Review article

Mining wastewater treatment technologies and resource recovery techniques: A review

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ABSTRACT

Mining wastewater can have adverse effects on the ecosystem; thus, treatment before discharging into the environment is of utmost importance. This manuscript reports on the effect of mining wastewater on the environment. Moreover, the currently used, effective and commercialised mine wastewater treatment technologies such as SAVMIN®, SPARRO®, Biogenic sulphide, and DESALX® are reported in this study. These technologies integrate two or more separation processes, which have been proven to be effective for the high recovery of salts and water for reuse. Some of the technologies reported can significantly recover salts and >95% of water. Modern pilot-stage and laboratory-scale treatment systems used for the recovery and removal of metals are also reported herein. Since some treatment technologies can generate highly toxic sludge and other waste products, the management of the generated waste was also considered. Some studies have focused on the treatment of wastewater at the laboratory level using the adsorption process. Most adsorbents exhibit promising results; however, there is insufficient research on reusability, toxic sludge management, and the economic analysis of the systems. Moreover, the implementation of adsorption systems in wastewater is necessary. Furthermore, the integration of treatment systems to recover precious metals at low concentrations is desirable in addition to water reclamation to achieve circular mine water.

1. Introduction

The mining industry contributes significantly to the world's economy. Mining resources are utilized for different purposes, including ornaments, jewellery, cable wires, building purposes, vehicles, electricity production, high-tech applications, etc. [1,2]. The process of mining and purification of mineral resources requires high volumes of water, which is released into the environment after use. The wastewater usually contains elevated levels of toxic organic pollutants such as flotation reagents and inorganic pollutants such as metal ions, which normally exceed the World Health Organization (WHO) discharge limits [3]. Mining wastewater discharge into the environment has been a major public concern as it can easily pollute water resources and negatively affect living organisms, including humans, aquatic animals, and plants [4,5]. In addition, freshwater supply is a challenge in many parts of the world, especially in arid and semi-arid areas. Thus, the treatment and purification of mining wastewater for reuse are essential to mitigate water scarcity [6,7]. There are several methods utilized for the treatment of mining wastewater, and these include evaporation and

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crystallization, biological processes, ion exchange, package plants, desalination, clarification, disinfection, zero liquid discharge, and membrane separation [8,9]. Most of the approved and commercialised treatment methods used cannot effectively remove all the elements in some wastewaters, or at least to the required concentration to deem the water safe for release into the environment or for reuse; hence, there is continuous research and development on wastewater treatment systems. Moreover, some of the treatment systems have high maintenance costs, high energy consumption, generate toxic sludge, and slow treatment processes. There is a need to come up with cheap and efficient treatment systems that can produce high-quality effluent whilst releasing small quantities of waste and those that can effectively scavenge precious metals to reduce environmental pollution and assist with the increasing demand for valuable metals.

A lot of research focusing on pollution prevention has been conducted and many treatment techniques focusing on wastewater treatment and resource recovery have been discovered [10–17]. There are few reviews that report on the progress in the development of mining wastewater treatment technologies [11], and thus far, there is no evidence of those that have focused on covering the full scope of real, pilot-stage, and laboratory-scale methods for the removal of toxic metals and the recovery of precious metals from mining wastewater. This review focuses on the effects of mining wastewater on the environment, the recovery of metal ions using different systems, and the effectiveness or ineffectiveness of these systems. Because removal is primarily focused on the separation of metals from wastewater, thereby generating bulky sludge made up of various components, the terms removal and recovery are employed independently in this study. The recovery process proceeds if the bulky sludge contains valuable metals, such as platinum group metals (PGMs), as covered in this review. This work aims to contribute to the understanding of existing commercialised and pilot-scale treatment technologies that target specific elements in wastewater. Recently developed laboratory-scale methods that address the shortcomings of current technologies are also reported.

2. Effects of mining wastewater on the environment

Mining extraction activities conducted underwater, open-pit, or underground produce large quantities of waste containing heavy metals, organic compounds, and unacceptable levels of salinity in wastewater, which can pollute local streams, wetlands, and groundwater, which can affect aquatic life and humans through the food chain [12,13]. Mining wastewater is generally highly acidic

Table 1
Reported environmental impacts caused by mining wastewater around the world.

Mine type	Environmental impacts	Study area	Reference
Antimony mining	Higher concentrations of Sb in plants, water, soils, and sediments	China, Guangxi, Hunan, Yunnan & Guizhou Province	[30]
Antimony–Arsenic ore mine	Contaminated streams	Australia, New South Wales	[31]
Asbestos mining	Increase in Cr and Ni metal concentrations in Bécancour River	Canada, Southern Quebec	[32]
Coal (mercury)	Sediments	China, Anhui Province	[33]
Coal mining	Damaged >10,000 km^2 of natural vegetation and agricultural land Consumed >2315 million m^3 of surface water and groundwater	China, Mongolia	[34]
Coal mining	Increased Zn and Ni concentrations, increased salinity, reduced taxonomic richness, and loss of pollution-sensitive macroinvertebrate groups	Australia, Sydney	[35]
Copper	Groundwater pollution	Serbia, Balkan Peninsula	[36]
Copper, Zinc, and Cadmium	Inhibition of enzyme activities and microbial biomass	China, Hunan Province	[37]
Diamond mining	Freshwater depletion	Democratic Republic of the Congo, Kananga and Kasai District	[38]
Gold mine	Increased levels of N_{total}, SO_4^{2-}, Sb, and electrical conductivity in the Seurujoki River	Finland, Kittilä	[5]
Gold mine	ASGM resulted in high concentrations of Hg in soil, sediment, and water	Senegal, Gambia	[25]
Gold mine	Land degradation, decreased water quality, airborne infections	Tanzania, Geita District	[39]
Gold mine	Contamination of Lake Charles with As and Hg	Canada, Nova Scotia	[40]
Gold mine	Significant Hg levels in fish from Atrato River	Colombia, Chocó	[41]
Gold mine	Concentrations of heavy metals on plant species and soil from Golden Pride and Geita mine	Tanzania, Nzega and Geita	[42]
Gold mine	Ni, Cd, Fe, Mn, As, and Hg concentrations in Lom River exceeded WHO standards	Cameroon, Adamawa region	[43]
Gold and copper mine	Water and soil pollution	Georgia, Kazreti	[44]
ASGM	Contamination of drinking water with Hg	Colombia, Suárez	[45]
ASGM	Hg contaminated the air	Colombia, Antioquia	[46]
Iron mining	Groundwater level decrease, waterborne pollution, dust pollution	China, Liaoning Nanfen, Mongolia Sanheing, and Sichuan Hongge	[47]
Lead–Zinc mining	Surface water contamination – Pb, Zn, and Cd concentration exceeded regulation values	Slovenia, Mezica area	[48]
Manganese mining	River water contamination	China, Xiushan County	[49]
Nitrate	High NO_3^- concentration in surface water	China, Huainan City	[50]
Phosphate	Aquatic life	Florida, Tampa Bay	[51]
Platinum mine	The concentration of Cr, Ni, Cd, Cu, Pb, Pt, and Zn in Hex River	South Africa, Rustenburg	[52]
Vanadium and titanium	Soil erosion and groundwater pollution	China, Panzhihua City	[53]

and has a high quantity of suspended solids. The acidity increases as a result of the high concentration of sulfates and metals in the water [14,15]. Unregulated or illegal mining activities of minerals such as gold also contribute massively to environmental pollution and negatively affect living organisms, including human beings, livestock, and aquatic animals. Human beings in direct and/or regular contact with waste from mining activities, such as mine workers, have been reported to suffer from cancer as well as respiratory and mental health conditions; a detailed report on these impacts is reported by Stephens et al. [16]. Mining activities result in acid mine drainage (AMD), heavy metal contamination and leaching, erosion and sedimentation, as well as processing chemical pollution [15]. Consequently, the mine health and safety acts were established together with numerous other legislation acts to regulate mining activities and wastewater management to restrict and prohibit the discharging of untreated wastewater into the environment.

A study conducted by Erasmus et al. [10] explored human health risks associated with the consumption of fish in the Hex River, Rustenburg, South Africa, which is contaminated with trace elements from the surrounding mines. The mines in this area are rich in Cr, Ni, Pt, and Cu resources, which have resulted in intense mining activities. Due to the extraction activities, trace elements (Pt, Cu, Cd, Cr, Zn, and As) were discovered in impoundments situated in the lower reaches (Bospoort Dam) and upper reaches (Olifantsnek Dam) of the Hex River. The authors evidenced adverse human health effects that were linked to the frequent consumption of contaminated fish from both impoundments. Unacceptable cancer risk values ($>10^{-4}$ for As, Cr, and Ni) were observed for all fish species, while Cd exhibited cancer risk values below 10^{-6}. Moreover, Ni, Cu, Zn, and Cd exceeded the standards of the water quality guidelines. Bospoort Dam posed higher human health risks as compared to Olifantsnek Dam [10]. Another study conducted by Li et al. [17] focused on the repercussions of phosphate mining activities on the rhizosphere bacterial communities of surrounding crops and vegetables in Sichuan, China. Rhizosphere bacteria are good for crop growth and development as well as enhancing soil nutrients, increasing plant disease resistance, and decomposing organic matter. The mining activities remarkably decreased the rhizosphere bacteria diversity of soybean, wheat, and lettuce in the area. The concentration of metals such as Cd, Pb, Zn, As, and Cr accumulating in the agricultural soil around this mine also increased. The study also found that the heavy metal contents exceeded the soil pollution threshold of the soil environment quality risk control standard for soil contamination of agriculture land (GB15618-2018) and affected the quality of vegetables and crops in the area [17]. Kurniawan et al. [13] have reported on the difficulty of separating heavy metals from the soil. Although several methods have been explored on a laboratory scale, the actual application of these methods in the real environment is not practical. Their work suggested the utilization of phytoremediation in conjunction with bioaugmentation as a viable technology for higher efficiencies. Other studies focusing on the effects of mining activities around the world are presented in Table 1.

Fig. 1 summarises the effects of mining wastewater on agriculture, marine life, soil, and waterbodies. These studies also show how these mining activities are affecting food security and human health. Supplementary Table S1 details the effects of metal ions which, are usually found in mining wastewater, on aquatic animals, humans, and plants. As indicated previously, illegal miners also contribute significantly to environmental pollution, especially since the usual mining regulations are not followed. South Africa, Ghana, Peru, and China are among the places where illegal mining on the surface and underground (closed, abandoned, and operating mines) is prominent [18–22]. Artisanal small-scale gold mining (ASGM) is a worldwide issue that has received a lot of attention, and there are numerous reports on its impacts. The miners have been using mercury (Hg) to recover Au for centuries. In the process, the minute pieces of gold mixed in sediments and soil are combined with Hg, which settles to form an amalgam. The extraction of Au is achieved by vaporising Hg [23]. The widespread use of mercury is attributed to its abundance and low cost [24]. Niane et al. [25], Mantey et al. [26], Soe et al. [27], Garcia-Ordiales et al. [28], etc. reported some incidents where the soil and aquatic ecosystems were contaminated by mercury (Hg). Niane et al. reported Hg and methylmercury (MeHg) contamination in the Kedougou region of Senegal during gold mining. High concentrations of Hg and MeHg were detected on the soil in the surrounding mining sites, rivers, and local
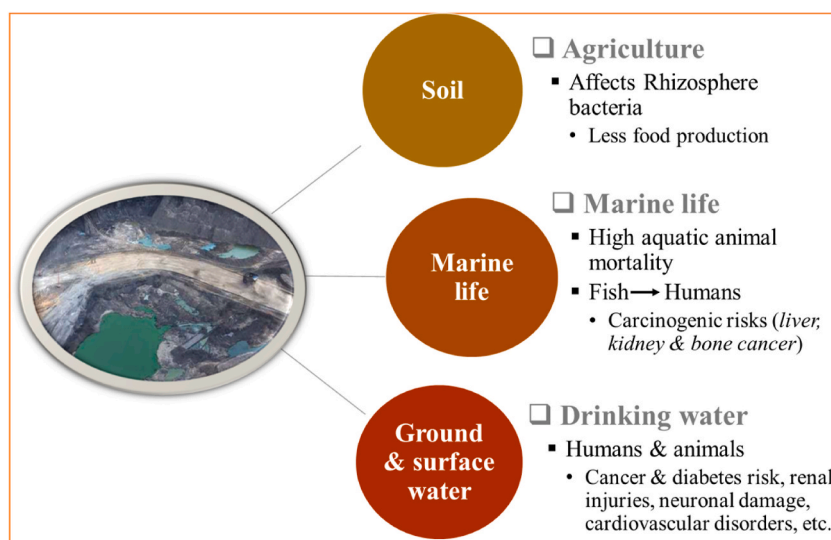

Fig. 1. A summary of mining effects on agricultural industry, marine life and drinking water.

water ponds [25].

Achina-Obeng and Aram [29] also reported the environmental impacts of ASGM in Ghana. The water and soil samples were collected from the Offin River and abandoned mine sites, and it was found that the pH, turbidity, conductivity, and the concentration of As, Pb, and Cd were above the WHO standards. Other metals such as Mn, Cu, Hg, and Fe were also high; thus, the river water could not be used for any purpose and the soil was found to be unfit for agricultural purposes. Based on the interviews conducted in the area, the illegal miners are aware of the environmental effects of their activities; however, they continue with their activities due to a lack of employment, other means of livelihood, and political influence. In their submission, they suggested engagements with stakeholders to create feasible policies that will benefit everyone and that include financial, technological, and technical skill investments. Legal mining sectors have progressed in ensuring less environmental contamination by mining wastewater and mitigating the excess use of freshwater in recovery processes. Some of the steps taken by legal mining industries to mitigate environmental pollution include the treatment of mine sludge and mining wastewater, reusing treated mining wastewater for recovery purposes, and following discharge limit guidelines.

3. Treatment of mining wastewater using real technologies

Several wastewater treatment methods and technologies have been tested on a laboratory scale, but their application on a large scale is limited. It is possible that even though some methods and technologies work very well on a laboratory scale, they may not be considered for large-scale use due to high costs and secondary pollution that could be toxic and not reusable. Such treatment techniques will not be environmentally friendly or economical. This section focuses on the application of mine wastewater treatment technologies that have been commissioned at mining sites and have been found to be successful and economical.

3.1. SAVMIN® technology

Mintek, South Africa, has come up with a mine water treatment technology called SAVMIN®, which was implemented in the Witwatersrand gold fields in South Africa [54]. The technology was first demonstrated using pilot plants at Stilfontein Gold Mine, Navigation Colliery, and Grootvlei Gold Mine, which are located in South Africa. The pilot plants proved that different qualities of wastewater from coal, gold, platinum, and base metal mines can be treated using SAVMIN®, which has been demonstrated to treat 4 m^3 of water per hour. In the first stage of this technology (flowchart shown in Fig. 2), the wastewater feed (normally around pH 3 and 4) is mixed with lime to raise the pH to more than 10 in a reactor, and metals can be precipitated as metal hydroxides [55]. During this stage, gypsum is also precipitated. A thickener is used to sediment the precipitates from the solution [56]. The resulting solution goes into the next stage whilst the sediment is released as waste or further processed to recover valuable metals. In the second stage, the pH of the solution from stage one is raised further using lime to supersaturate the solution with gypsum. The gypsum precipitate is either collected as a by-product or discarded as waste. In stage 3, aluminium hydroxide is added so that the pH of the gypsum-rich solution can be raised again to remove calcium and sulfate from the solution as an insoluble calcium-aluminium sulfate salt, which is called ettringite precipitate. The following equation demonstrates the process in stage 3 [54]:
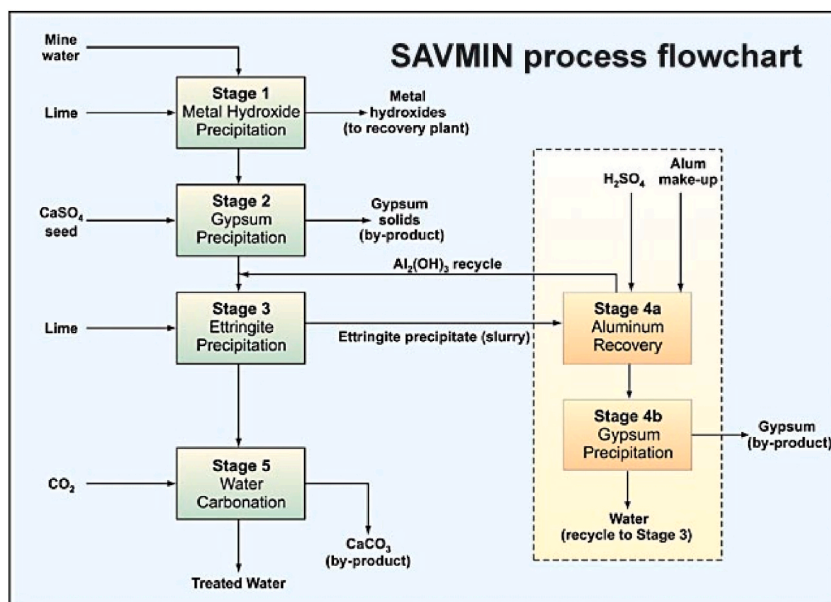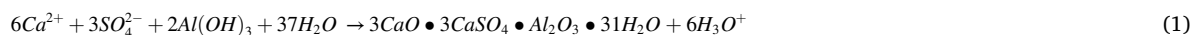

Fig. 2. SAVMIN process flowchart [57].

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3 + 37H_2O \rightarrow 3CaO \bullet 3CaSO_4 \bullet Al_2O_3 \bullet 31H_2O + 6H_3O^+ \tag{1}$$

The precipitate settles in a thickener and aluminium hydroxide is extracted from the ettringite precipitate using sulfuric acid in the stage 4 thickener. The overflow water from stage 3 is pumped into stage 5, where carbon dioxide is added to lower the pH so that calcium carbonate can be removed from the treated water. The results of the SAVMIN® process is potable water overflow from the thickener of stage 5 [54,56].

3.2. SPARRO® technology

A patented Slurry Precipitation and Recycle Reverse Osmosis (SPARRO®) process, which is a membrane desalination technique that uses seeded precipitation and RO, was developed to treat mine wastewater with high calcium and sulfate content (Fig. 3) [58]. This process was successfully tested at a pilot scale on mine water from the East Rand Proprietary Mines (ERPM) Hercules Shaft, South Africa. During seeded precipitation, pH is adjusted using lime or caustic soda and gypsum seeded crystals are added to enable precipitation where scaling compounds such as silica and calcium salts are removed. To prevent the scaling of the RO membranes, the precipitation of the scaling compounds occurs on the seed crystals and not on the tubular membranes. To ensure that membrane surfaces perform to their maximum capacity, all the precipitates are retained in a slurry suspension tank [59]. A cyclone separator is used to separate the crystal slurry from the solution and the recovered crystals can be reused with the new feed into the SPARRO system. In this process, the slurry of calcium sulfate seeds is recycled to enable the operation of the RO system at high recovery to reduce the quantity for brine disposal. This provides preferential precipitation sites for the supersaturating solution. Moreover, this process was developed to overcome the high recovery costs of mine wastewater treatment techniques by consuming minimal energy, having good calcium sulfate seed and brine mass balance control and treating a large amount of wastewater by reusing chemicals [60].

3.3. Biogenic sulfide technology

BQE Water, a Canadian company, has come up with biogenic sulfide technology. Unlike other discussed mine water treatment technologies that focus only on treatment, this technology (Fig. 4) also focuses on metal recovery. The technology has been applied to several gold mines, including the Lluvia de Oro gold mine site in Sonora, Mexico [61]. Since most gold deposits are rich in copper, gold mining has been a challenge due to the dissolution of copper by cyanide, which is used to leach gold. This results in a large amount of cyanide being used, leading to an expensive gold extraction process. The BQE Water technology focuses on the removal of copper from cyanide solution and the regenerated cyanide is used for gold extraction. This then reduces the consumption of cyanide and, consequently, the negative impact of gold mining on the environment. The Sulphidization-Acidification-Recycle-Thickening (SART) originally developed by SGS Lakefield and TeckCominco Ltd., was adapted in this technology. However, the chemical sulfide used in the SART process was replaced by low-cost biogenic hydrogen sulfide, which is produced by one of the BQE Water innovations. There are two main stages in this technology, *viz.*, biological and chemical [61]. In the biological stage, the elemental sulfur is fed sulfur-reducing bacteria in an anaerobic bioreactor containing acetic acid. This leads to the production of hydrogen sulfide gas. The gas is then transferred into the gas-liquid contactor tank, which contains contaminated water [62]. In the chemical stage, the metals in the contaminated water are selectively precipitated as sulfides using biogenic hydrogen sulfide. Filtration will then take place to separate the metals from the solution. The resulting treated water is either discharged into the environment or recycled. To recover the different valuable metals and remove toxic metals from the metal-bearing stream using this technology, different contractor and clarifier tanks are used in series [61]. The plant was designed to treat 12,000 m^3.day^{-1} of wastewater [62].
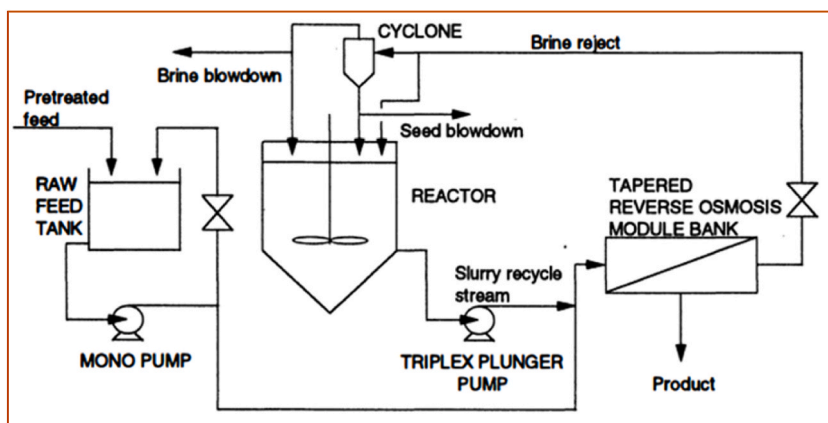

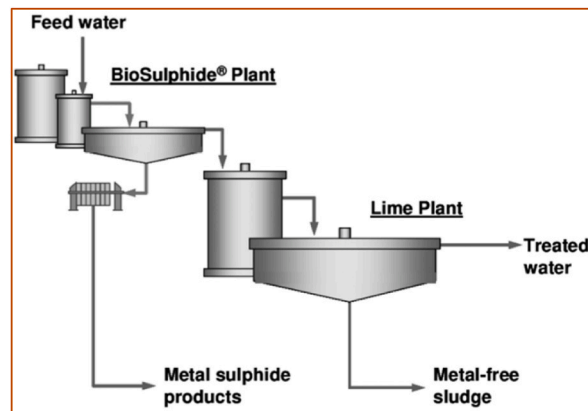**Fig. 3.** Schematic of SPARRO® technology [59].

Fig. 4. Biogenic sulfide process [63].

3.4. DESALX® technology

The Clean TeQ Water company came up with a zero liquid discharge (ZLD) water treatment plant called DESALX® for a gold mine in Victoria, Australia [64]. The underground mine had excess water that had to be treated to protect the environment. The main idea was to treat the mine wastewater so that it could be in a state that is acceptable for aquifer re-injection. The feed water from the mine has high concentrations of As, Mg, Sb, Ca, and SO_4^- [65]. Before the introduction of the feed water to DESALX®, Sb and As are reduced by the precipitation process (Fig. 5). The plant is also successful in treating the hardness of the water and reducing sulfate through a two-stage continuous ion exchange process in the adsorption column, where cations and anions are removed from the wastewater [64]. The resins will then move in counter-current form into the wash column and finally into the desorption column, where the adsorbed species will be detached from the resins using acid for cations and lime for anions (Fig. 5) [65]. The regenerated resins will then be washed back into the adsorption column to repeat the process. Although these species are removed, sodium and chlorine are not captured by the resins, so saline brines are avoided. The system can perform consistently across variable flow rates (from 20 to 80 $m^3\ h^{-1}$). To achieve consistent water recovery, the DESALX® system is automated and the water recovery is in excess of 90 % [64].

3.5. An overview and a critical analysis of the real technologies

Table 1 reports the common metals and anions that are normally found in mining wastewater (Hg, Cr, Ni, Cd, Cu, Pb, Pt, Zn, Fe, Mn, As, Sb, Au, V, N_{total}, sulfate, and nitrate). The above-discussed technologies are currently used for the treatment of Cu, Pt, As, Sb, Au, Mg, Ca, and sulfate. The focus on Au is on the fact that it plays a pivotal role in natural currency systems. Pt is one of the PGMs with high economic value; therefore, the recovery of these precious metals even at low concentrations is of great significance. Other metals, such as Sb and As are considered during water treatment since they are hazardous to human health and carcinogenic. High levels of Sb have already been reported in certain organs of fish [30]. The SAVMIN® technology, implemented at the Witwatersrand gold fields in
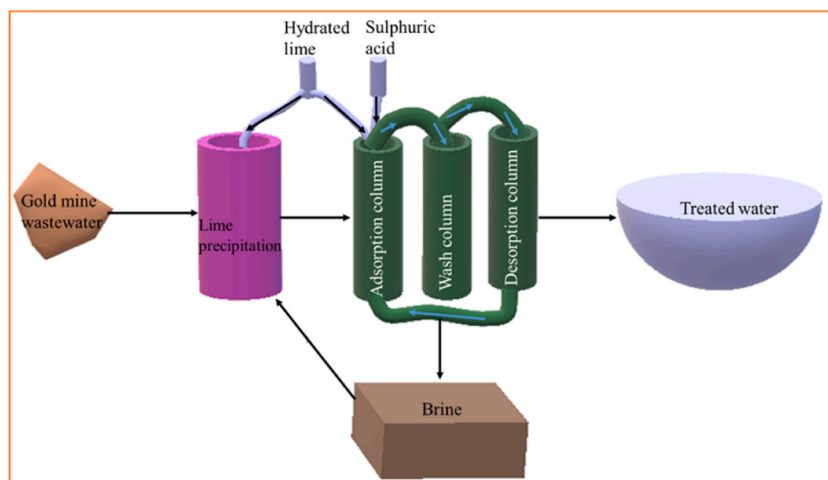

Fig. 5. The Clean TeQ Water company (DESALX®) process.

South Africa, was found to be efficient in the recovery of precious metals (Au and Pt) and the removal of unwanted metals and sulfate. Moreover, the SAVMIN® technology, which uses a chemical precipitation method, can treat mining wastewater until it reaches the potable stage. The chemical precipitation method is simple, safe to operate, and can utilize low-cost reagents. The disadvantage of this method is that it uses large volumes of chemicals, which in turn produce highly toxic sludge in large amounts. The primary purpose of the SAVMIN® technology is to treat mining wastewater with high sulfate content; therefore, mining plants such as those dealing with the extraction of gold from ores will benefit more from this technology due to the high concentrations of sulfate released from the process. In addition, the large amounts of metals that are normally released during ore processing will be removed using the SAVMIN® technology. Other industries, such as dyeing, pharmaceuticals, and aluminium production, which release large amounts of sulfate, can benefit from the SAVMIN® technology; however, some changes in the stages will have to be implemented due to the nature of the industries and the quality of wastewater produced. Industries with low concentrations of sulfate and metals will not benefit from this technology. The SPARRO® technology uses chemical precipitation as a pretreatment step and RO as a polishing step. This is highly recommended to avert fouling of the membrane, which ultimately prolongs the lifespan of the membrane. This technology consumes minimal energy, and the chemicals used for precipitation are recyclable. In addition, the use of RO membranes guarantees high-quality permeate, and the system requires a smaller footprint. The technology has been used for the treatment of mining wastewater with high sulfate and calcium contents. The SPARRO® wastewater technology can also be used in the removal of heavy metals from groundwater in pump-and-treat operations. The precipitation process can convert soluble heavy metals to precipitates, which can settle be subsequently filtered out of the water. To attain potable water, the reverse osmosis process will have to be used as a polishing step. Biogenic sulfide technology, on the other hand, is a combination of biological and chemical methods and focuses on the treatment of wastewater and the recovery of metals. The technology has been installed at a gold mining site for the removal of Cu from cyanide solutions and the regeneration of cyanide, which is then utilized in gold extraction. This practice abates the exhaustion of cyanide. Copper is normally used in the etching, electroplating, and metal finishing industries, among others, and the wastewater from these industries contains high concentrations of copper; hence, the biogenic sulfide technology can be adapted in these sectors for maximal copper removal. The DESALX® technology system's purpose is 100 % recovery of water for reuse and recovery of salts. This technology is operating in a gold mine in Australia, targeting As, Mg, Sb, Ca, and sulfate. The DESALX® technology consists of several phases. It has the precipitate process step to ensure Sb and As reduction, the ion exchange step to target the hardness of the water, and other steps focus on achieving ZLD and salt recovery. The technology can be regarded as one of the most advanced systems, even though it is costly. ZLD refers to a treatment process in which the system ensures that there will be no liquid effluent discharged into the environment [66]. Hence, DESALX® technology focuses on the recovery of water for reuse in industrial processes as well as the high recovery of salts and the reduction of environmental contamination. Due to its several treatment stages, which can change depending on the type of wastewater being treated, DESALX® technology is applicable to a wide spectrum of wastewaters. For instance, the effluent from pulp and paper mills, which contains a lot of organic matter and suspended solids, will benefit from this technology.

Fig. 6 shows the different phases (pretreatment, concentration and reduction (membrane processes), evaporation and crystallization) involved in the DESALX® technology. The pretreatment, which involves both biological and physicochemical processes, is utilized to reduce suspended solids, colloids, total alkalinity, and total hardness of the influent. In phase 2, the concentration and reduction processes are achieved through RO and electrodialysis membranes, etc. The purpose of this phase is to reduce the salt
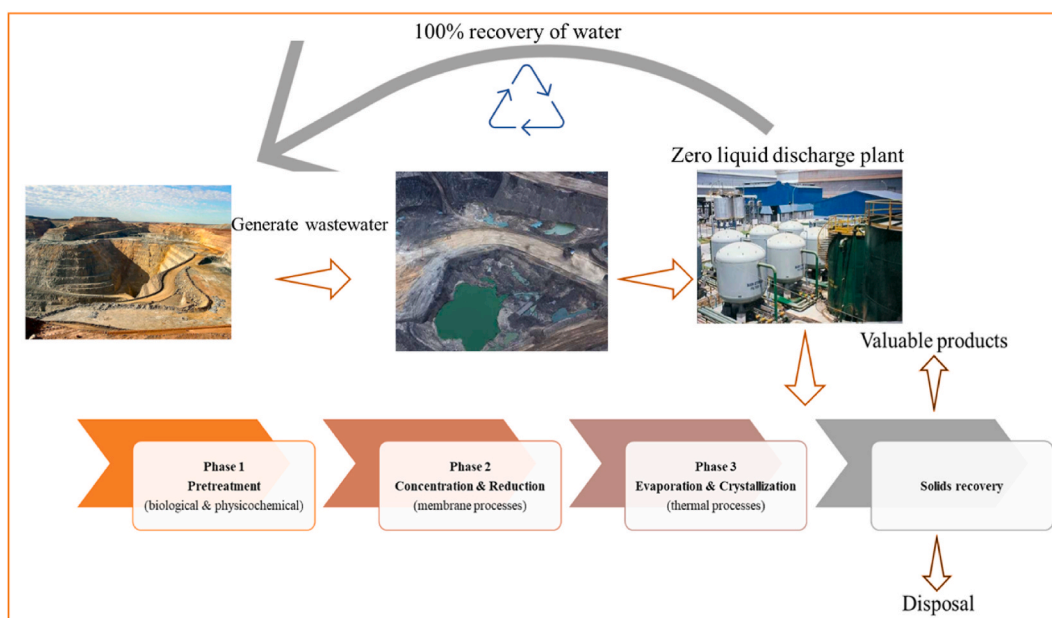

Fig. 6. Zero liquid discharge treatment of mining wastewater and recovery of solids process.

content of the influent. The evaporation and crystallization phases are attained through processes such as multi-effect evaporation (MED) and mechanical vapour recompression (MVR). Basically, it's the separation of water and salts to reach zero liquid discharge [67]. This technology has been applied in several industries, such as textiles, metals and mining, chemical processing, refining, food and beverage, microelectronics, etc. Regardless of the advantages and benefits, ZLD technologies have their shortcomings. Xiong and Wei discussed some of the challenges faced by ZLD technology used in the coal chemical industry in China [68]. The first issue is encountered in phase 1, where organics produced during the coal conversion process are not easily digestible with conventional biological processes and end up with recalcitrant organics in the wastewater. This then affects the separation process in phase 2 which becomes compromised due to membrane fouling, which automatically compromises the entire system. The second challenge is the cost of the system. There are several separation methods, such as RO, which are costly. Moreover, the system uses a large amount of chemicals and generates a large quantity of sludge. The high capital and energy consumption costs of the thermal system also add to the cost of the technology. Lastly, coal chemical industries generate about 10–100 thousand tons per year of mixed salts from wastewater crystallizers, which are supposed to be managed as hazardous waste in China. These industries are struggling with a practical way of disposing of these mixed salts [68].

The removal or recovery efficiency of the treatment technologies reported (SAVMIN®, SPARRO®, biogenic sulfide, and DESALX®) cannot be discussed in detail as there is limited information. There is no evidence of commercialised technologies that can treat wastewaters with high concentrations of silver (Ag), rhodium (Rh), palladium (Pd), and iridium (Ir). The SAVMIN® technology was reported to also remove base metals; however, they were not specified. Base metals can be easily removed from mining wastewater by adjusting the pH of the wastewater during precipitation processes. For instance, the pH required to precipitate ferric iron is 3.5, and other metals such as Zn, Mn, etc. require a pH ranging from 6 to 9. Therefore, the technologies mentioned can remove a wide range of toxic metals. However, there is also a need for the development and implementation of real technologies that can target metals that cannot be removed by existing technologies.

4. Treatment of mining wastewater using pilot-scale methods

The evaluation of treatment methods for mining wastewater at a pilot stage is limited in the literature. The development and implementation of pilot plants with promising laboratory-scale methods comes with many benefits for research. A pilot plant gives an insight into design conditions for full-scale implementation of the system, an economic perspective (operating costs and maintenance requirements) for suitable optimization before investment, can collect data from realistic environmental conditions for improvement of the ongoing operating systems, and can effectively test alternative treatment technologies. This section discusses pilot-stage treatment systems reported in the literature and the targeted pollutants.

4.1. Granular ferric oxyhydroxide (CFH-12)

There is only one study found in the literature that reported on the coagulation method for the removal of metals from mining wastewater. The coagulation technique discussed is a traditional water treatment system that uses coagulants to destabilize colloidal impurities to form large flocs for easy separation from water [69]. Zhang et al. [70] reported the removal of vanadium from mining wastewater at a closed mine located in Mustavaara, Finland, using granular ferric oxyhydroxide (CFH-12). Zhang et al. assessed two filter systems, pilot A (Fig. 7) and pilot B, which operated for 51 and 127 days, respectively. The short operation period of pilot A was attributed to a higher and very variable vanadium concentration (6.46–99.1 mg/L), whereas pilot B could operate for longer due to lower vanadium concentrations (0.443–2.32 mg/L). The results showed that the vanadium was effectively removed by both systems and that the filter beds were not fully saturated. The oxidized vanadium (5^+) was detected in the utilized CFH-12 sorbent, and the carbon was found to have increased in the content of the utilized sorbent, which was attributed to the adsorbed organic matter. The
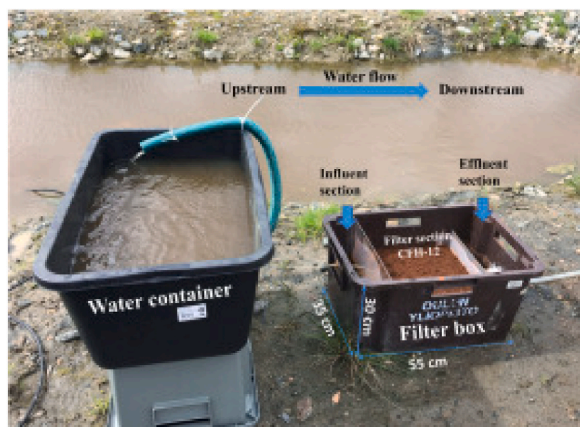

Fig. 7. Experimental setup of the pilot A filter systems. Reproduced with permission from Reference [70].

reporters recommended the use of the CFH-12-based coagulation method for vanadium removal as well as organic matter. Some of the reasons include ease of operation, stability of the sorbent throughout the operation period, easy scalability, low maintenance and regeneration, and reusability of CFH-12 [70].

4.2. Microfiltration/ultrafiltration-reverse osmosis

In the literature, a pilot study incorporating a pretreatment method and reverse osmosis membrane was reported by Grossi et al. [71], which assessed a pressure-driven oriented membrane system (microfiltration/ultrafiltration-reverse osmosis (MF/UF-RO)) for nitrogen-contaminated wastewater. Instead of using chemical precipitation as a pretreatment step as in SPARRO® technology, MF/UF membrane was used as a pretreatment step and reverse osmosis as a polishing step. Grossi et al. used MF/UF-RO (Fig. 8) to treat gold mining feed from the blasting stage collected from the mine located in Minas Gerais, Brazil. MF/UF membranes reduced fouling propensity and did not affect RO performance, making it feasible to operate at higher water recovery fractions. Consequently, the costs of increasing the permeate and decreasing the retentate volumes were reduced. A steady operation at a recovery fraction of around 80 % for RO at 6 bar was performed. After adjusting the pH as well as the ammonia and nitrogen concentrations, the effluent met the industrial reuse standards.

4.3. Sedimentation tank and Cocopeat filter bed

Samaniego and Tanchuling [72] reported the treatment of heavy metal-laden wastewater collected from a small-scale gold mining site in Paracale, Camarines Norte, Philippines, using a sedimentation tank (primary treatment) and a Cocopeat (coconut husk by-product) filter bed as an adsorbent (Fig. 9). The wastewater contained heavy metals such as Cd, Pb, As, Ba, and Hg, and physico-chemical parameters like turbidity, temperature, electrical conductivity, pH, oxidation-reduction potential, total dissolved solids (TDS), dissolved oxygen, total suspended solids (TSS), salinity, and colour were monitored. The pilot study operated for 50 days at a flow rate of 40 L/h for 3 h daily. The sedimentation phase reduced the concentration of heavy metals to 74.24 % (Cd), 98.82 % (Pb), 97.11 % (As), 39.75 % (Ba), and 97.02 % (Hg), and the Cocopeat adsorption filter bed further reduced the concentrations to 4.95 % (Cd), 0.97 % (Pb), 1.39 % (As), 28.00 % (Ba), and 2.91 % (Hg). The physico-chemical parameters and heavy metal concentrations were reduced to within the respective government regulatory limits for Philippine Class C waters. The adsorbent was not fully saturated and heavy metals accumulated 25 cm of the upper Cocopeat column. Further tests were suggested by the authors, where they would apply more volume of the feed to establish optimal conditions for HMs and TSS removal before a full-scale study.

4.4. Adsorption and constructed wetlands

Nguyen et al. [73] reported the treatment of mining wastewater containing As and other heavy metals such as Cd, Zn, Mn, and Pb. The wastewater was collected from the Pb–Zn Cho Don mine in northern Vietnam. A treatment system (Fig. 10) integrating a limestone dam (two reservoirs) and eight modules with different functions: a settling tank (MD1), an adsorbent tank (MD2) (modified iron-ore drainage sludge), and constructed wetlands (MD3–MD8) with common reeds (*Phragmites australis*) had a hydraulic loading rate of 5 $m^3.day^{-1}$. MD2 consisted of two compartments with 0.71 m^3 of total working time and 30 min of retention time. Therefore, waste-water flowed from MD1 to the first compartment of MD2, followed by the second compartment, which had ~138 kg of the adsorbent. The constructed wetlands (MD3–MD8) received wastewater from MD2. Limestone was utilized as a substrate material for *P. australis* growth in MD3–MD7, while MD8 used laterite. The adsorbent tank demonstrated higher removal efficiencies of As and heavy metals than the settling tank and constructed wetlands. In their findings, the higher removal efficiency of As (89.9 %) was obtained using laterite substrate, and limestone substrate was used for the removal of Cd, Zn, Mn, and Pb, which exhibited removal efficiencies of 93.3, 80.1, 99.5, and 66.7 %, respectively. The low removal of Pb was associated with constructed wetlands and different substrates.
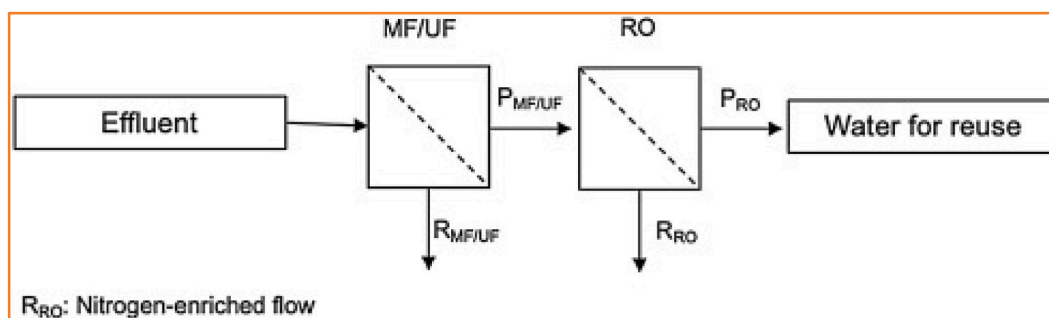

Fig. 8. Schematic of the proposed route of MF/UF-RO membrane system. Reproduced from Reference [71]. Elsevier 2021.
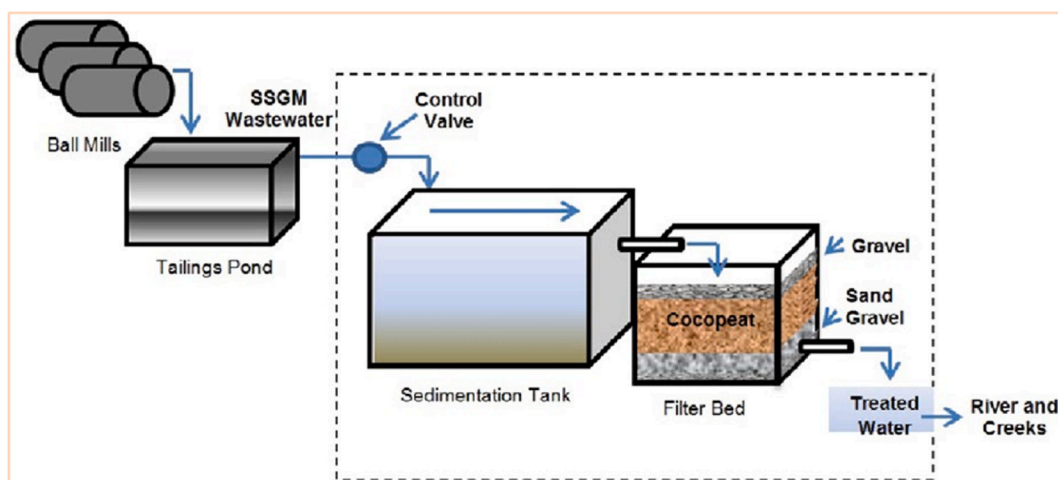
Fig. 9. Schematic of filter bed system installed in a small-scale gold mining processing plant [72].
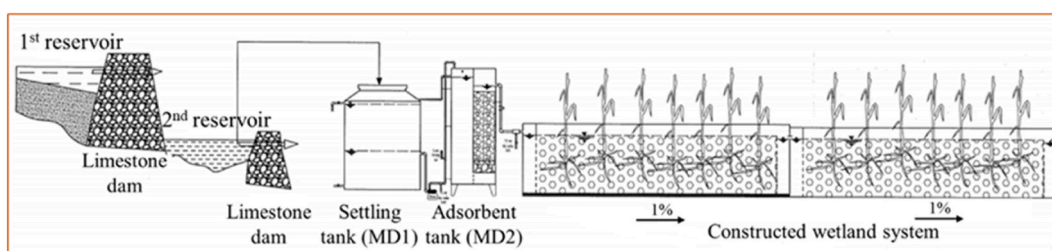

Fig. 10. Cross-section treatment system [73].

4.5. An overview and a critical analysis of the pilot stage technologies

The reported pilot treatment systems targeted many pollutants, such as V, N, Cd, Pb, As, Ba, Hg, As, Zn, and Mn. In the literature, there are a few pilot systems reported, including the CFH-12 coagulation method for vanadium removal, the MF/UF-RO system for nitrogen removal, the sedimentation tank and Cocopeat filter bed for the removal of Cd, Pb, As, Ba, and Hg, as well as adsorption and constructed wetlands for As, Cd, Zn, Mn, and Pb removal. The CFH-12 coagulation method used for the removal of vanadium could be operated for 51 and 127 days for high and low vanadium concentration areas, respectively. The possibilities of crystallization into goethite and the generation of toxic sludge, including management, were not addressed for this system. The system effectively removed vanadium; however, the lifespan of pilot A with high concentrations of vanadium was shorter. The removal of nitrogen using the MF/UF-RO system reduced fouling propensity; consequently, the system operated at higher water recovery fractions. The MF/UF-RO treatment system is technically and economically feasible, as the estimated operating costs of the system are US$ 0.488/m^3 and 55 % of expenditure is associated with the disposal of wastewater. It was suggested that the RO concentrate could be utilized for fertigation, which would subsequently decrease wastewater volume and associated disposal costs. Furthermore, the system has the potential to save ~367,000 m^3/year of freshwater, which is crucial. Therefore, the MF/UF-RO system has the potential for full-scale tests. On the other hand, the sedimentation tank and Cocopeat filter bed system, which were used for heavy metal removal, operated for 50 days at a flow rate of 40 L/h for 3 h daily. The system targeted crucial toxic metals (Cd, Pb, As, and Hg), which are the dominant pollutants (Table 1). Even though the system exhibited acceptable removal efficiency for the pollutants, the possibility of Hg leaching from the Cocopeat column was reported. The operation costs and toxic sludge management were not reported. The full potential of this system cannot be determined as it operates for only 3 h a day. Coupling this system with a pretreatment or polishing step would significantly enhance its efficiency and lifespan. Lastly, the adsorption and constructed wetlands system, which was operated for longer (4 months) compared to other pilot systems, exhibited promising results except for Pb. The system targeted very toxic metals such as Cd, As, Zn, and Pb. The concentrations of the pollutants after treatment were lower than the established limits by Vietnamese national regulations on industrial wastewater (QCVN 40:2011/BTNMT), which shows a clear indication that this system has the potential for a larger scale. However, the economic aspect and generated sludge management were not reported in this work. All these pilot treatment systems did not address the removal of Cr, Ni, Fe, and nitrate from mining wastewater, and these were also not addressed by real technologies. In addition, there are no pilot-stage systems that address the recovery of precious metals from mining wastewater.

5. Treatment of mining wastewater using laboratory scale methods

At the laboratory scale, there's a lot of work done on developing novel materials for the recovery and removal of precious and toxic metals. The adsorption treatment process has received a lot of attention from researchers for the treatment of mining wastewater. During the adsorption process, pollutants in the wastewater bind to the surface of a solid substance which may be through physisorption, chemisorption, or biosorption [74]. Physisorption is when pollutants mechanically lock up molecules through weak van der

Table 2
Laboratory scale treatment methods for recovery of precious metals.

Recovery method	Metals	Wastewater source	Mechanism	Recovery efficiency (%) or loading capacity $(mg.g^{-1})$	Reference
APDEMS-functionalized bentonite	Pd(II), Ir(III), Rh (III)	PGEs processing plants	Adsorption	>99 %	[102]
B-QUAT EDA	$[IrCl_6]^{2-}$	Model mining ww	Ion exchange	3.80 mg g^{-1}	[105]
B-QUAT TMDA				6.49 mg g^{-1}	
B-QUAT HMDA				13.07 mg g^{-1}	
B-QUAT OMDA				19.29 mg g^{-1}	
B-QUAT DMDA				27.09 mg g^{-1}	
B-QUAT DDMDA				4.36 mg g^{-1}	
DONA-MOF	Au(III)	Simulated ww	Adsorption	1st – 5th cycle: 99.8 −89.3 %	[100]
Egg-shell membrane	Au^{3+}, Pd^{2+}, Pt^{4+}	Simulated ww	Adsorption	250, 110, 50 mg g^{-1}	[106]
EDA	Pt, Pd	Model mining ww	Ion exchange	7.42, 4.32 mg g^{-1}	[107]
DETA	Pt, Pd			2.58, 1.08 mg g^{-1}	
TETA	Pt, Pd			0.47, 0.39 mg g^{-1}	
TAEA	Pt, Pd			0.79, 0.83 mg g^{-1}	
F-QUAT EDA	$[IrCl_6]^{2-}$	Model mining ww	Ion exchange	5.98 mg g^{-1}	[97]
F-QUAT TMDA				7.95 mg g^{-1}	
F-QUAT HMDA				15.23 mg g^{-1}	
F-QUAT OMDA				21.71 mg g^{-1}	
F-QUAT DDMDA				9.70 mg g^{-1}	
F-QUAT DMDA				1st – 3rd cycle: 32.9–32.6 mg g^{-1}	
F-QUAT HMDA-methyl	$[IrCl_6]^{2-}$	Model mining ww	Ion exchange	1st – 3rd cycle: 15.2–14.8 mg g^{-1}	[95]
F-QUAT HMDA-ethyl				1st – 3rd cycle: 9.7–8.5 mg g^{-1}	
F-QUAT HMDA-benzyl				1st – 3rd cycle: 42–41.6 mg g^{-1}	
Graphene oxide	Au(CN)$_2^-$	Simulated ww	Adsorption	130 mg g^{-1}	[108]
ICF	Pd(II)	Hydrometallurgy ww	Adsorption	99.5 %	[104]
Lyophilized *Galdieria sulphuraria* cells	Au	Simulated ww	Adsorption	35 ± 2.5 mg g^{-1}	[109]
MOF-AFH	Pd(II) Au(III)	Simulated ww	Adsorption	1st – 4th cycle: 99.7 −91.7 % 1st – 4th cycle: 99.1 −92.0 %	[110]
MOR-2-QAS	Pt(II), Pd(II)	Simulated ww	Adsorption	>90, 93 %	[111]
Ni$_{0.6}$Fe$_{2.4}$O$_4$-MTD	Au(III)	Laboratory ww	Adsorption	1st – 4th cycle: 91.2 −82.5 %	[99]
PDMC-SNP	Au(III)	Simulated ww	Adsorption	1st – 10th cycle: 81.93 −76.33 %	[101]
Puromet MTS9850	Pt, Pd, Rh	Refining process	Ion exchange	98.0, 99.9, 74.4 %	[112]
Puromet MTS9200	Pt			97.0 %	
PMCS	Au(III)	Simulated ww	Adsorption	1st – 3rd cycle: 99.07 −94.77 %	[98]
Si-EDA	Pt, Pd	Model mining ww	Adsorption	0.24, 0.14 mg g^{-1}	[113]
Si-DETA	Pt, Pd			0.40, 0.16 mg g^{-1}	
Si-TETA	Pt, Pd			0.00, 0.25 mg g^{-1}	
Si-TAEA	Pt, Pd			0.29, 0.15 mg g^{-1}	
Si-QUAT EDA	$[IrCl_6]^{2-}$	Model mining ww	Ion exchange	4.56 mg g^{-1}	[96]
Si-QUAT TMDA				6.88 mg g^{-1}	
Si-QUAT HMDA				14.63 mg g^{-1}	
Si-QUAT OMDA				19.01 mg g^{-1}	
Si-QUAT DDMDA				8.90 mg g^{-1}	
Si-QUAT DMDA				1st – 3rd cycle: 29.4–28.6 mg g^{-1}	
Yeast-functionalized zeolite	Pd(II), Ir(III), Rh (III)	PGEs processing plants	Adsorption	206 mg g^{-1}	[103]

Notes: EDA = ethylenediamine; TMDA = tetramethylenediamine; HMDA = hexamethylenediamine; OMDA = 1,8-diaminooctane; DMDA = 1,10-diaminodecane; DDMDA = 1,12-diaminododecane; F-QUAT = functionalized quaternary; DETA = diethylenetriamine; TETA = triethylenetetramine; TAEA = tris-(2-aminoethyl)amine; APDEMS = 3-aminopropyl(diethoxy)methylsilane; MOR-2-QAS = metal-organic resins-quaternary ammonium; DONA = 4,4′,4″,4‴-((1,4,8,11-tetraazacyclotetradecane-1, 4, 8, 11-tetrayl) tetrakis(methylene)) tetrabenzoic acid; AFH = 2,6-amino-pyridine on 3-formyl-4-hydroxybenzoic acid; PMCS = pyridine-modified chitosan; ICF = ion-imprinted chitosan fiber; PDMC-SNP = poly(methacryloxyethyl-trimethyl ammonium chloride)-Silica nanoparticles.

Waals forces, hydrogen bonding, polarity, and dipole-dipole interactions [75,76]. The physical process is more desirable due to its ability to form multilayer adsorption, thereby leading to high adsorption capacity and the possibility of reversibility [77]. Chemisorption, on the other hand, involves chemical bonding or electron transfer between the adsorbate and the surface. The chemical process is limited to monolayer adsorption, which is irreversible, making the adsorbent difficult to regenerate and reuse [78,79]. Biosorption is a fast and reversible process where the ions in wastewater bind onto functional groups present on biomass surfaces. Biosorption is considered to be more effective, eco-friendly, and cost-effective as it uses biological materials from agriculture and industrial waste [80]. It involves various mechanisms such as ion exchange, absorption, complexation, and precipitation [81]. The choice of the adsorbent is essential, as it plays a vital role in the removal efficiency of pollutants from wastewater. Thus, an adsorbent with properties such as high porosity (high surface area ≡ high absorption capacity), high selectivity, enough active sites on the surface, a short adsorption period, and high stability is more desirable [82]. Furthermore, the sorption process depends on the pH, contact time, adsorbent dosage, and temperature of the feed [83,84]. Some of the adsorbents that have been used for the treatment of wastewater include agricultural waste, biosorbents, industrial waste, miscellaneous sorbents, and natural materials [74]. In summary, physical, biological, and physico-chemical processes are more advantageous than chemical processes [85].

5.1. The recovery of precious metals in mining wastewater

The supply and demand of precious metals such as Ag, Pt, Au, Rh, Ir, and Pd have rapidly increased over the years due to their extensive use in medical, urban, and industrial applications [86]. Precious metals are attractive due to their properties such as excellent electrical and thermal conductivity, corrosion resistance, strong chemical stability, catalytic activity, and high coordination ability [87,88]. For instance, Pd is used in electronics on computer hard disk drives, while Ag and Au are used in bonding wires, contacts, switches, etc. [88]. In medicine, platinum is used as a cancer drug [89,90], while gold has found application in the treatment of rheumatoid arthritis [91,92]. Silver has antimicrobial properties [93,94]. The mining industry is the main source of extracting these precious metals, which generates a large amount of wastewater containing the extracted and other metals. Therefore, efficient recovery of these precious metals from mining wastewater before discharge into the environment is important, as this can also prevent environmental pollution. In addition, the extraction of precious metals from secondary sources is considered a crucial step to mitigate scarcity. However, the concentration of these metals in secondary sources is low but significant, which is why efficient, highly selective, economical, and sustainable technologies are required. Some of the methods being used for the recovery of precious metals at the industrial level include chemical precipitation, membrane separation, ion exchange, biological processes, etc. Like any other method, these methods have their shortcomings, such as high maintenance and operating costs, low efficiencies for low concentrations of ions, high costs, low selectivity, etc. [86]. The high demand for precious metals and the shortcomings of the existing methods are the main motivations for continuous research for effective economic recovery systems.

Table 2 shows that at the laboratory scale, considerable work has been done on the recovery of precious metals, and the adsorbents used show high efficiencies; however, it's impossible to conclude on their reusability potential as few studies have conducted it. The reports that conducted reusability studies include adsorbents such as functionalized quaternary hexamethylenediamine (F-QUAT HMDA) [95], silica gel quaternary 1,10-diaminodecane (Si-QUAT DMDA) [96], functionalized quaternary 1,10-diaminodecane (F-QUAT DMDA) [97], MOF-2,6-amino-pyridine on 3-formyl-4-hydroxybenzoic acid (AFH), pyridine-modified chitosan (PMCS) [98], $Ni_{0.6}Fe_{2.4}O_4$-MTD [99], 4,4',4'',4'''-((1,4,8,11-tetraazacyclotetradecane-1, 4, 8, 11-tetrayl) tetrakis(methylene)) tetrabenzoic acid-metal organic framework (DONA-MOF) [100], and poly(methacryloxyethyltrimethyl ammonium chloride) (PDMC-SNP) [101]. These adsorbents showed potential for multiple adsorption cycles. Two studies reported the use of biosorbents for the recovery of metals: lyophilized *Galdieria sulphuraria cells* and eggshell membrane for the recovery of Au and Pd, Pt, and Au, respectively. Utilizing biosorbents with high absorption capacity and selectivity is encouraged as it is cost-effective and eco-friendly. One study estimated the cost of their operating treatment system, which is crucial for upscaling tests [102]. The high adsorption capacity of the reported treatment systems was attributed to.

- The positively charged surface of the adsorbent (yeast-functionalized zeolite) favoured Pd(II) and Ir(III), as they are negatively charged at a highly acidic pH, while $[RhCl(H_2O)_5]^{2+}$ and $[RhCl_2(H_2O)_4]^+$ were repelled by the adsorbent [103].
- The large surface area and suitable HOMO-LUMO thermodynamic parameters obtained for F-QUAT HMDA-benzyl resulted in a high loading capacity for $[IrCl_6]^2$. This electron-withdrawing benzyl group lowered the charge density of the quaternary diammonium centre and the charge delocalizing ability resulted in a stronger ionic strength [96].
- Si-QUAT DMDA and F-QUAT DMDA's higher loading capacities were attributed to their higher binding capacities, indicating a strong bond between adsorbate and adsorbent. As the methylene spacers between the cationic centres increased, the Ir loading capacities increased as well in both studies [96,97].
- Ion exchange between gold ions and amines or chlorine groups on the surface of the PDMC-SNP adsorbent was attributed to its high loading capacity [101].
- High adsorption of Pd(II) on imprinted chitosan fiber (ICF) was attributed to the electrostatic attraction between protonated amine groups ($-NH_3^+$) and $PdCl_4^{2-}$ [104].

5.2. The removal of toxic metals in mining wastewater

Mining processes can release significant amounts of toxic metals, such as Pb, Hg, As, Cu, Ni, Cd, etc., into the environment, thus negatively affecting the ecosystem. Table 1 and Supplementary Table S1 show the effects of the toxic metals which primarily come

from the recovery of precious metals such as gold, tailings disposal, and wastewater around the mining areas. The real and pilot treatment systems reported in Sections 3 and 4 did not address the removal of toxic pollutants such as Cr, Ni, Fe, and nitrate. At the laboratory scale, one of the frequently investigated removal methods is the adsorption process (Table 3). And this might be due to its ease of design and operation, wide range of available adsorbents, less energy required, flexibility, and cost-effectiveness [84]. Just like biological and chemical precipitation processes, the adsorption process produces sludge and the regeneration of spent adsorbent is energy-consuming, insufficient, and results in high costs [114]. Nonetheless, research on the adsorption process is increasing and most adsorbents exhibit high removal efficiency. It was noted that the removal of As, Hg, and Sb has received a significant amount of attention from the researchers. This can directly be linked to the numerous incidences reported in Table 1 and the severe impacts these metals have on the environment. The highly toxic and strong carcinogenicity of As has been the main drive behind numerous treatment methods investigated. Bio-adsorbents (palm oil fuel ash (POFA) [115] and chitosan [116]), submerged aquatic plants (*Egeriadensa*, and *Hydrilla verticillata, Cabomba piauhyensis*) [117] and metal-organic frameworks integrated with iron nanoparticles [118,119], and birnessite [120] are some of the materials utilized for the adsorption of As. Iron nanoparticles were used for modification of ZIF-8 MOF and chitosan, and the interest in Fe NPs use can be attributed to their excellent magnetic properties, large surface area, sufficient active sites, and outstanding adsorption towards As [116,118,119]. The removal efficiency ranged between 93.7 and 100 %. Liu et al. [120] tested the reusability of their system through five cycles by electrochemically adsorbing birnessite for As(III) and As(V). The removal efficiency was 96.9–90.1 and 98.1–85.1, respectively. Increasing the voltage of the system resulted in an increased adsorption capacity of As. Reduction of adsorbent upon the cathode was found to generate additional adsorption sites for As, and the re-oxidation of Mn^{2+} on the birnessite anode provided feasible contact between the adsorbent and As, thereby enabling oxidation and adsorption of As. Mercury, which is mostly found in gold mining processing, is one of the major environmental pollutants in various areas, as seen in Tables 1 and 3 Numerous adsorbents have been successfully used for the reduction of mercury concentration levels, as the removal

Table 3
Laboratory scale treatment methods for removal of toxic metals.

Removal method	Metals	Wastewater source	Mechanism	Removal efficiency (%)	Reference
Activated carbon	Hg(CN)$_2$	Simulated effluent	Adsorption	81	[122]
Aspergillus niger	Cr(VI)	Mining effluent	Adsorption	96	[125]
APDC	Hg	Gold ores	Precipitation	98.9	[126]
Biochar	CN, Cr, Fe, Zn, Ni, Pb, Mn and Cu	Gold mining	Adsorption	75, 78, 74, 87, 82, 70, 85, and 90	[127]
Birnessite	As(III) As(T)	Mining effluent	Adsorption	1st – 5th cycle: 96.9 −90.1 1st – 5th cycle: 98.1 −85.1	[120]
CNT/COF–OH	U(VI)	Rare earth tailings	Adsorption	96.7	[128]
Carica papaya stem	ZnCl$_2$	Mining effluent	Adsorption	95	[129]
Chitosan	Cu(II), Hg(II), Pb(II), Zn(II)	Gold mining	Adsorption	97.8, 98.0, 94.1, 71.3	[130]
Egeriadensa, and *Hydrilla verticillata Cabomba piauhyensis*	As, Zn, Al	Gold mine	Adsorption	95.2, 93.7, 83.8	[117]
Fe–Al bimetallic particles	Hg	Gold processing	Adsorption	82	[121]
Fe-Chitosan-coated carbon electrode	As(III)	Mining effluent		96.4	[116]
Granular TiO$_2$	As(III) & As(V) Sb(V)	Mining effluent	Adsorption	74 & 94 76–92	[131]
Lemon peel	Cu	Copper mining	Adsorption	89	[9]
Limnocharis flava	Hg	Gold mine	Wetland system	90	[132]
MD and d-LLE	Cu	Gold mining	Membrane & solvent extraction	99.3	[133]
Moringa oleifera seeds	Cd(II), Hg(II), Fe(II)	Gold mining	Adsorption	91.66, 92.30, 24.48	[43]
Palm oil fuel ash	As	Gold mining	Adsorption	100	[115]
Palm oil fuel ash	Hg	Gold mining	Adsorption	96.77	[134]
Palm shell fly ash	Hg^{2+}	Gold mining	Adsorption	100	[135]
PTC coagulant	Al, Cu, Fe, Mn, Zn	Coal mining	Coagulation	98, 69.9,95.5, 97.7, 79.2	[136]
rGO-Fe/Ni	Sb(III) Sb(V)	Acid mine	Adsorption	1st – 4th cycle: 100 −72.7 1st – 4th cycle: 87.9 −12.1	[137]
ZIF-8	Sb(V)	Gold mining	Adsorption	73.6	[138]
ZIF-8@FeNPs	As(V)	Mining effluent	Adsorption	94.27	[118]
ZIF-8@FeNPs	Sb(V), As(V), Pb(II)	Mining effluent	Adsorption	1st – 4th cycle: 89.7 −39.1, 93.9, 99.1	[119]

Notes: APDC = ammonium pyrrolidine dithiocarbamate; CNT = carbon nanotubes; COF = covalent organic framework; MD = membrane distillation; d-LLE = dispersive liquid-liquid extraction; PTC = polytitanium tetrachloride; rGO = reduced graphene oxide.

efficiency reached more than 90 % for the reported processes except for Fe–Al bimetallic particles [121] and activated carbon (AC) [122], which exhibited 82 and 81 %, respectively. *Limnocharis flava*, palm oil fuel ash (POFA), palm shell fly ash (PSFA), and ammonium pyrrolidine dithiocarbamate (APDC) were also used as adsorbents for Hg in gold mining wastewater. These adsorbents exhibited removal efficiencies of 90, 96.77, 100, and 98.9 %, respectively, with PSFA adsorbent showing the highest performance. Zhang et al. [123] reviewed alternative methods being adopted by other gold mining industries. A novel eco-friendly synthetic gold lixiviants (NESGLs), Jinchan, with partial properties of cyanide, was developed by Guangxi Senhe High Technology. NESGLs were found to be less toxic than cyanide and have comparable recovery efficiency to cyanide [124]. Guo et al. [124] reported gold extraction using the eco-friendly lixiviant "Jinchan" and under optimum conditions, the recovery efficiency was 90.8 %. Ultrasound and ultrafine grinding pretreatment further improved recovery efficiency to 91.8 and 96.9 %, respectively. The effective ingredient in Jinchan is carbonized sodium cyanurate and other compositions used for leaching and stability of complex ions include thiourea, carbonate, polymerized ferrous sulfate, and alkali. The chemical reaction equation for gold leaching by Jinchan is as follows:

$$8C_6H_3O_3N_6Na_3 + 4Au + 2H_2O + O_2 \rightarrow 4NaAu(C_6H_3O_3N_6Na_2)_2 + 4NaOH \tag{2}$$
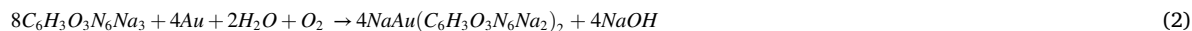
5.3. An overview and a critical analysis of the laboratory scale technologies

The exploration of bio-based materials as absorbents for heavy metals is observed in Table 3. The wide use can be attributed to their wide range of natural properties, cost-effectiveness, reusability, and ease of operation, and it significantly reduces the accumulation of agro-waste in the environment. The functional groups present on the surface of these bio-based materials are responsible for the effective adsorption of heavy metals. For instance, palm oil fuel ash (POFA), which is an agricultural by-product, consists of polar groups, namely siloxanes (Si–O–Si) and silanols (Si–OH), the hydroxide ions that are responsible for the formation of metal hydroxide with metals [139]. *Moringa oleifera* seeds are known for their coagulating properties, which are comparable to alum properties. The nitrogen- and oxygen-donating amino and carboxylate functional groups are responsible for the charge neutralization and ion adsorption between the metals and coagulant dimeric proteins [43]. Chitosan, a biopolymer that is mostly extracted from crustacean shells, has excellent adsorption capacity, biodegradability, and biocompatibility, and it's easy to produce. Its hydroxy and amino functional groups are responsible for the adsorption of metal ions, which happens either via hydrogen bonding, chelation, or electrostatic attraction [140,141]. In addition, carbon-rich materials like biochar, graphene oxide, activated carbon, etc. are being used as well. At the lab and pilot scale, the usage of these bio-based materials is conceivable; however, for real technologies, this approach may encounter problems, including insufficient production.

The laboratory-scale recovery and removal systems addressed all the precious metals (Ir, Pt, Pd, Rh, and Au) present in mining wastewater. However, the removal of toxic metals, especially Cr, Ni, and Fe, which were not addressed by commercialised and pilot systems, was reported in laboratory-scale tests. It is worth noting that the adsorption method is the most commonly reported for the recovery or removal of these precious and toxic metals from mining wastewater at the laboratory scale. In addition, there are few studies reported in the literature on the recovery of precious metals from real mining wastewater. Some of the aspects that are considered when transitioning to pilot testing are the reusability of the adsorbents, estimation of operating costs, environmental friendliness, and recovery and removal efficiency of the system. Therefore, these studies should address all these aspects to give a better account of the systems being tested. In addition, since all these laboratory-scale systems use the adsorption method, the issue of managing the generated sludge should be addressed to avoid secondary pollution. The laboratory-scale methods reported in Table 3 investigated the removal of the mentioned metals as well as Cr, CN⁻, and Ni. Therefore, there is a need to upscale these reported methods to test their potential on a pilot scale.

6. Summary and perspectives

The impact of mining wastewater on the environment and living organisms, including aquatic life, humans, and plants, as reported around the world was reviewed. Overall, the reports indicated that mining influents are a threat to the ecosystem and their effect has to be minimised as it keeps getting worse. There is therefore a need to remove toxic elements from mining wastewater before discharge into the environment. The currently used mining wastewater treatment technologies and methods were discussed. Technologies such as SAVMIN®, SPARRO®, biogenic sulfide, and DESALX® are among the approved and commercialised techniques for the treatment of mining wastewater and have been applied on a large scale. Pilot-stage treatment systems were also reported. Information on the operating costs of the systems is not provided, except for the MF/UF-RO system. Moreover, there is no discussion on sludge management resulting from the systems. There is a need for research and development of pilot-scale systems for the recovery and removal of Rh, Pd, Ir, Cr, CN⁻, and Ni since available research only focuses on laboratory scale. The adsorption treatment method, which has been widely investigated at the laboratory scale for both the recovery of precious metals and the removal of toxic metals, was discussed. There are few reports exploring alternative membrane-based, ion exchange, and chemical precipitation processes, or integrated systems, at the laboratory level. Simpler, more effective, less energy intensive and affordable treatment processes that can be integrated into the ZLD system should be developed. Moreover, the integration of several treatment systems can remarkably reduce the shortcomings of each system. The ultimate goal is to reuse permeate in mining operations, as this can significantly reduce the use of freshwater, especially in regions facing water scarcity. More work must be done on upscaling and performing cost-effective pilot tests, exploring environmentally friendly adsorbents, and developing strategies focused on reducing or avoiding secondary pollution.

Data availability statement

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

CRediT authorship contribution statement

Funeka Matebese: Conceptualization, Writing – original draft, Writing – review & editing. **Alseno K. Mosai:** Conceptualization, Writing – original draft, Writing – review & editing. **Hlanganani Tutu:** Supervision, Writing – review & editing. **Zenixole R. Tshentu:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

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

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e24730.

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