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Algae, biochar and bacteria for acid mine drainage (AMD) remediation: A review

Tianhao Du, Anna Bogush, Ondřej Mašek, Saul Purton, Luiza C. Campos



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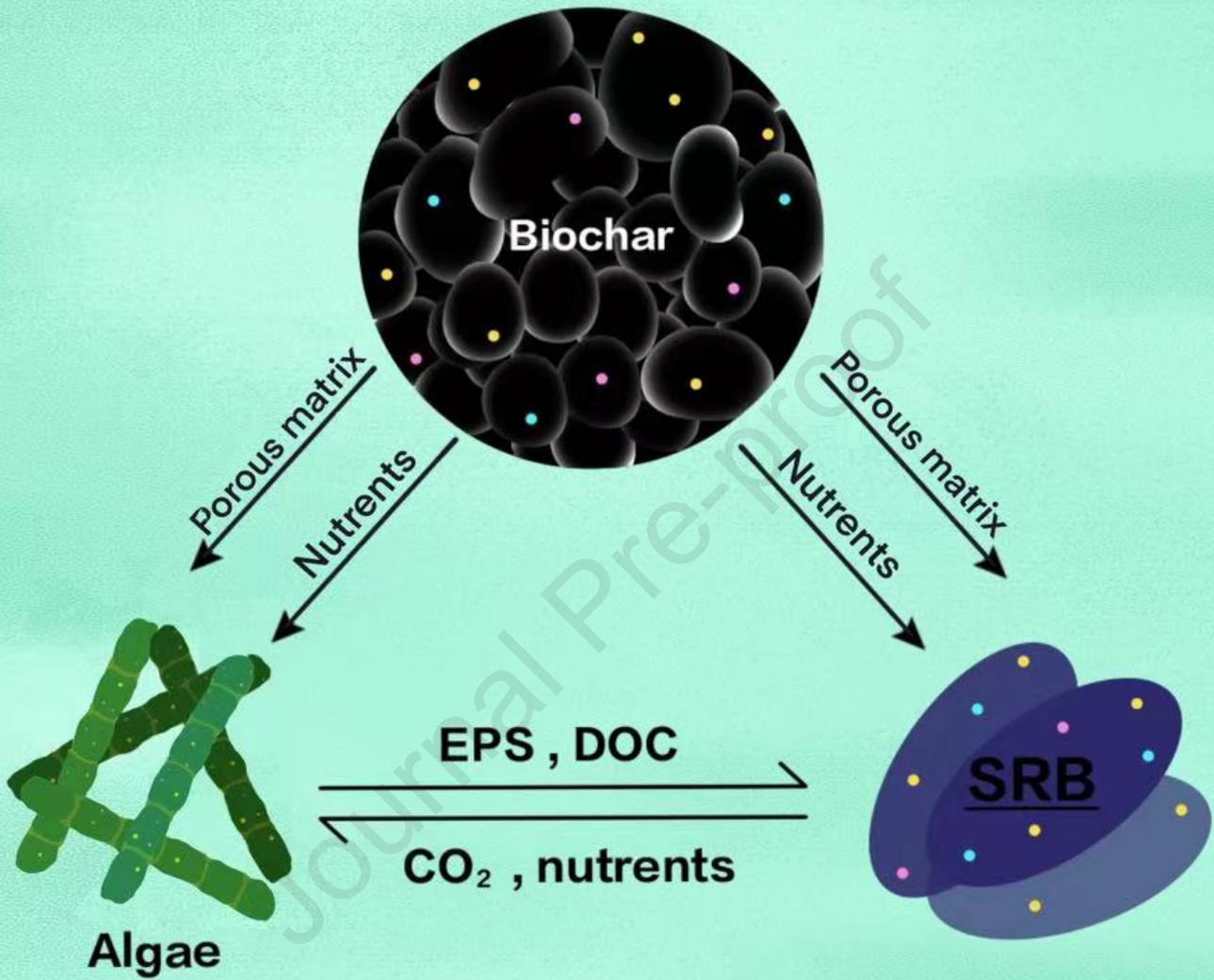
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Author contributions

Tianhao Du: Investigation, methodology, writing - original draft, visualisation. **Anna Bogush:** Conceptualisation, supervision, writing - review & editing. **Ondřej Mašek:** Conceptualisation, writing - review & editing. **Saul Purton:** Conceptualisation, supervision, writing - review & editing. **Luiza C. Campos:** Conceptualisation, supervision, project administration, writing - review & editing.



Acid mine drainage

1 **Algae, biochar and bacteria for Acid Mine Drainage (AMD)**
2 **remediation: a review**

3

4 Tianhao Du ^a, Anna Bogush ^b, Ondřej Mašek ^c, Saul Purton ^d, Luiza C. Campos ^{a*}

5

6 ^a Department of Civil, Environmental & Geomatic Engineering, Faculty of Engineering,
7 University College London, London, WC1E 6BT, United Kingdom

8 ^b Centre for Agroecology, Water and Resilience, Coventry University, Coventry, CV8
9 3LG, United Kingdom

10 ^c UK Biochar Research Centre, School of Geoscience, The University of Edinburgh,
11 Edinburgh, EH8 9YL, United Kingdom

12 ^d Department of Structural and Molecular Biology, Division of Bioscience, University
13 College London, London, WC1E 6BT, United Kingdom

14

15 * Corresponding author: Luiza C. Campos; Email: l.campos@ucl.ac.uk

16

17 **Abstract**

18 Acid mine drainage (AMD) is a global issue and causes harmful environmental
19 impacts. AMD has high acidity and contains a high concentration of heavy
20 metals and metalloids, making it toxic to plants, animals, and humans.
21 Traditional treatments for AMD have been widely used for a long time.
22 Nevertheless, some limitations, such as low efficacy and secondary
23 contamination, have led them to be replaced by other methods such as the bio-
24 based AMD treatments. This study reviewed three bio-based treatment
25 methods using algae, biochar, and bacteria that can be used separately and
26 potentially in combination for effective and sustainable AMD treatment to
27 identify the removal mechanisms and essential parameters affecting AMD
28 treatment. All bio-based methods, when applied as a single process and in
29 combination (e.g. algae-biochar and algae-bacteria), were identified as
30 effective treatments for AMD. Also, all these bio-based methods were found to
31 be affected by some parameters (e.g. pH, temperature, biomass concentration
32 and initial metal concentration) when removing heavy metals from AMDs.
33 However, we did not identify any research focusing on the combination of
34 algae-biochar-bacteria as a consortium for AMD treatment. Therefore, due to
35 the excellent performance in AMD treatment of algae, biochar and bacteria and
36 the potential synergism among them, this review provides new insight and

37 discusses the feasibility of the combination of algae-biochar-bacteria for AMD
38 treatment.

39

40 **Keywords: Acid mine drainage, treatment, sulfate reducing bacteria,**
41 **bioremediation, heavy metal**

42

43 **Abbreviations**

44 AMD Acid mine drainage

45 BET Brunauer-Emmett-Teller

46 EDX Energy Dispersive X-ray Analysis

47 EPS Extracellular Polymeric Substances

48 FTIR Fourier Transform Infrared

49 ROS Reactive Oxygen Species

50 SEM-EDX Scanning Electron Microscopy with Energy Dispersive X-ray

51 Analysis

52 SRB Sulfate reducing bacteria

53 XRD X-ray Diffraction Analysis

54 ZVC Zero-valent copper

55 ZVI Zero-valent iron

56

57 **1. Introduction**

58 Acid mine drainage (AMD) refers to the deposits and tailings generated by mine
59 site exploration. These deposits and tailings can be exposed to the natural
60 environment (water, air and microbial activity) and develop acidic conditions
61 that lead to the leaching of metals and metalloids (e.g. Fe, Al, Zn, Cu, Cd, Pb,
62 Hg, Ni, Co, Cr, As, Sb) (Alpers and Nordstrom, 1997; Bogush et al., 2016;
63 Favas et al., 2016; Hudson-Edwards et al., 2011; Nordstrom, 2011). Generally,
64 AMD comes from two main sources (Akcali and Kucuksezgin, 2011): 1) Primary
65 sources include mine rock dumps, tailing impoundment, underground and
66 open-pit mine works, pumped natural discharged underground water and
67 construction rocks; 2) Secondary sources include treatment sludge ponds, rock
68 cuts, and stockpiles.

69 Acid mine drainage is harmful to humans, animals, plants, and aquatic life
70 (Bogush and Lazareva, 2011; Kumari et al., 2010). For example, AMD causes
71 fish death by affecting the function of the gills, and increased turbidity from soil
72 erosion and precipitation layering on the riverbed can change the habitat for
73 aquatic organisms (Bogush and Lazareva, 2011; Kumari et al., 2010). Some
74 metals produced from the mining industry, such as Cd, Pb, Cu, Zn, Ni and Hg,
75 can accumulate in the human body and cause serious diseases. For example,
76 high levels of Hg in the body can cause Minamata disease, a neurological
77 disease that can cause numbness, muscle weakness, and even death.

78 Elevated Ni levels can cause a dry cough, chest pain, and nausea. High Pb
79 levels in humans can damage the nervous system and cause intellectual
80 disability, and high levels of Zn in the human body can cause vomiting, skin
81 inflammation and fever (Carolin et al., 2017). The biology of plants and aquatic
82 life can also be affected by metal toxicity. Furthermore, these organisms not
83 only act as receptors of the contamination but also as a pathway to humans via
84 food chains (Kumari et al., 2010). Even if the contamination comes from a single
85 point source, the impacts are not restricted to the local area but can also affect
86 distant regions, as water can carry the contamination along rivers or streams
87 (Bogush and Lazareva, 2011; Kumari et al., 2010).

88 The mining industry has played a vital role in the economies of many countries
89 and has supported their development for a long time. The total annual global
90 mineral production between 2013 and 2017 was approximately 17 billion MT
91 (Abinandan et al., 2018). Notably, the USA, China, Russia, Australia, and India
92 are the top five countries in the mining industry (Reichl et al., 2019). For
93 example, in 2017, China and the USA produced 4.1 and 2.0 billion MT of
94 minerals, respectively (Reichl et al., 2019). While the UK is, at present, not on
95 the list of top producers, with no active metal mining industry, it has a rich
96 mining history as the cradle of the industrial revolution, and therefore it has a
97 legacy of old mines with associated AMD still affecting large areas of the
98 country. Some abandoned mining sites in the UK still contribute significantly to

99 heavy metal contamination of rivers and streams (Johnston et al., 2008). For
100 instance, the Parys Mountain copper mine on the Welsh island of Anglesey
101 discharges 24 tonnes of Zn and 10 tonnes of Cu into the Irish sea every year
102 (Johnston et al., 2008). Because of these abandoned mining sites, 315 out of
103 7,816 water bodies in the UK, equating to 2,840 km of rivers, are contaminated
104 or potentially contaminated by AMD (Abinandan et al., 2018; Johnston et al.,
105 2008; Jones et al., 2016).

106 There are several established methods for treating AMD such as precipitation,
107 ion exchange, electrochemical, and membrane separation (Alcolea et al., 2012;
108 Genty et al., 2012; Taylor et al., 2005). For instance, the open limestone
109 channels (OLC) method uses a channel filled with limestone fragments to
110 neutralise and increase the alkalinity of AMD (Alcolea et al., 2012); anoxic
111 limestone drains (ALD) are buried limestone drainage lines with a gentle slope,
112 sealed with a low permeability liner and capped with clay to ensure air cannot
113 flow into the drain during operation (Taylor et al., 2005). These treatments have
114 advantages, including low cost and ease of management. However, they also
115 have certain limitations, for example, the need for a high quantity of limestone
116 and also the generation of a large amount of sludge (secondary contamination),
117 low efficacy, the inability to remove all metals/metalloids, and the need for a
118 relatively large area (Alcolea et al., 2012; Bogush et al., 2016; Dufresne et al.,
119 2015). Therefore, bio-based treatment approaches for AMD should be

120 considered as an attractive alternative due to their higher efficiency, lower
121 secondary contamination and potentially lower costs (I. Kim et al., 2014).

122 Bio-based treatment generally refers to the use of either dead/processed or
123 living biomass to reduce and remove heavy metals from AMD (I. Kim et al.,
124 2014). The common and suitable bio-based materials usually include algae,
125 biochar, and bacteria (Cai et al., 2021; Loreto et al., 2021; Orandi et al., 2012).

126 It is proven that each of these three treatments can remove metals from AMD
127 effectively and are cost-effective. However, the main bottlenecks of these three
128 AMD treatments are the lack of industrial AMD water treatment case studies for
129 algae, the use of rudimentary technologies in biochar recycling and recovery of
130 metals from biochar, and the need for highly effective carbon sources for
131 preparing sulfate reducing bacteria (SRB) immobilising (Almomani and Bhosale,
132 2021; Di et al., 2022; Shirvanimoghaddam et al., 2022).

133 This paper reviews (database: Scopus, Science Direct and Web of Science)
134 the use of algae, biochar, and bacteria separately and in combination for AMD
135 treatment due to their high capacities for metal removal. The paper also
136 discusses the removal mechanisms, parameters affecting metal removal,
137 efficacy, and examples of different treatment applications. The limitations and
138 gaps in existing studies are identified, and the recommendations for future
139 research are outlined.

140

141 **2. Algae application in AMD treatment**

142 A total of 14 studies were reviewed (screened from 1877 initial literature results
143 from 2006 to 2022) that focused on the use of algae for AMD treatment. Most
144 of these studies reported a relatively high removal efficiency, especially two
145 studies with dry biomass (Bansod & Nandkar, 2016; Khoubestani et al., 2015).
146 In terms of metal removal, most studies focused on Cu and Zn. The details of
147 metal removal by algae reported by different authors are summarised in Table
148 1 and discussed in the following sub-sections.

149 Table 1. Algae used for heavy metal removal from AMD.

Algal species	Growth method	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
<i>Klebsormidium</i> sp.	Algae were collected from the mine site and grown in Lab, Photo-rotating biological contactor (PRBC)	Cu 80-100, Mn 35-40, Mg 85-100, Ca 18-2, Ni 2.0-3.0, Zn 18-20, Na 20-25	Removal efficiency is 35%-50% by order Cu>Mn>Mg>Ca>Ni>Zn>Na	Orandi and Lewis (2013)
1. <i>Oedogonium crissum</i>			In all study pH conditions,	
2. <i>Klebsormidium klebsii</i>	Field growth and laboratory experiment	Al 4.8, Fe 79, Mn 51, Zn 550	<i>Oedogonium crassum</i> was considered to have the highest metal bioaccumulation rate	Oberholster et al. (2014)
3. <i>Microspora tumidula</i>				

150

151 Table 1. Algae used for heavy metal removal from AMD. (Continued).

Algal species	Growth method	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
		¹⁾		
<i>Stichococcus bacillaris</i>	Porous Substrate Bioreactor (PSBR)	Zn 2.0-3.0	Zn 15-19 mg g ⁻¹	Li et al. (2015)
<i>Sargassum</i> sp.	Laboratory experiment	Cu 20, Cr 20	Cu 71.4 mg g ⁻¹	Jacinto et al. (2009)
<i>Scenedesmus quadricauda</i>	Laboratory experiment with dry biomass	Cr 100	Cr 58.5 mg g ⁻¹ , Cr 46.5 mg g ⁻¹	Khoubestani et al. (2015)
<i>Chlorella</i> sp.	Stabilisation pond system	Zn and Pb 5.0-20	Zn 34.4 mg g ⁻¹ , Pb 41.8 mg g ⁻¹	Kumar and Goyal (2010)

152

153 Table 1. Algae used for heavy metal removal from AMD. (Continued).

Algal species	Growth method	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
<i>Ulothrix</i> sp.	Photrotating biological contactor (PRBC), algae collected from mine site	Cu 80-100, Ni 2-3, Mn 35-45, Zn 18-20, Sb 0.005-0.007, Se 0.03-0.04, Co 0.3-0.5, Al 0.07-0.09	The metal removal efficiency is 20-50% by order Cu>Ni>Mn>Zn>Sb>Se>Co>Al	Orandi et al. (2012)
<i>Nephroselmis</i> sp.	Pipe Insert Microalgae Reactor (PIMR), AMD pre-treated with active treatment	Fe 20.5 ± 9.8	Fe 24.2 mg g ⁻¹	Park et al. (2013)
<i>Spirogyra verrucosa</i>	Laboratory experiment with dry biomass	Mn 50	Mn 40.7 mg g ⁻¹ (80.2%)	Bansod and Nandkar (2016)

154

155 Table 1. Algae used for heavy metal removal from AMD. (Continued).

Algae species	Growth method	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
<i>Nannochloropsis</i> sp.	Lab-scale growth, modified with silica and followed by coating with magnetite particles	Cu 6.4-64	Cu 56 mg g ⁻¹ (87.5%)	Buhani et al. (2021)
<i>Nannochloropsis oculata</i>	Laboratory growth and experiment	Cu 16	Cu 99.9 ± 0.04% with 89.3 ± 1.92% by metabolism and 5 g/cell for adsorption	Martínez-Macias et al. (2019)

156

157 Table 1. Algae used for heavy metal removal from AMD. (Continued).

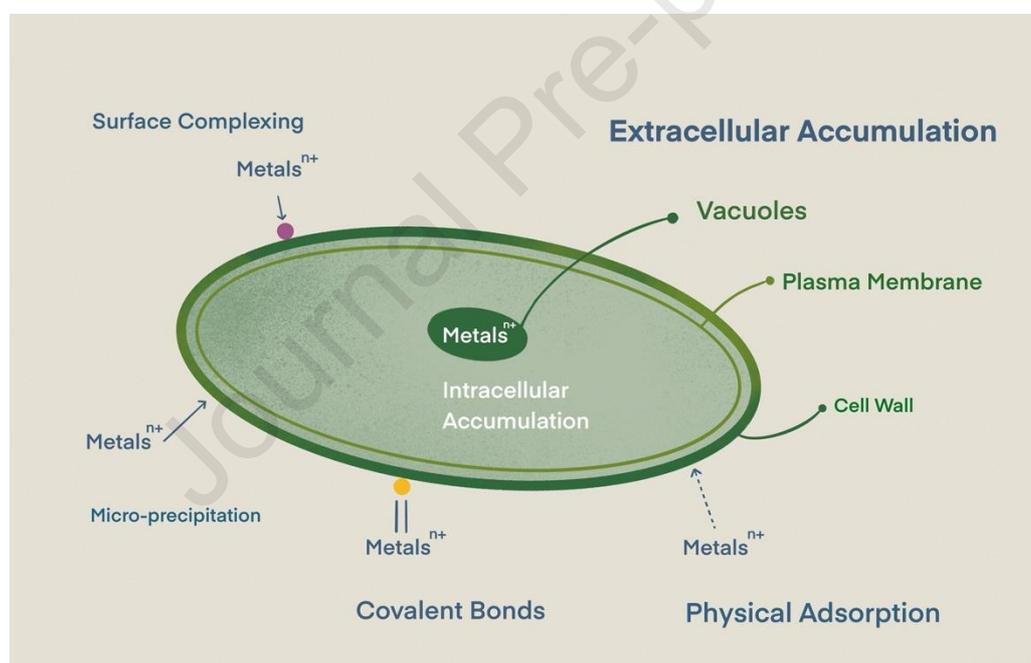
Algae species	Growth method	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
1. <i>Phormidium ambiguum</i>	Algae isolated from River Nile and Ain Helwan Spring & laboratory experiment	Cd, Pb and Hg are all 0.01	<i>P. typicum</i> had the highest removal efficiency of Hg 15.1 mg g ⁻¹ , Cd 5.5 mg g ⁻¹ and Pb 74.5 mg g ⁻¹	Shanab et al. (2012)
2. <i>Pseudochlorococcum typicum</i>				
3. <i>Scenedesmus quadricauda</i> var <i>quadrispina</i>				
<i>Chlorella vulgaris</i>	Lab-scale growth	Fe 788, Al 310, Mn 19.4	Removal efficacy for all metals reached approximate 99.9%	Brar et al. (2022)
1. <i>Spirulina platensis</i>	Lab-scale growth and dried with 100 °C oven	Al, Ni and Cu 2.5-100	<i>S. platensis</i> Ni 95%, Al 87%, Cu 62% <i>C. vulgaris</i> Ni 87%, Al 79.1% Cu 80%	Almomani and Bhosale (2021)
2. <i>Chlorella vulgaris</i>				

158

159 **2.1 Mechanism of metal removal by algae**

160 The process of heavy metal sorption by algae is complex. Generally, two stages
161 are involved (Bwapwa et al., 2017). The first is extracellular sorption, which is
162 rapid and can be assumed to be passive. This happens immediately after algae
163 are in contact with metals and involve the following mechanisms: the interaction
164 between metal ions and anionic cell ligands, micro-precipitation, surface
165 complexing, covalent bonds between metal ions and proteins and other
166 polymers. The second stage is intracellular accumulation. This is slower than
167 the first stage and is assumed to be active. The mechanisms involved are
168 species-specific and include, for example, phytochelation, which forms a metal
169 complex. Figure 1 illustrates some of the mechanisms of metal removal by
170 algae. Heavy metals are incorporated into algal vacuoles and then bonded with
171 proteins, DNA, and lipids. Also, algae cells, especially some resistance cells,
172 can effuse toxic metal complex substances, for example, Cu and Cd (da Costa
173 and de França, 2003; Levy et al., 2008; Worms et al., 2006). In addition, cell
174 walls, nuclei, mitochondria, chloroplasts, and some other parts of the cell may
175 be reinforced by the membrane, which works as a barrier in adapted cells (Chen
176 et al., 2012; Sandau et al., 1996; Tam et al., 1998). In these two stages, some
177 of the metals are taken by the surface, and others may be taken in the inner
178 cell due to metals' type and algae growth preference (Du et al., 2022). Surface
179 adsorption is essential since it represents the largest portion of the absorption

180 process (Chojnacka et al., 2005). Still, the relative importance of surface
 181 adsorption may vary depending on the metals and algae (Du et al., 2022).
 182 Nevertheless, the complexity of the algae surface makes it possible for various
 183 mechanisms to operate simultaneously (Monteiro et al., 2012). Generally, the
 184 ability to remove metals by different algal groups shows a decreasing order of
 185 *Chlorophyta* > *Phaeophyta* > *Rhodophyta* (Al-Shwafi and Rushdi, 2008).
 186 However, knowledge of the distribution of metals in/on the algal cell and the
 187 stage involved in metal removal processes still needs to be explored.



188
 189 Figure 1. The mechanisms of heavy metal removal by algae. Extracellular
 190 accumulation includes surface complexing, micro-precipitation, covalent
 191 bonds, and physical adsorption.

192 **2.2 Parameters that affect removal capacity by algae**

193 *a) pH*

194 In many studies, pH was considered the most critical parameter affecting the sorption
195 of metals by algae. According to Van Hille et al. (1999), a pH over 8 is required to
196 enable the precipitation of metals as hydroxides. If the pH decreases, the removal of
197 Zn is first to be affected, followed by Cu, Pb, and Fe, because different functional
198 groups can precipitate metals at different pH conditions (Chojnacka et al., 2005).
199 Monteiro et al. (2012) suggested an optimal pH range of 4.0–5.0 to remove Cu and
200 Cd and a pH of 2.0 for Co. Similarly, Khoubestani et al. (2015) indicated that the best
201 pH for Cr adsorption is 6.0, while Bansod and Nandkar (2016) reported that the best
202 pH condition for Mn removal is 5.0.

203 The differing optimal pH values for metal removal found in the different studies reflect
204 the different metal chemistry and different functional groups involved in the metal
205 removal process. Each functional group has distinct pH ranges for binding metal
206 cations (Monteiro et al., 2012). Under acidic conditions, a positive charge and
207 protonation will happen for specific functional groups associated with H⁺ because of
208 the repulsive forces (Khoubestani et al., 2015; Monteiro et al., 2012). Thus, some
209 functional groups are only available within a specific pH value. For instance, carboxyl
210 groups dominate at pH 2-5; phosphate becomes the main group at pH 5-9, while when
211 the pH increases to 9 and then up to 12, carboxyl, phosphate, and hydroxyl/amine

212 groups are all available (Bansod and Nandkar, 2016; Monteiro et al., 2012). The
213 general agreement is that at low pH, positively charged algae surfaces are the main
214 contributors to biosorption because the binding sites, surrounded by H⁺, attract metal
215 ions towards the algal surface. However, when the pH increases above 4.0, some
216 divalent metals, e.g. Zn and Cu, readily precipitate as hydroxide, thus reducing
217 biosorption (Bansod and Nandkar, 2016). In most cases, the initial pH of AMD is lower
218 than 4.0. Thus, strategies on how to reduce the negative effects caused by low pH
219 when exploring metal removal by algae should be considered, for example, isolation
220 of superior strains.

221 *b) Initial metal ion concentration*

222 Initial metal ion concentration is another critical parameter that can affect the efficiency
223 of algae in treating AMD. Most studies suggest that metal uptake positively correlates
224 with the initial metal ion concentration (Al-Rub et al., 2004; Monteiro et al., 2012, 2009).
225 This is due to higher initial metals concentration contributing to higher driving force,
226 which can overcome mass transfer resistances of metal ions between biomass and
227 solution and promote uptake (Al-Rub et al., 2004; Cruz et al., 2004). Also, collisions
228 between biomass and metal ions increase under higher metal concentrations,
229 enhancing the metal uptake process (Al-Rub et al., 2004). Monteiro et al. (2011) found
230 that the total Zn removal by *Scenedesmus obliquus* (mg Zn g⁻¹ algae) increased more
231 than ten-fold when the initial Zn concentration was increased from 10 mg L⁻¹ to 75 mg

232 L⁻¹. However, metal absorption is more effective at a lower initial metal concentration.
233 For example, Monteiro et al., (2009) reported that, although *Desmodesmus*
234 *pleiomorphus* adsorbed and totally removed more Zn at the higher initial Zn
235 concentration, it had higher removal efficacy of Zn at a relative lower Zn concentration
236 (1 mg L⁻¹) than higher Zn concentration (5-30 mg L⁻¹). This is because more binding
237 sites are available when the metal concentration is low (Khoubestani et al., 2015;
238 Mehta and Gaur, 2005). Nevertheless, the weakness of the two studies conducted by
239 Monteiro et al. (2011, 2009) is that the Zn concentration set in these studies was
240 relatively low, which cannot fully explain the relationship between initial ion
241 concentration and metal removal especially at high metal concentrations.

242 However, in a study by Bansod and Nandkar (2016) on Mn removal (with Mn
243 concentration of 10 mg L⁻¹ to 100 mg L⁻¹) by *Spirogyra 18errucose*, the total uptake
244 efficiency reached the highest level (40.66 mg g⁻¹) when the Mn concentration was 50
245 mg L⁻¹. When the concentration was over 50 mg L⁻¹, the percentage removal of Mn
246 did not continue to increase. Instead, it remained constant and even slightly decreased,
247 which is different from most of the studies mentioned above. This may be explained
248 by the research from Monteiro et al. (2012), who reported that this increase tends to
249 reach saturation after the threshold.

250 *c) Temperature*

251 Temperature is always considered an important parameter in both physicochemical
252 and biological reactions. However, based on the available literature, the effect of
253 temperature on heavy metal removal by algae is inconclusive. Some studies have
254 shown a positive correlation between heavy metal removal by algae and temperature
255 (Monteiro et al., 2012). Aksu (2002) reported increased Ni²⁺ biosorption by *Chlorella*
256 *vulgaris* with increased temperature from 15 to 45 °C. One reason for this could be
257 that increasing temperature may promote several active sites on algae to participate
258 in the biosorption (Mehta and Gaur, 2005).

259 On the other hand, several studies report a negative correlation between temperature
260 and the ability of algae to absorb heavy metals. For example, the biosorption of Cd²⁺
261 by both *Oedogonium* and *Sargassum* is reported to have a lower sorption efficiency
262 with increased temperature (Cruz et al., 2004; Gupta and Rastogi, 2008). The same
263 result was also reported by Aksu (2001) for Cd removal using *Chlorella vulgaris*. Cd
264 adsorption usually is exothermic, and thus the adsorption decreases with increasing
265 temperature (Aksu, 2001; Cruz et al., 2004).

266 Another group of studies observed almost no effect of temperature change on algae
267 sorption. For example, Cossich et al. (2002) reported that the use of *Sargassum* to
268 remove Cr showed the effect of temperature was not as significant as the effect of pH.
269 Likewise, these relationships between temperature and metal removal were also
270 reported by Mehta and Gaur, (2005). Overall, the general relationship between

271 temperature and metal removal effectiveness by algae is still unclear based on the
272 discussion above. For example, the types of algae and metal may both affect the
273 results. Also, seasonal parameters, such as precipitation and runoff, may cause the
274 initial metal ion concentration and temperature to vary with time in AMD sites (Du et
275 al., 2022). Therefore, a clear relationship between temperature and metal removal
276 efficiency should be investigated for different combinations of metals and algal species,
277 especially in practical AMD conditions.

278 *d) Biomass concentration*

279 Biomass concentration of algae can have significant effects on metal removal. Mehta
280 and Gaur (2005) reviewed several previous studies and indicated that the cell
281 concentration of *Chlorella* sp. negatively correlates with the binding of Cd per unit of
282 mass. Similarly, they reported a decreased sorption capacity per unit of mass of Cu
283 and Ni by increasing the *Chlorella vulgaris* concentration and decreased Pb sorption
284 by increasing *Spirulina maxima*. Monteiro et al. (2012) reviewed some studies and
285 reported this negative correlation. According to the literature, in most conditions, the
286 biomass concentration and metal adsorption capacity negatively correlate per unit
287 mass. The reason for this may be that the increase of biomass can lead to its partial
288 aggregation thus reducing the surface area for adsorption, and the increase of
289 biomass can also decrease the distance between the available adsorption sites
290 (Monteiro et al., 2012).

291 However, increasing biomass concentration may lead to a higher amount of heavy
292 metal removal (Mehta and Gaur, 2005). For example, Tam et al. (1998) reported that
293 Cu concentration in solution decreased with increasing algae cell concentration. The
294 increased metal removal with increasing biomass may be due simply to the increased
295 availability of metal-binding sites caused by increasing biomass amount (Khoubestani
296 et al., 2015).

297 Thus, the general agreement is that increasing biomass concentration can reduce the
298 algae removal capacity per unit mass. While it is possible that a higher biomass
299 concentration may increase the total amount of metal removed, this is not a
300 straightforward relationship (Mehta and Gaur, 2005).

301 **3. Biochar application in AMD treatment**

302 A total of 35 studies were reviewed (screened from 3788 initial literature results from
303 2006 to 2022) which were concerned with biochar treatments for AMD. These studies
304 used biochar with different feedstocks, pyrolysis methods, and modification methods.
305 The studies reported successful removal of heavy metals from AMDs, although with
306 different performances. The details of biochar used for metal removal from AMD
307 reported in different studies are summarised in Table 2 and discussed in the following
308 sub-sections.

309 Table 2. Biochar used for heavy metal removal from AMD.

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Hardwood	450	Cu 256, Zn 260	Cu 6.8 mg g ⁻¹ , Zn 4.5 mg g ⁻¹	Chen et al. (2011)
Corn straw	600	Cu 256, Zn 260	Cu 12.5 mg g ⁻¹ , Zn 11.0 mg g ⁻¹	Chen et al. (2011)
Corn straw	400	Cd 20, Pb 20	Cd 38.9 mg g ⁻¹ , Pb 29.0 mg g ⁻¹	Chi et al. (2017)
Hickory wood	Pre-treated by KMnO ₄ and then 600 °C pyrolysed	Pb 100, Cu 30, Cd 30	Pb 153 mg g ⁻¹ , Cu 34.2 mg g ⁻¹ , Cd 28.1 mg g ⁻¹	H. Wang et al. (2015)
Sugar cane	500	Pb 6.0-223	Pb 87.0 mg g ⁻¹	Abdelhafez and Li (2016)

310

311 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Orange peel	500	Pb 6.0-223	Pb 27.9 mg g ⁻¹	Abdelhafez and Li (2016)
Almond shell	650	Ni and Co 50-200	Ni 22.2 mg g ⁻¹ , Co 28.1 mg g ⁻¹	Kılıç et al. (2013)
Sewage sludge	550	Pb 100-1000	Pb 30.88 ± 0.95 mg g ⁻¹	Lu et al. (2012)
Peanut straw, soybean straw, Canola straw	400	Cu 15-960	Cu 37.12-89.6 mg g ⁻¹ , peanut > soybean > canola	Tong et al. (2011)
White birch, Black spruce	454, followed by KOH, CO ₂ and steam activation	Cu 100	Cu >99%	Braghiroli et al. (2019)

312

313

314

315 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
Papermill sludge	270-720	As 22.7, Cd 33.0	As 22.8 mg g ⁻¹ , Cd 41.6 mg g ⁻¹	Yoon et al. (2017)
Nutshells, Plum stones, Wheat straws, Grape stalks and Grape husks	600	Cd 11.2-168, Pb 20.7-310.5	Over 95% removal efficiency for all four biochar	Trakal et al. (2014)
Pistachio green hull	450	Cu 70-270	Cu 19.8 mg g ⁻¹ (62%)	Jalayeri and Pepe (2019)

316

317 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Olive pomace	Hydrothermal 300, pyrolysis 300 and 600	Cu 20	Cu 77.8%	Pellera et al. (2012)
Lolium perenne, Lolium perenne fibre, Miscanthus x giganteus, Salix viminalis, Fraxinus excelsior, Picea sitchensis	300, 450 and 600 slow-pyrolysis process	Zn 18.5 ± 2.10	Lolium perenne fibre has the best performance removal of Zn 93.0%	Hodgson et al. (2016)
<i>Platanus orientalis</i> Linn leaves	400, modified by H ₂ O ₂ , KMnO ₄ and K ₂ Cr ₂ O ₇	Cd 50	KMnO ₄ modified biochar reached the highest removal efficacy of Cd 54.7 mg g ⁻¹	Yin et al. (2022)

318

319 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Rice straw & Fe ₃ O ₄ & CaCO ₃	400	Cd and As 10-60	Cd 6.34 mg g ⁻¹ , As 10.1 mg g ⁻¹	Wu et al. (2018)
Rice husks	300, 500 and 700	Pb (concentration unknown)	Pb RH300 14.1 mg g ⁻¹ , RH500 21.7 mg g ⁻¹ , RH700 26.7 mg g ⁻¹	Shi et al. (2019)
Jarrah and pine wood chips	700	Cu 17.3-195, Zn 17.6-173	Cu 4.39 mg g ⁻¹ , Zn 2.31 mg g ⁻¹	Jiang et al. (2016)
Oakwood, Oakbark	400 and 450, followed by magnetic activation	Pb and Cd 1.0-100	Pb 100%, Cd 53%-99%	Mohan et al. (2014)

320

321 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Orange peel	400, 500, 600, 700, 800	Cd 100	Cd 115 mg g ⁻¹	Tran et al. (2016)
Sewage sludge	500 (for sewage sludge (Cs)), ZnCl ₂ activated (for sludge-based active carbon (SBAC)), modified by nitric acid at different concentration and temperature (MSBACs)	Pb 100-200	Pb MSBAC 26.6 mg g ⁻¹ , SBAC 17.0 mg g ⁻¹ , CS 4.42 mg g ⁻¹	Li et al. (2019)

322

323 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Dairy manure	350	Cu 0-320, Zn 0-325, Cd 0-560	Cu 54.4 mg g ⁻¹ , Zn 32.8 mg g ⁻¹ , Cd 51.4 mg g ⁻¹	Xu et al. (2013)
Poultry litter	400	Al 51, Cu 30.7, Zn 26.8	Al 100%, Cu 100%, Zn 99%	Oh and Yoon (2013)
Sesame straw	700	Pb, Cu, Cd, Zn and Cr are all 2.5-320	Pb 102 mg g ⁻¹ , Cu 55.0 mg g ⁻¹ , Cd mg g ⁻¹ , Zn 34.0 mg g ⁻¹ , Cr 65 mg g ⁻¹	Park et al. (2016)

324

325 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Rice husks	Hydrothermal 300, pyrolysis 300 and 600	Cu 20.0	Cu 90.1%	Pellera et al. (2012)
Common reed (Phragmites australis)	450	Fe 0.36 and 28.8, Al 0.13 and 10.99, Ni 0.07 and 0.39, Zn 0.03 and 0.19, Mn 0.37 and 5.08	Metal removal by 89.0%–98.0% (Fe≈Al>Ni≈Zn>Mn)	Mosley et al. (2015)
Sludge	300 (nano zero-valent)	Sb 10, 20 and 30	Sb 160.40 mg g ⁻¹	Wei et al. (2020)
Soy sauce residue	400 and modified by nanoscale FeS and chitosan	Cr 100-550	Cr 70.42 mg g ⁻¹ (76.07%)	Yang et al. (2021)

326

327 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
Oakwood, Oak bark, Pinewood Pine bark	400 and 600, fast pyrolysis	Cd, As, and Pb are all 0.01-0.10	Oak bark has the highest removal efficiency Pb 11.4 mg g ⁻¹	Mohan et al. (2007)
Aloe vera shell	700 followed by NiO.5ZnO.5Fe ₂ O ₄ magnetic nanoparticles supported	Ag 100	Ag 98.3% (244 mg g ⁻¹)	Beigzadeh and Moeinpour (2016)

328

329 Table 2. Biochar used for heavy metal removal from AMD. (Continued).

Biochar feedstock	Temperature for biochar production (°C)	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Spent coffee grounds	400	Cd 0.228, Cu 0.194, Pb 0.0156, Zn 0.0222	Cd 99%, Cu 88%, Pb >99%, Zn 99%	M.-S. Kim et al. (2014)
Canna indica	300, 400, 500 and 600	Cd 30-200	Cd 189 mg g ⁻¹	Cui et al. (2016)
Coconut shell	400, MgCl ₂ modification	Pb 1000, Cd 1000	Pb 271.53 mg g ⁻¹ , Cd 91.95 mg g ⁻¹	Wu et al. (2021)
Durian shell, <i>Robinia pseudoacacia</i>	500, Fe/Zn modification	Cd 30-300	Cd Durian shell biochar 99.81%, <i>Robinia pseudoacacia</i> biochar 71.08%	T. Yang et al. (2021)

330

331 **3.1 Heavy metal removal mechanisms**

332 Several mechanisms may be involved in removing heavy metals from
333 contaminated solutions using biochar. As presented in Figure 2, these
334 mechanisms include physical sorption, ion exchange, precipitation,
335 complexation, and electrostatic interaction. Solution pH, zero-point charge of
336 biochar, and temperature are the parameters that may affect this process
337 (Inyang et al., 2016).

338 Surface precipitation between metal ions and mineral components (anions)
339 such as PO_4^{3-} , CO_3^{2-} and OH^- is an essential mechanism in biochar metal
340 removal (Cui et al., 2016). Tran et al. (2016) studied the effects of orange peel
341 biochar on Cd^{2+} removal. They found that Cd^{2+} was removed by surface
342 precipitation, as $(\text{Cd}, \text{Ca})\text{CO}_3$ and Cd_3CO_3 were found by XRD after the
343 experiments. Also, the EDX results showed that Ca remained on the surface of
344 biochar, confirming surface precipitation. The same results of Cd^{2+} removal
345 were also reported by Cui et al. (2016) in an experiment conducted using
346 biochar from *Canna indica*. In addition, Cui et al. (2016) found that CO_3^{2-} was
347 the dominant mineral component when biochar was produced at a relatively
348 high pyrolysis temperature ($>500\text{ }^\circ\text{C}$). More CO_3^{2-} can be released into the
349 solution due to the incomplete cracking of carboxyl when the biochar pyrolysis
350 temperature is high, resulting in Cd^{2+} precipitating with ligands (Cui et al., 2016).
351 Likewise, another study using a pistachio green hull biochar to remove Cu gave

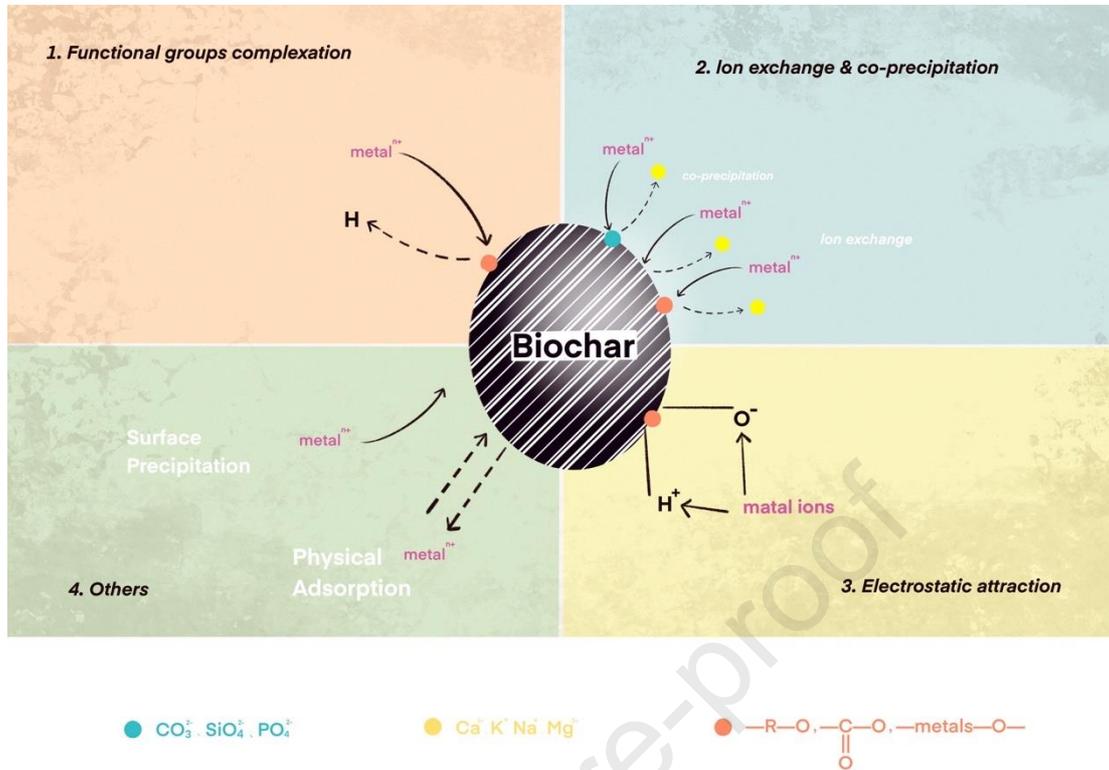
352 similar results (Jalayeri and Pepe, 2019). They reported that Cu-P, Cu-C and
353 Cu-Si were formed during experiments. The SEM-EDX image showed C, O,
354 Cu, P, S, Si, Fe and Ca on the biochar surface, and the FTIR spectra showed
355 the characteristic peaks of PO_4^{3-} and CO_3^{2-} , confirming this result.

356 Ion exchange, complexation, and electrostatic interaction are all associated
357 with functional groups on biochar (Tan et al., 2015). Under different pH
358 conditions, there would be various mechanisms for different metals. For
359 example, Abdel-Fattah et al. (2015) compared the simultaneous removal of
360 Mg^{2+} , Ca^{2+} , Pb^{2+} and Cr^{6+} by pinewood biochar in solution. They found that at
361 a pH of 6.0–7.0, Mg^{2+} , Ca^{2+} and Pb^{2+} were mainly removed by complexation
362 with C=O, C-O and phenolic O-H functional groups. In addition, it is worth
363 noticing that complexation between oxygen-containing functional groups and
364 heavy metals may be accompanied by H^+ release (Ding et al., 2016). The H^+
365 release would decrease the solution pH, which can be used as evidence to
366 determine if this complexation happened during the adsorption process (Tran
367 et al., 2016).

368 However, in acid conditions (pH 1.0) the mechanism of Cr^{6+} removal was mainly
369 electrostatic interaction between positively charged functional groups and
370 negatively charged chromate ion (CrO_4^{2-}) (Abdel-Fattah et al., 2015). This can
371 be explained by the fact that under low pH values, the biochar surface is highly
372 protonated, which promotes electrostatic interaction between ions. Conversely,

373 under high pH, biochar surface protonation is reduced to the lowest level. This
374 condition may contribute to the complexation between oxygen donors in
375 functional groups and metal ions (Abdel-Fattah et al., 2015).

376 Physical sorption by pores and surface area on the biochar surface is another
377 mechanism for metal removal. It can be concluded from the literature that
378 surface physical sorption had a limited effect or less significant contribution than
379 other mechanisms when using biochar to remove metals from solution. For
380 example, Poo et al. (2018) reported that physical sorption could be disregarded
381 when using algae-based biochar to remove Cu, Cd and Zn. Also, Tran et al.
382 (2016) reviewed several studies and summarised that physical sorption has
383 less importance than oxygen-containing function groups. However, physical
384 sorption was responsible for Mn removal in the simultaneous removal of Fe, Al,
385 Zn, Cu, As, and Mn by poultry litter biochar (Oh and Yoon, 2013). Unlike for
386 other metals, pH changes had no effects on Mn removal. Other mechanisms,
387 such as ion exchange or interactions between cations and electrons, may be
388 responsible for Mn removal, but this is still unclear (Oh and Yoon, 2013). Thus,
389 based on the discussion above, further detailed research is needed on the
390 mechanism of metal removal with biochar and the relative contributions of these
391 mechanisms. In addition, Mn removal by biochar is still poorly understood, and
392 more research is needed to determine the main mechanism of Mn removal.



393

394 Figure 2. The mechanisms of heavy metal removal by biochar, modified from

395

Tan et al. (2015).

396

3.2 Novel developments of biochar for AMD treatment

397

Novel developments of biochar focus mainly on pyrolysis methods and

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modification processes. Compared with conventional pyrolysis methods, some

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new trends of pyrolysis can improve the removal capacity of biochar (Wang et

400

al., 2020). For example, Wang et al. (2020) mentioned that microwave-assisted

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pyrolysis could change biochar morphology (for example, surface area) to

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make it more suitable for removing metals and organic pollutants. In addition,

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microwave pyrolysis can increase the number of biochar functional groups,

404

contributing to metal adsorption (Shirvanimoghaddam et al., 2022).

405 Hydrothermal pyrolysis is another novel pyrolysis method, used mainly for
406 feedstock with high water content, such as animal excreta and sewage sludge
407 (Shan et al., 2020). This method usually heats the feedstock at a relatively low
408 temperature (120-250 °C) without pre-drying (Xiang et al., 2020). Wang et al.
409 (2020) reviewed several studies on hydrothermal pyrolysis biochar and
410 concluded that hydrothermal pyrolysis could introduce more oxygen-containing
411 functional groups (-OH and -COOH) into biochar. Furthermore, hydrothermal
412 pyrolysis is a cost-effective and simple method, due to its lower heating
413 temperature, and there is no requirement for oxygen-limited conditions.

414 Recently, novel modification methods have enhanced biochar performance in
415 metal removal. Yin et al. (2022) compared three types of oxidant-modified
416 *Platanus orientalis* Linn leaf biochar (modified by H₂O₂, KMnO₄ and K₂Cr₂O₇,
417 respectively) for Cd removal. Among these three types of biochar, the KMnO₄
418 modified biochar had the best performance in removing Cd. It removed 98.57%
419 of Cd with the highest adsorption capacity of 54.7 mg g⁻¹. BET and FTIR
420 analyses confirmed that KMnO₄ modified biochar had a higher specific surface,
421 and MnO_x introduced by KMnO₄ can form inner-sphere complexes with oxygen-
422 containing groups and has a strong affinity for metal cations (Yin et al., 2022).
423 Ahmed et al. (2021) modified watermelon seed biochar with 30% H₂O₂ and
424 used it to remove Pb from the synthetic AMD water. Results showed that the
425 H₂O₂ could introduce more hydroxyl and carboxyl groups to modified biochar,

426 with a higher adsorption capacity (25.57-44.74 mg g⁻¹) than unmodified biochar
427 (10.82-32.07 mg g⁻¹). In addition, Wang et al. (2021) investigated Pb removal
428 by K₂FeO₄ modified sludge biochar. The adsorption capacity of K₂FeO₄
429 modified biochar was found to be six times higher than the original biochar due
430 to much more numbers of functional groups on the modified biochar.

431 Also, biochar modification by nanomaterials is another novel development of
432 biochar for metal removal. The nanomaterials used for biochar modification are
433 usually carbonaceous materials, metal oxides, and metals. Generally,
434 nanomaterial modification biochar has better physicochemical properties and
435 is more dispersible than conventional biochar (Zhao et al., 2021). Yang et al.
436 (2021) studied nano-FeS and chitosan-modified soy sauce residue biochar for
437 Cr removal. The results showed that when nano-FeS:chitosan:biochar mass
438 ratios were 1:1:1, the adsorption capacity reached its highest value of 103.9 mg
439 g⁻¹. This adsorption capacity was almost five times higher than conventional
440 soy sauce residue biochar (22.5 mg g⁻¹). Similar to the oxidant modified biochar,
441 nanomaterials can boost the adsorption capacity by increasing the specific
442 surface area and the number of oxygen-containing functional groups (Zhao et
443 al., 2021).

444 For the modified biochars mentioned above, almost all studies found that
445 modified biochar has a faster adsorption process when used for AMD treatment.
446 Ahmed et al. (2021), Wang et al. (2021) and Yin et al. (2022) confirmed that the

447 modified biochar could reach the adsorption equilibrium within 1 hour, while
448 conventional biochar may need 2-12 hours. The rapid adsorption process is
449 caused by the number of pore channels and functional groups on the modified
450 biochar that is sufficient to provide active sites (Yin et al., 2022).

451 In terms of pH, some modified biochar can still be affected by low pH conditions.
452 In general, the favourable pH for maximum adsorption is around 4-5 (Ahmed et
453 al., 2021; Yin et al., 2022). One reason for this is that, in acid conditions, H⁺ can
454 inhibit metal removal by strongly competing with metal ions for adsorption,
455 resulting in lower adsorption capacity (Yin et al., 2022). This competition may
456 also happen when using conventional biochar in a lower condition. However,
457 Ahmed et al. (2021) reported that competition for active sites between metal
458 ions and protons may happen in acidic conditions at the initial stages.
459 Nevertheless, the effect of H⁺ is considered a promoting factor at a low pH
460 range. They also reported that electrostatic repulsion has an inhibitory effect on
461 metal adsorption at low pH. The same reason (electrostatic repulsion) is also
462 mentioned in Cr adsorption by a nanoscale FeS/chitosan biochar (Y. Yang et
463 al., 2021). However, some modified biochar cannot be affected by extreme low
464 pH and reach the maximum adsorption. For example, Wang et al. (2021)
465 mentioned that K₂FeO₄ modified sludge biochar could reach the maximum Pb
466 adsorption capacity at pH 2. Yang et al. (2021) also reported nanoscale biochar
467 could achieve the maximum adsorption of Cr at pH 2. Compared with other

468 modified and conventional biochars, these biochars have a large abundance of
469 functional groups to resist the effects caused by low pH, which provides more
470 opportunities for complexation (Y. Yang et al., 2021). Thus, some modified
471 biochar may solve the problems caused by extreme low pH, which can be an
472 excellent advantage when used for AMD treatment.

473 However, both oxidant and nanomaterial introduce additional metals during the
474 modification process. Thus, it is necessary to assess the stability of these
475 methods and their environmental risks in further study. Also, due to the small
476 particle size of nanomaterials, nanomaterial modified biochar is dispersible and
477 difficult to separate from AMD, which may not be favourable for reuse and
478 recycling. Further research should consider an effective isolation and recycling
479 method to solve this problem (Zhao et al., 2021).

480 **3.3 Parameters that affect biochar adsorption capacity**

481 *a) Initial heavy metal concentration*

482 The initial heavy metal concentration in AMD solution can affect the adsorption
483 capacity of biochar. Liu and Zhang (2009) showed that with Pb concentration
484 increasing from 10 mg L⁻¹ to 20 mg L⁻¹, the adsorption capacity increased
485 approximately two-fold for pinewood and rice husk biochars. Kılıç et al. (2013)
486 used almond shell biochar (produced at 600 °C) to remove Ni and Co and found
487 similar trends. However, Pelleria et al. (2012) showed that increasing the initial
488 Cu concentration caused an increase in Cu removal per mass unit by biochar

489 but a decrease in total Cu removal produced from rice husk, olive pomace,
490 orange peel, and compost. The observed positive relationship between initial
491 metal concentration and biochar adsorption capacity may have two
492 explanations: firstly, the increased metal concentration may increase the
493 possibility of metal ions coming into contact with biochar; secondly, the increase
494 might be due to more metal ions in the solution inducing the release of H⁺ from
495 the surface of biochar, which then leads to more adsorption sites on the biochar
496 (Abdelhafez and Li, 2016; Liu and Zhang, 2009). Also, increasing metal
497 concentration can increase the driving force of mass transfer, which can cause
498 increased metal removal per mass unit (Pellera et al., 2012). The decrease in
499 metal removal by biochar may be explained by the saturation of active sites on
500 the biochar surface (Pellera et al., 2012).

501 *b) Biochar dosage*

502 Many studies have suggested that the biochar dosage is a critical parameter
503 that can affect the heavy metal removal capacity of biochar. Most of the
504 literature found that an increased ratio of biochar to water increased the total
505 amount of heavy metal removal but decreased the biochar removal efficiency.
506 For example, Chen et al. (2011) reported that in a Cu removal experiment by
507 corn straw biochar, the biochar adsorption dropped from 11.82 mg g⁻¹ to 1.18
508 mg g⁻¹ when increasing the biochar concentration from 1 g L⁻¹ to 50 g L⁻¹.
509 Meanwhile, the Cu removal rate increased from 19.7% to 98.3% due to the

510 increased biochar concentration. These findings are supported by other studies
511 (Pellera et al., 2012; Regmi et al., 2012; S. Wang et al., 2015). Based on the
512 findings from the literature, it is important to use appropriate biochar dosages
513 when removing metal, particularly for practical use. Appropriate biochar dosage
514 can be cost-effective and yield maximum results.

515 *c) pH of contaminated water*

516 The pH of contaminated water is another parameter that controls the
517 mechanisms of heavy metal removal by biochar. Many studies that used
518 biochar to remove Cu, Pb, and Cd demonstrated that a solution with pH around
519 5-6 was optimal for the highest metal removal efficiency (Abdelhafez and Li,
520 2016; Chen et al., 2011; Jiang et al., 2016; Liu and Zhang, 2009; Pellera et al.,
521 2012; H. Wang et al., 2015). However, there are also examples of better
522 removal efficiency at solution pH outside this range. For instance, Park et al.
523 (2017) reported that the adsorption of Cd using biochar reached a peak at
524 $\text{pH} > 8$. This was explained by electrostatic interaction between the metal ions
525 and biochar surface. At a lower pH, the excessive protonation of the biochar
526 results in competition for binding sites between H_3O^+ and Cd^{2+} , while at a higher
527 pH, the adsorbing sites are vacant for Cd adsorption.

528 Furthermore, other processes, such as metal precipitation/co-precipitation, can
529 occur at higher pH levels ($\text{pH} > 8$) (Park et al., 2017). In contrast, Abdel-Fattah
530 et al. (2015) showed that Cr removal by pinewood biochar (5 g L^{-1}) reached

531 maximum capacity (35.4 mg g^{-1}) at pH of 1. At low pH, the protonation favours
532 the formation of an ion-pair interaction mechanism between chromate anions
533 (HCrO_4^-) and the positively charged functional groups (Shaheen et al., 2019).

534 **4. Bacteria application in AMD treatment**

535 Forty studies were identified and selected for review (screened from 4041 initial
536 literature results from 2006 and 2022) from published literature on using
537 microbial treatments for AMD remediation. The metal removal efficiency
538 reported by these studies has a wide range, from 18% to 99%. In addition, these
539 studies used different carbon sources, for example, ethanol and organic waste.
540 A summary of the studies focused on metal removal by bacteria is shown in
541 Table 3 and discussed in the following sub-sections.

542 Table 3. Bacteria used for heavy metal removal from AMD.

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
Sulfate reducing bacteria (SRB)	Ethanol	Inversed fluidised bed bioreactors (IFBs)	Zn and Cu 25	Zn and Cu >90%	Janyasuthiwong et al. (2015)
SRB	Maise straw	Immobilised SRB sludge beads	Fe 469, Cu 88, Cd 92, Zn 128	Fe, Cu, Cd, and Zn >99.9%	Zhang et al. (2016)
SRB	Chitinous material	Sulfate-reducing bioreactors (SRBRs),	Cd 0.267, Fe 106, Mn 1.50, Zn 72.9	Cd 0.096 mg g ⁻¹ , Fe 0.748.30 mg g ⁻¹ , Mn 0.023 mg g ⁻¹ , Zn 3.07 mg g ⁻¹	Al-Abed et al. (2017)

543

544

545 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
SRB	Zero-valent iron (ZVI)	Continuous-flow bioreactors	Cu 50.0, Cd 10, Pb 2.4	Cu, Cd, Pb >99.8%	Ayala-Parra et al. (2016a)
SRB		acidophilic and autotrophic biocathode	Zn 15-40	Zn 25 mg g ⁻¹ (99%)	Teng et al. (2016)
SRB	Algae (<i>Chlorella sorokiniana</i>)	Permeable reactive barriers (PRB)	Cu 10-50	Cu >99.5%	Ayala-Parra et al. (2016b)
SRB	Graphene oxide	Laboratory-scale experiment	Ni 59.0, Cu 64, Fe 56, Cd 112, Cr 52, Pb 207, Ti 48	Ni 98.1%, Pb 97.1%, Ti 91%, Cu 89.2%, Fe 77.0%, Cd 51.5%, Cr 12.4%	Yan et al. (2018)

547 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
SRB	Manures, woodchips and sawdust, sugarcane waste and fodder	Bench-scale bioreactors	Fe 188.9, Cu 22.2, Zn 21.4, Mn 31.9, Ni 10.4, Co 1.2	Fe 51.49%–99.32%, Cu 84.95%–99.97%, Zn 35.11%–99.78%, Ni 17.87%–99.14%, Co 63.55%–99.02%, Mn 12.68%–73.86%	Choudhary & Sheoran (2012)
SRB	Ethanol	Anaerobic sequential batch reactor (ASBR)	Fe 100-400, Zn 20-40, Cu 5.0-10	Fe > 99.2%, Zn 100%, Cu > 93.3%	Costa et al. (2017)
<i>Acidithiobacillus ferrooxidans</i>	Glucose	Bio-mineralization system	Fe 4378	Fe 89%	X. Wang et al. (2021)

548

549 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
SRB	Ethanol	Sulfate reducing anaerobic membrane bioreactor (AnMBR)	Fe 37.5 ± 2.7, Cu 12.4 ± 0.7, Zn 2.50 ± 0.42, Co 2.50 ± 0.1, Mn 2.9 ± 0.2, Ni 1.42 ± 0.08, As 1.5 ± 0.18	Fe, Cu, Zn, Co, and Ni > 99.0%, Mn 76.0%-91.0%, As 41.0%-67.0%	Sahinkaya et al. (2019)
<i>Acidithiobacillus ferrooxidans</i>	ZVI	Laboratory-scale experiment	Fe 2234	Fe 98.4%	Wang et al. (2019)
SRB	Ethanol	Anaerobic sequential batch reactor (ASBR)	Fe 100, Zn 20, Cu 5.0	Fe, Zn and Cu > 99.0%	Castro Neto et al. (2018)

550

551 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
SRB	Ethanol	Laboratory-scale sulfate-reducing columns	Cu 100, Ni 10, Zn 10	Cu, Ni and Zn > 99.2%	Sierra-Alvarez et al. (2006)
SRB	Ethanol	Anaerobic bottles	Cu 10, Fe 55, Zn 32	Cu 99.99%, Fe 87.6%, Zn 99.9%	Zhao et al. (2018)
SRB	Leaves 6%, compost 9%, Fe (0) 3%, silica sand 30%, perlite 30%, limestone 22%	Fixed bed reactor	Cd 11, Cr 51, Cu 64, Zn 65, As 2.0	Cu, Zn, Cr, Cd, and As >98%	Cruz Viggi et al. (2010)

552

553 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
SRB	Limestone 40%, spent mushroom compost 30%, activated sludge 20% and woodchips 10%.	Up-flow anaerobic packed-bed bioreactor	Al 44, Fe 5.8, Cu 4.6, Pb 0.5, Zn 5.9	Fe, Pb, Cu, Zn and Al 87%-100%	Muhammad et al. (2018)
SRB	H ₂ S	Sulfidogenic bioreactor	Cu 325	Cu 90%	Silva et al. (2019)
SRB	Zero-valent iron (ZVI) and Zero-valent copper (ZVC)	Laboratory-scale experiment	Pb, Zn and Cu 50	Pb, Cu and Zn 100%,	Hu et al. (2018)
SRB	Ethanol	fluidised-bed reactor (FBR)	Cu 300, Fe 150	Cu and Fe >99%	Ucar et al. (2011)

554

555

556 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
SRB	Iron	Up-flow anaerobic multiple-bed (UAMB)	Cu 20, Fe 55	Cu 99%, Fe 86%	Bai et al. (2013)
SRB	Rice wine waste	Laboratory-scale experiment	Fe 192, Al 104	Al > 97%, Fe >87%	G.-M. Kim et al. (2014)
<i>Acidithiobacillus (Bacillus licheniformis, Bacillus firmus and Bacillus megaterium)</i>	Ethanol	Laboratory-scale experiment	As 100	As 90%-95%	Natarajan (2017)
SRB	Lignite	Activated lignite-immobilised SRB	Cu 10, Zn 20	Cu 99.59%, Zn 99.93%	Di et al. (2022)

557

558 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
SRB	Landfill leachate	Sulfidogenic fluidised-bed reactor	Cu 0.014, Fe 4.0, Zn 0.47, Cr 0.55	Cu, Fe, Cr, and Zn 82.0-99.9%	Sahinkaya et al. (2013)
SRB	ZVI	Glass batch reactors	Cr and Zn 10-90	Cr and Zn > 99%	Guo et al. (2017)
SRB	Sodium lactate	Laboratory-scale experiment	Zn 260	Zn under detection	Castillo et al. (2012)
SRB	Cow manure and activated sewage sludge	Cooperation with dried poultry litter pellets (400 °C) biochar	Fe 2460, Al 1295, Pb 1.2, Zn 19.2, Cr 0.3	Al, Cr, Fe, Pb and Zn 100%.	Giachini et al. (2018)
Iron-oxidising bacteria	Tryptone soy broth	Ceramic membrane bioreactor	Fe 250-3000	Fe 99%	Demir et al. (2020)

559 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L⁻¹)	Metal removal efficiency	Reference
SRB	Sodium lactate	Sodium alginate immobilised sulfate reducing bacteria	Cu and Zn 50-150	Cu 99%, Zn 95.8%	Gopi Kiran et al. (2018)
SRB	Sodium lactate	Laboratory-scale experiment	Ni, Cd, Zn, Pb, and Fe 5.0-50	Ni 97%, Cd 94.8%, Zn 94.6, Pb 94.4%, Fe 93.9%	Kiran et al. (2017)
SRB	Acetate,	Sulfidogenic up-flow anaerobic sludge blanket (UASB) reactor	Ni 50, Zn 50	Zn 99.99%, Ni 96.87%	Najib et al. (2017)

560

561 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

Bacteria species	Carbon source/electr on donor	Experiment methods	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
<i>Hermaacidophilic Archaea, Acidianus manzaensis</i>	—	Laboratory-scale experiment	Cu 64, Zn 65	Cu 2.88 mg g ⁻¹ , Zn 2.17 mg g ⁻¹	Li et al. (2020)
SRB	Chicken manure, dairy manure, and sawdust	Column reactor	Fe 599, Mn 29.6, Cu 30, Zn 50.4, Cd 12.2, Ni 16	Removal ability chicken manure > dairy manure > sawdust Cd and Ni 100%, Mn >60%	Zhang and Wang (2014)
SRB	Lactate	Laboratory-scale experiment	Ni 21.5	Ni 100%	Hu et al. (2020)
SRB	Bagasse	Maifanite-reinforced SRB, immobilised	Mn 6	Mn 63.87%	Bao et al. (2021)

562 Table 3. Bacteria used for heavy metal removal from AMD. (Continued).

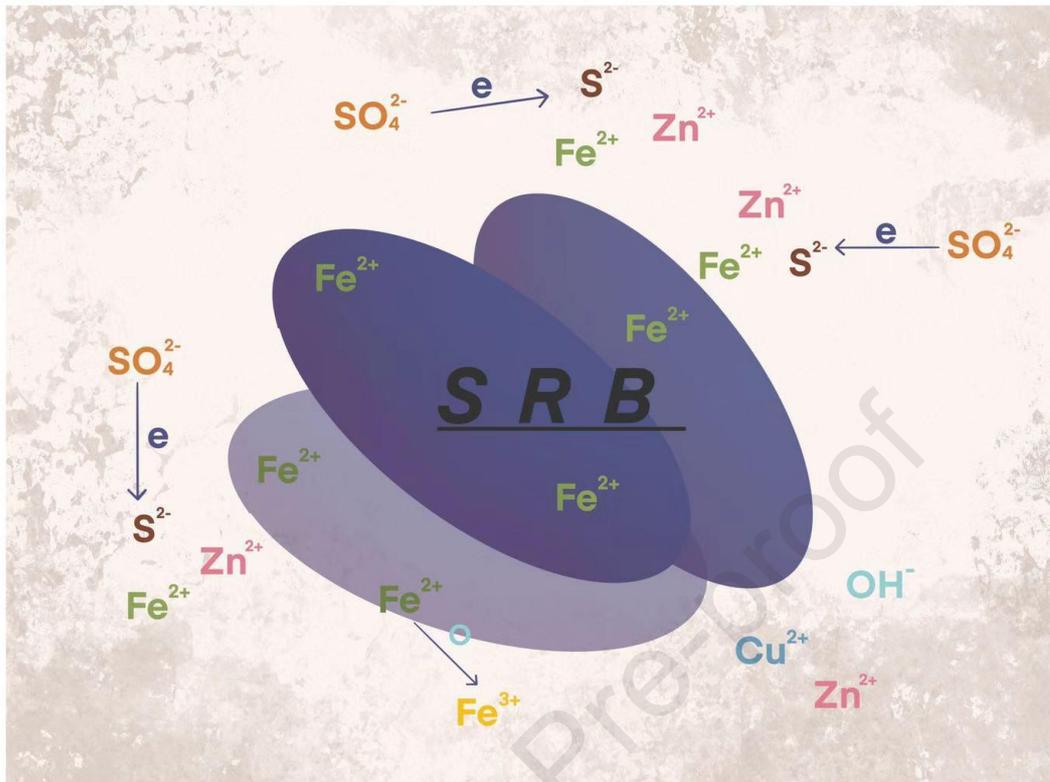
Bacteria species	Carbon source/electron donor	Experiment methods	AMD composition (mg L ⁻¹)	Metal removal efficiency	Reference
Fe–Mn oxidising bacteria (<i>Flavobacterium</i> , <i>Brevundimonas</i> , <i>Stenotrophomonas</i> and <i>Thermotonus</i>)	Glucose	Laboratory-scale experiment	Fe 100-1300, Mn 100-700	Fe 99.8%, Mn 99.6%	Hou et al. (2020)
<i>Acidiphilium multivorum</i> <i>Acidithiobacillus ferrooxidans</i>	—	Laboratory-scale experiment	Fe 1267	Fe 100%	Jin et al. (2020)
SRB	—	Inverse fluidised bed sulfidogenic bioreactor	Cd, Ni, Pb and Zn 10, Cu 50, Fe 150	Cd, Pb, Zn and Cu > 95%, Fe 90%, Ni 85%,	Kumar and Pakshirajan (2020)

563

564 **4.1 Mechanisms of metal removal by sulfate reducing bacteria**

565 Recent studies have focused on biological methods for removing heavy metals from
566 AMDs based on bacteria. Most of these studies used sulfate reducing bacteria (SRB)
567 and showed excellent results (Table 3). SRB are anaerobic microorganisms that use
568 sulfate as an electron acceptor, producing S^{2-} and increasing alkalinity in water,
569 resulting in the generation of insoluble metal sulphates. Thus, SRB can remove metals
570 dissolved in water (Sierra-Alvarez et al., 2006). Other mechanisms can contribute to
571 removing heavy metals from AMD by SRB, as shown in Figure 3. This may depend
572 on different metals, SRB species, and reaction conditions (Zhao et al., 2018). For
573 instance, Cu can be removed by extracellular chelating, whereas Zn and Fe can be
574 removed by bioprecipitation.

575 For multi-metal contaminated water like AMD, the variety of metal ions can also
576 influence the mechanism of metals removal (Zhao et al., 2018). This phenomenon was
577 also observed by Cruz Viggi et al. (2010), who found it is difficult to distinguish which
578 mechanism is involved in metal removal during the reaction with multi-metal water.
579 Nevertheless, based on the previous study of Cd removal by SRB, Cruz Viggi et al.
580 (2010) showed that sorption accounted for 94% of the removed Cd, and bioreduction
581 took up only 6% of total Cd removed. This result, however, can only explain the Cd
582 removal in this batch experiment. The contribution of different mechanisms for
583 different metals still requires further investigation (Cruz Viggi et al., 2010).



584

585 Figure 3. Proposed mechanism for bioremoval of heavy metal ions by SRB, modified
 586 from Zhao et al. (2018).

587 **4.2 Metals toxicity affecting sulfate reducing bacteria**

588 Although SRB can successfully remove heavy metals from AMDs, some studies found
 589 that heavy metals may be toxic to SRB (Alam and McPhedran, 2019; Gopi Kiran et al.,
 590 2018; Kiran et al., 2017; Teng et al., 2016; Wang et al., 2019; Zhang et al., 2016; Zhao
 591 et al., 2018). Alam and McPhedran (2019) summarised the findings of several studies
 592 regarding metal toxicity to SRB and pointed out that heavy metals mainly influence the
 593 activity of enzymes, induce protein denaturation, and compete with cations. These
 594 studies also indicated that different metals have different toxicity levels to SRB. For

595 example, Alam and McPhedran (2019) showed that Cd (6 mg L⁻¹), Cr (23 mg L⁻¹), Cu
596 (4 mg L⁻¹), Pb (25 mg L⁻¹), Ni (10 mg L⁻¹) and Zn (13 mg L⁻¹) could inhibit the activity
597 of SRB. However, Zhao et al. (2018) reported that, at 35 °C and pH 3, Cu is toxic to
598 SRB at 10 mg L⁻¹. In the study of Teng et al. (2016), Zn was found to have an inhibitory
599 effect on SRB when concentrations reached 40 mg L⁻¹.

600 However, many other studies observed that even a relatively high concentration of
601 metals in the water had no adverse effects on SRB activity. On the contrary, these
602 high concentrations could improve the ability of SRB to remove metals (Castro Neto
603 et al., 2018; Sierra-Alvarez et al., 2006). For example, Sierra-Alvarez et al. (2006)
604 showed no inhibition process in a column reactor at pH 4.5, even when the Cu
605 concentration reached 50 mg L⁻¹. Another study using an anaerobic stirred batch
606 reactor with Fe (100 mg L⁻¹), Zn (20 mg L⁻¹), and Cu (5 mg L⁻¹), found that these levels
607 did not affect SRB (Castro Neto et al., 2018). Therefore, the inhibition effect is
608 influenced not only by the concentration of metals but also by other experimental
609 conditions (e.g. pH and metal type). In general, pH for experimental inhibition
610 conditions is lower than 5 and higher than 9 (Kushkevych et al., 2019). Also, Hao et
611 al. (2008) indicated the inhibitory concentrations of some metals for SRB i.e. Zn 25-
612 40 mg L⁻¹, Pb 75-80 mg L⁻¹, Cu 4-20 mg L⁻¹, Cd 4-20 mg L⁻¹, Ni 10-20 mg L⁻¹ and Cr
613 60mg L⁻¹.

614 The difference in metal tolerance in the different experiments may be due to some
615 inorganic cations that can affect heavy metal toxicity for SRB by competing with metals
616 (e.g. Fe, Mg and Ca) for the anionic sites on the SRB surface (Kaksonen and Puhakka,
617 2007). Also, different metals have different toxicity for SRB (e.g. Cu is higher than Zn),
618 and a combination of various metal toxicity is higher than the sum of the individual
619 metal toxicities (Cossich et al., 2002; Utgikar et al., 2003). Another reason is that the
620 source of the SRB can affect their tolerance to metal toxicity. SRB collected from AMD
621 sites usually has a higher tolerance than those enriched in a batch experiment
622 because of the environment adaption (Kaksonen and Puhakka, 2007).

623 In order to avoid the toxicity effects on SRB, some studies have used SRB immobilised
624 in beads (Gopi Kiran et al., 2018; Zhang et al., 2016). These beads consisted of a
625 mixture of SRB, maize straw, zero valence iron, silicon sand, polyvinyl alcohol (PVA),
626 and sodium alginate. Immobilised SRB beads provided shelter for SRB, as well as a
627 relatively high specific surface area (Gopi Kiran et al., 2018). In addition, immobilised
628 SRB beads can increase biomass and retention time in reactors (Gopi Kiran et al.,
629 2018; Zhang et al., 2016). Thus, the SRB immobilised beads can be used to avoid the
630 toxicity effect on SRB caused by a high concentration of heavy metals (Zhang et al.,
631 2016). To increase the efficacy of SRB, other methods to reduce the effect of metals'
632 toxicity should be explored in future work.

633 **4.3 Metals removal by SRB**

634 Some metals such as Cu, Fe, Cd, Zn, and Pb can be almost entirely removed from
635 AMD by SRB, while SRB's ability to remove Mn is more varied among published
636 studies (Table 3). The removal efficiency of Mn in the solution was only around 50%,
637 compared to the over 80% for other metals that has been reported by some authors
638 (Bai et al., 2013; Muhammad et al., 2018; Sahinkaya et al., 2013; Zhang and Wang,
639 2014). There are two possible reasons for these observations. The first is the
640 potentially lower sorption affinity of Mn to organic waste (carbon source). The second
641 reason is the relatively higher solubility of MnS ($K_{sp} = 2.5 \times 10^{-13}$) compared to the
642 sulfide salt of other metals (Cd, Cu, Zn, and Fe). Thus, Mn^{2+} concentration is higher
643 than other metals in the water. Mn^{2+} presented in a dissolved state for almost the entire
644 reaction time (Muhammad et al., 2018), causing the removal efficiency to be
645 decreased (Zhang and Wang, 2014). Also, because of the complex interaction
646 between Mn and other metals, this solubility of Mn might be affected (Muhammad et
647 al., 2018). However, Mukwevho et al. (2019) reported that Mn removal efficiency could
648 reach 85.9%, which is much higher than the results obtained in previous studies
649 (~50%). Unfortunately, the reason for this is not clear.

650 The studies mentioned above did not investigate all experimental parameters in their
651 studies, and the higher removal efficiency (80.7%) had a better condition for SRB (pH
652 6 and 30°C) than that of the lower efficiency (74.8%), with conditions of pH 5 for 30°C

653 and 10°C. Thus, further research needs to be carried out to confirm whether pH and
654 temperature conditions can affect Mn removal by SRB.

655 **4.4 Carbon source and electron donor**

656 In the process of metal removal by SRB, the nature of the carbon source and electron
657 donor is an important factor affecting the metal removal efficiency. In general, lactate
658 is recommended by many studies (Alam and McPhedran, 2019; Gopi Kiran et al., 2018;
659 Kiran et al., 2017), as it supports SRB growth and performs better for metal removal
660 than other carbon sources. Ethanol is another popular carbon source that has been
661 used in many studies (Castro Neto et al., 2018; Janyasuthiwong et al., 2015; Natarajan,
662 2017; Sahinkaya et al., 2013; Sierra-Alvarez et al., 2006; Ucar et al., 2011). Ethanol
663 has been confirmed as effective in both reactor experiments, e.g. in an anaerobic
664 sequential batch reactor (ASBR) (Costa et al., 2017), and in small lab-scale
665 experiments, e.g. in an anaerobic reactor (Zhao et al., 2018). These studies reported
666 that ethanol could enhance SRB capacity to remove metals. Ethanol is also more
667 competitive in terms of kinetics when compared to lactate under room temperature
668 conditions (Nielsen et al., 2019), and is also cheaper than lactate (Alam and
669 McPhedran, 2019), making it more scalable.

670 In addition to these simple carbon sources (lactate and ethanol), some studies have
671 used complex organic matter, such as organic waste (e.g. maize straw, leaves and
672 cow manure) as carbon source (Choudhary and Sheoran, 2012; Cruz Viggi et al., 2010;

673 Giachini et al., 2018; G.-M. Kim et al., 2014; Muhammad et al., 2018; Sahinkaya et al.,
674 2013; Zhang et al., 2016). These organic sources are cheap and can contribute to
675 metal removal because most of them are porous materials. There is evidence that
676 SRB could be enhanced by using complex organic carbon sources (Nielsen et al.,
677 2019). Another advantage of complex organic carbon sources is that they can last
678 longer than simple carbon sources due to their more gradual degradation.
679 Nevertheless, for complex carbon sources, a disadvantage is that sulphate removal
680 yields are lower than those of simple carbon sources (Nielsen et al., 2019).

681 Besides using organic carbon as the electron donor in the removal of heavy metals by
682 SRB, some metals such as ZVI and ZVC are also used in many studies (Ayala-Parra
683 et al., 2016a; Guo et al., 2017; Wang et al., 2019; Yan et al., 2018). The ZVI can be
684 used by both SRB and *Acidithiobacillus ferrooxidans* in metal removal. Compared with
685 other control studies, ZVI can significantly increase mineral precipitation by enhancing
686 sulfate reduction and generating alkalinity in solution (Hu et al., 2018; Wang et al.,
687 2019). In the combination of ZVI and SRB, ZVI is a reducing agent that can enhance
688 anaerobic conditions and release Fe^{2+} , which is beneficial to SRB hydrogenase (Guo
689 et al., 2017). Also, ZVI can react with heavy metals such as Cr, which can reduce the
690 metals' toxicity to SRB (Guo et al., 2017). However, some disadvantages of ZVI have
691 also been reported, e.g. excessive ZVI is toxic to *Acidithiobacillus ferrooxidans*, and
692 the combination of ZVI and *A. ferrooxidans* results in Fe removal only. The addition of

693 ZVI did not affect the removal of Zn, Al, and Mn (Wang et al., 2019). Nevertheless, in
694 combination with SRB, ZVI can remove other metals except for Mn (Guo et al., 2017).
695 ZVC has higher removal efficiency than ZVI for Fe, but because ZVC can more easily
696 introduce Cu to the environment, most of the studies only used ZVI (Wang et al., 2019).
697 Overall, carbon sources for SRB in metal removal may vary in different conditions.
698 Factors to consider in selecting a carbon source include metal type, cost, and pH.
699 Further research should focus on finding long-lasting and cost-effective electron
700 donors for practical use.

701 **5. Combination of treatments for AMD**

702 ***5.1 Combination of algae and biochar***

703 Some studies reported the interactions between biochar and algae (Awad et al., 2017;
704 Jia et al., 2018; Kholssi et al., 2018; Magee et al., 2013; Zhang et al., 2019). In terms
705 of the inhibitory effects between biochar and algae, the result showed that in some
706 conditions, biochar could significantly inhibit the growth of algae. For example, Awad
707 et al. (2017) reported that rice husk biochar might reduce the production of green algae
708 (*Chlamydomonas. sp* and *Scenedesmus. sp*); Zhang et al. (2019) noted that pine
709 needle biochar has adverse effects on algae growth (*Scenedesmus obliquus*, and also
710 the bacterium *Photobacterium phosphoreum*) due to the presence of free radicals;
711 Magee et al. (2013) confirmed that oil mallee biochar could also inhibit the growth of
712 the test algae (*Chlorella vulgaris*) when adding the biochar at an induction phase (12h

713 after incubation of algae); Similar results were also reported by Jia et al. (2018) on the
714 interaction between apple tree biochar and three species of cyanobacteria
715 (*Oscillatoria. sp*, *Phormidium. sp* and *Nostoc. sp*). However, in Kholssi et al.'s (2018)
716 study, the growth of *Anabaena cylindrica* significantly increased with wood biochar
717 solid support compared with liquid media.

718 The inhibition caused by biochar to algae, as mentioned above, is mainly because 1)
719 porous biochar absorbs algae onto the biochar surface, which blocks nutrient uptake
720 and affects algae growth (Awad et al., 2017); 2) biochar can be suspended in solution
721 and the light intensity reduced, hence reduced algal photosynthesis (Jia et al., 2018;
722 Magee et al., 2013); 3) free radicals in biochar have biotoxicity for algae in solution
723 and reduce algal growth. These free radicals are produced during the biochar pyrolysis
724 processes and are influenced by the pyrolysis temperature. Free radicals may inhibit
725 the germination of seeds, cause growth retardation of roots, and damage the plasma
726 membrane of algae (Zhang et al., 2019); 4) reactive oxygen species (ROS) produced
727 by dissolved biochar can also damage algae by influencing algae photosynthetic
728 growth (Jia et al., 2018; Zhang et al., 2019).

729 Based on these findings, positive effects between algae and biochar are only valid for
730 specific algae and biochar (Kholssi et al., 2018). Some biochar can boost more
731 extracellular polymeric substances (EPS) of algal origin. These EPS may provide
732 important biological functions by excluding redundant glycogen in algal cells and

733 increasing cell numbers (Kholssi et al., 2018). Also, functional groups on the biochar
734 surface may contribute to the immobilisation of algae and promote algal growth (Shen
735 et al., 2017). In addition, although the porous structure of biochar may have adverse
736 effects on algal growth, porous biochar can serve as a suitable material for attachment
737 and increase the dispersibility of immobilised algae, thus increasing metal sorption
738 processes (Shen et al., 2017). Besides, quick passive adsorption by biochar can
739 increase the viability of algal cells and, as a result, enhance the metal removal
740 capacity (Shen et al., 2017).

741 Based on the work reviewed, the biochar-algae system in AMD metal removal has
742 been rarely studied. Two studies did a simple mixture of algae and biochar to remove
743 metals in the solution (Jiang et al., 2022; Shen et al., 2017). Shen et al. (2017) used a
744 combination of *Chlorella* sp. and water hyacinth biochar to investigate Cd removal.
745 The algae and biochar were mixed with a shaker by different algae: biochar ratios (1:4,
746 2:3, 3:2 and 4:1), and the Cd removal was conducted. It was found that the algal cells
747 were mainly attached to the biochar surface due to the electromagnetic effect. For the
748 Cd removal results, the maximum removal was 217.4 mg g⁻¹ when the algae and
749 biochar ratio reached 2:3. This result was better than the metal removals obtained for
750 algae only (169.9 mg g⁻¹) or biochar only (95.8 mg g⁻¹). Likewise, Jiang et al. (2022)
751 performed a similar study using a simple mixture of *Chlorella* sp. and coconut shell
752 biochar to remove Cd from synthetic AMD water. SEM morphology results showed

753 algae were attached very well to the visible pores on the biochar surface. The results
754 also showed that the biochar pores become rough after Cd adsorption. When using
755 algae and biochar together, the biochar became much rougher after Cd adsorption
756 than only biochar adsorption. This also indicated that algae-biochar Cd adsorption had
757 better Cd removal results than Cd adsorption by biochar only. Better Cd removals
758 with a mixture of algae and biochar were due to 1) the algae-biochar consortium has
759 a more negative charge on the surface. Also, the negative charge of the biochar
760 surface can boost the magnetic intensity surrounding the algae, which can enhance
761 the surface potential of biochar (Shen et al., 2017); 2) FTIR results confirmed that the
762 algae-biochar consortium has more types and greater numbers, of functional groups
763 (especially oxygen-containing functional groups) when compared to biochar or algae
764 alone, which may significantly contribute to the removal of Cd (Jiang et al., 2022; Shen
765 et al., 2017). The two studies mentioned above have confirmed that the biochar-algae
766 mixture may have a higher removal efficacy of Cd in solution. However, due to limited
767 studies of algae-biochar consortium on metal removal from AMD, more studies should
768 be conducted in the future to investigate the removal efficacy of this approach to
769 develop new preparation methods for combining algae and biochar. These preparation
770 methods would reduce the potential inhibition of algae growth caused by biochar and
771 potential blockage of the biochar pores by algae, as well as reducing the algae growth-
772 inhibitory caused by biochar, to optimise the metal removal result.

773 **5.2 Combination of algae and bacteria**

774 Several studies also used a combination of algae and bacteria for AMD treatment.

775 Sahoo et al. (2020) reported that an integrated bacteria (SRB)-algal (*Chlorella* sp.)

776 immobilised technology could remove over 95%-99% of metals from AMD in both

777 aerobic and anaerobic conditions. The same technology was also used by Li et al.

778 (2018a), which confirmed that an immobilised SRB-algae (*Scenedesmus obliquus*)

779 bead technology could remove up to 73.58% of sulfate and 98% of Cu. Similar results

780 (74.4% of sulfate and 91.7% of Cu) were also reported by Li et al. (2018a) with the

781 same immobilised technology in the anaerobic reactor (*Chlorella vulgaris*,

782 *Scenedesmus obliquus*, *Selenastrum capricornutum* and *Anabaena spiroides* with

783 SRB). In addition, Ayala-Parra et al. (2016b) reported that a permeable reactive barrier

784 (PRB) technology with SRB and *Chlorella sorokiniana* could remove over 99.5% of Cu

785 from AMD.

786 Russell et al. (2003) experimented with combining SRB with *Carteria* sp. and

787 *Scenedesmus* sp. for metal removal. The U and Mn were successfully removed, but

788 only *Scenedesmus* sp. showed a relatively high sulfate reduction rate (94.3 g g⁻¹

789 biomass), compared with *Carteria* sp. (43.5 g g⁻¹ biomass).

790 In the algae-SRB system, some studies confirmed that algae could serve as an

791 organic carbon source for SRB (Ayala-Parra et al., 2016b; Das et al., 2009a, 2009b;

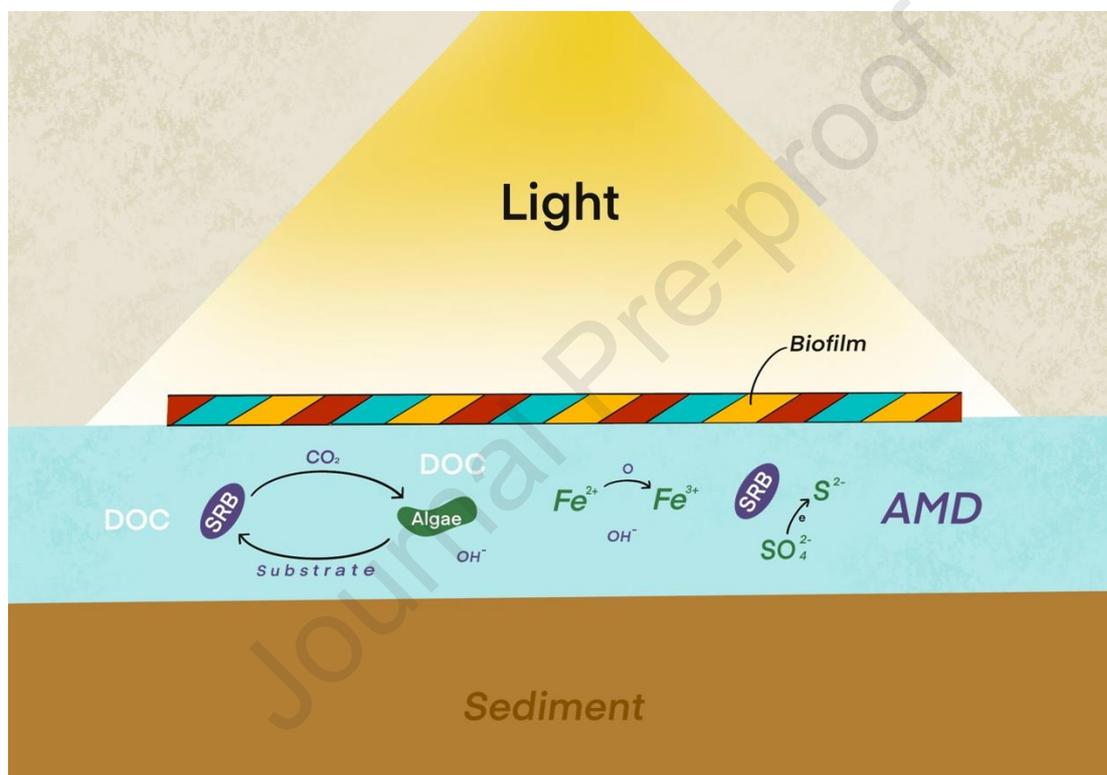
792 Faisal et al., 2020; Li et al., 2018b, 2018a; Russell et al., 2003). SRBs are carbon

793 limited in a natural AMD environment and need additional carbon sources for survival
794 and metal removal. Algae can generate dissolved organic carbon to feed the SRB as
795 a carbon source by photosynthesis and under the action of co-existing anaerobic
796 fermentative bacteria (Das et al., 2009a; Li et al., 2018b). EPS produced by algae can
797 also serve as nutrients for SRB (Das et al., 2009a). In return, CO₂ released by bacteria
798 is utilised by algae for growth in AMD conditions (Abinandan et al., 2018). In addition,
799 EPS produced by both microalgae and bacteria can chelate metal ions, decreasing
800 the concentration of the free form, which in turn makes the environment less
801 aggressive for the organisms to thrive in. From an evolutionary viewpoint, bacteria and
802 algae support each other for survival, growth, and even metal removal and sulfate
803 reduction in extreme conditions (Abinandan et al., 2018). The mutualism between SRB
804 and algae for bioremediation in AMD conditions is shown in Figure 4.

805 Nevertheless, in natural AMD conditions, the metal removal efficacy may be relatively
806 low when using algae as the organic carbon source because other microorganisms
807 compete for electron donors with SRB (Das et al., 2009a; Russell et al., 2003).

808 Immobilised SRB-algae systems and reactors can increase the efficacy of metal
809 removal by algae and SRB (Li et al., 2018b, 2018a; Sahoo et al., 2020). In an
810 immobilised SRB-algae system, SRB can use the secreted carbon source provided
811 by algae more efficiently because immobilised algae are in the vicinity of SRB (Li et
812 al., 2018b). For example, a bioreactor (anaerobic up-flow reactor) can continuously

813 provide a medium for SRB to grow and thus increase the metal removal efficiency (Li
 814 et al., 2018b). Thus, it can be concluded that the algae-bacteria system can have a
 815 high efficacy of metal removal when compared to individual algal or bacterial systems.
 816 Apart from the immobilised method, developing other ways to promote high
 817 effectiveness for SRB using algae as a carbon source is still needed.



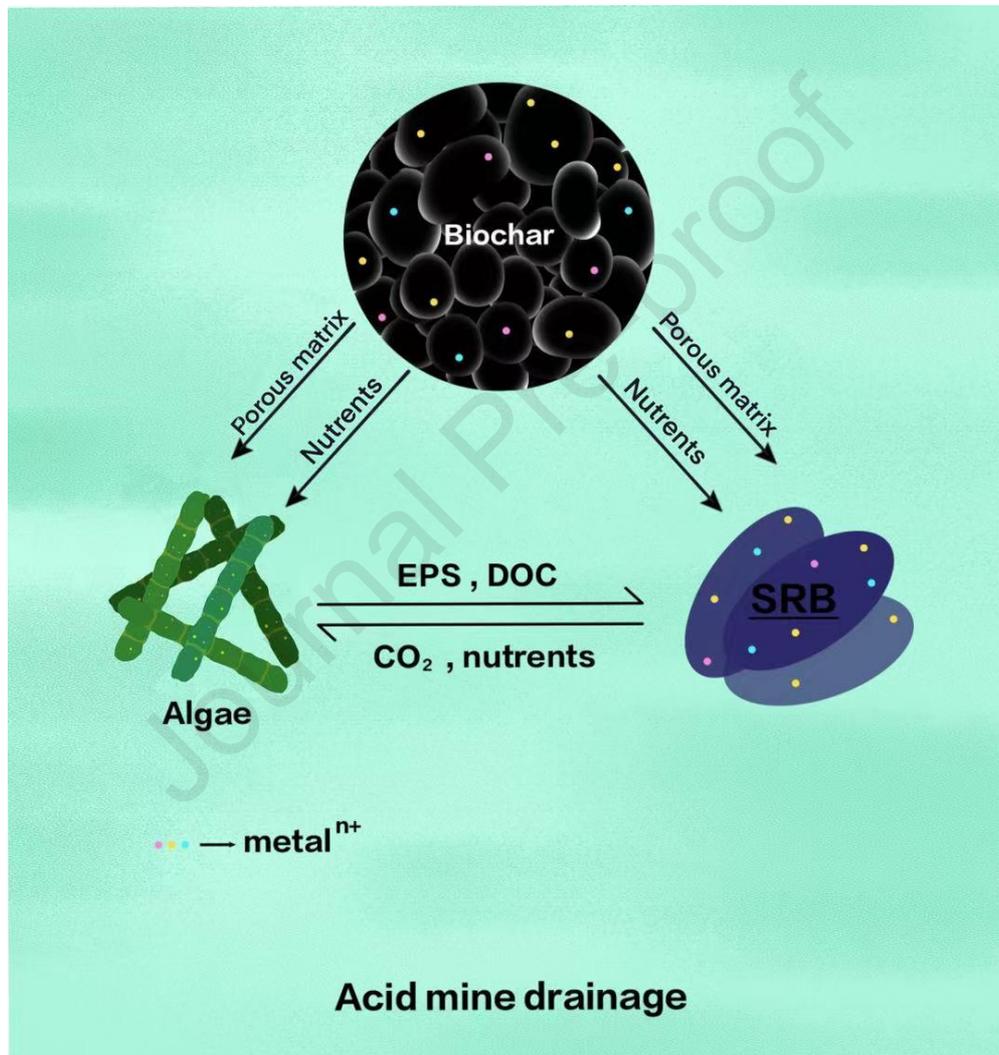
818
 819 Figure 4. Microalgal-bacteria synergism in biofilms of AMD, modified from Abinandan
 820 et al. (2018).

821 **5.3 Algae, bacteria, and biochar**

822 The authors have not found any study that has applied algae, bacteria, and biochar
 823 as a consortium to remediate and recover metals from AMD. In a natural AMD
 824 environment, bacteria and algae can be present as a consortium (Bernardez and de

825 Andrade Lima, 2015; Du et al., 2022). In addition, based on the discussion above, one
826 novel aspect of our exploratory approach is to use biochar as a porous support
827 medium for the growth of the algal-bacteria consortium (Figure 5). Biochar can act as
828 the “protective buffer” to provide a porous matrix for bacterial attachment since it can
829 trigger rapid passive uptake of some heavy metal ions, leading to less damage to cells
830 inside (Mehrotra et al., 2021; Retnaningrum et al., 2021). It was mentioned above that
831 algae could serve as a carbon source for bacteria (e.g. SRB), supporting their growth,
832 which in turn produce key nutrients and CO₂ required for the photosynthetic algae.
833 Biochar may not only provide a large surface area for biofilm production but may also
834 facilitate low-cost harvesting of the metal-laden algae and subsequent recovery of the
835 metal from ash by burning. Indeed, harvesting from bulk culture is one of the
836 bottlenecks to the commercialisation of microalgal technologies, as there is no cost-
837 effective harvesting method (Barros et al., 2015; Singh and Patidar, 2018). Moreover,
838 biochar contains K, P, Ca, etc. and would therefore be able to function as a nutrition
839 supply/growth medium for the consortium. Also, if AMD itself is inoculated with
840 nutrients, it may be possible that the biochar will adsorb further nutrients due to its
841 high adsorption capacity, attracting algae to grow on the surface of the biochar (Muñoz
842 and Guieysse, 2006). With the right environmental conditions, biochar may enhance
843 the self-aggregating process of algae-bacteria (Liu et al., 2017), providing an
844 optimised method to remediate and recover metals from AMD. The algae-bacteria-

845 biochar combination may be advantageous for use in AMD treatment with higher initial
 846 metal concentration (Mehrotra et al., 2021). Therefore, further research is
 847 recommended to explore the effectiveness of algae-bacteria-biochar consortium for
 848 AMD treatment.



849

850 Figure 5. The synergism of algae, bacteria, and biochar consortium in AMD.

851 6. Conclusion

852 6.1 Main findings

853 This review found that all three bio-based methods, when applied as a single process
854 and in combinations (e.g. algae-biochar and algae-bacteria treatments), are effective
855 treatments for AMD. The principal findings of the review are listed below.

- 856 • Most algae can reach at least 90% of removal efficacy via an extracellular stage
857 and then an intracellular stage when removing Cu, Zn, Fe, Cd and Cr from AMD.
858 *Chlorella vulgaris*, *Spirulina maxima*, *Oedogonium crissum* and some other
859 types of algae were found to be effective (over 70 mg. g⁻¹) in metal removal
860 from AMDs.
- 861 • Feedstock and pyrolysis temperature are two factors that can affect biochar
862 properties and influence the metal removal capacity of biochar. Most of the
863 biochar, for example, hardwood and fruit peel biochar, can reach a relatively
864 high metal removal efficacy (over 100 mg. g⁻¹). The mechanisms are mainly
865 physical sorption, ion exchange, precipitation, complexation, and electrostatic
866 interaction.
- 867 • SRB are the most common bacteria used in AMD treatments. It was found that
868 SRB has high metal and sulfate removal ability (60%-100%), mainly by
869 producing insoluble metal sulfide. SRB removal efficacy may be affected by the
870 carbon source. In general, complex carbon sources such as lactate works
871 better than simple carbon such as ethanol. In addition, *Acidithiobacillus*

872 *ferrooxidans* was also found to be an effective bacteria method for Fe removal
873 from AMDs.

874 • The combination of the bio-based methods (i.e. algae-biochar and algae-
875 bacteria) for AMD treatment was found to provide a relatively high removal
876 efficiency (over 200 mg. g⁻¹). Such methods have been observed to have higher
877 metal removal efficiency than those used as a single treatment.

878 **6.2 Limitations and future research**

879 The main limitations identified in previous studies and recommendations for future
880 research are:

- 881 • Algae may be inhibited by low pH when removing heavy metals from AMDs.
882 Thus, it needs to be further investigated to facilitate treatment. For example,
883 studies on isolating novel algae strains and modifying algae prior to treatment
884 to avoid the effects caused by pH and increase the removal efficacy should be
885 developed.
- 886 • The relationship between temperature and metal removal efficacy by algae is
887 still unclear. Further studies may focus on this to clarify this relationship and
888 establish the optimal temperature conditions for metal removal by algae.
- 889 • Secondary contamination and post-treatment recycling are the challenges in
890 AMD treatments by using biochar. The development of novel modifications to
891 overcome the limitations and increase metal removal capacity still needs to be

892 considered in future work. Also, recycling methods of metals and biochar,
893 especially nanoscale modified biochar, should be further investigated.

894 • When using bacteria in AMD treatment, the continuous addition of electron
895 donors is still a limitation. This may reduce the effectiveness of remediation
896 processes. Therefore, research may focus on effective alternative electron
897 donors, such as slow-release electron donors and low sulfate condition electron
898 donors. To reduce the toxicity caused by metals, the immobilised method for
899 bacteria may be considered.

900 • No studies focusing on the algae-bacteria-biochar combination for AMD
901 treatment were found. The authors of this review believe that this consortium
902 may provide a more sustainable and effective process to remove and recover
903 metals from AMD. Therefore, it is recommended that future studies investigate
904 the potential of this consortium.

905 • However, biochar may inhibit algae's growth, and algae and bacteria may block
906 the pore of biochar. Thus, preparation methods to combine algae, biochar, and
907 bacteria as a consortium are required. Also, the recovery of metals through the
908 consortium algae-biochar-bacteria should also be investigated. This should be
909 tested in lab and pilot-scale experiments for future practical applications.

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912 **Author contributions**

913 **Tianhao Du:** Investigation, methodology, writing - original draft, visualisation. **Anna**

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918 **Declaration of Conflicting Interests**

919 The authors declare that there is no conflict of interest.

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Highlights

- Algae-biochar-bacteria consortium is proposed as a novel method for acid mine drainage remediation.
- Sulfate reducing bacteria have little effect on Mn removal.
- Biochar can protect bacteria in heavy metals conditions by rapid removal of heavy metals.
- Algae growth may be inhibited by biochar in acid mine drainage conditions.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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