

## Active Physical Remediation of Acid Mine Drainage: Technologies Review and Perspectives

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### ABSTRACT

The successful acid mine drainage (AMD) treatment needs site-specific installation and implementation, as well as the deployment of technology that is compatible with the pollutants contained in the AMD. If key by-products of the AMD can be recovered, the financial sustainability of the AMD remediation method may be greatly improved. Additional research into novel and innovative solutions is necessary to advance in this direction. To accomplish this, it is necessary to have a complete awareness of current remediation technologies that are available and accessible. Active physical treatment methods such as ion exchange, adsorption, electrochemistry, and membrane techniques were examined in this article. Membrane technology excels in terms of ease of use, versatility, and environmental effect but produces brine streams the management of which remains vital for future adoption of the technology. Liquid membranes (LM), Micellar Enhanced Ultra-Filtration (MEUF), and Polyelectrolyte Enhanced Ultra-Filtration (PEUF) are all innovative membrane technologies that may provide some possibilities for metal recovery from chemical sludge and/or brine streams. Electrochemical technologies are considered an attractive alternative for AMD treatment, because they require only electricity as a consumable and can treat AMD to high standards by removing metals via (co)precipitation and sulfate via ionic migration (when an anion-exchange membrane is used in the configuration), while producing significantly less sludge. However, the accepted shortcomings include membrane/electrode fouling produced by (co)precipitates on the active surfaces necessary for the process, a lack of understanding regarding the effective scaling up to industrial scale, and the relatively expensive capital expenditure (CAPEX) required. The removal of heavy metals from AMD effluents by adsorption has a number of technical and environmental benefits, including high efficiency, and environmental friendliness. Despite its benefits, this technique has certain hurdles, such as the production process for low-cost adsorbents.

**Keywords:** Acid Mine Drainage; electrochemical; ion-exchange; adsorption; membrane processes; active physical treatment.

### INTRODUCTION

#### Environmental problems associated with AMD

Acid mine drainage is a long-standing environmental issue in many current and closed mines. AMD is distinguished by its low pH and high quantities of dissolved heavy metals and sulfates (Worlanyo et al., 2021). Arsenic and other metalloids add to the environmental dangers posed by AMD (Rezaie and Anderson, 2020). Untreated AMD can be harmful to receiving streams and rivers. In the worst-case scenario, river bottoms become coated with a layer of rust-like particles,

causing the pH to drop and all aquatic life to perish i.e. the extinction of flora and indigenous inhabitants, as well as higher forms of life, resulting in a reduction in biodiversity (Han et al., 2017). Dissolved metal levels in water may be harmful to aquatic ecosystems and possibly human health (e.g. zinc, chromium, mercury, arsenic) (Vardhan et al., 2019). This has an impact on the downstream beneficial users of receiving waters (fishing, aquaculture, irrigation, and so on), modifies essential life-supporting balances in water chemistry (e.g., the bicarbonate buffering system), and has an impact on groundwater quality (Al Nagggar et al.,

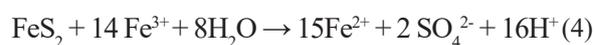
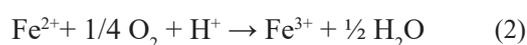
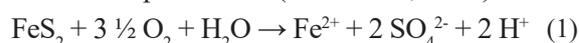
2018). Although the true scale of the environmental damage caused by mine water discharges is often difficult to determine accurately, it has been estimated that in 1989, approximately 19 300 km of streams and rivers as well as about 72 000 ha of lakes and reservoirs worldwide were seriously damaged by mining effluents (Sarmiento et al., 2009). AMD occurs in underground mines, waste rock piles, tailings dams or embankments, tailings storage facilities, and ore stockpiles (Shengo, 2021). These waste dumps often include finer particles than mined rock ore, and the AMD created at these locations is frequently more aggressive. Such mining waste disposal sites can continue to contribute to AMD generation for many years after mining operations have ceased. AMD can occur in the ground waters of deep mines, which is of little concern while the mine is actively producing and the water tables are artificially lowered through pumping. However, when mines are closed and abandoned and pumps are turned off, the water table rapidly rises, resulting in subsurface flooding and the discharge of contaminated groundwater, with potentially catastrophic environmental consequences. The early drainage from abandoned mines dissolves any acidic salt leftovers from the huge exposed surface of the underground workings, and it is often higher in acidity and metal concentration than the subsequent continuous discharge (Candeias et al., 2018).

The water contaminated by AMD must be treated to eliminate the metal and salinity concentrations, as well as increase the pH, before being discharged into the environment to avoid serious environmental damage. Several methods have been used to prevent the generation of AMD as well as to remediate, control, and minimize its consequences (Kefeni et al., 2017). Due to the high expenses of AMD treatment, it may be advisable to take steps to avoid, limit, delay, or stop the occurrence of AMD by implementing adequate measures to prevent or delay the migration of pollutants into the water supply. Underwater storage of mine tailings, land-based storage in sealed waste heaps, mixing of mineral wastes, entire solidification of tailings or the use of organic surfactants (biocides), and microencapsulation are some of these techniques (Sheoran et al., 2010).

### AMD formation

Because of anthropogenic activities, AMD, acidic, sulfur-rich wastewater is produced all over

the world. Although industrial processes such as galvanic processing and flue gas scrubbing at power plants add to the problem, the mining industry is still responsible for the majority of AMD production (Johnson and Santos, 2020). Metal leaching, ore washing, flotation, process water, boiler make-up, and extraction-resin regeneration are some of the mining activities. The greatest amounts of AMD are related with ground and surface water coming into contact with metal deposits, which are mostly sulfide ores associated with pyrite. Coal deposits also contain varying levels of pyritic and organic sulfur, both of which contribute to AMD production (Chaudhuri, 2022).



AMD is formed when pyrite is transformed to sulfates and iron oxyhydroxides by a mixture of chemical and biological processes (Park et al., 2019). This occurs when sulfide-bearing material is exposed to oxygen and water. Although this process happens naturally in iron-sulfide aggregated rocks, mining increases the amount of exposed sulfide minerals, which increases AMD formation (Schimmer and Deventer, 2018). Aerobic bacteria, such as *Acidithiobacillus ferrooxidans*, have a role in enhancing the rate of acid production (Inaba et al., 2019). At pH values above 4, iron-oxidizing bacteria such as *Gallionella ferruginea* can mediate AMD formation chemically or biologically, but at lower pH values, chemical iron oxidation is negligible (Stumm, and Morgan, 1970) and AMD formation is primarily the result of acidophilic iron-oxidizing bacteria activities (Yadollahi et al., 2021).

Bacterial activity, pH, pyrite chemistry and surface area, temperature, and oxygen content all influence the AMD production rates (Rambabu et al., 2020). The pH of polluted water decanting from mining operations can also be greater than 6, especially at discharge points with low dissolved oxygen concentrations. Iron and manganese will be in their reduced, more stable ( $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ) ionic forms in these anoxic circumstances. Although oxygenation will immediately drop the pH of most AMD streams due to the net acidity of the specific water, AMD streams may remain neutral to alkaline. Both “proton acidity” (i.e.,

hydrogen ion concentration) and “mineral acidity” contribute to total or net acidity (the combined concentration of soluble metals, notably iron, aluminum, and manganese, which produce protons when they hydrolyse).

According to reaction (1), when pyrite is first exposed during mining operations, it progressively oxidizes into dissolved iron, sulfate, and hydrogen. The rise in total dissolved solids and acidity of the water caused by the dissolved iron, sulfate, and hydrogen produces a drop in pH. Most ferrous iron will oxidize to ferric iron if the surrounding atmosphere is sufficiently oxidizing, according to reaction (2). Ferric iron precipitates as  $\text{Fe}(\text{OH})_3$  and jarosite at pH 2.3 to 3.5, leaving little  $\text{Fe}^{3+}$  in solution while simultaneously lowering the pH, as shown in reaction (3).

Any  $\text{Fe}^{3+}$  from reaction (2) that does not precipitate from solution via reaction (3) can be used in reaction (4) to oxidize further pyrite. When more  $\text{Fe}^{2+}$  ions are generated, the bacterial oxidation to  $\text{Fe}^{3+}$  continues, resulting in a propagation cycle, which continues until either ferric iron or pyrite is depleted. The breakdown of pyrite finally results in the creation of  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$  ions, resulting in acidic water with a pH as low as 2 (Singer and Stumm, 1970). Although reaction 4 is frequently used to depict the pyrite oxidation process, the principal oxidant is ferric iron rather than molecular oxygen (Evangelou, 2018). In addition, pyrite oxidation involves both oxygen-independent (ferric iron attack on the mineral, reducing it to the ferrous form) and oxygen-dependent processes. The oxidation of reduced sulfur intermediates to sulfate and the re-oxidation of ferrous to ferric iron are examples of these processes. The regeneration of ferric iron is thought to be the most important process in increasing pyrite oxidation (Johnson and Hallberg, 2005). The generation of AMD would be slowed or stopped if any of the processes represented by the equations 1–4 were slowed or stopped. Furthermore, it appears that water is required for this chemical reaction. The rate of pyrite oxidation increases with water vapor pressure until it equals that of immersed pyrite at 100% relative humidity. Given that the rate of the oxidation reaction increases as the concentration approaches saturation, it has been also suggested that water may not necessarily be a reactant, but rather a medium for the transfer of oxidation products from reaction sites. The absence of two of the three main reactants,

air and/or water, from the system would prevent pyrite from being oxidized.

Because the conversion of ferrous iron to ferric iron is slow at  $\text{pH} < 5$  under abiotic conditions, reaction (2) is often the rate-limiting step in pyrite oxidation. Because the Fe-oxidizing bacteria, particularly *Thiobacillus*, greatly accelerate this reaction, the bacterial activity is critical for the development of most AMD. A source of energy and a sufficient supply of oxygen, carbon dioxide, and vital nutrients are critical conditions for microbial sulfide mineral oxidation.

There are significant amounts of  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and other gases in mines. These gases aid the growth of bacterial cells. Bacteria use  $\text{CO}_2$  as their only carbon source, depleting the energy available from  $\text{Fe}^{2+}$  and sulfide mineral oxidation. Only a few types of bacteria can grow on the energy produced from the oxidation of  $\text{FeSO}_4$ .

## ACTIVE PHYSICAL TREATMENT OPTIONS

The AMD remediation methods typically focus on neutralizing the net acidity of water as well as removing dissolved metals and sulfate. The following are the primary factors that influence the choosing of AMD treatment technologies:

- a) Load of toxicity (water chemistry of the untreated AMD)
- b) Environmental objective (protection of mining site infrastructure, downstream aquatic ecosystems or water resources)
- c) Economic variables (capital and operating costs, availability of reagents/materials for treatment)

Because treatment procedures differ according to the analytical characteristics of each individual AMD stream, the most appropriate technology must be chosen based on the intended use of the treated water. The type of water contamination caused by mining operations is highly variable and is mostly determined by the geology of the mining areas and the chemicals employed to extract or concentrate minerals from the host rock. Water, valuable metals, and other substances collected throughout the treatment process all contribute to the sustainability of the AMD remediation method. Legislation governing treated water discharge practices may be the most influential factor in determining the type of treatment system to use for AMD remediation, but the

disposal of metals sludge and sediments, as well as increasingly stringent requirements for treated water, will influence the choice and, thus, the overall cost of AMD treatment. Sulfate limits in treated water discharged from processing plants may constrain the selection of a system to one that successfully removes sulfate, metals, and acidity from mine water. Costs that are not often considered in the technology selection process may include the transportation of liming materials. Due to the high cost of transportation and storage of chemicals, the cost of treating mine water in cold and isolated locations could increase by a factor of two or more. Due to the high cost of AMD treatment for the majority of mine operations, the selection of the “right” approach/technology and its successful implementation is frequently the first priority of any water management venture, as water is an integral and necessary part of any mining operation and thus a critical factor in the sustainability of the mining business. However, because mining occurs in a variety of geological regions with varying water availability, disposal, and pollution requirements, and because AMD can vary in volume and composition depending on the geology of the region where the decant occurs, no single treatment approach can provide a comprehensive solution. Depending on the site objectives and the composition of the wastewater generated during mining operations and/or closure, selecting a suitable AMD treatment approach will necessitate the use of fundamentally diverse technologies. Therefore, this paper examines in depth the physical treatment options that are currently in development/use, as well as their future prospects.

### Membrane based technologies

Possibly the most significant resource recovered during AMD remediation is high-quality water suitable for safe environmental discharge or reuse. Physical treatment technology using membranes has recently been investigated and even used as an additional stage in AMD remediation to give exceptionally high treated water (Abdullah et al., 2019). The membrane technology evolved primarily as a desalination and filtering technology unrelated to AMD treatment (Ali et al., 2018). Only recently, a confluence of factors, including cost reductions associated with membrane applications, increased understanding of the environmental impacts of AMD

pollution, and more stringent legislation governing discharge water quality, and has shifted the focus to the benefits of membrane technology. The ongoing development of membrane technology and processes has a direct impact on the potential use of this technology for AMD remediation, particularly in arid and semi-arid countries, such as South Africa, where the recovery of treated water for reuse is almost certainly worth more than the mere price of the treated water. The bare minimum treatment requirement for AMD remediation is based mostly on active chemical treatment to raise the pH and clarifier technology to extract metal-rich sludge and/or gypsum from the treated water. The membrane technology adds another degree of treatment, resulting in effluent of extremely high quality, suitable for reuse as drinking water. However, the generation of metals-rich sludge during neutralization operations and brines during membrane-based AMD remediation processes continue to be a severe concern. The membrane technology generates both high-quality treated water and a concentrated brine stream from which valuable components such as rare earth metals and precious metals can be recovered (Pramanik et al., 2017). Energy requirements, pre-treatment and final brine treatment or disposal have all been identified as potential roadblocks that must be addressed (Ahmad, 2020). The reduction and eventual reuse of these wastes continues to be a primary focus of current and future research.

### *Reverse osmosis and nanofiltration*

While reverse osmosis (RO) and nanofiltration (NF) technology were first developed for desalination applications, continued advancements have resulted in the use of membrane technology for wastewater remediation and potable water production (Srivastava et al., 2021). According to the available literature, some of the most notable applications of membrane technology for AMD remediation are the ability of the technology to remove metals and sulfides and the high quality of the final treated water (Menzel et al., 2021). This field of research includes studies into the feasibility of low-pressure RO applications for the efficient removal of heavy metals from wastewater using EDTA as a chelating agent (Dadari et al., 2021) and the use of composite membranes for heavy metals removal (Aloulou et al., 2020; Soonmin et al., 2020; Khademian et al., 2020;

Masoumi et al., 2021). Additionally, the RO technology has been used to remove trivalent chromium, cadmium, copper and lead from a variety of wastewaters (Salman et al, 2020; Samaei et al., 2020; Thaçi and Gashi, 2019). The removal of hazardous anions from water using RO and NF membranes indicates that the surface charge of the membranes has a significant effect on their retention characteristics (Kim et al., 2022). These results support conclusion that RO and NF membrane techniques are successful at extracting heavy metals ions from wastewater and may be useful for selective metal recovery from AMD (Qasem et al., 2021). Additionally, the amounts of ammonium and nitrate in mine water effluent were investigated successfully using RO and NF membranes (Grossi et al., 2021; Zou et al., 2019). Pre-filtration of the concentrated brine stream, on the other hand, remains crucial, and the concentrated brine stream can be treated in nitrifying-denitrifying bioreactors (Häyrynen et al., 2009). Application of this technology is the development of an AMD treatment facility near the town of Emalahleni, South Africa, to address the enormous volume of AMD generated by coal mining activities in the region (Grewar, 2019; Santos et al., 2021). The AMD treated at this facility is mostly derived from active and abandoned coal mining activities and is characterized by a high sulfate level and a relatively low metal content. The AMD remediation method involves chemical neutralization and sulfate removal in conjunction to ultra-filtration (UF), and reverse osmosis (RO), which provide water of drinkable quality that supplies 20% of the raw water supply in the town. Brine disposal is currently accomplished by the use of evaporation dams; however, the volume of brine produced continues to be an issue.

French Company Veolia has also developed a membrane based AMD treatment platform called AMDRO, which provide high quality treated effluent. Unlike the South African system, the Veolia system employs clarifying technology as a pre-filter before treating the low pH water with a first-pass RO membrane system, followed by pH adjustment with a second-pass RO system. This arrangement safeguards the membranes against scaling, a significant cost factor in membrane applications.

Although RO and UF employ comparable technologies for AMD remediation and the production of high-quality treated effluent, there is insufficient data to make meaningful comparisons.

Small, but significant variances may exist in terms of total water recovery, brine disposal options, and expenses associated with membrane cleaning and replacement. However, the RO plant in Emalahleni benefits from being operational at full capacity, but little information on comparable operational systems could be found in the literature or from technology vendors.

#### *Liquid membranes*

The use of liquid membranes to optimize metal removal from waste streams including AMD is currently being explored (Qasem, et al., 2021; Panayotova and Panayotov, 2021).

This technology combines metal extraction and stripping into a single operation. Bulk liquid membranes (BLM), emulsion liquid membranes (ELM), and supported liquid membranes (SLM) are all types of liquid membrane technology (Saik et al., 2020), as are multi-membrane hybrid systems (MHS) (Lee et al., 2018). While SLMs are the most stable of all LM technologies, polymer inclusion membranes (PIMs) are being developed as a more effective alternative (Zulkefeli et al., 2018). Metals are transported through these membranes via a carrier (ion-exchange or complexing agent). Zulkefeli et al. (2018) published a list of these carrier reagents that enable the selective removal of particular metal ions from solution. Valenzuela et al. (2009) developed a liquid membrane extraction system for copper removal from an AMD solution at a copper mine in central Chile, based on their research in liquid membrane technology. The extractor system consists of a copper extractant, a non-ionic commercial surfactant, an organic diluent, and sulfuric acid for metal acceptor stripping. The pH, mixing speed, and reactor design are all critical characteristics of this process. By combining the surfactant and extractant with the organic diluent, a primary emulsion is formed. This primary emulsion is then diluted 1:5 with the feed solution (AMD) to generate a double emulsion with the stripping liquid (primary emulsion) droplets encased by a layer of the feed solution. Suspended metal particles then travel spontaneously to the interior stripping liquid, where they are continuously enriched with copper. This initial stage of the method is highly particular for copper removal, and an additional step will be required to remove other metals. Copper is recovered using a sulfuric acid washing process. Although the loss of organic phase

solutions is said to be minimal, the final treated water quality is not discussed. This process may be sensitive to process control variables such as chemical dosing and stirring.

#### *Micellar enhanced ultrafiltration (MEUF)*

MEUF is another membrane-based technology that has been shown to enhance specific metal removal from AMD (Chen et al., 2020). The MEUF processes solubilize metal ions in oppositely charged micelles formed by ionic surfactants (Lin et al., 2021). The MEUF systems operate at a lower operating pressure (6–8 atm) than RO and NF processes [50]. MEUF has been examined for the removal of cationic pollutants ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Cd}^{2+}$ ) (Mirshakar et al., 2021). However, this work has not yet been extended to real multi-component systems (Yusaf et al., 2019), which is necessary for the effective commercialization of this technology in AMD treatment and metal recovery. Polymer enhanced ultrafiltration is a similar technique to low pressure membrane filtration in that it removes metals from a solution following the creation of metal-polyelectrolyte complexes utilizing natural or synthesized polyelectrolytes (Rodrigues et al., 2020). Additionally, experimental work is being conducted to determine the specific removal of chromium and copper from aqueous solutions utilizing the PEUF methods (Sánchez et al., 2018; Kochkodan et al., 2018). The pH of these metal ion-containing solutions has an effect on the net membrane surface charge, depending on the membrane manufacturing material(s). As a result, the effects of various membrane materials and composite materials used in PEUF processes are also being investigated (Qasem, et al., 2021), as is direct metal-membrane interaction and its effect on membrane fouling (Wenten, et al., 2020).

#### *Electrodialysis reversal treatment*

Electro dialysis reversal (EDR) is a membrane technique that has garnered significant attention in recent years (Patel et al., 2020). Direct electrical current is supplied across a stack of alternating anion- and cation-selective membranes in the EDR process. The anions in the raw feed are attracted to the anode but are unable to pass through the cation permeable membrane, resulting in their confinement or concentration in a concentration chamber. The cations, which are travelling in the opposite direction, are obstructed and concentrated in the

same chamber by the anion-permeable membrane. The chambers vacated by the ions are converted into dilution chambers, from which the desalinated product water is retrieved. The advantage of EDR over RO is that it requires minimal pre-treatment due to the periodic polarity reversals that promote membrane cleaning and hence reduce the likelihood of scaling (Honarparvar et al., 2021). Additionally, the EDR process allows for a wide range of working physical parameters such as pH and temperature, and unlike RO membranes, EDR membranes do not suffer from gradual compaction. All of these benefits result in lower operating costs for EDR plants [(Nayar, 2020). A few pilot scale plants have been established using the EDR technology, but on various types of waters (Elsaid et al., 2020). The EDR technology has been examined for the treatment of AMD in the Witwatersrand basin (Mogashane et al., 2020).

#### **Electrochemical treatment processes**

Numerous methods have been reviewed, tested and demonstrated that electrochemical approaches can be used to successfully treat AMD (Garcia-Rodriguez et al., 2020; Park et al., 2019). Electrochemical treatment is relatively costly in terms of capital and energy (Brewster et al., 2020). Electrocoagulation, electrofloatation, and electrodeposition are all examples of common electrochemical treatments (Das and Poater, 2021). Electrocoagulation is a process that generates coagulants in situ by electrically dissolving aluminum or iron ions from aluminum or iron electrodes (Shahedi et al., 2020). The anode generates metal ions, whereas the cathode emits hydrogen gas. Electrofloatation is a solid/liquid separation method that uses tiny bubbles of hydrogen and oxygen gases generated during water electrolysis to lift contaminants to the surface of a body of water (Ganiyu et al., 2020). Electrodeposition is a generally clean method that has demonstrated the metal recovery rates ranging from 40% to 90%, depending on the type of metal being removed (Sharma et al., 2020). Due to the relatively high cost of electrochemical treatment, AMD large scale applications of these procedures are uncommon.

#### **Ion exchange processes**

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex ion exchange resins are

typical ion exchangers. Ion exchangers are either cation exchangers that exchange cations or anion exchangers that exchange anions. The process of ion exchange may be used to remove potential scale forming ions as a pre-treatment or as a stand-alone desalination technique, although this option is usually limited to the water with salinity values of 3000 mg/l. Ion exchange can be used in a variety of bed configurations and with various resin types but the regeneration of the loaded resin is a critical component of the process and the required reagents are often expensive (Liu et al., 2021). GYP-CIX is a low cost ion-exchange technology for the removal of sulfate, calcium, magnesium and other ions from water (Öztürk and Ekmekçi, 2020). The products of the process are reusable/dischargeable water and solid gypsum product that might also have value, depending on local market potential; it has the potential of being the most cost-effective alternative for sulfate removal. AMD is fed counter-current through a fluidized bed of airlifted resin. Firstly, the cations are exchanged onto a resin and then the resin will be discharged into regeneration vessel. The Regeneration of the resin is achieved by the addition of sulfuric acid. The resin is then returned to the start of the loading section. After decarbonizing, the feed water passes through the anion exchange section. The resin from this section is regenerated by the addition of a lime solution to the regeneration vessel. In both regeneration sections, the sulfuric acid and lime solutions are seeded with gypsum crystals to enhance the precipitation process. The product from both the regeneration systems is solid gypsum precipitate (Range and Hawboldt, 2019). It was demonstrated that the feed TDS of 2000–4500 mg/l could be reduced to less than 240 mg/l and 54% of water as a worst case scenario can be recovered while reducing the salt load. The capital cost for an 80 Ml/d ion exchange plant was estimated at US\$26.7M. The operational costs were estimated at 60.4 c/kl. The brine disposal costs were estimated at US\$55.1 M. Therefore, the total desalination costs were estimated at US\$8 1.8 M (Schoeman and Steyn, 2001).

### **(Bio) adsorption processes**

Adsorption is the process by which a substance that was initially present in one phase is removed from that phase through accumulating at the interface between that phase and another solid

phase. Adsorption occurs because of surface energy. In a bulk material, all of the bonding requirements of the constituent atoms (whether ionic, covalent, or metallic) are supplied by other atoms in the substance. However, because the atoms on the adsorbent's surface are not completely covered by other adsorbent atoms, they can attract adsorbates. According to the features of the atom bonding, the absorption processes are classified as physisorption or chemisorption. Adsorption can also be caused by electrostatic attraction (Soliman and Moustafa, 2020). The treatment of AMD with various adsorbents has been extensively explored and described in the literature (Sadeghalvad et al., 2021). However, due to the relatively high cost of the adsorbent materials used, the majority of this study was conducted on a laboratory scale. Several widely used adsorption materials include zero valent iron nanoparticles (Vásquez et al., 2020; Diao et al., 2019), natural and synthetic zeolites (Lobo-Recio et al., 2021; Williams, 2018; Azizi et al., 2021), activated carbon (Serfontein et al., 2021; Nejadshafiee and Islami, 2020), as well as minerals such as apatite and clinoptilolite (Moodley et al., 2018; Prasad, 2018). Laboratory batch experiments demonstrated a considerable reduction in the concentrations of all pollutants monitored as a result of a rise in pH and a decrease in the oxidation–reduction potential associated with the application of zero valent iron nanoparticles (Klimkova et al., 2011). Adsorbent investigations with natural zeolites revealed that around 80% of metal was removed during the first 40 minutes of the reaction (Merrikhpour and Jalali, 2013) whereas using lignite as an adsorbent for AMD treatment resulted in almost complete metal removal (Olds et al., 2013). Activated carbon and zeolites synthesized from other adsorbent materials produced similarly favorable findings (Iakovleva and Sillanpää, 2013).

Numerous studies have been conducted so far on the use of low-cost adsorbents in AMD wastewater treatment. The adsorbent properties of agricultural wastes, industrial by-products and wastes, and natural compounds have been investigated (De Gisi et al., 2016; Lim and Aris, 2014). The cost of adsorbents is a constraint on AMD treatment. As a result of the search for a low-cost and readily available adsorbent, agricultural and biological materials have been investigated as prospective metal sorbents (Ahmaruzzaman, 2011; Bhuyan et al., 2021). The capacity of certain types of microbial biomass to accumulate

heavy metals from aqueous solutions is referred to as biosorption. Microbial biomass could be viewed as a biological ion exchanger (Kim and Park, 2021). Numerous microorganisms from various categories, including bacteria, fungus, yeasts, and algae, have been shown to bind a range of heavy metals to varying degrees (Pandey and Keshavkant, 2021). Biosorption is a technology that works well with dilute waste streams. Biosorbents can be formed from three types of biomass: non-living, algal, and microbial (Filote et al., 2020). Few researchers have also employed crab shells as an adsorption material to treat AMD, with good results (Lin et al., 2021). The adsorption of Zn and Cu from acid mine drainage using vegetative compost was also assessed (Westholm et al., 2014). Zhang (2018) explored the removal of Cu, Pb, and Zn from AMD using dairy manure compost. Potato peels, sawdust, blackgram husk, eggshell, seed shells, coffee husks, sugar-beet pectin gels, and citrus peels were also examined as non-living plant material for wastewater treatment (Anjum, 2017). Algae were evaluated as a natural biomass for metal removal from wastewaters due to their widespread availability, low cost, and high capacity for metal sorption (Bulgariu and Bulgariu, 2020). Such studies include the biosorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  using dried marine green macroalgae *Chaetomorpha linum* (Ajajbi and Chouba, 2009), the biosorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  using dried marine green macroalgae *Caulerpa lentillifera* (Bulgariu and Bulgariu, 2020), the biosorption of chromium from wastewater (Hariharan et al., 2020). The biosorption of heavy metals by dried sea green macroalgae (*C. linum*) was also examined (Santos et al., 2018), *Bacillus cereus* (Todorova et al., 2019), *Escherichia coli* (Khosravi et al., 2020; Abdelbary et al., 2019), and *Pseudomonas aeruginosa* (Chellaiyah, 2018) were all used in biosorption. Additionally, various fungi and yeast strains were used to absorb heavy metals from aqueous solutions, as detailed by Singh et al. (2022). The biosorption research is still in its development phase, with the majority of work being experimental in nature.

## PHYSICAL REMEDIATION OPTIONS: DECISION-MAKING FACTORS

Though there is a variety of physical technologies available at laboratory scale, most of these have not been efficiently deployed in pilot

or full-scale operations. Moreover, none of these methods are capable of treating all wastewater streams encountered in the mining industry, owing to the fact that each water stream is unique. Additionally, the outcome of treatment of these streams differs. In some instances, one wishes to recycle water, or to increase the water quality sufficiently for disposal into environmental bodies of water, or to recover specific components. Each of these systems is optimal for a particular wastewater stream and intended results. Table 1 outlines the present features of the physical technologies that may make them more or less desirable for deployment. The majority of AMD rehabilitation treatments begin with chemical neutralization and the controlled removal of metals and gypsum (Kaur et al., 2018). Depending on the specific needs for the treated water use, physical technology such as membrane-based technology is a great alternative for further treatment, up to and including drinking standards. The membrane technology is crucial in treating AMD and alleviating water constraint. Apart from addressing water constraint, the membrane technologies excel in terms of ease of use, versatility, and environmental impact (Moreira et al., 2022). However, all membrane processes generate brine streams, and lowering the volume of brine for disposal and/or treatment, as well as recoverable valuable by-products from these brine streams, is a critical component of future AMD treatment research (Mogashane et al., 2020). Liquid membranes, MEUF, and PEUF processes are new membrane technologies that may provide some answers to the recovery of metals from chemical sludge and/or brine streams. Liquid membrane applications are likely the most advanced at this moment in terms of technological maturity, with Cu (II) extraction pilot experiments already underway in Chile. However, the enhanced UF processes offer intriguing potential and should be more resilient, less reliant on chemical additives, and more cost effective than LM processes at large scale. One noteworthy downside of the upgraded UF technology is that experimental systems are currently confined to extracting a single metal species or separating no more than two metal species from a solution. Simultaneous separation of pure metals from the combination of metals as found in real AMD would be a quantum leap ahead in this area. The membrane fractionation of metals or metal complexes using chelating agents and/or surfactants may be the way ahead for metal separation,

purification, and concentration in the future. This is applicable not just to AMD treatment, but also to the treatment and recovery of valuable by-products from the waste streams of other metal industries, such as electroplating and smelting. Due to the high cost and infrastructure required to set up and maintain large-scale metal recovery plants, it would be more cost effective to treat just concentrated waste streams in this manner. The outcome of high-density sludge processes coupled with AMD neutralization, as well as the brine streams from membrane processes, may be good candidates for such metal recovery applications due to their small volume. The available literature and examples of recent large-scale use of membrane technology reveal that AMD remediation can now be enhanced to the point where reuse possibilities encompass both drinkable water production and

acceptable environmental discharge of treated AMD (Santoro et al., 2021; Kapoor et al., 2021). Regrettably, the practicality of future AMD remediation is intrinsically connected to the costs associated with the various techniques. While membrane treatment is costly, these direct process costs must be measured against the true value of the treated water, not against the value of other water suppliers, such as direct delivery of potable water from a national utility services. Although the membrane technology is a relatively new tool for pollution remediation, present and future research suggests that it has the potential to play a key role in future AMD remediation and the recovery of valuable by-products. The true value of AMD treated to a good quality for safe, beneficial environmental discharge or direct reuse as a source of potable water, may be much

**Table 1.** Summary of physical technologies for application in AMD remediation, their target area and the relative levels of maturity

Technology	Application	Target area of AMD remediation	Scale	Reference
RO	Final treatment of AMD following chemical neutralisation	High quality water for reuse	Commercial-scale	(Panayotov and Panayotov, 2021)
RO & NF	Metal species separation	Metal recovery	Experimental-scale	(Naidu et al., 2019; Chen et al., 2021)
Liquid membranes	Pilot-scale Cu(II) removal from AMD application in Chile	Cu ions removal from AMD	Pilot-scale	(Valenzuela et al., 2009)
MEUF	Micellar-enhanced UF dependent metal removal from aqueous solutions	Recovery of various metals from AMD and other process waste streams	Experimental-scale	(Yaqub and Lee, 2020; Lin et al., 2017)
PEUF	Polymer-enhanced UF dependent metal removal from aqueous solutions	Recovery of various metals from AMD and other process waste streams	Experimental-scale	(Huang and Feng, 2019; Lin et al., 2021; Panayotova and Panayotov, 2021)
Electro dialysis reversal treatment	AMD treatment	Water recovery	Pilot scale	(Scarazzato et al., 2020; Martí-Calatayud et al., 2014 ; Pulles, 2006; Range and Hawboldt, 2019)
Electrochemical treatment	Removal of metal from AMD and other waste waters	Metal removal	Commercial-scale	(Maarof et al., 2017)
Ion exchange process	Water with salinity values of 3000 mg/l	Removal of scale forming ions	Demonstration scale	(Vecino et al., 2021; Oyewo et al., 2018; van Rooyen and van Staden, 2020)
Ion exchange in fluidized bed (GYP-CIX)	AMD feed treatment	Recovery of ions from AMD and recovery of water	Demonstration-scale	(Klein et al., 2013; Mogashane et al., 2020)
Adsorption process	AMD treatment	Removal of heavy metals from wastewater through adsorption process	Experimental-scale	(Esmaeili et al., 2019 ; Feng et al., 2019)
Low cost adsorbent	Waste water treatment	Adsorption of heavy metals	Laboratory scale	(Levio-Raiman et al., 2021; Zheng et al., 2020; Iakovleva and Sillanpää, 2020 ; Carrillo-González et al., 2021)
Biosorption	Metal removal from AMD through adsorption	Metal removal	Experimental-scale	(Kim and Park, 2021; Hurtado et al., 2018; RoyChowdhury et al., 2019; Kanamarlapudi et al., 2018)
BioteQ Sulf IX	Treatment of industrial wastewater	Sulphate removal	Pilot-scale	(Fernando et al., 2018)

higher than the treatment expenses. However, if valuable by-products from the AMD remediation process can be obtained, the financial sustainability of AMD remediation will be considerably improved. These recoverable products may include sulfur and heavy metals, depending on the origins of certain AMD streams. The efficient recovery of these components, combined with the generation of high-quality water for reuse, will considerably boost the economic incentive for AMD treatment while also preserving the environment. Electrochemical technologies are considered an attractive alternative for AMD treatment, because they require only electricity as a consumable and can treat AMD to comparable standards by removing metals via (co)precipitation and sulfate via ionic migration (when an anion-exchange membrane is used in the configuration), while producing significantly less sludge. However, the acknowledged downsides include membrane/electrode fouling caused by (co)precipitates on the active surfaces necessary for the process, a lack of understanding regarding the effective scaling up to industrial scale of these processes, and the relatively high capital expenditure required.

## CONCLUSIONS

Mining is beneficial to the economy, but generally detrimental to the environment. Regulators and governments worldwide are becoming more aware of the environmental consequences of mining and taking steps to alleviate them. This has compelled mines to develop treatment methods and additional research is essential to ensure progress in the treatment of mine water at current and abandoned mine sites. The issue with AMD treatment is that it is frequently prohibitively expensive, and there is no universally acknowledged solution that is ecologically acceptable. Each treatment option carries its own set of costs and benefits. For the last half-century, the AMD treatment has been concentrated on water treatment and associated financial expenditures, oblivious to the downstream consequences of sludge formed during treatment activities. It has now become clear that any sustainable AMD treatment solution must break the waste cycle and strive for zero waste generation, as it is imperative to not only remove the legacy of decades of ineffective mine waste management, but also prevent the emergence of new. This will require mature

and legitimate technologies that holistically address the AMD concerns. This requires a thorough understanding of current remediation technology and tools. It is within this context that this paper has reviewed the active physical treatment methods such as ion exchange, adsorption, electrochemistry, and membrane technologies. The membrane technology is simple to use, versatile, and has a low environmental impact but generates brine streams; thus, limiting the volume of brine required for disposal and/or treatment, as well as collecting valuable by-products from these brine streams, is critical for future deployment. Liquid membranes, Micellar Enhanced Ultra-Filtration, and Polyelectrolyte Enhanced Ultra-Filtration are all innovative membrane technologies that may be used to recover metals from chemical sludge and/or brine streams. Liquid membrane applications are undoubtedly the most technologically advanced at the moment. Upgraded Ultra-Filtration (UF) methods, on the other hand, have tremendous potential because they should be more robust, less dependent on chemical additives, and more cost effective at scale than LM techniques. The electrochemical technologies are considered an attractive alternative for AMD treatment because they use only electricity as a consumable and can effectively treat AMD by removing metals via (co)precipitation and sulfate via ionic migration (when an anion-exchange membrane is used in the configuration), while producing significantly less sludge. However, recognized disadvantages include membrane/electrode fouling produced by (co)precipitates on the active surfaces of the process, a lack of understanding regarding effective scaling up to industrial scale, and the comparatively high capital expenditure required. Adsorption-based heavy metal removal from AMD effluents offers a number of technical and environmental advantages, including high efficiency, and environmental friendliness. Despite its advantages, this technique has challenges, including the production process for low-cost adsorbents.

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