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Review

Review of Constructed Wetlands for Acid Mine Drainage Treatment

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Abstract: The mining industry is the major producer of acid mine drainage (AMD). The problem of AMD concerns at active and abandoned mine sites. Acid mine drainage needs to be treated since it can contaminate surface water. Constructed wetlands (CW), a passive treatment technology, combines naturally-occurring biogeochemical, geochemical, and physical processes. This technology can be used for the long-term remediation of AMD. The challenge is to overcome some factors, for instance, chemical characteristics of AMD such a high acidity and toxic metals concentrations, to achieve efficient CW systems. Design criteria, conformational arrangements, and careful selection of each component must be considered to achieve the treatment. The main objective of this review is to summarize the current advances, applications, and the prevalent difficulties and opportunities to apply the CW technology for AMD treatment. According to the cited literature, sub-surface CW (SS-CW) systems are suggested for an efficient AMD treatment. The synergistic interactions between CW components determine heavy metal removal from water solution. The microorganism-plant interaction is considered the most important since it implies symbiosis mechanisms for heavy metal removal and tolerance. In addition, formation of litter and biofilm layers contributes to heavy metal removal by adsorption mechanisms. The addition of organic amendments to the substrate material and AMD bacterial consortium inoculation are some of the strategies to improve heavy metal removal. Adequate experimental design from laboratory to full scale systems need to be used to optimize equilibria between CW components selection and construction and operational costs. The principal limitations for CW treating AMD is the toxicity effect that heavy metals produce on CW plants and microorganisms. However, these aspects can be solved partially by choosing carefully constructed wetlands components suitable for the AMD characteristics. From the economic point of view, a variety of factors affects the cost of constructed wetlands, such as: detention time, treatment goals, media type, pretreatment type, number of cells, source, and availability of gravel media, and land requirements, among others.

Keywords: acid mine drainage; constructed wetland; passive treatment; metal removal

1. Physical-Chemical and Toxicological Characterization of Acid Mine Drainage

Acid mine drainage (AMD) forms when sulfide minerals are exposed to oxidizing conditions during and following mining operations, highway construction, and other large-scale excavations [1,2].

Although wastewaters with this composition are produced by different industrial operations, the mining industry is the major producer of such effluents [3]. Oxidation of sulfidic rocks in open pits, dumps, and reservoirs/tailings deposits, and operating effluents generated during the extraction processes of minerals are the main sources of contamination by mining activity.

In the extraction processes, the volume of waste varies with the ore processed. In the case of extraction of Pb-Zn from massive sulfide-rich rocks, between 60 and 80% constitute waste; in the extraction of Cu from porphyry, 97%–99.5% of the rock is discarded and in the case of gold, only 1% of the extracted rock is processed [4]. When the residues are forming sulfides, their exposure to oxygen and water, accompanied by microbial activity leads to the formation of sulfate, metal, and acid drainage called AMD.

The oxidation of metal sulfides is generally explained by pyrite ($FeS_{2(s)}$), the most abundant mineral:

$$FeS_{2(s)} + \frac{15}{4}O_2 + \frac{7}{2}H_2O \rightarrow Fe(OH)_{3(S)} + 2SO_4^{2-} + 4H^+ \quad (1)$$

The decrease in pH, due to oxidized pyrite, can accelerate the oxidation of other sulfuric minerals, such as stibnite, argentite, and stannite. Moreover, the AMD can leach metals/ecotoxic metalloids from geological materials. The resultant ecotoxic ions and acidity are significant threats to water resources [5]. The formation of AMD will depend on interactions between the microbiology and the mineralogical and geochemical conditions of the site [4]; in the case of limestone and silicates, these can attenuate the contamination (by increasing the pH and/or affecting the solubility of metals).

The formation of acid drainage is a complex geochemical and microbially mediated process, function of microbiological controls, depositional environment, acid/base balance of the overburden, lithology, mineralogy, and mine site hydrologic conditions [2,6].

The potential for a mine or its associated waste to generate acid and release contaminants depends on site-specific factors that can be categorized in three: generation factors (water, oxygen, bacteria), chemical control factors (ability of the rock or receiving water to either neutralize the acid or to change the effluent character by adding metals ions mobilized by residual acid), and physical factors (particle size, permeability, and physical weathering characteristics, hydrology) (Figure 1).

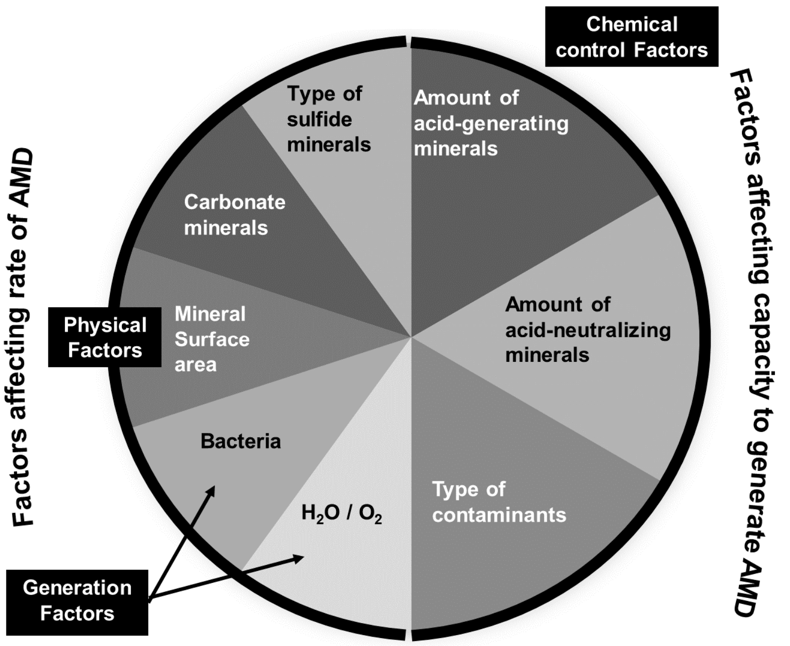

Figure 1. Factors that influence the formation of acid drainage.

There are methods to determine if a discrete volume of mining waste will generate acid and predict the quality of the drainage based on the rate of acid formation measured [7]. The results obtained from these methods can help to design an appropriate treatment system. Methods can be either static or kinetic tests. The former, predict drainage quality by comparing the sample maximum acid production potential (AP) with its maximum neutralization potential (NP) obtaining the net neutralization potential (NNP), NNP = NP − AP. A value of NNP < 0 indicates potential for the waste to form acid while a value of NP > 0 represents lower risk [8]. Examples of static tests includes acid base accounting (ABA), modified acid base accounting, British Columbia Research Initial Test (BC), alkaline production potential: sulfur ratio (APP:S) and net acid production test (NAP). On the other hand, kinetic tests attempt to mimic natural oxidation reactions of the field setting and provide information on the rate of sulfide mineral oxidation and acid production. Tests such as humidity cell, soxhelet extraction, column, British Columbia Research Confirmation, batch reactor, and field scale are examples of kinetic tests. Results from static and kinetic tests are used to classify mine wastes on the basis of their potential to generate acid [8].

Acid mine drainage has a high content of iron (Equation (1)), and sulfate promotes the oxidation of sulfur minerals bound to metals such as As, Cd, Co, Cu, Pb, and Zn [9]. Of all the pollutants of the watercourses, perhaps AMD is one of the most serious, due to its nature, extent, and difficulty of resolution. The rivers and aquifers affected by this type of pollution are characterized by their acidity, as well as by the high content of sulfates and heavy metals in their waters by the metallic content of their sediments [5]. Internationally, AMD and liquid waste generated during the extraction and processing of minerals under the term water impacted by mining (MIW) are grouped. The management, storage, and disposal of MIW is a major environmental problem in all mining areas [10]. Acid mine drainage is a persistent problem at active but also is an important problem at abandoned mine sites. From this perspective, countries such as Australia, the United States, and Canada consider monitoring programs that have enabled the cadastre of environmental liabilities to be developed and remedied. Due to this, Table 1 details the metal content of some aquifers contaminated with mining drainages in Germany, USA, Canada, Malaysia, Zimbabwe, among others.

The information provided in Table 1 is quite broad regarding the range in which the different minerals can be found in the MIW. As an example, it can be indicated that the concentration of SO_4^{2-} can vary between 19 mg/L (Mamut Mine, Malaysia) and 108 g/L (Aquifer near the Richmond mine). However, it is possible to state that all spills and/or discharges of MIW have acid characteristic (range pH 0.5–7.0).

High concentrations of metals can affect freshwater species, including microalgae, microcrustaceans, and fish [11]. An ecotoxicological assessment of mine water usually starts by assessing the concentrations of metals (e.g., Fe, Mn, Cu, As, Ba, Cd, Zn, Ni, and Pb) [12]. Metal distribution, speciation, and bioavailability in sediments and the water column can have deep impact by AMD toxicity. The environmental effects could be evaluated by biological assays using different species as it is mentioned in the following paragraphs [13].

Daphnia species (*sp*) have been used in standard toxicity tests for many years due to their high sensitivity, manageability, and high parthenogenetic reproduction rate, which ensures a uniform response [14,15]. Furthermore, these species play an important role in the aquatic food chain [16]. *Daphnia sp.* are non-selective filter-feeders, thus, the process of feeding has a direct influence on the physiological performance in terms of growth, metabolism, and reproduction [17]. On the other hand, most metals are plant growth inhibitors, exerting various adverse effects leading to phytotoxic responses and to decreased yield and quality of agricultural crops [18]. Phytotoxic effects caused by metals are related to oxidative stress. Concentrations between 1.5 and 10 mM of Cu and/or Zn inhibit germination and early growth of barley, rice, and wheat [19]. Cu, Zn, and other elements interfere with cellular division, diminish respiration at the roots, reduce water intake, and alter the transport and metabolism of various essential nutrients. As a consequence, inhibition in germination and in elongation of the radicle and epicotyl are determinant final points for assessment of AMD phytotoxic effects [20]. Chamorro et al. (2018) and Villamar et al. (2014) showed that the phytotoxic effects caused by metals produce an oxidative stress that inhibits germination. The AMD toxicity was evaluated on *Lactuca sativa* (lettuce), *Raphanus sativus* (radish), and *Triticum aestivum* (wheat), the results, expressed as the fraction of AMD resulting in 50% lethality (Lethal Concentration—LC_{50}) at 144 h, showed that wheat was more tolerant (LC_{50} = 62%) than radish (LC_{50} = 17.0%) or lettuce (LC_{50} = 21%). Also, AMD has been found to be very toxic to *Daphnia magna* (cladoceran) and *Danio rerio* (zebrafish) embryos, two of the best model organisms in aquatic ecology and ecotoxicology (LC_{50} < 1%) [21]. However, waters and soils of mine areas can be treated to avoid or minimize environmental damage.

The aim of this article is to present a broad perspective of the constructed wetlands CWs technology applied to the treatment of AMD to achieve high metal removal efficiencies. This review focuses on summarizing the main aspects of the mechanisms prevailing in these systems for metal removal, and the design and operation conditions are also presented in order to offer insights on how all the aspects can be adjusted for the characteristics of AMD.

Constructed wetlands systems are not a new technology but they are currently the most widely-used passive mine water treatment technology.

In the following sections the types of CWs, operational parameters, heavy metal uptake mechanisms by plants, microorganisms, and support material are emphasized and explained.

Table 1. Species content (mg/L) and pH of groundwater contaminated with MIW.

Description	pH	SO_4^{2-}	As	Cd	Cr	Cu	Fe	Zn	Ref.
Underground water near Königstein mine, Germany #	5.9	33			<0.02		1.5	<0.01	[22]
Unsaturated area near the Königstein mine, Germany *	1.9	12,322			0.97		1171	132	[22]
Aquifer near the Richmond mine, USA	0.5–1	20,000–108,000	3–222	4.0–19.0		120–650	13,000–19,000	700–2600	[23]
Aquifer affected by Carlton mine, USA	7	1292					0.01	0.04	[24]
Groundwater from different locations in the Cae mine, Canada	1.9–2.3	19–265				0.04–37	31,570–1100	1.3–120.0	[25]
Mine Mamut, Malaysia	2.6	14.8				299	443	90	[26]
Groundwater close to iron mine, Zimbabwe	1.5	355,425	72	3.7	18	20	132,909	55	[26]

Presence of Pb and Uranium in concentrations 0.01 mg/L and less than 0.02 mg/L; * Presence of Pb and Uranium in concentrations 2.1 mg/L and 12.3 mg/L, respectively.

2. Constructed Wetlands Applied to AMD Treatment: Types, Operational Parameters, and Efficiency

Treatment of AMD can be accomplished by either active or passive techniques. The former refers to the improvement of water quality by methods which require ongoing inputs of artificial energy and/or chemical reagents. On the other hand, passive techniques refer to the deliberate improvement of water quality using only naturally-available energy sources (e.g., gravity, microbial metabolic energy, photosynthesis) in systems which require only infrequent (although regular) maintenance in order to operate effectively over the entire system design life [27]. In practice, AMD active treatment refers to (though not exclusively) the continuous application of alkaline materials to neutralize acidic mine waters and precipitate metals, and passive treatment to the use of natural and constructed wetland ecosystems [28].

The origin of current passive mine water treatment technologies can be traced, to two independent observations in the eastern USA [29,30], to the effect that *Sphagnum* bogs naturally improved the quality of coal mine waters flowing into them [27]. These studies constitute the first attempts to construct wetlands specifically to treat polluted mine waters. Wetlands have the capacity to improve water quality by physical, chemical, microbial, and plant-mediated processes. These include oxidation, reduction, precipitation, sedimentation, filtration, adsorption, complexation, chelation, active plant uptake of metals and microbial conversion/immobilization mechanisms [31,32]. Constructed wetlands mimic the functions of natural wetlands with the objective to treat water. Typical components of CW are: soil bottom, vegetation, water surface, and it can also contain some kind of media (rock, gravel, soil, or others) [33].

There are two main criteria to classify constructed wetlands: water flow regime (surface and sub-surface) and type of macrophytic growth. Constructed wetlands with surface flow (water a relatively shallow depth, water is exposed directly to the atmosphere, circulating between the stems and leaves of the vegetation) can be classified according to the type of macrophytes (emergent, submerged, free floating and floating-leaved plants) [34].

SS-CW consists of a sealed basin, water level is below ground (0.3 to 0.9 m deep); water flow is through a sand or gravel bed; and roots penetrate to the bottom of the bed. According to the flow direction of the influent, they are divided into horizontal sub-surface flow wetlands and vertical flow SS-CW [34].

There are also hybrid or combined systems that incorporate different types of CW with the aim of exploiting the specific advantages of the different systems arrangements.

Constructed wetland systems are currently the most widely-used passive mine water treatment technology for at least four reasons: (i) aerobic wetlands are a proven technology in treating net-alkaline mine waters (iron as only pollutant), (ii) low cost compared to active treatment systems, (iii) have the ability of large wetland systems to cope with unforeseen fluctuations, and (iv) have landscape amenities of appeal to human visitors [27]. However, some characteristics of AMD such as high acidity and toxic metals concentrations are challenging for CW systems, but design criteria, conformational arrangements, and careful selection of each component must be considered to achieve the treatment.

Table 2 summarizes reports regarding the use of CW for AMD treatment to achieve metal removal. Constructed wetland systems have been used both at full scale to treat real AMD water near to mine sites and also at small or lab-scale in the pursuit of finding better conditions for higher metal removal efficiencies.

As it is shown, operational parameters are roughly reported, some studies reported hydraulic retention time but not the hydraulic load, etc. Under this scenario the comparison between the systems cannot be fair; however, some general conclusions about some aspects can be made.

Analyzing the performance of the type of wetland used, it can be observed that for some metals the removal efficiency varies when using surface or SS-CW. For instance, better removal had been achieved for Al, Mn, Ni, and Zn [35–38] in SS-CW as compared to surface CW. On the other hand, metals such as Fe can be removed efficiently by both types of CW systems with efficiencies up to 92.0% (Table 2).

In the attempt to achieve higher removal efficiencies different strategies can be applied to this technology. For example, the combining of surface flow wetlands with SS-CW (hybrid system) have been used. The study by Stottmeister and colleagues [39] demonstrated that this system can be successfully applied for As and Zn simultaneous removal. Actually, for the treatment of AMD with the presence of metals with high toxicity, such as Pb and As, in concentrations exceeding international guidelines, by CW, only surface flow CW and hybrids have been used. Nevertheless, only hybrid CW systems had been implemented for long term at small scale [39,40].

An important aspect regardless the type of artificial wetland and metals in the AMD, is that, according to the studies, at a pH value higher than 4.2 the removal efficiencies tend to be lower [35,39], in fact, at alkaline conditions the removal efficiencies are reported to be less than 34% [36].

Other studies have tested the use of combined substrate, for instance soil (75%), powdered goat manure (20%), and wood shavings (5%) in surface CW. The combined substrate used in the study by Sheoran (2017) was reported to promote sulfate reduction leading to an increase in pH from 3.16 to 7.20 and heavy metal removal from the AMD as a consequence [35].

The strategy of combining the mine effluent with wastewater can also be considered. Türker et al. (2013) [41] used small-scale, polyculture SS-CW to treat mine effluent (metal content of B, Ca, Mn, and Na) mixed with municipal wastewater (DQO = 62.1 mg/L). This study was performed at small scale under field conditions.

Regarding vegetation, studies revealed that species such as *Typha latifolia*, *Phragmites australis*, and *Juncus effuses* are the most used plants; however, it is not a rule and other species have been tested achieving good result for instance, *Desmostachya bipinnata*. Plant density is another parameter that is poorly described but it can be crucial for the correct performance of the system.

Since the CW system has different components, the metal removal is expected to occur in more than one of them, such as soil and substrate, and influenced by hydrology and vegetation [36] through different mechanisms. Moreover, the number and diversity of microorganisms found in each CW component is dependent of different factors such as wastewater type and characteristics, geography, among others, which are observed to influence the kinetics of metals removal [37].

Some studies have focused on report metal removal by analyzing water samples but just some of them have analyzed all the CW constituents (plants, media, water, etc.) to make a total balance and elucidate the contribution of each component. Hence, the knowledge and understanding of these main aspects based in scientific and practical experiences could lead to a better design and operation to achieve better results using the CW technology. In the following sections these aspects are explained and discussed in detail.

Table 2. Types of constructed wetlands applied to metal removal from acid mine drainage and their operational characteristics.

Type of CW	Influent Characteristics		Operational Parameters	Type of Vegetation	Removal Efficiency of Metal (%)	Reference
	Metal (mg/L)	**(a) SO_4^{2-} (mg L^{-1}) (b) pH (c) Alkalinity (mg/L $CaCO_3$)**	**(a) HRT (d) (b) Hydraulic load ($m^3/m^2 \cdot d$) (c) Scale**			
Surface Flow	Fe (260.5 ± 23.7) Zn (5.9 ± 0.3) Cu (1.44 ± 0.1) Cd (0.006 ± 0.0)	(a) 1336 ± 5.0 (b) 2.65 ± 0.02 (c) 0	(a) - (b) 0.033 (c) small-scale	*Carex rostrata* *Eriophorum angustifolium* *Phragmites australis*	−0.8–0.4 −3.4–8.5 50–57	[38]
	Al (30–100) Ca (-) Fe (200–250) Mg (30–100) Mn (30–100) S (-)	(a) 500–1000 (b) 2.6 (c) -	(a) - (b) - (c) full-scale	*Typhia latifolia*	23–30 5–8 25–31 17 18–19 17–18	[39]
	Fe (12.0) Al (11.3) Zn (0.385) Ni (0.388) Cu (0.03) Pb (0.01)	(a) 2610 (b) 2.54–2.99 (c) -	(a) - (b) - (c) lab-scale	*Chrysopogon zizanioides*	-	[41]
	Fe (44–205/1.3) Mn (5.9–7.4/0.2) Al (0.02–0.29/0.1) Zn (<0.009–0.03/<0.009) Cd (<0.006–0.02/<0.006) B (0.01–1.17/<0.006) As (0.0009–0.1/0.0004) Pb (<0.002–0.0022–<0.002)	(a) - (b) 6.3–7.2/5.7 (c) -	(a) - (b) 113.68/302.69/928.8 (c) full-scale	*Scirpus cyperinus* *Typha latifolia* *Juncus effusus*	97–98/10 47–79/40 - 33/- 100/- 52/- 99–100/- 26/-	[42]

Table 2. *Cont.*

Type of CW	Influent Characteristics: Metal (mg/L)	Influent Characteristics: (a) SO_4^{2-} (mg L^{-1}) (b) pH (c) Alkalinity (mg/L $CaCO_3$)	Operational Parameters: (a) HRT (d) (b) Hydraulic load ($m^3/m^2 \cdot d$) (c) Scale	Type of Vegetation	Removal Efficiency of Metal (%)	Reference
	Fe (17.861) Cu (14.620) Zn (29.367) Pb (1.753) Co (0.323) Ni (0.388) Mn (2.143)	(a) 395 (b) 2.93–3.31 (c) 0	(a) 1,2,3,4,7 (b) - (c) bench-scale	*Desmostachya bipinnata*	95–96 89–92 77–78 89–90 68–72 30–64 36–76	[43]
Subsurface flow	Al (12.6 ± 4.1) Fe (787 ± 121) Mn (10.9 ± 2.1)	(a) - (b) 3.38 ± 0.45 (c) -	(a) - (b) - (c)full-scale	*Typha latifolia* *Scirpus validus* *Bidens aristosa*	95.8 99.9 98.4	[40]
	B (187) Ca (54.9) Mn (19.6) Na (318)	(a) - (b) 8.96 (c) -	(a) 15 (b) 0.00078 (c) small-scale	*Typha latifolia* *Phragmites australis*	30–37 20–25 30–34 30–33.5	[38]
	Fe (1–191) Al (<1–48) Ca (64–170)	(a) 312–1603 (b) 3.4–6.1 (c) 0–54	(a) 2.4–27 (b) 0.12–0.75 (c) full-scale	-	0–92 0–90 (−8)–(−57)	[36]
	Fe (38.1) Mn (2.6) Ni (0.4) Zn (9.0)	(a) 292–377 (b) 4.2 (c) -	(a) 5 (b) 0.01 (c) small-scale	*Typhia latifolia*	98.6/89.8 75.5/−20.3 88.5/58.1 96.7/96.3	[43]
Hybrid (surface + subsurface flow)	Zn (1.8) As (0.5)	(a) 2000–3000 (b) 3.0 (c) -	(a) - (b) Batch system (c) small-scale	*Juncus effusus*	67 98	[44]
	Fe (166) Al (83) Mn (250)	(a) 1672 (b) 2.73–3.08 (c) 48-63.1	(a) 12 (b) 4.6 (c) full-scale	*Typha* sp. *Typha latifolia*	82.35 61.25 94.9	[45]

Note: - Information not reported.

3. Heavy Metal Uptake Mechanisms in Constructed Wetlands

In CW for AMD treatment systems metals are removed by a series of mechanisms that are usually attributed to a particular CW component. However, the removal of metals from aqueous solution comes from an interaction and synergetic effect between them. Each component of a CW system participates in metal removal: (i) the support material (mineral and/or organic) contributes to the removal mainly by adsorption processes, (ii) plants (emerging, floating and submerged) contribute mainly by direct uptake mechanisms, and (iii) microorganisms (bacteria and archaea) contribute by promoting reduction and subsequent precipitation of metals.

In this section, the role and removal mechanisms are described for each of these components, recommendations for better a performance are also mentioned.

3.1. Role of Vegetation on the Removal of Heavy Metals

Plants are one of the CW components whose participation can be underestimated. Despite the direct uptake, wetland plants act directly promoting adsorption and precipitation mechanisms assisted by bacteria and support material. Indirect contributions come from the formation of litter layer and organic particulate matter that contributes by trapping metals and lead to their sedimentation and by providing surface area and symbiosis between bacteria which promote mechanisms of metal reduction, adsorption, and precipitation. It is important to mention that wetland systems without plants are less efficient than those with vegetal material [46]. In this section plants' role in metal removal from acid solutions is described with emphasis in plant type and interactions between other CW components. Comments and recommendations to be considered for a better performance in metal removal are assessed.

3.1.1. Factors Involved in Metal Uptake Efficiencies by Plants

The plants commonly used in CW systems associated to mine drainage treatment are emergent, floating, and submerged plants. Emergent plants include species like *P. australis*, *P. arundinacea*, *T. dominguensis*, *T. latifolia*, *P. karka*, and *P. australis* [41,42,47]. The emergent plants promote the adsorption to the substrate and additionally they improve the removal by well know common processes like uptake and retention of heavy metals over its tissues. Floating plants, cannot promote the adsorption through the substrate, but they improve their adsorption to the plant biomass. Examples of floating plants includes species such as *Echhornia crassipes*, *Pistia stratiotes*, and *Salvinia herzoggi*. Finally, submerged plants, for instance, *Potamogeton* spp., *Ceratophylum demersum, Myriophylum spicatum*, and *Hydrilla verticillata* are suggested to be used on mine drainage treatment since they can accumulate metals in the hole biomass, but Fe precipitation over its roots can limit photosynthesis and their metal uptake [46].

Heavy metal removal efficiencies of CW are variable, and it depends on many factors, including AMD physical and chemical characteristics, support material composition, operation time, among others. According to the literature, to improve the plants performance on removal efficiencies, it is necessary to take into account the following approaches: (1) The use of local native plants is highly recommended, since they show better survival percentage and adaptation properties. For example, a CW treating Boron(B)-mine effluent and wastewater showed survival percentage of 87.5 and 100% of *T. latifolia* and *P. australis* obtained from natural wetland habitats at the same area, respectively [41]. However, this effect is more related to the variation of sensitivity to the environmental factors rather than metal tolerance properties [46]. (2) The plant growth stage in CW is also an important factor to improve heavy metal removal, since adult plants have much better ability to modify the environment and immobilize metals in the rhizosphere. In this stage, plants have much better developed aerenchymatous tissue, higher oxygen transport and a minor loss of radial oxygen. This also enhance the respiration of microbe in the rhizosphere promoting removal mechanisms by bacteria [47,48]. (3) The season, a parameter that cannot be controlled but that can be predicted and considered during the system design, also plays a role on the efficiency of heavy metal removal in CW since winter and summer weather have been shown a decreasing and increasing effect, respectively [35,46,47]. (4) The selection of the plant species is essential as metal uptake and accumulation capacities are specific and it has to be according to AMD characteristics in order to ensure the effectiveness of the system [41]. There are different reports with information about plants species and their accumulation towards specific heavy metals which can be consulted and considered for CW design [49–51]. For example, Leung et al. (2017) [47] compared the accumulation of Pb, Zn, and Cd concentrations in a CW receiving metals from mining facilities, where *T. latifolia* showed the highest content of these elements (3.4, 3.3, 0.06, and 0.01 g/m^2), compared to *C. Malacencis* (2.5, 1.2, 0.1, and 0.007 g/m^2) and *P. australis* (2.4, 1.6, 0.06, and 0.006 g/m^2). Türker et al. [41] also compared the accumulation of B by *T. latifolia* and *P. australis* in a polyculture CW receiving mining effluent, the results showed that *T. latifolia* can accumulate more B in its tissues (250 mg/Kg) than *P. australis* (38 mg/Kg). (5) Monoculture CWs have been reported more efficient for AMD treatment than polyculture CWs since the interspecific competition and overcrowding affects the nutrient availability and metal uptake rates [41].

Metals contained in AMD such as Zn, Cu, and Fe are reported as easy to remove in CW systems; conversely, elements like Mn, Ni, and B tend to be difficult to remove [35,41,42,46,52]. For instance, iron has been reported to be removed first from AMD solutions in bench scale studies, using *Demostachya bippinata* and organic substrate [43]. Some plant species, such as *P. australis*, has been shown to accumulate higher concentrations of Fe in roots and shoots (1100–1600 mg/Kg) [53]. Batty and Younger (2004) found that *P. australis* exposed to AMD show more Fe concentrations in its tissues, especially within or associated with plant roots, than those exposed to uncontaminated water [53].

Sulfate removal efficiencies in CW is still unclear, some authors report low or negligible removal [54] while other studies reported high rates of sulfate removal [43,55]. It has been reported that the presence of *T. latifolia* had a marginal effect on sulfate removal, but its carbon-rich litter greatly promoted sulfate removal [56].

Additionally, pH of the AMD is expected to influence the plant uptake content, for example B has shown a better uptake rate by plants of *Hordeum vulgare* in pH range from 6.3 to 7.5 and an inverse correlation between a pH increase and B plant tissue content [57].

Vegetation is an important component of CW used to treat AMD, plants produce synergy with other components, increasing the removal efficiencies for heavy metals. The principal mechanisms of plants in heavy metal removal includes: (1) chemical precipitation and sorption onto sediments assisted by macrophytes, (2) metal retention over plant tissues via filtration, adsorption, cation exchange, and changes induced in the rhizosphere, (3) retention and precipitation by symbiotic processes with root bacteria (e.g., formation of iron oxyhidroxydes layer, that also could adsorb other metals), and (4) direct uptake of metals by plant roots, (less than 2% of metals are reported to be uptake by plant roots, Marchand et al. (2010) [46], (see Figure 2). Other collateral processes are the accumulation of plant detritus or litter and suspended organic matter that act trapping metals [35,46,47,58,59].

On the other hand, most studies argued that plants generally have a low contribution on the heavy metal removal in CW, an argument generally based considering only the direct uptake mechanism and short time period experiments, where the participation of support material cover up the role of CW plants [53]. However, the role of plants as an essential component of constructed wetlands is well established and most studies comparing planted versus unplanted subsurface CW systems treating wastewaters, including AMD, show a significant and positive effect of pollutant removal by providing sites for metal precipitation and/or sedimentation [55,60]. Yet, most of the literature experiments do not include a control of unplanted units [53], hence comparison and conclusions about the importance of plants are difficult to state

The direct uptake by plants is usually calculated by measuring plant growth and metal content stored in plant tissues [53]. However, in big scale systems plant uptake tends to be negligible and difficult to measure at least in short time operations. Leung et al. (2017) [47] measured heavy metal concentrations in CW components receiving water from mining facilities and less than 0.1% of the removal of Pb, Zn, Cu, and Cd was associated to accumulation in the CW plants tissues.

Another important issue regarding plants in CW treating mine water is the presence of phytotoxic concentration metals, which can affect the plant growth, or create problems associated with reduced nutrient uptake due to the presence of high concentrations of metals and H^+ ions [61].

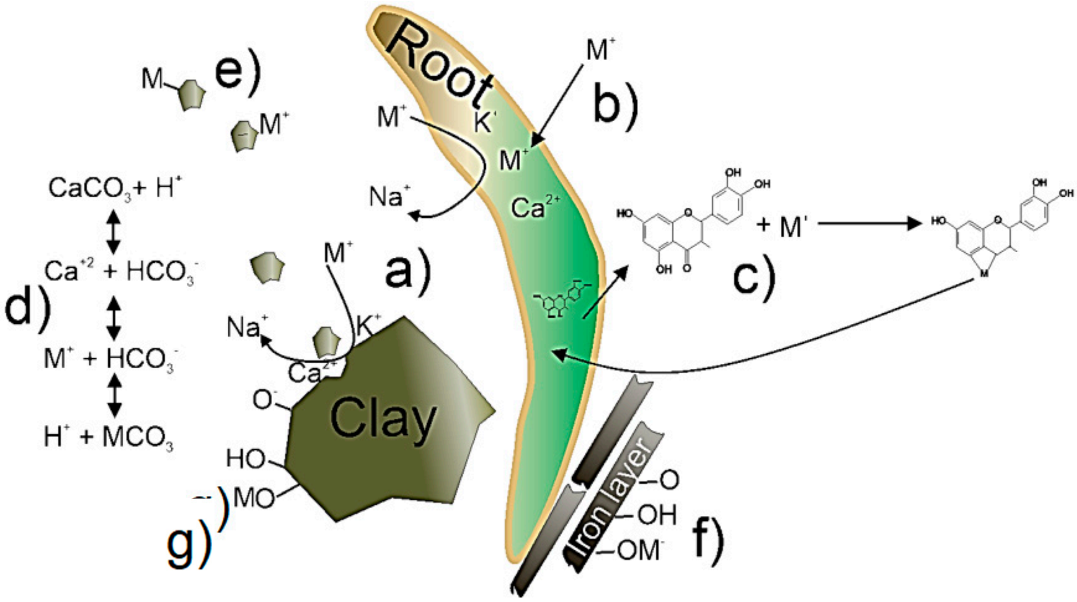

Figure 2. Metal removal mechanisms in constructed wetlands by plant and support material. (**a**) cation exchange; (**b**) plant uptake; (**c**) metal chelation by root exudates; (**d**) carbonate precipitation; (**e**) adsorption to particulate matter; (**f**) adsorption onto iron layer and (**g**) adsorption onto clay material.

3.1.2. Accumulation and Detoxification Mechanisms

The metal accumulation observed in CW systems plants is the result of the balance between accumulation, detoxification, and adaptability mechanisms. These mechanisms are multigenic and involved (i) biomineralization; (ii) the formation of complexes with glutathione, chelation with metallothioneins and phytochelatins; (iii) hyperactivity of antioxidant plant systems and chelation of heavy metals by root exudates. Biomineralization onto roots, leading to metal precipitation and intracellular biomineralization, e.g., iron plaque formation onto the plants root, has been proven to act as a barrier for metal uptake in plants due to metals affinity for Fe hydroxide (See Figure 2). The iron plaque has been observed in macrophytes like *Typha latifolia* and *Phragmites australis*, plants commonly used in CW systems. Intracellular sequestration of minerals occurs through the incorporation of metals in calcium oxalate crystals (CaOx) and calcium carbonates ($CaCO_3$). This phenomenon has been reported for Al, Pb, Cd, Zn, Mn, and Sr in *Ficus retusa*, *Nicotiana tabacum*, and *Solanum lycopersicum* [46,59,61,62].

The formation of complexes with glutathione, chelation with metallothioneins and phytochelatins and subsequent transport into the vacuole is another mechanism observed. The metal bind to the thiol group contained in these compounds to form a complex, it is a common mechanism that maintain low concentrations of free metals and metalloids in plant cytoplasm and an increase in its production is directly related to the increase of metal exposition [46,63], e.g., this effect was observed for Pb in *C. vulgaris*, Cr, Zn, Cd, and Hg in *R. sativus*, Al in *V. radiata* [64].

Plants exposed to metals are observed to develop an oxidative stress that is minimized by plants through antioxidant enzymes like catalase, peroxidase, ascorbate peroxidase, among others. Macrophytes such as *Alternanthera* sp., *Eclipta* sp., *Marselia* sp., *Typha* sp., and *Ipomea* sp. exposed to heavy metal industrial discharges, have shown a direct correlation of metal accumulation and the hyperactivity of antioxidants like catalase and peroxidase [65].

Root exudates secreted by plants can act as chelator of heavy metals. Root exudates includes organic acid fractions that occurs as anions in soils, these substances are associated to detoxification processes by chelating metals and converting them to inactive and non-toxic forms and reducing their intake rate [46,58]. For instance, Cu(II) as copper sulfate ($CuSO_4$) and copper nitrate ($Cu(NO_3)_2$) has been proved to induce the exudation of organic acids in *Typha latifolia* [66]. Other plants used in phytoremediation such as *Poa annua*, *Medicago polymorpha*, and *Malva sylvestris* showed a correlation between the higher concentrations of Cd, Cu, and Zn and the excretion of low molecular organic acids [67].

3.2. Contributions from Support Material to Metal Removal

The most common mineral support materials used in CWs for AMD treatment are: limestone, dolomitic limestone, gravel, coarse gravel, sand, sandy-soil, and bentonite. On the other hand, organic support material includes peat, cattle manure, pebbles, good shavings, goat manure, charcoal, and slag [43,51,53,55,61].

The main goal for the use of CW in the treatment of AMD is the reduction of the bioavailability of the heavy metals, and the metal removal contributions from support material includes: (1) cation exchange, is a short time retention that occurs when cations are attached to the surfaces of minerals and organic surfaces by electrostatic attraction, sometimes called outersphere complexation; (2) chemisorption, is a long-term immobilization and represents a stronger and permanent bonding compared to cation exchange, this mechanism involves ionic and especially covalent bonding, it is sometimes called innersphere complexation and (3) precipitation and co-precipitation, is an important adsorptive mechanism in support material and wetland sediments; this mechanism is enhanced by the increase of pH which results from the solubilization of some acid consuming minerals and carbonates formation; this specially occurs when limestone kind support material is dissolved by AMD solution. Limestone reacts with acidity present in the mine drainage to form free calcium (Ca^{2+}), dissolved carbon dioxide (carbonic acid, H_2CO_3) and bicarbonate (HCO_3^-) [35,68–70]. Elements such as Pb and Cu in general tends to be adsorbed most strongly than elements like Zn, Ni, and Cd. On the other hand, carbonate precipitation is especially effective for the removal of Pb, Ni, and Mn [44].

Generally, in new CW systems it can be observed a period of major efficient removal related to the initial filling of sorption sites on newly submerged clay minerals in the wetland base and buns [54].

Adsorption of metals to particulate matter, originated from the degradation of mineral and organic support material and plants, is also an important mechanism. More than 50% of the heavy metals can be easily adsorbed onto particulate matter in the wetland, and thus be removed from water by sedimentation [44].

In most of the CW systems for AMD treatment, the principal contaminant of concern is Fe though Al, Mn, and other metals can also be present in acidic mine waters [54] and are easily removed by increasing the pH in the system.

The final sink for elements is not usually explained, but Fe is suggested to precipitate as ferric oxide and ferric phosphate [54]. One of the techniques to quantify the "immobilization" of heavy metals in the system involves the use of sequential fractionation extractions which can provide evidence of the element fractionation in the substrate material [71].

Constructed wetland systems for AMD treatment can be amended and fed with organic matter in between the support material since the availability of organic matter (nutrients and carbon) enhances processes such as sulfate reduction promoting the removal of heavy metals such as Fe, Cu, Pb, Zn, and Ni [55]. This also provides the substrate or carbon source for anaerobic microorganisms that produces alkalinity [43]. The common organic amendments are wood chips, livestock manure, winery waste, crop residues, organic soil, municipal compost, municipal biosolids, and grain mill by-products [55]. However, a balance between mineral and organic support material need to be maintained since both materials contribute to the filtration of the precipitated forms of metals [55].

Some of the principal heavy metal removal mechanisms regarding plants and support material are shown in Figure 2.

3.3. Role of Microorganisms in CW Treating Acid Mine Drainage Containing Heavy Metals

Most of the constructed wetlands (CW) studies indicate that microorganisms are the main component of these treatment systems, because they interact more with wastewater, packing medium and vegetation to achieve the removal of contaminants [34,72–75].

Heavy metals removal by microorganisms, in any natural environmental system or open treatment system, could refer to bacteria; microalgae (especially *Chlorella* genus); bacteriophages and/or protozoa. However, protozoa are highly sensitive to heavy metals presence, including zinc and copper, for that reason they have been used as bioindicators of metal water contaminants [76–78].

Viruses have not presented a significant interaction with heavy metals, possibly due to the capsid protein structure that does not allow it to interact with the external environment. Also, when bacteria are under stress due to heavy metals, viruses have an opportunistic behavior [79].

Respect to microalgae, *Chlorella vulgaris* is being subject of bioremediation studies because it has shown tolerance and the presence of phytohormones that allow heavy metals accumulation [80,81], such as many other hydrophytes plants [82,83].

Despite this, the most viable option to apply constructed wetlands in mining are the subsurface type because they are more efficient in its operating control parameters such as hydraulic load, organic load, and plant density [47,84]. One characteristic of these systems is that residual water is never exposed to the surface and, therefore, they do not receive solar radiation, so microalgae cannot grow despite its ability to accumulate metals. In this sense the removal of heavy metals in constructed wetlands mediated by microorganisms, refers exclusively to the bacterial action and in anaerobic conditions also refers to archaeas [85–87].

Due to the physico-chemical characteristics of AMD such as pH between 0.5–5.0, sulfate concentration above of 400 mg/L, Eh above of 250 mV and high concentrations of Fe, Cu and/or Zn, only acidophilic bacteria or archaea can exist. To respect, [88] describes bacterial genus isolated in various AMD sites and its phenotypes (See Table 3).

Table 3. Genus and phenotype of microorganisms isolated from different mines. Modified of [88,89].

Genus	Phenotype	Mine Water Type
Leptospirillum spp.	iron-oxidizer, mesophile	Tin, Cooper, cooper with pH $\leq$ 1.0
Ferroplasma acidiphillum	iron-reducing heterotroph	Tin, cooper and copper wit pH $\leq$ 1.0
Acidocella spp.	iron-reducing heterotroph	Tin
Ferrimicrobium spp.	iron-oxidizing/reducing heterotroph, mesophile	Tin and copper wit pH $\leq$ 1.0
Acidimicrobium ferroxidans	Fe ox./red. Heterotroph, moderate thermophile	Copper with pH $\leq$ 1.0
Ferrovum myxofaciens	iron-oxidizer, psychrotolerant	Copper with pH $\leq$ 1.0
Thiomonas spp.	Iron-and sulfur-oxidizer, moderate acidophile	Coal, tin and copper
Halothiobacillus spp.	Iron-and sulfur-oxidizer, moderate acidophile	Tin
Acidobacterium-like spp.	iron-reducing heterotroph	Tin and copper
Ferroplasma spp.	iron-oxidizing/reducing heterotroph	Copper with pH $\leq$ 1.0

3.3.1. Microorganism Response to Heavy Metals Presence and Other Conditions of AMD

Perhaps the most known and studied mechanism of heavy metals removal by microorganisms is the reduction of SO_4^{2-}, and SO and subsequent precipitation of inorganic ions mediated by sulfur. This arises from the main known sulfur transformation processes in surface-flow constructed wetlands.

In anaerobic zones sulfur has been reduced to H_2S, this acid reacts with heavy metals releasing the hydrogen molecule and forming metal sulphides (e.g., FeS, ZnS) which quickly precipitate. In addition, the lowering of acidity in the system due to bacterial sulphate reduction to sulphide can prompt further precipitation of metals as hydroxides (e.g., Pb $(OH)_3$, Cd $(OH)_2$ and carbonates (e.g., $MgCO_3$) [89,90]. Figure 3 proposes the removal or tolerance mechanisms that exist within a wetland when metal sulphides interact with bacterial cells.

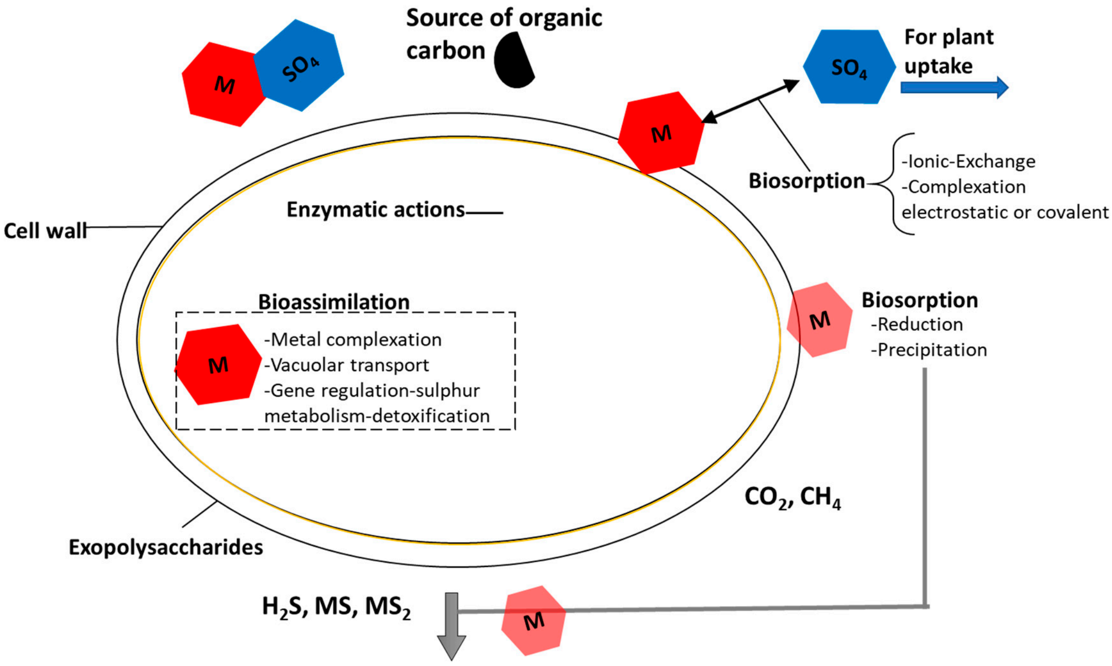

Figure 3. Possible mechanisms of bacteria present in constructed wetlands for the removal, transformation, and tolerance of heavy metals in acid mine drainage (AMD).

In CWs, anaerobic conditions could be propitiated, which are required for sulfatoreduction. However, it is necessary to consider, simultaneously, the operation of all components of CWs in absence of oxygen [91]. For example, sulfatoreduction implies metallic sulphides generation and subsequently its precipitated into the CW by chemical speciation. This process, in turn, results in clogging which is one of the disadvantages of CW [92–95].

3.3.2. Plant Growth Promoting Bacterium

Symbiosis between plants and rhizospheric bacteria could be the most beneficial dynamic population during bioremediation process of ADM in CW systems. In fact, it has been shown that the main factor in plants to accumulate heavy metals is the presence of rhizospheric bacteria, especially when they have developed some mechanism of tolerance towards metals, from symbiosis to synergism [44,96].

Plant growth promoting rhizobacteria (PGPR) is the term for a bacterium that promote photosynthetic organism's growth through compounds secretion such as indoleacetic acid (IAA), abscisic acid (AA) and auxins, besides behaving as hormones for plants, they offer protection from environmental stress of toxic substances [97,98], as heavy metals.

Isolations have been made to obtain PGPR identification in diverse geographic locations, and the following genera have been found, from higher to lower density, *Flavobacterium*, *Kleibsella*, *Rhizobium*, *Pseudomonas*, *Azospitillum*, *Actinoplanes*, *Agrobacterium*, *Azotobacter* and *Bacillus* [64,99,100]. In addition, Ashraf et al. (2017) presents in detail 16 plant species, medium heavy metal contaminants, and identified microbiota [100]. These species do not tolerate the most extreme acidic conditions reported in ADM, but they do develop at pH values above 2.5, so they may be applicable for bioremediation of AMD.

Microorganism development in a biofilm form is one of the main characteristics of CW in wastewater treatment, which is made up of 15% bacterial cells and 85% of cellular matrix [101,102], which is mainly constituted by extracellular polymeric substances (EPS) as polysaccharides and in lower proportion proteins, lipids, and humic acids [103,104]. All these organic substances have an adsorbent capacity of heavy metals by surface phenomena such as Van der Waals forces and chemisorption [92,93].

Also, biofilm contains channels within its structure, where water, enzymes and nutrients circulate. Through these channels different bacterial cells species establish symbiotic relationships and dependencies between them. The highlight relationship is communication through chemical signals called quorum sensing (QS) which regulate different gene expression, in distinct parts of bacterial population [94].

In this sense, different bacterial species present in biofilm make an important change in their metabolism, as those related to heavy metals detoxification. These detoxification mechanisms include chemical valence change by oxidation or reduction through specific enzymes. For example, the reduction of Hg^{2+} to Hg^0 by mercuric reductase enzyme allows metal volatilization before aqueous medium is affected. Similar mechanism occurs with Cr^{6+} when is reduced to Cr^{3+} through the ChrR reductase enzyme which is present in *Pseudomona putida* bacterium [95] as well as oxidases enzymes, which intervene to obtain As^{5+} from As^{3+}.

It has been reported that bacteria produce polythiol polypeptides in different environments with toxic metals such as Cd^{2+}, Ag, Cu, and Zn and this enzyme allowing an efflux ATPase which keeps low levels of inorganic toxins at intracellular levels [105,106]. Also, these organic substances promote the increasing of pH values.

Most of the heavy metals detoxification mechanisms of tolerance are mediated by mutant species, for example *Arthrobacter* spp. [107] or *Bacillus* spp. [108], which have been able to recombine DNA, and therefore incorporate at least one plasmid of some bacterial species that has expressed resistance as *Alcaligenes xylosoxydans* [109], *Arthrobacter* spp. [107], and *Bacillus* spp. [108].

For instance, two large plasmids (pMOL28 and pMOL30) were identified by Diels and Mergeay (1990) through *Alcaligenes eutrophus* isolation from decantation basin sediments from a zinc smelt factory with physico-chemical characteristics very similar to AMD [109]. The pMOL28 plasmid is resistant to nickel, cobalt, chromate, and mercury and pMOL30 is resistant to cadmium, cobalt, zinc, copper, lead, and mercury. When *A. eutrophus* species were introduced to contaminated soils with heavy metals it was found that native bacterial strains developed two plasmids with size very similar to those of *A. eutrophus*, which allowed these native strains to significantly increase their tolerance towards Cd, Co, and Zn.

On the other hand, Simmons et al. (2008) showed evidence of evolutionary processes which occur over a short time-scale period. DNA sequence obtained from a biofilm developed under acid mine drainage conditions was reconstructed, taking into account the effects of strains' genomic variations. The genetic sequence revealed species variations between *Leptospirillum* genus, in a short time, related with plasmid/phase-like regions, a variation at the nucleotide level [110].

3.3.3. Isolated Consortium from Acid Mine Drains

In addition to the obvious advantages of using AMD bacterial consortia to inoculate CW, such consortia may also have other environmental benefits. In fact, heavy metal-tolerant bacteria have been recently reported with positive changes in environmental systems. Specifically, they increment rates observed in carbon, nitrogen, and phosphorus assimilation. The study performed by Kuppusamy et al. (2016) [111] used heavy metal tolerant bacteria of *Trabulsiella* genus to remedy contaminated soils with petroleum aromatic hydrocarbons (PAH) [111]. After 90 days, bacteria colonization contributed to reduce the benzo (a) pyrene lifetime from 100 to 50 mg/L and PAH levels were reduced by 80%, suggesting that the aromatic compounds were used as carbon source since volatilization was not viable at the experimental conditions. In addition, nitrogen fixation and phosphorus solubilization were observed and correlated with a considerably increasing vegetation density and a 70% average reduction of LD_{50} in soil [111].

Furthermore, Amabilis-Sosa et al. (2015) [96] evaluated chemical oxygen demand (COD) and NH_4-N removal in subsurface constructed wetlands (CW) which were inoculated with five heavy metal tolerant bacteria strains isolated from Mexico center mining. The experiment was contrasted in real time with a CW system in same construction and operation characteristics as the inoculated ones, but with conventional bacteria (rhizospheres and wastewater).

Experiment was carried out for 156 days and the results indicated that tolerant bacteria CW exhibited a degradation rate constant of 0.92 d^{-1}, which is significantly higher than conventional bacteria CW (0.73 d^{-1}). Likewise, nitrification rate was 0.63 d^{-1} in CW inoculated with heavy metal-tolerant bacteria, while conventional bacteria CW was 0.38 d^{-1} [96].

The COD and nitrification removal rates were also higher than several reported in literature [73,84,112]. Although there are few studies on removal kinetics changes in organic compounds by heavy metal-tolerant bacteria, those results have been the most forceful.

4. Implementation of Constructed Wetlands (CW) for Mine Water Remediation: Scaling and Residues Generated

Since CW require minimal maintenance and can be applied at remote or at abandoned mine sites where the installation and maintenance of an active system would be difficult, they can be used to attenuate and mitigate the negative impact of AMD.

This technology, which combines naturally-occurring biogeochemical, geochemical, and physical processes, can be used for the long-term remediation of mine water. Depending on the size and design of this type of systems they would require rehabilitation every 5–10 years but their expected lifespan is around 20 years [113].

Constructed wetlands can also be considered cost-effective processes as long as the process is careful designed and constructed. A staged designed of the wetland system should be considered, as suggested by Wildeman et al. (1993) [114], which includes: (1) laboratory studies, (2) bench-scale studies, (3) pilot-scale systems, and (4) full-scale systems. Each of the stages allows to get important and valuable information that could lead to the development of optimum systems and a successful scaling of the CW system.

It has been reported that passive systems work well at low volume of AMD discharges (<0.45 $m^3/m^2 \cdot d$) containing moderate to high acidity and metals concentration, while they seem to be effective to treat larger flows (up to 11.25 $m^3/m^2 \cdot d$) for net alkaline water containing Fe [113].

The design factor is an important aspect to consider before implement the system. Data from literature report that design factors of 3.5 g acidity/$m^2 \cdot d$ (for anaerobic wetlands) and 10 g Fe/$m^2 \cdot d$ (aerobic and anaerobic wetlands) have been successfully used [113,115], in the case of vertical flow wetlands (VF-CW) a criterion for a long-term acidity removal rate of 35 g/$m^2 \cdot d$ has been reported [116].

In the United States the first large scale passive aerobic system (8.5 $m^3/m^2 \cdot d$ capacity) was built in 1992 by Tennessee Valley Authority in Alabama; and the West Fork Unit system (5.11 $m^3/m^2 \cdot d$ capacity) was the first large-scale anaerobic biotreatment system constructed in Missouri in 1996 built by Asarco Company for its underground lead mine.

In UK, passive treatment technology was implemented in the 1990s and recommended for the long-term remediation of mine waters such as acidic spoil heap leachate, deep mine drainage, spoil leachate, drift mine water, etc., wherever land availability is not unduly limiting [117]. Constructed wetland systems are reported as the most widely used passive mine water treatment technology for polluted mine waters [27].

There are some general established considerations to conduct the treatment, for example, if Fe, Mn and Al are the only contaminants of concern, the guiding principle is to neutralize the mine water using sulfate reduction and/or carbonate dissolution, and then use aerobic processes to strip the remaining metals from solution.

In cases where more toxic metals are present in the mine water, metal interactions and speciation, that could lead to the formation of toxic compounds, has to be considered [27].

In 2005, Skousen and Ziemkiewicz evaluated 116 systems comprised of eight system types treating AMD in eight states in the eastern of United States, and four years after 14 sites were re-evaluated for their performance [118]. Results from this study demonstrated that most of the passive systems were effective for more than five years. Regarding aerobic wetlands their results showed that those systems removed between 0.1 and 27 t of acid/year at costs ranging from \$23 to >\$7000/t/year over the expected 20-year lifetime. The anaerobic wetlands showed wide variation in acid removal (0 to 67.9 t/year of acid load treated (47.6 $g/m^2 \cdot d$)) and varied in treatment costs from \$341/t/year to \$4762/t/year. From this study authors also found that anaerobic wetlands were fairly robust systems that work well if not overwhelmed with acid or metal loads. The vertical flow wetlands (VF-CW) had removal efficiencies well above the design standards and iron was found to be the key element of concern, which causes systems to fail due to armoring or floc buildup.

Nowadays, it is considered that passive systems have substantially reduced water treatment costs at many mine sites due to its low capital, maintenance, and operating costs as compared to active systems.

A variety of factors affect the cost of constructed wetlands, such as: detention time, treatment goals, media type, pretreatment type, number of cells, source and availability of gravel media, and terrain [119].

The construction cost of a system can be roughly calculated based on accepted standard rates for building passive systems. These rates can vary and it is zone-dependent, data from 2005 established costs of \$3.25/m^3 for excavation, \$27/t of limestone, \$27/t of slag, \$27/m^3 of organic matter, costs for plants about \$0.50–1.00 per plant in the United States [118,119]. To the rates mentioned before other costs need to be considered related to the design and specific requirements of the wetland system. For example, the average wetland installation cost for a subsurface flow wetland treating wastewater is \$215,000/ha, while the average cost for a surface flow wetland is \$54,500/ha [119]. In developing countries and areas where land is available price can be lower than the cited above.

How long can a CW be operated? The accepted lifespan for passive system designs is 20 years [118], after that CWs would require to be dismantled and residues associated with the treatment must be properly disposed. Particularly in the case of mine water treatment, the fate of the toxic metals has to be monitored. Metals can undergo different transformations by means of processes such as oxidation-reduction, adsorption-desorption, complexation, etc. Therefore, the CW elements such as plants, soil, and media (rock, gravel, etc.) have to be analyzed for metal content and the long-term stabilities of residues need to be tested and evaluated to determine whether they will need to be removed or if special precautions are necessary for final storage. For example, a particular problem arising from the disposal of treatment residues generated by removal of arsenic is that arsenic can be highly mobile and has the potential to leach back to ground and surface waters [120].

The study conducted by Swash and Monhemius [121] focused on analyzing the solubility of residues formed during the effluent treatment of an acidic (pH 3 to 4) mine discharge enriched in iron (<100 mg/L), zinc (<80 mg/L), manganese (<20 mg/L), and arsenic (<2 mg/L) at the Wheal Jane constructed wetland facility in Cornwall, UK. Their results demonstrated that in the aerobic cells, the iron was precipitated as an amorphous (poorly crystalline goethite and ferrihydrite), orange-brown material, usually referred to as ochre, onto which arsenic (>0.1%) and trace amounts of base metals were adsorbed. Thus such residues have to be classified as hazardous waste according to UK landfill regulations. On the other hand, the anaerobic samples were composed mostly of carbonaceous material onto which inorganic elements were adsorbed or had precipitated. They were found to contain minimal amounts of toxic compounds and were considered to be less of a disposal problem [121].

Some studies recommend the harvest of plant material following by its transformation into methane (in anaerobic conditions) or to be used as compost or green fertilizers as the example of polyculture constructed wetland (PCW) designed to the phytoremediation of B mine effluents in field conditions [51].

Other suggested treatments include dewatering, densification, and solidification of the sludges as a prerequisite prior to landfilling to minimize any subsequent settling/subsidence of the landfill site, or solidification using cement or conversion to bricks as final disposal/recycling options.

Solidification/stabilization (S/S) is a feasible management method which includes a range of processes, normally used as a pre-landfill waste treatment that aims to make hazardous wastes safe for disposal [122].

Residues containing a high percentage of carbonaceous material can be disposed of separately, or incorporated into bricks, or dried and burnt to recover the contained metals (Zn, Pb, Cu, and Cd).

The caution of removal and disposal of the residual wastes from the site has to be considered from environmental, health, and cost effects since the costs associated to AMD treatment are much lower than undesirable effects.

5. Concluding Remarks

From all constructed wetlands arrangements sub-surface flow systems have been proven to be the most efficient systems for AMD treatment, mainly by promoting the complete interaction of water with support material and plant roots, and by providing anaerobic conditions that leads heavy metal removal by adsorption and precipitation mechanisms. The metal removal mechanisms are usually attributed to a particular CW component: (i) the support material (mineral and/or organic), which contributes to the removal mainly by adsorption processes, (ii) plants (emerging, floating and submerged) that contribute mainly by direct uptake mechanisms and (iii) microorganisms (bacteria and archaea) which contribute by promoting reduction and subsequent precipitation of metals. However, the removal of heavy metals from aqueous solution comes from an interaction and synergetic effect between them. From all CW components microorganisms are the most interactive ones. Specifically, microorganism-plant interactions play a crucial role on heavy metal removal, principally by the symbiosis that promotes plant growth and heavy metal tolerance mechanisms. Additionally, the formation of litter and biofilm layers as a result of natural CW processes, contributes trapping metals trough adsorption by organic surface groups at advanced stages of system operation.

Strategies for the improvement of heavy metal removal, includes the amendment of organic matter in between the mineral support material to increase heavy metal removal, principally by promoting plant growth, microorganism's establishment, and by trapping heavy metals. Inoculation of AMD with specialized bacterial consortiums into the CW systems also increase heavy metal removal, since most of heavy metals detoxification are mediated by mutant species that express resistance, and increase nitrogen, carbon, and phosphate fixation that subsequently promotes vegetation development. Additional recommendations include a careful vegetation selection and take into account seasonal effects on system operation.

The principal limitations for CW treating AMD is the toxicity effect that heavy metals produce on CW plants and microorganisms. However, these aspects can be solved partially by choosing careful constructed wetlands components suitable to the AMD characteristics. From the economic point of view, a variety of factors affect the cost of constructed wetlands, such as: detention time, treatment goals, media type, pretreatment type, number of cells, source and availability of gravel media, and land requirements, among others. To solve equilibria between systems requirements and costs, an experimental model must include: (1) laboratory studies, (2) bench-scale studies, (3) pilot-scale systems, and (4) full-scale systems. Each of the stages allows to get important and valuable information that could lead to the development of optimum systems and a successful scaling of the CW system. Depending on the size and design of this type of systems they would require rehabilitation every 5–10 years but their expected lifespan is around 20 years. Another important issue is the disposal of the residual waste produced by the system at the end of the operation. In general, the use of residual waste as a construction material is suggested. The caution of removal and disposal of the residual wastes from the site has to be considered from environmental, health, and cost effects, since the costs associated with AMD treatment are much lower than undesirable effects.

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