

# Wastewater Treatment in Mineral Processing of Non-Ferrous Metal Resources: A Review

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**Abstract:** Water used by mining enterprises needs to be comprehensively recovered and utilized to achieve clean production. This requires the effective treatment of mineral processing wastewater. Wastewater produced during non-ferrous metal mineral processing contains a complex mixture of pollutants at high concentrations, making comprehensive treatment difficult. Here, the sources of and hazards posed by wastewater produced during non-ferrous metal mineral processing are introduced and the techniques for removing heavy metal ions and organic chemicals are reviewed. Chemical precipitation and adsorption methods are often used to remove heavy metal ions. Chemical precipitation methods can be divided into hydroxide and sulfide precipitation methods. Organic chemicals are mainly removed using oxidation methods, including electrochemical oxidation, photocatalytic oxidation, and ultrasonic synergistic oxidation. External and internal cyclic utilization methods for treating wastewater produced by mineral processing plants are introduced, and a feasibility analysis is performed.



**Citation:** Meng, S.; Wen, S.; Han, G.; Wang, X.; Feng, Q. Wastewater Treatment in Mineral Processing of Non-Ferrous Metal Resources: A Review. *Water* **2022**, *14*, 726. <https://doi.org/10.3390/w14050726>

Academic Editor: Andrea G. Capodaglio

Received: 16 January 2022

Accepted: 22 February 2022

Published: 24 February 2022

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**Keywords:** cyclic utilization; mineral processing; non-ferrous metal; wastewater treatment

## 1. Introduction

Water is a basic natural resource and is essential to humans. Water resources are essential to almost all human activities and have various utilization values. Water resources must be adequate to meet the demands of economic (including scientific and technical), social, and domestic activities, and the environment [1–4]. Water demand has increased in recent decades due to population growth and industrial development. Many parts of the world are now in a state of water crisis exacerbated by water resource mismanagement [5]. Science-based water resource management is important for resolving water supply crises. The recycling and reutilizing of wastewater is generally acknowledged as being key to achieving sustainable water resource management. The natural purification of wastewater has disadvantages [6], such as requiring a long time period, being markedly affected by climate change, and having poor efficiency; therefore, it is important to develop efficient methods for treating and recovering wastewater.

Since the industrial era started, mining has led to rapid development, but also to many environmental problems, such as the pollution of air [7], soil [8–10], lakes [11], and the oceans [12], and the destruction of ecological systems [13,14]. Mineral processing wastewater produced at mining sites is an important source of environmental pollution. Mineral processing consumes large amounts of water and produces large amounts of wastewater, which accounts for 10% of total industrial wastewater around the world [15]. Mineral processing wastewater usually contains various heavy metal ions (e.g., Cd<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup>), fine suspended solids, organic chemicals, and other pollutants that pose serious risks to the environment [16–19]. Non-ferrous metal mineral processing produces

wastewater containing large amounts of various heavy metals, fine suspended solids, and organic chemicals due to the complex compositions of the minerals, the beneficiation processes applied, and the reagents used.

Fine suspended solids in non-ferrous metal mineral processing wastewater are generally removed through natural settling, flocculation and subsequent settling, and membrane separation [20]. The complex compositions of ores and the mineral processing methods used cause the wastewater produced to contain large amounts of heavy metal ions and organic chemicals. Removing organic chemicals and heavy metal ions is key to reutilizing non-ferrous metal mineral processing wastewater. Many techniques have recently been developed for removing heavy metal ions from wastewater, including chemical precipitation [21,22], adsorption precipitation [23–30], ion exchange [31,32], membrane separation [33–35], flocculation precipitation [36–38], and combined oxidation/coagulation [39], from which remarkable results have been found. These methods can effectively remove heavy metal ions from wastewater, and could be used to remove heavy metal ions from non-ferrous metal mineral processing wastewater. Most organic pollutants (e.g., sodium xanthate) in wastewater are difficult to remove using conventional treatment methods such as coagulation [40], adsorption [41], ion exchange [42], and chemical oxidation [43]. Efficient methods have been developed for removing organic pollutants from wastewater, including Fenton oxidation [44], electrochemical oxidation [45–48], and photocatalysis [49–51]. These methods could be used to remove common organic pollutants (e.g., xanthate) from non-ferrous metal mineral processing wastewater.

In this review, the sources of wastewater from non-ferrous metal mineral processing and its potential hazards, including heavy metal ions and residual flotation reagents, are introduced. Recent research progress on the treatment of heavy metal ions and residual reagents in wastewater from non-ferrous metal mineral processing is discussed. Furthermore, current approaches for the recycling of flotation wastewater from non-ferrous metal mineral processing are introduced.

## 2. Wastewater Sources and Hazards in Non-Ferrous Metal Mineral Processing

### 2.1. Wastewater Sources in Non-Ferrous Metal Mineral Processing

The different components of ore have different physical and chemical properties. Mineral enrichment can be achieved using one or more methods (e.g., flotation separation, electrical separation, gravity concentration, and magnetic separation), depending on the characteristics of the raw ore. Gravity concentration, electrical separation, and magnetic separation processes do not usually require reagents to be added, therefore, the wastewater can be recycled without treatment or after a simple settling treatment. Flotation wastewater includes wastewater from the flotation process (which contains a complex mixture of reagents) and wastewater from other processes, and, consequently, requires various treatments.

Wastewater from the flotation process includes tailing wastewater, concentrate wastewater, and raw ore washing water. Concentrate wastewater comprises the overflow water and filtered water produced during the concentrate dehydration process. This wastewater contains many flotation reagents, heavy metal ions, and suspended solids, which are generally difficult to remove. Tailing wastewater mainly comprises the overflow water and filtered water produced during the tailing dehydration process, and accounts for a large proportion (generally 50–70%) of the total wastewater produced at a processing plant. The raw ore must be flushed and deslimed if the mud content is too high, and the water used cannot be recycled without being treated.

Other types of wastewater are equipment water, wet dust removal equipment drainage water, ground flushing water, and wastewater from open pit mines. Equipment water comprises equipment cooling water and equipment shaft sealing water, including crushing water, high-pressure roller-grinding water, grinding equipment cooling water, and pulp pump shaft sealing water. Water produced by dust-cleaning equipment is discharged from the crushing and screening system and the belt conveying system. Ground washing

water from mineral processing workshops includes water from crushing and screening workshops, grinding workshops, and flotation workshops and mainly contains ore particles, flotation agents, and oil. The ore that accumulates in areas exposed to the open air for a long time period will be washed by natural rain. Mineral processing wastewater contains many types of sludge and mineral particles. The specific sources of mineral processing wastewater are summarized in Table 1.

**Table 1.** Sources of mineral processing wastewater.

Category	Source
Processing wastewater	<ol style="list-style-type: none"> <li>1. Concentrate wastewater</li> <li>2. Tailing wastewater</li> <li>3. Ore flushing water</li> </ol>
Other wastewater	<ol style="list-style-type: none"> <li>1. Equipment with water</li> <li>2. Drainage of wet dust cleaning apparatus</li> <li>3. Floor flushing water</li> <li>4. Mine acid wastewater</li> </ol>

## 2.2. Wastewater Hazards from Non-Ferrous Metal Mineral Processing

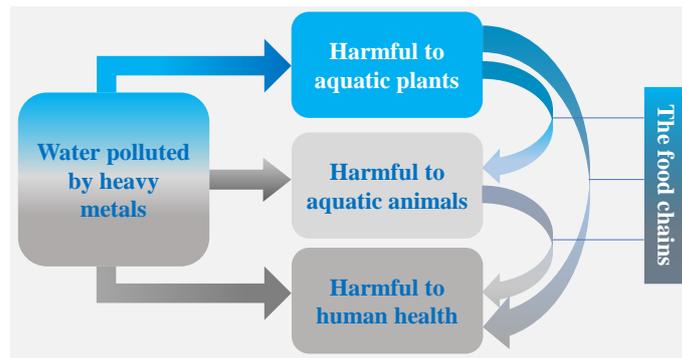
### 2.2.1. Hazards Posed by Heavy Metal Ions

The diversity of minerals in non-ferrous metal ore determines the variety and relatively high content of heavy metal ions in wastewater from mineral processing. Heavy metals are non-biodegradable inorganic pollutants that are difficult to remove from wastewater [52–54]. Therefore, heavy metals in wastewater discharged into the environment will readily accumulate in soil and water [55,56], and can affect humans. Heavy metal pollution occurs more rapidly, and becomes more widespread in water than soil due to the fact that water flows, taking heavy metals with it. Heavy metal pollution, therefore, has more serious environmental effects in water than soil. A certain degree of heavy metal pollution of water will endanger the aquatic ecosystem [57–60], and water polluted with heavy metals will have many adverse effects on aquatic plants and animals (Table 2).

**Table 2.** Hazards of heavy metal pollution to aquatic organisms.

Contaminated Organism	Specific Hazards
Aquatic plants	<ol style="list-style-type: none"> <li>1. Decreasing photosynthesis</li> <li>2. Inhibiting plant growth</li> <li>3. Causing plant atrophy and death</li> </ol>
Aquatic animals	<ol style="list-style-type: none"> <li>1. Causing metabolic disorders</li> <li>2. Causing organ damage</li> <li>3. Altering genetic information</li> </ol>

The potential hazards of water polluted by heavy metals to humans are also of great importance. It is possible for humans to directly drink contaminated water, touch water contaminated by heavy metals on their skin, or consume food contaminated by heavy metals through the food chain (Figure 1) [57–60]. Although some metals are necessary for human health, the body only tolerates very low levels, while elevated levels can be harmful [61]. Heavy metals, such as Pb, Cd, and Cr are of low value in human health functions, and are also harmful to human health when trace amounts are present in the body [62,63]. When heavy metals enter the body, they are deposited in the vital organs, such as the brain, kidneys, and stomach, and can eventually lead to illness and even death [64,65].



**Figure 1.** Potential hazards of heavy metals in water to biota.

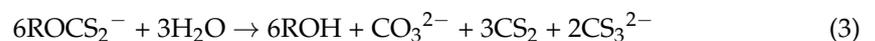
### 2.2.2. Hazards Posed by Reagent Residues

The chemical oxygen demand (COD), which is the oxygen equivalent that can be used by substances (generally organic) that, in turn, can be oxidized by a strong oxidant in water, is an important index of water quality [66]. The COD is an important parameter relating to organic pollutants, which is useful when studying river pollution and industrial wastewater and when operating and managing wastewater treatment plants. The COD can be determined rapidly. Persistent organic pollutants in industrial wastewater can have various negative effects on the environment. Some persistent organic pollutants can cause odor problems, pose risks to aquatic organisms, occur at saturated concentrations in soil, affect soil quality, discolor natural water, cause surface water eutrophication, and pollute surface layer water [67–69]. If not removed, many organic pollutants can adsorb to sediment and be deposited on river and lake beds, which can result in them having long-term toxic effects on aquatic biota. A river ecosystem will be destroyed if a large proportion of the aquatic biota dies. Humans that consume aquatic organisms from polluted water can absorb many toxins that can accumulate in the body. Some of these toxins may be carcinogenic or mutagenic, and therefore pose great risks to health. If polluted river water is used for irrigation, the plants and crops may be affected by the pollutants and may suffer poor growth.

Almost  $2 \times 10^9$  t of minerals (including ores of almost all non-ferrous metals, e.g., sulfide and oxide ores of copper, lead, and zinc) are processed by flotation each year around the world [66]. Organic collectors and regulators are widely used when non-ferrous metal ores are subjected to the flotation process [70] to achieve reasonable separation and ensure that the processing plants are economically effective. However, organic reagents used in the flotation process cannot be completely recovered, and reagent residues can enter the thickener with the washing water and subsequently enter the mineral processing wastewater. Organic reagents in wastewater from non-ferrous metal mineral processing plants can undergo various reactions to form products that are more harmful than the original reagents to the environment. For example, xanthate is a common collector used in non-ferrous sulfide ore flotation processes [70]. Xanthate can undergo various degradation reactions in wastewater at different pH values [71]. At acidic pH values, xanthate can undergo two degradation reactions, xanthogenate hydrolysis and xanthic acid decomposition, as shown below:

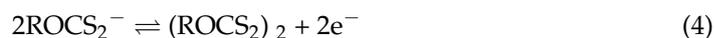


At alkaline pH values, xanthogenate can undergo the hydrolysis reaction shown below:



Trithiocarbonate ( $\text{CS}_3^{2-}$ ) produced in this reaction can decompose to form  $\text{CS}_2$  and  $\text{S}^{2-}$ .

Xanthate is sensitive to oxygen and undergoes the oxidation reactions shown below:



The production of  $(\text{ROCS}_2)_2$  will greatly increase the COD of wastewater, and this will increase the difficulty involved in treating the wastewater.  $\text{CS}_2$  produced through xanthic acid decomposition is toxic to humans because it can disrupt normal metabolism in cells and interfere with lipoprotein metabolism, resulting in vascular lesions, neuropathy, and damage to the main organs.

### 3. Wastewater Treatment in Mineral Processing of Non-Ferrous Metals

#### 3.1. Treatments for Heavy Metal Ions in Wastewater

Some metal oxides [72], carbon materials [73], biomass [74], and polymers [24] have been used to remove heavy metals from wastewater because they are cheap, have high adsorption efficiencies, are recyclable, and are very environmentally compatible. Adsorbents based on these materials can remove heavy metal ions through chemical reactions (e.g., coordination, ion exchange, oxidation–reduction, or precipitation) and physical interactions (e.g., electrostatic attraction, hydrogen bonding, or surface complexation).

##### 3.1.1. Chemical Precipitation

Chemical precipitation has been widely used to remove heavy metal ions from wastewater [75]. The chemical reagent reacts with heavy metal ions in wastewater to form insoluble precipitates [76]. The precipitates can then be removed from the wastewater using settling or filtration techniques. Chemical precipitation methods can be divided into hydroxide and sulfide precipitation methods. Hydroxide precipitation is economically viable, and many hydroxides have been used to precipitate metals from wastewater. Giannopoulou et al. [77] removed Ni from wastewater using a hydroxide method. When NaOH was added to wastewater containing Ni, the Ni precipitated as  $\text{Ni}(\text{OH})_2$ . The Ni removal efficiency was 99.76% at pH 10. After reducing Cr (VI) to Cr (III) using ferrous sulfate,  $\text{Ca}(\text{OH})_2$  or NaOH can be added to the precipitate and remove the Cr (III) from the wastewater (Figure 2) [75]. Adding a flocculating agent such as alum, a ferric salt, or an organic polymer to wastewater can accelerate precipitation [78]. The pH of the solution affects the precipitation of heavy metal ions into hydroxides. Various metal hydroxides are soluble in a narrow pH range, so heavy metals can be removed from the wastewater at a low cost using an appropriate pH and chemicals that are easy to treat.

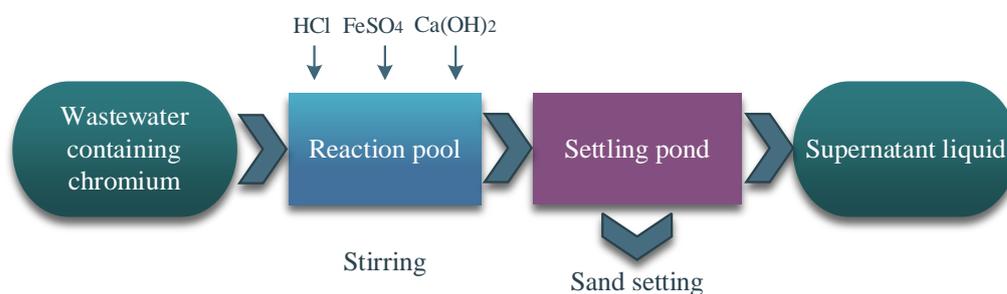
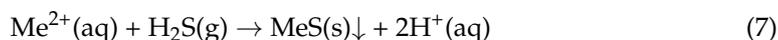
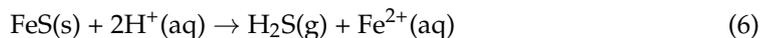


Figure 2. Schematic of Cr removal by  $\text{Ca}(\text{OH})_2$  precipitation.

Hydroxide precipitation is generally suitable for treating industrial wastewater containing heavy metals at high concentrations as simple mixtures. However, hydroxide precipitation has some problems, including producing a large amount of low-density sludge that is difficult to dehydrate, and the pH-influenced precipitation reagent releasing metal ions into the solution. Sulfide precipitation is also effective for removing heavy metal ions from wastewater. Metal sulfide precipitates are markedly less soluble than hydroxide precipitates. Metal ions can be quickly and selectively removed as sulfide precipitates.

The main reactions involved in sulfide precipitation are between  $\text{H}_2\text{S}$  and metal ions, as shown below [79]:



Metal sulfide sludge produced through sulfide precipitation settles faster and is treated more easily than sludge produced through hydroxide precipitation. However, there are some problems with the sulfide precipitation method, including that acidic conditions cause  $\text{H}_2\text{S}$  (which is toxic) to be produced. Sulfide precipitation, therefore, needs to be performed in a neutral or alkaline medium. Some examples of removal of metal ions by chemical precipitation are shown in Table 3.

**Table 3.** Chemical precipitation methods for removing heavy metals from wastewater.

Process	Removing of Metal Ions	Chemicals/Adsorbents Used	Removing (%)/ $Q_{\max}$	Experimental Conditions	References
Hydroxide precipitation	$\text{Cu}^{2+}, \text{Zn}^{2+}$	Apatite	>90	$\text{Ca}_5(\text{PO}_4)_3$ $\text{F}/\text{Ca}_5(\text{PO}_4)_3(\text{OH}) = 1:6$	[80]
	$\text{Cu}^{2+}$	CaO + biosorption	>99	pH = 12.5	[76]
	$\text{Zn}^{2+}$	CaO	>99	In the pH range of 9 to 10	[81]
	$\text{Ni}^{2+}$	NaOH	>99	pH = 10.0	[77]
	$\text{Cu}^{2+}, \text{Zn}^{2+}$	CaO	>99	In the pH range of 7 to 11	[82]
	$\text{Cr}^{3+}$	CaO and MgO	>99	pH = 8.0	[83]
Sulfide precipitation	$\text{Cu}^{2+}, \text{Zn}^{2+}$	$\text{H}_2\text{S}$	>90	pH = 3.0	[84]
	$\text{Hg}^{2+}$	Pyrrhotite and pyrite	>90	pH = 4.0	[85]

### 3.1.2. Ion Exchange

In the ion exchange method, harmful ions are removed from wastewater using an ion exchange material that can adsorb, bond, and exchange the ions. Ion exchange has been used to remove heavy metal ions from industrial wastewater due to the high capacities, high removal efficiencies, and other advantages of ion exchange materials [86,87]. Ion exchange materials can be classed as inorganic (e.g., zeolites [88]) or organic (e.g., ion exchange resins [89]). Cation exchange resins can be divided into strong acidic cationic resins containing sulfonic acid groups, and weak acidic cationic resins containing carboxylic acid groups.  $\text{H}^+$  in sulfonic acid or carboxylic groups in the cation exchange resin are exchanged for heavy metal ions in the solution being treated [90]. Both organic and inorganic ion exchange materials have limitations. Organic ion exchange resins are poorly thermally stable [91]. For example, the mechanical strengths and heavy metal removal abilities of ordinary organic ion exchange resins tend to be lower at high temperatures (e.g., for treating liquid radioactive waste) than at lower temperatures [92]. Inorganic ion exchange materials are poorly reusable, have low mechanical strengths, and are not resistant to some chemicals [93]. Inorganic–organic composite ion exchange materials have been developed to attempt to overcome these limitations of organic ion exchange resins and inorganic adsorbents [94]. Composite ion exchange materials combine the mechanical properties of organic polymers and the inherent properties of inorganic compounds, meaning they have advantageous mechanical properties, are chemically inert, are stable at high temperatures and when exposed to radiation, and can reproducibly and selectively remove heavy metal ions from solution [95–101]. Some examples of composite ion exchange materials are shown in Table 4.

**Table 4.** Sodium ion exchange capacities of composite ion exchange materials.

Composite Materials	Thermal Stability (°C)	IEC for Na Ions	References
n-Butylacetatezr (IV) iodate	200	0.78	[102]
Polyaniline Ti (IV) tungstate	300	0.78	[103]
Zirconium (IV) iodotungstate	400	0.68	[104]
Poly-orthotoluidine Zr (IV) iodate	100	0.85	[105]
Zirconium (IV) molybdo tungsto-vanadosilicate	100	0.86	[106]
Polyaniline Zr (IV) molybdophosphate	200	1.30	[107]

### 3.1.3. Adsorption

The adsorption method has great potential because the adsorbents that are used are cheap, the method is simple, and the adsorbents used can remove heavy metals from wastewater even at low concentrations [108]. The most common materials used to adsorb heavy metals from wastewater are activated carbon, polymers, and nanomaterials. These materials all have three characteristics [109], as follows: (i) a chemical structure containing chelating sites or ion exchange groups that can interact with heavy metal ions; (ii) a hydrophilic and three-dimensional network structure, providing a large area in contact with water; and (iii) low cost and availability from a wide range of sources. However, commercially available activated carbon can only be used at a large scale because it is expensive to produce and reuse [110]. Polymers and nanomaterials have therefore been used to remove metal ions from wastewater in many studies.

Polymers are particularly suitable adsorbents for removing metal ions from wastewater because they have high specific surface areas, are cheap to reuse, and are environmentally compatible [111–114]. However, polymer adsorbents have low adsorption capacities and poor selectivities, and need to be modified for practical use [115]. El et al. [115] synthesized a novel hyper-cross-linked nanoscale chelating resin with a high specific surface area (335 m<sup>2</sup>/g) and a mesoporous structure (2.882 nm diameter pores). At room temperature (25 °C), the adsorption capacities of the hyper-cross-linked nanoscale chelating resin for Pb, Cd, and Zn ions were 1.2 mmol/g (at pH 5.5), 1 mmol/g (at pH 6.0), and 0.9 mmol/g (at pH 6.3), respectively, which are much higher than the adsorption capacities of many other adsorbents. Ulusoy et al. [116] directly polymerized polyacrylamide in a suspension of bentonite and zeolite to produce a polyacrylamide–bentonite/zeolite composite material. At room temperature (25 °C) and pH 4.5, the adsorption capacity of the polyacrylamide–bentonite/zeolite for Pb (II) was 0.16 mmol/g. The adsorption capacities of the modified polymers used in previous studies as adsorbents for some metal ions in wastewater are summarized in Table 5.

Nanomaterial adsorbents are important for removing heavy metal ions from wastewater. Many nanoscale metal oxides, such as nano-alumina, nano-cerium oxide, nano-iron oxide, nano-magnesium oxide, nano-manganese oxide, and nano-titanium oxide, have been found to be promising adsorbents for removing heavy metal ions from aqueous solutions. Nano-oxide particles with certain characteristics (including a small volume, large specific surface area, and strong magnetism) have been found to strongly adsorb heavy metals [122–124]. Fang et al. [125] synthesized a puffed rice carbon with coupled sulfur and metallic iron composite nanomaterial that efficiently adsorbed Hg<sup>2+</sup> from an aqueous solution. The maximum adsorption capacity of the composite was 689.0 mg/g, which was achieved at pH 6. Nassar et al. [126] reported a maximum adsorption capacity of Fe<sub>3</sub>O<sub>4</sub> nanoparticles for Pb (II) ions of 36.0 mg/g, which is much higher than the adsorption capacities of common adsorbents (Table 6). Beneficial adsorption characteristics have been

found for nano-oxide particles modified with Mn. For example, Warner et al. [127] used nano-oxide particles with and without Mn doping to adsorb heavy metal ions, and found that Mn doping strongly improved the affinities and capacities of the particles for the heavy metals Ag, As, Cd, Co, Hg, Ni, Ti, and Zn. Iron-oxide-based nanomaterials have high heavy metal ion adsorption capacities and adsorption rates, are simple to use and regenerate, and can be used instead of poorly efficient adsorbents.

**Table 5.** Adsorption capacities of modified polymers and other adsorbents for metal ions.

Adsorbents	Metal Ions	Sorption Capacity (mmol/g)	Conditions	Reference
HCNSCR	Pb (II), Cd (II), and Zn (II)	1.2, 1, and 0.9	pH = 5.5, 6.0, and 6.3 25 °C	[115]
PAA-B/Z	Pb (II)	0.16	pH = 4.5 25 °C	[116]
Fe <sub>2</sub> O <sub>3</sub> -ceramisite (FOC)	Pb (II) and Zn (II)	0.08 and 0.11	pH = 5 25 °C	[117]
Olive stone activated carbon (COSAC)	Cd (II) and Pb (II)	0.53 and 0.54	pH = 5 30 °C	[118]
Amidoxime-modified poly (acrylonitrile-co-acrylic acid)	Cd (II) and Pb (II)	0.18 and 0.6	pH = 9 25 °C	[119]
Novel chelating sponge (PVA-M-H)	Ni (II) and Cd (II)	1.114 and 1.117	pH = 5.5 30 °C	[120]
Synthetic amberlite IR-120	Ni (II), Cu (II), and Cd (II)	0.819, 0.344, and 0.899	pH = 9 25 °C	[121]

HCNSCR, hyper-cross-linked nanoscale chelating resin; PAA-B/Z, polyacrylamide-bentonite/zeolite.

**Table 6.** Maximum Pb (II) adsorption capacities of various adsorbents.

Adsorbing Material	Maximum Adsorption (mg/g)	Reference
Nano oxide particle	36.0	[126]
Humic acid	22.7	[128]
Goethite	11.04	[128]
Montmorillonite	33	[129]
Al <sub>2</sub> O <sub>3</sub>	17.5	[130]
Diatomite	24	[131]
Activated carbon	21.5	[132]

### 3.2. Treatment of Residual Organic Reagents

Xanthate is the most common collector when treating sulfide and oxidized ores [133,134]. Methods for removing xanthate from mineral processing wastewater are summarized in this section. Xanthate can be removed from flotation wastewater using biological, chemical, and physical techniques (Table 7). Traditional physical treatments, such as physical precipitation and activated carbon adsorption, have some drawbacks, including high costs and poor reusability; therefore, these treatments are not widely used [135]. Common methods for degrading xanthates using oxidizing agents, such as chlorine or permanganate, can cause secondary contamination because harmful byproducts are created [136]. Using microorganisms to bioremediate wastewater often requires a long degradation time, and it is difficult to degrade pollutants at low concentrations using biological treatments [137]. The treatment methods mentioned above are “traditional”, however, advanced oxidation techniques that efficiently produce active substances and rapidly remove organic pollutants have been developed [138]. Novel oxidation techniques for degrading xanthate include Fenton oxidation and photocatalytic oxidation.

**Table 7.** Traditional treatments and advanced oxidation treatments for removing xanthate from wastewater.

	Progress	Characteristic
Traditional treatment technologies	Physical and chemical precipitation Activated carbon adsorption	High cost, poor reusability, and causes secondary contamination
Advanced oxidation technologies (AOTs)	Fenton oxidation Photocatalytic oxidation	High chemical activity and decontamination efficiency

### 3.2.1. Photocatalytic Oxidation

Photocatalysis is one of the best methods for degrading harmful organic pollutants in wastewater because it is environmentally benign, sustainable, and cheap [139]. Titanium dioxide (TiO<sub>2</sub>) is a photocatalytic material that has attracted much attention in recent years, and has often been found to be the optimal semiconductor photocatalyst [140,141]. However, TiO<sub>2</sub> has some disadvantages when used as a photocatalyst [142,143], including powder-like TiO<sub>2</sub> having a large bandgap (3.2 eV for anatase), photogenerated electron–hole pairs (e<sup>−</sup>/h<sup>+</sup>) readily and rapidly recombining, agglomeration occurring readily, and separation and recycling procedures being difficult; therefore, TiO<sub>2</sub> is not suitable for treating contaminated water [144].

The unsuitability of TiO<sub>2</sub> for use as a photocatalyst for treating wastewater can be solved to an extent by loading TiO<sub>2</sub> nanoparticles (TNPs) onto a supporting surface [145]. TNPs aggregate on the supporting material surface through various bonding methods, and the surface of the supporting material can act as an electron sink. The photocatalytic activity is markedly better in this composite material than in TiO<sub>2</sub> because less electron/hole recombination in the TiO<sub>2</sub> photocatalyst occurs. Some problems using TiO<sub>2</sub> to achieve photocatalysis have been solved using TiO<sub>2</sub> composites with silver orthophosphate (Ag<sub>3</sub>PO<sub>4</sub>) [146], BiOCl [139], clinoptilolite [145], and Nb<sub>2</sub>O<sub>5</sub> [147]. As shown in Table 8, the bandgaps were found to be narrower for composite photocatalytic materials than for TiO<sub>2</sub>, resulting in the response in the visible spectrum to be stronger for composite photocatalytic materials than for TiO<sub>2</sub>.

**Table 8.** Bandgap widths for synthesized composite photocatalytic materials and TiO<sub>2</sub>.

Material	Bandgap (eV)	Reference
TiO <sub>2</sub>	3.09	[145]
TiO <sub>2</sub> /Clinoptilolite	2.88	[145]
BiOCl/TiO <sub>2</sub> /Clinoptilolite	2.56	[139]
TiO <sub>2</sub> /Nb <sub>2</sub> O <sub>5</sub>	2.59	[147]
Ag <sub>3</sub> PO <sub>4</sub> /TiO <sub>2</sub>	2.05	[146]

Zhou et al. [139] synthesized novel ternary heterogeneous BiOCl/TiO<sub>2</sub>/clinoptilolite (BTC) photocatalysts using a hydrothermal method combined with a water bath precipitation method using clinoptilolite as the supporting material. BiOCl is a ternary layered oxide with an internal structure that provides adequate space to facilitate the separation of the photogenerated e<sup>−</sup>/h<sup>+</sup> pairs in the TNPs. Morphological analysis indicated that the clinoptilolite improved TNP dispersion on the composite surfaces. N<sub>2</sub> adsorption/desorption analysis indicated that there were many micropores in the BTC, which would provide it with a high adsorption capacity and ability to degrade xanthate. In degradation experiments, BTC was found to exhibit degradation rates for sodium ethyl xanthate, sodium butyl xanthate, and sodium isoamyl xanthate of 84.5%, 96.7%, and 99.2%, respectively. These data indicate that BTC performs well as a photocatalyst.

### 3.2.2. Fenton Oxidation

Fenton oxidation produces strongly oxidizing hydroxyl radicals (·OH) that can effectively degrade otherwise recalcitrant organic pollutants [148–150]. Fenton oxidation is

a promising water treatment technique because the reagents are cheap and the method is simple and effective [151,152]. However, the Fenton process has some drawbacks that prevent it being used widely in industrial-scale wastewater treatment plants [153]. Improving wastewater treatment methods using the Fenton oxidation process is a current focus of research, and remarkable progress has been made using improved Fenton oxidation processes to remove xanthate residues from wastewater.

Improved versions of the traditional Fenton oxidation process include ultrasonication–Fenton oxidation [154], photocatalysis–Fenton oxidation [155], and electrocatalysis–Fenton oxidation [156]. Ai et al. [157] investigated xanthate degradation using a combination of ultrasonication and Fenton oxidation, and a greater removal efficiency was found using the combined method than using Fenton oxidation alone. At pH 3, a  $\text{H}_2\text{O}_2$  concentration of 24 mg/L, and a  $\text{Fe}^{2+}$  concentration of 18 mg/L, 97.6% of the xanthate present was removed from real mineral processing wastewater, and the xanthate concentration in the treated wastewater met the relevant effluent discharge standard. Xanthate degradation in the ultrasonication–Fenton oxidation method [158–161] involves two processes. Ultrasonication causes the Fenton reagent to form more hydroxyl radicals ( $\cdot\text{OH}$ ) in the water than would otherwise be produced, and the high temperatures and pressures generated in the cavitation bubbles are conducive to the Fenton reaction. The ultrasonic waves also increase the degree of liquid mass transfer that occurs, so the reacting species come into more contact with each other, which increases the reaction efficiency. Garcia et al. [162] assessed ethyl xanthate removal, degradation, and mineralization in a simulated solar Fenton advanced oxidation process, and a kinetics study indicated that the process performed well (~99% of xanthate anions were removed). Electrocatalysis–Fenton oxidation and photocatalysis–Fenton oxidation are generally used as combined processes. Yang et al. [163] found that ethyl xanthate was effectively degraded using bismuth ferrites based on activated bentonite (A-BiFe/Bent in Table 9) as particle electrodes in a three-dimensional electro-Fenton system under visible light. At  $\text{Na}_2\text{SO}_4$  concentration of 0.10 mol/L, a concentration of bismuth ferrites based on activated bentonite of 1.0 g/L, an applied voltage of 10 V, an aeration intensity of 3.5 L/min, and at natural pH, the ethyl xanthate degradation efficiency and  $\text{COD}_{\text{Cr}}$  removal efficiency were 97.85% and 93.50%, respectively. These advanced oxidation processes can effectively remove xanthate from wastewater, often exhibiting removal efficiencies >95% (Table 9). However, homogeneous photocatalysis–Fenton oxidation has some clear disadvantages, including the aqueous solution having a low pH, and it being difficult to separate and reuse the iron ions in the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$  system. The latter will cause secondary pollution, which will increase the treatment cost; furthermore, the production of iron hydroxide sludge will cause other environmental problems [164–167]. Research into heterogeneous Fenton processes has therefore been performed. Composite heterogeneous catalysts, such as a bentonite-supported Fe (II)/phosphotungstic acid composite [168], acidified/calcined red mud [169], and modified fly ash [170], can overcome most of the problems associated with homogeneous Fenton processes and offer great potential for industrial applications.

**Table 9.** Xanthate degradation efficiencies achieved using various advanced oxidation processes.

Process	Conditions	Removal Rate of Xanthate (%)	Reference
Ultrasonic–Fenton oxidation	$c(\text{Fe}^{2+}) = 18 \text{ mg/L}$ $c(\text{H}_2\text{O}_2) = 24 \text{ mg/L}$ 40 kHz (Ultrasonic frequency) pH = 3	97.6	[157]
Photocatalysis–Fenton oxidation	$[\text{Fe}^{2+}]: [\text{H}_2\text{O}_2] = 1:40$ (Molar ratio) pH = 9 30mW/cm <sup>2</sup> (Irradiance)	99.1	[162]

Table 9. Cont.

Process	Conditions	Removal Rate of Xanthate (%)	Reference
Electrocatalysis–Fenton oxidation	c (Na <sub>2</sub> SO <sub>4</sub> ) = 0.10 mol/L c(A-BiFe/Bent) = 1 g/L U = 10 V Aeration intensity 3.5 L/min pH = 6.82	97.85	[163]

#### 4. Recycling and Utilization of Wastewater from Non-Ferrous Metal Mineral Processing

Mineral processing, particularly for non-ferrous metal production, consumes large amounts of freshwater resources. Many mineral processing plants are situated in remote mining areas to minimize transportation costs and limit the effects of the plants on humans; however, some such areas have inadequate freshwater supplies. It is therefore important to recycle the water using mineral processing plants and to develop efficient wastewater treatment processes, liquid–solid separation processes, and dehydration steps [171]. The effective recycling of flotation wastewater is key to recycling mineral processing wastewater.

##### 4.1. Effects of Recycling Wastewater on Flotation Processes

Flotation wastewater has different qualities to freshwater; thus, using recycled water in a flotation process usually negatively affects mineral recovery and the concentrate quality [172]. The accumulation of dissolved inorganic and organic compounds in the water used in the flotation process can alter the chemical properties of the system. When recycling flotation wastewater, the accumulation of reagents and heavy metal ions in the wastewater can cause the flotation production index to weaken. The main factors affecting the recycling of flotation wastewater for further flotation processes include the presence of ions that cannot be removed, flotation reagent residues, and suspended solids. Cations and anions on the mineral surfaces, and calcium or magnesium ions in hard water, can affect the flotation process. When flotation wastewater is reused, reagent residues can be both beneficial and detrimental to the flotation process. The benefit is that some collector will remain in the flotation wastewater, so less fresh collector will need to be added when the wastewater is reused. The adverse effects of using recycling water are shown in Table 10.

Table 10. Adverse effects of using recycling water on flotation.

Factors	Potential Effects
Inevitable ions	1. Consumption of flotation reagents. 2. Activation of gangue mineral. 3. Depression of the target mineral.
Residual reagents	1. May have a depressive effect on the purpose mineral. 2. May activate the gangue mineral, making it difficult to separate the target mineral from the gangue mineral. 3. Could interact with inevitable ions to form complex, colloidal substances, etc., reducing the efficiency of flotation.
Suspended solids	1. The surface of mineral particles could be covered by suspended solids, which affects the adsorption of reagents on the mineral surface. 2. The colloidal group generated by suspended solids will increase the pulp viscosity.

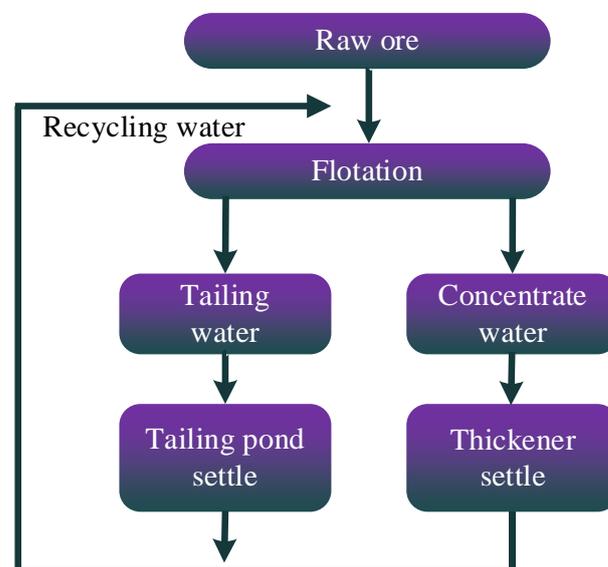
##### 4.2. Processes Involved in Recycling Flotation Wastewater

Wastewater recycling in the flotation process can be divided into two categories, known as external and internal recycling [172–175]. External recycling is where the total amount of wastewater is simply settled and used in different parts of the flotation process.

Internal recycling is where the water recovered from different parts of the process is returned to the corresponding loop.

#### 4.2.1. External Recycling

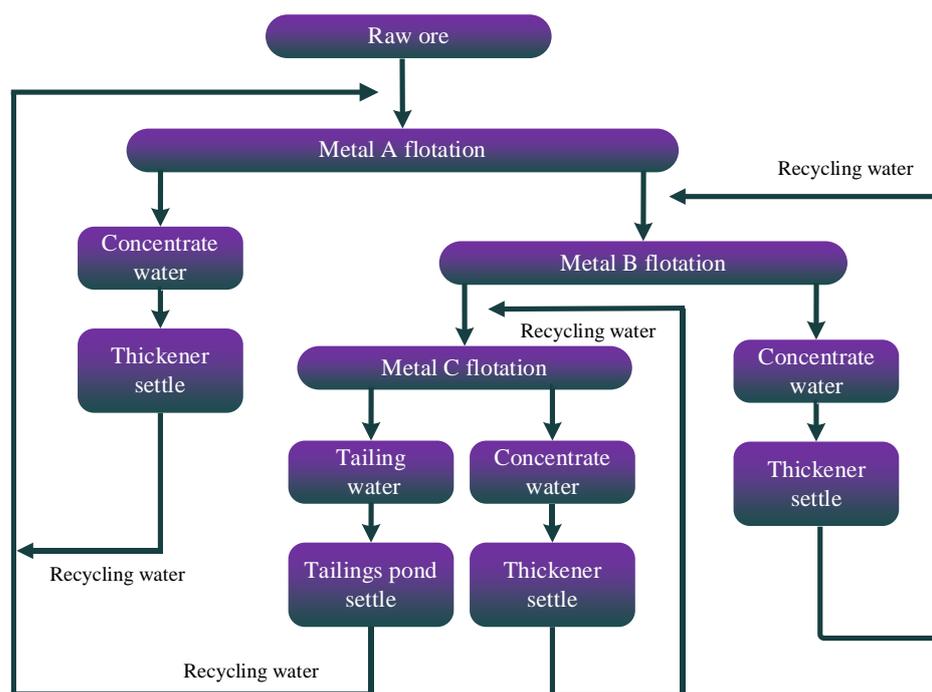
The external recycling process (Figure 3) is mainly used for the flotation concentrate and tailing pond overflow water, which are allowed to settle naturally and then directly reused in the flotation process. Alternatively, depending on the reagent residue and heavy metal ion concentrations, the total amount of wastewater may be mixed with some new water before being used in the flotation process. This technique has various advantages, being relatively simple, cheap, and convenient, and is widely used in industrial plants. However, external recycling has some disadvantages. Mixing wastewater from different processes means the wastewater is usually of a complex composition. The reagent residue and heavy metal ion concentrations in the water increase as the number of cycles increase. Various chemical reactions occur between the anionic reagent residues and metal cations in the wastewater, causing the wastewater composition to become more complex. This may ultimately adversely affect the flotation index.



**Figure 3.** Schematic diagram of external recycling process of flotation wastewater.

#### 4.2.2. Internal Recycling Process

The internal recycling process (Figure 4) involves selecting when to use recycled mineral processing wastewater according to the quality of the wastewater. The most common internal recycling process is described here. In the polymetallic flotation process, wastewater derived from the processing of a single metal concentrate is filtered and passed into a concentrating basin, in which purification treatments targeted at specific impurities are performed. The wastewater is then reused in the previous stage of the flotation process. This internal recycling process has four advantages and maintains a stable flotation index. These advantages are: (i) a smaller volume of wastewater needs to be treated compared to when wastewater is not recycled, (ii) few heavy metal ions and flotation reagents need to be removed, which greatly decreases the difficulty and cost of treating the wastewater, (iii) reagent residues in the wastewater are effectively utilized, which decreases the required reagent dose, (iv) the flotation process is cheaper compared to when wastewater is not recycled. However, more multiple return water cycles are required, and the process is more complex and difficult to manage when internal recycling is performed than when direct recycling of whole wastewater is performed.



**Figure 4.** Internal recycling process of flotation wastewater. Metals A, B, and C represent different valuable metals in polymetallic mineral processing.

## 5. Conclusions

Heavy metals (e.g., copper, lead, and zinc) and xanthate are the main pollutants in non-ferrous metal mineral processing wastewater; therefore, it is important to remove these pollutants from wastewater before the wastewater is reused or released. Removing these pollutants can allow the effects of using recycled wastewater on mineral separation to be controlled, and can improve the wastewater utilization rate and decrease the pollution of the environment surrounding a mineral processing plant. Few practical studies of mineral processing wastewater treatments have been performed. The methods previously used to treat wastewater containing heavy metals and organic chemicals in various industries and laboratories are summarized above.

Chemical precipitation and adsorption methods are generally used to remove heavy metal ions from wastewater. Chemical precipitation is suitable for removing Cr, Cu, Hg, Ni, Zn, and other heavy metals from wastewater. Hydroxide precipitation can be used to economically and effectively treat wastewater containing a small number of heavy metals at high concentrations. Sulfide precipitation is more easily achieved than hydroxide precipitation because metal sulfides are more stable than metal hydroxides in sediment. Alternatively, adsorption is simpler to perform and cheaper than precipitation. Many high-performance polymers and modified nanomaterials have been developed that can be used to adsorb heavy metal ions from mineral processing wastewater.

The efficient degradation of organic reagents (e.g., xanthate) using advanced oxidation techniques has been achieved in the laboratory; thus, advanced oxidation techniques would be worth considering for treating non-ferrous metal mineral processing wastewater. The cost of an ultrasonic device needs to be considered before deciding to use the ultrasonic oxidation process, and electric consumption needs to be considered before using an oxidation process. Photocatalytic oxidation will be the most cost-effective treatment because sunlight is free. The only drawback of photocatalytic oxidation is that variations in light intensity will cause a variable xanthate degradation rate. Few treatments for removing fine suspended solids have been developed, possibly because fine suspended solids have little environmental impact and due to the long time period required for the natural settlement of fine suspended solids. Few studies of comprehensive treatment techniques for heavy

metal ions and organic reagents have been published. Developing such methods will be key to achieve efficient recycling of wastewater produced during the beneficiation process. Research into the comprehensive treatments of various pollutants in wastewater should be performed.

Recycling flotation wastewater is an effective way of preserving water resources and achieving clean production processes. Most mineral processing wastewater is produced during the flotation process. Flotation wastewater can be recycled using external or internal recycling processes. Recycling flotation wastewater has the advantages of decreasing production costs and environmental impacts. Recycling flotation wastewater can decrease the consumption of water and the quantities of reagents required for the flotation process, which will decrease production costs. Recycling flotation wastewater can also minimize the amount of wastewater discharged, and therefore decrease the impacts of mineral processing on the environment. Overall, recycling flotation wastewater is an important way of decreasing production costs and environmental impacts, and should be a top priority to allow the sustainable development of mining enterprises.

**Author Contributions:** S.M.: Data curation, Formal analysis, Investigation, Methodology, Software, Visualization, Writing—original draft, Writing—review & editing. S.W.: Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing—review & editing. G.H.: Formal analysis, Investigation, Methodology, Visualization, Writing—review & editing. X.W.: Investigation, Methodology, Visualization, Writing—review & editing. Q.F.: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was financially supported by Ten Thousand Talent Plans for Young Top-notch Talents of Yunnan Province (No. YNWR-QNBJ-2018-051).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

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