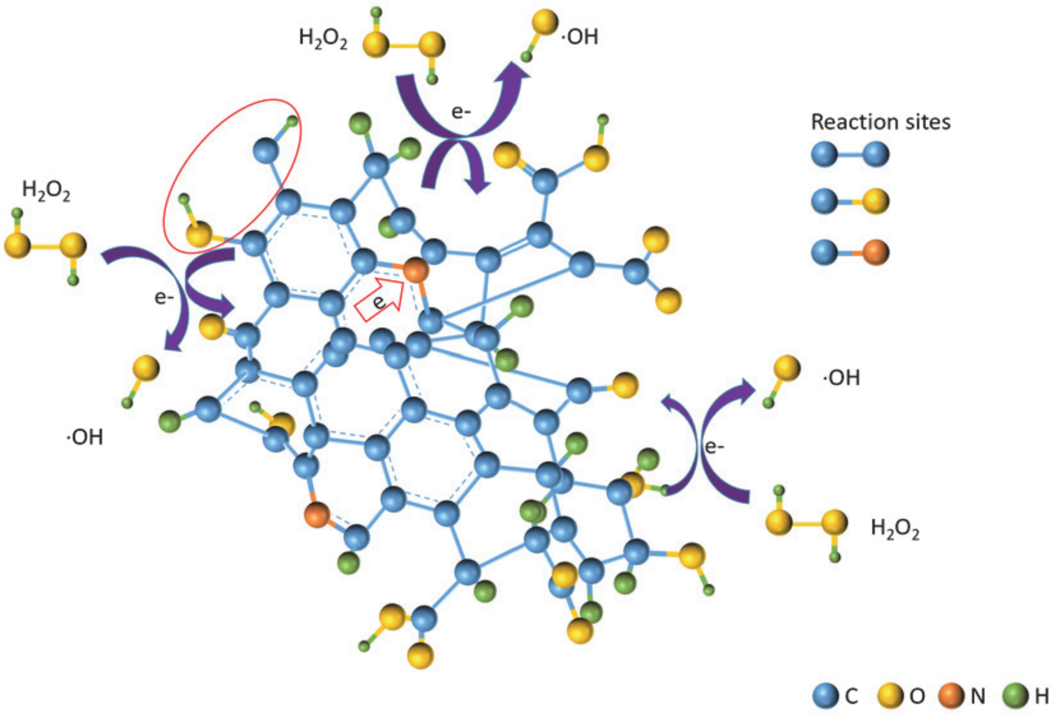

Fig. 5. The mechanisms involved in the biochar ·OH based advanced oxidation process. Reprinted with permission from Ref. Luo et al. (2019b).

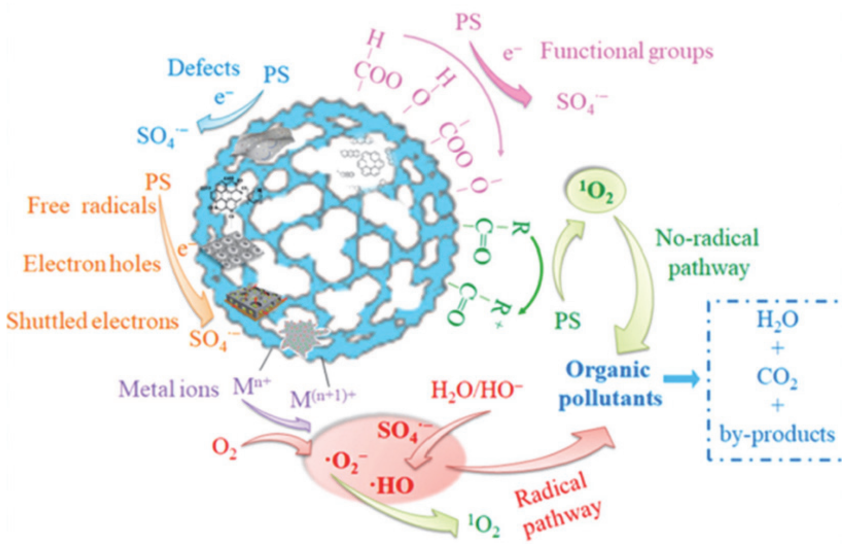

Fig. 6. The mechanisms involved in the biochar $SO_4^{\cdot\cdot}$ − based advanced oxidation process. Reprinted with permission from Ref. Zhao et al. (2021b).

removed BPA in the sludge vulcanized biochar/PS system. Electrochemical analysis of PMS activated positively charged C and S atoms to generate $^1O_2$ to degrade BPA. Previous studies have indicated that the formation of $^1O_2$ is closely related to dissolved oxygen and HCO_3^- in water, and the dissolved oxygen content has a great influence on the results in the non--free dominated degradation process (Wang et al. 2020).

In sludge biochar, the carbon element is the main factor in the electron transfer process. The pollutants are firstly adsorbed into the pores of the sludge biochar. The electron transfer with the carbon material as the conductor contacts the pollutants with PS and degrades them by oxidation (Kappler et al. 2014). To explore the mechanism of electron transfer, electrochemical methods are usually used to measure conductivity and detect the electron transfer process between the sludge biochar, PS and pollutants. In the process of activating PMS by sludge biochar (SSB), Wang et al. used the pollutant BPA PMS as an electron donor and acceptor, respectively. Anionic radical $-SO_5^-$ was generated by PMS (1). React rapidly with adjacent water molecules. (2) Generate $^1O_2$ to oxidize BPA, and heavy metals in the biochar form an unstable complex with PS on the surface (3). Weak electron transfer is performed within the complex, and the oxidation occurred on the surface of (4) (Wang et al. 2020).

$$SSB + HSO_5^- \rightarrow SO_5^- + H^+ \quad (1)$$

$$2SO_5^- + H_2O \rightarrow 2HSO_4^- + 1.5\,^1O_2 \quad (2)$$

$$SSB + S_2O_8^{2-} \rightarrow [PMS\text{-}SSB] \quad (3)$$

$$[PMS\text{-}SSB] \rightarrow SO_4^{2-} + SSB \quad (4)$$

Yang and his team studied that in the water hyacinth based sludge biochar (BC-OH-700)/PS system, the combined action of surface electrostatic adsorption and electron transfer showed excellent adsorption and degradation effects on tetracycline. The active site changed the potential distribution to strengthen the electrostatic adsorption and improve the electron transfer rate. The increase of electron transfer rate also promotes the production of $^1O_2$, thus improving the catalytic efficiency as shown in Figure. 7 (Yang et al. 2022).

Yu et al. doped nitrogen in magnetic sludge biochar/PS system and proposed three internal electron transfer pathways for magnetic Fe species, N, and sludge biochar catalytic sites. Activated PDS was more effective for tetracycline degradation compared to graphitized carbon (Yu et al. 2019). On the other hand, increasing the degradation reaction temperature can enhance chemisorption and improve the electron transfer efficiency between pollutants and PS. This was beneficial for catalytic degradation (Duan et al. 2017).

Conclusion

As a raw material for the synthesis of biochar, sludge needs more experimental and analytical work to find suitbal pathways for improving its performance due to its diverse production conditions and complex components. The works focused on sludge biochar that have been carried out untill now is mainly focused on two aspects. One is to improve the adsorption performance of sludge biochar through structural improvement and other ways; The other aspect is to improve the catalytic ability of sludge biochar in AOPs system through modification methods such as heteroatom doping. Due to the characteristics of sludge, the developments of these two applications are both limited by high operating costs and the risk of secondary pollution. Therefore, how to use more effective pyrolysis methods to avoid the leaching of heavy metals in the process of synthesizing biochar, and how to make a use of various substances (such as metal ions and carbon sources) contained in sludge from different sources for promoting its catalytic function in the treatment of various

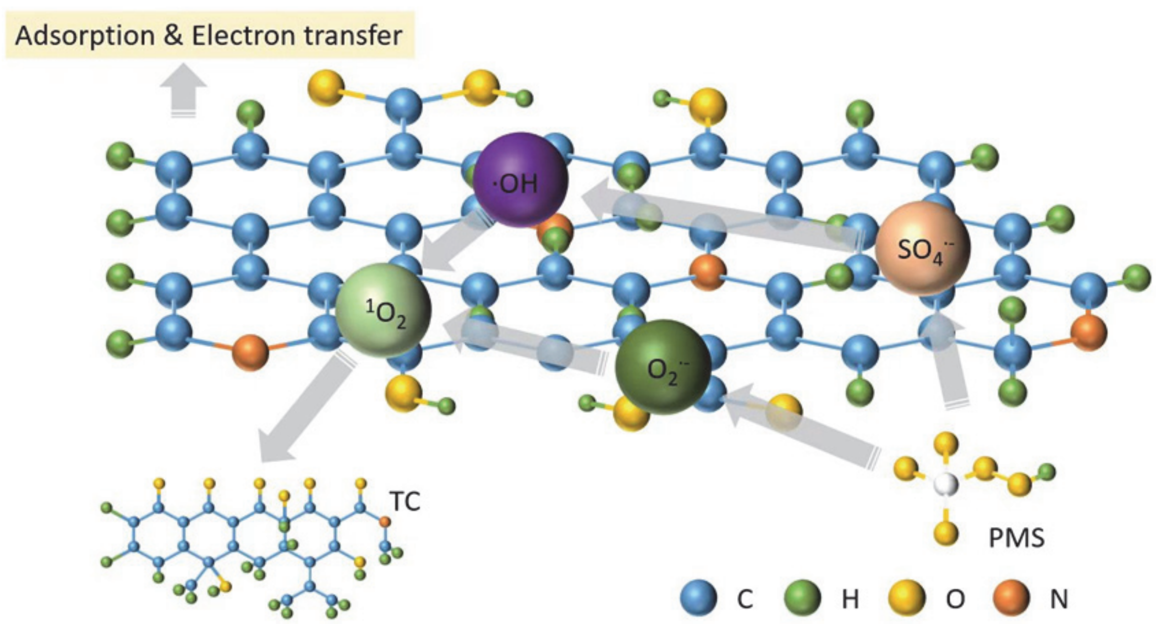

Fig. 7. Water caltrop-based carbon catalysts for cooperative adsorption andheterogeneous activation of peroxymonosulfate for tetracycline oxidationvia electron transfer and non-radical pathway Ting et al. (2022b).

types of wastewater are the future research directions, with a expectation to providing reference ways for the combined treatment of biological waste and solid waste and realizing the recycling of resources.

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