1	A critical review of biochar-based materials for the remediation of
2	heavy metal contaminated environment: applications and practical
3	evaluations
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19 Abstract

The contamination of heavy metals (HMs) in the environment has aroused a 20 global concern. The valid remediation of HM contaminated environment is a highly 21 significant issue. Biochar an alternative to carbon materials has been vastly 22 23 documented for the remediation of HM contaminated environment. However, there are some possible imperfections to meet the actual remediation tasks as the finite 24 properties of raw biochar, and the remediation process is complex and unexpectedly. 25 This review focuses on the progress made on environmental HM remediation by 26 27 biochar-based materials within the past six years. The property analysis and key modifications of biochar are summarized inspired by their applicability or necessity 28 for HM decontamination, the environmental remediation as well as the implicated 29 30 mechanisms are thoroughly elaborated from multiple pivotal sides. The evaluations of practical application associated with biochar amendment are also presented. Finally, 31 some pertinent improvements and research directions are proposed. To our knowledge, 32 33 this article is the first time to make a systematic summary on the reliability and practicability of biochar-based materials for environmental HM remediation, and 34 critically pointed out the existing issues to facilitate the judicious design of biochar-35 based materials and understanding the trends in this field. It is also aims to provide 36 reference for subsequent research and propel practical application. 37

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39 Keywords: Heavy metals; Biochar; Property improvement; Remediation
40 mechanisms; Practical application evaluations

## 41 **1. Introduction**

Heavy metal (HM) contamination is an alarming global environmental problem 42 43 (Bolisetty et al., 2019). The notorious highly toxicity, carcinogenicity and nondegradability of HMs, and the potential to bioaccumulate in living organisms, have 44 posed a serious threat to human health and entire biosphere (Cremazy et al., 2018; Li 45 et al., 2018a). Various anthropogenic activities, industrial manufactures, and 46 environmental catastrophes have ineluctably aggravated the exchange of HMs to 47 environment (Sun et al., 2018). However, the remediation of HM contaminated 48 environment is still a significant and challenging project. The world will face with 49 deterioration of available soil and water imputes the pollution of these resources. 50 Accordingly, it is indispensable to find ways to decontaminate HMs from 51 52 environment.

Remediation techniques for HM contaminated environment include adsorption 53 (Ali and Gupta, 2006), membrane technology (Shannon et al., 2008), ion exchange 54 55 (Ge and Li, 2018), coagulation, electrochemical treatment (Wang et al., 2020d), soil washing and phytoremediation (He et al., 2019). Majority of them are complex and 56 costly as well as often generate considerable chemical residues (Tan et al., 2020; Yang 57 et al., 2020c). Alternatively, adsorption is deemed as a relatively feasible way for the 58 cleanup and recycle of HMs (Deng et al., 2020b). In this regard, carbon materials 59 (Yang et al., 2019), clay minerals (Ray et al., 2019) and aquatic plant (Cheng et al., 60 2019) have been broadly reported for precluding toxic HMs. Carbon materials (e.g. 61 biochar, activated carbon, graphene oxide, and carbon nanotubes) are well recognized 62

with tailorable properties and multifunctionality for effective remediation of HM
contaminated environment (Song et al., 2020a; Yang et al., 2019). Wherein, biochar
shows fascinating preponderance due to the cost-effectiveness, local availability, biorenewability, and environmental benignity (Dong et al., 2017).

Biochar has versatile applications (Wang et al., 2019a; Yang et al., 2020a; Ye et 67 al., 2020b; Zhang et al., 2019b) and this review centers on the application of HM 68 remediation in contaminated soil and water environment. Biochar can be derived 69 from plant tissues (Bakshi et al., 2018; Shaheen et al., 2018), wastewater solids (Liu 70 71 et al., 2018e), various residues (Xu et al., 2019a), animal wastes (Liu et al., 2019) and non-conventional materials (Zhou et al., 2020b) via pyrolysis, hydrothermal 72 carbonization, gasification and torrefaction at low temperatures (<700°C) and low or 73 74 no oxygen conditions (Yang et al., 2020c). Different feedstocks and preparation avenues have substantial influence on intrinsic properties of biochar and directly 75 affect the extent and control mechanisms of HM remediation (Wu et al., 2019). 76 77 Furthermore, the environmental status also has an impact on HM remediation. Sufficient understanding the mechanisms can help to cultivate application-oriented 78 biochar-based materials with well-ordered structure and remarkable surface 79 chemistry, which is something needed to work on further. Undoubtedly, the 80 physicochemical characteristics of materials are crucial to its application. The 81 mechanisms will be explored in molecular-level by analyzing biochar-based material 82 83 construction and properties, and its role in the interaction with HMs.

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Previous reviews on the remediation of HM contaminated environment by

biochar mainly focused on the utilization of pristine biochar. As the research 85 progresses, it commits to tailor the physicochemical properties (e.g. functional 86 groups (FGs), specific surface area (SSA), porosity, roughness, and species 87 composition) of pristine biochar to enhance its selectivity, activity, separability and 88 structural stability (Cui et al., 2019; Karunanayake et al., 2018; Kim et al., 2019; 89 Ling et al., 2017), thereby improving the remediation efficacy for HMs. While there 90 is still less portion of review articles about these modified biochar-based materials 91 for the remediation of HM contaminated environment. Although the unlimited 92 93 potential of biochar-based materials, many practical matters have to be faced in its application. Meanwhile, it is requisite to evaluate its practical application with the 94 increasing distribution and commercial production of biochar internationally 95 96 (Alhashimi and Aktas, 2017). However, the summary of practical application evaluations of biochar-based materials for the remediation of HM contaminated 97 environment is still bare so far. Namely, the full-scale evaluations regarding recovery 98 and regeneration, economic efficiency, aging and disintegration, potential 99 environmental risks, which has recently been highlighted. 100

Anyhow the treatment of HM contaminants in the environment is of critical incident. Using biochar-based materials as remediation materials is a sustainable and practical strategy. As abovementioned, this updated review (based on studies from 2016 to 2021) presents a critical summary regarding analysis and improvement of biochar properties, various biochar-based materials for the remediation of HM contaminated environment and the mechanisms from multiple aspects, as well as the 107 correlated evaluations of practical application. Besides, possible improvements and 108 perspectives are also proposed. This paper is to illustrate the admirable remediation 109 performance and optimization of biochar-based materials for various HMs. It is also 110 hoped that this review can enlighten researchers and push forward the progress of 111 practical remediation of HM contaminated environment by biochar-based materials.

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## 2. Property analysis of biochar

Understanding biochar properties through characterization benefits to its 113 efficient application (such as formulating the outcome-oriented property 114 115 modification of biochar for HM capture) owing to the subtle relationships between biochar properties and its environmental applications (Xiao et al., 2018; Zhou et al., 116 2020c). And to adequately decipher the role of respective components of biochar-117 118 based materials in capturing HMs, characterization is the prerequisite. Moreover, material characterization has emerged as an independent research field and has 119 drawn increasing research interests (Igalavithana et al., 2018a; Khiari et al., 2020), 120 121 thereby it is meaningful to summarize the analysis techniques.

The commonly used analysis techniques for biochar are shown in Fig. 1, i.e., 122 proximate and ultimate analyses, Brunauer-Emmett-Teller (BET), 123 Barret-Joyner-Halender (BJH), scanning electron microscopy (SEM), high-124 resolution transmission electron microscopy (HR-TEM), scanning transmission 125 electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDX), X-ray 126 photoelectron spectroscopy (XPS), Fourier transform-infrared spectroscopy (FT-IR), 127 Raman spectroscopy, Böehm titration, thermo-gravimetric analyzer (TGA), X-ray 128

diffraction (XRD), X-ray fluorescence spectroscopy (XRF), solid-state nuclear
magnetic resonance (NMR), electron spin resonance (ESR), electron paramagnetic
resonance (EPR), scanning transmission soft X-ray microscopy (STXM),
synchrotron-based near-edge X-ray absorption fine structure spectroscopy
(NEXAFS), X-ray absorption near-edge structure spectroscopy (XANES) and
extended X-ray absorption fine structure spectroscopy (EXAFS).



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Fig. 1. Summary of analysis techniques for biochar.

The interaction affinity between HMs and biochar can be disclosed via the XPS 137 and FT-IR. FT-IR is usually carried out to identify the FGs and mineralogy on 138 biochar surface before and after contacting with HMs to explore the interaction 139 mechanisms. Table 1 lists the corresponding wavenumbers of stretching vibration of 140 chemical groups that frequently seen in biochar-based materials from FT-IR spectra. 141 Typically, the strong Pb-O interaction on materials was suggested by FTIR spectra of 142 before and after biochar-metal interaction, which was further illustrated by XPS 143 analysis of Pb-laden biochar (Wan et al., 2020a). 144

materials by 1 1 m analys	(modified from (stang et al., 2017)).
Wavenumbers (cm <sup>-1</sup> )	Chemical groups
3600~3200	hydroxyl (O–H)
2950~2850	aliphatic CH <sub>x</sub> (C–H, CH <sub>2</sub> or CH <sub>3</sub> )
1740~1700	carboxyl (-COO-), ketones (C=O)
1630~1600	aromatic compounds (C–C), ketonic acids and quinones (C–O)
~1440	aromatic (C=C)
~1375	aliphatic CH <sub>x</sub> (CH <sub>2</sub> or CH <sub>3</sub> ), phenolic hydroxyl (O–H)
~1260	-COO-
1110~1030	С-О-С
900~750	aromatic C–H

**Table 1.** The stretching vibration of common chemical groups in biochar-basedmaterials by FTIR analysis (modified from (Jiang et al., 2019) ).

147	Advanced spectroscopy techniques such as NEXAFS, STXM, XANES and
148	EXAFS have higher resolution and sensitivity, are valuable tools for accurately and
149	deeply probing metal-biochar interactions. However, accounts the relatively less
150	accessibility, these techniques in biochar characterization are not universal. Wei et al.
151	used STXM and Cr K-edge XANES to determine the Cr species sorbed by carbon-
152	coated montmorillonite nanocomposite (CMt) (Wei et al., 2019a). These analyses
153	showed that Cr(VI) was reduced to Cr(III) at pH 2 or 8, wherein Cr(OH) <sub>3</sub> precipitate
154	(65.4% for pH 2, 96.2% for pH 8) and Cr(III)-acetate complex (31.4% for pH 2, 3.3%
155	for pH 8) were the main species. The FTIR and C K-edge XANES further indicated
156	that phenolic groups of CMt serve as electron shuttles to reinforce Cr(VI) reduction.
157	Ahmad et al. indicated that Pb was immobilized by forming stable
158	chloropyromorphite through EXAFS quantification of Pb speciation in biochar
159	unamended/amended soils (Ahmad et al., 2016). The information about in-situ
160	metal-biochar interactions is significant for evaluating the actual status of biochar-
161	based materials to remediate HM contaminated environment.

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Though each analysis technique has its own unique merits, none of these

valent iron; HAP, hydroxyapatite; LDHs, layered double hydroxides; GO, graphene
oxide; CNTs, carbon nanotubes.)

180 **3.1. Magnetization and activation** 

181 The magnetization and activation of biochar can improve its defects such as 182 difficulty in separation and limited ability to remediate HMs, which is the key for 183 efficient utilization of biochar-based materials. Magnetization and/or activation have 184 been used as pre-treatments for further modifications in most studies. Meanwhile, 185 some considerations for magnetization and activation of biochar are also noteworthy.

Magnetization avoids the inconvenience and time-consuming defects of 186 customary separation methods, which allows spent biochar-based materials to be 187 lightly separated by external magnets (Fig. 3) to decrease the recovery costs. 188 189 Furthermore, the inserted magnetic iron particles can serve as active sites (Yang et al., 2016b; Ye et al., 2020a; Zhao et al., 2019b). Whilst some studies shown that 190 magnetized biochar was less capable of removing HMs than non-magnetized biochar 191 (Karunanayake et al., 2018; Lu et al., 2018), it possibly because magnetized 192 modification may unintended destroy the structure of original biochar. Carefully, it 193 may form different phases ( $Fe_xO_y$  and  $Fe_x(OH)_y$ ) that containing non-magnetic phases 194 on biochar surface, and it is better to synthesize magnetic biochar in alkaline media to 195 form magnetic Fe<sub>x</sub>O<sub>y</sub> (Reguyal et al., 2017). Last but not least, whether to magnetize 196 before or after pyrolysis is a matter worth considering. Wan et al. reported that 197 biochar magnetization after pyrolysis with a stronger metal(loid) adsorption capacity, 198 whereas pyrolysis after magnetization fixed iron oxides on biochar and implying a 199

200 higher magnetic recovery and metal(loid) removal (Wan et al., 2020b).

Activation of biochar covers physical activation and chemical activation. 201 202 Physical (i.e., steam) activation can raise the SSA and pore volume of biochar, but decrease the surface polar FGs and hydrophilic nature (Wang et al., 2019b). The C=O 203 and C-O ratios of biochar both decreased after steam activation, while increased O-204 C=O for HM adsorption (Wang et al., 2019b). Steam activation has disadvantage of 205 relatively high costs. In comparison, using CO2 as gas medium or adding some 206 chemicals (e.g. KHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>) during pyrolysis perhaps a more 207 208 viable activation route for the fabrication of biochar-based materials with hierarchical porous structure (Kim et al., 2019; Wan et al., 2020a). Chemically activated biochar 209 can be prepared by oxidant, acidic or alkaline treatments such as H<sub>2</sub>O<sub>2</sub> (Dong et al., 210 211 2017), KMnO<sub>4</sub> (Yin et al., 2020), HCl (Liu et al., 2018b), HNO<sub>3</sub> (Deng et al., 2020a), H<sub>3</sub>PO<sub>4</sub> (Chen et al., 2020b), CH<sub>3</sub>COOH (Liu et al., 2020a), NaOH (Choudhary et al., 212 2020), KOH (Liang et al., 2020), K<sub>3</sub>PO<sub>4</sub> (Zhang et al., 2019c). Chemical activation 213 214 not only improve the SSA, porosity, polarity and charge characteristics of biochar, but also increase the oxygen-containing FGs and active sites for the chemisorption of 215 HMs. However, noting that certain activation could be a double-edged sword if 216 activator concentration is used inappropriately. For instance, high KOH concentration 217 would cause the lignin structure inside biochar to expand to hinder the stabilization of 218 HMs (Wang et al., 2020b). Generally, activators with moderate concentrations are 219 220 recommended.

produced co-pyrolyzed biochars by mixing bone meal (BM) and triple superphosphate 239 (TSP) with wood chips or switchgrass biomass, respectively (Zhao et al., 2016). 240 Numerous particles appeared on TSP-biochar composites, which could block active 241 carbon sites to lower carbon decomposition. Moreover, C–O–PO<sub>3</sub> or C–P groups were 242 composed during co-pyrolysis and the FGs (C=O, -C=C, C-P, P-O-C, P-O-P, -P=O) 243 of composites were more than pristine biochar reflected by XPS and FTIR spectra 244 (Zhao et al., 2016). BM-biochar composite also enhanced Cd, Cu, and Pb 245 immobilization by 1, 2, and 4 times. 246

Co-pyrolytic biochar be utilized for the remediation of HM contaminated environment is still at an exploratory stage. Whether the co-pyrolysis of multiple raw materials will yield other unanticipated effects remains further clarification. Anyway, if suitable biowaste feedstocks are selected and in a proper blending ratio, copyrolysis of different wastes could be a way of "triple wins". It not only safe treating these wastes more economically, but also producing in-situ modified biochar-based materials with exceptional properties for secluding HMs from environment.

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### **3.3.** Nanomaterials-biochar composites

The incorporation of low-cost biochar with expensive nanomaterials creates costeffective nanocomposites with outstanding structural natures, high reactivity, plentiful active sites and synergies (Lin et al., 2019; Liu et al., 2020b; Tan et al., 2016). Hereby, biochar frequently as a host to distribute and stabilize nanomaterials to maximize both superiorities for remediation of HM contaminated environment. In this area, nanometal oxide/hydroxide, functional nanoparticles, and carbon nanomaterials (Fig. 2) are the primary coated nanomaterials.

Biochar-based nanocomposites be warranted to have better physicochemical 262 properties than pristine biochar (Liang et al., 2017; Liu et al., 2016b). Metal 263 oxide/hydroxide-biochar nanocomposites were vastly reported in literatures as their 264 increased binding sites, SSA, CEC and metal-O groups for isolating HMs (Liang et 265 al., 2017; Wei et al., 2019b). For example, the 29.90% (w/w) MgO nanoparticles 266 coated on fresh biochar enhanced its SSA from 0.07 to 26.56 m<sup>2</sup> g<sup>-1</sup> (Shen et al., 267 2019), and could increase the exchangeable ions (Ling et al., 2017), which 268 significantly facilitated Pb removal and immobilization. The pathway of MgO 269 embedding during pyrolysis was depicted in eqs 1-3 (Ling et al., 2017). Note that 270 (MgOH)Cl and MgCl<sub>2</sub> may mixed with MgO on biochar surface. Iron nanoparticles 271 272 (consisted of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and ZVI) evenly dispersed on nanocomposite created a new chemical bond of Fe=O, more C-O and C=O groups compared to pure biochar 273 (Cui et al., 2019). nZVI is one of the most used nanomaterials owing to its unmatched 274 characters such as large SSA, luxuriant active sites and strong redox capacity for HMs 275 (Bakshi et al., 2018; Zhu et al., 2017; Zou et al., 2016). C=C/C=O bonds or iron 276 oxides formed and nanoscale Fe<sup>0</sup> core-Fe<sub>3</sub>O<sub>4</sub> shell were constituted on the 277 surface/channels/pores of nZVI-assisted biochar composites, but SSA decreased since 278 the embedding of iron nanoparticles (Zhu et al., 2017). Additionally, rod-shaped HAP 279 nanoparticles imbedded to biochar improved its rough surface, porosity, functionality, 280 281 ash contents, and provided more available binding sites for HMs (Chen et al., 2021; Jung et al., 2019). Mg/Fe-LHD-biochar displayed a 3-D network with highly 282

283	developed polyporous structure, and a superior co-adsorption ability of anions and
284	cations (Zhang et al., 2018). (Liu et al., 2016a) shown that CNTs or GO decoration
285	strengthened the SSA and thermal stability but diminished the pore volume of biochar,
286	introduced more FGs (-OH and -COOH) and aromatic compound groups as well, and
287	enhanced the sorption by 0.5–1.0 and 2.0–5.0 times for Pb(II) and Cd(II), respectively
288	$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 2H_2O + 4H_2O\uparrow $ (1)

289 
$$MgCl_2 \cdot 2H_2O \rightarrow (MgOH)Cl + H_2O\uparrow + HCl\uparrow$$
 (2)

$$290 \quad (MgOH)Cl \to MgO + HCl\uparrow \tag{3}$$

291 Hereinbefore, the purity of artificial produced nanoparticles should be measured and deliberated in future studies. Crucially, the selection of proper ratio of 292 nanomaterials to biochar matrix is a factor for further researches. If biochar matrix is 293 294 insufficient, the aggregation of nanomaterials on biochar cannot be completely suppressed and clog biochar pores, while excessive biochar will block the active sites 295 of nanomaterials, which all adverse to reduce HMs (Dong et al., 2017; Lyu et al., 296 2017; Zhu et al., 2017). Since the wide application of nanomaterials, more splendid 297 properties of cost-effective biochar-based nanocomposites and co-doping of various 298 nanoparticles need to be further expanded. 299

#### 300

### **3.4.** Polymer-biochar composites

301 Studies have attested that polymer-modified composites are promising to trap 302 HMs (Deng et al., 2019; Luo et al., 2021b; Ray et al., 2019). The grafting 303 modification using polymers (Fig. 2) can introduce hydroxyl, carboxyl, and N-304 containing groups (e.g., -NH, -NH<sub>2</sub>, -C-N, and -C=N) to enhance chemical reactivity of biochar toward HMs (Deng et al., 2017; Wang et al., 2020a; Yang et al.,
2019; Zhang et al., 2019e). Moreover, it also can improve the charge reversal, O/C
and N/C ratios, hydrophobicity and mechanical strength of biochar and normally
construct stable-porous gel beads (Dhiman et al., 2021; Zhang et al., 2019e; Zhang et al., 2019f; Zhao et al., 2019a).

Polymer-grafted biochar usually has special ameliorative properties that 310 enhance its adsorption and chelation of HMs (Qi et al., 2021; Zhang et al., 2019f; 311 Zhao et al., 2019a; Zhou et al., 2017). Typically, Deng et al. revealed that the 312 modification of pyromellitic dianhydride and chitosan increased amino groups (N 313 content increased from 2.49% to 9.35%) and O-containing FGs (N-H, N-C=O, C=C, 314 C–OH, COOH), as well as enlarged SSA (from 32.1 to 62.6 m<sup>2</sup> g<sup>-1</sup>) and pore volume 315 (from 0.038 to 0.096 cm<sup>3</sup> g<sup>-1</sup>) of biochar (Deng et al., 2017), resulting the elevated 316 removal of Pb and Cd by approximately 10% and that of Cu by 2.5 times. Inimitable 317 grapefruit peel biochar/pectin/alginate hydrogel beads had bead-like forms with 318 inner-porous structures to disperse and sorption metal ions into the inner active sites 319 of composite (Zhang et al., 2019f). Both of the Cu(II) sorption ability and 320 mechanical strength significantly increased with increasing pectin contents. 321 Chemically stable poly(acrylic acid) grafted chitosan-biochar composite was 322 fabricated through two-step strategy (Fig. 4b) (Zhang et al., 2019e). Abundant 323 surface FGs (i.e., hydroxyl, carboxyl, and amine) were successfully introduced, 324 which contribute greatly to the efficient and selective removal of HMs in-wastewater. 325 Peculiarly, chitosan/clay/biochar composites is a desired modification which with a 326

hybrid organic-inorganic nature for HM immobilization (Arabyarmohammadi et al., 2017). However, heating temperature may affect subsequent modification of biochar with polymers. Acrylonitrile only successfully modified the corncob biochars which pyrolyzed at low temperature ( $350^{\circ}$ C) since the lignin of biochar primarily destroyed at above 400°C, yet the graft of C=N groups is hard to achieve on –OH of benzene ring (Luo et al., 2018).

Overall, polymer-biochar composites have appreciable application prospects, but it is still in its infancy for remediation of HM contaminated environment, especially in soil. For manufacturing novel efficient biochar-based materials to meet the remediation demand, a delicate balance between pyrolysis temperature, biochar feedstocks, polymer types and grafting amounts is suggested to be deeply discussed.

#### 338 **3.5. Natural mineral-biochar composites**

Abundant natural minerals have advantages of high SSA, adsorption sites, large 339 ion exchange capacity and even electroconductibility (Han et al., 2019; Song et al., 340 341 2020b), have been used for biochar modification. Natural mineral-biochar composites also possess introduced mineral elements such as Na, Ca, Al, Fe, Mg and 342 Si (Chen et al., 2019b; Tang et al., 2021; Zhu et al., 2020b) and ions such as  $CO_3^{2-}$ , 343 SiO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> (Deng et al., 2020b; Han et al., 2019; Lahori et al., 2019). 344 Types of natural minerals (Fig. 2) are adopted for revising the above properties and 345 anti-degradation of biochar to improve its HM adsorption efficiency by ion exchange, 346 347 electrostatic interaction and co-precipitation (Jung et al., 2018; Li et al., 2020b; Sun et al., 2020; Xia et al., 2019). 348

349	For instance, biochar loaded montmorillonite greatly changed morphology,
350	protected its structure, added oxygen-containing FGs (hydroxyl, oxygen content was
351	over 30 %) and more active sites for Zn(II) removal (Song et al., 2020b). After pyrite
352	modification, the composite had higher SSA, enhanced electron transport, new
353	Fe(II)-S groups, more O-containing FGs and reaction sites than pristine biochar,
354	which facilitated Cr(VI) removal by 3-25 times (Tang et al., 2021). Excitingly,
355	inserting minerals to hydrochar which retains abundant oxygen-containing FGs but
356	fewer mineral components would have a synergistic reinforcing remediation for HM
357	contaminated environment. Moreover, negatively charged minerals are more likely
358	to bond to the acidic surface of hydrochar (Jung et al., 2018). Calcite-impregnated
359	hydrochar had a larger SSA (21.62 vs 11.54 m <sup>2</sup> g <sup>-1</sup> ), pore volume (0.064501 vs
360	0.025247 cm <sup>3</sup> g <sup>-1</sup> ) and looser structure than hydrochar, as well as ample oxygen-
361	containing FGs and calcite provided active sites (Ca content increased from 1.0% to
362	5.1%) for Cu(II) precipitation (Chen et al., 2019b). Specially, the physical
363	combination of biochar and geo-/mineral-materials can increase the alkalinity, CEC
364	and surface activity of soil, thus may enhance the immobilization of multi-HMs
365	(Lahori et al., 2019).

The development of various natural minerals through scientific means adhered to biochar for remediation of multi-HM contaminated environment are required. Among which mineral modified hydrothermal carbon generally superior than modified pyrolytic carbon in performance despite the lower SSA and porosity of hydrochar (Song et al., 2020b). Meanwhile, it should be noted that pyrolysis temperature may affect the carbon fractions and porosity of mineral modified biochar.
Rawal et al. unveiled that in the presence of iron-clay mineral, biochar developed a
higher pore volume at lower temperatures, while caused a reduction in pore volume
and increase in acidic functionalities (especially the phenolic species) and aromatic
condensation degree at higher temperature (Rawal et al., 2016).

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### **3.6.** Other biochar-based composites

Biochar-based composite fabricated by incorporation with exogenous modifier is considered as a desirable strategy to improve the properties of raw biochar. Apart from the aforementioned composites, other modifications such as monatomic doping and microorganism assistance are incrementally described in the literatures.

Monatomic doping is generally a specific modification for the target HMs. 381 382 O'Connor et al. synthesized a sulfur-modified biochar which increased the S content (from 0.2% to 13.04%) in biochar, and elevated  $Hg^{2+}$  adsorption and immobilization 383 by ~73% due to S had a strong affinity for Hg (O'Connor et al., 2018). For 384 complicated environmental media, biochar modified by robust polyatomic-doping 385 for chemical reactivity segregation of HMs is encouraged. Biological modification is 386 also an underlying platform for improving the ability of biochar to immobilizing 387 specific HMs by increasing multi-sorption sites or changing the ambient 388 environmental conditions such as microbial balance and stimulating microorganism 389 activities (Chen et al., 2019a; Qi et al., 2021). Nevertheless, microbial-assisted 390 biochar-based materials still in its embryonic stage and more further studies are 391 demanded to determine their stability and environmental behaviors from a broad 392

4.1. Remediation and mechanisms of biochar-based materials for HM 409 contaminated soil 410

Soil polluted by HMs is widespread in most parts of the world and HM 411 concentration often exceeds the background values. The fractions of HMs in soil can 412 be classified into individual fraction of exchangeable, carbonate-bound, (Fe/Mn) 413 oxyhydroxide, organically-bound and residual (Li et al., 2019; Mujtaba Munir et al., 414 2020b). The flexible applications of biochar-based materials in soil have great 415 benefits, such as immobilizing HMs by reducing their mobility and/or bioavailability. 416

417

### **4.1.1.** Selection of feedstocks and modifications

Biochar-based materials used to effectively remediate HMs have a variety of 418 biomass feedstocks and different abilities. The biochar of different feedstocks 419 420 prepared by (Xu et al., 2020) have reduced extractable Pb and Cd in soil ranked by 22.61%-71.01% (kitchen waste), 18.54%-64.35% (corn straw), and 3.28%-60.25% 421 (peanut hulls), respectively. The better immobilization performance for kitchen 422 423 waste biochar perhaps owing to its better CEC which from more alkaline metals (e.g. Na, K, Mg, and Ca) in the kitchen residues. Zhang et al. used P-modified biochars 424 (i.e., wood, bamboo, corn stalks and rice husks) to remediate HMs in soil (Fig. 5a) 425 (Zhang et al., 2019c). 60 days of incubation experiments showed that both 426 extractability of Cd(II) and Cu(II) decreased by 2~3 times through the P compounds 427 in modified biochars precipitated or complexed with HMs (Fig. 5a). Additionally, the 428 429 immobilization efficiency of modified cornstalk and rice husk biochars on Cu(II) and Cd(II) was on average 19-33% and 14-24% higher than the other two modified 430

biochars. It may be because the high Si content of these two feedstocks is conducive 431 to the firmly binding of P compounds to their modified-biochar surfaces. But the 432 433 extractability and mobility of As(V) increased regardless of feedstocks (Zhang et al., 2019c). Besides, hazardous wastes such as antibiotic residues (Hu et al., 2019) and 434 industrial sludges (Tian et al., 2020), recovering and utilizing as biochar precursors 435 is an emerging research hotspot. Collect seemly feedstocks to make biochar with 436 added-value, and some ingenious modifications can be adopted to manufacture well-437 designed biochar-based materials for HM contaminated soil amendment in future 438 439 studies.

Utilizing phosphorus-loaded biochars seem to be a promising tool for the 440 immobilization of HMs (e.g. Pb, Zn, Cu and Cd) and supplement of phosphorus 441 442 nutrients to improve soil properties (Zhao et al., 2016). For instance, the addition of phosphorus-modified rape straw biochar significantly decreased ecological risks and 443 extracted concentrations (5.9-81.7%) of HMs (Pb>Cu>Cd) in soil by the 444 precipitation and complexation of phosphate/-OH/-COOH with metals directly, and 445 indirectly by raising soil pH and available P amount (Gao et al., 2020). However, 446 special attention should be taken when applying phosphorus-loaded biochars to treat 447 contaminated soil with As (Yin et al., 2016; Zhang et al., 2019c) or Cr (Xu et al., 448 2019b) existed, there might be a negative feedback. It is probably attributed to the 449 fact that phosphorus is an analogue of As/Cr and can compete for binding sites when 450 added to soil (Yin et al., 2016). Therefore, attention should be paid to whether the 451 modified components in biochar-based materials are contrary to the intrinsic 452

its remediation for Cd(II) and Cu(II) in soil. Reproduced with permission (Zhang et
al., 2019c). (b) Schematic illustration of As(III) removal mechanism using BMN.
Reproduced with permission (Cui et al., 2019). (c) The feedback mechanism
between soil nitrification and Cd availability by N fertilizers-biochar treatments.
Reproduced with permission (Zhao et al., 2020).

#### 461 **4.1.2. Internal mineral components of biochar-based materials**

Some studies have shown that mineral components such alkali or alkaline earth 462 metals (i.e., oxides/hydroxide, phosphate, carbonate, silicate, or sulfate forms) as 463 464 inherent in biochar-based materials, have indispensable role (i.e., co-precipitation) in HM immobilization in soil (Li et al., 2020b; Lin et al., 2019; Tian et al., 2020; Zhang 465 et al., 2019c). Chen et al. reported that Cd-phosphate and Cd-carbonate formed on P-466 enriched biochar represented the main reduction of  $Cd^{2+}$  toxicity (Chen et al., 2020a). 467 Silicate in rice straw/husk derived biochar had momentous contribution to reduce the 468 bioavailability and extractability of Zn or Al (Wu et al., 2019) and Cd (Huang et al., 469 2020) by sorption and (co)precipitation. Accordingly, biochar raw materials rich in 470 certain special components are selected afterwards, and sensible mineralogical 471 modifications are carried out. After heat treatment, the obtained biochar-based 472 materials can be endowed with copious mineral constituents for HM immobilization. 473

474

#### **4.1.3.** Fabrication conditions

Fabrication conditions of biochar-based materials have crucial effects on its HM immobilization performance, particularly the heating temperature and medium gas during pyrolysis. Lincomycin mycelial fermentation residue was pyrolyzed in

478	$N_2/CO_2$ and different temperatures (300~800°C) to produce different biochar for Pb
479	immobilization (Liu et al., 2018d). The study expressed that Pb immobilization rate
480	increased significantly with increasing pyrolysis temperature, and decreased slightly
481	at the final 800°C. But Pb immobilization by CO <sub>2</sub> -biochar at high temperatures
482	(≥700°C) was notably stronger than that of N <sub>2</sub> -biochar. Spectral analysis also shown
483	that the main Pb precipitates were PbC <sub>2</sub> O <sub>4</sub> and Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH for 300℃ -biochar and
484	PbCO <sub>3</sub> and Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH for 700 <sup>°</sup> C -biochar, wherein more PbCO <sub>3</sub> in CO <sub>2</sub> -biochar
485	than that in N <sub>2</sub> -biochar. Finally, 700°C-CO <sub>2</sub> -activated biochar exhibited the highest
486	Pb immobilization (60%) in soil as the mechanisms of elevated alkalinity and more
487	carbonate and available phosphorus for Pb immobilization (Liu et al., 2018d).
488	Another study reported that CO <sub>2</sub> -biochar mobilized the available As compared to N <sub>2</sub> -
489	biochar due to the increased soil pH, while both biochars immobilized the available
490	Pb, Cd, and Zn (Igalavithana et al., 2018b). Furthermore, CO <sub>2</sub> -biochar highly
491	increased the Mn and Fe oxides, hydroxide, and organically bound Pb in soil.
492	Biochar prepared at high temperature has higher ash content and hence a higher
493	alkalinity (Jin et al., 2016; Singh et al., 2012), and majority of HMs (e.g. Pb, Cd, Cu,
494	Zn, Ni) immobilization in soil is positively allied to biochar alkalinity (Li et al.,
495	2020b; Liu et al., 2018b; Liu et al., 2018d; Wang et al., 2020b). Interestingly, HM
496	immobilization by different temperatures-derived biochars may also influenced by
497	soil conditions. Low temperature-biochars immobilized Zn(II) and Cd(II) better than
498	high temperature-biochars under acidic environment, but the results were opposite
499	under alkaline environment (Qian et al., 2019).

#### 500 **4.1.4. Soil conditions**

Soil pH and organic carbon contents importantly regulate the geochemical 501 behavior of HMs. The availability of most HMs decreased with soil pH increased (Li 502 et al., 2019; Wang et al., 2020b; Zhu et al., 2020b), and increasing biochar dosage 503 caused an upward in soil pH (Wu et al., 2020b). Cui et al. reported that palm waste 504 derived magnetic biochar-nanocomposite could increase soil pH and decrease the 505 available As(III) concentration (Cui et al., 2019). As(III) removal could via three 506 pathways (Fig. 5b): (1) electrostatic adsorption of As(III) anions; (2) oxidation of 507 508 As(III) to As(V) by reactive oxygen species; and (3) immobilization of As species by Fe-nanoparticles. On the contrary, it is stated that As become more bioavailable with 509 soil pH increasing thanks to its mostly existence form is negatively charged free state 510 511 (Wu et al., 2020b). The above contradiction perhaps ascribed to no significant correlation between pH changes and HM availability when biochar was added to 512 alkaline soils (Zhang et al., 2016). However, not all biochar amendments can rise 513 soil pH and apparently remediate HM contaminated soil (Liu et al., 2019). This may 514 be because the potential binding sites for HMs are occupied by other ions or 515 substances, or soil pH and organic carbon affect the interaction of HMs with biochar-516 based materials. 517

Attention also should be paid to the functions of redox-active components such as mineral species and organic matters in soil environment. The interactive effects of biochar and soil oxide minerals can markedly impact the immobilization pathways of HMs (Wu et al., 2019). (Xu et al., 2019e) and (Liu et al., 2019) elucidated that

biochar applied to soil rich in iron and organic acids could promote Cr(VI) reduction, 522 however, soil rich in iron but less organic acids may have an unwanted inhibition. 523 524 The association of naturally abundant iron minerals and biochar-based materials in soils is an important environmental behavior (Liu et al., 2021; Wu et al., 2020a), but 525 526 whether it has a positive effect on the remediation of HMs remains controversial. More studies are desired to reveal the influences of soil redox-active components on 527 the remediation of various HMs especially redox reactive metals by biochar-based 528 materials. 529

530 **4.1.5** 

# **4.1.5.** Coexistence of multiple HMs

Multiple HMs usually coexist in contaminated soil, and there seemingly 531 competitive between them. In general, this competitiveness is affected by various 532 533 factors, such as electronegativity, hydration radius, hydrolysis constant, and carried charges of metals (Gao et al., 2020; Liu et al., 2018b; Mujtaba Munir et al., 2020a), 534 and the ability of different metals to complex with FGs on biochar-based materials is 535 discrepant (Mujtaba Munir et al., 2020b). Calcium-based magnetic biochar (Wu et 536 al., 2020b), goethite modified biochar (Zhu et al., 2020b) and magnetic macro-537 porous biochar sphere (Liu et al., 2020b) had a better stabilization ability on Cd than 538 As in co-contaminated soil due to the elevated pH and CEC. In this respect, it may 539 indeed be the electrostatic repulsion/attraction of anionic As and cationic Cd with the 540 electronegative surface of biochar. Carefully, the sorption competitiveness of HMs 541 on biochar prepared by different production methods is different. Wan et al. used red 542 cedar sawdust to synthesize magnetic biochar-based adsorbents via three production 543

procedures: (1) pyrolysis before magnetization (PM); (2) pyrolysis after 544 magnetization (MP); (3) pyrolysis before magnetization and again after 545 magnetization (PMP) (Wan et al., 2020b). The removal rates of HMs from multi-546 contaminated soil slurry in the order of: PMP treatment: Pb (32%) >As (28%) >Cd 547 (25%); PM treatment: Pb (24%) > As (23%) > Cd (16.9%); MP treatment: Cd (23%) > 548 Pb (15.1%) > As (4.7%). Biochar-based materials basically had a better 549 immobilization for Pb than Cd in soil due to the smaller hydration radius of Pb (Lu 550 et al., 2018; Xia et al., 2019). 551

552 **4.1.6. Effects of microbial communities** 

Biochar-based materials can influence HM behavior by some indirect effects 553 such as changing microbial activities in soil (Song et al., 2021; Zhao et al., 2020). 554 555 Biochar could stimulate the activity of metal-reducing bacteria to accelerate arsenic mobility, and Geobacter might lead to the reduction of As(V) in the presence of 556 biochar (Qiao et al., 2018). Similarly, biochar application can also affect Cr 557 558 immobilization and bioavailability by stimulating electron transfer of Geobacter (Xu et al., 2019b) and Shewanella (Liu et al., 2021) to induce Fe-plaque formation and 559 Fe dissimilatory reduction for Cr segregation or reduction. The addition of N 560 fertilizers combined with biochar almost halved soil available Cd and greatly 561 increased nitrification through boosting ammonia-oxidizing bacteria recovery in 562 biochemical processes, and available Cd continuously decreased under this 563 expedient feedback mechanism (Fig. 5c) (Zhao et al., 2020). Overall, adding biochar 564 can stimulate microorganism metabolism, and mediating ambient environment 565

mineralization or translate electrons to immobilize HMs. On the other hand, biochar 566 can directly immobilize HMs and protect microorganisms from pressure, which is a 567 568 pleasant feedback (Zhao et al., 2020). However, the relative process is so complex and poorly determined. Current studies mainly focus on raw biochar, while the 569 570 interaction between modified biochar-based materials and microorganisms and their impact on HM remediation and the mechanisms, as well as when inputting other 571 nutrients such as N and P fertilizers and at different soil oxygen conditions, also need 572 to be comprehensively discussed. 573

574

# 4.1.7. Amendment of contaminated sites

The remediation of HM contaminated soil by biochar-based materials is diverse. 575 Biochar with more polar groups, had high capability to decrease the 576 phytoavailability of HMs (Zhang et al., 2016), and inhibit the biotoxicity and uptake 577 of Cd (Qiao et al., 2017), Cu<sup>2+</sup> and CuO NPs (Sima et al., 2017) by plant cells. And 578 improve the stability of microbial communities under HM pressure in soil (Li et al., 579 580 2018b) by reducing available HMs and supplementing available carbon, minerals and habitat (Igalavithana et al., 2019). In field trials, some other techniques may be 581 needed later to regenerate the contaminated sites or field soil. Shen' group conducted 582 a long-term field remediation in Castleford, UK by applying hardwood biochar to a 583 contaminated site (Shen et al., 2016). It reduced the carbonic acid-extractable Ni(II) 584 and Zn(II) by 83-98%, and decreased the leachabilities of HMs over three years, but 585 586 grass on the site still failed to germinate.

587 Various biochar-based materials and their immobilization performance for HMs

in soil and the remediation mechanisms are presented in Table 2. Types of biochar-588 based materials have been adopted for the remediation of HM contaminated soils 589 and achieved certain effects. The modification of biochar using nutrients may have a 590 dual effect, i.e., stabilize HMs effectively and improve soil properties. Furthermore, 591 biochar incorporating with mineral materials may also have synergies on the 592 bioavailability, transformation and accumulation of HMs in soil. However, most of 593 the research have been done under short-term incubation conditions in laboratory, 594 the results of field trials may vary greatly as the complexity of soil. The long-term 595 stability of immobilized HMs remains unclear and it demands to verify the 596 practicality of biochar-based materials in soil amendment. Other issues are the 597 impacts of microorganisms, planted plants or natural conditions (e.g. weathering, 598 599 surface runoff, migration, acid rain) on HM remediation under actual conditions also require added studies to explore. 600

Feedstock of biochar	Modification/A ssistant method	Production conditions	Soil environment	Incubation conditions	HMs	Soil remediation effects	Mechanisms	Ref.
Lincomycin mycelial fermentation residue	CO <sub>2</sub> -activation	700°C, 2 h	Artificial Pb contaminated soil	4 weeks, pH 2.88 ± 0.05	Pb (1250 mg/kg)	The highest Pb immobilization rate was 60%	Precipitation	(Liu et al., 2018d)
Corncob	MgO-coated modification by MgCl <sub>2</sub>	600°C, 1 h	Pb contaminated soil washing residue	28 days, pH 9.14	Pb (3410 mg/kg)	A reduction in leachable Pb from 10.63 to 5.24 mg/L (reduced by 50.71%)	Cation- $\pi$ interaction, surface adsorption, precipitation	(Shen et al., 2019)
Rice husk	KOH- activation	300°C, 1 h	Soil washing residue from a contaminated site in Guangzhou, China	21 days, pH 9.19 ± 0.02	Pb (3952.71 ± 72.74 mg/kg), Cd (136.77 ± 3.48 mg/kg)	The metal concentrations in TCLP leachates decreased significantly, Cd and Pb immobilization was a gradually developed process	Surface complexation between oxygen-containing FGs (hydroxyl, carbonyl and ester) and metals, and a shift in metal fractions from mobile forms to immobile forms	(Wang et al., 2020b)
Pinewood sawdust	A one-pot lime- assisted hydrothermal synthesis approach	220°C, 4 h	Artificial Pb- and Cd-contaminated soil	2 weeks	Pb (1000 mg/kg), Cd (5 mg/kg)	The leaching toxicity of Pb and Cd and the acid-soluble Pb and Cd decreased by 34.5% and 8.1%, 54.0% and 27.0%, respectively	Surface complexation, precipitation and cation-π interaction	(Xia et al., 2019)
Rice straw	Thiol- modification	500°C, 5 h	Surface layer (0–20 cm) soil from a contaminated vegetable field	28 days, pH 7.42	Cd (9.18 mg/kg), Pb (1182 mg/kg)	Reduced the available Cd and Pb by 34.8–39.2 % and 8.6 %– 11.1 %, respectively	The thiol groups on biochar form complexes with metals	(Fan et al., 2020)
Bamboo	Mixed with hydrothermally treated coal	550°C	An agriculture field soil at depths of 0– 20 cm near a coal mining area	45 days, pH 6.23 ± 0.19	Cd (4.80 ± 0.56 mg/kg), Cr (18.04 ± 1.97 mg/kg), Pb (25.87 ± 2.28 mg/kg)	Reduced the soil pore-water Cd, Cr, and Pb contents, decreased HM availability by 52–78%, reduced extractable Cd and Pb contents by 80% and 68%, respectively	The hydroxyl, carboxyl, carbonyl, and amide groups on composites immobilize Cd(II), Cr(VI) and Pb(II) by adsorption and forming metal carbonates, phosphates complexation, and precipitates	(Mujta ba Munir et al., 2020b)

Table 2. Summary of various biochar-based materials and their immobilization performance for HMs in soil and the remediation mechanisms

Feedstock of biochar	Modification/A ssistant method	Production conditions	Soil environment	Incubation conditions	HMs	Soil remediation effects	Mechanisms	Ref.
Kenaf bar	Loading nZVI using FeSO4·7H2O	600°C, 2 h	A farmland soil (15– 30 cm) and artificially spiked with CdCl <sub>2</sub> ·2.5H <sub>2</sub> O	240 min, pH 4.50 ± 0.3	Cd (10 mg/kg)	The residual fractions of Cd significantly increased by nearly 45%	Physical-chemisorption, Cd precipitation formed by surface complexation of Cd(II) with iron hydroxides	(Diao et al., 2020)
Corn stalk	Loaded by mixed bacteria of <i>Bacillus</i> <i>subtilis</i> , <i>Bacillus cereus</i> , and <i>Citrobacter</i> sp.	350∘C, 2 h	Artificial U and Cd co-contaminated Sandy-loam	75 days, pH 6.9	Cd (2.5 mg/kg), U (28.9 mg/kg)	Improved soil properties and microbial metabolic activities, the reduction in the DTPA- extractable U and Cd (69.1 % and 58.2 %) was achieved with the 3% amendment	Improved soil properties of increased –OH, –COOH and negative charge for electrostatic interaction with HMs, responsibility of mixed bacteria cells due to their surface FGs for biosorption of HMs	(Qi et al., 2021)
Sodium alginate	Porous magnetic biochar sphere loaded with Fe <sub>3</sub> O <sub>4</sub> and FeCl <sub>2</sub> hydrates nanoparticles	300°C, 2 h	Shale-derived soil samples from a agricultural soil	48 h, pH 5.5	Cd(II) $(2.81 \pm 0.02 \text{ mg/kg})$ , As(V) $(60.23 \pm 0.39 \text{ mg/kg})$	The bioavailable Cd and As(V) decreased from $1.55 \pm 0.08$ to $0.32 \pm 0.04$ mg/kg and $1.26 \pm 0.003$ to $0.85 \pm 0.01$ mg/kg, respectively	Electrostatic interactions between biochar spheres and HMs	(Liu et al., 2020b)
Rice straw	Modification with calcium carbonate and iron oxide	400°C, 2 h	Top layer (0–20 cm) of a paddy field co- contaminated by multiple metals	160 days, pH 4.65	Cd (46.89 μg/g), As (3.01 μg/g)	Decreased the bioavailability of Cd and As, and reduced extractable Cd and As by 23%–64% and 12 %, respectively	Adsorption for As and Cd; cation exchange (for Cd); co-precipitation of Cd with other hydroxide precipitates; the formation of bidentate chelate and ternary surface complexes on the surface of iron oxide	(Wu et al., 2020b)
Wheat straw	Goethite- modification with KOH and Fe(NO <sub>3</sub> ) <sub>3</sub> solution	600°C, 1 h	Soil contaminated by multiple contaminants nearby the local poultry farm	45 days, pH 5.2	As $(67.48 \pm 0.94 \text{ mg/kg})$ , Cd $(1.01 \pm 0.19 \text{ mg/kg})$	Decreased the available Cd and As by 74.1% and 58.7%, respectively	Surface complexation and co- precipitation; –OH group of iron hydroxides interacted with the adsorbed As (H <sub>2</sub> AsO <sup>4–</sup> or HAsO <sub>4</sub> <sup>2–</sup> ) to form an inner-sphere complex (iron hydrogen arsenate hydrate)	(Zhu et al., 2020b)

4.2. Remediation and mechanisms of biochar-based materials for HM
 602 contaminated water

Excess HMs (e.g. Pb, Cd, Cr, Cu, As, Hg, Ni, U) in water is a serious environmental concern in view of the toxic effects of HMs on aquatic ecosystems and human health (Ling et al., 2017). There is an urgent need for technically viable and cost-effective strategy to treat HMs. Many studies have certified that biocharbased materials can decontaminate HMs from water by adsorption with various mechanisms.

### 609 **4.2.1. Selection of feedstocks and modifications**

The selection of biomass feedstocks is vital (Yi et al., 2019). Typically, 610 MgO@N-biochar derived from N-enriched T. angustifolia had plentiful 611 612 exchangeable ions and N-containing FGs (Ling et al., 2017). A large selective and rapid adsorption of Pb<sup>2+</sup> (893 mg g<sup>-1</sup>) within 10 min was obtained through surface 613 adsorption, ion exchange and surface coordination of Pb<sup>2+</sup> with C=O or O=C-O, 614 pyridonic, pyridinic, and pyrrolic N. The N functionalities such as amino, pyrrole, 615 and pyridine groups could intensify the adsorption ability of biochar-based materials 616 (Chen et al., 2018a). Relatively speaking, the amino FGs modified carboxymethyl 617 chitosan coated sewage sludge-biochar exhibited a lower sorption ability for Pb(II) 618  $(210.00 \text{ mg g}^{-1})$  in an equilibrium time of 60 min (Ifthikar et al., 2018). As described 619 above, it evidenced that natural N enrich in biomass is likely more important than 620 introducing N through modification, or the partial role of MgO nanoparticles on 621 MgO@N-biochar in HM adsorption. In this way, it is better to choose feedstocks 622

rich in one or more elements that can self-doping some special components throughthermal treatment, and/or then proceed to further modification.

625 Reasonable use of modifiers is critical for target HM removal. The combination of biochar with phosphate can upgrade biochar performance and lower 626 eutrophication risks of utilizing phosphate materials (Yang et al., 2021), which 627 provides a promising direction for the removal of multiple HM. Biochar-628 orthophosphate composite was used for Pb removal (Gao et al., 2019), wherein the 629 formed potassium metaphosphate and phosphorus devoted clearly to Pb removal by 630 forming Pb-precipitates (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl, Pb<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, and Pb<sub>n/2</sub>(PO<sub>3</sub>)<sub>n</sub>). Phosphate in 631 biochar-based composites could precipitate with many HMs (e.g. Pb, Cu, Cd) (Zhao 632 et al., 2016), and commonly has a selective adsorption for  $Pb^{2+}$ . 633

634

### **4.2.2.** Fabrication conditions

The synthesis procedure of biochar-based materials, such as pyrolysis 635 temperature and auxiliary process, has a nonnegligible impact on its binding ability 636 637 for HMs. Treatment by ball-milling could effectively lower the positive charge of biochar by exposing large numbers of FGs on absorbents (Tang et al., 2021; Xiao et 638 al., 2020). Xiao et al. prepared micro-nano-engineered nitrogenous biochars (MBC) 639 by pyrolyzing cow bone meal at different temperatures (300, 450 and 600°C) for 2 h 640 and engineered with the assistance of ball-milling technique (Xiao et al., 2020). The 641 HM adsorption capacities of MBC were better with increase in pyrolysis temperature, 642 in which MBC600 had the best adsorption capacities for Cd(II) (165.77 mg  $g^{-1}$ ), 643 Cu(II) (287.58 mg  $g^{-1}$ ) and Pb(II) (558.88 mg  $g^{-1}$ ). Surface complexation, cation 644

exchange, chemical precipitation, electrostatic interaction and cation- $\pi$  bonding were 645 regarded as the mechanisms. Higher pyrolysis temperature derived biochar 646 apparently has a better adsorption effect on HMs in water (Park et al., 2019). Whilst 647 with increasing pyrolysis temperature, crop residue-biochar yields declined 648 consistently (Zhang et al., 2020b), as well as a higher aromatic structure and few 649 polar FGs of biochar (Zhou et al., 2016). Modified biochar also perhaps had a 650 presentation of characteristic shortage and distorted structure with the raised 651 pyrolysis temperature (Song et al., 2020b). To sum up, an intelligent synthesis 652 conditions of biochar-based materials and assistive technology should be adopted for 653 different cases. 654

#### 655

### 4.2.3. Physicochemical properties of biochar-based materials

656 Active binding sites is more crucial than microstructure to determine the HM adsorption performance of biochar-based materials (Liang et al., 2017; Tian et al., 657 2020). Bakshi et al. fabricated ZVI-biochar complexes with more binding sites 658 659 through pyrolyzing magnetite suspension treated red oak (RO)/switchgrass (SG) at 900°C (Bakshi et al., 2018). Higher As(V) adsorption capacity (15.58 mg  $g^{-1}$  for 660 ZVI-RO, 7.92 mg g<sup>-1</sup> for ZVI-SG) was obtained contrast to magnetite/RO/SG only 661 and physical mixtures of RO/SG + magnetite (all <1.6 mg g<sup>-1</sup>), and surface 662 adsorption, intraparticle diffusion, reduction of As<sup>5+</sup> to As<sup>3+</sup> and As<sup>3+</sup> was co-663 precipitated with Fe<sup>3+</sup> denoted the major reaction course. Developed microstructure 664 will facilitate the exposure of active sites. However, contemporary research major 665 concerned with the modification of single microstructure or surface chemistry. 666

667 Integration modification of the two features should be priority in future research.

668

# **4.2.4.** Coexistence of multiple HMs

669 To meet practical demand, increasing studies have implemented the application of biochar-based materials in polymetallic systems, and described the remediation 670 behaviors. Magnetic nZVI-biochar had high affinity for multiple HMs, wherein the 671 major removal channels for Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cr<sup>6+</sup> were stronger reduction and 672 complexation, and for  $Cd^{2+}$ ,  $Ni^{2+}$ , and  $Zn^{2+}$  were coprecipitation and complexation 673 (Zhu et al., 2017). The binding strength of HMs was ordered as 674 Cu<sup>2+</sup>>Pb<sup>2+</sup>>Cd<sup>2+</sup>>Ni<sup>2+</sup>>Zn<sup>2+</sup>>Cr<sup>6+</sup> that determined by Langmuir model (Zhu et al., 675 2017). In the study of (Deng et al., 2020a), electrostatic effect and ion exchange 676 between N-containing groups and Cr/Sb contributed to the binary adsorption of 677 678 amino-functionalized hydrochar (NMSH). Whilst the competitive adsorption was attributed to O-containing FGs of NMSH reduced Cr(VI) to Cr (III) rather than 679 Sb(V), and some Cr(VI) at adsorption sites were replaced by Sb(V) at high initial 680 concentration (>80 mg  $L^{-1}$ ). Generally, the dominant removal mechanisms in the 681 reaction system and the innate characteristics of metal ions all affect their removal 682 efficiency and priority. Recently, (Fan et al., 2020) corroborated that thiol-modified 683 rice straw biochar (RS) selectively adsorbed Cd<sup>2+</sup> instead of Pb<sup>2+</sup> in binary-metal 684 systems via surface complexation, attributing to thiol-modification increased the 685 content of thiol groups (more favorable interaction with  $Cd^{2+}$ ) (Fan et al., 2020) on 686 RS but lost carboxyl groups (more favorable to adsorb  $Pb^{2+}$ ) (Tian et al., 2020). In 687 brief, the sorption sites of HMs could be different or overlapped on biochar surface. 688

689 Outcome-oriented modification of biochar-based materials are required for target 690 HMs in polymetallic systems, and the biochar-based materials which could achieve 691 comprehensive removal of multi-HMs are highly recommended.

692

# 4.2.5. Aquatic pH conditions

693 Ambient pH conditions have considerable influence on the adsorption behavior of biochar-based materials for HMs by changing adsorbent surface charge and 694 adsorbate species. H<sub>3</sub>PO<sub>4</sub>-modified jute fiber biochar with abundant acidic groups 695 (phosphonic acid and carboxyl) was used to remove Cr(VI) (>98%) within a wider 696 operating pH range (1-6) (Chen et al., 2020b), which involved adsorption and 697 surface reduction processes (Fig. 6a). While, Cr(VI) removal by KOH-modified 698 biochar was dependent on pH, and the efficiency dropped sharply to below 30% 699 700 when pH>3. pH and charge distribution on biochar played a pivotal part in Cr(VI) adsorption since Cr(VI) exists as anion species (HCrO<sub>4</sub><sup>-</sup> or CrO<sub>4</sub><sup>2-</sup>) (Dong et al., 701 2017; Wang et al., 2020c). In contrast, the removal of Pb(II) (Ifthikar et al., 2018; 702 703 Shen et al., 2021) and Cu(II) (Zhang et al., 2019f) was positively correlated with pH 704 because of the strong electrostatic attraction and hydroxide precipitation between cationic HMs and biochar-based materials at high pH. Thus, proper pH regulation 705 should also be made according to the form of metal ions, and make efforts to 706 develop biochar-based materials with a wide pH operating range for HM removal. 707

Additionally, Zhong et al. clarified that the roles of redox-active moieties (i.e., phenolic–OH, quinoid C=O, and semiquinone-type persistent free radicals (PFRs)) of biochar in promoting As(III) oxidation was strongly pH dependent in water (Fig. dependent As(III) oxidation by rice husk-derived biochar in water. Reproduced with
permission (Zhong et al., 2019). (c) A proposed mechanism of heterocyclic Ndopants changing PFRs intensity and governing the transformation of Cr(VI).
Reproduced with permission (Zhu et al., 2020a).

722 **4.2.6. Free radicals of biochar-based materials** 

Recently, the effects of free radicals (FRs) in biochar-based materials 723 mentioned above on reactive transformation and removal of redox-sensitive metals 724 (Cr, As, etc.) have also been approved in other studies (Xu et al., 2019c; Zhong et al., 725 726 2018). These studies pointed that biochar-based materials could act as electron donor and shuttle to support redox reaction during sorption process. Typically, Zhu et al. 727 disclosed that the heterocyclic-N within nitrogen-doped biochar (with the N content 728 729 of 1.76%~12.72%) planed modulatory PFRs as redox-sites by forming carboncentered radicals and boosting their concentration by Lewis acid-base interaction, 730 thus further improving the transformation of Cr(VI) into Cr(III) (Fig. 6c) (Zhu et al., 731 2020a). What's more, this sorption-redox process in biochar is more resistant to 732 environmental factors than radicals-chain reaction. Wherein structural characteristics 733 should be considered when interpreting the redox properties of biochar. A larger SSA 734 would expose more redox-active moieties and creating better redox properties (Li et 735 al., 2020a; Ren et al., 2021). The ratio of electron donors to acceptors (Zhou et al., 736 2020a) and peripheral salt ion concentrations (Luo et al., 2020) maybe factors 737 affecting biochar redox properties as well. However, most of studies have merely 738 centered on biochar-based materials as adsorbents to adsorb HMs in water. The roles 739

of their redox-active moieties to HMs and the electron transfer mechanisms involvedduring sorption process need more inquiry.

### 742 **4.2.7. Development of innovative assistive technologies**

The combination of experiment and theoretical calculation will helps to 743 understand mechanisms precisely, so as to determine the contributions of biochar's 744 FGs to formulate exclusively designed biochar's functionalities. In 2018, Chen et al. 745 prepared mesoporous cellulose biochars (MCB) with newly introduced N and 746 increased O content, while CB only had hydroxyl groups (Chen et al., 2018a). The 747 adsorption capacity for Cd(II) of MCB (368.8 mg  $g^{-1}$ ) was about 4 times higher than 748 that of CB. The micro-mechanism analyzed by DFT calculation showed that 749 aromatic and FGs could respectively provide  $\pi$  electrons and lone pair electrons for 750 751 Cd(II) adsorption, and the N-functionality modification showed better than Ofunctionality modification and hydroxyl groups had the weakest binding ability for 752 Cd(II). In 2020, Zhu et al. reported that biochars with more pyrrolic N have better 753 adsorption performance as pyrrolic N contributed dramatically to the increased 754 intensity of PFRs and improved Cr(VI) transformation by DFT calculation results 755 (Zhu et al., 2020a). 756

Understanding molecular-level mechanisms will help to define the reaction pathways between HMs and biochar-based materials, and choose judicious materials in different hydrochemistry. Alam'group combined spectroscopic and surface complexation modeling approach to describe the molecular-scale adsorption of Ni(II) and Zn(II) on five biochars (Alam et al., 2018a). The reactivity of biochars to

762	Ni(II)/Zn(II) directly related to the position densities of biochars, and Ni(II)/Zn(II)
763	adsorption was primarily occurred via proton-active -OH and -COOH groups on
764	biochar surface. Later, this team studied Uranium (U) removal as well and found U
765	adsorption was strongly affected by aqueous U(VI) speciation according to modeling
766	analysis (Alam et al., 2018b). These results disclosed that -OH and -COOH in
767	biochar was the main substances complexing with metals in contaminated water
768	(Alam et al., 2018a; Alam et al., 2018b). Therefore, to enhance the decontamination
769	of HMs, biochar-based materials should be selected case-by-case based on their
770	physiochemical properties. Further investigations want at molecular-level by
771	applying some advanced techniques and innovations to identify whether FGs
772	existing in biochar with low concentration but have high affinity for HM binding.

773 Various biochar-based materials and their adsorption capacities for HMs in water and the removal mechanisms are presented in Table 3. The superior biochar-774 based materials, have a large pH operating range (2-7) and strong anti-interference 775 ability for purifying HM contaminated water. Thereby suggesting that biochar-based 776 materials may be supposed to treat various real water bodies. Langmuir and pseudo-777 second-order are the suitable models for fitting the HM adsorption process in most 778 circumstances (Table 3), which signifying monolayer homogenously adsorption and 779 the pronounced role of chemical forces (Chen et al., 2018a). It is conflicted to 780 compare the adsorption performance of individual biochar and the mechanism also 781 be distinguishing. In order to be more targeted, the existing forms of HMs and the 782 properties of biochar-based materials should be thought over. The roles of FRs in 783

784	biochar for decontaminating HMs is still incomplete and in-depth studies are needed.
785	Applying theoretical calculations, advanced spectroscopic techniques and modeling
786	innovations will be hot trends to study the remediation behaviors of specific HMs at
787	molecular-level to fabricate smart biochar-based materials. Adsorption is actually a
788	complicated process, however, lacks real field trials and attempts are required in this
789	aspect.

#### 792 **4.3. Column study for HM decontamination**

Column operation namely continuous adsorption is suitable for revealing the 793 794 potential of practical applications. The effects of column systems depending on inlet fluid concentration, bed height, pressure drop and flow rate, etc. (Wan et al., 2020a). 795 796 Fixed bed columns have the advantages of simplicity, large processing capacity and feasible in laboratory scale, being the preferred choice of most researchers. The 797 knowledge of breakthrough curves is the fundamental to design continuous flow 798 systems, which generally be determined experimentally or modeling in terms of 799 800 kinetic behavior and isotherm models (Rosales et al., 2017).

Instead of activated carbon, biochar was supported in packed bed column filters 801 for high strength wastewater treatment (Huggins et al., 2016). In 2019, Wei et al. 802 used 2 g Fe-NN/BFs packed in one fixed-bed column (100 mm length × 12 mm 803 diameter) to remove As(III) and As(V) ( $C_0=275 \ \mu g \ L^{-1}$ ) from As-spiked groundwater, 804 the effective bed volume (BV) was 9.04 mL and flow rate was 2.26 mL min<sup>-1</sup> (Wei 805 et al., 2019b). The results revealed that breakthrough point was set as 10 mg  $L^{-1}$ , the 806 effective treatment volume (ETV) was 350 BV for As(III) and 1350 (BV) for As(V) 807 in the first cycle, and the ETV for As(III) and As(V) were still 270 BV and 1210 BV 808 after five regeneration cycles, respectively. Attractively, the ETV of As(III) and As(V) 809 by tandem two columns were 7.14 times (2500 BV) and 2.15 times (2900 BV) 810 higher than a single column treatment, respectively. Furthermore, it achieved 11,000 811 BV after a month of continuous operation in the treatment of As-spiked natural 812 groundwater (As(V): 25  $\mu$ g L<sup>-1</sup>, As(III): 25  $\mu$ g L<sup>-1</sup>), which suggested that Fe-813

NN/BFs could withstand for long-term removal of As in groundwater (Wei et al., 814 2019b). Dramatically, Zhang et al. successfully ran column leaching experiments 815 under stimulated rainfall events to examine the practical performance of 816 Mg/Fe@LDH-BC in farmland (Zhang et al., 2018). The 3.0% addition of 817 Mg/Fe@LDH-BC into soils could obviously reduce the leaching of HMs and ions 818 simultaneously, with reduction rates of >90, >60, and >40% for HMs,  $NH_4^+-N$ , 819 NO<sub>3</sub><sup>-</sup>-N, respectively. In brief, biochar-based materials have proved practical 820 application potential for HM retention based on its exceptional performance in 821 column studies in water or soil systems. Note, yet, structural stability is an ideal 822 characteristic for adsorbent materials in column processes, especially in prolonged 823 use (Wei et al., 2019b). 824

825 Particularly, stormwater columns amended with wood waste biochar and food waste compost removed more than 50-70% of influent metals, and the co-existing 826 kaolinite enhanced metal removal by biochar owing to its abundant active sites (Sun 827 et al., 2020). Ashoori's group aged the biochar-woodchip amended columns for 8 828 months, and continuous exposure to synthetic stormwater which containing trace 829 organic contaminant and HMs for 5 months (Ashoori et al., 2019). It was observed 830 that the removal efficiencies were >80% for Cu, Ni, Pb and Cd, and for Zn was 831 about 50% in column treatment. These results further suggested that biochar-based 832 materials are expected to be desirable and recalcitrant in field-scale bioretention 833 834 systems to remove HM contaminants.

835

## **5.** Evaluations of practical application

The potential of biochar-based materials in the remediation of HM 836 contaminated environment has triggered wide interests. Up to now, published 837 reviews have focused on the application benefits of biochar, while little attention has 838 been paid to assessing its practical application. For the sake of applying biochar-839 based materials more correctly, their recovery and regeneration performance, cost-840 effectiveness, aging and disintegration, and toxicological effects should be evaluated 841 prior to put into large-scale application. This chapter will summarize the above four 842 843 aspects.

844 **5.1. Recovery and regeneration** 

From any practicability point of view, it is indispensable to evaluate the 845 846 recovery and regeneration performance of materials (Imran et al., 2020). Many engineered biochars with high HM decontamination performance were doped with 847 magnetic materials, which allowed their readily separation and recovery by external 848 magnetic fields in practical application. Noteworthily, when biochar are applied in 849 soil system, biochar particles can be packed into porous sponges, filter papers or 850 other large-volume carriers to facilitate the separation, recovery and regeneration 851 (Cui et al., 2019). 852

The choice of desorbent and its concentration is vastly critical for regeneration. Desorption can be fulfilled by proton exchange using inorganic acid (e.g. HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) (Karunanayake et al., 2018; Kołodyńska et al., 2017) and organic acid (e.g. CH<sub>3</sub>COOH and citric acid) (Ling et al., 2017), by precipitation using alkali

(e.g. NaOH, ) (Deng et al., 2020b), by chelation (e.g. EDTA) (Zhang et al., 2019d; 857 Zhang et al., 2019e), by ion exchange (e.g. NaCl, CaCl<sub>2</sub>, and KH<sub>2</sub>PO<sub>4</sub>) (Jung et al., 858 2019; Wan et al., 2020a) or even by physical washing using water (Zhu et al., 2017). 859 Compared to HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>, HCl had a better desorption effect on bivalent metal 860 861 ions, which presumably because the smaller ionic size of Cl<sup>-</sup> is more competitive than NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (Alqadami et al., 2018). Prudently, nitrogen FGs of regenerated 862 biochars may be destroyed under alkaline conditions, leading to a sharp decrease in 863 nitrogen content (Liang et al., 2020). 864

Systematically study of selecting a benign regenerant should be conducted to 865 enhance the regeneration ability/stability of biochar-based materials. Ideally, the 866 biochar-based material components and loaded HMs do not react irreversibly with 867 868 selected eluent. Jung et al. collected and soaked Cu(II)-loaded hydroxyapatite/biochar in 40 mL pH 2.0 HCl solution and 0.1M KH<sub>2</sub>PO<sub>4</sub> solution 869 (Jung et al., 2019). They found that Cu(II) removal decreased from 99.79% to 24.06% 870 after 1 cycle that desorption by HCl, while still exhibited >88% Cu(II) removal after 871 3 cycle that desorption by KH<sub>2</sub>PO<sub>4</sub>. It is possibly that hydroxyapatite dissolved in 872 strong acidic solution and caused obvious destruction of material structure, yet 0.1M 873 KH<sub>2</sub>PO<sub>4</sub> is an ideal eluent (Jung et al., 2019). It should be pointed out that H<sub>2</sub>SO<sub>4</sub> 874 may be unadaptable as an eluent for Pb<sup>2+</sup> account to the low solubility of lead 875 sulphate (Kołodyńska et al., 2017; Zhang et al., 2019d). 876

877 Research have certified that biochar-based materials have delightful recovery 878 and regeneration performance (Table 3). Briefly, an optimal eluent is one that

desorbs HMs completely without any damage to the structure and functionality of adsorbent. It also preferably homologous to material properties that eluent can reinforce these properties (e.g. exchangeable ions, FGs and charge) for HM purification. The best is to allow the recovery and reuse of materials and HMs simultaneously. The fabrication of biochar-based materials with robust structural stability ought to be done as well.

885 **5.2. Cost-benefit analysis** 

Cost-benefit analysis of biochar-based materials should be carried out before 886 887 making the final recommendations for practical applications (Zhang et al., 2021). In comparison to other carbon materials, biochar has the preponderance of cheap and 888 widespread feedstocks, facile production procedure and no other energy 889 890 consumption during application. Great stability and reusability can also lower its commercial application costs to a certain extent. Furthermore, biochar-based 891 materials have abundant binding sites for HMs after engineering changes, but the 892 cost of used chemical modifiers needs attention. Certainly, the alternatives of 893 minerals/chemicals-containing waste liquor/matters to chemical modifiers to modify 894 raw biochar will become popular. 895

There is witness that biochar, if engineered unerringly for HM remediation task, could be at least as effective as activated carbon with a lower cost (Alhashimi and Aktas, 2017; Ashoori et al., 2019). In a study, biochar offered better HM treatment data for high-strength wastewater than activated carbon and coupled with additional lifecycle benefits (Huggins et al., 2016). As a reference, Wei et al. synthesized Fe-

901 NN/BFs with high efficiency for As removal in long-term application. This 902 engineered biochar costs approximately US\$  $5.14 \times 10^{3}$ /t, which much lower than 903 activated carbon (US\$  $7.5 \times 10^{4}$ /t) and multi-walled carbon nanotubes (US\$  $7.5 \times$ 904  $10^{4}$ /t) (Wei et al., 2019b). While, note that the production of biochar on small-scale 905 units and transport charges may decline the benefits: cost ratio (Sohail et al., 2020).

Generally speaking, biochar-based materials have relatively high environmental and economic benefits for the practical remediation of HM contaminated environment. It is recommended that in future studies, empirical formulas between the costs of raw material preparation–production–transport–regeneration–posttreatment of used biochar-based materials should be established through repeated tests to quantify their cost-benefits.

#### 912

#### **5.3.** Effects of aging and disintegration

In practical applications, biochar-based materials are susceptible to aging and disintegration ascribe to natural conditions (e.g. acid rain, surface runoff, weathering) and microbial activity. The characteristic alterations of biochar-based materials along with the change of environment, which leads to changes in the stability and timeliness of HM immobilization. Therefore, the effects of aging and disintegration of biochar-based materials on HM remediation in long-duration practical application should be considered.

920 The aging of biochar-based materials has both positive and negative effects. 921 Current researches mostly using chemical reagents (H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> or NaOH) 922 to simulate aging treatments under lab-scale and suggested an increase in

surface oxygen-containing FGs, expansion of SSA, and much more developed 923 mesopores of aged biochars (Liu et al., 2020c; Wang et al., 2019c). Oxidative ageing 924 925 of biochar/hydrochar could also alleviate the competitive adsorption of HMs (Liu et al., 2020c). Intriguingly, a study declared that soil minerals could relieve the surface 926 aging of biochar (Yang et al., 2016a), so there have to execute more field trials to 927 appraise the effects of actual aging. Aging of biochar-based materials may also 928 substantially elevate their mobility underground (Wang et al., 2019c) and reverse the 929 sorption capacity, but biochar derived organic matter have a positive effect on 930 sorption (Mia et al., 2017). Attractively, an acidic soil amended by wood chip 931 biochar showed obviously fortified Cu and Cd adsorption after 15 months of aging 932 (Rechberger et al., 2019). It attributed to the formation of organic FGs on aged 933 934 biochar and increasingly Cu adsorbed to biochar organic phase (9.2% to 40.7%). However, it predicted that the adsorption ability for HMs in biochar amended soils 935 would drop to the level of untreated soil after 2.5 years of aging (Ren et al., 2018), 936 and immobilized HMs are likely to release back into environment in long-period 937 aging (Qian et al., 2019). Meanwhile, the effects of biological aging of biochar-based 938 materials induced by environmental biomes on HM remediation, and whether the 939 tiny environmental impurities will fill the pores of biochar during natural aging, 940 remains to be future verified. 941

942 Unlike bio-chemical aging, the physical disintegration of biochar-based 943 materials under prolonged application is always be neglected. The disintegration of 944 biochar-based materials switches them to microscale and nanoscale fragments,

therefore being more likely to dissolve, aggregate and move (Liu et al., 2018a; Shen 945 et al., 2020). This consequence may be the principal reason for the deterioration of 946 947 remediation performance, and will cause adsorbed HMs to be released back into environment. As the non-degradability of HMs, it is inevitable to manufacture 948 designed biochar with anti-disintegration properties. Luckily, biochar was easy to 949 form a more crystal structure and recalcitrant constitutions to prevent disintegration 950 at higher pyrolysis temperature and a excellent HM adsorption performance 951 simultaneously (Zhang et al., 2020b). 952

#### 953 **5.4. Environmental risks: Dust, HMs, PAHs, Free radicals**

While seeing the unlimited potential of biochar-based materials in HM remediation, we cannot ignore some environmental risks it may poses. The pollution originated from biochar application, such as HMs, PAHs and FRs in biochar matrix, and the flotage of ultrafine biochar dust may accelerate the environmental risks. An assessment of the risk levels of these contaminants in biochar-based materials is essential before practical application.

With different feedstock, pyrolysis temperature and modification, the asprepared biochar-based materials generally have different environmental risk levels. The typical contaminants in biochar are HMs and PAHs. The contents and leaching risks of HMs in biochar derived from HM contaminated feedstocks or biochar-based materials modified with metallic-materials should be guaranteed within safe limits. It was reported that total Cr, Pb, Ni and Cd contents in swine manure biochars were within safe levels, while Zn and Cu contents were exceeded the limitations

967	recommended by the International Biochar Initiative (416 and 143 mg $kg^{-1}$ for Zn
968	and Cu, respectively) (Xu et al., 2019d), and the same trend of HM leaching
969	occurred in cow manure biochar as comparison with the Environmental Protection
970	Agency (EPA.U.S.) thresholds (Zhang et al., 2020a). Delightfully, the leaching
971	concentrations of Cd from the low temperature (400°C)-phytoremediation residue
972	biochars were $0\sim0.3593$ mg L <sup>-1</sup> , which were lower than the US EPA threshold (0.5
973	mg $L^{-1}$ ) and there were not detectable in high temperature (>500 °C)-biochars (Zhang
974	et al., 2020c). PAHs have chronic toxicity (Mayer et al., 2016), were formed during
975	pyrolysis of plant-based biomass. Along with aging conditions and types of biochar,
976	the content of PAHs would vary and in most cases that a decrease in total PAHs
977	content (Oleszczuk and Koltowski, 2018). Although biochar-based materials has
978	strong adsorption potential for PAHs (Mayer et al., 2016; Sigmund et al., 2017),
979	there is a lack of investigation on the exposure of desorbed PAHs from biochar-based
980	materials after long-term environmental aging. FRs generated in biochar production
981	have also been concerned recently. FRs could promote the formation of reactive
982	oxygen species (Luo et al., 2021a; Yang et al., 2020b; Yang et al., 2020d), thereby
983	irritating organisms to undergo oxidative reactions. Apart from the vigorous role on
984	HM immobilization (Zhong et al., 2019; Zhu et al., 2020a), several studies have
985	shown that FRs have toxic effects on organisms (Lieke et al., 2018; Liu et al., 2018c;
986	Wang et al., 2021). The persistence and composition of these FRs and their risks to
987	environment desire thorough research.

Biochar-induced dust emissions and its hidden toxicity are emerging

environmental worry (Gelardi et al., 2019). As noted above, biochar may contain 989 substances that are toxic to organisms, while dust could exacerbate the transmission 990 991 risks of these substances in environment. A study has elucidated that the particulate nature and size distribution of biochar were associated with cytotoxic effects, and 992 dust formed during production and field applications of biochar probably pose a 993 health risk (Sigmund et al., 2017). It is necessary to consider the unrealized exposure 994 of relevant workers to dust, and suggests to take safety precautions when biochar-995 based materials for environmental HM remediation. 996

997 At present, although it is impossible to develop clean biochar-based materials that do not contain any hazardous substances, some measures can be taken to reduce 998 their potential risks. For instance, choosing appropriate raw materials and/or 999 1000 pyrolysis temperatures can abatement the amounts of PAHs, labile HMs, and FRs in biochar matrix (Huang et al., 2019; Jin et al., 2016; Stefaniuk et al., 2016). Huang et 1001 al. showed that with the decreased contents of metals and phenolic compounds in 1002 1003 feedstocks, PFRs amounts in obtained biochar decreased sharply (Huang et al., 2019). There was evidence that the bioavailability of HMs and PAHs in biochar 1004 significantly decreased when pyrolysis temperature was above 600°C (Jin et al., 1005 2016; Zhang et al., 2019a). But another study claimed that increasing pyrolysis 1006 temperature, the contents of PAHs and HMs (Cd, Cr, Cu, Pb, Mn) and the toxicity 1007 level in biogas solid residue derived biochar increased (Stefaniuk et al., 2016). This 1008 contradictory implied that the relevant study is still in its infancy, which deserve 1009 unremitting experiments to construct biochar with low environmental risks. 1010

1011 Additionally, co-pyrolysis of HMs-containing feedstocks (e.g. sludge, animal wastes, 1012 hyperaccumulator) with clean feedstocks (e.g. plant-based biomass) or chemicals 1013 (e.g. phosphate, alkali, chlorinating agents) can stabilize the unstable HMs of 1014 feedstocks onto biochar matrix (Devi et al., 2020; Xia et al., 2020; Xu et al., 2019d). 1015 This co-pyrolysis can also enhance the ability of biochar-based materials to 1016 immobilize environmental HMs.

1017

# **6. Conclusions and perspectives**

Overall, this review highlighted the utilization and desirable potential of biochar-1018 1019 based materials for the remediation of HM contaminated environment, and pointed out the feasibility of practical application. This remediation mission is directly (i.e., 1020 biochar-based materials interact with HMs) and indirectly (i.e., biochar-based 1021 1022 materials through amending the ambient environment to affect HMs) acted by biochar-based materials in the complex and changeable environmental system. In 1023 addition, spent biochar-based materials can be recovered and regenerated by selecting 1024 suitable eluents, which possess certain economic benefits. Whilst the effects of aging 1025 disintegration of biochar-based materials in long-range environmental 1026 and applications, as well as their potential environmental risks demand full-scale 1027 exploration. In short, the remediation of HM contaminated environment by biochar-1028 based materials will further develop to close in the practicality in near future. 1029

1030 HM remediation performance is directly related to biochar feedstocks, 1031 production conditions, modification methods, target HMs and environmental 1032 conditions. Some refractory bio-wastes with hetero-element enrichment will indeed be

preferred feedstocks in future research. Certainly, proper modification strategies on 1033 pristine biochar will greatly improve the HM remediation performance. Moreover, 1034 adopting advanced analysis techniques for analyzing the physicochemical properties 1035 of biochar-based materials before and after applications and further discussed couple 1036 with theoretical calculation will helpful to reveal the underlying remediation 1037 mechanisms. Even though there have been vast related studies in this field, several 1038 improvements and potential research directions can be proposed from the rapidly 1039 updated research data. As follows: 1040

(1) Choosing feedstocks rich in some specific endogenous components to prepare
self-doped biochar for target HM remediation. Furthermore, carbonization
technologies integrate with other technologies (e.g. ultrasonic assisted, ball
milling and microwave assisted) to form hybrid systems to fabricate efficient
engineered biochar.

(2) Utilizing optimal modification to develop designed biochar for target HMs. Insitu modification by co-pyrolysis of multiple feedstocks, functionalization by
inexpensive natural polymers, mineral impregnation modification of hydrochar,
combined modification of microstructure and surface chemicals rather than
individually, or hybrid organic-inorganic natural biochar composites that
prepared by combining polybasic modifications, are directions that worth
considering.

1053 (3) The integrated roles of redox-active moieties such as FRs in biochar-based
 1054 materials on HMs and the electron transfer mechanisms involved, as well as the

1055 influence factors on these moieties in HM immobilization are encouraged to1056 deeply study.

(4) It is necessary to investigate the interaction between biochar-based materials and
environmental minerals after it is applied to the real environment, whether a
biofilm will form on the surface of materials after a period of aging, and whether
these changes have a positive or negative effect on the alleviation of
environmental HMs.

1062 (5) Biological-modified biochar has great environmental benefits for the
1063 remediation of HM contaminated environment. To stabilize the composite
1064 technology of microbial-biochar and realize standardized production in large1065 scale, which will be beneficial to promote the practical applications.

1066 (6) To research HM remediation by well-designed biochar-based materials under
1067 actual operating conditions such as bioreactors, tertiary water treatment and field
1068 environment, and evaluate the long-term stability of immobilized/adsorbed
1069 metals.

1070 From a practical application perspective, biochar-based materials should be 1071 economically feasible and environmentally sound. After remediation, it is of great 1072 significance for the recovery and reutilization of biochar-based materials and 1073 adsorbed metals. The trace hazardous substances contained in biochar-based 1074 materials can be effectively controlled or reduced through administrating the raw 1075 materials and production conditions. It is needed to develop relevant detection 1076 technologies and formulate normative regulations to prevent environmental pollution

1077 caused by the extensive application of unqualified biochar. Of course, structural
1078 stability of biochar-based materials is a fundamental characteristic for playing its
1079 subsequent remediation role. To achieve practical application, here are some
1080 perspectives:

(1) To develop a technology to regularly recover the spent biochar-based materials
 in environment, and select eluents that can provide biochar with some ions, FGs
 and improved charges that are conducive to HM decontamination. Besides, non renewable spent biochar can use for energy production to elevate the economic
 performance.

1086 (2) Although iron/phosphorus-modified biochars are relatively effective
 amendments for HM contaminated environment, applying such biochar-based
 materials requires further risk assessments about the numerous iron/phosphorus
 in environment.

1090 (3) To explore adaptable decoration methods/techniques for producing engineered1091 biochar with high mechanical strength and resistant to physical disintegration.

1092 (4) Pilot-scale tests are needed to verify the release and toxicity of hazardous
1093 substances from biochar-based materials and the toxic effects of biochar-induced
1094 dust.

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