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10 ABSTRACT

Natural-aged microplastics with changed surface properties accumulate, 11 12 redistribute and spread in all water fields as carriers of hazardous substances. The combined hazard of co-contamination of microplastics and hazardous substances 13 expands the ecological risks, which urgently needs to design treatment schemes for 14 15 pollutant removal from microplastics. In this paper, a facile and applicable magnetic biochar with porosity and graphitization (PGMB) was prepared for realizing the goal 16 of metal removal from the microplastics. Heterogeneou 17 persulfate (PS) activated by PGMB achieved the decomposition of organics, with the decrease of more 18 than 60% of the attached Pb on the surface of m cropl 19 stics, and the adsorbed metal (c) is much higher than that by the amount by PGMB in this system (31.99 m 20 individual PGMB group (7.07 mg/). A 21 alysis demonstrated that the organic layer covered on the microplastic ce venthe long-term weathering provided the key 22 decomposition and peeling were the critical steps in 23 sites for metal sorptio wh spared PGMB was responsible for activating PS to produce 24 whole process. T reactive species for decomposing the organic matter accompanied with detaching 25 metals from microplastic surface, also would keep the role for re-adsorption of the 26 27 released metals and separation from aqueous phase by magnetic force. The influences of natural environmental factors including salinity, common matrix species, and 28 temperature on the performance of PGMB/PS system for metal removal from 29 microplastics were discussed to illustrate the universality of the scheme in saline or 30

organic-rich waters. The results of this study provided underlying insights for removing metals from microplastic surface, and decreasing the harm risks in the co-contamination of microplastics and hazardous substances.

- 34
- Keywords: Natural-aged microplastics; Attached Pb; Organic matter; Biochar;
 SR-AOPs

t corter to

37 **1. Introduction**

The prevalence, distribution and influence of plastic particles in the natural 38 environment have received considerable attention of scientists and government 39 managers. The annual production amount of waste plastics had been reported to 40 surpass 348 million tons (Shen et al., 2019a), and these various plastics are released 41 42 into aquatic environment through irresponsible handling, illegal dumping and aquaculture activities. Processes of fragmentation and embrittlement would occur on 43 the discarded plastics when they are exposed to solar radiation, temperature change, 44 physical effects of wind currents and waves, as well as the biological effects 45 (Fotopoulou & Karapanagioti, 2015; Shen et a 209c). The fragmented plastic 46 e defined as microplastics, which particles whose diameter is smaller that of m 47 48 become the focus of research owing to their potential toxic risk in aquatic ecosystem and human health (Farrell & on. 2019; Tanaka et al., 2013). Because of the small 49 gested food and the ubiquitous distribution whether 50 dimension that similar to the microplastics are regarded as a huge threat to aquatic 51 suspended or der 52 organisms through inadvertent ingestion, entanglement and smothering. The hard-digestible microplastics can block the esophagus, but also lead to a false sense of 53 fullness (Mrosovsky et al., 2009; Taylor et al., 2016; Wright et al., 2013). Besides the 54 physical harms of microplastics, a related concern is the attachment and enrichment of 55 hazardous substances onto the surface of microplastics causing chemical toxicity. As a 56 result, microplastics act as a component of the suspended load shown precise role for 57

58 long-range transport of contaminants (Holmes et al., 2014; Huffer & Hofmann, 2016; Shen et al., 2019b). Many researches have indicated that microplastics could act as 59 vectors to increase metals and organic chemicals exposure in organisms (Hodson et al., 60 2017; Koelmans et al., 2016; Massos & Turner, 2017). Furthermore, the microplastics 61 along with the adsorbed hazardous substances can not only raise the risk of 62 63 inflammation and immune impairment on organisms (Carbery et al., 2018), but also be capable of promoting the bioaccumulation and biomagnification of hazardous 64 65 contaminants via the food chain. Considerable research efforts have been devoted to the disorption behaviors of 66 hazardous substances onto different types of microplastes (Huffer & Hofmann, 2016; 67 In both the microplastic types and Wu et al., 2019; Xu et al., 2018) that append 68 69 pollutant properties. Due to the wide distribution of microplastics likely to be exposed to heavy metals and organic atarts in natural environment, microplastics exhibit 70 ption of harmful substances. The properties of 71 substantial potential m cherity, specific surface area, degree of crystalline structure, and 72 microplastic such 73 abundance of rubbery (Brennecke et al., 2016) show significant impacts on adsorption behavior of persistent organic pollutants through hydrophobic interactions, electrostatic 74 forces, H-binding and noncovalent bonds (Wu et al., 2019; Zhang et al., 2018a). 75 Attaching charged metal ions onto inherently neutral surface of plastics seems to be 76 infeasible, since the microplastic surface has no inherent characteristics for extra 77 attraction to metal ions. However, the natural-aged microplastics suspended in aqueous 78

environment with loss of physical integrity for a long-term basis can gain charges and a 79 larger surface area by surface modification of biofilm formation, weathering, and 80 81 attrition or precipitation of inorganic minerals. These surface changes endow aged microplastics with accessibility to hazardous substance, and metal adsorption was 82 found to be considerably greater to aged microplastics than to virgin microplastics 83 84 (Holmes et al., 2014; Kalcikova et al. 2020). Studies confirmed that pollutant adsorption on microplastic surface was improved in the presence of organic matter 85 especially the humic acid than fulvic acid, which was resulted som the π - π conjugation 86 between humic acid and microplastic that provided a suitable and charged surface for 87 attraction and adsorption of various pollutants (Thanget al., 2018a). Although the 88 by e not been formally established, health effects of ingesting microplastic 89 alon been verified due to the combined toxic 90 higher toxic effects on aquatic life had 91 function of hazardous subst and microplastics (Dong et al., 2019; Turner & hed that aged microplastics with biofouling was tested 92 Holmes, 2015). Resear a cor for adsorbing silv a environmentally relevant concentrations, and showed more 93 94 adsorbed amount and intensive subsequent leaching of silver. The following toxicological experiments proved that aged microplastics attached with silver had high 95 96 ecotoxicological potential on daphnids Daphnia magna, yet little toxicity could be found by pristine microplastics (Kalcikova et al. 2020). Surprisingly, little attention has 97 been committed to remove the attached hazardous substances from microplastics for 98 decreasing the risk of co-contamination. On the basis of the above views, it can be 99

100 concluded that the organic matter layer (biofilm) formed naturally over time on the 101 microplastic surface endows the microplastic surface with the ability to adsorb metals 102 through bridging role. In order to achieve the purpose of removing heavy metals from 103 microplastics, the decomposition and exfoliation of the organic layer adhering to the 104 microplastic surface is crucial.

105 Microplastics exposed to the aquatic environment are gradually coated by a layer of inorganic and organic substances, which provides available surface for the 106 microorganisms f rming 107 colonization of to inhabit followed biofilm (Oberbeckmann et al., 2015; Rummel et al., 2017; Zhang 108 et al., 2018b). The subsequent formation of conditioning layer containing according anisms (live or dead) 109 taple (EPS) shows great potential for and the embedded extracellular polymeters sub 110 organic layer that bears the bridging role, 111 metal adsorption. For transforming the advanced oxidation processe cially he sulfate radical-based one (SR-AOPs) has 112 g organic matter by in-situ generated reactive species 113 hopeful prospects in decomp al., 2019; Oh et al., 2016; Tang et al., 2018; Yi et al., 2019). 114 (Liu et al., 2019; Heterogeneous catalysis for SR-AOPs is of great interest to many researchers, in which 115 the selection and preparation of catalysts are the focus of research (Gong et al., 2009; 116 Wang et al., 2019a; Xu et al., 2012). Biochar-based material with high graphitization is 117 increasingly reported as a promising redox-active catalyst to mineralize organics into 118 carbon dioxide and water by the active sites of defects and versatile functional groups 119 (Chen et al., 2018; Oh et al., 2018; Wang et al., 2019b; Zhang et al., 2019). Besides the 120

carbon matrix, biochar with appropriate pore structure can be used as a carrier to 121 support transition metals and their oxides which configured with variable valence to 122 coordinate the activation process of persulfate (PS) (Fu et al., 2019; Yu et al., 2019). Fe 123 is considered as a better alternative of transition metals, not only because of its wide 124 range of sources and hypotoxicity, more importantly, attributed to its inherent 125 126 magnetism which provides a beneficial opportunity to achieve material recycling (Yu et al., 2019). In addition to the function of catalyst, the performance of biochar as 127 adsorbent to immobilize metal ions had been intensively investigation gated Ye et al., 2017a; 128 Zeng et al., 2019; Zhang et al., 2013). Owing to the abundant functional groups and 129 large cation exchange capacity (Song et al., 2019a; Xione et al., 2018), biochar exhibits 130 the efore provides a powerful platform considerable adsorption capacity for metal cons 131 tached from the microplastic surface and reduces 132 for re-immobilizing metals that are the mobile form of metal. 133

he view of removing metals from microplastics by 134 This paper first p opos matter layer covered on the surface, in order to alleviate the 135 decomposing the d potential harms of microplastics as vectors to transport hazardous substances and 136 reduce the co-contamination. Considering the additional chemical toxicity of heavy 137 metals attached to aged-microplastics, sulfate radical-based AOPs were regarded as 138 novel and cost-effective technology to remove heavy metals from the surface of the 139 microplastic, as well as separating the released heavy metals from the water 140 simultaneously by magnetic catalyst. Lead (Pb), a frequently detected heavy metal in 141

aquatic environment, is treated as a representative target pollutant. In this study, a 142 highly efficient biochar-based catalyst containing ferromagnetic property was prepared 143 by modification of K₂FeO₄ (a green and multi-functional water treatment agent playing 144 the role to improve pore formation and graphitization). The performance of prepared 145 biochar-based catalyst to activate persulfate for decomposition of organic matter 146 147 covered on microplastic surface and to achieve immobilization and recovery of the released metal ions was explored. The main research purposes are to (1) explore the 148 decomposition of the organic matter layer through SR-AQPs whic PS is activated 149 by biochar-based catalyst; (2) determine the content change of metal on the 150 microplastic surface during the experiment; (3) disc ss the effects of coexisting 151 warer, salinity and temperature on the substances (inorganics and organics) in transformed 152 netal removal from microplastics; and (4) 153 performance of PGMB/PS system for analyze the main treatment echinisms involved in degradation of organics, 154 separation of attached p microplastics, and re-adsorption of released metal. 155 letal 156

- 157 **2. Materials and methods**
- 158 2.1 Materials

159 Natural-aged (beached) plastics were sampled from bottomland of Dongting Lake, 160 a wetland located in Hunan Province, China. In the laboratory, the sand on the plastic 161 surface was carefully removed by soaking in ultrapure water, and then the dried 162 samples pass through a 20-mesh sieve to ensure that the particle dimensions fall into the range of microplastics definition. Standard Lead reserve solution, potassium ferrate (K_2FeO_4), sodium persulfate ($Na_2S_2O_8$, PS) were purchased from Shanghai Chemical Corp. Besides, all used solutions were prepared in high purity ultrapure water (18.25)

- 166 M Ω cm) which was produced by Ulupure (UPRII-10 T) laboratory water system.
- 167 2.2 Synthesis of biochar-based catalyst
- 168 Straw collected from shallow flats of Dongting Lake was washed and shattered to a particle size of < 0.15 mm as precursor. Then, the straw powders were immersed in 169 100 mL aqueous solution of K₂FeO₄ (0.1 M) with continuous tirring lasting for 12 h. 170 Undergone vacuum drying at 80 $^{\circ}$ C overnight, the acquired solid was transferred into a 171 quartz boat and annealed in tube furnace at a temperature of 900 °C for a residence 172 time of 2 h at continuous flow of N_2 gas. The cabonized black solid after naturally 173 graphitization as well as magnetism was cooling with porous structure, improve 174 denoted as PGMB. 175
- 176 2.3 Characterization m mode

The surface norphological and structural differences between virgin and aged microplastics were characterized via field emission scanning electron microscope (SEM, QUANTA Q400, USA). Surface functional groups of microplastics in different states were qualitatively detected by fourier transform infrared spectrum (FTIR, Nicolet 5700 Spectrometer) recorded in the range of 4000-400 cm⁻¹. The zeta potentials analysis used to determine the surface charge of microplastics was performed by Electroacoustic Spectrometer (ZEN3600 Zetasizer, UK). EDX elemental 184 mapping was used to discover the variation of Pb on microplastic surface before and185 after adsorption equilibrium, as well as undergone treatment of SR-AOPs.

- 186 In addition, the surface properties of the prepared biochar were also characterized.
- 187 X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, USA) with the calibration
- of C1s at 284.8 eV was applied to test the chemical states of element under an Al-Kα
- 189 X-ray radiation. The pore characteristics of biochar-based catalyst were calculated by
- 190 automatic surface-area porosity analyzer (Quantachrome Instrum Quadrasorb EVO,
- 191 USA) on the basis of N_2 isotherms at 77.3 K.
- 192 2.4 Treatment Experiments



Microplastics (MPs) that had been pre-wetter were poured into 250 mL conical 193 at a concentration of 10 mg/L. Moderate flask containing 100 mL solution of P 194 shaking was carried out in a thermortatic 195 haker to establish the adsorption-desorption equilibrium over night (pre rin ent confirmed that the equilibrium state was 196 apacity was calculated by $q_t = (C_0 - C_t) V/m (C_0 (mg/L))$: reached at 6 h). The ad orpti 197 is a solution; C_t (mg/L): residual Pb concentration at t; V (mL): 198 initial Pb concentr 199 reaction solution volume; m (mg): the mass of the microplastic) and taken as the amount of Pb that adhered onto the microplastic surface prior to the SR-AOPs 200 treatment. In a typical treatment process, 15 mg of the synthesized biochar was 201 suspended in above solution, followed by adding a certain amount of Na₂S₂O₈ 202 (maintaining final solution containing 0.25 mM PS) to trigger the oxidation reaction. 203 The solution samples were withdrawn at each time interval and used for determination 204

of parameters in solution after filtration by 0.45 µm PVDF disposable filters. After four 205 hours of experiments, the attached metal onto the microplastic surface were extracted 206 by digestion with acid and measured by atomic absorption spectrometry (PEAA700, 207 USA), and the attached content of Pb on microplastics was calculated by $q_m = C_1 * V_0 / m_1$ 208 $(C_1 \text{ (mg/L)})$: Pb concentration in digestion solution; $V_0 \text{ (mL)}$: volume of digestion liquid; 209 210 m_1 (mg): the mass of the microplastic involved in digestion). The differences in metal 211 amount of MPs before experiment, and Fe leaching from PGBC after reaction were detected through coupled plasma mass spectrometry (ICP-212 Aglent 7800). The transformation of organic matter in solution across the treament was measured by 213 three-dimensional excitation and emission matrix floorescence spectroscopy (3D 214 trophotometer. EMMs) recorded on FluoroMax-4 fluoresence 215

- 216
- 217 **3. Results and discussion**
- 218 **3.1 Characterization**

First of all, it concide visually distinguished between natural-aged and virgin MPs on the basis of their external surface color (Fig. S1). The darker color was assigned to the aged MPs resulted from the attachment of organisms, such as algaes, mosses, microbes and their secretions on the microplastic surface. More detailed differences in surface morphology of microplastics can be observed by SEM images (Fig. 1). Virgin microplastics were in the uniform shape of fragments with smooth and flat surface (Fig. 1b), since they were derived from the artificially mechanical fragmentation of

commercial plastics. Notably, the natural-aged MPs displayed changes in the 226 morphology, roughness and chemical properties on surface compared with virgin ones. 227 The surface of aged MPs was rougher and presented macroscopic networks of 228 microcracks with covering protrusions and deposition owing to chain scission of the 229 polymer and mineral adhesion, showing the characteristics of porous polymer. Table S1 230 231 shows the differences of metal content between virgin and natural-aged microplastics determined by ICP-MS under the same digestion condition. It can intuitively 232 to mileral deposition, demonstrate that the metals such as Mg, Al, Mn and Fe, related 233 are much more abundant in weathered microplastics than in the virgin ones. The huge 234 difference in Cd content could be explained by the fact that Cd was accumulated over a 235 vere collected from shallow flats of long period on natural-aged microplastic 236 whic Dongting Lake where was polluted by . The wrinkled and aggregated structure of 237 specific surface area and more potential adsorption aged MPs might result in la 238 sites for metal captur also could reveal the affinity of microplastics for 239 w wheir tendency for surface biofouling. 240 different organism

The surface functional groups of microplastics before and after weathering were characterized by FTIR and shown in Fig. 1c. Variations in absorption peak position and peak intensity can be observed between them. Different from the spectrum of virgin microplastic, a broadened new peak located at ~1030 cm⁻¹ was detected on the aged microplastic, which is attributed to the C–O–C stretching vibration of ester. In addition, the new bands appearing at peak position of 535, and 785 cm⁻¹ are assigned to the

in-plane bending vibration of the C=O in aliphatic ketone and the oscillations of C-O 247 of hetero-aromatic ring, respectively. These variations in oxidation peaks of aged MPs 248 are derived from the long-term photo-oxidation by reaction with atmospheric oxygen 249 during light irradiation assisted with biodeterioration, when plastic was exposed to the 250 natural environment (Fotopoulou & Karapanagioti, 2015; Zhu et al., 2019). Besides the 251 252 hetero-aromatic ring structure which was not found in the virgin MPs, the peak positioned at ~ 670 cm⁻¹ in spectrum of aged microplastic could be derived from the 253 C-P vibration of phosphorus-containing compounds, which 254 be a proof for the organics covering on the surface of natural-aged microplastic. 255

The Zeta potentials of aged and virgin suspended microplastics under different pH 256 state charges. According to the results values were investigated, which reflected the s 257 obtained by Fig. 1f, the negative values f both MPs in a near-neutral pH manifested 258 microplastics could be stabil and minimally aggregated in the natural aquatic 259 article electrostatic repulsion (Li et al., 2018). The 260 environments, owing 5 int oplastics showed electronegative on a pH range of 2~6 and 261 surface of aged i decreased gradually with increasing pH value. Compared with the virgin MPs, the aged 262 MPs accumulated more negative charges on surface, and the zero point of charge 263 (pH_{zpc}) drop from 3.06 examined by virgin MPs suspension to less than 2.00 by aged 264 MPs suspension, which was accounted for the changes in physico-chemical properties 265 of aged microplastic surface or the adhesion of negatively charged organic matter and 266 minerals onto the surface in natural environment for long time. 267

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269 **3.2 PS/PGBC** performance for metal removal from microplastic surface

Surface modification of aged MPs was formed by long-term weathering, 270 UV-induced photo-oxidation, high temperature and humidity, and typical conditions 271 encountered at beaches. These variations endow microplastic with larger specific 272 273 surface area, porosity and oxygen-containing functional groups, as well as turning charge through biofilm formation and mineral precipitation Holmes et al., 2014; 274 Turner & Holmes, 2015). The more heterogeneous and reactive surface induces greater 275 adsorption capacity of aged MPs than that of the virgin ones by electrostatic 276 interactions, cation exchange and co-precipitation. Figu S2 shows a time-dependent 277 adsorption process and kinetics curve atural-aged MPs, whose saturated 278 Pb adsorption capacity can reach as high as 0.15 mg/g, confirming the strong adsorption 279 performance of aged MPs n respect of the transport and behavior of 280 ble ompared with the equilibrium adsorbed amount of Pb 281 metals in aquatic envir nme calculated to be 4.63 mg/g under the same surrounding 282 by virgin microp conditions, it could be further clarified that the organic layer as well as the deposited 283 minerals on MP surface formed by weathering was of great importance for metal 284 accumulation. 285

The Pb content attached to the microplastic surface was calculated to be 19.83 mg/g measured by the acid digestion method, which was very close to the adsorbed amount calculated by the Pb concentration in solution at the equilibrium of adsorption

(20.15 mg/g). Therefore, it is convincing that the content of Pb attached onto the 289 microplastic surface before SR-AOPs treatment was calculated by equilibrium 290 adsorption with Pb concentration in the solution at the subsequent experiments. 291 Undergone adsorption-desorption equilibrium within 24 h, samples were exposed to 292 different treatment of individual PGMB, PS, and SR-AOPs treatment with PS activated 293 by PGMB lasting for 4 h. As shown in Fig. 2a, compared with the negligible Pb 294 removal from microplastic surface under non-treatment, treatment by PGMB, and PS 295 alone, successful combination system of PGMB and PS is like v to invoire the removal 296 improvement for attached Pb on microplastic surface with an over 60% removal 297 efficiency (calculated by the ratio of Pb content on Min after SR-AOPs treatment to 298 the Pb content on MPs after adsorption). To identify the changes in Pb on microplastic 299 surfaces, elemental mapping analysic under scanning transmission electron microscopy 300 characterize the element distribution. The evident (STEM) mode was carried 301 Pb ribution on microplastic surfaces before and after 302 contrast differences GMB/PS system could be observed on Fig. 1. This was a 303 oxidation treatment strong evidence for Pb distribution with large amount on the surface of microplastics 304 after adsorption operation (Fig. 1d), while the signal of the attached Pb was 305 significantly reduced after the SR-AOPs reaction by PGMB/PS system (Fig. 1e). 306

It is worthwhile mentioning that the adsorbed amount of Pb on biochar surface was observed to increase significantly from 7.07 mg/g at treatment of PGMB individual to 31.29 mg/g at PGMB/PS treatment, which not only proved that the

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prepared biochar has excellent adsorption properties for metals, but also indirectly 310 verified the advanced oxidation process of PS activated by PGMB would help the 311 attached Pb to fall off from the microplastic surface and thereby provide more 312 opportunities for metal removal. To gain more insight, we explored the variation of Pb 313 concentration in different parts (MPs, PGMB, and solution) with different periods, as 314 315 shown in Fig. 2b. It could be found that once the AOPs were triggered by adding biochar into vessels, PGMB can rapidly adsorb metal in the solution while activate PS 316 to destroy the organic matter covered on microplastic surface for th 317 Pb detachment from surface. The fluctuating Pb concentration in solution reflected the process of Pb 318 desorption from microplastic surface and re-adsorption onto PGMB. Until the end of 319 soluton changed little compared with that the reaction, the Pb concentration in the 320 before AOPs treatment, reflecting a concentration of mobile Pb would not be 321 at th he congical risk of Pb in the solution could be increased, which indicated 322 effectively controlled. ontact time increased, the attached content of Pb on 323 AS th microplastics surfa gradually decreased, while the adsorbed amount of Pb on PGMB 324 significantly increased, realizing the transfer of metal from microplastic to biochar 325 surface and achieving the purpose of metal separation through magnetic force (Scheme 326 1). 327

Concerning the potential vehicle role of microplastics for transfer of chemicals from river to ocean, the influences of various factors in the natural environment on the performance of PGMB/PS system for metal removal need to be further discussed. The

performance of the PGMB/PS system from adsorption to separation removal of metal 331 on microplastic surface under different salinity gradients is shown in Fig. 3a. A distinct 332 decrease of the attached Pb on microplastic surface could be found within the NaCl 333 electrolyte, which may be explained by the competition of sodium ion for occupying 334 the adsorption site, and shielding negative charge of the microplastic surface to reduce 335 336 electrostatic attraction. Although the final attached content of Pb was lower in the salinity group than in the control, the metal removal efficiency from the microplastic 337 surface slightly decreased with the increase of salinity, due to 338 low asic adsorption. NaCl exhibited an inhibitory effect on the detachment of Pa from the microplastic 339 surface, as Cl⁻ can be served as radical scavenger (Yang t al., 2018; Zhou et al., 2019) 340 dversely affected the exfoliation and to produce less reactive chlorine radica 341 hat sible explanation is that the microplastic 342 breaking of organic layers. Anoth r po particles tend to be agglome at higher salinity, which is determined by the less 343 ind th eric effect with compression of the electrical double 344 electrostatic repulsion rner & Holmes, 2015), reducing the opportunities of contact 345 layer (Li et al., between the microplastic surface and the reactive species generated on the surface of 346 biochar, followed by a decrease in degradation toward organic matter on MP surface. 347 348 In order to deeply investigate the practical application, several common matrix species were discussed systematically for their effects on metal removal by PGMB/PS 349 system. Figure 3b displays the different attached amount of Pb on solid (MPs and 350

351 PGMB) as well as the metal removal efficiency in the presence of various (in)organics.

The pH buffering action of HCO_3^- and $HPO_4^{2^-}$ resulted from hydrolysis can alkalinize 352 the solution to a certain extent, where an alkaline environment would benefit the 353 precipitation or complexation of Pb and reduce the amount of available Pb(II) for 354 adsorption in solution. In terms of the metal removal from microplastic surface based 355 on the radical oxidation, there is no denying that HCO_3^- and HPO_4^{2-} have great 356 potential as scavenger to immediately capture radicals (Song et al., 2019b; Ye et al., 357 2019a), thereby inhibiting the decomposition of organic matter and removal of metal 358 on surface. The difference between the two groups of HPO_4^{2-} is the 359 adsorbed amount of Pb on PGMB at the end of treatment. It may arise from the fact 360 that the biochar surface is still attractive for adsorption of metals or their 361 1e he metals in HPO_4^{2-} group tended precipitation generated in the HCO₃⁻ grd 362 to generate soluble complexes by chenting effect. A decreasing tendency in the 363 aurtice was found as the humic acid (HA) content attached amount of Pb on MP 364 increased, which was a aribu o the extra interaction of HA as organic ligands with 365 suble complex compounds with stable chemical properties. It 366 metals to produce should be mentioned that there seems to be no significant effect of added amount of 367 HA with regard to the metal removal from microplastic surface. It indicated that HA is 368 more likely to affect the metal chelated affinity partition, and influence limitedly the 369 oxidation performance of reactive species generated by PGMB/PS system. 370

371 Considering that microplastics have experienced numerous seasonal cycles in 372 nature, the effects of ambient temperature on metal removal from microplastic surface

by PGMB/PS system were further explored. On the basis of the results in Fig. S3, it 373 can be concluded that higher temperature showed slight inhibited effect on Pb 374 adsorption to microplastic surface. Two possible explanations are responsible for this 375 phenomenon: (1) high temperature favors the thermal motion of molecules in solution, 376 thereby enhancing the Pb(II) mobility; (2) metal attachment on microplastics 377 378 dominated by physical interaction is a reversible process, where the temperature rise is more conducive to the occurrence of desorption reaction. In addition, temperature is 379 observed to have a remarkable impact on metal removal being vior from microplastic 380 surface. More radical generation by PS decomposition at higher temperature could 381 account for the larger removal efficiency of metal as hore radicals were involved in 382 ste the microplastic surface. Based on decomposing the organic matter that attacked 383 the observation on Fig. S3, Pb adserption h by PGMB is a spontaneous, endothermic 384 process dominated by chemi nte action, indicating warming is likely to inspire 385 sorbed amount on biochar surface. 386 more metal recovery th hi

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388 **3.3 Mechanism exploration**

The surface properties of the prepared PGMB were characterized to gain more insight into its ability to activate PS decomposition and adsorb metal. As can be seen from Fig. 4a, a plenty of hollow tubes consisted of thin-walled carbon with rough surface was observed by SEM, on which many small bumps were assigned to be iron-containing particles. The uneven surface and the abundant pores on it provide a

platform for the occurrence of various reactions. The BET specific surface area of 394 PGMB was calculated to be about 76.316 m^2/g testing by N₂ isotherms at 77K. A 395 IV-type isothermal curve with a large hysteresisloop demonstrated the characteristic of 396 mesoporous, where the average pore size was detected to be 3.732 nm based on pore 397 size distribution by the BJH model. Appropriate specific surface area and pore size 398 399 distribution improved the surface accessibility for drawing PS melocules and metals to trigger surface reaction. The graphitic structure and crystallinity of the prepared PGMB 400 were provided by XRD patterns (Fig. 4b). A diffraction pear appearing at 26.5 ° was 401 ascribed to the (002) plane of graphite, demonstrating the ocally ordered carbon 402 Three structure even with the introduction of iron. typical characteristic peaks 403 corresponding to Fe⁰ were found at 20 44.6°, 65.2° and 82.3° in XRD 404 Talu spectrum, respectively, indicating that F is the most important form of iron in the 405 intensively investigated to exhibit strong activation prepared biochar. Fe⁰ had b 406 ability for PS decomposition to its low valence state, it can not only produce more 407 neous transportation of electrons from Fe⁰ to PS, but also 408 radicals by the he continuously and slowly provide Fe(II) for radical generation (Eqs. 1~3), avoiding the 409 quenching reactions between Fe(II) ion and $SO_4^{\bullet-}$ (Oh et al., 2010; Peluffo et al., 2016). 410 The other two weak peaks locating at 30.5 ° and 43.3 ° were indexed to the (220), and 411 (400) crystal planes of Fe₃O₄, further confirming the ferromagnetism of PGMB which 412 allows metal could be separated from aqueous phase. The VSM magnetization curve 413 (Fig. S4) of the recovered PGMB was examined with saturation magnetization value of 414

55.51 emu/g for verifying the magnetic properties of PGMB after the whole treatment. 415 X-ray photoelectron spectroscopy was performed to analyze the valence state of each 416 417 element in PGMB. There are three fitted peaks in high-resolution spectrum of C1s shown in Fig. 4e, positioned at 284.8, 286.2, and 288.8 eV, corresponding to C=C 418 bonds in aromatic ring, C-O (alkoxy), and ketonic C=O, respectively, in which 419 420 carbonyl and ketone groups had been proved to be the active site for triggering advanced oxidation processes (Duan et al., 2016; Shao et al., 2018; Ye et al., 2020). 421 Moreover, most of the oxygen-containing functional group, 422 such 2 C=O (ketonic group), COOH (carboxyl), and H-O located at 530.2, 531.7, and 533.3 eV, respectively, 423 detected in the O1s high-resolution spectrum vere regarded as sites for metal 424 et al., 2017b). Figure 4g and h display adsorption (Tan et al., 2015; Ye et al., 20 425 the binding energies of Fe 2p peakeat 7 0.9, and 724.1 eV referring to the 2p_{3/2} and 426 $2p_{1/2}$ orbit of Fe, respectively ad litional satellite peaks of PGMB appeared in the 427 p after the AOPs reaction suggested the increase in 428 high-resolution spectrum of which was due to the participation of low valence Fe in PS 429 oxidation state Fe activation with Fe cycle (Eqs. 3~7). 430 101 (1)

$$431 \equiv Fe^{\circ} + H_2O \rightarrow \equiv Fe(II) + OH + H_2 \tag{1}$$

$$432 \equiv \mathrm{Fe}^{0} + \mathrm{O}_{2} + 2\mathrm{H}_{2}\mathrm{O} \rightarrow 2 \equiv \mathrm{Fe}(\mathrm{II}) + 4 \mathrm{OH}^{-}$$

$$\tag{2}$$

433
$$\equiv Fe^0 + 2 S_2 O_8^{2^-} \rightarrow 2 \equiv Fe(II) + 2 SO_4^{\bullet^-} + 2 SO_4^{2^-}$$
 (3)

434
$$\equiv \operatorname{Fe}(\mathrm{II}) + \operatorname{S_2O_8}^{2^-} \rightarrow \equiv \operatorname{Fe}(\mathrm{III}) + \operatorname{SO_4}^{\bullet^-} + \operatorname{SO_4}^{2^-}$$
(4)

$$435 \equiv \text{Fe}(\text{III}) + 2 \text{ H}_2\text{O} \rightarrow \equiv \text{Fe}(\text{III})\text{OOH} + 3 \text{ H}^+$$
(5)

436
$$2 \equiv Fe(III)OOH + 2 SO_4^{2-} + 2 H_2O \rightarrow 2 \equiv Fe(II) SO_4 + 4 OH^- + H_2 + O_2$$
 (6)

437
$$\equiv \operatorname{Fe}(\operatorname{III}) + \operatorname{S}_2 \operatorname{O}_8^{2^-} \to \equiv \operatorname{Fe}(\operatorname{II}) + \operatorname{S}_2 \operatorname{O}_8^{\bullet^-}$$
(7)

438
$$\equiv C - OOH + S_2 O_8^{2-} \rightarrow \equiv C - OO^{\bullet-} + SO_4^{\bullet-} + HSO_4^{-}$$
(8)

$$439 \equiv C - OH + S_2 O_8^{2-} \rightarrow \equiv C - O^{\bullet-} + SO_4^{\bullet-} + HSO_4^{-}$$
(9)

440
$$\equiv Quinones + H_2O \rightarrow 2 \equiv Semiquinone^{-} + 2H^+$$
 (10)

441
$$\equiv Semiquinone^{\bullet-} + S_2 O_8^{2-} \rightarrow SO_4^{\bullet-} + \equiv Quinones$$
 (11)

442

To shed light on the role of the organic layer cover 443 rface on metal attachment by microplastics, we deeply studied the reactionship between the 444 decomposition degree of organic matter on mic oplanic surface by acid or alkali 445 on the surface, thus illustrating the treatment with the adsorbed amount 446 Þ Pb feasibility of separating metals from nich plastic surface through the decomposition of 447 organic matter covering on nsilering the different solubility of organic matter 448 alkali, the aged-microplastics were shaken in different under the condition of 449 .cid s contents of organic matter coated on microplastics (different 450 solutions to obtain TOC values in aqueous phase). The pre-treated microplastics were dried and used to 451 explore their ability of metal adsorption. As shown in Fig. S5, it should be pointed out 452 that the microplastic with the least amount of remaining organic matter on surface, 453 reflected by the largest TOC value after the treatment of alkali liquor, resulted in the 454 smallest metal adsorption capacity. The values of TOC in the pretreatment solution 455 were inversely proportional to the amount of metal adsorbed on the microplastic 456

457 surface (Fig. S5b), which proved that the decomposition of organic matter on the
458 microplastic surface can achieve metal detachment and removal from microplastics.

459 In order to further confirm the decomposition and mineralization of the organic matter, 3D EMM spectra was carried out to identify the transformation and evolution 460 of organic matter in solution across the oxidation process by PGMB/PS system. A 461 462 sample of the solution, oscillated for 24 hours with adding the same amount of microplastic as above experiment, showed the multiple peaks before SR-AOPs reaction 463 (Fig. 5a). Based on spectrum elucidation, there were mainly see kip is of fluorescent 464 peak positioned at Ex/Em of: 1) 250-300/280-380 nm (peak A associated with 465 including ryptophan microbial by-product-like substances 466 and tyrosine), h fulvic acid-like compounds), and 250–290/400–500 nm (peak B associated 467 320-380/400-490 nm (peak C ated with humic acid-like compounds), 468 ssoc respectively. When the sample s c lleved by the reaction time of 1 hour (Fig. 5b), 469 k A that closely related to biology decreased markedly, 470 the fluorescence signal of the pert of organic matter is most sensitive to the oxidation reaction 471 which proved that by PGMB/PS system. Undergone 2 hours of oxidation process, the intensity of the B 472 and C peaks drop sharply even almost disappeared, describing that the fulvic acid-like 473 474 and humic acid-like substances were decomposed by a large amount during this period, and they may be degraded into other intermediate products or mineralized thoroughly 475 to produce CO₂ and H₂O. Extending the reaction time to 4 h (Fig. 5d), the fluorescence 476 intensity of B and C peak abnormally increased dramatically, revealing that the organic 477

substances originally covered onto the microplastic surface were destroyed and 478 decomposed thereby released into solution. The FTIR spectrum of the microplastic that 479 undergone the whole SR-AOPs was performed to analyze the transformation in surface 480 properties in comparison with the microplastic before reaction (Fig. S6). The changes 481 in either position or intensity of peaks associated with the covered organics on surface 482 at 1420~1300 (carboxylate) and 900~600 cm⁻¹ provided a supplementary explanation 483 for the variation in coverage status of the organics on microplastic surface in the 484 485 oxidation process. The role of reactive species in the detachment of attached netals from microplastic 486 surfaces and the types of active substances involved in the decomposition of organic 487 xperiments. Methanol (MeOH) and matter can be analyzed by radical ca 488 ure tio of 1000 to PS, were adopted as the 489 tert-butyl-alcohol (TBA), at a mean r scavengers of both sulfate and fox yl radicals, and hydroxyl radicals, respectively, to 490 pecie he moderate degree of reduction in metal removal 491 consume the reactive et on Fig. 6a, which preliminarily indicated that both SO_4 and 492 efficiency was pro •OH were produced according to Eqs. 3~11, and participated in the metal removal 493 process. Taking the hydrophilicity of scavengers but the radical generated on surface 494 into account, the more hydrophobic scavenger for simultaneously capturing both 495 radicals was applied. In the presence of phenol, the metal removal efficiency was 496 found to be considerable decline from 60.45% to 37.55%, confirming the important 497 role of radicals on metal detachment from microplastic surfaces. Electron paramagnetic 498

resonance (EPR) spectrum with DMPO as spin trapping agents is a powerful evidence 499 (Fig. 6b), in which the emergence of characteristic peaks of DMPO- SO_4^{\bullet} and 500 501 DMPO-•OH adducts directly illustrated the generation and revolution processes of reactive species on system. The metal removal by PGMB/PS system still proceeded 502 even if the radicals were trapped, which was likely due to that the specific pathway of 503 504 PS activation by carbon-based catalyst (non-radical degradation) continued to be a great impetus to organics decomposition (Luo et al., 2019; Zhu at al., 2018). The sharp 505 decrease in the metal recovery by PGMB is owing to the at that the coverage of 506 hydrophobic substances on the surface restricts its adsorption site or accessible 507 pathway, as well as less Pb detached from microplatic and released into solution. 508

509 4. Conclusions

In conclusion, the removal of the 510 attached heavy metals from natural-aged microplastics was first achie the advanced oxidation reaction of PS activated by 511 char. The PGMB/PS system with reactive species 512 the prepared ferromagnetic acisal pathway was proposed to transform and decompose the generation and no 513 covered organic matter (formed by long-term exposure to the environment) which 514 acted the bridging role for metal adsorption on natural aged-microplastic surface. The 515 516 metals that subsequently released from microplastic surface were re-immobilized by biochar with favorable specific surface area and abundant versatile functional groups, 517 exhibiting great potential regarding the metal separation from aqueous phase through 518 magnetic force. The anti-interference tests demonstrated that regardless of the 519

differences in processing efficiency, the relatively less contents of metal were eventually remained on microplastic after reaction under various surrounding conditions. These new overall understandings provide novel opportunities for reducing the risks of microplastic pollution in water environments, especially the co-contamination of hazardous substances and microplastics.

525

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References

533	
534	Brennecke, D., Duarte, B., Paiva, F., Cacador, I., Canning-Clode, J. 2016. Microplastics as vector for
535	heavy metal contamination from the marine environment. Estuarine Coastal and Shelf Science
536	178 , 189-195.
537	Carbery, M., O'Connor, W., Palanisami, T. 2018. Trophic transfer of microplastics and mixed
538	contaminants in the marine food web and implications for human health. Environment
539	International 115 , 400-409.
540	Chen, X., Oh, W., Hu, Z., Sun, Y., Webster, R.D., Li, S., Lim, T. 2018. Enhancing sulfacetamide
541	degradation by peroxymonosulfate activation with N-doped graphene produced through
542	delicately-controlled nitrogen functionalization via tweaking thermal annealing processes.
543	Applied Catalysis B: Environmental 225, 243-257.
544	Dong, Y., Gao, M., Song, Z., Qiu, W. 2019. Adsorption mechanism of As(IV) on polytetrafluoroethylene
545	particles of different size. Environmental Pollution 254 (Pt A), 1993.
546	Duan, X., Sun, H., Ao, Z., Zhou, L., Wang, G., Wang, S. 2015, Unwinning the active sites of
547	graphene-catalyzed peroxymonosulfate activation. Carbon 107, 371, 78.
548	Farrell, P., Nelson, K. 2013. Trophic level transfer of microplastic: Mytilus edulis (L.) to Carcinus
549	maenas (L.). Environmental Pollution 177, 1-3.
550	Fotopoulou, K.N., Karapanagioti, H.K. 2015. Surface reporties of beached plastics. Environmental
551	Science & Pollution Research International 22, 147, 1 022-32.
552	Fu, Y.K., Qin, L., Huang, D.L., Zeng, G.M., Lai, A.Li, B.S., He, J.F., Yi, H., Zhang, M.M., Cheng, M.,
553	Wen, X.F. 2019. Chitosan functionalized activated coke for Au nanoparticles anchoring: green
554	synthesis and catalytic activities hyperogenation of nitrophenols and azo dyes. Applied
555	Catalysis B: Environmental 2 5. (1774)
556	Gong, J.L., Wang, B., Zeng, G.M., Yang, P., Niu, C.G., Niu, Q.Y., Zhou, W.J., Liang, Y. 2009. Removal
557	of cationic dyes from aquious solution using magnetic multi-wall carbon nanotube
558	nanocomposite as dsorbunt. Journal of Hazardous Materials 164(2-3), 1517-1522.
559	Hodson, M.E., Duffur-Hodson, C.A., Clark, A., Prendergast-Miller, M.T., Thorpe, K.L. 2017. Plastic
560	Bag Derived-dicroplastics as a Vector for Metal Exposure in Terrestrial Invertebrates.
561	Environmental Science & Technology 51(8), 4714-4721.
562	Holmes, L.A., Turner, A., Thompson, R.C. 2014. Interactions between trace metals and plastic
563	production pellets under estuarine conditions. Marine Chemistry 167, 25-32.
564	Huffer, T., Hofmann, T. 2016. Sorption of non-polar organic compounds by micro-sized plastic particles
565	in aqueous solution. Environmental Pollution 214, 194-201.
566	Kalcikova, G., Skalar, T., Marolt, G., Kokalj, A.J. 2020. An environmental concentration of aged
567	microplastics with adsorbed silver significantly affects aquatic organisms. Water Research
568	175 (2020), 115644.
569	Koelmans, A.A., Bakir, A., Burton, G.A., Janssen, C.R. 2016. Microplastic as a Vector for Chemicals in
570	the Aquatic Environment: Critical Review and Model-Supported Reinterpretation of Empirical
571	Studies. Environmental Science & Technology 50(7), 3315-3326.
572	Li, S., Liu, H., Gao, R., Abdurahman, A., Dai, J., Zeng, F. 2018. Aggregation kinetics of microplastics in

- aquatic environment: Complex roles of electrolytes, pH, and natural organic matter.
 Environmental Pollution 237, 126-132.
- Liu, Y., Liu, Z., Huang, D., Cheng, M., Zeng, G., Lai, C., Zhang, C., Zhou, C., Wang, W., Jiang, D.,
 Wang, H., Shao, B. 2019. Metal or metal-containing nanoparticle@ MOF nanocomposites as a
 promising type of photocatalyst. Coordination Chemistry Reviews 388, 63-78.
- Luo, R., Li, M., Wang, C., Zhang, M., Nasir Khan, M.A., Sun, X., Shen, J., Han, W., Wang, L., Li, J.
 2019. Singlet oxygen-dominated non-radical oxidation process for efficient degradation of
 bisphenol A under high salinity condition. Water Research 148, 416-424.
- 581 Massos, A., Turner, A. 2017. Cadmium, lead and bromine in beached microplastics. Environmental 582 Pollution **227**, 139-145.
- 583 Mrosovsky, N., Ryan, G.D., James, M.C. 2009. Leatherback turtles: the menace of plastic. Marine
 584 Pollution Bulletin 58(2), 287-9.
- 585 Oberbeckmann, S., Löder, M.G.J., Labrenz, M. 2015. Marine microplastic-associated biofilms a review.
 586 Environmental Chemistry 12(5), 551.
- 587 Oh, S.Y., Kang, S.G., Chiu, P.C. 2010. Degradation of 2,4-dinitrotoluere by persurfate activated with 588 zero-valent iron. Science of the Total Environment **408**(16), **16**(4-2)
- Oh, W., Lisak, G., Webster, R.D., Liang, Y., Veksha, A., Giannis, A., Mot 2018. Lim, J., Lim, T. 2018.
 Insights into the thermolytic transformation of light cellulosic biomass waste to redox-active carbocatalyst: Durability of surface active sites. Applied Catalysis B: Environmental 233, 120-129.
- Oh, W.D., Dong, Z.L., Lim, T.T. 2016. Generation of staffice indical through heterogeneous catalysis for
 organic contaminants removal: Current development, challenges and prospects. Applied
 Catalysis B: Environmental 194, 169 201.
- Peluffo, M., Pardo, F., Santos, A., Romero, X 2015. Use of different kinds of persulfate activation with
 iron for the remediation of a PAA-comminated soil. Science of the Total Environment 563,
 649-656.
- Rummel, C.D., Jahnke, A., Corochova E., Kühnel, D., Schmitt-Jansen, M. 2017. Impacts of Biofilm
 Formation on the Fate and Potential Effects of Microplastic in the Aquatic Environment.
 Environmenal Science & Technology Letters 4(7), 258-267.
- Shao, P., Tian, J., Yan, F., Duan, X., Gao, S., Shi, W., Luo, X., Cui, F., Luo, S., Wang, S. 2018.
 Identification and Regulation of Active Sites on Nanodiamonds: Establishing a Highly Efficient
 Catalytic System for Oxidation of Organic Contaminants. Advanced Functional Materials
 28(13), 1705295.
- Shen, M., Zeng, G., Zhang, Y., Wen, X., Song, B., Tang, W. 2019a. Can biotechnology strategies
 effectively manage environmental (micro)plastics? Science of the total environment 697,
 134200.
- Shen, M., Zhang, Y., Zhu, Y., Song, B., Zeng, G., Hu, D., Wen, X., Ren, X. 2019b. Recent advances in toxicological research of nanoplastics in the environment: A review. Environmental Pollution 252(Pt A), 511-521.

Shen, M., Zhu, Y., Zhang, Y., Zeng, G., Wen, X., Yi, H., Ye, S., Ren, X., Song, B. 2019c. Micro(nano)plastics: Unignorable vectors for organisms. Marine Pollution Bulletin 139, 328-331.

- Song, B., Chen, M., Ye, S.J., Xu, P., Zeng, G.M., Gong, J.L., Li, J., Zhang, P., Cao, W.C. 2019a. Effects
 of multi-walled carbon nanotubes on metabolic function of the microbial community in riverine
 sediment contaminated with phenanthrene. Carbon 144, 1-7.
- Song, B., Zeng, Z.T., Zeng, G.M., Gong, J.L., Xiao, R., Ye, S.J., Chen, M., Lai, C., Xu, P., Tang, X.
 2019b. Powerful combination of g-C3N4 and LDHs for enhanced photocatalytic performance:
 a review of strategy, synthesis, and applications. Advances in Colloid and Interface Science
 271(101999), 1-17.
- Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., Yang, Z. 2015. Application of biochar for the
 removal of pollutants from aqueous solutions. Chemosphere 125, 70-85.
- Tanaka, K., Takada, H., Yamashita, R., Mizukawa, K., Fukuwaka, M.A., Watanuki, Y. 2013.
 Accumulation of plastic-derived chemicals in tissues of seabirds ingesting marine plastics.
 Marine Pollution Bulletin 69(1-2), 219-22.
- Tang, L., Liu, Y., Wang, J., Zeng, G., Deng, Y., Dong, H., Feng, H., Wang, J., Peng, B. 2018. Enhanced
 activation process of persulfate by mesoporous carbon for degradation of aqueous organic
 pollutants: Electron transfer mechanism. Applied Catalysis B: Environmental 231, 1-10.
- Taylor, M.L., Gwinnett, C., Robinson, L.F., Woodall, L.C. 2016. Plast microSpheringestion by deep-sea
 organisms. Scientific Reports 6, 33997.
- Turner, A., Holmes, L.A. 2015. Adsorption of trace metal by microplastic pellets in fresh water.
 Environmental Chemistry 12(5), 600.
- Wang, H., Zeng, Z., Xu, P., Li, L., Zeng, G., Xiao, R., Ten, A. Huang, D., Tang, L., Lai, C., Jiang, D.,
 Liu, Y., Yi, H., Qin, L., Ye, S., Ren, X. Tang, Y. 2119a. Recent progress in covalent organic
 framework thin films: fabrications, applications and perspectives. Chemical Society Reviews
 48(2), 488-516.
- 638 Wang, W.J., Zeng, Z.T., Zeng, G.M., Zha Xi b, R., Zhou, C.Y., Xiong, W.P., Yang, Y., Lei, L., Liu, 639 Y., Huang, D.L., Cheng, M., Fu, Y.K., Luo, H.Z., Zhou, Y. 2019b. Sulfur doped tubular g-C3N4 as novel photocatalyst for destruction of 640 carbon quantum dots lo aed h clive degradation under visible light. Chemical Engineering Journal 641 Escherichia coli and 642 378, 122-132
- Wright, S.L., Thompson, P.C., Galloway, T.S. 2013. The physical impacts of microplastics on marine
 organisms: a review. Environmental Pollution 178, 483-92.
- Wu, P., Cai, Z., Jin, H., Tang, Y. 2019. Adsorption mechanisms of five bisphenol analogues on PVC
 microplastics. Science of The Total Environment 650, 671-678.
- Kiong, W.P., Zeng, Z.T., Li, X., Zeng, G.M., Xiao, R., Yang, Z.H., Zhou, Y.Y., Zhang, C., Cheng, M., Hu,
 L., Zhou, C.Y., Qin, L., Xu, R., Zhang, Y.R. 2018. Multiulti-walled carbon
 nanotube/aminomino-functionalized -53 (Fe)composites: remarkabl adsorptive removal of
 antibiotics from aqueous solutions. Chemosphere 210, 1061-1069.
- Ku, B., Liu, F., Brookes, P.C., Xu, J. 2018. Microplastics play a minor role in tetracycline sorption in the
 presence of dissolved organic matter. Environmental Pollution 240, 87-94.
- Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z., Huang, C., Xie, G.X.,
 Liu, Z.F. 2012. Use of iron oxide nanomaterials in wastewater treatment: A review. Science of
 the Total Environment 424, 1-10.
- 456 Yang, Y., Zhang, C., Lai, C., Zeng, G., Huang, D., Cheng, M., Wang, J., Chen, F., Zhou, C., Xiong, W.

657 2018. BiOX (X=Cl, Br, I) photocatalytic nanomaterials: Applications for fuels and 658 environmental management. Advances in Colloid and Interface Science 254, 76-93. Ye, S., Zeng, G., Wu, H., Zhang, C., Dai, J., Liang, J., Yu, J., Ren, X., Yi, H., Cheng, M., Zhang, C. 659 660 2017a. Biological technologies for the remediation of co-contaminated soil. Critical Reviews in 661 Biotechnology 37(8), 1062-1076. 662 Ye, S.J., Yan, M., Tan, X.F., Liang, J., Zeng, G.M., Wu, H.P., Song, B., Zhou, C.Y., Yang, Y., Wang, H. 663 2019a. Facile assembled biochar-based nanocomposite with improved graphitization for 664 efficient photocatalytic activity driven by visible light. Applied Catalysis B: Environmental 250, 665 78-88. Ye, S.J., Zeng, G.M., Tan, X.F., Wu, H.P., Liang, J., Song, B., Tang, N., Zhang, P., Yang, Y.Y., Chen, Q. 666 667 2020. Nitrogen-doped biochar fiber with graphitization from Boehmeria nivea for promoted 668 peroxymonosulfate activation and non-radical degradation pathways with enhancing electron 669 transfer. Applied Catalysis B: Environmental 269(118850), 1-11. 670 Ye, S.J., Zeng, G.M., Wu, H.P., Liang, J., Zhang, C., Dai, J., Xiong, W.P., ong, B., Wu, S.H., Yu, J.F. 2019b. The effects of activated biochar addition on remediation 671 of co-composting elenc with contaminated wetland soil. Resources Conservation and 672 278-285. W.P., Wan, J., Xu, P.A., 673 Ye, S.J., Zeng, G.M., Wu, H.P., Zhang, C., Liang, J., Dai, J., Liu, Z.F., 674 Cheng, M. 2017b. Co-occurrence and interactions of pollutants, and their impacts on soil 675 remediation-A review. Critical Reviews in Environmental Science and Technology 47(16), 676 1528-1553. 677 Yi, H., Yan, M., Huang, D.L., Zeng, G.M., Lai, C H10, X.Q., Qin, L., Liu, S.Y., Liu, X.G., Li, X.Y. 2019. Synergistic effect of artificial enzyme B.S., Wang, H., Shen, M.C., Fu, Y.K., C. 678 eco-filendly and efficient biomimetic photocatalysis. 679 and 2D nano-structured Bi2WO6 680 Applied Catalysis B: Environmenta 250.` 2-62. eng, Y., Liu, Y., Feng, H., Chen, S., Ren, X. 2019. 681 Yu, J., Tang, L., Pang, Y., Zeng, G., Na slude rived biochar catalysts for persulfate activation: Internal 682 Magnetic nitrogen-dope m. Clemical Engineering Journal **364**, 146-159. 683 electron transfer me Viao, L., Zeng, G., Liang, J., Zhang, C., Yu, J., Fang, Y., Song, B. 2019. Zeng, Z., Ye, S., Wu, H., 684 Research o nable efficacy of g-MoS2 decorated biochar nanocomposites for 685 removing tetra vcline hydrochloride from antibiotic-polluted aqueous solution. Science of the 686 Total Environment 648, 206-217. 687 Zhang, H., Wang, J., Zhou, B., Zhou, Y., Dai, Z., Zhou, Q., Chriestie, P., Luo, Y. 2018a. Enhanced 688 689 adsorption of oxytetracycline to weathered microplastic polystyrene: Kinetics, isotherms and 690 influencing factors. Environmental Pollution 243(Pt B), 1550-1557. 691 Zhang, L.H., Zhang, J.C., Zeng, G.M., Dong, H.R., Chen, Y.N., Huang, C., Zhu, Y., Xu, R., Cheng, Y.J., 692 Hou, K.J., Cao, W.C., Fang, W. 2018b. Multivariate relationships between microbial 693 communities and environmental variables during co-composting of sewage sludge and 694 agricultural waste in the presence of PVP-AgNPs. Bioresource Technology 261, 10-18. 695 Zhang, P., Tan, X.F., Liu, S.B., Liu, Y.G., Zeng, G.M., Ye, S.J., Yin, Z.H., Hu, X.J., Liu, N. 2019. Catalytic degradation of estrogen by persulfate activated with iron-doped graphitic biochar: 696 697 Process variables effects and matrix effects. Chemical Engineering Journal 378, 122-141... 698 Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., Bolan, N.S., Pei, J., Huang, H. 2013. Using

- biochar for remediation of soils contaminated with heavy metals and organic pollutants.
 Environmental Science & Pollution Research 20(12), 8472-83.
- Zhou, C., Zeng, Z., Zeng, G., Huang, d., Xiao, R., Cheng, M., Zhang, C., Xiong, W., Lai, C., Yang, Y.,
 Wang, W., Yi, H., Li, B. 2019. Visible-light-driven photocatalytic degradation of
 sulfamethazine by surface engineering of carbon nitride: Properties, degradation pathway and
 mechanisms. Journal of Hazardous Materials 380, 120815.
- Zhu, K., Jia, H., Zhao, S., Xia, T., Guo, X., Wang, T., Zhu, L. 2019. Formation of Environmentally
 Persistent Free Radicals on Microplastics under Light Irradiation. Environmental Science &
 Technology 53(14), 8177-8186.
- Zhu, S., Huang, X., Ma, F., Wang, L., Duan, X., Wang, S. 2018. Catalytic Removal of Aqueous
 Contaminants on N-Doped Graphitic Biochars: Inherent Roles of Adsorption and Nonradical
 Mechanisms. Environmental Science & Technology 52(15), 8649-8658.
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Accepted

- 712 Figure captions
- Fig. 1 SEM images of natural-aged (a) and virgin microplastic surface (b); FTIR 713 714 spectrums of natural-aged and virgin MPs (c); Pb elements on aged MPs before (d) and 715 after (e) SR-AOPs in PGMB/PS system by EDS mapping analysis; and Zeta potentials of natural-aged and virgin MPs at different pH ranging from 2.0-6.0 (f). 716 717 Fig. 2 Pb content on solid (MPs and PGMB) at each stage 718 in different treatment 719 groups. 720 Scheme 1. Proposed mechanism of SR-AOPs performance by PGMB/PS system for 721 organics degradation and metal detachment from ural-aged microplastic surface. 722 723 non-matrix species (b) on Pb content and metal Fig. 3 Effect of salinity (a) 724 6mremoval efficiency from ace by PGMB/PS system. 725 726 Fig. 4 SEM image (a), XRD pattern (b), N₂ adsorption-desorption isotherm (c), 727 pore-size distribution curve (d) of the prepared PGMB, the high resolution XPS 728 spectrum of C 1s (e), O 1s (f); Fe 2p before (g) and after AOPs treatment (h) in PGMB. 729 730 731 Fig. 5 3D-EEM fluorescence spectroscopy of the water sample before SR-AOPs reaction (a); the sample undergone oxidation reaction by PGMB/PS system for 1 h (b), 732

733 2 h (c), and 4 h (d).

734

- Fig. 6 Metal removal with additions of various scavengers (a); and EPR spectrum of
- species adducts trapped by DMPO in PGMB/PS system.

