

METHODS FOR MANGANESE REMOVAL FROM WASTEWATER: REVIEW AND COMPARATIVE ANALYSIS

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ABSTRACT. Manganese plays a vital role as an essential micronutrient in numerous biological processes, but when its concentration is elevated in aquatic systems, it becomes a pollutant which induces considerable environmental problems. A great part of the heavy industry, like mining, metallurgy, chemical production, and battery manufacturing, generates wastewater streams containing manganese ions in a wide concentration range (1–200 mg/L). In the context of increasing environmental problems and progressively stricter regulatory standards, the implementation of sustainable manganese removal technologies becomes a necessity. The current review provides a comparative analysis of contemporary techniques for manganese removal from wastewater, including chemical oxidation and precipitation, adsorption, membrane-based processes, as well as biological and electrochemical approaches. The analysis shows that although most technologies achieve removal efficiencies above 90%, they cannot satisfy all criteria simultaneously. It was found that hybrid and integrated systems are a promising practical solution.

Key words: wastewater treatment, manganese removal, sustainable water management.

МЕТОДИ ЗА ОТСТРАНЯВАНЕ НА МАНГАН ОТ ОТПАДЪЧНИ ВОДИ: ОБЗОР И СРАВНИТЕЛЕН АНАЛИЗ

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РЕЗЮМЕ. Манганът играе жизненоважна роля като основен микроелемент в множество биологични процеси, но когато концентрацията му се повиши във водните системи, той се превръща в замърсител, който причинява значителни екологични проблеми. Голяма част от тежката промишленост, като минното дело, металургията, химическата промишленост и производството на батерии, генерираят потоци от отпадъчни води, съдържащи манганови йони в широк диапазон на концентрация (1–200 mg/L). В контекста на нарастващите екологични проблеми и все по-строгите регулаторни стандарти, прилагането на устойчиви технологии за отстраняване на манган се превръща в необходимост. Настоящият преглед предоставя сравнителен анализ на съвременните техники за отстраняване на тези йони от отпадъчни води, включително химическо окисление и утаяване, адсорбция, мембранни процеси, както и биологични и електрохимични подходи. Анализът показва, че въпреки че повечето технологии постигат пречиствателен ефект над 90%, те не могат да отговорят на всички критерии едновременно. Установено е, че хибридните системи са обещаващо практическо решение.

Ключови думи: пречистване на отпадъчни води, отстраняване на манган, устойчиво управление на води.

Introduction

Mining and mineral processing are central to modern industrial supply chains, providing the metals and mineral raw materials required for construction, transport, and energy transition technologies. However, these activities are inherently water-intensive and disruptive to natural systems, as they mobilise large volumes of solids and generate process-affected waters throughout the mine life cycle. The most persistent pressures typically originate from tailings storage facilities and waste-rock dumps (via seepage and runoff), as well as from process circuits where reagents, fine particles, and dissolved species interact with water. Under increasing water scarcity, stricter permitting frameworks, and rising societal expectations, mine water management is evolving from a compliance-driven task to a core operational function linked to water efficiency, reuse, and long-term liability reduction (Matebese et al., 2024; de Lima et al., 2025).

A key pathway of water degradation in mining environments is the formation of acid mine drainage (AMD), driven primarily by sulphide mineral oxidation and often enhanced by microbial activity. AMD is characterised by low pH and elevated concentrations of sulphate and dissolved metals, which complicate both prevention and treatment strategies. In recent years, the field has moved beyond conventional “one-size-fits-all” neutralisation approaches towards more systematic and comparative evaluation of prevention measures (e.g., covers and oxygen barriers), passive and semi-passive systems, and active chemical or physicochemical treatment systems.

Increasingly, these approaches are assessed using sustainability-oriented metrics, including reagent consumption, sludge generation, energy demand, and overall environmental footprint (Yang et al., 2023; Nguengang & Ambushe, 2025).

At the same time, mine-impacted waters are no longer viewed solely as waste streams requiring disposal, but as potential sources of reusable water and recoverable materials. This shift aligns with broader circular economy principles and has driven growing interest in integrated and hybrid treatment systems (i.e., multi-step process systems) designed to maximise water recovery while enabling selective removal or recovery of metals and salts. However, this “treatment + recovery” paradigm introduces a critical trade-off: secondary residues (e.g., sludges and concentrates) may remain hazardous or difficult to valorise, meaning that overall sustainability performance depends strongly on downstream residue management (Matebese et al., 2024; Mahlohla et al., 2026).

Within this context, manganese (Mn) represents a particularly persistent and technically challenging contaminant in mine drainage and metallurgical wastewater. In contrast to Fe and Al, which are readily removed as hydroxides during pH adjustment, Mn removal is governed primarily by sorption and redox-controlled precipitation processes. These mechanisms are highly sensitive to Eh–pH conditions, competing ions, and the presence of reactive or catalytic surfaces, which limits process robustness under variable water chemistries. As a result, Mn frequently emerges as a “polishing-stage” constraint,

even when bulk metal removal has already been achieved (Neculita & Rosa, 2019).

From an operational and design perspective, this challenge is further amplified by the wide variability of Mn concentrations in mine-affected waters, ranging from a few mg/L to over 100 mg/L depending on geological and site-specific conditions (Doyle & Figueroa, 2024). Such variability reduces the effectiveness of single-step treatment approaches and necessitates adaptable, matrix-specific process configurations that can reliably meet discharge or reuse criteria.

Manganese also presents a dual sustainability concern. While it is an essential micronutrient, elevated concentrations in aquatic systems pose risks to ecosystems and human health, particularly where impacted waters interact with drinking water sources. A systematic review focusing on school-age children reported consistent associations between higher Mn exposure via drinking water and adverse cognitive or neurobehavioral outcomes (Iyare et al., 2019). In the European context, Mn is regulated as an indicator parameter in the Drinking Water Directive, with a parametric value of 50 µg/L, reinforcing the need for effective Mn control in water management strategies (Directive (EU) 2020/2184).

A wide range of Mn removal technologies has been developed, typically classified into chemical methods (neutralisation and oxidative precipitation), physicochemical approaches (adsorption, ion exchange, membrane processes), and biological and emerging electrochemical techniques. Nevertheless, the literature consistently highlights a key limitation: few technologies simultaneously achieve low residual Mn concentrations, low reagent and energy consumption, resilience to variable water matrices, and minimal secondary waste generation. This trade-off underpins the growing emphasis on integrated and hybrid treatment systems as more realistic and scalable solutions for industrial application (Bao et al., 2025).

The aim of this study is to provide a critical and sustainability-oriented overview of contemporary methods for manganese removal from wastewater, with particular focus on mining and metallurgical effluents. The paper evaluates removal mechanisms and controlling parameters, compares technology performance under realistic water matrices, and proposes practical criteria for process selection and integration in the context of increasingly stringent environmental and resource-efficiency requirements.

This review is based on a structured literature survey conducted using major scientific databases, including Scopus, Web of Science, and ScienceDirect. The search strategy combined keywords related to manganese occurrence and removal in industrial water, such as “manganese removal”, “Mn(II) oxidation”, “mine drainage”, “acid mine drainage (AMD)”, “metallurgical wastewater”, “adsorption”, “membrane processes”, “biological treatment”, and “electrochemical treatment”. Boolean operators (AND/OR), truncation and phrase searching were used to refine results, while backward and forward citation tracking was applied to key papers to capture additional relevant studies (Patil et al., 2016; Bao et al., 2025).

The primary time window considered spans from 2016 to 2026, to capture recent technological developments and emerging trends, while selectively including earlier seminal studies where needed for mechanistic understanding (e.g. Mn(II) oxidation kinetics and catalytic effects). Inclusion criteria comprised peer-reviewed journal articles reporting quantitative performance data (e.g. removal efficiency, residual Mn

concentrations, or adsorption capacities), clearly defined operational conditions (e.g. pH, oxidant dose, current density, pressure, contact time), and applicability to realistic or representative water matrices (e.g. mine drainage, metallurgical effluents, industrial wastewater). Studies using purely synthetic solutions were included primarily when they provided mechanistic insights and/or parametric data useful for process comparison (Patil et al., 2017).

Exclusion criteria included non-peer-reviewed sources, studies lacking quantitative evaluation of Mn removal, and works not directly related to aqueous systems. The selected literature was analysed comparatively, with emphasis on dominant removal mechanisms, operational constraints, secondary waste generation (sludge or concentrate), and practicality for mining and metallurgical settings.

Manganese in mining and metallurgical wastewater

Manganese is widely encountered in mining and metallurgical wastewater due to its natural abundance in ore deposits and its mobilisation during extraction, beneficiation, and metallurgical processing. In mine drainage, Mn frequently appears alongside Fe, Al and sulphate, yet tends to persist longer during treatment because it is less readily removed by simple neutralisation compared with Fe/Al (Neculita & Rosa, 2019). Reported Mn concentrations in mining-impacted water commonly range from a few mg/L to tens of mg/L, and can be higher at specific sites. For example, an AMD stream used for staged recovery contained 41.8 mg/L Mn (with co-occurring metals) (Shekarian et al., 2022), while a pilot mine-drainage bioreactor study treated influent containing ~20 mg/L Mn(II) together with ~6 mg/L Zn(II) (Watanabe et al., 2024). Such co-contamination is important because competing ions and matrix composition influence both Mn speciation and removal performance.

In aqueous systems, manganese predominantly occurs as dissolved Mn(II) under reducing to mildly oxidising conditions. Higher oxidation states (Mn(III)/Mn(IV)) form sparingly soluble oxides/oxyhydroxides, but their formation is often kinetically limited under circumneutral conditions unless catalysed by existing MnO_x surfaces, reactive media, or microbial activity (Watanabe et al., 2024). Consequently, pH and redox potential (Eh) are key control variables: Mn(II) oxidation becomes more favourable with increasing pH, yet may remain slow without catalytic pathways. This is reflected in the operational reality that purely aeration-based or passive oxidation approaches may deliver incomplete Mn removal unless pH/alkalinity and catalytic surfaces are favourable (Neculita & Rosa, 2019; Lafont et al., 2026).

Complexation with inorganic ligands (e.g., carbonate, sulphate) and competition with major cations (Ca²⁺, Mg²⁺) and transition metals can further shift Mn speciation and influence its reactivity and treatability. These interactions help explain why Mn can remain in solution after Fe removal and why Mn compliance often becomes the limiting step in mine water treatment systems (Neculita & Rosa, 2019; Bao et al., 2025). Table 1 summarises well-known technologies into chemical, physicochemical, membrane-based, and biological/electrochemical categories to support a structured comparison and a decision-oriented synthesis (Bao et al., 2025).

Chemical methods (neutralisation/precipitation and oxidative precipitation)

Chemical treatment remains the backbone of manganese removal in many mining and metallurgical applications because it is relatively robust, scalable, and compatible with existing infrastructure. Conventional neutralisation typically targets hydroxide precipitation, but Mn(II) requires higher alkalinity than

Fe/Al to reach low dissolved concentrations. In AMD systems, Mn precipitation during “classical” hydroxide neutralisation often starts around pH ~9, while high Mn recovery may require pH ~10.5, which increases alkali consumption and sludge production (Shekarian et al., 2022). These requirements are a major reason why Mn removal is frequently staged (e.g. Fe/Al removal at lower pH followed by dedicated Mn removal at higher pH) (Bao et al., 2025).

Table 1. Comparative decision matrix for manganese removal technologies in mining and metallurgical wastewater

Technology group	Typical Mn range (mg/L)	Target role	Key advantages	Key limitations	Sensitivity to water matrix	Residuals / by-products	Typical application stage
Chemical precipitation (pH control)	>10-100+	Bulk removal	Simple, widely applied, cost-effective for high loads	Requires high pH for Mn, incomplete removal at low concentrations	Moderate-high (pH, alkalinity, competing ions)	Large sludge volumes	Primary treatment
Oxidative precipitation	5-100	Bulk + improved removal	Enhances Mn removal efficiency, relatively robust	Oxidant demand, kinetics can be slow without catalysts	High (Eh, pH, catalytic surfaces)	Metal-rich sludge	Primary / secondary
Adsorption	<10-50	Polishing / selective removal	High selectivity (material-dependent), flexible	Limited capacity, regeneration required	High (competing ions, ionic strength)	Spent sorbents / regeneration waste	Tertiary (polishing)
Ion exchange	<20	Polishing / selective removal	High efficiency at low concentrations	Fouling, sensitivity to competing ions, regeneration chemicals	Very high	Regeneration brine	Tertiary (polishing)
Coagulation–flocculation	Variable	Support / polishing	Improves solid–liquid separation, simple operation	Limited for dissolved Mn(II) without prior oxidation	Moderate	Chemical sludge	Secondary / polishing
Membrane processes (NF/RO)	<50 (feed-dependent)	Advanced removal / reuse	Very low residual concentrations, enables water reuse	Fouling, scaling, high energy demand	Very high	Concentrate stream	Advanced / reuse
Biological systems	<1-50	Sustainable removal	Low chemical input, potential for passive operation	Sensitive to environmental conditions, slower kinetics	High (pH, temperature, variability)	Biogenic solids	Passive / semi-passive
Electrochemical methods	1-100	Controlled removal	Reduced chemical addition, <i>in situ</i> oxidant generation	Energy demand, electrode stability, scale-up challenges	Moderate	Sludge / electrode wear products	Emerging / hybrid

Oxidative precipitation targets the conversion of soluble Mn(II) to insoluble Mn(III/IV) oxides using oxidants, such as oxygen (aeration), chlorine-based oxidants, permanganate, persulphate, or ozone. A key point is that, although Mn(II) oxidation can be thermodynamically favourable near neutral pH, reaction kinetics are often the true bottleneck, necessitating either longer contact times or catalytic surfaces/media to achieve practical rates (Neculita & Rosa, 2019; Bao et al., 2025). Within AMD contexts, oxidative precipitation has been reported to enable high Mn removal at milder pH. For instance, oxidative precipitation using permanganate has been reported to achieve ~99% Mn recovery at pH ~7 (as discussed in the context of AMD treatment and recovery) (Shekarian et al., 2022).

Oxidative precipitation can be leveraged not only for removal but for resource recovery. Shekarian et al. (2022) developed a chemical-free process using ozone oxidative precipitation, achieving >95% recovery of Co and Mn from AMD and producing a solid with ~54.6% Mn, highlighting the potential to couple treatment with value generation. Nevertheless, oxidant demand and performance remain strongly dependent on water matrix (alkalinity, organics, competing reductants), and practical design typically balances chemical consumption against residence time and downstream solids separation (Bao et al., 2025).

A persistent operational challenge across chemical approaches is the generation of Mn-bearing sludge (often mixed

with Fe/Al hydroxides/oxides). Sludge volumes, stability, and disposal options can dominate capital expenditure (CAPEX), operating expenditure (OPEX), and sustainability impacts, particularly where elevated pH operation is required for Mn (Neculita & Rosa, 2019; Bao et al., 2025). Accordingly, chemical methods are most advantageous for bulk removal at moderate-high Mn concentrations, often followed by polishing steps when very low residual Mn targets are required.

Physicochemical methods (adsorption, ion exchange, coagulation/flocculation)

Physicochemical methods are commonly applied as polishing steps or where selective removal at lower Mn concentrations is required. Adsorption performance depends on surface chemistry, available binding sites, and competition with co-ions. Recent studies show that material modification can substantially increase Mn uptake. For example, potassium permanganate-modified bamboo biochar achieved a Langmuir maximum adsorption capacity of 21.277 mg/g compared with 0.803 mg/g for the unmodified biochar (Wilamas et al., 2023).

In addition to chemically modified systems, biomass-derived adsorbents obtained from industrial residues have also demonstrated promising performance (removal efficiencies above 84.62%). For instance, raw walnut and cherry wood shavings and their corresponding biochars produced via pyrolysis exhibited Mn(II) adsorption capacities in the range of approximately 2.1–2.5 mg/g, with biochars showing improved performance due to increased surface area and porosity (Lavrova and Yavorov, 2026). While these capacities are lower than those reported for highly engineered or chemically modified sorbents, they are comparable to other low-cost lignocellulosic materials and offer advantages in terms of availability, sustainability, and process simplicity.

In complex real matrices, adsorption can remain effective but typically requires higher doses and longer contact times: pruning-derived biochar achieved a maximum Mn removal of 86.2% at pH 7, 0.2 g/L adsorbent dose, and 180 min contact time (Rabiee Abyaneh et al., 2024). Overall, these results support the use of adsorption primarily as a polishing or selective step, especially after upstream processes reduce competing loads.

Ion exchange (IX) can provide high selectivity under controlled conditions but is sensitive to competing cations typical of mine water ($\text{Ca}^{2+}/\text{Mg}^{2+}$). Quantitative resin performance data demonstrate both capacity and selectivity constraints. For example, Purolite S950 achieved Langmuir maximum loadings of ~37.9 – 41.5 mg/mL-resin for Mn^{2+} , with kinetics consistent with pseudo-second order behaviour and pore-diffusion control (Amengol et al., 2024). Such data are valuable for comparative assessment, but practical application must account for regeneration chemical demand and the handling of concentrated regenerant brines (Bao et al., 2025).

Coagulation/flocculation can assist Mn removal mainly when Mn is present in particulate/colloidal form or after partial oxidation generates MnO_x particles that can be aggregated and separated. In most mining/metallurgical cases, coagulation is not a stand-alone Mn(II) solution but a supporting step integrated with oxidation and solid-liquid separation (Patil et al., 2016; Bao et al., 2025). Overall, physicochemical methods are most effective when combined with upstream conditioning (pH/oxidation) and selected based on matrix composition,

regeneration strategy, and secondary waste management requirements.

Membrane-based processes (UF/NF/RO and hybrids)

Membrane technologies are increasingly considered where stringent discharge limits or water reuse goals justify higher costs and operational complexity. Ultrafiltration (UF) is generally ineffective for dissolved Mn(II) unless preceded by oxidation that converts Mn into filterable particulate forms, whereas nanofiltration (NF) and reverse osmosis (RO) can achieve high Mn rejection through size/charge exclusion (Patil et al., 2016; Bao et al., 2025).

Quantitative studies demonstrate the strong role of water chemistry in membrane performance. In a polyamide nanofiltration and ultrafiltration membrane (PA-NF/PA-UF) study using synthetic groundwater with 50 mg/L Mn, the best permeate quality for Mn was achieved at pH 9, reaching 0.4 mg/L Mn with PA-NF, while very poor performance was observed at acidic pH (e.g. 42.2 mg/L Mn in permeate at pH 3) (Norherdewati et al., 2017). The same work indicates Mn rejection increased from ~26% at pH 5 to >70% at pH 7 and >95% at pH 9, highlighting that pH-dependent speciation and membrane surface charge strongly influence Mn separation. A parametric nanofiltration study using a spiral-wound hydrophilised polyamide (HPA-400) nanofiltration membrane reported a maximum Mn rejection of 92.58% at 100 mg/L feed, 9 bar TMP, and 1.050 L/min feed flow (Patil et al., 2017).

Reverse osmosis (RO) can achieve very high Mn removal but shifts the challenge toward concentrate management and scaling control. For example, RO treatment of raw freshwater retained ~99% of Mn^{2+} (alongside Fe^{2+}), demonstrating high intrinsic rejection under controlled conditions (Livinalli et al., 2023). In mining/metallurgical matrices, however, fouling and scaling risks (sulphate, hardness, suspended solids) typically require robust pre-treatment and careful antiscalant/cleaning strategies, while the reject stream may require additional treatment or secure disposal (Bao et al., 2025). Consequently, membrane systems are most often implemented as part of hybrid systems rather than as stand-alone Mn solutions.

Biological and electrochemical approaches

Biological manganese removal leverages Mn-oxidising microorganisms that catalyse Mn(II) oxidation to insoluble MnO_x under suitable conditions. While traditionally applied in drinking water and passive systems, recent mine-relevant studies demonstrate strong performance when biogeochemical conditions are engineered appropriately. Watanabe et al. (2024) operated *in situ* continuous-flow bioreactors for mine drainage (influent ~20 mg/L Mn(II)) and achieved >98% Mn(II) removal at a hydraulic retention time of 0.5 days without organic substrate amendment, with biogenic Mn oxides accumulating on limestone carriers. Such results support the potential of semi-passive or biologically assisted systems for mine water, provided stability can be maintained across seasonal and influent variability.

Biological filtration evidence from related water treatment contexts also highlights the achievable low residual Mn under

favourable conditions. Biological granular activated carbon (GAC) filtration reduced Mn(II) from 400 µg/L to 10 µg/L after a ~20-day start-up period, outperforming sand filtration under unchlorinated conditions (Chen et al., 2023). Although this is not a mining matrix *per se*, it provides quantitative criteria for biologically mediated Mn removal and underscores sensitivity to disinfectants/oxidant residuals.

Electrochemical approaches, in particular electrocoagulation (EC), offer controlled *in situ* generation of coagulants and reactive species, potentially reducing chemical dosing and simplifying automation. Safwat et al. (2023) reported a maximum Mn removal of 96.5% after 60 min at initial pH 7 and current density 10 mA/cm² (with electrolyte support), while Mn removal in real wastewater reached 91.3% after 60 min, alongside substantial COD reduction. In another study, combining ultrasound with electrocoagulation achieved 89.0% Mn removal, though the authors highlight that cost and equipment considerations can limit scalability depending on configuration (Posavčić et al., 2022). The key barriers remain energy demand, electrode passivation, sludge handling, and scale-up reliability - yet EC is increasingly attractive as a flexible

polishing or hybrid component when conventional precipitation alone cannot meet discharge targets (Bao et al., 2025).

Comparative discussion and selection criteria

Selecting an appropriate Mn removal strategy requires multi-criteria evaluation that balances performance with matrix compatibility, cost, and sustainability (Figure 1). Across mining and metallurgical applications, literature consistently indicates that no single technology is universally optimal. Instead, performance is strongly shaped by influent chemistry (pH, alkalinity, sulphate, hardness), co-metals, and target residual Mn levels (Neculita & Rosa, 2019; Bao et al., 2025). For high Mn loads, chemical neutralisation/oxidation remains the most common bulk approach, but may require elevated pH (often ≥9) unless oxidants/catalysts are used (Shekarian et al., 2022). Where very low residual Mn is required, adsorption/ion exchange or membranes can serve as polishing steps, though at the cost of regeneration or concentrate management (Patil et al., 2017; Livinalli et al., 2023; Amengol et al., 2024).

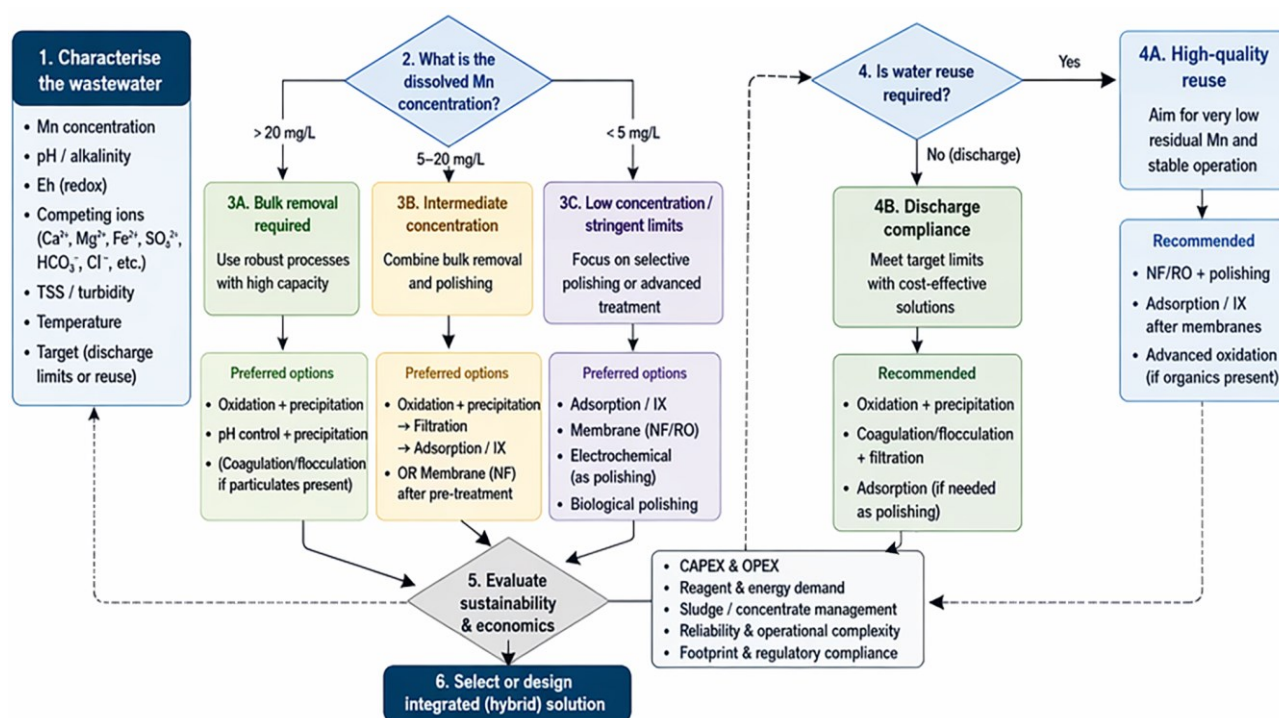


Fig. 1. Decision framework for selecting and integrating manganese removal technologies

Biological and electrochemical methods provide promising pathways to reduce chemical consumption or improve selectivity, but site-specific validation is essential. For mine drainage specifically, pilot evidence shows that biologically driven Mn oxidation can reach >98% removal under engineered conditions (Watanabe et al., 2024), while EC can deliver >90% removal within short reaction times (Safwat et al., 2023). Overall, integrated systems, consisting of bulk removal followed by targeted polishing, remain the most realistic configuration for consistent compliance under variable industrial conditions (Bao et al., 2025; Neculita & Rosa, 2019). However, the process selection should be driven by Mn concentration thresholds and matrix complexity rather than nominal removal efficiency alone.

Conclusions

Manganese removal from mining and metallurgical wastewater remains challenging due to Mn(II) persistence, kinetic limitations of oxidation near neutral pH, and strong sensitivity to water matrix composition. Chemical precipitation and oxidative precipitation are robust for bulk removal but often generate sludge and may require high pH unless oxidants/catalysts are used. Physicochemical and membrane methods can achieve deeper removal, but introduce regeneration or concentrate management constraints. Emerging biological and electrochemical approaches can reduce chemical inputs and deliver high efficiencies under controlled conditions, yet require

careful scale-up and stability assessment. Consequently, hybrid and decision-based treatment design remains the dominant direction for practical implementation.

Acknowledgements. This research is in performance of Project BG05SFPR001-3.004-0002-C02 “Development and improvement of professional and interdisciplinary education in technical and economic sciences and enhancement of the research capacity of the extractive industry through project-based doctoral studies” funded by Programme “Education”, co-funded by the European Union.

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