Activation of persulfate by swine bone derived biochar: Insight into the specific role of different active sites and the toxicity of acetaminophen degradation pathways

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¹⁷ Abstract

18 Recently, persulfate (PS) activation system has grown up as a primary branch of 19 advanced oxidation processes, and biochar has been recognized as a potential 20 nonmetal material in this field. However, few studies have focused on the 21 corresponding relationship between actives sites on biochar and active species in 22 AOPs. To pave this way, similar biochar (obtained from different pyrolysis 23 temperature) with different functional structures were involved. In this study, biochar 24 derived from swine bone (BBC) was applied in PS activation system to degrade 25 acetaminophen (ACT). The results showed that both radical and non-radical pathway 26 worked in the PS/BBCs systems, and the degradation rate (from 0.1042 to 0.4364 27 min⁻¹) climbed with the increase of pyrolysis temperature (from 700 to 900 °C). To 28 probe into the corresponding relationship between functional structure and active 29 species, the effect of pyrolysis temperature on functional structure was analyzed. It 30 came out that 1) defects could act as active sites for various active species; 2) 31 persistent free radicals could do favor to the generation of ${}^{1}O_{2}$ and O_{2} ; 3) 32 hydroxyapatite in swine bone only served as hard templet for the porous structure. 33 ACT degradation process was measured by Liquid chromatograph-mass spectrometer, 34 and Scendesmus obliguus was applied to investigate the toxicity of PS/BBCs system. 35 It illustrated that the existence of SO₄⁻⁻ mainly contributed to the generation of high 36 toxic intermediates (such as biphenyl and diphenyl ether) in the PS/BBCs system. 37 Furthermore, the enhancement of adsorption capacity would mitigate the toxicity of 38 PS/BBCs systems to some extent.

³⁹ Keywords: Biochar; Catalysis; Intermediates; Toxicity; Persulfate activation
 ⁴⁰ system

⁴¹ **1. Introduction**

Advanced oxidation processes (AOPs), including photocatalysis (Li et al., 2020; Zhang et al., 2019), electrocatalysis (Huang et al., 2020; Liu et al., 2019), Fenton oxidation (Li et al., 2019; Luo et al., 2020), ozonation (Levanov et al., 2019), and thermal activation (Sun et al., 2020), etc.. AOPs have been extensively applied to decompose refractory organic matter. Over the past decade, persulfate (PS) activation system has gradually grown as a promising option in AOPs, for it is efficient and economical (Tang et al., 2018; Yang et al., 2020).

49 Up to now, numerous studies have been launched to develop efficient catalyst to 50 activate PS. Among the available carbonaceous materials, biochar attracts much 51 attention for its simple design and low cost. However, conventional biochar cannot 52 activate PS efficiently without heteroatom doping or metal loading. Undeniably, 53 heteroatom doping and metal loading process would increase the cost and induce a 54 risk of metal leaching. Thus, it is urgent to develop an available and efficient pristine 55 biochar to activate PS. Swine bone is mainly composed of collagen and 56 hydroxyapatite (HOP), which is different from other biomass. Moreover, the swine 57 bone derived biochar (BBCs) exhibited relatively high specific surface area and 58 performed well in supercapacitor (Huang et al., 2011). Thus, BBCs were regarded as a 59 promising option in PS activation system, and our previous study verified this 60 inference (Zhou et al., 2019). That is, BBCs could efficiently activate PS to degrade

⁶¹ organic pollutants without the heteroatom doping or metal loading.

62 On account of the complex composition of biochar, the specific roles of different 63 active sites on biochar remain vague. To pave this way, study has been launched to 64 investigate the roles of different oxygen-containing groups (Zhou et al., 2020). 65 However, other functional structures on biochar have not been further discussed. As is 66 well-known, pyrolysis temperature could influence functional structures. To be 67 specific, Li and his groups reported that the specific surface area of biochar increased 68 with the climb of annealing temperature and mesopores were principally formed in 69 the temperature holding stage of thermal treatment (Zhu et al., 2018). It has been 70 proved that annealing temperature could not only influence the oxygen content of 71 biochar, but also vary the proportion of different oxygen-containing groups (Klupfel 72 et al., 2014). Furthermore, the annealing temperature could change the amount and 73 type of defects and persistent free radicals (PFRs) on biochar (Andrews et al., 2001; 74 Fang et al., 2015). In addition, acid/ alkali treatment is a common approach to vary the 75 composition and pore structure of biochar (Fu et al., 2018; Huang et al., 2011). In this 76 regard, the role of different functional structures might be able be deduced by 77 comparing the mechanism of different homologous biochar. Accordingly, in order to 78 further dig into the specific role of different functional structures, BBCs obtain by 79 acid treatment and different pyrolysis temperature were introduced in PS activation 80 system.

⁸¹ With the explosion of research on PS activation system, some studies have ⁸² focused on its environmental risk. It has been reported that PS activation system

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83	might produce intermediates that possess higher toxicity than the pollutant itself
84	(Cheng et al., 2020; Yang et al., 2019). SO4 in PS activation system might attack
85	phenols to generate phenoxy radicals, which could induce the formation of biphenyls
86	and diphenyl ethers. Furthermore, Ji and co-workers reported that nitrogen dioxide
87	radicals were detected in SO4 based oxidation system when nitrophenols were
88	denoted as the targeted contaminant. However, except for the denitration process, the
89	renitration process might also take place in this system, which might lead to the
90	formation of toxic polynitrophenols (Fu et al., 2019; Ji et al., 2019). Moreover, it has
91	been reported that dissolve organic matter (DOM) and PFRs on biochar showed
92	toxicity to organisms (Ruan et al., 2019; Sun et al., 2021). Thus, it is necessary to
93	assess the comprehensive environmental risk of PS activation system. With respect to
94	PS/BBCs system, the pyrolysis temperature would influence the amount of DOM
95	(Chen et al., 2015) and alter the functional structure on BBCs, which would result in
96	different proportion of degradation mechanisms. Finally, a difference in toxicity
97	would be observed.
98	In this study, acetaminophen (ACT) was selected as the target pollutant. As a

ophen (ACI) ıy, g ոլ 99 typical pharmaceutical and personal care product (PPCPs), ACT is usually applied as 100 an analgesic. Up to now, ACT was widely detected around the world (Vo et al., 2019). 101 The concentration of ACT could reach 12.5 ng/L in surface water in China, and it has 102 been recorded as the PPCPs with the highest concentration (Sun et al., 2016). The 103 leakage of ACT would do harm to the ecological environment and human health (Du 104 et al., 2020). It has been reported that the effective concentration of ACT to Daphnia magna was 50 mg/L in 24 h (Henschel et al., 1997). AOPs have been proved as an
 efficient method to treat with ACT in aqueous media (Bicalho et al., 2020), thus
 PS/BBCs system was applied to deal with ACT in aqueous media.

108 Overall, in order to investigate the roles of different functional structures in PS 109 activation system, BBCs treated with acid and different temperatures were introduced 110 in PS activation system. Nitrogen adsorption and desorption analysis, Raman 111 spectrometer, X-ray photoelectron spectrometer (XPS) and electron paramagnetic 112 resonance (EPR) spectrometer were applied to probe the change in functional 113 structure of BBCs. Ulteriorly, Scendesmus obliquus were applied to investigate the 114 toxicity of PS/BBCs system. Combining the results of toxicity experiment and 115 degradation mechanism, the environmental risk of different degradation mechanisms 116 could be roughly deduced. This study can not only give information for the further 117 oriented synthesis of biochar, but also drive the downstream application of PS 118 activation system.

¹¹⁹ **2. Materials and methods**

¹²⁰ 2.1 The preparation of catalysts

¹²¹ The biochar used in this study was derived from swine bone. The de-fatted ¹²² spareribs were washed and dried at 80 °C to remove the impurity on swine bone. ¹²³ Furthermore, BBCs were synthesized according to previous study (Huang et al., 2011; ¹²⁴ Zhou et al., 2019). Concretely, in order to facilitate subsequent operations spareribs ¹²⁵ were pre-carbonated at 450 °C under N₂ atmosphere. Then, the collected particles ¹²⁶ were sifted after ground for further carbonization (700 °C, 800 °C or 900 °C). Finally,

127	the product was soaked in 6 M HNO ₃ for 12 h, then the obtained material was rinsed
128	until the filtered solution was neutral. The acid treatment could not only change the
129	pore structure of BBC, but also deactivate PFRs on BBCs. The pyrolysis temperatures
130	were set as 700 °C, 800 °C, and 900 °C (hold for 2 h), and the BBCs were labeled as
131	BBC-700, BBC-800, and BBC-900, respectively. Moreover, the sample carbonized at
132	900 °C without acid treatment was labeled as BBC-AW.

¹³³ 2.2 Catalytic procedure

134 All experimental groups were conducted in 100 mL beakers. Magnetic stirring 135 apparatus was applied to equally distribute the material and PS in water. In order to 136 avoid the influence of adsorption process, the adsorption experiment (1 hour) was 137 carried out before the addition of PS. Specifically, 0.1 g/L prepared BBCs were added 138 in 50 mL ACT (20 mg/L) solution, then, the adsorption began. After 1 h adsorption, 1 139 g/L PS was added to the beaker to launch the PS activation process. The experimental 140 conditions were determined based on the empirical value of previous studies (Zhou et 141 al., 2019; Zhou et al., 2020), and all batches were taken in the same conditions. The 142 samples (1.5 mL) were collected at 0, 1, 5, 10, 15, 20 min. Before the concentration 143 measurement, the sample was filtered by nylon filter (0.22 µm), and 0.5 mL methanol 144 was applied to inhibit the effect of residual radicals. Moreover, all batches were taken 145 at room temperature, and the initial pH was controlled at around 6.

Active species capture experiments were taken to assess the role of different active species in the PS/BBCs system. Benzoquinone (BQ, 1 mM), NaN₃ (1 mM), ethanol (EtOH, 0.75 M), and tert-Butyl alcohol (TBA, 0.75 M) were applied as the

149	quenching agents for $O_2^{\bullet, 1}O_2$, $SO_4^{\bullet, \bullet}$, and $\bullet OH$, respectively. The corresponding agent
150	was added into the ACT solution before the adsorption process.
151	Furthermore, to quantify the rate of catalytic reaction, all batches were fitted by
152	pseudo-first order kinetics based on Langmuir-Hinshelwood model. The results
153	showed that reactions involved in this study abided by the first order kinetics equation
154	(Eq. (1)).
155	$In(C_t/C_0) = -k_{obs}t $ ⁽¹⁾
156	C_0 and C_t are the label of initial concentration and the real-time concentration of ACT,
157	k_{obs} is defined as the pseudo-first-order rate constant for each batch.
158	2.3 Characterization of catalyst
159	Raman spectra (Horiba Scientific LabRAM HR Evolution) and XPS (Thermo
160	Scientific K-Alpha) were applied to analyze the functional groups and characteristics
161	of the catalyst in this study. Nitrogen adsorption and desorption analysis was
162	conducted on Quantachrome Autosorb AS-1 to investigate the BET surface area of
163	BBCs. Magnettech MiniScope MS 5000 was applied to analyze the persistent free
164	radicals (PFRs) on biochar, and EPR spectra in aqueous media were taken on Bruker
165	ER200-SRC. Total organic carbon (TOC) was measured on TOC-L CPN Shimadzu.
166	2.4 Analysis
167	The concentration of ACT was analyzed on Agilent 1200 (equipped with C18
168	column (5.0 μ m, 4.6 mm x 250 mm)). The mobile phase was ultrapure water and
169	methanol (70:30, v/v). The column temperature was 40 °C. Furthermore, the flow rate
170	set as 1 min/L, and the UV detector worked at 243 nm. Liner sweep voltammetry

171	(LSV) and electrochemical impedance spectroscopy (EIS) were taken on CHI760E
172	electrochemical workstation. To verify the existence of different active species, ESR
173	was measured in liquid phase (Bruker ER200-SRC), 2,2,6,6-tetramethylpiperidine
174	(TEMP) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were selected as the trapping
175	agents to verify the exist of active substance. Moreover, SO4 and [.] OH were detected
176	in deionized water, while O2 was detected in methanol circumstance. The
177	degradation pathway of ACT was determined by liquid chromatograph-mass
178	spectrometer (LC-MS), and the mobile phase consisted of buffer A (0.1% formic acid
179	in water) and buffer B (0.1% formic acid in acetonitrile).

Furthermore, the toxicity of different PS/BBCs systems were assessed by Scendesmus obliquus. As a kind of green algae, Scendesmus obliquus was a common option to evaluate the toxicity in aqueous media. The inhibition rate of Scendesmus obliquus in 96 h was applied to assess the toxicity of the mixed solutions during the activation reaction (Scendesmus obliquus was bought from the Freshwater Algae Culture Collection at the Institute of Hydrobiology), and the detailed information was presented in supported information (Text S1).

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3. Results and discussion



In our previous studies, the catalytic capacity of BBCs has been proved (Zhou et al., 2019). To be specific, BBCs could effectively activate PS to degrade refractory contamination, and the radical pathway (SO_4^{--} , •OH and O_2^{--}) and non-radical pathway (electron transfer pathway and ${}^{1}O_2$) both took effort in this system.

193	Subsequently, chemical deactivation method was applied to explore the roles of
194	different oxygen-containing groups in the PS/BBCs systems (Song et al., 2021; Zhou
195	et al., 2020). The results showed that 1) C=O could do favor to electron transfer
196	pathway; 2) -OH and -COOH might be conducive to radical pathway (SO ₄ and •OH)
197	(Zhou et al., 2020). However, the roles of other functional structures on BBCs in PS
198	activation system remain unclear. In this study, several approaches were tried to
199	investigate the specific role of other functional structures on biochar in PS activation
200	system.

201 To explore the role of other functional structures on biochar, different BBCs were 202 introduced in PS activation system. As mentioned in section 2, BBC-700, BBC-800, 203 BBC-900, and BBC-AW were involved into the PS activation system. The k_{obs} of 204 BBC-700, BBC-800, BBC-900, and BBC-AW under preset conditions was 0.1042, 205 0.32933, 0.4364, 0.1427 min⁻¹, respectively (Fig. 1). With the climb of annealing 206 temperature, an upward tendency of degradation rate could be observed. The results 207 of TOC further verified this conclusion. After 1 h catalytic reaction, the mineralization 208 rate of PS/BBC-900 system could reach 83.5% (Fig. S1). Besides, the kobs of 209 PS/BBC-900 system was much higher than that of PS/BBC-AW system, which 210 illustrated that acid treatment could effectively boost the catalytic capacity of BBC 211 (The results of Fig. 2 will be further evaluated in section 3.2).



Fig. 1 (a) Catalytic performance of BBC-700, BBC-800, BBC-900, and BBC-AW
(degradation rate in 20 min), (b) the corresponding pseudo-first-order rate constants.
[ACT] = 20 mg/L, [PS] = 1 g/L, [BBCs] = 0.1 g/L, [Temp] = 298 K.

216 Generally, the catalyst in the PS activation system takes effect by radical and non-217 radical pathway. In order to distinguish the mechanism of PS/BBCs systems, active 218 species capture experiments, EPR spectra, and electrochemical tests (LSV and EIS) 219 were carried out. The active species capture experiments illustrated that SO₄⁻⁻, 'OH, 220 O_2 , and 1O_2 could assist the degradation of ACT in the PS/BBCs system (Fig. 2 and 221 Fig. S2). Moreover, the existence of SO_4 , O_2 , O_2 , and O_2 were further verified 222 by EPR spectra (Fig. S3). It is obvious that the inhibition effect of trapping agents was 223 weak in the PS/BBC-900 system. Moreover, O_2 and 1O_2 exhibited a relatively minor 224 role in the PS/BBC-900 system. In the PS/BBC-800 system, active species played a 225 vital role, among which O2[•] was the most important participant. Specifically, the 226 degradation rate of PS/BBC-800 decreased from 0.32933 to 0.0688 min⁻¹ after the 227 addition of BQ. With respect to PS/BBC-700 system, the degradation process was 228 primarily contingent on O2⁻⁻ and ¹O2. In the PS/BBC-900, PS/BBC-800 and PS/BBC-229 700 system, the inhibition effect of NaN₃ presented similar trend with BQ, it might because O_2^{--} could be converted into 1O_2 in PS activation system (Eq. (2-3)). However, the role of O_2^{--} could be distinguished from 1O_2 in the PS/BBC-AW system. The difference in the role of O_2^{--} and 1O_2 might be due to the lack of 'OH and H⁺. As is shown in Fig. 2d, the addition of 'OH trapping agent showed a weak inhibitory effect (from 0.14 min⁻¹ to 0.13 min⁻¹) in the PS/BBC-AW system.

$$^{\bullet}OH + O_2^{\bullet-} \rightarrow {}^{1}O_2 + OH^{\bullet}$$
⁽²⁾

(3)

$$2H^+ + 2O_2^{\bullet} \rightarrow {}^1O_2 + H_2O_2$$

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Fig. 2 Active species capture experiment (corresponding pseudo-first-order rate constants) of (a) BBC-900, (b) BBC-800, (c) BBC-700, (d) BBC-AW. [ACT] = 20 mg/L, [PS] = 1 g/L, [BBC] = 0.1 g/L, [Temp] = 298 K. The dosage of the trapping agents: [EtOH] = 0.75 M, [TBA] = 0.75 M, [BQ] = 1 mM, [NaN₃] = 1 mM.

243	LSV is usually applied to evaluate the electron transfer capacity of PS activation
244	system. The increase of the current indicates the enhancement of electron transfer
245	capacity. As shown in Fig. S4, only when the PS, BBCs, and ACT existed at the same
246	time, the current would reach the peak. It indicated that electron transfer process took
247	effect in every PS/BBCs system. Moreover, the enhancement of current was most
248	obvious in the PS/BBC-900 system. It manifested that electron transfer pathway
249	played a central role in the PS/BBC-900 system. This conclusion was further verified
250	by the results of EIS (Fig. 3b). It is widely considered that the radius of the arc is the
251	representation for impedance, and a smaller radius illustrates a stronger ability for
252	electron transfer (Lai et al., 2018). According to the equivalent circuit fitting, the
253	interface charge transfer resistances of BBC-AW, BBC-700, BBC-800, and BBC-900
254	were 11390, 3005, 1112, and 431 Ω , respectively. Obviously, BBC-900 had the lowest
255	impedance. It was in line with the current signal in LSV. As a result, non-radical
256	pathways and radical pathway both existed in all PS/BBCs systems, and the
257	proportion of non-radical pathway increased with the increase of annealing
258	temperature. Furthermore, acid treatment did favor to the electron transfer pathway.



Fig. 3 (a) LSV measured with the bare GCE electrode by BBCs in the presence of PS or ACT, (b) EIS Nyquist plots of bare GCE and BBCs/GCE with frequency range from 0.01 Hz to 10^5 Hz, and the insert was the equivalent circuit diagram. [ACT] = 20 mg/L, [PS] = 1 g/L, [BBC] = 0.1 g/L, [Temp] = 298 K.

²⁶⁴ 3.2. The functional structure analysis of BBC

Firstly, the active sites for non-radical pathway were investigated. As is known to all, the non-radical pathway relies on the formation of ternary system (catalyst, PS and pollutant), and the radical pathway can be induced by the collision between catalyst and PS (Tang et al., 2018). In this regard, comparing the functional structures of used BBC-900 and BBC-900 treated with PS could give information for the mechanism of non-radical pathway.

271 Defect is a common active site in PS activation system. It exhibits a high redox 272 potential, which could promote the electron transfer between PS and catalyst (Duan et 273 al., 2015b). Furthermore, the graphitized structure could facilitate the electron transfer 274 capacity of carbonaceous materials (Ye et al., 2019a). Raman spectra was taken to 275 investigate the roles of defects and graphitized structure in the PS/BBCs system. The 276 peaks at 1350 cm^{-1} (D) and 1580 cm^{-1} (G) are the signal for the defects and graphite 277 structure, respectively. The G peak is caused by the high-frequency E_{2g} phonon at the 278 Brillouin zone center, and the appearance of D peak relates to the defects in six-atom 279 benzene rings (Ferrari and Basko, 2013). Generally, the intensity ratio of D and G 280 (I_D/I_G) is defined as the indicator to evaluate the graphitization degree (or defective 281 level) of materials (Wan et al., 2020; Wan et al., 2019). After reacting with PS, the value of I_D/I_G decreased from 1.1104 to 1.0771, and it further decreased to 1.0407 when ACT was added into the system (Fig. 4a). The result illustrated that the introduction of ACT could further consume the defects on BBC-900. Consequently, it is reasonable to infer that the defects could be regarded as the active sites for nonradical pathway (electron transfer pathway).

287 H₂O₂ has been applied as oxidizing agent to modify the oxygen-containing 288 groups on biochar surface (Zhang et al., 2018). As a typical peroxide, PS might have a 289 similar effect on oxygen-containing groups. In this study, XPS was applied to probe 290 the variation of oxygen-containing groups on BBC-900. The Fig. 4b-d exhibited the O 291 1s high resolution of BBC-900, BBC-900 treated with PS, and BBC-900 treated with 292 PS and ACT. Obviously, the PS could oxidize the C-O on BBC-900, the proportion of 293 C-O declined from 68.24% to 53.79%. Interestingly, the proportion of C-O on BBC-294 900 reached 60.85% when ACT was introduced. It illustrated that the PS could 295 oxidize the oxygen-containing groups of BBC-900, and ACT might inhibit this 296 oxidation process. This might be ascribed to the competitive adsorption of ACT and 297 PS, which might inhibit the oxidation process of PS/BBCs systems. On the one hand, 298 -OH and -COOH could adsorb organic contaminants by hydrogen bond (Ahmad et al., 299 2014; Yang et al., 2021). On the other hand, it also has been reported that -OH and -300 COOH could act as the adsorption site for PS (Ren et al., 2020a). To be specific, -OH 301 obtained the highest PS adsorption energy (-2.99 eV versus -2.37 and -2.69 eV of 302 C=O and -COOH, respectively) among the oxygen-containing groups (Ren et al., 303 2020b). Given these, instead of promoting the electron transfer process, -OH and -

304 COOH mainly do favor to the adsorption process in the PS/BBCs systems.



306 Fig. 4 (a) Raman spectra of BBC-900, and O1s spectrums of (b) BBC-900, (c) BBC-307

900 treated with PS, (d) BBC-900 treated with PS and ACT.

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308 To further figure out the functional structures that would influence the catalytic 309 performance of BBCs, the properties of BBC-700, BBC-800, BBC-900 and BBC-AW 310 were characterized. Firstly, nitrogen adsorption and desorption analysis were taken to 311 investigate the pore structure and specific surface area of BBCs. The results showed 312 that BBC-900 obtained the highest specific surface area (1199.920 m²/g), and the 313 specific surface area of BBC-700, BBC-800, and BBC-AW were 603.375, 922.040, 314 and 43.560 m²/g, respectively. In addition, the pore volumes of BBC-700, BBC-800, 315 BBC-900, BBC-AW were 0.454, 0.958, 1.420, 0.137 cm³/g, respectively. The growth 316 trend of catalytic capacity was the same as that of specific surface area (Fig. 1). 317 Furthermore, aside from BBC-AW, the correlation (positive linear relationship, $R^2 =$ 318 0.94743) between k_{obs} and specific surface area was strong (Fig. S5). However, the 319 linear relationship did not exhibit between degradation rate and other functional 320 structures (such as defects, oxygen-containing groups). This might support that 321 specific surface area was an important influence factor for degradation rate. 322 Interestingly, the relatively low specific surface area of BBC-AW did not completely 323 inhibit the degradation of ACT. Consequently, the worked active sites on BBC-AW 324 were quite different from other BBCs in this study. Taking radical trapping 325 experiments into consideration, a distinct inhibitory effect of BQ to PS/BBC-AW 326 could be seen. It manifested that the unique active sites on BBC-AW would do favor 327 to the generation of O_2 .

328 It has been reported that the defect on biochar could promote the generation of 329 O_2 ⁻⁻ and 1O_2 (Zhou et al., 2020), Raman spectra were applied to access the role of 330 defects in the PS/BBCs systems. The I_D/I_G of BBC-AW was 1.1662, while the I_D/I_G of 331 BBC-700, BBC-800, and BBC-900 was 1.2075, 1.3811, and 1.1104, respectively. 332 Obviously, with the increase of carbonization temperature, the value of ID/IG 333 experienced a trend of rise first and decline at last, and it was consistent with previous 334 studies. Concretely, the relatively low annealing temperature could decrease the 335 oxygen content on carbonaceous materials and form defects, and the relatively high 336 temperature would remove defects (such as bond rotations and non-hexagonal rings) 337 to generate graphitized structure (Andrews et al., 2001; Cheng et al., 2019).

338 Interestingly, the variation of I_D/I_G roughly synchronized with the change in the 339 proportion of SO₄⁻⁻ and 'OH. It might support that the defect was the active sites for 340 SO_4 and OH. Moreover, the weak correlation between k_{obs} and I_D/I_G could be 341 observed. It might be originated from the confluence of defects and graphitization 342 degree, both of which could benefit the catalysis performance (Lai et al., 2020; Ye et 343 al., 2019b). As is well known, the high graphitization degree can facilitate the electron 344 transfer process and defects can act as active sites in PS activation system. As 345 presented in Fig. 5a, BBC-AW did not indicate a distinct superiority in defects. So, 346 O₂⁻⁻ generated in the PS/BBC-AW system did not trigger by defects.



Fig. 5 (a) The nitrogen adsorption/desorption isotherms of BBCs, (b) the Raman
 spectra of BBCs.

³⁵⁰ Ulteriorly, PFRs could serve as active sites in PS activation system (Yang et al., ³⁵¹ 2016). ESR was used to measure PFRs on BBCs. The result showed that g factor of ³⁵² BBC-AW was around 2.0055, which could be categorized as the oxygen-centered ³⁵³ PFRs (Fang et al., 2014; Lomnicki et al., 2008). The intensity of PFRs suffered an ³⁵⁴ obvious decline after the PS activation process, and the acid treatment almost wiped ³⁵⁵ off PFRs on BBC-AW (Fig. 6a). In addition, Fang and co-workers reported that PFRs ³⁵⁶ could activate the O_2 to generate O_2^{--} (Fang et al., 2015). Consequently, it was ³⁵⁷ reasonable to regard PFRs as the unique active sites on BBC-AW to generate O_2^{--} .



Fig. 6 (a) ESR spectra of BBC-AW, BBC-900, and used BBC-AW, (b) XPS survey of
 BBC-700, BBC-800, BBC-900, and BBC-AW.

361 XPS was applied to assess the surface elements distribution of BBCs. As shown 362 in Fig. 6b the oxygen content dropped with the climbing of annealing temperture. The 363 XPS survey illustrated that BBC-700, BBC-800, BBC-900 had similar elementary 364 composition. The C 1s high resolution spectrum illustrated that the sp³ carbon (C-C) 365 proportion of BBC-700, BBC-800 and BBC-900 was 68.14%, 73.24% and 41.98%, 366 respectively. Furthermore, BBCs showed a similar propotion of C=O (Fig. S6). 367 However, the striking difference in oxygen content would result in a quantitative 368 diffrence in C=O. It has been repeatly reported that C=O could be denoted as the 369 active sites for electron transfer pathway, but the quantity of C=O did not affet the 370 propotion of electron transfer pathway in this study (Fig. 3). Adsorption capacity 371 might be the answer for this contradiction (Fig. S7) (Ren et al., 2020a; Yu et al., 2020). 372 As mentioned above, the PS adsorption capacity was closely related to the catalytic 373 permofmance of catalysts, whereas excess oxygen-contianing groups on carbonaceous 374 materials might hinder the approach of PS (Ren et al., 2020b). Noteworthy, -OH and -375 COOH have been reported as the active sites for 'OH and SO₄. The active species 376 capture experiment showed that the varation trend of 'OH and SO₄.⁻ proportion was 377 inconsistent with the quantity of -OH and -COOH on BBCs. Thus, there might be 378 other active sites that do favor to the production of 'OH and SO4'. Taken the results 379 of Raman spectra into consideration, defects might be the active sites for 'OH and 380 SO_4 .

381 Interestingly, there was an peak around 400 eV in the XPS survey of BBC-700, 382 BBC-800, BBC-900, which was identified as the signal for N 1s (Fig. 6b). Morever, N 383 content decreased with the increase of annealing temperature. The N content might be 384 derived from acid treatment (HNO₃). However, the characteristic peak of nitrate 385 should be attached to 405 eV. Thus, there must be other source for N (Rignanese et al., 386 1997). The collagen in swine bone might be the answer. It was obvious that the 387 decrease of the N content might be due to the cleaving of the C-N bond (Duan et al., 388 2015a; Ye et al., 2020). Although the doped N was regarded as the active sites, the N 389 content of BBCs demonstrated a negative correlation with the degradation rate of 390 ACT. It meant that the N in BBCs was not the main active sites in the PS/BBCs 391 system.

³⁹² As is shown in Fig. 6b, the elementary composition of BBC-AW was obviously ³⁹³ different from the other BBCs. The distinct peak of Ca 2p and P 2p might be generate

394	form the residue of HOP, and acid treatment could wipe off the inorganic component
395	in BBC-AW (Fig. 6b). In regard of the different degradation mechanisms of BBCs,
396	HOP was preliminarily identified as an active ingredient in the PS/BBC-AW system.
397	In order to verify this conjecture, pure HOP and HOP after annealing (900 °C) were
398	involved in this study (Fig. S7). The result showed that the HOP could do little to the
399	degradation of ACT. With respect to the results of BET, the specific surface area of
400	BBCs soared from 43.56 to 1199.920 m^2/g after acid treatment. Thus, HOP might
401	serve as the natural hard templet in swine bone to form pore strucure. Morever, the
402	increase of specific surface area would also contribute to the boosting of BBCs
403	catalytic capacity after acid treatment (Fig. 1).

404 To sum up, in the PS/BBCs system, PFRs might do favor to the formation of O_2 . 405 and defects could be the active sites for SO4⁻⁻, 'OH, and electron transfer process. 406 Moreover, HOP could not activate PS to degrade ACT, it only acted as the hard 407 templet to form pore structure, which would benefit both radical and non-radical 408 pathway.

409

3.3. The degradation pathway of ACT and toxicity experiment

410 LS-MS was applied to probe the ACT degradation pathway in the PS/BBCs 411 system. The intermediates were listed in Table S3, and the possible degradation 412 pathway of ACT was deduced (Fig. 7). In the PS/BBCs system, ACT was mainly 413 degraded by two pathways. In pathway I, active species might attack the acetyl amino 414 group, to generate product A. Then, the hydroxylation of benzene ring could be 415 observed. Thereafter, the benzene ring opening might be implemented by two

416	approaches. On the one hand, the product B could be directly oxidized to aliphatic
417	chain (product E) (Bicalho et al., 2020). On the other hand, the quinone structure
418	(product C) was unstable, which might contribute to the opening of the ring.
419	According to previous study, SO4 could attack the phenolic compounds to generate
420	phenoxy radicals, which possessed a long lifetime, then, the phenoxy radicals might
421	conduce to the formation of biphenyls and diphenyl ethers (Ji et al., 2019). In this
422	study, products H and I were detected in the PS/BBCs system (pathway II). Note-
423	worthily, the two pathways mentioned above both existed in all PS/BBCs systems.
424	The difference was mainly exhibited in the emerging time of products H and I. After
425	10 min reaction, the products H and I were detected in the PS/BBC-700 system,
426	whereas it took more than 30 min for discovering product H and I in the PS/BBC-900
427	system. As mentioned in section 3.1, radical (SO4 , 'OH and O2) and non-radical
428	pathways (¹ O ₂ and electron transfer pathway) were worked in all PS/BBCs system.
429	Radical pathway (SO ₄ and [•] OH) dominated the PS/BBC-700 system, and electron
430	transfer pathway played a central role in the PS/BBC-900 system. Thus, SO4 and
431	'OH would evoke the generation of the biphenyls and diphenyl ethers in the PS/BBCs
432	systems. However, it has been proved that 'OH primarily attacked the substituents on
433	ACT benzene ring, then the hydroquinone or 4-benzoquinone was generated to assist
434	the benzene ring opening (de Luna et al., 2013; Li et al., 2014). Given these, it was
435	reasonable to infer that radical pathway (SO4 ^{•-}) was the main cause for the generation
436	of products H and I. It was in line with the previous study that the radical (SO_4^{-})
437	induced the formation of biphenyls and diphenyl ethers (Ji et al., 2019).



⁴³⁹ **Fig. 7** Proposed degradation pathway of ACT in the PS/BBCs system

It has been reported that the biphenyls and diphenyl ethers generated in PS
activation system showed a higher toxicity than the pollutant itself (Ji et al., 2019;
Yang et al., 2019). This environmental risk might limit the downstream application of
PS activation system. Consequently, the toxicity of PS/BBCs systems was compared
to investigate the inducement of the toxicity.

The variation in toxicity during the ACT degradation pathway was assessed by *Scendesmus obliquus* (inhibitory in 96 h). The results showed that only 5% *Scendesmus obliquus* was inactivated by 20 mg/L ACT. In addition, the toxicity climbed with as the catalytic reaction progress (Fig. S8). The evaluation of toxicity might be due to three reasons: 1) the generated intermediates had high toxicity (Yang et al., 2019); 2) the radical in the PS/BBC system might kill the *Scendesmus obliquus* ⁴⁵¹ (Fan et al., 2013; Zhang et al., 2020); 3) the DOM desquamated from BBCs might do
⁴⁵² harm to *Scendesmus obliquus*.

453 Relative to PS/BBC-800 system, the increase rate of inhibition gradually declined 454 after 30 min in the PS/BBC-700 and PS/BBC-900 system. It might be ascribed to the 455 relative high proportion of radical pathway (SO4⁻⁻ and 'OH) in the PS/BBC-800 456 system (Fig. 2 and Fig. S2). As mentioned above, the biphenyls and diphenyl ethers 457 would emerge after 30 min in the PS/BBC-900 system, while the increase rate of 458 PS/BBC-900 toxicity descend after 30 min. It might prove that the high toxic 459 intermediates were not master for the removal of Scendesmus obliguus in the 460 PS/BBCs activation system.

461 Furthermore, the inhibition rate of PS/BBCs system was compared when ACT 462 was completely removed. As shown in Fig. S2, ACT was completely removed in 5 463 min in the PS/BBC-900 system, and time was prolonged to 20 min and 30 min in the 464 PS/BBC-700 and PS/BBC-800 system, respectively. According to the toxicity 465 experiment, when the concentration of ACT decreased to 0, the inhibition rates of 466 Scendesmus obliguus in the PS/BBC-900, PS/BBC-800, and PS/BBC-700 were 467 24.22%, 30.16%, and 65.77%, respectively. Obviously, the inhibition rate of PS/BBC-468 700 system exceeded that of PS/BBC-800 (65.77% versus 30.16%). Considering that 469 PS/BBC-800 system exhibited a relatively high proportion of SO₄⁻⁻ and ⁻OH than 470 PS/BBC-700 system, the radicals and high toxic intermediates might not the major 471 cause for the high toxicity of PS/BBC-700 system. Therefore, the DOM on BBC-700 472 was denoted as the primary origin of toxicity in the PS/BBC-700 system. Chen and

473	his group proved that the amount of DOM on biochar would decrease with the
474	increase of pyrolysis temperature (Xiao and Chen, 2017), and the DOM on biochar
475	might be toxic to blue-green algae and eukaryotic green algae (Sun et al.,
476	2021).Interestingly, the Scendesmus obliquus inhibition rate exhibited a negative
477	linear correlation ($R^2=0.9895$) with specific surface area of BBCs (Fig. S9). Since
478	specific surface area is closely related to adsorption capacity of BBCs, it is reasonable
479	to believe that the excellent adsorption capacity would mitigate the toxicity caused by
480	PS activation system.
481	Overall, according to the result of LC-MS, the generation of high toxic

intermediates required the existence of SO₄⁻⁻. Furthermore, the environmental risk
caused by PS activation system might owe to the existence of radicals, generation of
high toxic intermediates and the exfoliation of DOM. However, the appearance
toxicity of PS/BBCs system did not exhibit an obvious correlation with these factors,
for the adsorption capacity of BBCs could relieve the toxicity induced by PS
activation process.

⁴⁸⁸ **4.** Conclusion

⁴⁸⁹ To sum up, all types of BBCs in this study could activate PS to degrade ACT. ⁴⁹⁰ Furthermore, the degradation rate of ACT climbed with the increase of pyrolysis ⁴⁹¹ temperature, and the degradation rate could reach 0.4364 min⁻¹. The results showed ⁴⁹² that 1) PFRs could do favor to the generation of $O_2^{\cdot-}$; 2) Defects not only could ⁴⁹³ induce the production of SO₄⁻⁻ and [•]OH, but also could promote electron transfer ⁴⁹⁴ process; 3) HOP in swine bone contributed little for the catalytic capacity of BBCs, ⁴⁹⁵ and it only served as a hard template to create porous structure in BBCs.

496 LC-MS results illustrated that ACT was degraded by two main pathways in the 497 PS/BBCs system. Taken the degradation mechanism of PS/BBCs into consideration, 498 the generation of high toxic intermediates might be related to the emergence of SO_4 . 499 Moreover, the toxicity test showed that all PS/BBCs systems were toxic to 500 Scendesmus obliguus, and the inhibition was more than 80% in 96 h. It could infer 501 that the environmental risk caused by PS activation system might owe to the existence 502 of radicals, generation of high toxic intermediates and the exfoliation of DOM. 503 Nevertheless, excellent adsorption ability of BBCs can alleviate the environmental 504 risk caused by PS activation system. Conclusively, purposefully increasing the 505 specific surface area and reducing the active sites for SO₄⁻⁻ production might be 506 beneficial to mitigate the toxicity of PS activation systems.

507

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