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REVIEW OF TREATMENT TECHNOLOGIES FOR HEAVY METALS FROM ACID MINE DRAINAGE

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The mining activity generates acid drainages that cause a dispersion of heavy metals in the water and soils. Water pollution by heavy metals is a problem in mining areas. Heavy metals have serious effects on the environment and health exposed in various toxicological studies. Over the years, several technologies have been developed to reduce and eliminate heavy metal from acid mine drainages, among others: ion exchange, electrochemical reduction, reverse osmosis, precipitation chemistry, membrane filtration, coagulation and flocculation, adsorption and biosorption. Besides these methods allow the minimization or elimination of the contaminant, they also have disadvantages such as high requirements for reagents and / or energy, generation of toxic sludge and other waste products. This study makes a bibliographic analysis of the most relevant studies on these methods and evaluates the different technologies for heavy metal removal in the particularities of mine drainage.

Keywords: *Heavy metals; micro basin; mining; water problems.*

REVISIÓN DE TECNOLOGÍAS DE TRATAMIENTO PARA METALES PESADOS PROVENIENTES DE DRENAJE ÁCIDO DE MINA

La actividad minera genera drenajes ácidos que ocasionan una dispersión de metales pesados en el agua y suelos. La contaminación hídrica por metales pesados es una problemática en zonas de explotación minera. Los metales pesados tienen graves efectos sobre el medio ambiente y la salud reflejados en diversos estudios toxicológicos. A lo largo de los años se han desarrollado varias tecnologías para disminuir y eliminar las concentraciones de metales pesados provenientes de drenajes ácidos de mina, entre otros: el intercambio de iones, la reducción electroquímica, la ósmosis inversa, la precipitación química, la filtración por membrana, la coagulación y floculación, la adsorción y la biosorción. Si bien estos métodos permiten la minimización o eliminación del contaminante, también tienen desventajas como altos requerimientos de reactivos y/o energía, generación de lodo tóxico y otros productos de desecho. Este estudio realiza un análisis bibliográfico de los estudios más relevantes sobre estos métodos y evalúa las distintas tecnologías para eliminación de metales pesados en las particularidades de drenaje de minas.

Palabras clave: *Drenajes ácidos de mina; metales pesados; tratamientos de agua.*

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1. Introduction

Pollution from mining is a major problem in many parts of the world. Several examples of contamination from mining waste are observed in the United States of America (Kleinmann, 1989), Canada (Sracek et al., 2004), and in other parts of the world including Africa, South America, Europe, Australia, and Asia.

Mining activities generate solid and liquid wastes that are potentially hazardous to water resources and the environment (Akcil & Koldas, 2004; Duruibe et al., 2007). Mine water, also known as acid mine drainage (AMD) or acid rock drainage, is considered as one of the main water pollutants in many countries with historical or current mining activities (Simate & Ndlovu, 2014; Yadav & Jamal, 2016). AMD causes severe environmental pollution due to its high acidity, heavy metal content, and sulfate content (Kefeni, Msagati & Mamba, 2017).

AMD has resulted in heavy metals being widely discharged into the environment (Duruibe et al., 2007). This presents a particular concern because heavy metals become potentially hazardous to human health when their concentrations increase above background levels (Gaikwad & Gupta, 2008). Heavy metals also have high persistence in the environment (Zhao et al., 2016). This implies both a current and future risk.

In Milluni in Bolivia, where mining activities have remained largely unregulated (Salvarredy-Aranguren et al., 2008), AMD is one of the most important causes of heavy metal contamination in surface water. With a focus on the Milluni region, this study reviews different techniques for removing heavy metals from AMD wastewater with the aim of identifying the advantages, limitations, and potential applicability of these different treatments.

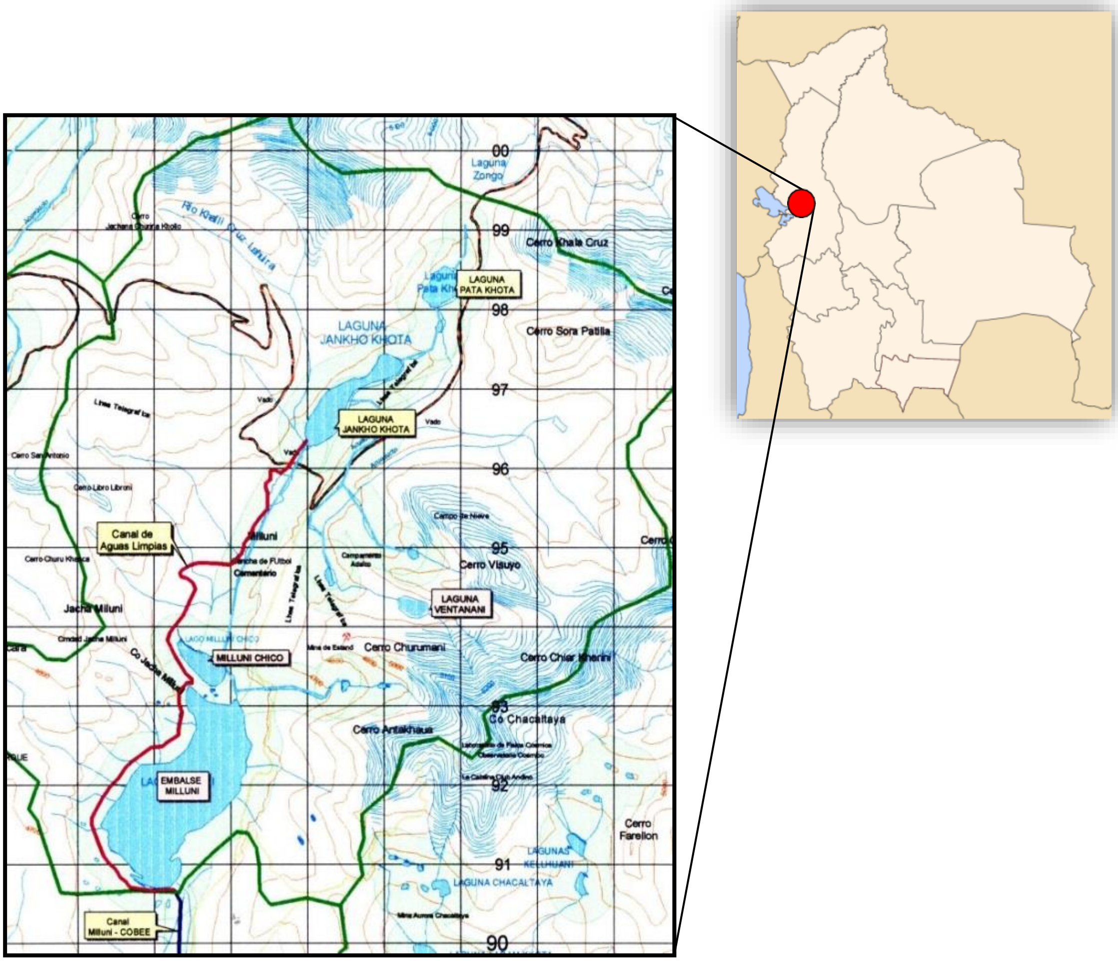
1.1 Mining in the Milluni region

The Milluni Valley is located 4,500 m above sea level in the Bolivian Tin Belt, which consists of massive sulfide deposits in the Eastern Andes. This 40 km^2 area is part of the basin system of the Altiplano Plateau that presents extreme climatic conditions otherwise typical of the area (Ahlfeld, Schneider-Scherbina & Bolivia, 1964).

The Milluni Valley has a typical U-shaped geomorphology as a product of the last glacial regression. There are four lagoons in the upper Milluni Basin: Pata Khota Lagoon, Jankho Khota Lagoon, Milluni Chico Lagoon, and Milluni Grande Lagoon (Iltis, 1988). The first two of these are natural lagoons and receive waters from the snowmelt of Huayna Potosí Mountain. Here, water pollution is very low or completely absent. The third lagoon, Milluni Chico, is an artificial lagoon with an irregular shape, which captures mine-draining waters to prevent them from entering the Milluni Grande Lagoon (Figure 1).

The surface water bodies in Milluni contribute to a storage dam located in the Milluni Grande Lagoon. This dam has an area of 2,450,000 m^2 and a capacity of 10,000,000 m^3 (Raffaillac, 2002). The Milluni Basin provides the largest contribution to the water supply for La Paz and, for this reason, water quality in this area is a matter of great importance. Milluni Mine operated from 1940 until 1990, principally extracting Sn, Zn, and Pb. A very large volume of sulfide-rich mine waste has been deposited in the area as a result of a range of mining activities that employed a variety of separation techniques (Ríos, 1985). Even though widespread mining activities stopped around 20 years ago, the impact of mining waste on water quality remains a serious national environmental problem (Salvarredy-Aranguren et al., 2008). Another problem that has arisen in recent decades is small-scale mining, which exists without any regulation. For the most part, this activity is intermittent and illegal, and so very little information exists about its impact on water quality.

Figure 1: Location of Milluni



Note: ALBA, Milluni, 2005

1.2. Acid mine drainage

AMD is produced when sulfide-bearing material is exposed to oxygen and water. The production of AMD usually, but not exclusively, occurs in rocks containing iron sulfide. Although this process occurs naturally, mining can promote AMD generation simply through increasing the quantity of sulfide exposed at the Earth's surface. Naturally occurring bacteria can accelerate AMD production by assisting in the breakdown of sulfide minerals (Akcil & Koldas, 2004; Simate & Ndlovu, 2014).

AMD poses a severe pollution problem to current and future generations, especially due to its low pH and high concentration of potentially toxic dissolved metals, metalloids, and sulfates (Anawar, 2015; Kefeni, Msagati & Mamba, 2017). The most frequent AMD pollutants are Fe, Mn, Al, and SO_4, with locally important contributions from other metals and metalloids including Zn, Cu, As, Ni, Cd, and Pb (Younger, 2004). Once AMD is generated, it is difficult to prevent major environmental problems where mining activities are or have been common (Qureshi, Maurice & Ohlander, 2016). AMD compromises the environmental quality of surface and groundwater systems by destroying aquatic life and increasing human health risks (Kefeni, Msagati & Mamba, 2017).

1.3. Effects of heavy metals on human health

The term 'heavy metal' is applied to a group of elements having atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0. Examples are lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), and copper (Cu) (Srivastava & Majumder, 2008). Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants in the environment (Thayer & Brinckman, 1982). In particular, heavy metals are considered especially dangerous contaminants in freshwater reserves.

Heavy metal toxicity has proven to be a major threat to humans and there are several health risks associated with it (Jaishankar et al., 2014). While heavy metals are required in small amounts to maintain good health, in larger amounts they can become toxic (Raja Rajeshwari & Namburu, 2014). Toxic concentrations can damage the functioning of vital organs including the brain, lungs, kidneys, and liver, and they can also affect the composition of blood. Long-term exposure can lead to degenerative physical, muscular, and neurological problems that imitate diseases such as multiple sclerosis, Parkinson's disease, Alzheimer's disease, and muscular dystrophy (Jaishankar et al., 2014). Repeated long-term exposure to some heavy metals and their compounds have also been linked to human cancers (Raja Rajeshwari & Namburu, 2014).

2. Treatments to remove heavy metals from water

Remediation options for waters contaminated with heavy metals as a result of AMD include: monitored natural attenuation; physical intervention to minimize the release of pollutants; and active and passive water treatment technologies (Younger, 2004). The following sections outline water treatment technologies (both active and passive) that are more widely used to remove heavy metals from water.

2.1. Chemical precipitation

Chemical precipitation is one of the most well-established and widely used methods for removing metals from wastewater (Gautam et al., 2016). As the name implies, chemicals are used to react with heavy metal ions to form insoluble precipitates that can subsequently be separated from water by filtration or sedimentation (Fu & Wang, 2011; Zhao et al., 2016). Conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation. As an alternative, many companies use chelating precipitants to precipitate heavy metals from aqueous systems (Matlock, Henke & Atwood, 2002). Mirbagheri and Hosseini (2005) used $Ca(OH)_2$ and NaOH to remove Cu(II) and Cr(VI) ions from wastewater, reducing the concentration of chromate from 30 mg/L to 0.01 mg/L and copper from 48.51 mg/L to 0.694 mg/L. Özverdi and Erdem (2006) investigated the use of pyrite and synthetic iron sulfide to remove Cu^{2+}, Cd^{2+}, and Pb^{2+}. The mechanism governing the metal-removal process was chemical precipitation at low pH (<3) due to H_2S generation and adsorption at a higher pH (3–6).

2.2. Ion exchange

The ion exchange process is a widely used approach for removing heavy metals from wastewater using synthetic or natural solid ion-exchange resins, which have the specific ability to exchange cations with metals in the wastewater (Cavaco et al. 2007; Fu & Wang, 2011). Synthetic resins are commonly used for their efficiency and absolute removal capabilities. For example, Alyüz and Veli (2009) demonstrated the removal of Ni and Zn aqueous solutions using synthetic resins. However, naturally occurring silicate minerals and natural zeolites have also been extensively applied given their relatively low cost, prevalence, and often outstanding metal-adsorption capabilities under different experimental conditions (Ostroski et al., 2009).

2.3. Adsorption

Adsorption is a process in which a single or group of ions/compounds are accumulated on the surface of another solid or liquid (Silver & Phung, 1996). The substance on which the adsorption takes place is known as adsorbent and the substance that is adsorbed is called the adsorbate (Gautam et al., 2016). The effectiveness of this process is dependent on the adsorbent material (Zhao et al., 2016). For example, activated carbon (AC) is the most widely used adsorbent, and a large number of researchers have studied AC in the context of heavy metals (Jusoh et al., 2007; Kang et al., 2008).

The search for other low-cost and easily available adsorbents to remove heavy metal ions has become an important research focus. To date, hundreds of studies on the use of low-cost adsorbents for heavy metal wastewater treatment have been reported (Fu & Wang, 2011). Kobya (2004) studied the removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon. Sud, Mahajan, and Kaur, (2008) reviewed agricultural waste material as a potential adsorbent for the removal of heavy metal ions from aqueous solutions. Wan Ngah, and Hanafiah, (2008) studied the removal of heavy metal ions from wastewater using chemically modified plant wastes as adsorbents. Indeed, some treated adsorbents show good adsorption capacities with respect to Cd, Cu, Pb, Zn, and Ni.

2.4. Biosorption

Biosorption of heavy metals from aqueous solutions is a relatively new process that has been identified as a very promising process. Typical biosorbents can be derived from three sources, as follows (Apiratikul & Pavasant, 2008):

- Non-living biomass, such as potato peels (Aman et al., 2008);
- Algal biomass, such as the dried marine green macroalga *Chaetomorpha linum*, which is used for the biosorption of Cu^{2+} and Zn^{2+} (Ajjabi & Chouba, 2009);
- Microbial biomass, such as *Escherichia coli*, which is used for biosorption (Souiri et al., 2009).

Biosorbents have a wide range of sources, however, research into the optimization of different biosorbents under a range of operating conditions is still in the theoretical and experimental stages (Fu & Wang, 2011).

2.5. Wetlands

There are two types of wetlands, natural and constructed. Natural wetlands are characterized by water-saturated soils with supporting vegetation. It was first noted that AMD can be ameliorated through naturally occurring sphagnum moss bogs (Yadav & Jamal, 2016). In comparison, constructed wetlands utilize organic substrates to support bacterially mediated sulfate reduction and dissolved metal removal from AMD (Ayora et al., 2016).

Wetlands are broadly classified as either aerobic or anaerobic. Aerobic wetlands are shallow ponds usually designed to promote the precipitation of metal oxides or hydroxides by providing aeration and suitable retention times. They are vegetated with emergent plant species and contain an approximate 15- to 25-cm water level to maintain aerobic conditions. This approach requires longer retention time and a large surface area for successful treatment of mine water (Sheoran & Sheoran, 2006). Anaerobic wetlands are typically modifications of natural wetlands with emergent vegetation, but also contain a 30–60 cm organic layer over a 15–30 cm bed of limestone. Alternatively, a mixed layer of organic matter and limestone can be applied to a depth of approximately 50–100 cm (Zipper, Skousen & Jage, 2011). Some examples demonstrating how this passive treatment technology has been developed recently are provided by Pat-Espadas et al. (2018).

2.6. Coagulation and flocculation

Coagulation and flocculation followed by sedimentation and filtration are also employed to remove heavy metals from wastewaters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Many coagulants are widely used in conventional wastewater treatment processes such as aluminum, ferrous sulfate, and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. Flocculation involves the action of polymers to form bridges between the flocs and the binding the particles into large agglomerates or clumps. Once suspended, particles are flocculated into larger particles, and they can usually be removed or separated by filtration, straining, or floatation. Currently, many kinds of flocculants are widely used in the treatment of wastewater including Polyaluminium Chloride PAC, polyferric sulfate (PFS), and polyacrylamide (PAM) (Fu & Wang, 2011).

Generally, coagulation and flocculation cannot completely remove heavy metals from wastewater (Chang & Wang, 2007). Therefore, these processes must be followed by other treatment techniques to be completely successful. For example, Plattes et al. (2007) employed the precipitation, coagulation, and flocculation processes using ferric chloride to remove tungsten from wastewater. Acidic conditions ($pH < 6$) proved most successful in their study, removing 98–99% of tungsten from the treated waters.

2.7. Flotation

Originating in the mineral processing industry, flotation can be employed to separate heavy metals from liquid phases via bubble attachment. Dissolved air flotation (DAF), ion flotation, and precipitation flotation are the main techniques used for the removal of metal ions from solution (Fu & Wang, 2011). DAF is the most commonly used among these for the purification of metal-contaminated wastewater (Gautam et al., 2016), which has been studied since the 1990s (Waters, 1990) and continues to be the subject of ongoing development.

2.8. Membrane filtration

Membrane filtration is a pressure-driven separation process for heavy metals that can be enhanced by treating membranes with suitable chemical materials (Zhao et al., 2016). The membrane processes used to remove metals from the wastewater are ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis (Fu & Wang, 2011). These technologies, as outlined in the following sections, are the most promising for minimizing water consumption via wastewater reclamation (Liu et al., 2011).

2.8.1. Ultrafiltration (UF)

On the basis of pore size (of the range 2–50 nm) and the molecular weight of the separating compounds (1000–100,000 Da), UF, which is an energy intensive process, works at low transmembrane pressures for the removal of dissolved and colloidal materials (Zhao et al., 2016). Particles that are larger than the pore size of UF membranes are trapped, while dissolved metal ions (in the form of hydrated ions or low-molecular-weight complexes) pass through easily (Vijayalakshmi et al., 2008).

To obtain high removal efficiency of metal ions, micellar-enhanced ultrafiltration (MEUF) and polymer-enhanced ultrafiltration (PEUF) processes have been proposed (Fu & Wang, 2011).

In the MEUF process, metal ions are captured within surfactant micelles and they form large metal-surfactant structures (Liu et al., 2016). For example, Zeng et al. (2011) demonstrated the use of MEUF for the removal of Cd(II) from synthetic wastewater. In the PEUF process, water-soluble polymers form complexes with metal ions and form macromolecules with higher molecular weights, which are then retained when pumped through a UF membrane (Landaburu et al., 2009). Molinari, Poerio, and Argurio, (2008) used this process in the selective separation of Cu^{2+}, and Ni^{2+} from aqueous media during a complexation-ultrafiltration process.

2.8.2. Nanofiltration (NF)

NF is the intermediate process between UF and RO (Fu & Wang, 2011). The application of NF processes for AMD treatment has recently attracted attention due to its high capacity for salt and metal retention (Kefeni, Msagati & Mamba, 2017). In this process, the molecular weights of the separating compounds range between 200 Da and 1000 Da, with pore diameters varying from 0.5 nm to 2 nm (Khedr, 2008). NF is a promising technology for the removal of heavy metal ions including Ni (Murthy & Chaudhari, 2008).

2.8.3. Reverse osmosis (RO)

RO, which involves membranes with a pore size of < 2 nm, works on the principle of size exclusion and solution diffusion through a semipermeable membrane (Greenlee et al., 2009). A significant advantage of RO over other traditional water treatment technologies is the ability to reduce the concentrations of other ionic contaminants as well as dissolved organic compounds (Fu & Wang, 2011); RO can remove more than 99% of all dissolved minerals (Akpor & Muchie, 2010). For example, Cu^{2+} and Ni^{2+} ions were successfully removed using RO, and rejection efficiencies of up to 99.5% were achieved using Na2EDTA (Mohsen-Nia, Montazeri & Modarress, 2007).

2.8.4.Electrodialysis (ED)

With the addition of electric potential, ED is another membrane separation process that employs ion-exchange membranes through which ionized species in a solution can pass. These membranes can be divided as two basic types: (1) cation-exchange membranes, in which cations move toward a cathode; and (2) anion-exchange membranes, in which anions migrate to an anode (Chen, 2004). In one example, Lambert et al. (2006) studied the separation of Cr(III) from sodium ions using ED with modified cation-exchange membranes.

2.9. Electrochemical treatments

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Given the stringent environmental regulations regarding wastewater discharge, electrochemical technologies have regained worldwide importance over the last two decades (Wang, Hung & Shammas, 2007). For example, Chartrand and Bunce (2003) described the electrolysis of synthetic AMD solutions containing Fe, Cu, Ni, and mixtures of these metals using flow-through cells divided by ion-exchange membranes. They showed that ions could be successfully removed using this process.

3. Synthesis and discussion

Table 1 summarizes the advantages and limitations of the reviewed techniques for wastewater treatment involving heavy metals. The most suitable treatment techniques depend on the initial concentrations of the metal, the composition of the wastewater, capital investment and operational costs, plant flexibility and reliability, and environmental impact (Kurniawan et al., 2006).

Table 1: Processes for the removal of heavy metals

Process	Advantages	Limitations
Chemical precipitation	Well established Easy to apply	Generates sludge and dangerous by-products Hazardous chemicals are used in the process Not economical when metal ion concentrations are high due to the high demand for chemicals
Ion exchange	High efficiency Fast process	Requires pretreatment High operating costs High costs involved in the regeneration of resins For large quantities of competing mono and divalent ions, ion exchange is almost totally ineffective
Adsorption	Low cost in some cases Easy operation Reusability and recyclability of the sorbent	Effectiveness is dependent on the adsorbent materials Generation of sorbents with heavy metals Difficulty separating sorbents and heavy metals
Biosorption	Low cost Easy operation Rapid adsorption	Effectiveness is dependent on the adsorbent materials Generation of biomass with heavy metals Difficulty separating sorbents and heavy metals
Wetlands	Low operating and maintenance costs Requires a large area	High initial cost of construction depending on the conditions for plant growth Generation of biomass with heavy metals Long remediation time
Coagulation and flocculation	Various heavy metals can be treated	Must be followed by other treatment techniques to be completely efficient
Floatation	High metal selectivity Shorter retention times	High initial capital cost High maintenance and operation costs Still under study and development
Membrane filtration (UF, NF, RO, and ED)	Highly efficiency High separation selectivity Space saving Easy operation Fast process	Requires pretreatment High operating costs High energy consumption
Electrochemical treatment	Low operating cost	Large capital investment High energy consumption

Note: Data from Gaikwad and Gupta (2008); Akpor and Muchie (2010); Fu and Wang (2011); Simate and Ndlovu (2014); Yadav and Jamal (2016); Zhao et al. (2016); and Kefeni, Msagati, and Mamba, (2017).

The selection of adequate treatments for the removal of heavy metals from mine wastewater should be considered an important component of any effective and integrated management strategy for mining activities and their impacts, such as AMD pollution.When designing wastewater treatments for a particular region, the efficiency, duration, and costs of implementation, operation, and maintenance are significant parameters that must be taken into account. In the case of the Milluni region of Bolivia, the key factors to consider are an altitude of more than 4,500 m above sea level, extreme climatic conditions typical of the Altiplano Region, and its crucial function as the main water supply for La Paz. Limitations such as prolonged treatment durations, climatic and altitudinal effects on any chosen treatment, the use of hazardous chemicals, the generation of large volumes of polluting byproducts, and treatment efficiencies that depend on many factors that are difficult to control pose risks to the success of mining wastewater treatment in this area. Therefore, membrane filtration and ion exchange are suggested as the most suitable techniques for the treatment of AMD in the Milluni region.

4. Conclusions

Removal of heavy metal ions from wastewater can be accomplished using various active or passive technologies. For the Milluni region of Bolivia, two techniques have been identified as being most suitable: (1) ion exchange and (2) membrane filtration, especially RO.

It should also be considered that each mine is unique in terms of its potential to generate AMD. Therefore, the nature and size of associated risks and the feasibility of different mitigation options will vary from one site to another. There are no standardized methods to classify, measure, and reduce the risk of AMD. For this reason, the selection of appropriate treatments must be made on a case-by-case basis.

In future research, the combination of the most efficient technologies identified here with other types of treatments should be considered in depth, with the aim of optimizing the elimination of heavy metals from AMD and improving water quality.

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