REVIEW ARTICLE

Sulfate-radicals Advanced Oxidation Processes by Biochar-based Catalysts and Applications in the Degradation of Endocrine Disrupting Chemicals in Wastewater: A Review

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ABSTRACT

Increasing input of endocrine disrupting chemicals (EDCs) has been increasing rapidly nowadays. Various wastewater treatment technologies have been studied to remove EDCs in water and wastewater. Due to its high oxidation potential and other benefits over other tertiary wastewater treatments, the establishment of advanced oxidation processes based on sulfate radicals (SR-AOP) has been of attention in recent years. There are numerous activation methods to produce sulfate radicals from peroxymonosulfate (PMS) and peroxydisulfate (PDS) such as ultrasound, transition metals, and the use of carbon catalysts. This review manuscript focuses to provide the latest overview of different methods of PDS and PMS activation and different utilization of this technology focusing on water and wastewater treatment. Besides that, this article also focused on the utilization of carbon-based catalysts as a substitute for metal catalysts as an activator in the SR-AOP process. This review also aims to discuss the perspectives for the biochar-based catalyst application and expand their potential for removing organic pollutants.
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INTRODUCTION

Nowadays, rapid development and urbanization have caused increasing input of organic pollutants such as endocrine-disrupting chemicals (EDCs) into the environment. These EDCs contributes to diseases and dysfunctionality in human and wildlife. EDCs cannot be withdrawn from the waters through conventional wastewater treatment processes. Therefore, past research has studied non-conventional methods for the elimination of EDCs from aqueous solutions (1). Various wastewater treatment methods have been studied for the effective removal of organic pollutants which include nanofiltration, photocatalysis, and advanced oxidation process (AOP). Among these, AOP has gained great interest due to its high potential to remove organic pollutants in wastewater. Recent studies showed that advanced treatments have been used to remove EDCs which is by using sulfate-radical based oxidation (SR-AOP) technology from peroxydisulfate (PDS) and peroxymonosulfate (PMS). In comparison, PDS offers a lower cost, is able to persist in the water longer, and has higher redox potential than PMS (2), making PDS a more feasible choice.

Currently, various methods of activating PDS and PMS have been developed which include ultrasound, transition metals, carbon catalysts, heat, etc. Among these methods, PDS activation by homogenous/ heterogenous catalysts defined as metal and carbon-based catalysts have gained interest from researchers. However, the durability of PDS activators by utilizing metal-based catalysts is argumentative owing to metal leaching during the process (3). Therefore, carbon-based materials have been issued as a positive and effective alternative in activating PDS. Recently, biochar technology shows promise in reducing climate change and refining soil quality, as well as lessening waste and generating energy as a by product. Biochar has a stronger adsorption capacity, larger surface area, or ample surface functional groups (SFG), which portrays a new type of carbon material with significant implications in wastewater treatments (4). Several studies have shown the application of biochar in activating PDS and PMS to be used in the degradation of

aqueous pollutants. Wang et al. described that biochar derived from sewage sludge was able to activate PMS and was then utilized to degrade triclosan in wastewater (5). Several studies discovered that the performance of catalytic biochar can be further improved with Nitrogen-doping (6). N-doping showed the most functional doping to produce active sites on biochar for PDS and PMS activation. A study by Zhu et al. produced nitrogen-doped biochar (N-doped biochar) at various temperatures and observed the mechanisms for organic pollutants' degradation (7). Therefore, this article reviewed the research development of biochar-based catalyst to activate PDS in an advanced oxidation process and its mechanism towards the degradation of organic pollutants.

ENDOCRINE DISRUPTING CHEMICALS

Environmental issues are a main global concern. Among all issues, water pollution is said to be one of the highest menacing sources of environmental problems to living health. Water is one of the critical essentials for domestic industrial and natural usage. Due to the increasing population and industrial sector, water quality is deteriorating causing a significant consequence to the environment. This led to the demand for access to clean water increasing significantly (8). Total change in land-based activities might be the main source of water pollution in river systems. Land-based activities may include agriculture and industry, residential development, and deforestation (9). Untreated and inadequately treated wastewater is one of the main roots of water pollution (10).

The improper discharge of wastewater causes the natural water bodies to be contaminated with organic and inorganic pollutants (11). These contaminants comprise endocrine-disrupting chemicals (EDCs), personal care products, heavy metal ions, dyes, pharmaceuticals, pesticides, etcetera (12). These compounds are harmful that cause hazardous consequences for humans and the environment. EDCs can be found in aquatic systems including underground water, wastewater, and drinking water (13). EDCs defines as exogenous chemicals or chemicals mixture that disrupts the endocrine function not only in the human body but also wildlife. It exists either in synthetic or natural compounds that are discharged to the aquatic environment from industrial wastewater, livestock wastes, and domestic sewage effluents (14). Figure 1 shows an overview of human exposure to EDCs. Humans can be exposed to EDCs either through natural or synthetic sources. The natural source is hormones such as progestogen, androgen, estrogen, and etcetera. The excretion of these hormones will then be absorbed in the soil and influence the composition of groundwater. The exposed

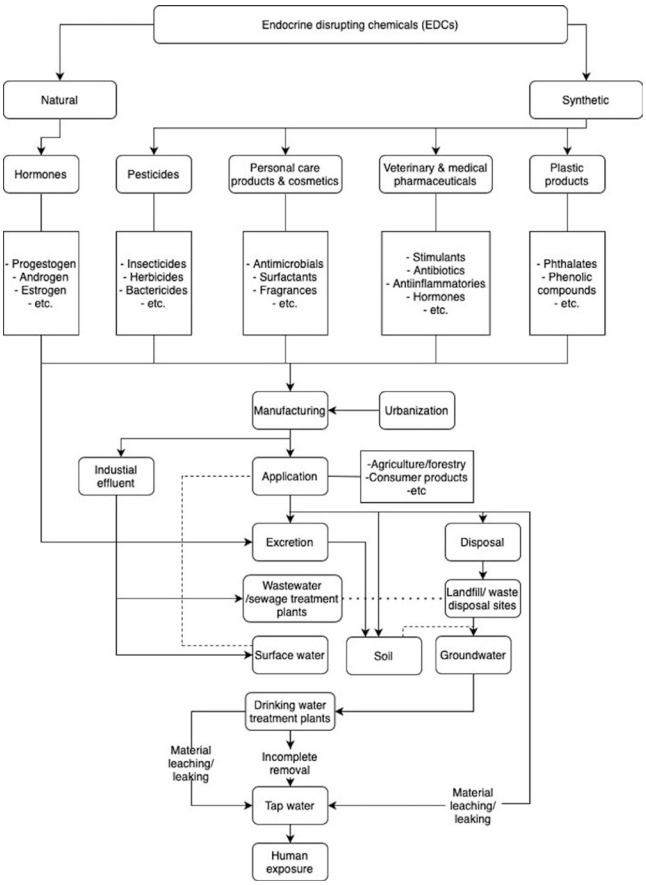

Figure 1 : Overview of human exposure to EDCs. Adapted from ref. (65).

groundwater will then be processed into drinking water in the water treatment plants. However, incomplete removal of the EDCs in the groundwater will then be passed into the tap water and simultaneously exposed to humans after consumption. Meanwhile, synthetic sources of EDCs may originate from pesticides, personal care products and cosmetics, veterinary and medical pharmaceuticals, and plastic products. These sources mainly originate from manufacturing and industrial effluent.

Industrial chemicals and pesticides produced from industrial effluent can leach into groundwater and soil, which later then make their way into the food chain. Some products manufactured in the industry such as products with fragrances, lotions, cosmetics, household chemicals, anti-bacterial soaps, and fabrics treated with flame retardants can leach EDCs and are then exposed to the consumers (14). Another example of EDC sources is processed foods produced in the industry. Materials used in processing, manufacturing, transportation, and storage contain traces of EDCs which can accumulate in processed foods. Besides that, soy-based products contain phytoestrogens, which are chemicals produced by plants that mimic estrogen hormones which if consumed by humans, will disrupt the natural hormones in the body (14). Furthermore, household dust may also contain EDCs such as flame retardants,

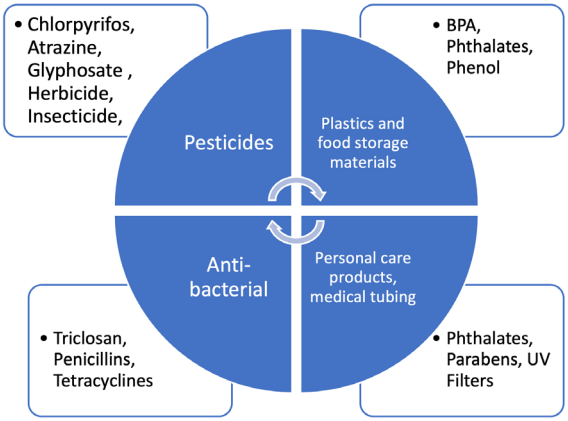

Figure 2 : Common classes of EDCs. Adapted from ref. (15).

lead, and polychlorinated biphenyls (PCBs) from furniture or weathering construction material (14). Figure 2 shows the common classes of EDCs (15).

WASTEWATER TREATMENT METHODS

Various wastewater treatment methods have been investigated by past researchers for the effective removal of organic pollutants which include nanofiltration, photocatalysis, and advanced oxidation process (AOP).

Nanofiltration (NF) is a pressure-drive membrane process using a nanoporous membrane to selectively separates contaminates in water (16). NF is a liquid-separation technology similar to the characteristic of reverse osmosis. NF membranes' pore size ranges from 1 to 10 nm, slightly larger than that of reverse osmosis membranes (16). NF has the possibility to degrade EDCs in wastewater as the size of most EDCs is inside the range of NF's molecular weight cut-off (200 – 1000 Da) (17). Figure 3 shows the classification of membranes according to different particle sizes.

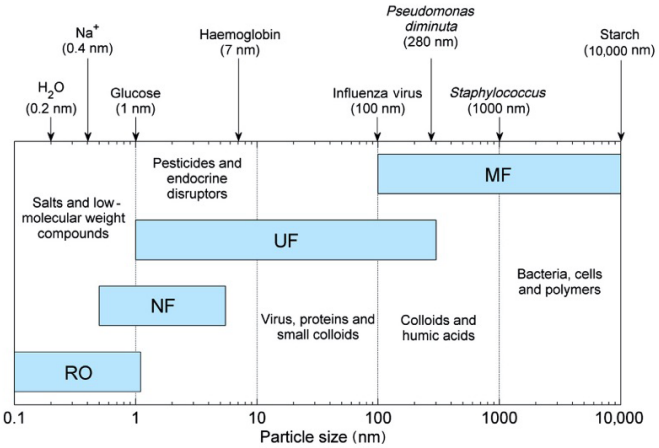

Figure 3 : Classification of Membranes according to particle size. Adapted from ref. (66).

Dai et al established MoS2 nanosheets to polyamide (PA) NF membrane to create nanochannels and hydrophilic surface in the PA rejection layer, to intensify the elimination of hydrophobic EDCs from water. Their outcomes revealed MoS2 nanosheets enhanced EDCs degradation by 6 times larger than conventional PA NF membranes (17). Emek et al examined the performance of NF membranes for the degradation of EDCs from textile industries' wastewater sources. Their experimental outcomes revealed that 10 out of 17 EDCs from textile wastewater sources were treated below their detection values limit with NF. However, compounds such as naphthalene, di-sec-octyl phthalate, and butyl phthalate were not efficient to use the NF membrane (18).

Another wastewater treatment method is photocatalysis. This method utilizes the energy produced by light and converts it to a higher energy level to drive a chemical reaction (19). Previous studies concluded that photocatalysts can degrade persistent organic compounds with the help of the absorption of light in the water (20). Titanium dioxide (TiO_2) and zinc oxide (ZnO) is the most utilized photocatalyst in the photocatalysis process. During the process, reactive oxygen species (ROS) such as hydroxyl radicals (.OH) and superoxide radical anions ($.O_2^-$) were produced when the photoinduced holes and electrons reacted with water (H_2O), oxygen (O_2), and hydroxyl radicals.

The removal of persistent organic pollutants then occurred to the existence of these ROS (21). Plenty of past research has shown significant results by utilizing photocatalysts in wastewater treatment. A study by Babu et al revealed that 98% of methyl orange degradation was achieved by utilizing CuO-TiO_2/rGO catalyst utilizing a UV light source (22). Besides that, Alvarez et al showed that degradation of amitrole was achieved at 96.90% by using an X-Ni catalyst with also utilizing a UV light source (23).

ADVANCED OXIDATION PROCESS (AOP)

AOP is based on the in situ generation of strongly reactive free radicals species which are able to partially or totally oxidize complex organic molecules (24). The advanced oxidation process based on the production of hydroxyl radicals (.OH) in water purification is the most common treatment compared to other disinfectant agents such as chlorine, ozone, or permanganate (25). The AOP concept later then has been widened to the oxidative processes with sulfate radicals (SO_4.-). Hydroxyl radicals are reliable in breaking organic compounds as they are high in redox potential (2.8 eV) and are non-selective (26). Table I showed the oxidation potential of commonly used oxidants.

Table I : Oxidation potential of commonly used oxidants (25)

Oxidant	Oxidant potential (eV)
Fluorine [F_2]	3.0
Hydroxyl radical [$HO^{\cdot}$]	2.8
Sulfate radical [$SO_4^{\cdot}$]	2.5-3.1
Ozone [O_3]	2.1
Persulfate [$S_2O_8^{2}$]	2.1
Peroxymonosulfate [HSO_5^{-}]	1.8
Hydrogen peroxide [H_2O_2]	1.8
Permanganate [MnO_4^{-}]	1.7
Chlorine dioxide [ClO_2]	1.5
Chlorine [Cl_2]	1.4

Garrido et al stated that ·OH's reaction with organic contaminants leads to the formation of carbon radicals (R or R-HO) that can create organic peroxyl radical (ROO) with O_2 (26). These ·OH's reaction causes the generation of more reactive species namely hydrogen peroxide, therefore, chemical destruction and mineralization of organic compounds then might occur (25). Nevertheless, these hydroxyl radicals have a limited lifetime, therefore activation is required to produce free-radical or non-radical reactive species with higher reactivity. Common activation methods are by using oxidizing agents (hydrogen peroxide and ozone), catalysts, and irradiation (ultrasound or ultraviolet light) (25). In UV-based AOP, the most often catalyst used to generate these radicals is Titanium dioxide (TiO_2), where TiO_2 particles produce and excite positive holes in the valence band with an oxidative capacity and negative electron at the conduction band. With the reaction of O_2.-, H_2O, and OH- at the surface of TiO2, these holes and electrons are able to increase the generation of hydroxyl radicals (25).

In other ways, the utilization of iron as a catalyst is also widely studied with O3 and H_2O_2 as catalysts called as Fenton process that can generate strong reactive oxygen species (ROS) including ·OH and SO_4.-. Generally, ·OH is generated through electron transfer but it is also can be produced by Fenton reagents (Fe^{2+} and H_2O_2). These reagents are added to wastewater which then reacts to form hydroxyl radicals (27). Operating parameters such as H_2O_2 and Fe^{2+} concentrations, reaction temperature, and pH value will affect the Fenton process efficiency (27). Hence, the optimal molar ratio of hydrogen peroxide to ion needs to be determined accordingly to minimize unwanted scavenging (25). In wastewater, Fe^{3+} forms iron sludge that requires to be removed which leads to an increase in operational cost. Deng et al stated that the ·OH generation in the Fenton process gives effective results in acidic pH conditions but since the optimal pH is 2.8, the practice is quite restricted for treating wastewater (25) (26). Therefore, catalysts such as Fe(II), Fe(III), Cu(II), metal foam-based catalysts, and nano zero-valent iron (28) are utilized to replace Fe^{2+} to overcome this limitation (27). Qi et al observed that by utilizing $CuCo_2O_4$ nano-catalyst for metacycline degradation, the degradation efficiency is 38.4% when the dosage is 5.0 mg and increased to 89.1% when the dosage is 12.0 mg (29). Besides that, Nasseh et al. were able to achieve 84.29% degradation efficiency by utilizing 0.1 g/L synthesized $FeNi_3/SiO_2$ magnetic nano-catalyst to degrade metronidazole (30).

Ozonation is another type of AOP, where ozone having a 2.07 V oxidation potential can react with wastewater to form hydroxyl radicals (27). To enhance the degradation efficiency of pollutants, homogenous and heterogenous catalysts are introduced in the ozonation AOP. Transition metal ions or liquid catalysts such as Mn^{2+}, Fe^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, and Ag^{2+} are utilized to enhance degradation efficiency by exciting ozone to produce higher amounts of hydroxyl radicals (27). Oh et al proved that by increasing ozone dosage from 3 ppm to 7 ppm, the degradation of tetracycline occurs faster at 5 min reaction time, the tetracycline concentration was 40 mg/L at 3 ppm ozone and 20 mg/L at 7 ppm ozone introduction (31). However, ozonation AOP has high manufacturing costs and complex equipment. Therefore, it has not been used on a large scale although it has a strong oxidizing ability and lesser secondary pollution compared to other methods (28). Table II shows the mechanisms for pollutant removal by different AOP types.

SULFATE-BASED AOP

Currently, the usage of PMS and PDS in the activation of ROS has gained interest in water purification (32) (33) (34). Although, direct reaction with pollutants occurs at a very low rate so activation is required to generate sulfate radicals. PDS and PMS are activated to form ROS for organic pollutants removal. Between the two, PDS holds more advantages due to its lower cost, improved stability, and higher redox potential compared to PMS (26). PDS is a strong oxidant with a standard oxidation potential of 2.01 V. Table III showed the chemical properties of PDS and PMS.

Numerous activation methods have been employed for the activation of PDS which includes ultraviolet (UV) irradiation, heat, elevated pH, transitional metals, and carbon-based catalysts which will form more powerful sulfate radicals (25). Equation (1) showed PDS activated by UV radiation:

Table II : Mechanisms For Pollutant Removal By Different AOP Types (24)

AOP types	Oxidant for advanced oxidation	Other occurring mechanisms
O_3	OH·	Direct O_3 oxidation
O_3/H_2O_2	OH·	Direct O_3 oxidation
O_3/UV	OH·	UV photolysis
UV/TiO_2	OH·	UV photolysis
UV/H_2O_2	OH·	UV photolysis
		H_2O_2 oxidation
Fenton reaction	OH·	Iron coagulation
		Iron sludge-induced adsorption
Photo-Fenton reaction	OH·	Iron coagulation
		Iron sludge-induced adsorption
		UV photolysis
Ultrasonic irradiation	OH·	Acoustic cavitation generates transient high temperatures (>5000 K) and pressures (>1000 atm), and produce H·and HO_2·, besides OH·
Heat/persulfate	SO_4^-	Persulfate oxidation
UV/persulfate	SO_4^-	Persulfate oxidation
		UV photolysis
Fe (II)/persulfate	SO_4^-	Persulfate oxidation
		Iron coagulation
		Iron sludge-induced oxidation
OH^-/persulfate	SO_4^-/ OH·	Persulfate oxidation

Table III : Chemical properties of PDS and PMS (27)

	PDS	PMS
Formula	$S_2O_8^{2}$	HSO_5^-
Molecular weight (g/mol)	192.12	113.07
Redox potential (V)	2.1	1.8
O-O bond dissociation energy (kJ/mol)	140	140.213
O-O bond length (A)	1.453	1.497

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-} \quad (1)$$

Ultraviolet irradiation is considered a productive way for the activation of PDS for decomposing the organic compounds in water (35). Zhang et al proved that the addition of 2 mM of PDS activated by UV attained 100% removal of 20 mg/L trimethoprim at an absorbed dose of 400 Gy (36). Shah et al revealed the degradation of chlorendic acid escalated to 95% from 82% in the attendance of PMS, showing the synergistic effect of hydrogen sulfate and UV radiation (37). However, owing to the active species interaction, PDS and PMS activation by radiation might have a side reaction. Therefore, further research should be done to explore the aforementioned matter (35). Metal oxide and transition metal can be classified into heterogeneous and homogenous subject to the existing form of metal oxide and transition metals. Amongst the homogenous metal oxide and ions, silver ion was demonstrated to be

the most effective for PDS activation, while cobalt ion (Co^{2+}) reveal the best-activated conduct for PMS (35). Equation (2) showed the activation of PDS by transition metals:

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{\cdot-} + SO_4^{2-} + M^{n+1} \qquad (2)$$

The most commonly studied metals were iron and its oxide because of its advantages of being cost-effective, and non-toxic in contrast to other transition metals (35). However, in homogenous systems, the limitation is that a high amount of organic pollutants in wastewater requires a high amount of metal ions for organic pollutant degradation. In return, high amounts of metal ions in the effluent existed and thus are difficult to be recovered (35). Heterogenous metal-based activation may overcome this limitation. Nevertheless, it depends on the surface properties of the material (35).

Various factors may affect the efficiency of SR-AOPs, among these, the effect of pH has the highest influence on the degradation of organic pollutants (38). Increasing the pH of the wastewater to 8-9, sulfate radicals are converted to hydroxyl radicals thus engaging in the degradation of organic pollutants (39). Besides pH, the effect of reaction temperature also plays a crucial role in the degradation efficiency of organic pollutants in SR-AOP. Zhang et al studied the degradation efficiency of Rhodamine B (RhB) at various temperatures, with the aid of an Ag@CuO-activated catalyst. Based on their findings, it is observed that at a higher temperature, a higher degradation was achieved. The time to achieve 95% degradation at 20 °C was 36 min, meanwhile, at 30 °C, 40 °C, and 50 °C, the time was 24 min, 19 min, and 15 min respectively (40).

Genc et al evaluated the degradation efficiency of pollutants in olive oil mill wastewater with microwave-activated persulfate process. At 30 min, the removal rate of pollutants was 63.38% under optimal conditions of persulfate anion dosage of 266 g/L, reaction time 23.58 min, initial pH 2, and microwave power of 567 W (41). Liu et al studied the degradation of RhB dye in wastewater with PMS activated by Я-MnO2 and within 5 minutes the catalytic system achieved 100% RhB degradation (42). Yin et al investigated the degradation of Sulfamethoxazole (SMX) in pharmaceutical wastewater by PDS with the aid of Fe-based metal-organic frameworks (MOF) and achieved a degradation rate of 100% within 3 hours of reaction time (43).

CARBON-BASED CATALYSTS FOR PDS/PMS ACTIVATION

An efficient and inexpensive activator to generate suitable reactive species is one of the main problems in persulfate-based advanced oxidation processes. Although the performance of homogeneous or heterogeneous catalysts based on transition metals has been extensively studied, metal leaching of catalysts is generally unavoidable and poses additional environmental problems (44) (45) (46). Various studies have been issued in recent years on the use of carbonaceous materials such as carbon nanotubes, graphene, graphene oxide, and activated carbon as metal-free persulfate activators (38, 47-49). Among these, activated carbon derived from biomass has emerged as an extensive approach for environmental applications (50) (51) (52). This is because of its unique properties of having a huge specific surface area (SSA) and pore volume, excellent thermal and chemical stability, and is also cost-effective (32). Duan et al suggested that metal-free catalysts have shown potential in catalytic superoxide activation and oxidation (53). Biochar is a porous carbonaceous material produced by decomposing biomass feedstock which includes organic waste materials such as manures, sewage sludge, algae, wood chip, and crop and forest residues (2, 54, 55). Li et al synthesized rice straw biochar modified with cooper oxide (RSBC-CuO) in activating PDS in removal of SMX in pharmaceutical wastewater and within 30 min, achieved 100% removal efficiency (56).

The pyrolysis process is the most standard technique used in biochar catalyst preparation for catalytic degradation. Pyrolysis is carried out at a temperature between 300 to 900 °C under oxygen-limited conditions (57). Pyrolysis temperature, reaction time, and pyrolysis atmosphere are the operating parameters that is a vital role in biochar formation, which affects the yield of biochar and its surface properties (58). Different pyrolysis temperatures will affect the reactivity of biochar-based catalysts as it greatly reflects on the biochar's physical and chemical properties (59). Wang et al. developed and compared sludge-derived biochar (SBC) with pyrolysis temperatures of 600 °C and 700 °C, and discovered that biochar at 600 °C has a catalytic activity of 20% lesser than biochar at 700 °C. This might be due to the rise in carbon content and reduction in the biochar's specific surface area (5).

Studies have shown that doping heteroatoms such as sulfur (S), nitrogen (N), boron (B), and phosphorus (P) can improve metal-free catalysts' catalytic activity for decomposing persistent organics pollutants (60). The heteroatom introduction into catalyst materials can produce surface defects and therefore replace the intrinsic characteristics of the biochar which improves pore diameter and specific surface area, also increasing the active sites of the biochar (48). Comparing the heteroatoms, N-doped carbon materials have numerous N functional groups and higher defective sites, thus exhibiting excellent

catalytic activity (61). A study by Xu et al successfully produced N-doped biochar by using a ball milling process with ammonium hydroxide. The nitrogen-doped biochar was then utilized for the adsorption of carbon dioxide and reactive red (62). Besides that, Mian et al developed nitrogen-doped biochar from sewage sludge processed by a single-step pyrolysis approach by the addition of different ratios of melamine with the biochar. The nitrogen-doped biochar was then utilized as a catalyst for the activation of peroxymonosulfate (PMS) (63).

Another study developed microporous N-doped biochar attained from crop straws with ammonium chloride as the nitrogen precursor. By doping the biochar with ammonium chloride, the biochar increased in microporosity to 71.5%, with an atomic nitrogen percentage of 8.8, relatively about 15 to 20 times higher than that of the initial biochar (64). Tian et al have proposed the usage of $NaHCO_3$ for creating functional (S co-doped, N or N) porous with low-cost carbon precursors, wheat flour, and a few doping agents (32). It was then discovered that this porous carbon shows great results in applications such as water rectification, supercapacitors, and CO_2 uptake oxygen reduction reaction (ORR) (32).

CONCLUSION

The application of sulfate radicals in advanced oxidation processes for the treatment of water and wastewater has grown significantly over the years. In this article, different methods of activation of sulfate radicals from PDS and PMS have been discussed focusing on the utilization of a carbon-based catalyst, biochar as a metal-free catalyst alternative. Metal catalysts are the most widespread activation method for SR-AOP, however, the main disadvantages of metal leaching and high concentration of ions in the water have moved researchers to find a greener alternative. Carbon-based catalysts give good results with the advantages of having a big specific surface area (SSA) and pore volume, great chemical and thermal stability, and are also cost-effective. It is important to know in depth the synthesis process of the biochar such as pyrolysis temperature, reaction time, and pyrolysis atmosphere in order to improve their structure to obtain an optimum catalytic activation of the radicals. The combination of heteroatoms such as sulfur, phosphorus, boron, and nitrogen can further enhance the catalytic activity. Currently, most of the studies on heteroatom-doped biochar catalysts focus on the N-doped biochar, due to having numerous N functional groups and higher defective sites, thus exhibiting excellent catalytic activity. In our perspectives, the application of SR-AOP by biochar in the degradation of EDCs includes (1) Development of low-cost efficient catalysts. In the field of SR-AOPs, the production of efficient and cost-effective catalysts is still the main focus of future research. Researchers need to study how to reduce the cost of catalyst preparation as the process requires high temperature and high pressure. (2) Improve toxicological studies of catalysts in the environment. Some catalysts may contain ingredients that are harmful to the environment. Therefore, it is necessary to consider the leaching of harmful ingredients into the environment and the impact on the environment.

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REFERENCES

1. Vieira WT, de Farias MB, Spaolonzi MP, da Silva MGC, Vieira MGA. Removal of endocrine disruptors in waters by adsorption, membrane filtration and biodegradation. A review. Environmental Chemistry Letters. 2020;18(4):1113-43. doi: 10.1007/s10311-020-01000-1.
2. Duan X, Zhang C, Wang S, Ren N-q, Ho S-H. Graphitic biochar catalysts from anaerobic digestion sludge for nonradical degradation of micropollutants and disinfection. Chemical Engineering Journal. 2020;384:123244. doi: 10.1016/j.cej.2019.123244.
3. Jindo K, Mizumoto H, Sawada Y, Sanchez-Monedero MA, Sonoki T. Physical and chemical characterization of biochars derived from different agricultural residues. Biogeosciences. 2014;11(23):6613-21. doi: 10.5194/bg-11-6613-2014.
4. Xiang W, Zhang X, Chen J, Zou W, He F, Hu X, et al. Biochar technology in wastewater treatment: A critical review. Chemosphere. 2020;252:126539. doi: 10.1016/j.chemosphere.2020.126539.
5. Wang S, Wang J. Activation of peroxymonosulfate by sludge-derived biochar for the degradation of triclosan in water and wastewater. Chemical Engineering Journal. 2019;356:350-8. doi: 10.1016/j.cej.2018.09.062.
6. Oh W-D, Lim T-T. Design and application of heterogeneous catalysts as peroxydisulfate activator for organics removal: an overview. Chemical Engineering Journal. 2019;358:110-33. doi: 10.1016/j.cej.2018.09.203.
7. Zhu S, Huang X, Ma F, Wang L, Duan X, Wang S. Catalytic removal of aqueous contaminants on N-doped graphitic biochars: inherent roles of adsorption and nonradical mechanisms. Environmental science & technology. 2018;52(15):8649-58. doi: 10.1021/acs.est.8b01817.
8. Ashraf M, Maah M, Qureshi A, Gharibreza M, Yusoff I. Synthetic polymer composite membrane

for the desalination of saline water. Desalination and Water Treatment. 2013;51(16-18):3650-61. doi: 10.1080/19443994.2012.751152.
9. Afroz R, Banna H, Masud MM, Akhtar R, Yahaya SR. Household's perception of water pollution and its economic impact on human health in Malaysia. Desalination and Water Treatment. 2016;57(1):115-23. doi: 10.1080/19443994.2015.1006822.
10. Nasrollahzadeh M, Sajjadi M, Iravani S, Varma RS. Starch, cellulose, pectin, gum, alginate, chitin and chitosan derived (nano) materials for sustainable water treatment: A review. Carbohydrate polymers. 2021;251:116986. doi: 10.1016/j.carbpol.2020.116986.
11. Zhao F, Sillanpдд M. Cross-linked chitosan and β-cyclodextrin as functional adsorbents in water treatment. Advanced Water Treatment: Elsevier; 2020. p. 161-264.
12. Abhinaya M, Parthiban R, Kumar PS, Vo D-VN. A review on cleaner strategies for extraction of chitosan and its application in toxic pollutant removal. Environmental Research. 2021;196:110996. doi: 10.1016/j.envres.2021.110996.
13. Lv X, Xiao S, Zhang G, Jiang P, Tang F. Occurrence and removal of phenolic endocrine disrupting chemicals in the water treatment processes. Scientific reports. 2016;6(1):1-10. doi: 10.1038/srep22860.
14. Al Sharabati M, Abokwiek R, Al-Othman A, Tawalbeh M, Karaman C, Orooji Y, et al. Biodegradable polymers and their nano-composites for the removal of endocrine-disrupting chemicals (EDCs) from wastewater: A review. Environmental Research. 2021;202:111694. doi: 10.1016/j.envres.2021.111694.
15. Society E. 2023 [cited 2023 29 May]. Available from: https://www.endocrine.org/topics/edc/what-edcs-are/common-edcs.
16. Ahmad Fauzi Ismail, Takeshi Matsuura. 4 - Nanofiltration. Membrane Separation Processes: Elsevier; 2022. p. 61-8.
17. Dai R, Han H, Wang T, Li X, Wang Z. Enhanced removal of hydrophobic endocrine disrupting compounds from wastewater by nanofiltration membranes intercalated with hydrophilic MoS2 nanosheets: Role of surface properties and internal nanochannels. Journal of Membrane Science. 2021;628:119267. doi: 10.1016/j.memsci.2021.119267.
18. Emek A, Yilmazer C, Cinar S, Kiraz O, Paşaoğlu M, Tasdemir R, et al. Removal of endocrine-disrupting chemicals from textile industry effluents by nanofiltration. Desalination and Water Treatment. 2021;211. doi: 10.5004/dwt.2021.26542.
19. Yang X, Wang D. Photocatalysis: from fundamental principles to materials and applications. ACS Applied Energy Materials. 2018;1(12):6657-93. doi: 10.1021/acsaem.8b01345.
20. Koe WS, Lee JW, Chong WC, Pang YL, Sim LC. An overview of photocatalytic degradation: photocatalysts, mechanisms, and development of photocatalytic membrane. Environmental Science and Pollution Research. 2020;27:2522-65. doi: 10.1007/s11356-019-07193-5.
21. Han M, Zhu S, Lu S, Song Y, Feng T, Tao S, et al. Recent progress on the photocatalysis of carbon dots: Classification, mechanism and applications. Nano Today. 2018;19:201-18. doi: 10.1016/j.nantod.2018.02.008.
22. Babu SG, Karthik P, John MC, Lakhera SK, Ashokkumar M, Khim J, et al. Synergistic effect of sono-photocatalytic process for the degradation of organic pollutants using CuO-TiO2/rGO. Ultrasonics sonochemistry. 2019;50:218-23. doi: 10.1016/j.ultsonch.2018.09.021.
23. Alvarez MA, Orellana-Garcна F, Lopez-Ramon MV, Rivera-Utrilla J, Sanchez-Polo M. Influence of operational parameters on photocatalytic amitrole degradation using nickel organic xerogel under UV irradiation. Arabian journal of chemistry. 2018;11(4):564-72. doi: 10.1016/j.arabjc.2016.10.005.
24. Hu P, Long M. Cobalt-catalyzed sulfate radical-based advanced oxidation: a review on heterogeneous catalysts and applications. Applied Catalysis B: Environmental. 2016;181:103-17. doi: 10.1016/j.apcatb.2015.07.024.
25. Deng Y, Zhao R. Advanced oxidation processes (AOPs) in wastewater treatment. Current Pollution Reports. 2015;1:167-76. doi: 10.1007/s40726-015-0015-z.
26. Garrido-Cardenas JA, Esteban-Garcна B, Agьera A, Sбnchez-Pйrez JA, Manzano-Agugliaro F. Wastewater treatment by advanced oxidation process and their worldwide research trends. International Journal of Environmental Research and Public Health. 2020;17(1):170. doi: 10.3390/ijerph17010170.
27. Wang J, Zhuan R. Degradation of antibiotics by advanced oxidation processes: An overview. Sci Total Environ. 2020;701:135023. doi: 10.1016/j.scitotenv.2019.135023.
28. Ma D, Yi H, Lai C, Liu X, Huo X, An Z, et al. Critical review of advanced oxidation processes in organic wastewater treatment. Chemosphere. 2021;275:130104. doi: 10.1016/j.chemosphere.2021.130104.
29. Qi Y, Mei Y, Li J, Yao T, Yang Y, Jia W, et al. Highly efficient microwave-assisted Fenton degradation of metacycline using pine-needle-like CuCo2O4 nanocatalyst. Chemical Engineering Journal. 2019;373:1158-67. doi: 10.1016/j.cej.2019.05.097.
30. Nasseh N, Taghavi L, Barikbin B, Nasseri MA, Allahresani A. FeNi3/SiO2 magnetic nanocomposite as an efficient and recyclable heterogeneous fenton-like catalyst for the oxidation of metronidazole in neutral environments:

Adsorption and degradation studies. Composites Part B: Engineering. 2019;166:328-40. doi: 10.1016/j.compositesb.2018.11.112.
31. Oh J, Medriano CA, Kim S. The effect of tetracycline in the antibiotic resistance gene transfer before and after ozone disinfection. Desalination and Water Treatment. 2014;57(2):646-50. doi: 10.1080/19443994.2014.986828.
32. Tian W, Zhang H, Qian Z, Ouyang T, Sun H, Qin J, et al. Bread-making synthesis of hierarchically Co@ C nanoarchitecture in heteroatom doped porous carbons for oxidative degradation of emerging contaminants. Applied Catalysis B: Environmental. 2018;225:76-83. doi: 10.1016/j.apcatb.2017.11.056.
33. Wang J, Wang S. Reactive species in advanced oxidation processes: Formation, identification and reaction mechanism. Chemical Engineering Journal. 2020;401. doi: 10.1016/j.cej.2020.126158.
34. Ding Y, Wang X, Fu L, Peng X, Pan C, Mao Q, et al. Nonradicals induced degradation of organic pollutants by peroxydisulfate (PDS) and peroxymonosulfate (PMS): Recent advances and perspective. Sci Total Environ. 2021;765:142794. doi: 10.1016/j.scitotenv.2020.142794.
35. Wang J, Wang S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. Chemical Engineering Journal. 2018;334:1502-17. doi: 10.1016/j.cej.2017.11.059.
36. Zhang Z, Yang Q, Wang J. Degradation of trimethoprim by gamma irradiation in the presence of persulfate. Radiation Physics and Chemistry. 2016;127:85-91. doi: 10.1016/j.radphyschem.2016.06.019.
37. Shah NS, Khan JA, Ala'a H, Sayed M, Murtaza B, Khan HM. Synergistic effects of HSO5− in the gamma radiation driven process for the removal of chlorendic acid: a new alternative for water treatment. Chemical Engineering Journal. 2016;306:512-21. doi: 10.1016/j.cej.2016.07.031.
38. Wu S, Yang D, Zhou Y, Zhou H, Ai S, Yang Y, et al. Simultaneous degradation of p-arsanilic acid and inorganic arsenic removal using M-rGO/PS Fenton-like system under neutral conditions. J Hazard Mater. 2020;399:123032. doi: 10.1016/j.jhazmat.2020.123032.
39. Lee J, von Gunten U, Kim JH. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. Environ Sci Technol. 2020;54(6):3064-81. doi: 10.1021/acs.est.9b07082.
40. Zhang T, Zhou T, He L, Xu D, Bai L. Oxidative degradation of Rhodamine B by Ag@ CuO nanocomposite activated persulfate. Synthetic Metals. 2020;267. doi: 10.1016/j.synthmet.2020.116479.
41. Genз N, Durna E, Kayapinar Cicigьn HK. Response Surface Modeling and Optimization of Microwave - Activated Persulfate Oxidation of Olive Oil Mill Wastewater. CLEAN – Soil, Air, Water. 2019;48(1). doi: 10.1002/clen.201900198.
42. Liu Y, Qu R, Li X, Wei Y, Feng L. A bifunctional beta-MnO(2) mesh for expeditious and ambient degradation of dyes in activation of peroxymonosulfate (PMS) and simultaneous oil removal from water. J Colloid Interface Sci. 2020;579:412-24. doi: 10.1016/j.jcis.2020.06.073.
43. Yin R, Chen Y, He S, Li W, Zeng L, Guo W, et al. In situ photoreduction of structural Fe(III) in a metal-organic framework for peroxydisulfate activation and efficient removal of antibiotics in real wastewater. J Hazard Mater. 2020;388:121996. doi: 10.1016/j.jhazmat.2019.121996.
44. Huang B-C, Jiang J, Huang G-X, Yu H-Q. Sludge biochar-based catalysts for improved pollutant degradation by activating peroxymonosulfate. Journal of Materials Chemistry A. 2018;6(19):8978-85. doi: 10.1039/C8TA02282H.
45. Liu L, Corma A. Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. Chem Rev. 2018;118(10):4981-5079. doi: 10.1021/acs.chemrev.7b00776.
46. Tian D, Zhou H, Zhang H, Zhou P, You J, Yao G, et al. Heterogeneous photocatalyst-driven persulfate activation process under visible light irradiation: From basic catalyst design principles to novel enhancement strategies. Chemical Engineering Journal. 2022;428. doi: 10.1016/j.cej.2021.131166.
47. Chen X, Oh W-D, Lim T-T. Graphene-and CNTs-based carbocatalysts in persulfates activation: Material design and catalytic mechanisms. Chemical Engineering Journal. 2018;354:941-76. doi: 10.1016/j.cej.2018.08.049.
48. Duan X, Indrawirawan S, Sun H, Wang S. Effects of nitrogen-, boron-, and phosphorus-doping or codoping on metal-free graphene catalysis. Catalysis Today. 2015;249:184-91. doi: 10.1016/j.cattod.2014.10.005.
49. Ozyildiz G, Olmez-Hanci T, Arslan-Alaton I. Effect of nano-scale, reduced graphene oxide on the degradation of bisphenol A in real tertiary treated wastewater with the persulfate/UV-C process. Applied Catalysis B: Environmental. 2019;254:135-44. doi: 10.1016/j.apcatb.2019.04.092.
50. Oliveira CYB, Oliveira CDL, Prasad R, Ong HC, Araujo ES, Shabnam N, et al. A multidisciplinary review of Tetradesmus obliquus: a microalga suitable for large - scale biomass production and emerging environmental applications. Reviews in Aquaculture. 2021;13(3):1594-618. doi: 10.1111/raq.12536.
51. Thomas P, Lai CW, Bin Johan MR. Recent developments in biomass-derived carbon as a potential sustainable material for super-capacitor-based energy storage and environmental applications. Journal of Analytical and Applied

Pyrolysis. 2019;140:54-85. doi: 10.1016/j.jaap.2019.03.021.
52. Varma RS. Biomass-Derived Renewable Carbonaceous Materials for Sustainable Chemical and Environmental Applications. ACS Sustainable Chemistry & Engineering. 2019;7(7):6458-70. doi: 10.1021/acssuschemeng.8b06550.
53. Duan X, Sun H, Wang S. Metal-free carbocatalysis in advanced oxidation reactions. Accounts of Chemical Research. 2018;51(3):678-87. doi: 10.1021/acs.accounts.7b00535.
54. Du J, Kim SH, Hassan MA, Irshad S, Bao J. Application of biochar in advanced oxidation processes: supportive, adsorptive, and catalytic role. Environmental Science and Pollution Research. 2020;27(30):37286-312. doi: 10.1007/s11356-020-07612-y.
55. Zhao C, Shao B, Yan M, Liu Z, Liang Q, He Q, et al. Activation of peroxymonosulfate by biochar-based catalysts and applications in the degradation of organic contaminants: A review. Chemical Engineering Journal. 2021;416:128829. doi: 10.1016/j.cej.2021.128829.
56. Li W, Liu B, Wang Z, Wang K, Lan Y, Zhou L. Efficient activation of peroxydisulfate (PDS) by rice straw biochar modified by copper oxide (RSBC-CuO) for the degradation of phenacetin (PNT). Chemical Engineering Journal. 2020;395:125094. doi: 10.1016/j.cej.2020.125094.
57. Cha JS, Park SH, Jung S-C, Ryu C, Jeon J-K, Shin M-C, et al. Production and utilization of biochar: A review. Journal of Industrial and Engineering Chemistry. 2016;40:1-15. doi: 10.1016/j.jiec.2016.06.002.
58. Amin FR, Huang Y, He Y, Zhang R, Liu G, Chen C. Biochar applications and modern techniques for characterization. Clean Technologies and Environmental Policy. 2016;18:1457-73. doi: 10.1007/s10098-016-1218-8.
59. Singh BP, Cowie AL, Smernik RJ. Biochar carbon stability in a clayey soil as a function of feedstock and pyrolysis temperature. Environmental science & technology. 2012;46(21):11770-8. doi: 10.1021/es302545b.
60. Zhou X, Zeng Z, Zeng G, Lai C, Xiao R, Liu S, et al. Persulfate activation by swine bone char-derived hierarchical porous carbon: multiple mechanism system for organic pollutant degradation in aqueous media. Chemical Engineering Journal. 2020;383:123091. doi: 10.1016/j.cej.2019.123091.
61. Zhang X, Wang Y, Du Y, Qing M, Yu F, Tian ZQ, et al. Highly active N, S co-doped hierarchical porous carbon nanospheres from green and template-free method for super capacitors and oxygen reduction reaction. Electrochimica Acta. 2019;318:272-80. doi: 10.1016/j.electacta.2019.06.081.
62. Xu X, Zheng Y, Gao B, Cao X. N-doped biochar synthesized by a facile ball-milling method for enhanced sorption of CO2 and reactive red. Chemical Engineering Journal. 2019;368:564-72. doi: 10.1016/j.cej.2019.02.165.
63. Mian MM, Liu G, Zhou H. Preparation of N-doped biochar from sewage sludge and melamine for peroxymonosulfate activation: N-functionality and catalytic mechanisms. Science of The Total Environment. 2020;744:140862. doi: 10.1016/j.scitotenv.2020.140862.
64. Cao J, Yang Z-h, Xiong W-p, Zhou Y-y, Peng Y-r, Li X, et al. One-step synthesis of Co-doped UiO-66 nanoparticle with enhanced removal efficiency of tetracycline: Simultaneous adsorption and photocatalysis. Chemical Engineering Journal. 2018;353:126-37. doi: 10.1016/j.cej.2018.07.060.
65. S. Y. Wee and A. Z. Aris, "Occurrence and public-perceived risk of endocrine disrupting compounds in drinking water," Clean water, 2019.
66. H. T. Madsen, "Chapter 6: Membrane Filtration in Water Treatment - Removal of Micropollutants," in Chemistry of Advanced Environmental Purification Processes of Water, 2014, pp. 200-202.