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Published PDF deposited in Coventry University's Repository

Original citation:

Du, T, Bogush, A, Mašek, O, Purton, S & Campos, LC 2022, 'Algae, biochar and bacteria for acid mine drainage (AMD) remediation: A review', *Chemosphere*, vol. 304, 135284. <https://doi.org/10.1016/j.chemosphere.2022.135284>

DOI 10.1016/j.chemosphere.2022.135284

ISSN 0045-6535

Publisher: Elsevier

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

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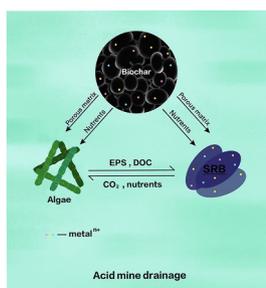
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HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Y Yeomin Yoon

Keywords:

Acid mine drainage
Treatment
Sulfate reducing bacteria
Bioremediation
Heavy metal

ABSTRACT

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

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Abbreviations

AMD	Acid mine drainage
BET	Brunauer-Emmett-Teller
EDX	Energy Dispersive X-ray Analysis
EPS	Extracellular Polymeric Substances
FTIR	Fourier Transform Infrared
ROS	Reactive Oxygen Species
SEM-EDX	Scanning Electron Microscopy with Energy Dispersive X-ray Analysis
SRB	Sulfate reducing bacteria
XRD	X-ray Diffraction Analysis
ZVC	Zero-valent copper
ZVI	Zero-valent iron

1. Introduction

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

Acid mine drainage is harmful to humans, animals, plants, and aquatic life (Bogush and Lazareva, 2011; Kumari et al., 2010). For example, AMD causes fish death by affecting the function of the gills, and increased turbidity from soil erosion and precipitation layering on the riverbed can change the habitat for aquatic organisms (Bogush and Lazareva, 2011; Kumari et al., 2010). Some metals produced from the mining industry, such as Cd, Pb, Cu, Zn, Ni and Hg, can accumulate in the human body and cause serious diseases. For example, high levels of Hg in the body can cause Minamata disease, a neurological disease that can cause numbness, muscle weakness, and even death. Elevated Ni levels can cause a dry cough, chest pain, and nausea. High Pb levels in humans can damage the nervous system and cause intellectual disability, and high levels of Zn in the human body can cause vomiting, skin inflammation and fever (Carolin et al., 2017). The biology of plants and aquatic life can also be affected by metal toxicity. Furthermore, these organisms not only act as receptors of the contamination but also as a pathway to humans via food chains (Kumari et al., 2010). Even if the contamination comes from a single point source, the impacts are not restricted to the local area but can also affect distant regions, as water can carry the contamination along rivers or streams (Bogush and Lazareva, 2011; Kumari et al., 2010).

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

(Johnston et al., 2008). For instance, the Parys Mountain copper mine on the Welsh island of Anglesey discharges 24 tonnes of Zn and 10 tonnes of Cu into the Irish sea every year (Johnston et al., 2008). Because of these abandoned mining sites, 315 out of 7816 water bodies in the UK, equating to 2840 km of rivers, are contaminated or potentially contaminated by AMD (Abinandan et al., 2018; Johnston et al., 2008; Jones et al., 2016).

There are several established methods for treating AMD such as precipitation, ion exchange, electrochemical, and membrane separation (Alcolea et al., 2012; Genty et al., 2012; Taylor et al., 2005). For instance, the open limestone channels (OLC) method uses a channel filled with limestone fragments to neutralise and increase the alkalinity of AMD (Alcolea et al., 2012); anoxic limestone drains (ALD) are buried limestone drainage lines with a gentle slope, sealed with a low permeability liner and capped with clay to ensure air cannot flow into the drain during operation (Taylor et al., 2005). These treatments have advantages, including low cost and ease of management. However, they also have certain limitations, for example, the need for a high quantity of limestone and also the generation of a large amount of sludge (secondary contamination), low efficacy, the inability to remove all metals/metalloids, and the need for a relatively large area (Alcolea et al., 2012; Bogush et al., 2016; Dufresne et al., 2015). Therefore, bio-based treatment approaches for AMD should be considered as an attractive alternative due to their higher efficiency, lower secondary contamination and potentially lower costs (Kim et al., 2014b).

Bio-based treatment generally refers to the use of either dead/processed or living biomass to reduce and remove heavy metals from AMD (Kim et al., 2014b). The common and suitable bio-based materials usually include algae, biochar, and bacteria (Cai et al., 2021; Loreto et al., 2021; Orandi et al., 2012). It is proven that each of these three treatments can remove metals from AMD effectively and are cost-effective. However, the main bottlenecks of these three AMD treatments are the lack of industrial AMD water treatment case studies for algae, the use of rudimentary technologies in biochar recycling and recovery of metals from biochar, and the need for highly effective carbon sources for preparing immobilised sulfate reducing bacteria (SRB) (Almomani and Bhosale, 2021; Di et al., 2022; Shirvanimoghaddam et al., 2022).

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

2. Algae application in AMD treatment

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

2.1. Mechanism of metal removal by algae

The process of heavy metal sorption by algae is complex. Generally, two stages are involved (Bwapwa et al., 2017). The first is extracellular sorption, which is rapid and can be assumed to be passive. This happens immediately after algae are in contact with metals and involve the following mechanisms: the interaction between metal ions and anionic cell ligands, micro-precipitation, surface complexing, covalent bonds between metal ions and proteins and other polymers. The second stage is

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> 2. <i>Klebsormidium klebsii</i> 3. <i>Microspora tumidula</i>	Field growth and laboratory experiment	Al 4.8, Fe 79, Mn 51, Zn 550	In all study pH conditions, <i>Oedogonium crissum</i> was considered to have the highest metal bioaccumulation rate	Oberholster et al. (2014)
<i>Stichococcus bacillaris</i> <i>Sargassum</i> sp.	Porous Substrate Bioreactor (PSBR) Laboratory experiment	Zn 2.0–3.0 Cu 20, Cr 20	Zn 15–19 mg g ⁻¹ Cu 71.4 mg g ⁻¹	Li et al. (2015) 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)
<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)
<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)
1. <i>Phormidium ambiguum</i> 2. <i>Pseudochlorococum typicum</i> 3. <i>Scenedesmus quadricauda</i> var <i>quadrispina</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)
<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> 2. <i>Chlorella vulgaris</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)

intracellular accumulation. This is slower than the first stage and is assumed to be active. The mechanisms involved are species-specific and include, for example, phytochelation, which forms a metal complex. Fig. 1 illustrates some of the mechanisms of metal removal by algae.

Heavy metals are incorporated into algal vacuoles and then bonded with proteins, DNA, and lipids. Also, algae cells, especially some resistance cells, can effuse toxic metal complex substances, for example, Cu and Cd (da Costa and de França, 2003; Levy et al., 2008; Worms et al., 2006). In

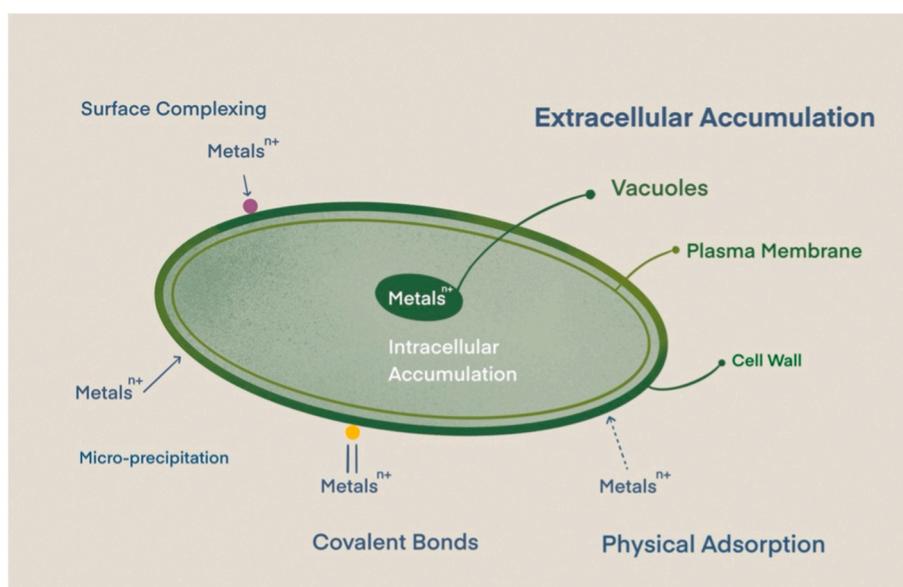


Fig. 1. The mechanisms of heavy metal removal by algae. Extracellular accumulation includes surface complexing, micro-precipitation, covalent bonds, and physical adsorption.

addition, cell walls, nuclei, mitochondria, chloroplasts, and some other parts of the cell may be reinforced by the membrane, which works as a barrier in adapted cells (Chen et al., 2012; Sandau et al., 1996; Tam et al., 1998). In these two stages, some of the metals are bound to the surface, and others may be accumulated within cell due to metals' type and algae growth preference (Du et al., 2022). Surface adsorption is essential since it represents the largest portion of the absorption process (Chojnacka et al., 2005). Still, the relative importance of surface adsorption may vary depending on the metals and algae (Du et al., 2022). Nevertheless, the complexity of the algae surface makes it possible for various mechanisms to operate simultaneously (Monteiro et al., 2012). Generally, the ability to remove metals by different algal groups shows a decreasing order of *Chlorophyta* > *Phaeophyta* > *Rhodophyta* (Al-Shwafi and Rushdi, 2008). However, knowledge of the distribution of metals in/on the algal cell and the stage involved in metal removal processes still needs to be explored.

2.2. Parameters that affect removal capacity by algae

a) pH

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

The differing optimal pH values for metal removal found in the different studies reflect the different metal chemistry and different functional groups involved in the metal removal process. Each functional group has distinct pH ranges for binding metal cations (Monteiro et al., 2012). Under acidic conditions, a positive charge and protonation will happen for specific functional groups associated with H⁺ because of the repulsive forces (Khoubestani et al., 2015; Monteiro et al., 2012). Thus, some functional groups are only available within a specific pH value. For instance, carboxyl groups dominate at pH 2–5; phosphate becomes the main group at pH 5–9, while when the pH increases to 9 and then up to 12, carboxyl, phosphate, and hydroxyl/amine groups are all available (Bansod and Nandkar, 2016; Monteiro et al., 2012). The general agreement is that at low pH, positively charged algae surfaces are the main contributors to biosorption because the binding sites, surrounded by H⁺, attract metal ions towards the algal surface. However, when the pH increases above 4.0, some divalent metals, e.g. Zn and Cu, readily precipitate as hydroxide, thus reducing biosorption (Bansod and Nandkar, 2016). In most cases, the initial pH of AMD is lower than 4.0. Thus, strategies on how to reduce the negative effects caused by low pH when exploring metal removal by algae should be considered, for example, isolation of superior strains.

b) Initial metal ion concentration

Initial metal ion concentration is another critical parameter that can affect the efficiency of algae in treating AMD. Most studies suggest that metal uptake positively correlates with the initial metal ion concentration (Al-Rub et al., 2004; Monteiro et al., 2009, 2012). This is due to higher initial metals concentration contributing to higher driving force, which can overcome mass transfer resistances of metal ions between biomass and solution and promote uptake (Al-Rub et al., 2004; Cruz et al., 2004). Also, collisions between biomass and metal ions increase under higher metal concentrations, enhancing the metal uptake process (Al-Rub et al., 2004). Monteiro et al. (2011) found that the total Zn

removal by *Scenedesmus obliquus* (mg Zn g⁻¹ algae) increased more than ten-fold when the initial Zn concentration was increased from 10 mg L⁻¹ to 75 mg L⁻¹. However, metal absorption is more effective at a lower initial metal concentration. For example, Monteiro et al. (2009) reported that, although *Desmodesmus pleiomorphus* adsorbed and totally removed more Zn at the higher initial Zn concentration, it had higher removal efficacy of Zn at a relative lower Zn concentration (1 mg L⁻¹) than higher Zn concentration (5–30 mg L⁻¹). This is because more binding sites are available when the metal concentration is low (Khoubestani et al., 2015; Mehta and Gaur, 2005). Nevertheless, the weakness of the two studies conducted by Monteiro et al. (2011, 2009) is that the Zn concentration set in these studies was relatively low, which cannot fully explain the relationship between initial ion concentration and metal removal especially at high metal concentrations.

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

c) Temperature

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

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

Another group of studies observed almost no effect of temperature change on algae sorption. For example, Cossich et al. (2002) reported that the use of *Sargassum* to remove Cr showed the effect of temperature was not as significant as the effect of pH. Likewise, these relationships between temperature and metal removal were also reported by Mehta and Gaur (2005). Overall, the general relationship between temperature and metal removal effectiveness by algae is still unclear based on the discussion above. For example, the types of algae and metal may both affect the results. Also, seasonal parameters, such as precipitation and runoff, may cause the initial metal ion concentration and temperature to vary with time in AMD sites (Du et al., 2022). Therefore, a clear relationship between temperature and metal removal efficiency should be investigated for different combinations of metals and algal species, especially in practical AMD conditions.

d) Biomass concentration

Biomass concentration of algae can have significant effects on metal removal. Mehta and Gaur (2005) reviewed several previous studies and indicated that the cell concentration of *Chlorella* sp. negatively correlates with the binding of Cd per unit of mass. Similarly, they reported a decreased sorption capacity per unit of mass of Cu and Ni by increasing

the *Chlorella vulgaris* concentration and decreased Pb sorption by increasing *Spirulina maxima*. Monteiro et al. (2012) reviewed some studies and reported this negative correlation. According to the literature, in most conditions, the biomass concentration and metal adsorption capacity negatively correlate per unit mass. The reason for this may be that the increase of biomass can lead to its partial aggregation thus reducing the surface area for adsorption, and the increase of biomass can also decrease the distance between the available adsorption sites (Monteiro et al., 2012).

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

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

3. Biochar application in AMD treatment

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

3.1. Heavy metal removal mechanisms

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

Surface precipitation between metal ions and mineral components (anions) such as PO_4^{3-} , CO_3^{2-} and OH^- is an essential mechanism in biochar metal removal (Cui et al., 2016). Tran et al. (2016) studied the effects of orange peel biochar on Cd^{2+} removal. They found that Cd^{2+} was removed by surface precipitation, as $(\text{Cd}, \text{Ca})\text{CO}_3$ and Cd_3CO_3 were found by XRD after the experiments. Also, the EDX results showed that Ca remained on the surface of biochar, confirming surface precipitation. The same results of Cd^{2+} removal were also reported by Cui et al. (2016) in an experiment conducted using biochar from *Canna indica*. In addition, Cui et al. (2016) found that CO_3^{2-} was the dominant mineral component when biochar was produced at a relatively high pyrolysis temperature ($>500^\circ\text{C}$). More CO_3^{2-} can be released into the solution due to the incomplete cracking of carboxyl when the biochar pyrolysis temperature is high, resulting in Cd^{2+} precipitating with ligands (Cui et al., 2016). Likewise, another study using a pistachio green hull biochar to remove Cu gave similar results (Jalayeri and Pepe, 2019). They reported that Cu-P, Cu-C and Cu-Si were formed during experiments. The SEM-EDX image showed C, O, Cu, P, S, Si, Fe and Ca on the biochar surface, and the FTIR spectra showed the characteristic peaks of PO_4^{3-} and CO_3^{2-} , confirming this result.

Ion exchange, complexation, and electrostatic interaction are all associated with functional groups on biochar (Tan et al., 2015). Under different pH conditions, there would be various mechanisms for different metals. For example, Abdel-Fattah et al. (2015) compared the simultaneous removal of Mg^{2+} , Ca^{2+} , Pb^{2+} and Cr^{6+} by pinewood

biochar in solution. They found that at a pH of 6.0–7.0, Mg^{2+} , Ca^{2+} and Pb^{2+} were mainly removed by complexation with $\text{C}=\text{O}$, $\text{C}-\text{O}$ and phenolic $\text{O}-\text{H}$ functional groups. In addition, it is worth noticing that complexation between oxygen-containing functional groups and heavy metals may be accompanied by H^+ release (Ding et al., 2016). The H^+ release would decrease the solution pH, which can be used as evidence to determine if this complexation happened during the adsorption process (Tran et al., 2016).

However, in acid conditions (pH 1.0) the mechanism of Cr^{6+} removal was mainly electrostatic interaction between positively charged functional groups and negatively charged chromate ion (CrO_4^{2-}) (Abdel-Fattah et al., 2015). This can be explained by the fact that under low pH values, the biochar surface is highly protonated, which promotes electrostatic interaction between ions. Conversely, under high pH, biochar surface protonation is reduced to the lowest level. This condition may contribute to the complexation between oxygen donors in functional groups and metal ions (Abdel-Fattah et al., 2015).

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

3.2. Novel developments of biochar for AMD treatment

Novel developments of biochar focus mainly on pyrolysis methods and modification processes. Compared with conventional pyrolysis methods, some new trends of pyrolysis can improve the removal capacity of biochar (Wang et al., 2020). For example, Wang et al. (2020) mentioned that microwave-assisted pyrolysis could change biochar morphology (for example, surface area) to make it more suitable for removing metals and organic pollutants. In addition, microwave pyrolysis can increase the number of biochar functional groups, contributing to metal adsorption (Shirvanimoghaddam et al., 2022). Hydrothermal pyrolysis is another novel pyrolysis method, used mainly for feedstock with high water content, such as animal excreta and sewage sludge (Shan et al., 2020). This method usually heats the feedstock at a relatively low temperature (120–250 °C) without pre-drying (Xiang et al., 2020). Wang et al. (2020) reviewed several studies on hydrothermal pyrolysis biochar and concluded that hydrothermal pyrolysis could introduce more oxygen-containing functional groups ($-\text{OH}$ and $-\text{COOH}$) into biochar. Furthermore, hydrothermal pyrolysis is a cost-effective and simple method, due to its lower heating temperature, and there is no requirement for oxygen-limited conditions.

Recently, novel modification methods have enhanced biochar performance in metal removal. Yin et al. (2022) compared three types of oxidant-modified *Platanus orientalis* Linn leaf biochar (modified by H_2O_2 , KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, respectively) for Cd removal. Among these three types of biochar, the KMnO_4 modified biochar had the best performance in removing Cd. It removed 98.57% of Cd with the highest adsorption capacity of 54.7 mg g^{-1} . BET and FTIR analyses confirmed that KMnO_4 modified biochar had a higher specific surface, and MnO_x

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	Wang et al. (2015)
Sugar cane	500	Pb 6.0-223	Pb 87.0 mg g ⁻¹	Abdelhafez and Li (2016)
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	Kiliç 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)
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)
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)
Platanus orientalis 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)
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)
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)
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 1 mg g ⁻¹ , Zn 34.0 mg g ⁻¹ , Cr 65 mg g ⁻¹	Park et al. (2016)
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. (2021b)
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)
Spent coffee grounds	400	Cd 0.228, Cu 0.194, Pb 0.0156, Zn 0.0222	Cd 99%, Cu 88%, Pb >99%, Zn 99%	Kim et al. (2014c)
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, Robinia pseudoacacia	500, Fe/Zn modification	Cd 30-300	Cd Durian shell biochar 99.81%, Robinia pseudoacacia biochar 71.08%	Yang et al. (2021a)

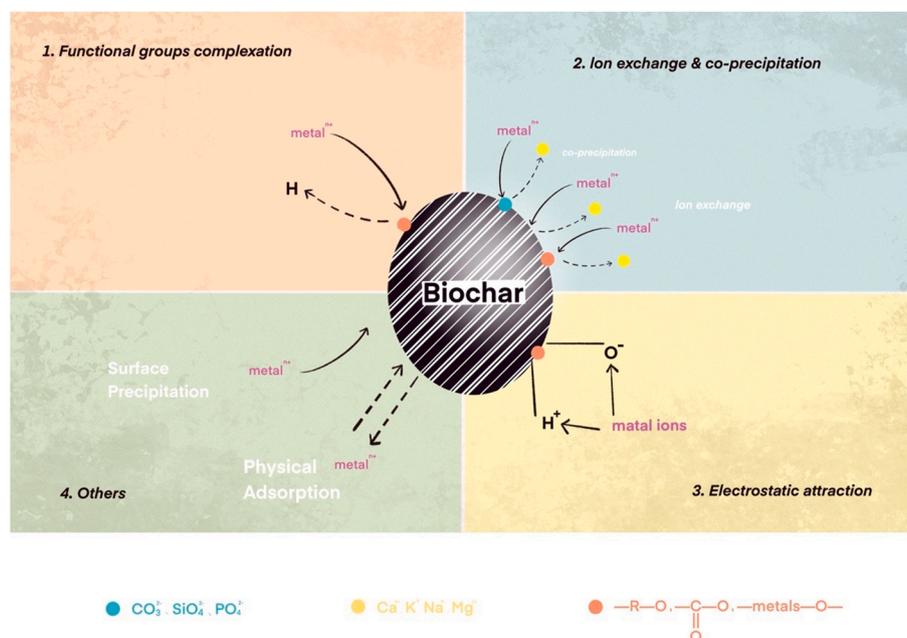


Fig. 2. The mechanisms of heavy metal removal by biochar, modified from Tan et al. (2015).

introduced by $KMnO_4$ can form inner-sphere complexes with oxygen-containing groups and has a strong affinity for metal cations (Yin et al., 2022). Ahmed et al. (2021) modified watermelon seed biochar with 30% H_2O_2 and used it to remove Pb from the synthetic AMD water. Results showed that the H_2O_2 could introduce more hydroxyl and carboxyl groups to modified biochar, with a higher adsorption capacity ($25.57\text{--}44.74\text{ mg g}^{-1}$) than unmodified biochar ($10.82\text{--}32.07\text{ mg g}^{-1}$). In addition, Wang et al. (2021a) investigated Pb removal by K_2FeO_4 modified sludge biochar. The adsorption capacity of K_2FeO_4 modified biochar was found to be six times higher than the original biochar due to much more numbers of functional groups on the modified biochar.

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

For the modified biochars mentioned above, almost all studies found that modified biochar has a faster adsorption process when used for AMD treatment. Ahmed et al. (2021), Wang et al. (2021a) and Yin et al. (2022) confirmed that the modified biochar could reach the adsorption equilibrium within 1 h, while conventional biochar may need 2–12 h. The rapid adsorption process is caused by the number of pore channels and functional groups on the modified biochar that is sufficient to provide active sites (Yin et al., 2022).

In terms of pH, some modified biochar can still be affected by low pH conditions. In general, the favourable pH for maximum adsorption is around 4–5 (Ahmed et al., 2021; Yin et al., 2022). One reason for this is that, in acid conditions, H^+ can inhibit metal removal by strongly competing with metal ions for adsorption, resulting in lower adsorption capacity (Yin et al., 2022). This competition may also happen when using conventional biochar in a lower condition. However, Ahmed et al.

(2021) reported that competition for active sites between metal ions and protons may happen in acidic conditions at the initial stages. Nevertheless, the effect of H^+ is considered a promoting factor at a low pH range. They also reported that electrostatic repulsion has an inhibitory effect on metal adsorption at low pH. The same reason (electrostatic repulsion) is also mentioned in Cr adsorption by a nanoscale FeS/chitosan biochar (Yang et al., 2021b)). However, some modified biochar is not affected by extreme low pH and can reach the maximum adsorption. For example, Wang et al. (2021a) mentioned that K_2FeO_4 modified sludge biochar could reach the maximum Pb adsorption capacity at pH 2. Yang et al. (2021b) also reported nanoscale biochar could achieve the maximum adsorption of Cr at pH 2. Compared with other modified and conventional biochars, these biochars have a large abundance of functional groups to resist the effects caused by low pH, which provides more opportunities for complexation (Yang et al., 2021b). Thus, some modified biochar may solve the problems caused by extreme low pH, which can be an excellent advantage when used for AMD treatment.

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

3.3. Parameters that affect biochar adsorption capacity

a) Initial heavy metal concentration

The initial heavy metal concentration in AMD solution can affect the adsorption capacity of biochar. Liu and Zhang (2009) showed that with Pb concentration increasing from 10 mg L^{-1} to 20 mg L^{-1} , the adsorption capacity increased approximately two-fold for pinewood and rice husk biochars. Kılıç et al. (2013) used almond shell biochar (produced at $600\text{ }^\circ\text{C}$) to remove Ni and Co and found similar trends. However, Pellera et al. (2012) showed that increasing the initial Cu concentration caused an increase in Cu removal per mass unit by biochar but a decrease in total Cu removal produced from rice husk, olive pomace, orange peel, and compost. The observed positive relationship between initial metal

concentration and biochar adsorption capacity may have two explanations: firstly, the increased metal concentration may increase the possibility of metal ions coming into contact with biochar; secondly, the increase might be due to more metal ions in the solution inducing the release of H^+ from the surface of biochar, which then leads to more adsorption sites on the biochar (Abdelhafez and Li, 2016; Liu and Zhang, 2009). Also, increasing metal concentration can increase the driving force of mass transfer, which can cause increased metal removal per mass unit (Pellera et al., 2012). The decrease in metal removal by biochar may be explained by the saturation of active sites on the biochar surface (Pellera et al., 2012).

b) Biochar dosage

Many studies have suggested that the biochar dosage is a critical parameter that can affect the heavy metal removal capacity of biochar. Most of the literature found that an increased ratio of biochar to water increased the total amount of heavy metal removal but decreased the biochar removal efficiency. For example, Chen et al. (2011) reported that in a Cu removal experiment by corn straw biochar, the biochar adsorption dropped from 11.82 mg g^{-1} to 1.18 mg g^{-1} when increasing the biochar concentration from 1 g L^{-1} to 50 g L^{-1} . Meanwhile, the Cu removal rate increased from 19.7% to 98.3% due to the increased biochar concentration. These findings are supported by other studies (Pellera et al., 2012; Regmi et al., 2012; Wang et al., 2015b). Based on the findings from the literature, it is important to use appropriate biochar dosages when removing metal, particularly for practical use. Appropriate biochar dosage can be cost-effective and yield maximum results.

c) pH of contaminated water

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

Furthermore, other processes, such as metal precipitation/co-precipitation, can occur at higher pH levels ($\text{pH} > 8$) (Park et al., 2017). In contrast, Abdel-Fattah et al. (2015) showed that Cr removal by pinewood biochar (5 g L^{-1}) reached maximum capacity (35.4 mg g^{-1}) at pH of 1. At low pH, the protonation favours the formation of an ion-pair interaction mechanism between chromate anions ($HCrO_4^-$) and the positively charged functional groups (Shaheen et al., 2019).

4. Bacteria application in AMD treatment

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

4.1. Mechanisms of metal removal by sulfate reducing bacteria

Recent studies have focused on biological methods for removing

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

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

4.2. Metals toxicity affecting sulfate reducing bacteria

Although SRB can successfully remove heavy metals from AMDs, some studies found that heavy metals may be toxic to SRB (Alam and McPhedran, 2019; Kiran et al., 2017, 2018; Teng et al., 2016; Wang et al., 2019; Zhang et al., 2016; Zhao et al., 2018). Alam and McPhedran (2019) summarised the findings of several studies regarding metal toxicity to SRB and pointed out that heavy metals mainly influence the activity of enzymes, induce protein denaturation, and compete with cations. These studies also indicated that different metals have different toxicity levels to SRB. For example, Alam and McPhedran (2019) showed that Cd (6 mg L^{-1}), Cr (23 mg L^{-1}), Cu (4 mg L^{-1}), Pb (25 mg L^{-1}), Ni (10 mg L^{-1}) and Zn (13 mg L^{-1}) could inhibit the activity of SRB. However, Zhao et al. (2018) reported that, at 35°C and pH 3, Cu is toxic to SRB at 10 mg L^{-1} . In the study of Teng et al. (2016), Zn was found to have an inhibitory effect on SRB when concentrations reached 40 mg L^{-1} .

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

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

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)
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)
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	Biominalization system	Fe 4378	Fe 89%	Wang et al. (2021b)
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)
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%	Viggi et al. (2010)
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)
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%	Kim et al. (2014a)
<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)
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)
SRB	Sodium lactate		Cu and Zn 50-150	Cu 99%, Zn 95.8%	Kiran et al. (2018)

(continued on next page)

Table 3 (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 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)
<i>Hermoacidophilic 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)
Fe–Mn oxidising bacteria (<i>Flavobacterium, Brevundimonas, 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>	—	Laboratory-scale experiment	Fe 1267	Fe 100%	Jin et al. (2020)
<i>Acidithiobacillus ferrooxidans</i>	—	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)

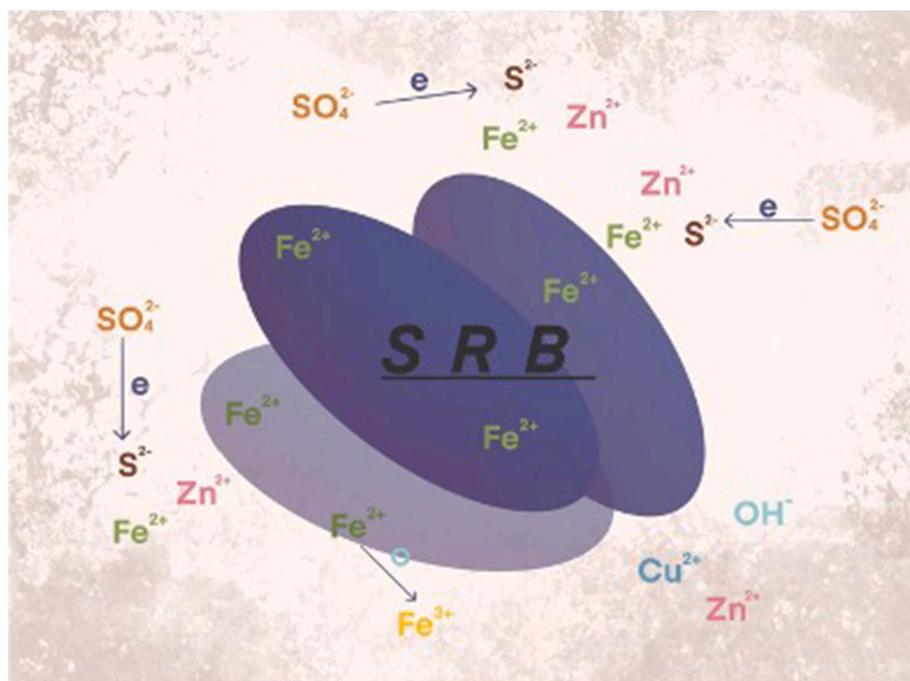


Fig. 3. Proposed mechanism for bioremoval of heavy metal ions by SRB, modified from Zhao et al. (2018).

environment adaptation (Kaksonen and Puhakka, 2007).

In order to avoid the toxicity effects on SRB, some studies have used SRB immobilised in beads (Kiran et al., 2018; Zhang et al., 2016). These beads consisted of a mixture of SRB, maize straw, zero valence iron, silicon sand, polyvinyl alcohol (PVA), and sodium alginate. Immobilised SRB beads provided shelter for SRB, as well as a relatively high specific surface area (Kiran et al., 2018). In addition, immobilised SRB beads can increase biomass and retention time in reactors (Kiran et al., 2018; Zhang et al., 2016). Thus, the SRB immobilised beads can be used to avoid the toxicity effect on SRB caused by a high concentration of heavy

metals (Zhang et al., 2016). To increase the efficacy of SRB, other methods to reduce the effect of metals' toxicity should be explored in future work.

4.3. Metals removal by SRB

Some metals such as Cu, Fe, Cd, Zn, and Pb can be almost entirely removed from AMD by SRB, while SRB's ability to remove Mn is more varied among published studies (Table 3). The removal efficiency of Mn in the solution was only around 50%, compared to the over 80% for

other metals that has been reported by some authors (Bai et al., 2013; Muhammad et al., 2018; Sahinkaya et al., 2013; Zhang and Wang, 2014). There are two possible reasons for these observations. The first is the potentially lower sorption affinity of Mn to organic waste (carbon source). The second reason is the relatively higher solubility of MnS ($K_{sp} = 2.5 \times 10^{-13}$) compared to the sulfide salt of other metals (Cd, Cu, Zn, and Fe). Thus, Mn^{2+} concentration is higher than other metals in the water. Mn^{2+} presented in a dissolved state for almost the entire reaction time (Muhammad et al., 2018), causing the removal efficiency to be decreased (Zhang and Wang, 2014). Also, because of the complex interaction between Mn and other metals, this solubility of Mn might be affected (Muhammad et al., 2018). However, Mukhethwa et al. (2019) reported that Mn removal efficiency could reach 85.9%, which is much higher than the results obtained in previous studies (~50%). Unfortunately, the reason for this is not clear.

The studies mentioned above did not investigate all experimental parameters in their studies, and the higher removal efficiency (80.7%) had a better condition for SRB (pH 6 and 30 °C) than that of the lower efficiency (74.8%), with conditions of pH 5 for 30 °C and 10 °C. Thus, further research needs to be carried out to confirm whether pH and temperature conditions can affect Mn removal by SRB.

4.4. Carbon source and electron donor

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

In addition to these simple carbon sources (lactate and ethanol), some studies have used complex organic matter, such as organic waste (e.g. maize straw, leaves and cow manure) as carbon source (Choudhary and Sheoran, 2012; Vigi et al., 2010; Giachini et al., 2018; Kim et al., 2014a; Muhammad et al., 2018; Sahinkaya et al., 2013; Zhang et al., 2016). These organic sources are cheap and can contribute to metal removal because most of them are porous materials. There is evidence that SRB could be enhanced by using complex organic carbon sources (Nielsen et al., 2019). Another advantage of complex organic carbon sources is that they can last longer than simple carbon sources due to their more gradual degradation. Nevertheless, for complex carbon sources, a disadvantage is that sulfate removal yields are lower than those of simple carbon sources (Nielsen et al., 2019).

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

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

5. Combination of treatments for AMD

5.1. Combination of algae and biochar

Some studies reported the interactions between biochar and algae (Awad et al., 2017; Jia et al., 2018; Kholssi et al., 2018; Magee et al., 2013; Zhang et al., 2019). In terms of the inhibitory effects between biochar and algae, the result showed that in some conditions, biochar could significantly inhibit the growth of algae. For example, Awad et al. (2017) reported that rice husk biochar might reduce the production of green algae (*Chlamydomonas* sp and *Scenedesmus* sp); Zhang et al. (2019) noted that pine needle biochar has adverse effects on algae growth (*Scenedesmus obliquus*, and also the bacterium *Photobacterium phosphoreum*) due to the presence of free radicals; Magee et al. (2013) confirmed that oil mallee biochar could also inhibit the growth of the test algae (*Chlorella vulgaris*) when adding the biochar at an induction phase (12 h after incubation of algae); Similar results were also reported by Jia et al. (2018) on the interaction between apple tree biochar and three species of cyanobacteria (*Oscillatoria* sp, *Phormidium* sp and *Nostoc* sp). However, in Kholssi et al. (2018)'s study, the growth of *Anabaena cylindrica* significantly increased with wood biochar solid support compared with liquid media.

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

Based on these findings, positive effects between algae and biochar are only valid for specific algae and biochar (Kholssi et al., 2018). Some biochar can boost more extracellular polymeric substances (EPS) of algal origin. These EPS may provide important biological functions by excluding redundant glycogen in algal cells and promote increases in cell numbers (Kholssi et al., 2018). Also, functional groups on the biochar surface may contribute to the immobilisation of algae and promote algal growth (Shen et al., 2017). In addition, although the porous structure of biochar may have adverse effects on algal growth, porous biochar can serve as a suitable material for attachment and increase the dispersibility of immobilised algae, thus increasing metal sorption processes (Shen et al., 2017). Besides, quick passive adsorption by biochar can increase the viability of algal cells and, as a result, enhance the metal removal capacity (Shen et al., 2017).

Based on the work reviewed, the biochar-algae system in AMD metal removal has been rarely studied. Two studies did a simple mixture of algae and biochar to remove metals in the solution (Jiang et al., 2022; Shen et al., 2017). Shen et al. (2017) used a combination of *Chlorella* sp. and water hyacinth biochar to investigate Cd removal. The algae and

biochar were mixed with a shaker in different algae: biochar ratios (1:4, 2:3, 3:2 and 4:1), and the Cd removal was measured. It was found that the algal cells were mainly attached to the biochar surface. For the Cd removal results, the maximum removal was 217.4 mg g^{-1} when the algae and biochar ratio reached 2:3. This result was better than the metal removals obtained for algae only (169.9 mg g^{-1}) or biochar only (95.8 mg g^{-1}). Likewise, Jiang et al. (2022) performed a similar study using a simple mixture of *Chlorella* sp. and coconut shell biochar to remove Cd from synthetic AMD water. SEM morphology results showed algae were attached very well to the visible pores on the biochar surface. The results also showed that the biochar pores become rough after Cd adsorption. When using algae and biochar together, the biochar became much rougher after Cd adsorption than only biochar adsorption. This also indicated that algae-biochar Cd adsorption had better Cd removal results than Cd adsorption by biochar only. Better Cd removals with a mixture of algae and biochar were due to 1) the algae-biochar consortium has a more negative charge on the surface. Also, the negative charge of the biochar surface can boost the magnetic intensity surrounding the algae, which can enhance the surface potential of biochar (Shen et al., 2017); 2) FTIR results confirmed that the algae-biochar consortium has more types and greater numbers, of functional groups (especially oxygen-containing functional groups) when compared to biochar or algae alone, which may significantly contribute to the removal of Cd (Jiang et al., 2022; Shen et al., 2017). The two studies mentioned above have confirmed that the biochar-algae mixture may have a higher removal efficacy of Cd in solution. However, due to limited studies of algae-biochar consortia on metal removal from AMD, more studies should be conducted in the future to investigate the removal efficacy of this approach to develop new preparation methods for combining algae and biochar. These preparation methods would reduce the potential inhibition of algae growth caused by biochar and potential blockage of the biochar pores by algae, as well as reducing the algae growth-inhibition caused by biochar, to optimise the metal removal result.

5.2. Combination of algae and bacteria

Several studies also used a combination of algae and bacteria for AMD treatment. Sahoo et al. (2020) reported that an integrated bacteria (SRB)-algal (*Chlorella* sp.) immobilised technology could remove over 95%–99% of metals from AMD in both aerobic and anaerobic conditions. The same technology was also used by Li et al. (2018a), who confirmed that an immobilised SRB-algae (*Scenedesmus obliquus*) bead technology could remove up to 73.58% of sulfate and 98% of Cu. Similar results (74.4% of sulfate and 91.7% of Cu) were also reported by Li et al. (2018a) with the same immobilised technology in the anaerobic reactor (*Chlorella vulgaris*, *Scenedesmus obliquus*, *Selenastrum capricornutum* and *Anabaena spiroides* with SRB). In addition, Ayala-Parra et al. (2016b) reported that a permeable reactive barrier (PRB) technology with SRB and *Chlorella sorokiniana* could remove over 99.5% of Cu from AMD.

Russell et al. (2003) experimented with combining SRB with *Carteria* sp. and *Scenedesmus* sp. for metal removal. The U and Mn were successfully removed, but only *Scenedesmus* sp. showed a relatively high sulfate reduction rate (94.3 g g^{-1} biomass), compared with *Carteria* sp. (43.5 g g^{-1} biomass).

In the algae-SRB system, some studies confirmed that algae could serve as an organic carbon source for SRB (Ayala-Parra et al., 2016b; Das et al., 2009a,b; Faisal et al., 2020; Li et al., 2018a,b; Russell et al., 2003). SRBs are carbon limited in a natural AMD environment and need additional carbon sources for survival and metal removal. Algae can generate dissolved organic carbon by photosynthesis to feed the SRB under the action of co-existing anaerobic fermentative bacteria (Das et al., 2009a; Li et al., 2018b). EPS produced by algae can also serve as nutrients for SRB (Das et al., 2009a). In return, CO_2 released by bacteria is utilised by algae for growth in AMD conditions (Abinandan et al., 2018). In addition, EPS produced by both microalgae and bacteria can chelate metal

ions, decreasing the concentration of the free form, which in turn makes the environment less challenging for the organisms to thrive in. From an evolutionary viewpoint, bacteria and algae support each other for survival, growth, and even metal removal and sulfate reduction in extreme conditions (Abinandan et al., 2018). The mutualism between SRB and algae for bioremediation in AMD conditions is shown in Fig. 4.

Nevertheless, in natural AMD conditions, the metal removal efficacy may be relatively low when using algae as the organic carbon source because other microorganisms compete for electron donors with SRB (Das et al., 2009a; Russell et al., 2003). Immobilised SRB-algae systems and reactors can increase the efficacy of metal removal by algae and SRB (Li et al., 2018a, 2018b; Sahoo et al., 2020). In an immobilised SRB-algae system, SRB can use the secreted carbon source provided by algae more efficiently because immobilised algae are in the vicinity of SRB (Li et al., 2018b). For example, a bioreactor (anaerobic up-flow reactor) can continuously provide a medium for SRB to grow and thus increase the metal removal efficiency (Li et al., 2018b). Thus, it can be concluded that the algae-bacteria system can have a high efficacy of metal removal when compared to individual algal or bacterial systems. Apart from the immobilised method, developing other ways to promote high effectiveness for SRB using algae as a carbon source is still needed.

5.3. Algae, bacteria, and biochar

The authors have not found any study that has applied algae, bacteria, and biochar as a consortium to remediate and recover metals from AMD. In a natural AMD environment, bacteria and algae can be present as a consortium (Bernardez and de Andrade Lima, 2015; Du et al., 2022). In addition, based on the discussion above, one novel aspect of our exploratory approach is to use biochar as a porous support medium for the growth of the algal-bacteria consortium (Fig. 5). Biochar can act as the “protective buffer” to provide a porous matrix for bacterial attachment since it can trigger rapid passive uptake of some heavy metal ions, leading to less damage to cells inside (Mehrotra et al., 2021; Retnasingrum et al., 2021). The algae could serve as a carbon source for bacteria (e.g. SRB), supporting their growth, which in turn produce key nutrients and CO_2 required for the photosynthetic algae. Biochar may not only provide a large surface area for biofilm production but may also facilitate low-cost harvesting of the metal-laden algae and subsequent recovery of the metal from ash by burning. Indeed, harvesting from bulk culture is one of the bottlenecks to the commercialisation of microalgal technologies, as there is no cost-effective harvesting method (Barros et al., 2015; Singh and Patidar, 2018). Moreover, biochar contains K, P, Ca, etc. and would therefore be able to function as a nutrition supply/growth medium for the consortium. Also, if AMD itself is inoculated with nutrients, it may be possible that the biochar will adsorb further nutrients due to its high adsorption capacity, attracting algae to grow on the surface of the biochar (Muñoz and Guieysse, 2006). With the right environmental conditions, biochar may enhance the self-aggregating process of algae-bacteria (Liu et al., 2017), providing an optimised method to remediate and recover metals from AMD. The algae-bacteria-biochar combination may be advantageous for use in AMD treatment with higher initial metal concentration (Mehrotra et al., 2021). Therefore, further research is recommended to explore the effectiveness of algae-bacteria-biochar consortium for AMD treatment.

6. Conclusion

6.1. Main findings

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

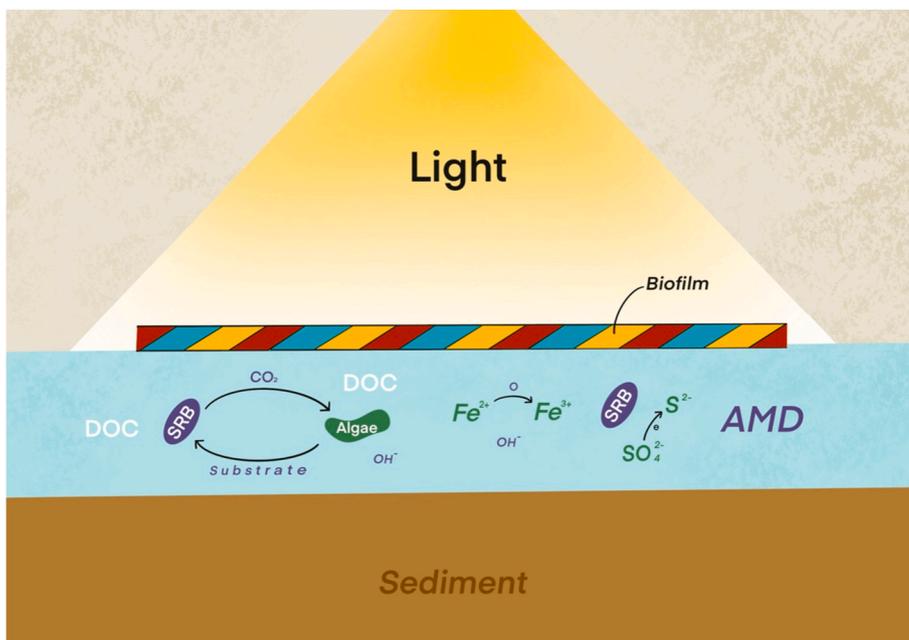


Fig. 4. Microalgal-bacteria synergism in biofilms of AMD, modified from Abinandan et al. (2018).

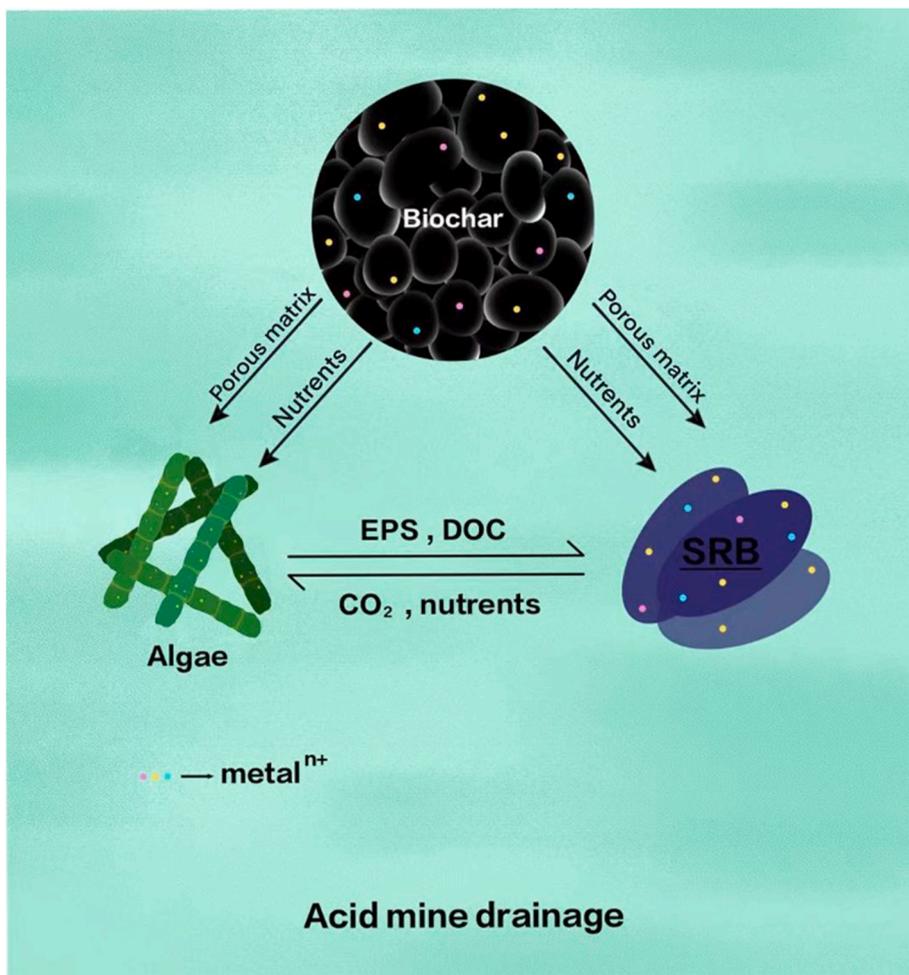


Fig. 5. The synergism of algae, bacteria, and biochar consortium in AMD.

- Most algae can reach at least 90% of removal efficacy via an extracellular stage and then an intracellular stage when removing Cu, Zn, Fe, Cd and Cr from AMD. *Chlorella vulgaris*, *Spirulina maxima*, *Oedogonium crissum* and some other types of algae were found to be effective (over 70 mg. g⁻¹) in metal removal from AMD.
- Feedstock and pyrolysis temperature are two factors that can affect biochar properties and influence the metal removal capacity of biochar. Most of the biochar, for example, hardwood and fruit peel biochar, can reach a relatively high metal removal efficacy (over 100 mg. g⁻¹). The mechanisms are mainly physical sorption, ion exchange, precipitation, complexation, and electrostatic interaction.
- SRB are the most common bacteria used in AMD treatments. It was found that SRB has high metal and sulfate removal ability (60%–100%), mainly by producing insoluble metal sulfide. SRB removal efficacy may be affected by the carbon source. In general, complex carbon sources such as lactate works better than simple carbon such as ethanol. In addition, *Acidithiobacillus ferrooxidans* was also found to be an effective bacterial method for Fe removal from AMD.
- The combination of the bio-based methods (i.e. algae-biochar and algae-bacteria) for AMD treatment was found to provide a relatively high removal efficiency (over 200 mg. g⁻¹). Such methods have been observed to have higher metal removal efficiency than those used as a single treatment.

6.2. Limitations and future research

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

- Algae may be inhibited by low pH when removing heavy metals from AMDs. Thus, it needs to be further investigated to facilitate treatment. For example, studies on isolating novel algae strains and modifying algae prior to treatment to avoid the effects caused by pH and increase the removal efficacy should be developed.
- The relationship between temperature and metal removal efficacy by algae is still unclear. Further studies may focus on this to clarify this relationship and establish the optimal temperature conditions for metal removal by algae.
- Secondary contamination and post-treatment recycling are the challenges in AMD treatments by using biochar. The development of novel modifications to overcome the limitations and increase metal removal capacity still needs to be considered in future work. Also, recycling methods of metals and biochar, especially nanoscale modified biochar, should be further investigated.
- When using bacteria in AMD treatment, the continuous addition of electron donors is still a limitation. This may reduce the effectiveness of remediation processes. Therefore, research may focus on effective alternative electron donors, such as slow-release electron donors and low sulfate condition electron donors. To reduce the toxicity caused by metals, the immobilised method for bacteria may be considered.
- No studies focusing on the algae-bacteria-biochar combination for AMD treatment were found. The authors of this review believe that this consortium may provide a more sustainable and effective process to remove and recover metals from AMD. Therefore, it is recommended that future studies investigate the potential of this consortium.
- However, biochar may inhibit algae's growth, and algae and bacteria may block the pore of biochar. Thus, preparation methods to combine algae, biochar, and bacteria as a consortium are required. Also, the recovery of metals through the consortium algae-biochar-bacteria should also be investigated. This should be tested in lab and pilot-scale experiments for future practical applications.

Author contributions

Tianhao Du: Investigation, Methodology, Writing – original draft,

Visualisation. **Anna Bogush:** Conceptualisation, Supervision, Writing – review & editing. **Ondrej Mašek:** Conceptualisation, Writing – review & editing. **Saul Purton:** Conceptualisation, Supervision, Writing – review & editing. **Luiza C. Campos:** Conceptualisation, Supervision, Project administration, Writing – review & editing.

Funding

This research has not received funds from any grant funding agency.

Declaration of conflicting interests

The authors declare that there is no conflict of interest.

Declaration of competing interest

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.

Data availability

No data was used for the research described in the article.

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