

The following publication Wan, Z., Sun, Y., Tsang, D. C., Iris, K. M., Fan, J., Clark, J. H., ... & Ok, Y. S. (2019). A sustainable biochar catalyst synergized with copper heteroatoms and CO₂ for singlet oxygenation and electron transfer routes. *Green Chemistry*, 21(17), 4800-4814 is available at <https://doi.org/10.1039/C9GC01843C>.

1 **Sustainable biochar catalyst synergized with copper heteroatoms and CO₂ for singlet**
2 **oxygenation and electron transfer routes**

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17

18 **Abstract**

19 We have developed a sustainable graphitic biochar for environmental remediation from wood waste through
20 catalytic pyrolysis under the synergistic effects between CO₂ and Cu heteroatoms, which for the first time are
21 found to significantly enhance the oxygen functionalities, defective sites, and highly ordered sp²-hybridized
22 carbon matrix. The copper-doped graphitic biochar (Cu-GBCs) were further characterized by XRD, FTIR,
23 Raman, XPS, etc., revealing that the modified specific surface area, pore structure, graphitization, and active
24 sites (*i.e.*, defective sites and ketonic group) on the Cu-GBCs corresponded to the synergistic Cu species
25 loading and Cu-induced carbon-matrix reformation under CO₂ environment during pyrolysis. The catalytic
26 ability of the Cu-GBCs was evaluated using the ubiquitous peroxydisulfate (PDS) activation system for the
27 removal of various organic contaminants (*i.e.*, Rhodamine B, phenol, bisphenol A, and 4-chlorophenol), and
28 gave the highest degradation rate of 0.03122 min⁻¹ in comparison with those of pristine GBCs and N₂-
29 pyrolyzed Cu-GBCs ranging from 0.0056 to 0.0094 min⁻¹. The synergistic effects were attributed to the
30 encapsulated Cu heteroatoms, evolved ketonic groups, and abundant unconfined π electrons within the carbon
31 lattice. According to scavenger experiments, ESR analysis, and the two-chamber experiments, selective and
32 sustainable non-radical pathways (*i.e.*, singlet oxygenation and electron transfer) mediated by Cu-induced
33 metastable surface complex were achieved in the Cu-GBC/PDS system. This study offers the first insights
34 into the efficacy, sustainability, and mechanistic roles of Cu-GBCs as an emerging carbon-supported catalyst,
35 and facilitates the development of biochar-based materials as sustainable catalysts in green environmental
36 remediation.

37

38 **Keywords:** engineered biochar; heteroatoms doping; charcoal; non-radical activation; sustainable waste
39 management; green and sustainable remediation.

40 1. Introduction

41 As one of the environmentally friendly and low-cost carbonaceous materials, biochar (BC) has been
42 extensively employed in agricultural and environmental applications,¹⁻³ such as soil
43 amendment/stabilization,⁴⁻⁶ carbon sequestration,⁷⁻⁹ water/wastewater treatment,¹⁰⁻¹⁵ and catalytic biomass
44 conversion.^{16,17} The versatile physicochemical properties of biochar are primarily determined by its intrinsic
45 atom arrangement of carbon matrix, structural defective sites, pore structure, and surface functional groups.<sup>1,
46 18, 19</sup> Considering the large-scale production potential and sustainability of selected biomass wastes as
47 renewable carbonaceous materials at the present time, biochar stands out as an economic and abundant carbon
48 material with excellent adsorptive capability and potential catalytic activity for green and sustainable
49 remediation.¹⁹⁻²¹ Engineered metal-biochar composites with modified physicochemical properties have been
50 fabricated by introducing various multivalent transition metal components (Fe^0 ,^{15,22,23} Fe_3O_4 ,²⁴⁻²⁶ Co ,^{27,28} etc.)
51 into the carbon lattice to evolve versatile active sites. To date, despite its high efficiency, the application of
52 active multivalent transition metal-functionalized biochar unavoidably causes metal leaching into the
53 environment, which is potentially hazardous and detrimental to sustainable development (clean water and
54 aquatic life).²⁹ The establishment of a low-toxicity transition metal-biochar composite is thus imperative.

55 In this study, Cu was employed as the metal heteroatom for its inherent catalytic capacity and low toxicity,³⁰
56 while the lignin-rich wood waste was adopted as the feedstock, which results in macro- and meso-porous
57 structure for housing Cu species. Recent studies have revealed that biochar fabricated in CO_2 medium could
58 increase surface defects and oxygen-containing functional groups that significantly enhanced its catalytic
59 performance.^{24,27,28,31,32} The catalytic reforming of carbon matrix and the potential interactions with copper
60 heteroatoms during CO_2 pyrolysis are yet to be revealed, particularly for the physicochemical properties,
61 surface structure, and interfacial chemical behaviour of the resulting Cu-biochar composites for catalytic
62 applications.

63 The heterogeneous peroxydisulfate (PDS, $S_2O_8^{2-}$) activation system has been widely employed on
64 engineered biochar. As an emerging green oxyanion, PDS can be directly activated by external energy input
65 (heat, ultraviolet light, ultrasound, *etc.*) or various metal-based catalysts to generate robust sulphate radicals
66 ($SO_4^{\bullet-}$) that exhibit higher redox potential ($E^0 = 2.5\text{--}3.1$ V) and longer half-life period ($t_{1/2} = 30\text{--}40$ μ s) than
67 $\bullet OH$ ($E^0 = 1.9\text{--}2.7$ V, $t_{1/2} = 3\text{--}10$ μ s) over a wide range of pH values (pH = 2–8).^{33,34} Organics degradation
68 based on radical pathways often requires intensive energy or chemical input that would limit its field
69 application, and the generated radicals would demonstrate non-selective oxidation capability (*e.g.*, self-
70 scavenging effects, highly chlorinated byproducts),^{30,35} wherein the induced cannibalistic surface oxidation
71 reaction would lead to the irreversible oxidation of carbon framework.³⁶ Thus, PDS activation *via* a more
72 sustainable pathway is highly desirable. Zhang et al. reported that copper species could activate PDS to
73 degrade chlorophenols *via* a non-radical pathway by forming a metastable complex on its surface.³⁰ Zhu et al.
74 found that crystallographic manganese oxide could activate PDS to generate singlet oxygen (O_2^1) other than
75 commonly reported free radicals (*e.g.*, $\bullet OH$, $SO_4^{\bullet-}$, and $O_2^{\bullet-}$) for the degradation of aqueous contaminants.³⁷
76 In addition, various carbonaceous materials (*e.g.*, activated carbon, carbon nanotube, and graphene oxide
77 (GO)) are also capable of catalysing PDS for organic degradation *via* electron transition through graphitic
78 matrix, which potentially are even more efficient than transition metal oxides (*e.g.*, Fe_3O_4 , Co_3O_4 , and α -
79 MnO_2).³⁸ This superior performance could be possibly ascribed to the well-defined sp^2 -hybridized carbon
80 matrix with versatile catalytic centre (*e.g.*, defects and ketonic groups) and abundant unconfined π -electrons.¹⁸
81 ³⁹⁻⁴¹ In a recent study, graphitic biochar (GBC, pyrolyzed over 700 °C) was employed for its large specific
82 surface area (SSA), ordered sp^2 -hybridized structure, and tuneable defect sites as redox centre for catalytic
83 degradation.⁴² Thus, it is hypothesized and then verified in this study that the introduction of low-toxicity
84 copper heteroatoms into the graphitic biochar matrix can enable the complimentary coupling of the catalytic

85 centre and graphitic matrix of carbonaceous materials. This technique is more economic, scalable, and
86 sustainable for green remediation applications *via* the non-radical PDS activation route.

87 In this study, Cu-doped GBC composites were synthesized through a one-step pyrolysis of CuCl₂-
88 pretreated waste-wood at 900 °C with continuous CO₂ purging as the reactive medium (in comparison to N₂
89 purging). The objectives of this research were to: (i) articulate the interactions of CO₂ medium and doped
90 copper heteroatoms for tailoring the physicochemical properties, surface structure, and interfacial chemical
91 behaviour of the resultant Cu-GBC composites, and (ii) capitalize on the evolution of sustainable pathways
92 for non-radical PDS activation and catalytic degradation of various organic contaminants (*i.e.*, Rhodamine B
93 (RB), phenol (PN), bisphenol A (BPA), and 4-chlorophenol (4-CH)). The results of this study are conducive
94 to improving the future design of high-efficiency, engineered metal-biochar composites as green catalysts.

95

96 **2. Experimental**

97 *2.1. Materials and chemical reagents*

98 Apple-tree waste wood (collected from Guiyang Province, China) was selected as the feedstock of waste
99 biomass. All the chemicals were of analytical reagent grade and solvents were of high-performance liquid
100 chromatography (HPLC) grade. Ultrapure water (UW, 18.2 MΩ cm⁻¹) obtained from a Millipore Milli-Q
101 Water Purification System (Milford, USA) was used for all experimental solutions.

102 *2.2. Preparation of Cu-GBC composites*

103 Before use, wood waste was cut into small pieces (< 5 cm), washed with ultrapure water (UW) for several
104 times, oven dried at 80 °C overnight, then crushed by a high-speed rotary pulverizer, and finally sieved
105 through a 120-mesh (particle size < 0.125 mm). The suspension of biomass with Cu²⁺ was prepared by mixing
106 20 g wood with predetermined amounts of CuCl₂•6H₂O in 1 L UW in a glass beaker, which was then agitated
107 at 350 rpm for 24 h with a magnetic stirrer to maintain a uniform concentration. After heated under continuous

108 stirring at 80 °C for 12 h with a thermostat water bath to evaporate the water, the mixture was completely
109 dried at 80 °C for 24 h in an oven. Next, the samples were placed in a tubular furnace with a medium heating
110 rate of 5 °C min⁻¹ to reach desired 900 °C, and the same temperature was maintained for 2 h under CO₂
111 purging at 500 mL min⁻¹.⁴² For comparison, the pristine BC was also prepared without metal impregnation
112 process. After naturally cooling down to room temperature inside the furnace, the stabilized samples were
113 collected, rinsing with UW/alcohol three times, ground and passed through 200-mesh (pore size < 0.075 mm)
114 sieve, and stored in an airtight container for further use.

115 The obtained products are denoted as Cu-GBCXC or Cu-GBCXN, where the X (5, 10, and 20 %) and C/N
116 represent the copper calculated mass ratio after wet digestion (Cu/BC, wt.%) and the purging gas (*i.e.*, CO₂ or
117 N₂) during pyrolysis, respectively.

118 2.3. Microscopic characterization of Cu-GBC composites

119 The characteristics of the GBC and Cu-GBC composites were determined *via* employing the Brunauer-
120 Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) porosity, scanning electron
121 microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), Raman
122 spectroscopy, Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and X-ray
123 photoelectron spectroscopy (XPS). Detailed information on the characterization methods is available in the
124 Supporting Information.

125 2.4. Catalytic degradation of various organic contaminants by Cu-GBC composites

126 The organic removal experiments were performed at 25 ± 1 °C under intensive mixing by a thermostatic
127 oscillator (180 rpm). The solution pH was adjusted to 5.8 ± 0.2 using 0.1 M NaOH or HNO₃. To investigate
128 the removal kinetics of various organic contaminants (*i.e.*, RB, PH, BPA, and 4-CH) by Cu-GBC composites,
129 0.3 g L⁻¹ suspensions of Cu-GBC composites and 2 mM PDS (determined according to preliminary results)
130 were reacted with 100 mL UW containing 0.1 mM organic contaminants, while a similar reaction with GBC

131 was also conducted for comparison in 250-mL conical flasks. The commercial metal and metal-free catalysts
132 (Fe_3O_4 , Fe_2O_3 , zero valent iron (ZVI), CuO, CoO, MnO_2 , ZnO, and GO) were also evaluated for PDS
133 activation. At predetermined time interval for sampling, aliquot sample of 1 mL was withdrawn from the
134 conical flask to a glass vial, and then further oxidation reactions were immediately stopped by adding excess
135 EtOH to quench all the generated radicals and leach out adsorbed organics. Same batch experiments
136 quenching with NaNO_2 were also conducted to differentiate the contribution of adsorption and catalytic
137 degradation. Then, the sample was filtered through a 0.45- μm pore-size polytetrafluoroethylene (PTFE)
138 membrane (Millipore, USA) and analysed for the organic concentration. After the reaction, the Cu-GBC
139 suspension was centrifuged, and the catalyst was collected and recovered by acetone (solid/acetone, 1:158,
140 wt. %).

141 The scavenging experiments were performed to illustrate the contribution of different reactive oxygen
142 species (*i.e.*, $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, $\text{O}_2^{\cdot-}$, and O_2^1) by using 4 M ethyl alcohol ($\text{C}_2\text{H}_6\text{O}$, EtOH) (for $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$), 0.5
143 M tert-Butanol (TBA) (for $\cdot\text{OH}$), 0.05 M chloroform (CF) (for $\text{O}_2^{\cdot-}$), and 0.01 M furfuryl alcohol (FFA) (for
144 O_2^1), respectively.²⁹ Potassium iodide (KI, 10 mM) and pure acetone were chosen as inhibitors of non-radical
145 pathway to suppress the surface-bound reactive species formation and direct contact between organic
146 contaminants and carbon matrix, respectively.⁴² Similar experiments (without extra PDS addition) using the
147 composites pretreated by excess PDS (1 M) were performed to identify the contribution of organic removal
148 *via* metastable complex.⁴³ The metal-free Cu-GBC composites (treated with ethylene-diamine-tetraacetic
149 acid (EDTA)) and phenol-free GBC (treated with glycerol) were also employed (Supporting Information).²⁶
150 To identify the direct electron-transfer process during PDS activation, a two-chamber reactor separated by
151 proton exchange membrane (PEM), equipped with carbon fibre electrodes, connected *via* electric wire, and
152 loaded with Cu-GBC composite as an activator was prepared to separate organic contaminants from PDS
153 (Supporting Information).

154 *2.5. Analytical methods*

155 The concentrations of organic pollutants were analysed by a UV-Vis spectrophotometer at a wavelength of
156 554 nm (UV-1100, China, limit of detection (LOD) of 0.1 mg L⁻¹) or a high-performance liquid
157 chromatography (HPLC, Hitachi, Japan, LOD of 0.1 mg L⁻¹). The total organic carbon (TOC) was measured
158 with a TOC analyser (SSM-5000A, Japan, LOD of 0.1 mg L⁻¹). The PDS concentration was determined by
159 UV-Vis spectrophotometry (Optizen Pop, South Korea, LOD of 0.1 mg L⁻¹). The metal concentration was
160 tested by an inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific, USA,
161 LOD of 0.1 µg L⁻¹). The electron spin resonance (ESR) spectra were obtained using an EMX10/12
162 spectrometer (Bruker, Germany). The solution pH was measured by a digital pH meter (Thermo 911600,
163 USA). Detailed information on the analytical methods is available in the Supporting Information.

164 Calibration of standard organic/inorganic concentrations was carried out prior to each analysis. Standards
165 were analysed every 10 samples for quality assurance and quality control. All experiments were performed
166 in triplicate, and the results are presented as mean ± standard deviations.

167

168 **3. Results and discussion**

169 *3.1. Physiochemical properties and crystalline structure of Cu-GBC composites*

170 Selected physiochemical properties of GBC and the synthesized Cu-GBC composites after different Cu
171 impregnation under N₂ or CO₂ environment are summarized in Table 1. After wet digestion, the total Cu
172 content in the Cu-GBC composites was shown to range from 3.8 ± 1.1 to 23.2 ± 5.5 wt. %. These results
173 suggest that copper was successfully loaded with the biochar framework after impregnation and pyrolysis
174 processes.

175 The specific surface area (SSAs) and total pore volume of GBC fabricated in a CO₂ environment (358 m²
176 g⁻¹ and 0.323 cm³ g⁻¹) were significantly higher than those generated in a N₂ environment (68.3 m² g⁻¹ and

177 0.0516 cm³ g⁻¹). The CO₂ medium promoted the formation of both micropores (219 m² g⁻¹) and meso/macro-
178 pores (139 m² g⁻¹), which should enhance the site accessibility of BC-based catalysts.^{24, 31, 32} The SSA
179 increased from 358 m² g⁻¹ for the control CO₂-GBC to 388 m² g⁻¹ and 468 m² g⁻¹ for the Cu-GBC5C and Cu-
180 GBC10C, respectively, which might be attributed to the pore structure evolution in catalytic graphitization
181 after metal impregnation. Moreover, the external surface area and micropore volume also increased from 139
182 to 175 m² g⁻¹ and 0.121 to 0.156 cm³ g⁻¹ (*i.e.* 39.2–53.1% of total pore volume), respectively, suggesting the
183 more significant formation of both mesopores (2–50 nm) and micropores (< 2 nm) in the Cu-GBC10C. Thus,
184 the Cu-induced catalytic graphitization of carbon matrix during pyrolysis could possibly generate more zero-
185 dimensional point defects (*i.e.*, vacancy and edge sites) and three-dimensional volume defects (*i.e.*, lattice
186 disorder and void).⁴⁴ However, excess Cu loading caused a sharp decrease in SSA (4.89 m² g⁻¹) for the Cu-
187 GBC20C, which might result from the pore blockage after Cu precipitation. As shown in Figs. 1a and S1, N₂
188 adsorption curves of all the composites exhibited the typical type-IV adsorption/desorption isotherms with
189 H4-type hysteresis loop at medium relative pressure ($P/P_0 = 0.45\text{--}0.95$), which further demonstrated the
190 existence of micropores and mesopores derived from capillary condensation,⁴⁵ corresponding to the average
191 pore size data of GBC and Cu-GBC composites in Table 1. Compared with the control CO₂-GBC, the pH of
192 the Cu-GBCXC composites decreased from 10.5 to 10.3–8.51, which is attributed to the hydrolysis of Cu²⁺
193 and/or the generation of acidic functional groups (*e.g.* phenolic and carboxylic groups).⁴⁶ The pH value at the
194 point of zero charge (pH_{zpc}) increased (Fig. S2) after copper encapsulation owing to an increasing positive
195 surface charge after the incorporation of copper atoms, which is expected to tailor the electronic states of the
196 adjacent carbon *via* charge transport to modulate the electron density.³⁸ The SEM-EDX analysis of the GBC
197 and Cu-GBC composites are presented in Figs. S3, S4, and S5. In contrast to the relative smooth surface with
198 multilayer structure on the N₂-GBC (Fig.S3a-b), porous channels and more mesopores were observed on the
199 surface of CO₂-GBC (Fig.S3c-d). With respect to Cu-GBC5C, the Cu particles exist mainly in the interior

200 micropores of the flaky cracking GBC surface (Fig. S3e). As the Cu loading increased, *i.e.*, for Cu-GBC10C,
201 Cu particles with diameters ranging from micro- to nano-scale became evident (Fig. S4c-d). These particles
202 were evenly distributed in the pores and on the surfaces of bulkier dendritic flocs, up to a particle size of 400–
203 500 nm. In contrast, obvious particle aggregation into discrete spheres of $\sim 10\ \mu\text{m}$ was observed in the Cu-
204 GBC20C (Fig. S3f). These findings are consistent with the variation in surface area and pore size distribution
205 of the Cu-GBC composites (Table 1). EDX analysis (Fig. S5) revealed the co-existence of Cu, O, C, Ca, Mg,
206 and P elements on the Cu-GBC10C surfaces, suggesting the possible formation of Cu-O-C bond which could
207 lead to the denser local electronic states of the carbon/metal framework at the interaction region. The
208 significantly higher oxygen content (21.1 wt. %) of Cu-GBC10C compared with that of the Cu-GBC10N
209 (1.83 wt. %) indicated that more oxygen could be introduced into the carbon matrix under CO_2 medium,
210 which favoured the encapsulation of Cu species with the oxygen-containing functionalities acting as the
211 anchoring sites. Besides, the induced edges terminated with hydrogen and oxygen atoms on sp^2 -hybridized
212 carbon were reported to possess high affinity to absorb oxyanions.^{18,47}

213 The XRD patterns of the GBC and Cu-GBC composites are shown in Fig. 1b. In the case of the N_2 -GBC,
214 the carbon matrix demonstrated a broad peak at 2θ value of $20\text{--}25^\circ$, which can be assigned to graphite
215 corresponding to the amorphous plane of (002) in carbonaceous materials.⁴⁸ Nonetheless, the spectra of the
216 CO_2 -GBC presented the characteristic peaks at 29.41° , 35.93° , 39.42° , 47.14° , and 47.42° attributed to the
217 (104), (110), (113), (024), and (018) planes of calcite, respectively, as typical ash component of waste wood.⁴⁹
218 ⁵⁰ As for the Cu-GBC composites, the characteristic peaks at 35.04° , 38.48° , and 50.43° were assigned to the
219 (002), (111), and (112) planes of CuO ,^{51,52} while the peaks at 43.29° and 74.13° corresponded to the (111) and
220 (220) planes of Cu^0 ,⁵³ respectively. Particularly, in contrast with the N_2 -pyrolysis, the CO_2 environment may
221 have suppressed the crystalline sizes of CuO (0.61 vs. 0.89 nm) and Cu^0 (1.97 vs. 2.28 nm) particles based on
222 the Debye-Scherrer calculation.⁴³ Thus, copper heteroatoms can be successfully grafted in the framework of

223 BC, and thereby likely to significantly increase its catalytic reactivity by forming Lewis acid-alkaline pairs to
224 catalyze PDS (*i.e.* electrons donation)^{54, 55} or evolving surface metastable complex (*i.e.* non-radical
225 pathway).³⁰ Besides, the absence of a calcite peak in the Cu-GBC XRD pattern suggests the doped copper
226 heteroatoms saturated the exchangeable sites that originally held Ca.¹⁵

227 The Raman spectra of the GBC and Cu-GBC further elucidated physical characteristics of the
228 carbonaceous materials, as shown in Fig. S6. The two peaks at 1310 and 1590 cm^{-1} correspond to the
229 characteristic D and G bands of carbon, *i.e.* defects of sp^3 C and in-plane vibrations of sp^2 C in curved
230 graphitized carbon sheet.^{40,56} In all samples, the Raman spectra were deconvoluted into eight peaks that were
231 assigned to sp^2 C-H of aromatic rings (S^1) at 1060 cm^{-1} , $C_{\text{aromatic}}-C_{\text{alkyl}}$ (S) at 1185 cm^{-1} , Aryl-alkyl ether (S^2)
232 at 1230 cm^{-1} , defect bands and small ordered fused benzene rings (D) at 1310 cm^{-1} , methyl group and
233 amorphous carbon (V^1) at 1380 cm^{-1} , semicircle ring breathing (V) at 1465 cm^{-1} , aromatics with 3–5 rings
234 (G^1) at 1540 cm^{-1} , and highly ordered sp^2 graphitic carbon (G) at 1590 cm^{-1} .^{57,58} The area ratios of the D peak
235 to the G peak (A_D/A_G) and the sum of G, V, and V^1 peaks ($A_D/A_{(G+V+V^1)}$) of the CO_2 -pyrolyzed composites
236 are greater than that of the N_2 environment, suggesting that CO_2 medium induced more fused aromatic rings
237 and structural edge defects within the BC matrix during the pyrolysis of GBC and Cu-GBC composites.⁵⁹⁻⁶¹
238 This can be attributed to the enhanced dehydrogenation of organic matters (*viz.* $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$; biomass
239 $\rightarrow \text{BC} + \text{tar} + \text{C}_n\text{H}_m$) at high temperature with CO_2 purging, which could generate more vacancy and zigzag
240 edges as structural-dimensional defects.⁴⁴ After Cu impregnation with higher content, the ratios of A_D/A_G and
241 $A_D/A_{(G+V+V^1)}$ also increased (Fig. S6c-d). This result suggests that enhanced catalytic graphitization of BC
242 occurred during the synthesis of the Cu-GBC composites, which accounted for more newly formed volume
243 defects (*e.g.* void).⁶² Intriguingly, the Cu-GBC10C composite exhibited both a higher level of graphitization
244 and defects than the lab-synthesized GO (Fig. S7b) prepared in our recent study,⁶³ which could possibly

245 contribute to an improved performance in the catalytic activation of PDS for organics degradation with
246 abundant free-flowing π electrons and defective sites.

247 3.2. Surface chemical behaviour and thermal stability of Cu-GBC composites

248 FTIR spectra helped to determine the functional groups on the surfaces of the GBC and Cu-GBC
249 composites (Fig. 1d). In the case of the N₂-pyrolyzed composites, the broad spectral band with a weak peak
250 at 3429 cm⁻¹ was attributed to the presence of the O–H stretching vibration in alcoholic and phenolic –OH
251 groups. The high-temperature pyrolysis (*i.e.* 900 °C) diminished most of the functional groups ubiquitously
252 presented in low-temperature BCs, which is consistent with previous findings that dehydration of cellulosic
253 and ligneous components at high temperature (>700 °C) tend to decompose majority of the aliphatic and
254 phenolic organic compounds.^{46, 64, 65} After Cu impregnation and pyrolyzed in CO₂ environment, the band
255 disappeared for –OH and C–H at 3429 and 835 cm⁻¹, respectively, whereas an aromatic C=O stretching
256 vibration in conjugated ketones and quinones evolved at 1659 cm⁻¹.⁶⁶ This result also suggests that catalytic
257 reformation and condensation of carbon matrix might occur during the synthesis of the Cu-GBC
258 composites,^{27, 67} which may account for more graphitic carbon observed in the Raman spectra. It should be
259 noted that the produced ketonic group (C=O) is indispensable for the activation of PDS and the generation of
260 singlet oxygenation for organics degradation.^{18, 39, 42, 68, 69}

261 TG-STA was employed to verify the generation of ketonic group (C=O) during the aforementioned
262 catalytic reformation. As shown in Fig. 2, the mass decay (TG) of raw wood waste exceeded 80 % and the
263 broad peak (*peak 1*) at 345.5 °C in derivative thermogravimetry (DTG) was consistent with the dehydration
264 of cellulosic or ligneous components and the lignin/cellulose-derived transformation at mid-level pyrolytic
265 temperature (200-550 °C).^{46, 64} With respect to biochar composites, CO₂-pyrolyzed biochar exhibited higher
266 mass decay values compared with the N₂-pyrolyzed biochar, especially for Cu-GBC10C (69.9 %, compared
267 to 82.9 % of Cu-GBC10N). Two apparent peaks at 643.6 °C (*peak 2*) and 634.8 °C (*peak 3*) for CO₂-GBC

268 and Cu-GBC10C DTG curves both correspond to the decomposition of conjugated ketones (C=O),⁶⁴ while
269 Cu induced more oxygen groups compared with sole CO₂ medium, suggesting copper heteroatoms and CO₂
270 medium both could increase the oxygen levels during the pyrolytic process.

271 The XPS data indicated that the GBC was composed of C 1s and O 1s, whereas the Cu-GBC composites
272 incorporated C 1s, O 1s, and Cu 2p. In all samples, the C 1s spectra were composed of five different peaks
273 that were assigned to O=C–OH at 288.8 eV, C=O at 286.6 eV, C–O at 285.8 eV, C–C at 285.4 eV, and C=C
274 at 284.8 eV, while the three fitted peaks of O 1s could be assigned to O–C=O at 533.6eV, O–C at 532.2 eV and
275 O=C at 530.8 eV.⁷⁰ As the Cu impregnated biomass was pyrolyzed under CO₂ purging, there was a significant
276 increase in the content of O=C (from 17.7 % to 41.1 %) compared to CO₂-GBC (Figs. 3b and S8). This
277 observation corroborates the transformation of O–C (532.2 eV) into O=C (530.8 eV) *via* Cu-induced catalytic
278 oxidation process.⁴⁰ Duan et al. reported that the species other than the amount of oxygen groups were the key
279 factor to the inherent catalytic capability of carbonaceous materials, and both the oxygen levels and species
280 of oxygen groups should be carefully optimized.¹⁸ In this research, copper heteroatoms are favoured to tune
281 the oxygen groups by transforming more oxygen functionalities into ketonic C=O which would account for
282 the better catalytic performance of Cu-GBC10C (data shown later).

283 Additionally, as shown in Figs. 3c and S10 CuO shake-up (943.8 eV) accounted for only 19.9% and slight
284 increases were observed after reaction (from 19.9 % to 20.6 % for CuO, 27.8 % to 36.3 % for Cu²⁺), which
285 ruled out the electron donation or sole CuO-induced non-radical pathway as the primary reaction route. It has
286 been reported that metal-O-C bond could give rise to denser local electronic states evolving more reactive
287 sites,³⁸ and similar synergism between Cu and graphitic carbon could explain the phenomenon in this work.
288 Therefore, the CO₂ environment and Cu doping favoured the formation of ketonic groups during the
289 pyrolysis,^{15,71,72} and ultimately the *sp*²-hybridized carbon framework was converted into one of a more active
290 nature after accommodating copper heteroatoms and tuned oxygen functionalities.

291 3.3. Cu-GBC performance for PDS activation and catalytic degradation of organic contaminants

292 A typical rhodamine dye of RB was chosen as the target organic pollutant to evaluate the catalytic
293 performance of synthesized composites for PDS activation and the kinetic data were fitted using a pseudo-
294 first-order kinetics model.^{30,37,73} The waste wood biomass (5 g) was combusted in air to obtain its ash (0.48
295 g), which can barely activate PDS for RB degradation, indicating that the metal residues in the biomass do
296 not contribute to the catalytic oxidation on GBCs. The adsorptive removals of RB were insignificant on GBCs
297 and Cu-GBC10N, while PDS alone could not oxidize the dye (< 5 %) without the presence of catalysts (Fig.
298 S11). In contrast, Cu-GBC10C showed notable RB adsorption (~ 40 %), which might be due to the enriched
299 oxygen functionalities on the material surface. The larger SSA (468 m² g⁻¹, Table 1) and higher graphitic level
300 of Cu-GBC10C might also contribute to larger active region for an improved adsorption capacity. However,
301 Cu-GBC5C and Cu-GBC20C demonstrated unfavourable adsorptive performance due to the lack of SSA
302 and active sites (data not shown herein). An 86.4 % degradation rate of RB was achieved in the Cu-
303 GBC10C/PDS system in 30 min, demonstrating a better degradation efficiency than most commercial
304 heterogeneous catalysts (metal-based systems: CuO, ZVI, Fe₂O₃, Fe₃O₄, ZnO, CoO, and MnO₂), while a
305 degradation rate of 22.3 % was obtained by Cu-GBC10N (Fig. 4a). Additionally in Fig. S12, compared to the
306 pristine BC (N₂-GBC, 0.0056 min⁻¹ with 7.8 % degradation removal; CO₂-GBC, 0.0071 min⁻¹ with 15.6 %
307 degradation removal) and Cu-GBC10N (0.0094 min⁻¹ with 22.3 % degradation removal), Cu-GBC10C
308 (0.03122 min⁻¹ with 86.4 % degradation removal) gave rise to a 5.60-, 4.46- and 3.32-fold enhancement of
309 the degradation rate might be a result of the larger surface area, higher graphitization degree, and more active
310 sites (*i.e.* C=O in ketonic group). This may indicate a synergism of the Cu catalytic reformation and CO₂
311 purging during pyrolysis. Therefore, Cu-GBC10C was chosen as the representative catalyst for the
312 subsequent comparative, kinetic, and mechanism studies.

313 Fig. S13 shows that ~ 90 % removals of RB, PH, and BPA at 0.1 mM could be rapidly achieved within 30
314 min. In contrast, Cu-GBC10C achieved inferior 4-CH oxidation (39.8 %). This lower performance probably
315 indicates that organic pollutants (*e.g.* RB, PH, and BPA) with lower ionization potential (IP) (IP = 7.4–8.5)
316 were more prone to be oxidized by mild reactive oxygen species (ROSs) (*e.g.* $^1\text{O}_2$) generated in Cu-GBC/PDS
317 system *via* a non-radical pathway, which is consistent with previous findings that some highly-graphitic
318 carbonaceous materials (*e.g.* CNTs and carbonized N-containing polymers, *etc.*) and metal oxides (*e.g.* CuO
319 and $\beta\text{-MnO}_2$, *etc.*) tended to exhibit a higher selectivity towards electron-rich phenolic compounds.^{30, 37, 39, 40}
320 When the concentration of organics increased to 0.5–0.6 mM, 40.3 and 79.7 % removals of RB and PH were
321 obtained in 30 min, possibly limited by the insufficient PDS or active sites.

322 To affirm the key step of determining the reaction rate (at pH = 5.8 ± 0.2), the pseudo-first-order kinetics
323 was employed to calculate the observed rate constant (k_{obs}) in the first 30 min at different catalyst loadings,
324 PDS dosages, or organic concentrations. The increased PDS concentration from 1 to 5 mM gave a minor
325 improvement of k_{obs} (Fig. 5b). Catalyst loading (0.1–0.5 g L⁻¹) and initial RB concentration (0.05–0.6 mM)
326 posed more significant impacts on the removal rate constants (Fig. 5a&c). The curves between logarithms of
327 k_{obs} and dosages of Cu-GBC10C, PDS, and RB were plotted accordingly, showing good linearity between
328 $\ln(k_{obs})$ with $\ln(\text{Cu-GBC10C})$ ($R^2 = 0.983$), $\ln(\text{PDS})$ ($R^2 = 0.821$), and $\ln(\text{RB})$ ($R^2 = 0.965$) (Fig. 5d). In
329 addition, the positive correlation ($R^2 = 0.999$) was established between the adsorbent dosage (g L⁻¹) and
330 adsorptive removal rate (k_{obs}) (Fig. 5d). The slopes of $\ln(k_{obs})$ against $\ln(\text{Cu-GBC10C})$, $\ln(\text{PDS})$, $\ln(\text{RB})$, and
331 $\ln(\text{adsorbent})$ were estimated to be 0.968, 0.095, -0.653, and 0.860, respectively, which can be taken as the
332 orders of reactivity in the overall organic removal rate. The lowest reaction order of PDS suggested that the
333 active sites for PDS adsorption are limited, and self-scavenging effect or cannibalistic surface oxidation
334 reaction could also be ruled out accordingly, demonstrating the features of a typical non-radical activation.³⁶
335 ⁷⁴ The higher reaction orders with respect to Cu-GBC10C, RB, and adsorbent concentrations indicated that

336 the adsorption of organic compounds on the Cu-doped GBC might be the key step determining reaction rate
337 for the non-radical oxidation.^{30,37,42,75}

338 3.4. Contribution of radical and non-radical pathways to PDS activation and organics degradation

339 In previous studies, it has been discovered that the persistent free radicals (PFRs) were formed from the
340 decomposition of organic structure (*i.e.* hydroquinone) in BCs derived at moderate temperatures
341 (300–500 °C),⁷⁶ which served as the redox centres to deliver electrons to PDS to evolve sulfate radicals.²⁶
342 However, Ruan et al. noted that pyrolysis of different biomass (*e.g.* pinewood, rice husk, and cow manure
343 *etc.*) at temperature > 700 °C generally removed all PFRs due to the elimination of oxygen functionalities and
344 condensation/graphitization of carbon clusters.⁷⁷ In this work, the removal rate of phenol-free GBC
345 (Supporting Information) is comparable to GBC, indicating that PDS activation by PFRs on highly graphitic
346 BCs for catalytic degradation can be ruled out.

347 More interestingly, the radical quenching tests (Fig. 6a and Table 2) indicate that the addition of free radical
348 scavengers, *i.e.* EtOH ($k_{\text{SO}_4^{\cdot-}} = (1.6-7.7) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{OH}} = (1.2-1.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), TBA ($k_{\text{SO}_4^{\cdot-}} = (4.0-9.5)$
349 $\times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{OH}} = (3.2-7.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), and CF ($k_{\text{O}_2^{\cdot-}} = (1.1-3.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) had an insignificant
350 impact on organic removal with a 3.2, 0.19, and 9.4% decrease in removal efficiency.^{42, 54, 78, 79} This implies
351 that Cu-GBC10C/PDS is an oxidative system relying on not free radicals but non-radical pathways due to the
352 absence of DMPO–SO₄ characteristic signal peaks (1:1:1:1:1, $\alpha\text{N} = 13.2 \text{ G}$, $\alpha\text{H} = 9.6 \text{ G}$, $\alpha\text{H} = 1.48 \text{ G}$),
353 although DMPO–OH characteristic signal peaks (1:2:2:1, $\alpha\text{H} = \alpha\text{N} = 14.9 \text{ G}$) were observed in the ESR
354 spectra (Fig. 4c). The generation of hydroxyl radicals might result from the oxidation of adsorbed water on
355 graphitic carbonaceous material surface which has been reported in some dimensional-structured nanocarbon
356 system.¹⁸ However, the impact of radical quenching on reaction rate was moderate with 31.7 %, 9.1 %, and
357 39.1 % rate decline, respectively, indicating that the scavengers with nonpolar properties might suppress the
358 anchoring of RB on the hydrophobic surface of Cu-GBC10C.

359 To further investigate the interfacial reaction, KI and pure acetone were employed to quench the direct
360 surface contact between PDS/RB and the carbon matrix,^{80, 81} respectively. The almost unaffected organic
361 removal with excess KI (10 mM) addition suggests that the enhanced anionic strength could not affect the
362 strong interaction between Cu-GBC10C and PDS. The dramatically suppressed effect of pure acetone
363 (0.00211 min^{-1} with 18.9 % removal) further indicates the surface-confined organic adsorption could be vital
364 for the total oxidation,⁴² suggesting that the degradation occurred in the carbon matrix other than the bulk
365 solution corroborating the non-radical culture. Recent studies have reported that ketonic- and quinone-like
366 moieties on graphitic carbon with strong nucleophilic nature and high electron density can catalyze PDS to
367 produce $^1\text{O}_2$ under mild condition.^{39, 42, 82} Thus, FFA ($k^1_{\text{O}_2} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) was used to scavenge $^1\text{O}_2$ in the
368 reaction. FFA (0.01 M) significantly reduced the RB removal efficiency to 50.0 % (0.00593 min^{-1}) in 120
369 min, indicating that $^1\text{O}_2$ contributed to a large portion (nearly half) of the catalytic oxidation. A trapping agent
370 of TEMP was used to detect the production of $^1\text{O}_2$ without light. A characteristic three-line signal of TEMPN
371 adducts (Fig. 4d, 1:1:1, $\alpha = 16.9 \text{ G}$) appeared, which can be assigned to the oxidation of TEMP by $^1\text{O}_2$. In
372 contrast with other GBC composites, the intensities of TEMPN and DMPO-OH in Cu-GBC10C increased
373 sharply, implying that Cu-GBC10C possessed the highest reactivity, which originated from the encapsulated
374 copper heteroatoms and the evolved ketonic groups (C=O) on Cu-GBC10C at the edges of the carbon
375 matrix.⁸³ Moreover, the PDS-pretreated Cu-GBC10C achieved an 8.15 % RB degradation without extra PDS
376 addition, whereas those for the Cu-free CO_2 -GBC and EDTA-pretreated Cu-GBC10C (2.12–2.31 %) were
377 negligible (Fig.S14). Thus, it can be inferred that C=O would induce the surface metastable complex between
378 copper heteroatoms and PDS (*i.e.* $\equiv\text{Cu}-\text{O}_3\text{SOOSO}_3^-$ or $\equiv\text{Cu}^{\text{II}}-\text{O}_3\text{SOOSO}_3^-$) susceptible to accepting
379 electrons from electron-rich phenolic compounds for $^1\text{O}_2$ generation,⁶⁸ which may correspond to a significant
380 peak shift at 531 nm in the UV-vis spectra of the Cu-GBC10C (Fig.4b). This observation corroborates the C
381 1s spectra depicting a lower C=O ratio (from 41.1 to 17.4 %) for the Cu-GBC10C after PDS activation.

382 3.5. PDS reduction and RB oxidation in two chambers separated by a proton exchange membrane

383 As presented above, the empirical results supported a significant role of $^1\text{O}_2$ in PS activation *via* a non-
384 radical reaction pathway, whereas the RB removal pathway was not completely terminated in the presence of
385 $^1\text{O}_2$ quenchers. Moreover, in the Cu-GBC mediated non-radical pathway, an electron-transfer process from
386 organics and donation of free-flowing π electrons by GBC to activated surface metastable complexes *via* the
387 conductive surface of carbonaceous materials was expected due to the differences of inherent redox potentials
388 between organic pollutant and PDS molecules.⁶¹ Thus, the electron-transfer non-radical pathway was further
389 identified by examining Cu-GBC10C-mediated electron transfer from organic substrates to PDS using a PEM
390 that physically partitioned the reaction system into two chambers containing PDS and RB (Fig. 7). In this
391 system, free electrons were transported from the anode to the cathode through the connected wire. The Cu-
392 GBC10C particles were homogeneously dispersed in the bulk solution under vigorous shaking to achieve
393 sufficient contact with the electrodes, *i.e.* carbon fibre brushes with high SSA. As a PEM with high water
394 impermeability is likely to reject organic/inorganic impurities and ROSs (*e.g.* $\cdot\text{OH}$, and $^1\text{O}_2$), simultaneous
395 RB oxidation and PDS reduction in the physically separated chambers (*i.e.* anode and cathode) would be
396 strong proofs for the electron-transfer mechanism, in which Cu-GBC10C mediate electron transfer from
397 organics to PDS.

398 As shown in Fig. 7, increased amounts of reactants (5-fold catalyst and oxidant addition) were added in the
399 anode chamber (no oxidant) and cathode chamber (no pollutant), respectively. Control group experiments
400 were conducted detaching the linking wire between the two electrodes, and the results indicated that RB
401 concentration in the cathode chamber declined to less than 5 % in 360 min due to the adsorption by the
402 employed Cu-doped biochar, as around 10 % PDS concentration decomposed simultaneously. This result
403 may indicate the formation of metastable complex. Moreover, the PDS-saturated state of the catalyst was
404 reached after 360 min. A continuous PDS decrease ($55.6 \pm 3.13\%$ in 4320 min) could be achieved in a wire-

405 connected group compared with the wire-detached control ($90.8 \pm 3.25\%$ in 4320 min), which confirmed that
406 the PDS was activated without direct contact with pollutant. Neither PDS nor RB was detected in the opposite
407 side of PEM, thus the continuous PDS concentration decline in the separated chambers could prove the
408 hypothesis of electron transfer pathway not relying on ROSs. The overall schematic diagram of the plausible
409 mechanistic routes (singlet oxygenation and electron transfer) is presented in Fig. 8.

410 3.6. Effect of pH values and reusability/recyclability

411 Fig. S15 presents the influence of initial pH values on the organics (*i.e.* RB and PN) degradation by the Cu-
412 GBC10C. It can be seen that performance of the Cu-GBC10C was highly pH dependent and the degradation
413 of PN steadily decreased with pH increasing from 3.0 to 9.0. However, in the case of RB, efficiency rose with
414 increasing pH values from 3.0 to 5.8 followed by pronounced lower RB removal as the solution pH further
415 elevated to 9. Fig. S15 displays the highest degradation efficiency of PN and RB as 82.1 % and 86.4 % at pH
416 value of 3.0 and 5.8, respectively. The obvious difference of organic removal by the Cu-GBC10C at fluctuated
417 pH values can be probably ascribed to the composite surface charge, organic speciation, and Cu dissolution.
418 As illustrated in Fig. S1, zeta potential presented an obvious decrease as pH increased. When pH was higher
419 than 2.08, zeta potential was negative, which was undesirable to the removal of negative-
420 charged/deprotonated organics (RB- $pK_a = 3.5$ and PN- $pK_a = 9.8$).^{84, 85} Meanwhile, the surface of Cu-
421 GBC10C became more negatively charged with the increase of pH, which leases to more unfavourable
422 interaction with anionic PDS ($S_2O_8^{2-}$) forming a metastable complex.⁸⁶ In addition, an acidic environment at
423 lower pH (*i.e.* pH = 3.0–6.0) adversely affected organics degradation by the Cu-GBC10C due to the inevitable
424 Cu dissolution ($0.014\text{--}0.925\text{ mg L}^{-1}$), which led to the lower organic removal capacity.³⁰

425 Reusability/recyclability is one of the most important indicators evaluating the sustainability of Cu-
426 GBC10C. The removal efficiency decreased from 95.8 to 30.6% after four cycles probably because the
427 carbon matrix partially collapsed, the Cu nanoparticles were exhausted by chemical reduction, and the

428 degradation intermediates covered active sites. Noticeably, Cu-GBC10C maintained 73.2% of the RB
429 removal efficiency *via* an acetone regeneration process after four cycles, suggesting that the Cu-GBC10C has
430 good reusability/recyclability and stability.

431

432 **4. Conclusions**

433 Through the integrated analysis of the surface characteristics and contaminant interactions, we
434 demonstrated that the highly graphitic Cu-doped biochar fabricated in CO₂ environment manifested a superior
435 catalytic performance of PDS activation for degradation of various organic contaminants, out-performing
436 most popular heterogeneous catalysts. Selective degradation routes like singlet oxygenation and mediated
437 electron transfer were validated as the predominant non-radical mechanisms. In addition, the organics
438 adsorption was identified as the key step determining the reaction rate. The scientific merits of this paper are
439 highlighted as follows: (i) a new approach for utilizing waste biomass to synthesize value-added products
440 with versatile metal-heteroatoms-induced active sites and high graphitization employing greenhouse gas CO₂;
441 (ii) a highly reactive, selective, green, and stable method for catalytic degradation of aqueous organic
442 contaminants with sustainable, cost-effective, environmental-benign composites; (iii) deepened mechanistic
443 insights into the synergistic effects of the copper heteroatoms and CO₂ environment during metal-impregnated
444 biomass pyrolysis and catalytic degradation. Therefore, the Cu-GBC10C composites are fast, sustainable,
445 green, and potentially low-cost catalysts suitable for the practical treatment of organic-contaminated waters.

446 **Conflicts of interest**

447 The authors declared that we have no conflicts of interest to this work.

448

449 **Acknowledge**

450 The authors appreciate the financial support from the Hong Kong Research Grants Council (PolyU 15217818
451 and E-PolyU503/17) for this study. The support of the University Research Facility on Chemical and
452 Environmental Analysis (URFCE) of PolyU is also acknowledged.

453

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