Biochar in Remediation of Organic Pollutants in Water

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Biochar is a biological material for environmental remediation due to its low-cost precursor (waste), low toxicity, and diversity of active sites, along with their facile tailoring techniques. Due to its versatility, biochar has been employed as an adsorbent, catalyst (for activating hydrogen peroxide, ozone, persulfate), and photocatalyst. Biochar could also be applied in remediation of organic pollutants in water.



1. Introduction

Over the past few years, the rapid growth of various industries has led to the release of toxic pollutants to the environment. In particular, various refractory pollutants such as antibiotics, phenolic compounds, dyes, and heavy metals are detected in numerous water bodies and soil ^{[1][2][3][4][5]}. In particular, pollution due to refractory pollutants in water bodies is of emerging concern due to its greater mobility compared to soil. While these pollutants pose a threat to public health, they also disrupt the microbial ecosystem ^{[6][7]}. For instance, the release of trace antibiotics will lead to the development of multidrug-resistant strains, which will result in less effective clinical treatment effects of conventional antibiotics ^[7]. Phenolic compounds such as chlorophenols are toxic and may induce carcinogenic and mutagenic effects. In order to alleviate this problem, methods such as adsorption ^[8], membrane separation ^[9], and advanced oxidation processes (AOPs) ^[10] can be used to treat the wastewater before it is discharged into the environment. Generally, adsorption and membrane separation involve the separation of pollutants and water without destroying the pollutants, while AOPs utilizes reactive oxygen species (ROS) generation for organics mineralization.

Recently, biochar has gained attention in various environmental remediation applications. Biochar can be obtained by the direct carbonization of organic wastes in an oxygen-deficient environment. Compared with other carbonbased materials, some of the advantages of using biochar for environmental remediation include low production cost (cheap raw materials), relatively simple preparation methods (facile pyrolysis of biomass), and eco-friendly (waste recovery). Furthermore, the properties of biochar can be engineered more easily (compared with other carbon allotropes) by changing the synthesis parameters (e.g., synthesis temperature and duration) ^{[11][12]}, careful selection of biomass as a precursor ^[13], and functionalization (e.g., heteroatom doping, oxygen tuning, and defects) ^{[14][15]}. Numerous reviews on the use of biochar in specific environmental applications are available ^{[16][17][18][19][20][21][22]}, howbeit, with modest emphasis on comparing biochar performance and the mechanism of treating organic pollutants under different systems for finding superior applications of biochar and to fully realize its potential. For instance, Dai et al. ^[21] discussed the employment of biochar as an adsorbents for organic pollutants, however, without discussing biochar potential in other pollutant remediation systems. Similarly, Zhou et al. ^[19] and Zhao et al. ^[23] reviewed biochar as AOPs catalyst and persulfate activator, respectively, without comparison against other systems (e.g., adsorption, O₃ activation).

2. Applications of Biochar in Environmental Remediation

2.1. Adsorption

Adsorption is a common technique to remove organic pollutants. Due to its relatively low operational cost, adsorption is widely utilized for water remediation. **Table 1** presents an overview of the performance of biochar as an adsorbent for various organic pollutants. The criteria for an effective adsorbent include having high SSA and porosity along with the abundance of active sites. Generally, the adsorption process relies on the liquid–solid intermolecular attraction between the adsorbate and the adsorbent, which leads to the accumulation of solute molecules on the adsorbent surface ^[24]. The adsorption mechanisms between the biochar and organic pollutant occur through physical and chemical interactions, including H-bonding, hydrophobic interactions, electrostatic attraction, π - π EDA interactions, complexes adsorption, Lewis acid–base interactions, pore filling, partition uncarbonized fraction, dipole–dipole interactions, Coulombic attraction, spectrometer exchange, and acceptor interactions ^[22]. The adsorption process undertaken is controlled by the nature of the adsorbate, biochar properties, and operational condition (i.e., pH, pressure of water matrix, rate). The adsorption process is divided into three stages. First, there is external mass transfer of organic pollutants from the aqueous solution to the biochar surface (external diffusion), which is followed by the diffusion of organic molecules into the pores of biochar (internal diffusion) and ending with the adsorptive interactions (**Figure 1**) ^{[14][25]}.



Figure 1. Mechanism of phenol adsorption by N-doped biochar. Reprinted with permission from Li et al.^[14]. Copyright 2019 American Chemical Society.

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref
Peanut shellsPyrolysis: 700 °C	 [DEP] = 20 mg L⁻¹, [Biochar] = 1 g L⁻¹, pH = 7 	• Oxidized S and pyridinic N were crucial in the adsorption process	
 N, S co-doping: Thiourea + biochar, pyrolysis: 350 °C, 1 h 	• Q_e of 3.60 ± 0.20 mg g ⁻¹ and k ₂ of 0.04 ± 0.05 g mg ⁻¹ min ⁻¹ in 4 h	 Removal efficiency remained ≥80% after 5 cycles (used biochar was washed with methanol) 	[<u>26</u>]
 Hickory sawdust + boric acid Pyrolysis: 700 °C, 2 h 	 [SMX] = 50 mg L⁻¹, [Biochar] = 0.5 g L⁻¹, pH = 5 	• Enhanced porosity and SSA by boric acid activation promoted better adsorption capacity	[27]
	 Q_e of 94.76 mg g⁻¹ in 240 min 	• Adsorption capacity and SSA were in well agreement (R ² = 0.9091), indicating that adsorption followed the pore-filling process	
		- Adsorption capacity decrease from 94.76 to 64.62 mg g $^{-1}$ after 5 cycles (NaOH	

Table 1. An overview of biochar preparation and performance in adsorption of organic pollutants.

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref
-		treatment of used catalyst after every cycle)	
 Tapioca peels + S doping Pyrolysis: 800 °C, 3 h, N₂ atmosphere 	 [RhB] = 25 mg L⁻¹, [Biochar] = 2 g L⁻¹, pH = 8 92.6% removed in 120 min 	 Biochar had homogeneous surface interactions with RhB via monolayer adsorption system Adsorption was controlled by H-bonding, surface interaction, and electrostatic attraction Adsorption efficiency decreased with each cycle (NaOH treatment of used catalyst after every cycle) 	[28]
 Livistona chinensis Pyrolysis: 500 °C, 4 h, N₂ atmosphere 	 [MG] = 150 mg L⁻¹, [Biochar] = 1 g L⁻¹, pH = 7 ± 0.5 99.7% removed in 24 h 	 Adsorption was best described by Langmuir isotherm model (R² = 0.97) 	[29]
 Grapefruit peel Pyrolysis: 400 °C, 2 h Modification with FeSO₄ and FeCl₃ 	 [BPA] = 150 mg L⁻¹, [Biochar] = 1 g L⁻¹, pH = 7 ± 0.5 Saturated adsorption capacity 9.7098 mg g⁻¹ after 150 min 	 Chemical adsorption is rate control step in adsorption with non-uniform adsorbent and evenly distributed energy of surface adsorption Adsorption mechanism was controlled by a variety of forces (i.e., π-π EDA interaction, H-bond, etc.) 	[<u>30]</u>
 Sawdust + Zn and Fe loading Pyrolysis: 600 °C, 2 h, N₂ atmosphere 	 [TET] = 150 mg L⁻¹, [Biochar] = 1 g L⁻¹, pH = 6 	 Adsorption process was controlled by chemisorption H-bond between OH of TET and OFGs biochar along with the π-π EDA interactions promote fast sorption 	[<u>31</u>]

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref	
-		 After desorption (using NaOH treatment), the adsorption decrease from 91.6% to 89% after 3 cycles 		
 Rice straw Pyrolysis: 700 °C, 2 h H₃PO₄ treatment 	 [TC] = 120 mg L⁻¹, [Biochar] = 2/3 g L⁻¹ Qe of 166.3 mg g⁻¹ in 192 h 	 Π-π EDA interactions and H-bonding are ascribed as primary sorption mechanisms 	[<u>32</u>]	
Domelo neolo		 Adsorption efficiency remained similar at pH 3–10 but significantly decreases at higher pH 		
 Pomeio peeis Pyrolysis: 450 °C, 15 min 	• [CIP] = 50 mg L ⁻¹ , [Biochar] = 0.1 g L ⁻¹ , pH = 3–10	- Adsorption mechanisms encompassed π - π EDA interaction, H-bonding, and hydrophobic interaction	[<u>33</u>]	
 Chitosan treatment for chitosan–biochar hydrogel beads 	 Sorption capacity of 36.72 mg g⁻¹ 2 2 	 OFGs groups such as -OH and -COOH on biochar make it more hydrophilic for ₃ hydrophobic interaction with CIP 		ever,
		• F and N heteroaromatic ring of CIP allow it to act as π electron acceptor		pecies) and i.e., b
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^[34], is highly preferable in water treatment because its decomposition products are only oxygen and hydrogen, which is considered environmentally friendly to water treatment [35]. The H₂O₂ structure encompasses an O-O bond distance of 1.460 Å with a dissociation energy of 377 kJ/mol. In a biochar/H2O2 system, the electron transfer process from biochar to H2O2 molecules induces the breakage of the O-O or O-H bond for subsequent ROS formations. Table 2 overviews the performance and mechanism of H_2O_2 activation by biochar catalysts.

Table 2. An overview of biochar preparation and performance in H_2O_2 activation for organic pollutants removal.

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref
Maize straw + Fe- impregnation	• [SMX] = 10 μ M, [Biochar] = 1 g L ⁻¹ , [H ₂ O ₂] = 3 mM, pH = 5	 C-OH activates H₂O₂ to produce 'OH, HO₂', and alkyl radicals to degrade SMX 	[<u>36</u>]

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref
 Pyrolysis: 700 °C, 2 h, N₂ atmosphere 	• 100% removed in 2 h		
 Sewage sludge Pyrolysis: 500 °C, 4 h, N₂ atmosphere Acid (HNO₃) treatment 	 [CIP] = 10 mg L⁻¹, [Biochar] = 1 g L⁻¹, [H₂O₂] = 10 mM, pH = 7.4 93% removed in 24 h 	 Single-electron transfer from biochar PFRs to H₂O₂ induced *OH generation Consumption of sp.³ and sp.² carbons indicated and electron transfer regime from amorphous carbon to graphitic carbon, as the latter serves as a reactive site C=O, pyridinic N, and pyridinic N were active sites for the activation by electron transfer to H₂O₂ 	[<u>37]</u>
 Wheat straws Pyrolysis: 700 °C, 2 h, N₂ atmosphere 	 [SMT] = 13.7 μM, [Biochar] = 1 g L⁻¹, [H₂O₂] = 3 mM, pH = 5 100% removed in 2 h 	 SSA and porosity were crucial in SMT adsorption and catalytic *OH generation Biochar surface acidity was negatively correlated with catalytic activation, whereas surface basicity was positively correlated with catalytic activation Excessive SMT adsorption prior to activation hindered H₂O₂ activation 	[38]
 Biogas residue + KHCO₃ activation Pyrolysis: 800 °C, 3.5 h, N₂ atmosphere Acid (HCI) washing 	 [Benzene] = 10 μM, [Biochar] = 1 g L⁻¹, [H₂O₂] = 3 mM, pH = 5 	 OFGs, C=C, pyridinic N, and graphitic N allowed electron transfer for 'OH, 'O₂⁻, and ¹O₂ formation ¹O₂ generation dominated the catalytic reaction 	[<u>39</u>]

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref	
 Sewage sludge Pyrolysis: 600 °C, 30 min Pyrolysis + kaolin: 1100 °C, 30 min, N₂ atmosphere 	 [CIP] = 10 mg L⁻¹, [Biochar] = 0.2 g L⁻¹, [H₂O₂] = 10 mM, pH = 4 <30% removed after 1 h of adsorption and 80% removed after 20 min from H₂O₂ addition 	 Large SSA and inorganic groups enhance CIP adsorption ·O₂⁻ is formed by reactions of *OH and H₂O₂ 	<u>[40]</u>	
 Pig manure Pyrolysis: 500 °C, 2 h, N₂ atmosphere 	 [TC] = 30 mg L⁻¹, [Biochar] = 0.5 g L⁻¹, [H₂O₂] = 5 mM, pH = 7.4 100% removed in 240 min 	 Electron transfer pathway from PFRs to H₂O₂ was responsible for *OH formation TC adsorption can block the active site and minimize reactions between PFRs and H₂O₂, lowering activation performance Removal efficiency decreased from 100% to 74.5% in 4th run 	[<u>41</u>]	
 Sugarcane residues + Fe impregnation Pyrolysis: 600 °C, 4 h 3 	 [OG] = 0.1 g L⁻¹, [Biochar] = 0.5 g L⁻¹, [H₂O₂] = 0.075 g L⁻¹, pH = 5.5 99.7% removed within 2 h 	 HO₂[•] and [•]OH are a function of H₂O₂ concentration Catalytic degradation preferred lower pH due to the higher oxidative potential of HO₂[•] and [•]OH, slower decomposition of H₂O₂ to H₂O and O₂, and formation of inner-sphere complexes of Fe oxides and OG 	[42]	so di
 Sugarcane bagasse + steel pickling waste liquor Pyrolysis: 400 °C, 2 h, N₂ 	 [MNZ] = 40 mg L⁻¹, [Biochar] = 0.3 g L⁻¹, [H₂O₂] = 5 mM, pH = [45] 5.61 3 100% removed within 2 h 	[<u>44</u>] • Surface-bounded [•] OH were the major ROS responsible for degradation ³	[<u>43</u>] i /) ;	imite vith s acl vation ance

Table 3. An overview of biochar preparation and performance in O_3 activation for organic pollutants removal.

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref
 Coking wastewater treatment sludge Pyrolysis: 700 °C, 2 h, N₂ atmosphere 	 [Phenol] = 0.2 g L⁻¹, [Biochar] = 1 g L⁻¹, [O₃] = 14 ± 1 mg L⁻¹, 1.0 L min⁻¹ 95.4% removed in 30 min 	 C-O and C=O served as active sites for ozone catalytic decomposition C=O adsorbed dissolved O₃ and initiated its rapid decomposition for ·O₂⁻ generation C=O was oxidized into O-C=O after reaction Presence of HCO₃⁻ promoted *OH and HCO₃* formation, reacting with O₃ for *O₂⁻ generation Removal efficiency decreased from 95.4% to 59.3% in 4th cycle 	[<u>46</u>]
 Activated petroleum waste sludge Pyrolysis: 850 °C, 1 h, N₂ atmosphere 	 [Benzoic acid] = 100 mg L⁻¹, [Biochar] = 1 g L⁻¹, [O₃] = 20 mg min⁻¹, pH = 3.8–10.0 ≥95% removed in 30 min 	 Functional C groups, Si-O groups, metallic oxides of Zn, Al, Fe, and Mg are expected as the active sites Reaction was suggested to be mediated by 'OH Excessive adsorption under acidic conditions leads to competition with ozonation process Removal efficiency fell to 79.1% in 5th cycle 	[47]
 Peanut shell Pyrolysis: 600 °C, 4 h, N₂ atmosphere 	 [KET] = 2 mg L⁻¹, [Biochar] = 500 mg L⁻¹, [O₃] = 0.5 L min⁻¹, pH = 6 ± 0.1 99.9% removed in 3 min 	 O₃ direct or indirect attack on C=O, C=C, and -OH on biochar initiated radical chain reactions Delocalized π-electrons react with H₂O to form hydroxide OH⁻ and H₃O⁺ that will 	[<u>48</u>]

Biochar Precursor and Synthesis	Performance	Removal Mechanism Re	ef
		yield HO ₂ , O_2^- , and O_4^- after reaction with O ₂	
4° 4	 ¹O₂, [•]O₂⁻, and [•]OH were the main species responsible for degradation 	gra M:	
		 Removal efficiency decreased to 94.8% in 5th cycle 	e

Table 4. An overview of biochar preparation and performance in PS activation for organic pollutants removal.

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref
 Food waste digestate Pyrolysis: 800 °C, 2 h, N₂ atmosphere 	 [X-3B] = 1 g L⁻¹, [Biochar] = 0.5 g L⁻¹, [PDS] = 1.5 mM, pH = 3.78 85.72% removed in 30 min 	 sp.² carbon served to produce radicals by PDS activation in an electron-accepting process Graphitic and pyridinic N facilitated ROS generation C=O contributed to ¹O₂ formation Removal efficiency decreased from 85.72% to 32.53% at 30 min in 2nd cycle 	<u>[49]</u>
 Peanut shells Pyrolysis: 900 °C, 2 h, N₂ atmosphere 	 [SMT] = 40 µM, [Biochar] = 0.2 g L⁻¹, [PMS] = 1 mM, pH = 6 98.3% removed in 120 min 	 Sieving to small-sized biochar (0–75 μm) enhanced PDS activation due to more graphitic and aromatic carbon, COOH content, and higher SSA COOH groups promoted SO₄^{*-} and [*]OH formation Biochar mediated electron transfer from SMT to PDS Electron-rich active sites transfer electrons to PDS for SO₄^{*-}, [*]OH, ¹O₂, and [*]O₂ generation 	[50]

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref
 Spent tea leave Pre-oxidation: 250 °C, 0.5 h, air environment Pyrolysis: 500 °C, 1 h, N₂ atmosphere 	 [CTC] = 50 mg L⁻¹, [Biochar] = 0.1 g L⁻¹, [PDS] = 1 g L⁻¹, pH = 6.0 97.4% removed in 90 min 	 Pre-adsorption was beneficial to the subsequent catalytic degradation Delocalized π-electrons and Fe facilitated SO₄^{•-}, [•]OH, and ¹O₂ generation 	[<u>51</u>]
 Dairy manure Anaerobic digestion: 37 °C, 35 days Pyrolysis: 800 °C, 2 h, N₂ atmosphere 	 [SMX] = 15 mg L⁻¹, [Biochar] = 1 g L⁻¹, [PMS] = 2.5 mM, pH = 5.56 90.2% removed in 60 min 	 Defects were positively correlated with degradation potential (R² = 0.92) Electron-rich C=O promoted *O₂⁻ and ¹O₂ generation Graphitic N accelerated electron transfer from carbon to O₂ for ¹O₂ formation Pyridine N was not an active site Graphitic structure facilitated electron transfer between SMX and PMS Removal efficiency decreased from 90.2% to 62.5% in 5th cycle 	[<u>52</u>]
 Straw Pyrolysis: 700 °C, 2 h, N₂ atmosphere N doping: Thiourea + biochar, pyrolysis: 800 °C, 2 h, N₂ atmosphere 	 [TC] = 20 mg L⁻¹, [Biochar] = 200 mg L⁻¹, [PDS] = 2 mM, pH = 7 97% removed in 60 min and 100% in 120 min 	 Reaction mainly relied on nonradical electron transfer between TC and PDS due to enhanced graphitization degree Radicals had no effect on TC degradation Removal efficiency decreased from 100% to 55% in 3rd cycle 	[53]

Biochar Precursor and Performance Synthesis	Removal Mechanism	Ref
 [SMX] = 500 µg L⁻¹, [Biochar] = 100 mg L⁻¹, [PI = 500 mg L⁻¹ Pyrolysis: 850 °C, 1 h 96% removed in 120 min 	 PS] Reaction controlled by either electron transfer/¹O₂ control surface-bound radicals 	[<u>54]</u>
• Wheat straw + B doping • Pyrolysis: 900 °C, 2 h, N ₂ atmosphere • KOH activation: 600 °C, 2 h, N ₂ atmosphere • Acid (HCl) washing	 B species acted as Lewis acid sites enhancing PDS adsorption L⁻¹, Defects and sp.²-conjugated π-system facilitated electron transfer B substitution in carbon matrix enhanced catalyst stability due to active sites reversible transformation during catalytic activation Removal efficiency decreased from 92% to 90% in 5th cycle 	[<u>55</u>]
 [MB] = 8 mg L⁻¹ [Biochar] = 0.2 [Biochar] = 0.2 L⁻¹, [PMS] = 0.4 L⁻¹, pH = 3-4 Pyrolysis: 800 °C, 2 h >95% removed 30 min 	 Synergy between S and N moieties altered surrounding electron density OH, SO₄^{•-}, and ¹O₂ participated in the catalytic reaction Removal rate decreased gradually from 0.202 min⁻¹ to 0.019 min⁻¹ in 4th cycle 	[<u>56</u>]
• Corncob + N doping • [SDZ] = 10μ M, [Biochar] = 3 g • Pyrolysis: 700 °C, 2 h, N ₂ atmosphere = 7 • 96.2% removed 10 min	 Pyridinic and pyrrolic N at edge sites disturbed electron density to create active sites pH Graphitic N was not well correlated with catalytic activity 	[<u>15</u>]

Biochar Precursor and Synthesis	¹ Performance	Removal Mechanism	Ref	_
		 PDS was reduced at electron-rich N while SDZ was oxidized around adjacent electron-deficient C 		-
		 Reaction was dominated by an electron transfer regime that was unaffected by inorganic anions except NOM 		
		 Removal efficiency decreased from 96.5% to 83.0% after 3 cycles 		
	• [OG] = 50 mg L ⁻¹ ,	 Quaternary N induces asymmetric spin density and low electron density to adjacent carbons, facilitating the chemical bonding with negatively charged O atoms of the O-O bond in PDS for free radicals formations 		_
 Wetland plants (reed) + N doping Pyrolysis: 900 °C, 90 	[Biochar] = 0.2 g L ⁻¹ , [PDS] = 2 mM pH = 9.5 ± 0.8	 Large SSA and π-π interactions between OG aromatic rings graphitic carbon structure enhanced adsorption 	[<u>57]</u>	
min, N_2 atmosphere	100% removed in60 min	- Catalytic activity was governed by nonradical pathway of surface-activated PDS complexes and $^{1}\mathrm{O}_{2}$		
		 Removal efficiency decreased from 98.3% to 45.0 ± 2.0% after 5 runs 		
 Spirulina residue + N doping Pyrolysis: 900 °C, 90 	 [SMX] = 20 mg L⁻¹ ² [Biochar] = 0.5 g ⁴ L⁻¹, [PDS] = 6 mM 	 Biochar provided electron-mediating medium between SMX and PDS for nonradical degradation 	[58]	Typical onmen atalyst
 Acid (HCI)_washing cb 	 100% removed in 45 min 	 N doping caused a redistribution of charge densities in graphitic carbons where PDS [59] then bond with positively charged O atoms adjacent to N dopants to enhance activation performance 		tocataly le excit nigrate e electr
[<u>60][6</u>	2	vb		e cataly 1 electr

donors, respectively. The e_{cb}^- can reduce O_2 to generate O_2^- whereas h_{vb}^+ can react with the OH⁻ to generate OH. Nonetheless, O_2^- can only be generated when the CB potential is more negative than the reduction potential

Biochar Precurso Synthesis	er and Performance	Removal Mechanism	Ref	y positive
	2	 Surface-activated metastable PDS/carbon 		
		complex participated in reaction		onaceous
		 Removal efficiency decreased from 100% to 42.51% after 3 cycles 		e organic

Table 5. An overview of biochar preparation and performance as photocatalyst activation for organic pollutants removal.

Biochar Precursor and Synthesis	Performance	Removal Mechanism	Ref
 Pine needles Pyrolysis: 500 °C 2 h 	 [DEP] = 20 mg L⁻¹, [Biochar] = 0.2 g L⁻¹, pH = 7, 100 W Hg lamp (350-450 nm) 72 3% removed within 	 *OH was dominate species contributing to 76.7–82.8% DEP removal UV irradiation excited quinone-like moieties to singlet states and then rapidly went through an intersystem crossing to yield excited triplet states that further reacted with dissolved oxygen by energy transfer to form ¹O₂ PFRs can mediate electron transfer to O₂ for *OH 	[65]
500 0,211	120 min	 formation Electron transfer from VB to CB and electron-hole pairs formation allows electrons transfer to redox- active functional groups defects to form relatively stable PFRs 	
 Wheat straw Pyrolysis: 500 °C, 2 h 	 [DEP] = 20 mg L⁻¹, [Biochar] = 0.2 g L⁻¹, pH = 7, 100 W Hg lamp (350–450 nm) 60.9% removed within 120 min 	 *OH was dominate species contributing to 76.7– 82.8% DEP removal UV irradiation excited quinone-like moieties to singlet states and then rapidly went through an intersystem crossing to yield excited triplet states that further reacted with dissolved oxygen by energy transfer to form ¹O₂ 	[65]

Biochar Precursor and Synthesis	Performance	Removal Mechanism	
		 PFRs can mediate electron transfer to O₂ for °OH formation Electron transfer from VB to CB and electron–hole pairs formation allows electrons transfer to redox-active functional groups defects to form relatively stable PFRs 	
		• More amounts of phenolic structures and defects on ball-milled biochar aided in $\cdot O_2^-$ generation	
 Poplar woodchips 	 [EFA] = 20 mg L⁻¹, [Biochar] = 0.2 g L⁻¹, pH = 7, 500 W Xe lamp (UV cut-off filter), pH = 6.8 80.2% removed after 1.5 	• OFGs, particularly O-C=O, was important in ROS generation	
 Pyrolysis: 300 °C, 3 h 		• OFGs acted as CB and defects acted as VB, forming a semiconductor-like structure	[<u>66</u>]
• Ball milling	h under dark and 2.5 h under illumination	- Excited electrons after light exposure react with O_2 to form O_2^-	
		- h^+ on the defects with strong oxidative and ${\rm O_2}^-$ will attack EFA	

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decontamination of organic pollutants from water by different applications. Among the numerous applications of biochar in wastewater treatment, adsorption, H₂O₂ activation, O₃ activation, PS activation, and photocatalysis hold the superlative potential in the treatment of organic pollutants. These applications were compared with respect to performance, mechanism of removal with emphasis on pollutant-biochar interactions and biochar active sites' involvement, tolerance to changes in water pH, stability of biochar after consecutive cycles of pollutant treatment, and economic factors. Each application has its own advantages and limitations. Adsorption is superior in terms of simplicity of operational procedures, ability to remove oxidation-resistant pollutants, and cost-wise. AOPs utilize more active sites of biochar and are able to mineralize organics pollutants or form less resistant organic byproducts, so they can be treated by conventional methods. All AOPs have their own advantages. For instance, PS activation is effective in utilizing all of the biochar active sites along with having a monopoly on the capability to produce SO4 -. H2O2 is a safe oxidant with nonharmful decomposition products (hydrogen and oxygen). O3 is a strong oxidant with various activation pathways. Photocatalysis does not require the use of any oxidant. Nonetheless, limitations are present in each application. (i) The low durability of biochar active sites during AOPs is repeatedly reported. In addition, (ii) the performance of pristine biochar for environmental remediation of organic pollutants is often slow with low efficiency. (iii) The cost of light source during photocatalytic reactions is a drawback. (iv) Adsorption is unable to mineralize or degrade organic pollutants. (v) Biochar-pollutant and biocharoxidant interactions are highly influenced by water pH changes, hindering its application in real wastewater. To enhance biochar performance in environmental remediation, several suggestions can be made:

- The fabrication of robust biochar with high graphitization and aromaticity degree can prevent poor durability. In addition, compositing with polymers can protect the active site of biochar from cannibalistic reactions and can also simplify the separation of the catalyst.
- Heteroatom (i.e., N, S, B, F, P) doping is often found to have a fruitful effect on the performance of biochar in environmental remediation. However, co-doping and triple-doping are rarely reported. Hence, more studies are needed on multi-doped biochar, with systematic investigations on the interactions between the multi-dopants within the biochar structure and its effect on the biochar performance. Moreover, as heteroatomic doping of biochar can be achieved by in situ and post-treatment methods, a comparison between the two techniques is needed to determine the most efficient method.
- For photocatalytic applications, LED lamps can be used instead of conventional light sources to avoid an additional cost of electricity and better utilization of energy.
- Synergistic removal by adsorption with other AOPs methods may provide constructive results. Nonetheless, the optimization of adsorption contribution is crucial to avoid undesirable competition over biochar active sites and hinder removal performance.
- Specific tailoring of biochar active sites that are unlikely to be affected with pH changes and/or can produce species that are resistant to changing pH (i.e., nonradical pathways) can endow the biochar with better performance over different water matrixes.

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