

Cyanide speciation as the determinant of treatment performance: A critical review of removal, destruction and recovery routes for cyanide-bearing wastewater

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ABSTRACT

Cyanide-containing wastewater is a multicomponent system: cyanide occurs as free cyanide, within weak acid dissociable (WAD) cyanide and stable metal-cyanide complexes, and alongside thiocyanate, metals, and other impurities. The chemical form of cyanide and the composition of the aqueous matrix govern treatment performance, which makes direct comparison between technologies difficult. This review covers physical and physicochemical, chemical, electrochemical, photochemical, and biological methods; for each group, it examines the process mechanism, the target cyanide species, the treatment conditions, the secondary streams generated, the scope for recovery, and the level of technological maturity. Removal, destruction, and recovery of cyanide are treated as distinct outcomes because an identical removal efficiency may conceal a fundamentally different final fate of the pollutant. No universal treatment technology exists, and data obtained on model solutions cannot always be transferred to real multicomponent effluents. For concentrated process streams, the feasibility of cyanide extraction and reuse should be assessed first; where recovery is not viable, destructive processes followed by deep polishing are applied. Further work requires testing on real wastewater, lower energy and reagent consumption, smaller volumes of secondary waste, scale-up of promising processes, and integrated schemes in which recovery, destruction, and polishing are matched to the characteristics of the specific stream.

Keywords: cyanide-containing wastewater, cyanide speciation, cyanide detoxification, cyanide recovery, adsorption, chemical oxidation, biological treatment, electrochemical treatment.

INTRODUCTION

Cyanide-containing wastewater is generated in gold and silver mining and processing, electroplating, metallurgy, as well as the coke-chemical and chemical industries (Vaca-Escobar et al., 2024; Kuyucak and Akcil, 2013). Gold mining is a major source of such effluents, since cyanidation is used to extract gold from ores and concentrates (Adams, 2016; Botz et al., 2016). The wastewater and recycled process water generated

are multicomponent: besides cyanides, they contain thiocyanates, non-ferrous and heavy metal compounds, flotation reagents, sulphides, and thiosulphates (Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024). Their composition depends on the feed material processed and on the flow-sheet applied (Adams, 2016; Botz et al., 2016).

Treatment of these waters is complicated by the diversity of cyanide species present (Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024). In industrial effluents, cyanide occurs as free cyanide

(CN⁻ and HCN), as weak acid dissociable metal-cyanide complexes (WAD cyanide) and as more stable metal complexes (Jaszczak et al., 2017; Botz et al., 2016). Thiocyanates and complexes of iron, zinc, nickel, and other metals may be present at the same time (Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024). Treatment performance is therefore assessed from the cyanide species present and the composition of the aqueous matrix rather than from total cyanide alone (Dong et al., 2021; Vaca-Escobar et al., 2024).

Physical and physicochemical, chemical, electrochemical, photochemical, and biological methods have been developed for the treatment of cyanide-containing wastewater. Among the chemical routes, alkaline chlorination, the SO₂/air (INCO) process, ozonation, and hydrogen peroxide oxidation are the best studied (Botz et al., 2016; Vaca-Escobar et al., 2024). These processes are rapid and supported by extensive operating experience, but they consume reagents, generate secondary products and destroy cyanide irreversibly (Botz et al., 2016; Vaca-Escobar et al., 2024).

Physical and physicochemical methods separate, concentrate and extract cyanide; they include adsorption, ion exchange, membrane processes and recovery operations (Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024). Recovered cyanide can be returned to the process circuit (Botz et al., 2016). In exchange, concentrated secondary streams are produced that themselves require further treatment (Vaca-Escobar et al., 2024).

Biological methods exploit the ability of microorganisms and other biological systems to transform cyanide and associated compounds. They act on several pollutants simultaneously and reduce the demand for chemical reagents (Alvillo-Rivera et al., 2021; Berkinbayeva et al., 2025a). Their performance depends on the concentration and speciation of cyanide, temperature, wastewater composition, and the stability of operating conditions (Luque-Almagro et al., 2016).

Integrated schemes combining separation, recovery, destruction, and deep polishing are applied to complex multicomponent effluents. Sequential treatment addresses both cyanide and the associated pollutants, but it complicates the flowsheet and requires that each stage be justified (Dong et al., 2021; Vaca-Escobar et al., 2024).

Direct comparison of these technologies is difficult (Dong et al., 2021; Vaca-Escobar et al., 2024). Cyanide removal efficiency alone is an insufficient basis for selecting a method, since

the concentration in the aqueous phase decreases through separation, recovery, and destruction alike (Botz et al., 2016; Vaca-Escobar et al., 2024). The speciation and initial concentration of cyanide, the wastewater composition, the treatment conditions, reagent and energy consumption, secondary waste, the scope for recovering valuable components, and the industrial maturity of the technology all have to be taken into account (Dong et al., 2021; Vaca-Escobar et al., 2024).

This review critically examined physical and physicochemical, chemical, electrochemical, photochemical, and biological technologies for the treatment of cyanide-containing wastewater. It addressed the relationship between cyanide speciation and treatment outcome, the correspondence between laboratory data and industrial applicability, and the advantages and limitations of each group of methods. On this basis, selection criteria that account for wastewater composition, the scope for recovering valuable components, and process maturity, together with the current limitations and the directions for further work were formulated.

To move beyond a descriptive inventory, the evidence was compared using a common framework: (i) wastewater type and cyanide fraction measured; (ii) initial and final concentrations; (iii) removal mechanism and final cyanide fate; (iv) contact time, reagent demand and energy input; (v) transformation products and secondary residues; (vi) scale and technological readiness; and (vii) the extent to which cost and environmental burdens were quantified. Only the studies reporting an initial cyanide concentration were retained in the quantitative comparison. Where a study did not report a resource or waste metric, this was stated explicitly, rather than inferred. This framework was used below to distinguish high analytical removal from complete detoxification and from industrial readiness.

CHEMICAL FORMS OF CYANIDE AND WASTEWATER CHARACTERISTICS

The composition of cyanide-containing wastewater depends on the source of its generation, on the features of the technological process, and on the associated inorganic and organic components. Cyanides are used or formed in the cyanide leaching of precious metals, in electroplating, in the coke-chemical industry, and in organic synthesis (Kuyucak and Akcil, 2013; Vaca-Escobar

et al., 2024). The problem is most acute at plants processing gold-bearing feed: their recycled and waste waters contain, in addition to cyanides, non-ferrous metal ions, flotation reagents, sulphides, thiosulphates, and other impurities. The content of individual components is governed by the flowsheet applied, the mineralogy of the feed processed, and the water-circuit arrangement of the plant (Adams, 2016; Botz et al., 2016).

Cyanide is present in these waters in several chemical forms. In the literature on the treatment of gold-plant effluents, cyanide compounds are classified according to the stability of the complexes they form. The first group comprises free cyanides, chiefly CN^- and HCN . The second comprises weak acid dissociable (WAD) cyanides, in particular the complexes of zinc, cadmium, nickel, copper, and silver. The third comprises more stable complexes that dissociate only under severe conditions, namely the complexes of iron, cobalt, gold, and mercury (Jaszczak et al., 2017; Vaca-Escobar et al., 2024). Therefore, total cyanide aggregates the compounds that differ sharply in chemical stability and in amenability to treatment (Vaca-Escobar et al., 2024).

The ratio between molecular HCN and the cyanide ion CN^- is governed by the acid-base conditions of the medium. A decrease in pH promotes the formation of volatile hydrogen cyanide, whereas the ionic form predominates in alkaline media, which is why many chemical detoxification processes are operated at controlled alkaline pH (Botz et al., 2016; Vaca-Escobar et al., 2024). In real tailings water from the Muteh gold processing plant, complete cyanide removal was obtained at pH 12.3 and elevated temperature, and cyanate was the principal oxidation product (Khodadad et al., 2008). The pH thus determines both the form in which cyanide exists as well as the safety and efficiency of the technologies used to destroy it.

A further complication arises from the complexes that cyanide forms with metals. The effluents from gold recovery plants contain cyanide complexes of iron, zinc, nickel, and other metals, while part of the cyanide is present as the simple salts NaCN , KCN , and $\text{Ca}(\text{CN})_2$. The interaction of soluble cyanides with components of the liquid and solid phases yields both soluble and sparingly soluble complex compounds (Jaszczak et al., 2017; Vaca-Escobar et al., 2024). The cyanide species present and their concentrations depend on the mineralogy of the ore, the ionic composition of the water, and the cyanide

concentration in the process solutions (Adams, 2016; Botz et al., 2016). Direct comparison of methods is difficult as a result, particularly where some studies determine free cyanide and others WAD or total cyanide (Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024).

Besides cyanides themselves, related compounds are present in process solutions. The most important is thiocyanate (SCN^-), which forms through the interaction of cyanide with sulphur-bearing compounds and sulphide minerals such as pyrrhotite, pyrite, chalcopyrite, and arsenopyrite (Adams, 2016; Botz et al., 2016). Thiocyanate is less toxic than cyanide, but it is taken into account in treatment design because its chemical and process behaviour differ. Some chemical and biological processes act on cyanide and thiocyanate simultaneously (Luque-Almagro et al., 2016; Vaca-Escobar et al., 2024).

Cyanate (CNO^-) is an intermediate or final product of several chemical cyanide destruction processes. Under oxidative treatment, CN^- is converted to cyanate, which then undergoes further transformation (Botz et al., 2016; Vaca-Escobar et al., 2024). Assessing a technology solely by the disappearance of the initial CN^- therefore, does not describe the environmental outcome in full: the transformation products formed and the need for their removal or further oxidation must also be considered (Vaca-Escobar et al., 2024).

The composition of real industrial effluents is further complicated by heavy and non-ferrous metals, so treatment is rarely confined to the removal of cyanide alone (Pérez-Cid et al., 2020; Goyburo-Chávez et al., 2024). Processes acting simultaneously on cyanide, thiocyanate, arsenic and other components have been developed for such streams. The schemes combining the SO_2/air (INCO) process with subsequent ozonation have been proposed, in which the bulk of the cyanide is removed in the first stage while ozone lowers the residual cyanide concentration, destroys thiocyanate and other reduced compounds as well as removes arsenic and heavy metals (Li and Jiang, 2014). Different treatment mechanisms thus operate in sequence, addressing several pollutants of a complex industrial stream.

The initial pollutant concentration also influences the choice of method. For relatively concentrated cyanide-containing process solutions, both destruction and recovery of cyanide are considered (Kuyucak and Akcil, 2013; Botz et al., 2016). Recovery methods include ion exchange,

electrodialysis, reverse osmosis, and the acidification-volatilisation-reneutralisation (AVR) process (Kuyucak and Akcil, 2013; Botz et al., 2016). For highly concentrated solutions, AVR is already applied in practice: the HCN released on acidification is stripped, absorbed in an alkaline solution, and the NaCN obtained is returned to the cyanidation circuit (Botz et al., 2016). For the deep polishing of less concentrated streams, adsorption, membrane or biological processes become more relevant (Vaca-Escobar et al., 2024).

A cyanide-containing effluent cannot be regarded as a single-component system containing only CN^- . The chemical form of cyanide, its concentration, metal-cyanide complexes, thiocyanate, cyanate, heavy metals, and other constituents together form a matrix that directly determines the applicability of a treatment technology (Dong et al., 2021; Vaca-Escobar et al., 2024). A method is therefore selected on the basis of the characteristics of the raw effluent, the cyanide species determined, the final transformation products and the need to remove associated pollutants, rather than on a single reported cyanide removal efficiency (Dong et al., 2021; Vaca-Escobar et al., 2024). The principal cyanide forms and related compounds encountered in such wastewaters are summarised in Table 1.

PHYSICAL AND PHYSICOCHEMICAL METHODS

Unlike chemical and biological processes, which convert cyanide into less toxic compounds,

physical and physicochemical methods operate through phase separation, sorption, concentration, or extraction of the pollutants. This group includes adsorption, ion exchange, membrane technologies such as reverse osmosis, and cyanide recovery processes (Kuyucak and Akcil, 2013; Botz et al., 2016). Such an approach lowers the cyanide concentration in the water treated and, in some cases, allows cyanide to be recovered and reused. In physical separation, however, the pollutant is not destroyed: it is transferred to a concentrate, a sorbent, or another phase, which subsequently requires regeneration or further detoxification (Botz et al., 2016; Vaca-Escobar et al., 2024).

Adsorption is the most widely used of the physicochemical approaches: cyanide compounds are concentrated on the surface of a solid material through physical or chemical interactions. Activated carbons, natural and modified zeolites, mineral and other carbon-bearing materials, and biosorbents have all been investigated as sorbents (Iakovleva et al., 2018; Mondal et al., 2019). Activated carbon stands out for its high specific surface area and its ability to combine sorption with catalytic mechanisms. Adsorption performance depends on the cyanide species, pH, temperature, sorbent dose and characteristics, contact time, and the composition of the aqueous matrix (Iakovleva et al., 2018; Vaca-Escobar et al., 2024).

The role of activated carbon is not limited to the physical retention of the pollutant. Under certain conditions, catalytic transformation of cyanide proceeds on its surface, and modification of the carbon surface alters the affinity of

Table 1. Main cyanide forms and related compounds in cyanide-containing wastewater

Form/ compound	Principal examples	Characteristics	Significance for treatment	References
Free cyanide	CN^- , HCN	The form most readily available for chemical transformation; the CN^-/HCN ratio depends on pH	Can be removed by chemical oxidation and by biological and other methods; strict pH control is required	Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024
WAD cyanides	Complexes of Zn, Cd, Ni, Cu, Ag	Relatively less stable metal-cyanide complexes	Dissociation of the complexes must be taken into account; performance depends on the metal and on process conditions	Botz et al., 2016; Kuyucak and Akcil, 2013
Stable metal- cyanide complexes	Complexes of Fe, Co, Au, and others	Higher chemical stability	Can be considerably more difficult to destroy; should be considered separately from free CN^- when technologies are compared	Jaszczak et al., 2017; Vaca-Escobar et al., 2024
Thiocyanate	SCN^-	Formed, in particular, through the interaction of cyanide with sulphur-bearing compounds and sulphide minerals	Can be removed by chlorine or ozone oxidation and by biological treatment	Luque-Almagro et al., 2016; Vaca-Escobar et al., 2024
Cyanate	CNO^-	May be formed on oxidation of CN^-	Must be considered as a cyanide transformation product, together with the scope for its further removal or conversion	Botz et al., 2016; Vaca-Escobar et al., 2024

the material for different cyanide species and the mechanism of their removal (Botz et al., 2016; Vaca-Escobar et al., 2024). Carbon materials are therefore used both as stand-alone sorbents and as components of more complex systems in which separation is combined with chemical or electrochemical stages (Botz et al., 2016).

Adsorption is technologically simple, but its limitations are considerable. The sorption capacity of the material is finite, so it has to be regenerated or replaced periodically. Regeneration produces a concentrated secondary stream, and where regeneration is not feasible, the spent sorbent requires safe handling. Adsorption performance also depends on the wastewater composition, pH, cyanide speciation, competing ions, and the surface characteristics of the material (Iakovleva et al., 2018). High laboratory performance of novel sorbents must therefore be assessed together with regenerability, material stability, and the scope for scale-up (Vaca-Escobar et al., 2024).

In ion exchange, dissolved ionic forms of the pollutants interact with the functional groups of an ion-exchange material. The material can be regenerated, which makes the process attractive for recovering cyanide compounds from certain process solutions. The main obstacles are competing ions, fouling of the ion-exchange material and the need to treat the regeneration solutions (Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024). In the literature on the treatment of cyanide-containing recycled and waste waters, ion exchange is considered alongside electrodialysis, reverse osmosis and the AVR process as one of the approaches to cyanide separation and recovery (Botz et al., 2016).

Membrane technologies separate the components of wastewater selectively, yielding a treated stream and a concentrate that retains the pollutants. They include reverse osmosis and other membrane processes. They provide deep water purification without the addition of large quantities of chemical oxidants. Membrane separation itself, however, does not destroy cyanide and generates a concentrated stream that requires further handling. Membrane fouling, the need for feed pretreatment and operating costs are further constraints (Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024).

Membrane processes have also been verified on real industrial effluents. In a pilot study, reverse osmosis was applied on-site to treat the effluent of a gold cyanidation process. The system removed 99.79% of total cyanide and 98.17% of total arsenic, with the initial total cyanide concentration

in the membrane feed varying over the wide range of 110–1620 mg/L (Goyburo-Chávez et al., 2024). The significance of these data lies in their having been obtained during pilot operation on a real multicomponent effluent. The high cyanide removal from the permeate, however, characterises the efficiency of separation, rather than chemical destruction of the pollutant: the composition and subsequent fate of the concentrate generated remain open questions.

Membrane and other physicochemical processes serve both as stand-alone methods and as stages of multistage treatment. Preliminary removal of suspended and interfering components reduces the load on the membrane system, while subsequent chemical, sorption, or other treatment polishes the streams obtained. This matters all the more for complex industrial effluents, in which a single process rarely removes all the pollutants present (Dong et al., 2021; Vaca-Escobar et al., 2024).

A separate line of development is the recovery of cyanide rather than its destruction. This is significant for gold mining, where residual cyanide in process solutions is simultaneously a hazardous pollutant and a process reagent that, upon complete oxidative destruction, loses irreversibly. Extraction and recovery technologies developed for such streams include ion exchange, electrodialysis, membrane separation, and the acidification-volatilisation-reneutralisation (AVR) process (Kuyucak and Akcil, 2013; Botz et al., 2016).

The AVR process converts cyanide to HCN by acidification, after which the hydrogen cyanide is separated and absorbed in an alkaline solution. The cyanide obtained is returned to the process circuit, and in this respect AVR differs fundamentally from oxidative destruction (Kuyucak and Akcil, 2013; Botz et al., 2016). Handling HCN imposes stringent requirements on equipment integrity, process control, and safety.

The mechanisms of physical and physicochemical technologies differ: surface sorption, membrane separation, concentration, and cyanide recovery. Their common advantage is the extraction of the pollutant without obligatory chemical destruction, which matters in closed process circuits (Botz et al., 2016; Dong et al., 2021). Concentrates, loaded sorbents, and regeneration solutions mean, at the same time, that a high cyanide removal from the aqueous phase is not equivalent to its ultimate detoxification. Assessment of such processes therefore requires removal, extraction,

concentration, recovery, and destruction of cyanide to be distinguished (Vaca-Escobar et al., 2024).

More broadly, the recovery of associated metals can improve the resource efficiency of waste-management systems. Microwave-assisted pretreatment followed by acid leaching has, for example, been investigated to enhance zinc recovery from mineral residues (Kenzhaliyev et al., 2025). Although this approach does not constitute cyanide treatment, it illustrates the potential integration of wastewater detoxification with the recovery of valuable components from associated solid residues.

In practice, physical and physicochemical methods operate as part of an overall strategy for managing cyanide-containing streams. The choice between adsorption, membrane separation, ion exchange, and recovery is determined by the concentration and speciation of cyanide, the associated pollutants, the treatment depth required, and the scope for returning the reagent to the process (Kuyucak and Akcil, 2013; Botz et al., 2016). Comparison of technologies also takes into account the composition of the real effluent, the stability of the cyanide complexes, the secondary streams generated, and the technological maturity of the process (Dong et al., 2021; Vaca-Escobar et al., 2024).

CHEMICAL METHODS

Chemical methods of detoxifying cyanide-containing wastewater are the most extensively studied and the most widely applied. In contrast, physical processes separate, concentrate or extract the pollutant, chemical treatment converts cyanide into less toxic compounds or binds it into sparingly soluble or stable species. Depending on the reagent and the conditions, this may involve oxidation of free cyanide and metal-cyanide complexes, conversion of cyanide to cyanate with subsequent decomposition, precipitation or complexation. Among the destructive technologies, oxidation with active-chlorine reagents, the SO_2/air (INCO) process, ozonation and hydrogen peroxide treatment are the best studied and the most widely practised (Botz et al., 2016; Vaca-Escobar et al., 2024).

Alkaline chlorination is one of the traditional methods, using chlorine-bearing reagents including sodium and calcium hypochlorite as oxidants. An alkaline medium is maintained to prevent the release of HCN and to direct the oxidation of cyanide. The reaction of CN^- with hypochlorite forms

cyanogen chloride (CNCl) as an intermediate, which converts rapidly to cyanate, CNO^- , in alkaline media; an excess of oxidant ensures the further transformation of cyanate (Botz et al., 2016; Vaca-Escobar et al., 2024). Hence, the requirement for strict pH control in alkaline chlorination.

In laboratory experiments with real wastewater from the Muteh gold mine containing about 270 mg/L cyanide, NaOCl and $\text{Ca}(\text{OCl})_2$ were investigated at pH 6–13 and 25–50 °C. At pH 12.3 and elevated temperature, the cyanide determined was removed completely, and cyanate was the principal oxidation product (Khodadad et al., 2008).

The performance of hypochlorites has also been assessed by modelling cyanide oxidation in tailings-pond water from the Muteh gold mine using PHREEQC. At 12 °C and pH 12–13, increasing the $\text{Ca}(\text{OCl})_2$ concentration from 0.71 to 1.43 g/L raised the calculated cyanide removal from 97.01% to 99.20%, whereas increasing NaOCl from 1.72 to 5.18 g/L raised it only from 95.46% to 95.90% (Tavasoli et al., 2019). Removal efficiency can thus be interpreted only together with the reagent dose and the treatment conditions.

Alkaline chlorination is simple and rapid, but the use of active chlorine carries substantial limitations. The intermediate formation of toxic CNCl requires alkaline conditions, under which it converts rapidly to CNO^- . Chlorine-bearing oxidants are also consumed by associated components, including thiocyanate and sulphides, which increases reagent demand and complicates process control (Botz et al., 2016; Vaca-Escobar et al., 2024). Alkaline chlorination should therefore be evaluated in terms of cyanide removal together with active-chlorine consumption, pH and the final composition of the treated water.

Hydrogen peroxide is the second widely used oxidant and an alternative to chlorine-bearing reagents. No active chlorine is introduced into the water, but process performance depends on the cyanide species, the oxidant dose, pH, catalysts and the wastewater composition (Kuyucak and Akcil, 2013; Vaca-Escobar et al., 2024). Catalytic oxidation of cyanide by H_2O_2 , in particular in the presence of copper compounds, accelerates the process, although part of the oxidant is consumed in side reactions in a real multicomponent matrix (Amaouche et al., 2019; Vaca-Escobar et al., 2024). The search for alternative oxidants continues: the use of sodium percarbonate for cyanide detoxification in gold mine tailings has been investigated, for example (Berkinbayeva et

al., 2025b). The SO_2/air process, known as INCO, has achieved wide industrial application. It employs SO_2 , air, lime, and copper compounds as a catalyst; free cyanide and a number of metal-cyanide complexes undergo oxidative treatment, and the final detoxification outcome depends on the process conditions and on the stability of the particular cyanide species (Botz et al., 2016; Vaca-Escobar et al., 2024).

The principal advantage of INCO is its accumulated industrial experience, which many newer methods lack, their performance having been demonstrated largely at laboratory scale. Comparative assessment of a technology, therefore, considers not only cyanide removal but also process maturity, operating requirements, reagent consumption, and the secondary products generated (Botz et al., 2016; Vaca-Escobar et al., 2024).

Ozonation is a further route for the oxidative destruction of cyanide. Ozone oxidises free cyanide and a number of metal-cyanide complexes to cyanate, although the stability of individual complexes appreciably limits performance. The reaction rate and the subsequent transformation of CNO^- depend on pH, solution composition, and mass-transfer conditions (Botz et al., 2016; Vaca-Escobar et al., 2024).

In comparing ozone with chlorine-bearing oxidants, cyanide removal is considered together with the secondary products formed, oxidant consumption, and equipment requirements. Ozone is generated on-site and introduced into the liquid

phase, so performance depends on gas-liquid mass transfer. In return, no chlorine-bearing oxidant enters the water treated (Botz et al., 2016; Vaca-Escobar et al., 2024).

The combined use of O_3 and H_2O_2 belongs to advanced oxidation. The performance of this combination depends strongly on the composition of the water treated, since the constituents of a real industrial effluent affect the consumption of oxidants and of reactive species. The results obtained on model solutions must therefore be transferred to real multicomponent waters with caution (Dong et al., 2021; Vaca-Escobar et al., 2024).

The development of oxidative technologies has led to advanced oxidation processes (AOPs), in which highly reactive species are generated: $\text{O}_3/\text{H}_2\text{O}_2$ systems, catalytic ozonation, UV-activated oxidants, and others. These achieve deeper destruction of components that are difficult to oxidise. An $\text{MgO}/\text{O}_3/\text{persulphate}$ catalytic system was tested on real industrial cyanide-containing water with an initial cyanide concentration of 173 mg/L, and cyanide was oxidised completely under optimised conditions (Behnami et al., 2021). Another example of intensification is the combination of ozonation with electrocoagulation in the treatment of real metallurgical wastewater (Das et al., 2021). Assessment of AOPs and hybrid oxidative processes must address oxidant and energy consumption, catalyst properties, intermediate products, and the scope for scale-up simultaneously (Vaca-Escobar et al.,

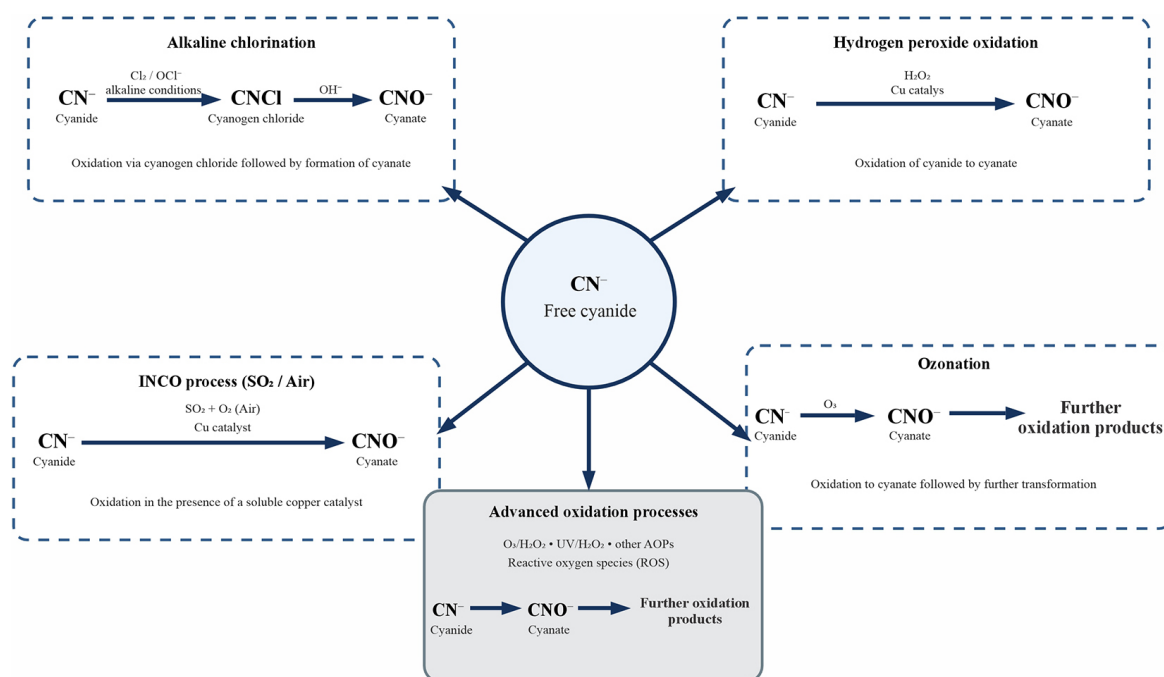


Figure 1. Main pathways of chemical transformation of cyanide during wastewater treatment

2024). The main pathways of chemical cyanide transformation during wastewater treatment are shown in Figure 1.

Chemical detoxification of cyanide-containing effluents is not limited to oxidation. Pollutants are bound and precipitated using iron and copper compounds and other reagents, an approach suited to complex wastewaters containing cyanide complexes and metals together (Dong et al., 2021; Vaca-Escobar et al., 2024).

Precipitation is also applied to the removal of stable cyanide complexes. The outcome here is determined by the form of the metal-cyanide complex, the precipitating reagent, pH, and the associated components. A solid phase is formed that has to be separated and disposed of safely (Dong et al., 2021; Vaca-Escobar et al., 2024).

Chemical methods act comparatively rapidly, handle concentrated cyanide-containing streams and, in part, have undergone long industrial validation. The process is controllable and the cyanide concentration falls quickly. In exchange, oxidants have to be consumed, pH and redox conditions controlled, and intermediate and secondary products and sludges managed. Destructive chemical methods also lose cyanide irreversibly as a process reagent, and in this respect, they differ fundamentally from extraction and recovery processes (Botz et al., 2016; Vaca-Escobar et al., 2024).

A chemical technology cannot be selected on the basis of maximum cyanide removal alone. Sound comparison requires the initial and final concentrations, the cyanide species determined, reagent consumption, pH, treatment duration, the presence of thiocyanate and metal-cyanide complexes, the secondary products and sludges formed, energy consumption, and the degree of industrial validation (Dong et al., 2021; Vaca-Escobar et al., 2024). For concentrated process solutions, chemical destruction should be weighed against prior extraction and recovery of cyanide (Kuyucak and Akcil, 2013; Botz et al., 2016).

BIOLOGICAL METHODS

Biological methods exploit the ability of microorganisms and other biological systems to transform cyanide and associated compounds. Physical processes separate or concentrate the pollutant, whereas biological treatment converts it into less hazardous products. This approach is particularly well suited to multicomponent

mining effluents, since biological systems remove not only cyanide but also cyanate, thiocyanate, nitrogen compounds, and certain metals (Alvillo-Rivera et al., 2021; Berkinbayeva et al., 2025a).

Biological treatment relies on the ability of certain microorganisms to use cyanide, or its transformation products, in their metabolism. Bacteria, fungi, microalgae, and microbial consortia have been studied for cyanide biodegradation, and they differ in transformation mechanism and in tolerance to environmental conditions (Anning et al., 2020; Alvillo-Rivera et al., 2021). Among bacteria, members of the genus *Pseudomonas* and other cyanide-degrading microorganisms isolated from contaminated environments have been studied most frequently (Razanamahandry et al., 2016; Luque-Almagro et al., 2016).

The performance of a biological process is determined both by the microbial species and by the environmental conditions. The concentration and speciation of cyanide, temperature, pH, the sources of carbon and nutrients, dissolved oxygen, and toxic associated components all affect biomass activity (Luque-Almagro et al., 2016; Alvillo-Rivera et al., 2021). Biodegradation depends appreciably on pH, the initial cyanide concentration, and the cultivation conditions of the microorganisms (Jiang et al., 2022; Alvarado-López et al., 2023).

Biological systems can act on several compounds simultaneously. Under aerobic conditions, microbial communities transform thiocyanate, and specialised systems are adapted to multicomponent cyanide-containing streams (Mekuto et al., 2016; Alvillo-Rivera et al., 2021). This is a substantial advantage for such wastewaters, since thiocyanate and metal-cyanide compounds accompany free cyanide in mining process streams (Botz et al., 2016; Vaca-Escobar et al., 2024).

Beyond studies of individual microorganisms, bioreactor systems, microbial consortia and technologies based on immobilised biomass are being developed. Industrial applicability is constrained by process duration, the tolerance of the microorganisms to changes in loading and the ability to maintain the required conditions during continuous operation (Alvillo-Rivera et al., 2021; Kenzhaliyev et al., 2026).

In addition to bacteria, cyanide is removed by microalgae and by mixed phototrophic-bacterial systems in which biological transformation of the pollutants is combined with phototrophic processes. A recent example is a continuous stirred photobioreactor with an algal-bacterial

system investigated for the bioremediation of cyanide-containing water (AbdelMaged and El-Rakaiby, 2025).

Fungi represent a further option for biological treatment. Fungal microorganisms transform cyanide enzymatically and are considered alongside bacterial systems and microbial consortia. Practical application requires data on microbial tolerance, transformation kinetics, and performance in the treatment of real multicomponent effluents (Anning et al., 2020; Alvillo-Rivera et al., 2021).

Immobilisation of microorganisms and the formation of biofilms retain biomass within the reactor and yield more stable systems for continuous operation, particularly where the hydraulic loading and the composition of the incoming effluent fluctuate. Immobilisation and the establishment of robust microbial communities are regarded as means of improving the stability of biological processes (Mekuto et al., 2016).

A bioreactor must provide contact between the microorganisms and the pollutants, transfer of oxygen and nutrients, and retention of active biomass. In developing an industrial technology, the decisive step is the transition from batch laboratory experiments to continuous systems and to testing on real multicomponent wastewater (Alvillo-Rivera et al., 2021; Kenzhaliyev et al., 2026). Studies of natural biodegradation within gold mine tailings environments show that microbial processes need to be examined in real cyanide-containing matrices (Welman-Purchase et al., 2024).

Biological treatment also encompasses phytotechnologies based on higher aquatic plants and algae. Such systems remove residual concentrations of cyanide and other pollutants under comparatively mild conditions. The use of *Eichhornia crassipes* for cyanide removal has been confirmed by experimental studies of the phytotechnological treatment of aquatic systems (Singh and Balomajumder, 2021).

Biodegradation and biosorption need to be distinguished. In the former, the pollutant undergoes biochemical transformation; in the latter, it is bound by biological material and transferred from the aqueous phase onto the biosorbent. Biosorption is attractive for the availability of the biological feedstock and the mild treatment conditions, but industrial application requires data on sorption capacity, material regeneration, the secondary streams generated, and performance in continuous systems on real aqueous matrices (Anning et al., 2020; Vaca-Escobar et al., 2024).

The principal groups of biological systems used for the treatment of cyanide-containing waters, together with the key factors governing cyanide biodegradation, are summarised in Figure 2.

Biological methods require smaller quantities of strong chemical oxidants, act on several pollutants at once, and are suited to use as a deep polishing stage (Alvillo-Rivera et al., 2021). Under stable conditions, they deliver high treated-water quality, and recent work on biological detoxification confirms this for cyanide-containing mining

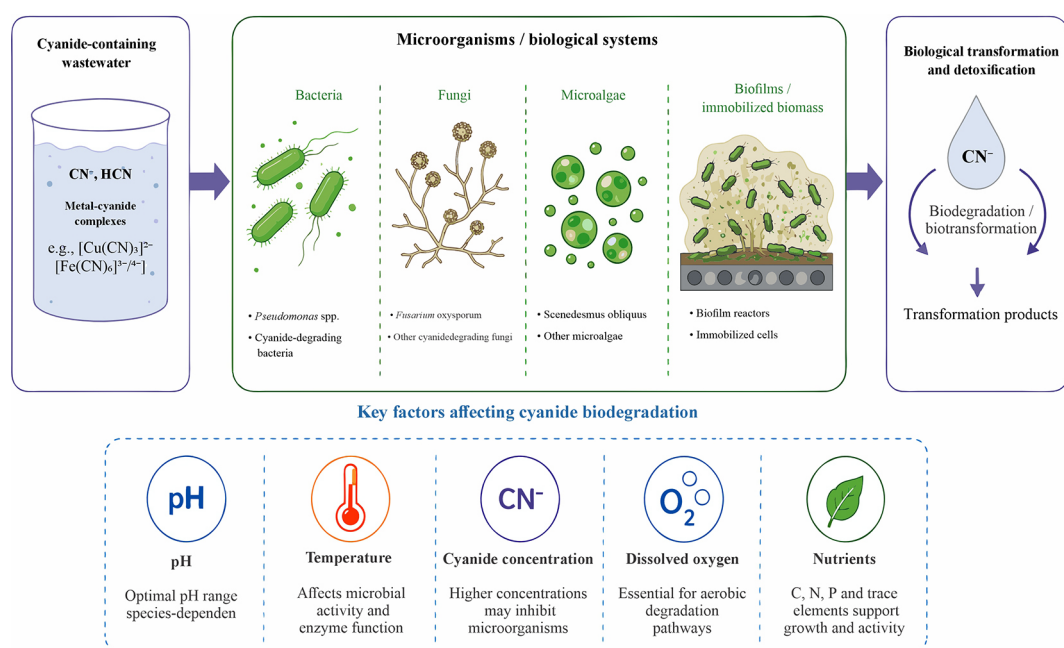


Figure 2. Biological approaches and key factors affecting cyanide biodegradation in wastewater

waters. Biological processes combine well with chemical and physicochemical ones: pretreatment relieves the toxic load on the biomass, while the biological stage removes the residual pollutants (Mekuto et al., 2016; Alvillo-Rivera et al., 2021).

The limitations of biological methods are also considerable. Their performance is sensitive to temperature, pH, the concentration and speciation of cyanide, the availability of nutrients and oxygen, and the presence of toxic associated components (Luque-Almagro et al., 2016; Alvillo-Rivera et al., 2021). High cyanide concentrations inhibit microbial activity: studies of bacterial systems show a pronounced dependence of biodegradation on the initial cyanide loading (Alvarado-López et al., 2023; Jiang et al., 2022). Treatment also takes longer than intensive chemical oxidation, which is taken into account when practical applicability is assessed (Alvillo-Rivera et al., 2021).

A separate difficulty is the gap between model solutions and real industrial effluents. A laboratory solution containing a single source of CN^- bears little resemblance to water from a gold mining plant containing metal-cyanide complexes, SCN^- , metals and other constituents (Welman-Purchase et al., 2024; Vaca-Escobar et al., 2024). A high degree of biodegradation obtained in a controlled model system is not necessarily reproduced in a multicomponent industrial matrix (Alvarado-López et al., 2023; Alvillo-Rivera et al., 2021). The prospects of a biological technology are therefore assessed with reference to the composition of the raw effluent, the cyanide species measured, the initial loading, the residence time, temperature, bioreactor configuration, and process stability under variable loading.

Biological treatment does not replace physical and chemical technologies; it constitutes a distinct group of processes with its own field of rational application. Its strength is the combined action on cyanide, thiocyanate, and related pollutants under comparatively mild conditions (Anning et al., 2020; Berkinbayeva et al., 2025a). Development is proceeding from individual laboratory cultures towards microbial consortia, immobilised biomass and continuous bioreactor systems (AbdelMageed and ElRakaiby, 2025). The most rational arrangement combines biological treatment with prior physicochemical or chemical reduction of a high pollutant load, leaving the biological stage to polish residual cyanide, thiocyanate and nitrogen compounds (Mekuto et al., 2016; Alvillo-Rivera et al., 2021).

ELECTROCHEMICAL AND PHOTOCHEMICAL METHODS

Electrochemical and photochemical methods form a distinct line of development. They use electrical energy, electrochemically generated active species, or radiant energy to destroy, oxidise or remove cyanide compounds. Their appeal lies in reduced direct consumption of certain chemical reagents, in the intensification of oxidation, and in the possibility of combining cyanide removal with the recovery of associated metals (Betancourt-Buitrago et al., 2019; Vaca-Escobar et al., 2024). Practical performance depends on the wastewater composition, solution conductivity, electrode material, and electrical parameters or, alternatively, on the characteristics of the radiation source and the catalyst.

Electrochemical oxidation proceeds through electron transfer at the electrode surfaces or through the reaction of cyanide with active oxidising species generated within the electrochemical system itself. In direct oxidation, the pollutant is converted at the anode surface; in indirect oxidation, intermediate oxidants are formed first and then react with cyanide in the bulk solution (Berenguer et al., 2017; Vaca-Escobar et al., 2024). The process rate is controlled through current density, potential, and other electrical parameters, but performance and energy consumption depend strongly on the conductivity and composition of the solution treated.

Electrochemical oxidation suits streams with sufficient conductivity and pollutant concentration. As the cyanide concentration and conductivity fall, ohmic losses and background electrochemical reactions become more important, and electrical energy is used less efficiently. Results obtained for concentrated model solutions cannot, therefore, be transferred to dilute multicomponent industrial effluents without assessing energy and matrix effects (Berenguer et al., 2017; Vaca-Escobar et al., 2024).

Electrochemical processes are suitable not only for cyanide destruction but also for the simultaneous recovery of metals. This is significant for electroplating and mining effluents, in which cyanide occurs together with Cu, Zn, and other metals. In the photoelectrocatalytic treatment of cyanide-containing water, 96.90% of total cyanide was removed with the simultaneous recovery of 99.76% of Cu and 90.56% of Zn over 4 h

at an applied voltage of 2.5 V (Wei et al., 2022). Assessment of an electrochemical technology, therefore, covers both the degree of cyanide destruction and the scope for returning valuable metallic components.

Electrocoagulation is the second electrochemical route. Dissolution of sacrificial electrodes generates coagulating species directly in the water treated, and the pollutants are bound and removed together. The outcome is governed by the electrode material, current density, interelectrode distance, pH, and the chemical composition of the water; a sludge that requires subsequent handling is also produced. In an optimisation study of the electrocoagulation treatment of a cyanide-containing effluent in an airlift reactor, 98.27% cyanide removal was reported at a current density of 68 A/m² and a treatment time of about 57.5 min (Zmirli et al., 2023).

Electrochemically intensified processes also include hybrid systems in which the electrical action is combined with chemical oxidants or mineral reagents. Here the electrochemical generation of active species, the chemical destruction of the pollutant and, in certain cases, metal recovery operate simultaneously. The integration of ozonation with electrocoagulation has been investigated, for example, for cyanide removal from real metallurgical wastewater (Das et al., 2021). In comparing hybrid processes, it is important to separate the contribution of the electrochemical stage itself from that of the additional reagents: a high removal efficiency cannot be attributed to the electrical action alone (Vaca-Escobar et al., 2024).

Photochemical methods destroy cyanide compounds using the energy of light, either directly or indirectly. In photocatalytic systems, a semiconductor material absorbs photons, electron-hole pairs are formed, and reactive species that oxidise the pollutant are then generated (Betancourt-Buitrago et al., 2019). Photochemical action is combined with H₂O₂, O₃, and other oxidants to give photo-assisted advanced oxidation processes.

Photochemical processes reduce the direct consumption of conventional oxidants and use radiant energy to intensify oxidation reactions. Practical performance depends on the light transmittance of the water, turbidity, the concentration of suspended solids, the intensity and spectrum of the radiation, the properties and stability of the photocatalyst, and the presence of constituents competing for reactive species (Betancourt-Buitrago et al., 2019; Vaca-Escobar et al., 2024).

For real effluents from gold mining operations, these limitations are particularly pronounced. Photocatalytic treatment of a real industrial matrix has nevertheless been demonstrated experimentally. A GO/TiO₂/ZSM-5 composite was applied to a real effluent from the Hexi gold mine with an initial total cyanide concentration of 71.56 mg/L: after preliminary adsorption and 3 h of photocatalytic treatment, 92.91% of total cyanide was removed, together with 82.53% of Cu and 100% of Zn (Pan et al., 2022a). This is stronger evidence than results obtained on transparent model solutions, although the study itself remains at a laboratory scale.

In another study, an Ag-modified coralloid titanosilicate (CTS-Ag) was investigated for the removal of free cyanide and Cu and Zn cyanide complexes from a real wastewater. Removals of 98.00% for cyanide, 99.41% for Cu, and 98.44% for Zn were achieved (Pan et al., 2022b). The photocatalytic system thus acts on both free CN⁻ and metal-cyanide complexes. Scalability, however, is constrained by the preparation and regeneration of the functional catalyst and by the provision of effective irradiation.

Ozone oxidation is also intensified by physical means. Ultrasonic enhancement of the ozonation of cyanide-containing wastewater improves mass transfer and cyanide oxidation (Zhang et al., 2022). Combining physical intensification with chemical oxidation is of interest, but its practical assessment must account for the additional energy consumption.

The destruction of stable metal-cyanide complexes is a separate task. Cyanide in industrial effluents occurs not only in the free form but also in complexes of differing stability, so removal efficiencies reported for free CN⁻, WAD cyanide, and total cyanide are not interchangeable (Jaszczak et al., 2017; Vaca-Escobar et al., 2024). Electrochemical and photochemical studies should state the cyanide species determined and consider the fate of the metal after the complex has been destroyed. A single figure for cyanide removal, without specification of the species analysed, leads to invalid comparison between technologies (Vaca-Escobar et al., 2024).

Electrochemical and photochemical processes integrate readily into combined systems. An electrochemical stage couples cyanide oxidation with metal recovery, while photochemical action is combined with an electric field or with additional oxidants. The work of Wei et al. (2022),

with simultaneous photoelectrocatalytic cyanide destruction and Cu and Zn recovery, exemplifies such a combination of functions. Other studies demonstrate the coupling of electrochemical processes with ozonation and of physical intensification methods with oxidative technologies (Das et al., 2021; Zhang et al., 2022). The more mechanisms that operate simultaneously, the harder it becomes to determine the contribution of each stage and the greater the need for a separate assessment of energy and material costs.

Energy consumption is the key criterion for assessing electrochemical technologies. Cyanide removal alone is insufficient for comparing studies: current density, voltage, treatment duration, solution conductivity, electrode material, and service life, and the need to add an electrolyte are all required. For photochemical processes, the power and spectrum of the radiation source, the treatment duration, the dose and stability of the photocatalyst, any additional oxidants, and the performance on a real aqueous matrix are considered in the same way (Betancourt-Buitrago et al., 2019; Vaca-Escobar et al., 2024).

Electrochemical and photochemical methods extend the capabilities of conventional cyanide-containing wastewater treatment: they destroy cyanide, recover associated metals, or intensify oxidation. The process is controllable, and several functions can be combined within a single technological system. They are constrained by energy consumption, dependence on water composition and conductivity, the condition of the electrodes or photocatalysts, and the shortage of large-scale operating data for a number of the newer processes (Betancourt-Buitrago et al., 2019; Vaca-Escobar et al., 2024). The prospects of these technologies will be established by the transition from laboratory experiments on model solutions to long-term pilot trials on real multicomponent industrial effluents.

COMPARATIVE ASSESSMENT AND TECHNOLOGY SELECTION

No universal method exists for the treatment of cyanide-containing wastewater. A process is selected according to the characteristics of the specific stream rather than the cyanide removal efficiency attainable. The principal criteria are the chemical form and initial concentration of cyanide, the presence of metal-cyanide complexes and thiocyanate, the content of associated metals,

the composition of the aqueous matrix, the treated-water quality required, reagent and energy consumption, the secondary waste generated, the scope for recovering valuable components and the industrial maturity of the technology (Dong et al., 2021; Vaca-Escobar et al., 2024).

In comparing methods, removal, destruction and recovery must be distinguished. A high cyanide removal from the aqueous phase does not imply chemical destruction. In membrane separation, adsorption and ion exchange, cyanide is concentrated in another phase: in a concentrate, a loaded sorbent or a regeneration solution (Botz et al., 2016; Vaca-Escobar et al., 2024). Chemical, electrochemical, and biological processes, by contrast, transform the original cyanide compounds. Identical cyanide removal values reported for different technologies therefore do not describe an identical final fate of the pollutant (Dong et al., 2021; Vaca-Escobar et al., 2024).

The absence of destruction is not necessarily a shortcoming. For the process solutions with a high residual cyanide content, concentration opens a route to extraction and return to the production circuit. Recovery approaches, including AVR, ion exchange, electrodialysis, and membrane separation, allow cyanide to be regarded not only as a pollutant but also as a recoverable process reagent (Kuyucak and Akcil, 2013; Botz et al., 2016). In selecting a strategy, the case for irreversible destruction is weighed against the possibility of prior extraction and reuse.

Sound comparison also requires knowledge of the chemical form of cyanide determined. Free cyanide, WAD cyanides, and more stable metal-cyanide complexes differ in reactivity and stability, so the same technology performs differently depending on the composition of the feed stream (Jaszczak et al., 2017; Vaca-Escobar et al., 2024). Thiocyanate, metals, suspended solids, and other constituents of industrial effluents also exert an influence. Comparison of studies that do not specify the cyanide species determined and the characteristics of the raw aqueous matrix leads to an incorrect assessment of technology performance (Dong et al., 2021; Vaca-Escobar et al., 2024).

A further criterion is the level of technological maturity. High performance in a batch laboratory experiment on a synthetic solution is not equivalent to demonstrated performance in the long-term treatment of a real industrial effluent. Alongside removal efficiency, the type of water investigated, the scale of the process, the duration of operation,

Table 2. Standardised comparison of representative cyanide-treatment studies reporting an initial cyanide concentration

Method	Wastewater and cyanide fraction	C ₀ , mg/L	Final concentration, mg/L; removal, %	Conditions, time and reported inputs	Mechanism, cyanide fate and secondary stream	Scale and readiness	Reference
Reverse osmosis	Real gold-cyanidation effluent; total CN	110–1620*	C _{final} ≈0.60 mg/L; 99.79%	On-site pilot RO; pressure, energy demand and operating cost NR	Separation, not destruction; cyanide retained in membrane concentrate; concentrate management NR	Pilot; real wastewater	Goyburo-Chávez et al. (2024)
Calcium alginate hydrogel adsorption	Real electroplating wastewater; free CN	51,190 ± 415	7667 ± 79 mg/L after two cycles; 85.02 ± 0.15%	Two 30-min cycles; CAB/wastewater ratios 1.5:1 then 1:1 (v/v); room temperature; 120 rpm; energy and cost NR	Separation by sorption; cyanide transferred to loaded hydrogel; regeneration/disposal not evaluated	Batch laboratory; real wastewater	Pérez-Cid et al. (2020)
NaOCl or Ca(OCl) ₂ oxidation	Real gold-mine tailings water; cyanide fraction not specified	270	C _{final} not quantified; complete removal reported	pH 6–13; 25–50 °C; complete removal at pH 12.3 and higher temperature; oxidant dose NR	Destruction; cyanide oxidised mainly to cyanate; chlorine-bearing intermediates require alkaline control	Batch laboratory; real wastewater	Khodadad et al. (2008)
MgO/O ₃ /persulphate	Real chromium-electroplating wastewater; cyanide	173	C _{final} not quantified; 100% oxidation within 70 min	pH 11; MgO-catalysed ozonation with persulphate; 70 min; reagent demand, energy and cost NR	Destruction; cyanate and ammonium formed first, followed by nitrate and bicarbonate; residual sulphate/persulphate require monitoring	Batch laboratory; real wastewater	Behnami et al. (2021)
Sodium percarbonate oxidation	Real gold-mine tailings liquor; free CN	443.2	0.05 mg/L; >99.99%	3.5 g/L percarbonate; pH 10; 20–25 °C; 300 rpm; 8 h; estimated operating cost US\$0.7–1.0/t tailings	Destruction by radical oxidation toward cyanate; carbonate accumulates and post-treatment neutralisation is required	Batch laboratory; pilot validation required	Berkinbayeva et al. (2026)
GO/TiO ₂ /ZSM-5 photocatalysis	Real gold-mining effluent; total CN	71.56	≈5.07 mg/L †; 92.91%	Pre-adsorption followed by UV irradiation for 3 h; catalyst dose, irradiation energy and cost NR	Combined adsorption and oxidation; Cu removal 82.53% and Zn removal 100%; catalyst recovery/reuse burden not quantified	Batch laboratory; real wastewater	Pan et al. (2022a)
Native bacterial consortium	Synthetic alkaline wastewater; free CN	120	≈2.4 mg/L †; 98%	pH >9.2; up to 15 d; nutrient, aeration and energy demand NR	Biological destruction; transformation products and excess-biomass management NR	Batch laboratory; synthetic matrix	Alvarado-López et al. (2023)
Algal–bacterial photobioreactor	Synthetic mixed wastewater; KCN in feed	200 mg/L KCN	Complete KCN removal reported; failure at 250 mg/L KCN	HRT 3.5 d; pH 7.5–8; room temperature; 150 rpm; 12/12 h light/dark; 5000–7000 lx; no added fertiliser at stable load	Biological destruction; KSCN was not removed; biomass formed and settled naturally	Continuous laboratory, 106 d; synthetic matrix	AbdelMageed and ElRakaiby (2025)

Note: * Range recorded in the membrane feed during pilot operation. † Calculated from the reported initial concentration and removal efficiency. CAB, calcium alginate hydrogel beads; HRT, hydraulic retention time; NR, not reported; RO, reverse osmosis. Values and limitations are reported without inference where the source did not provide a metric.

reagent and energy consumption, the secondary streams generated, and the operational complexity are all taken into account (Dong et al., 2021; Vaca-Escobar et al., 2024). This is how technologically mature processes are distinguished from promising methods whose performance has so far been demonstrated mainly at the laboratory scale. Representative published results for the technologies discussed are collated in Table 2.

The expanded comparison shows that similar analytical removal values may correspond to different environmental outcomes. For example, reverse osmosis achieved 99.79% removal during

pilot treatment of a real gold-cyanidation effluent, whereas 98% biodegradation by a bacterial consortium was obtained using synthetic alkaline wastewater over a substantially longer period. Reverse osmosis and calcium alginate adsorption transfer cyanide to a concentrate or loaded sorbent, while hypochlorite, MgO/O₃/persulphate, and sodium percarbonate treatments chemically transform it. Biological systems avoid concentrated chemical oxidants but require longer treatment periods and have so far been validated mainly at the laboratory scale. These differences confirm that removal percentage alone cannot serve as a

technology-selection criterion. A rational treatment strategy is developed from the characteristics of the specific cyanide-containing stream. For relatively concentrated process solutions holding a large quantity of potentially recoverable cyanide, the first step is to assess the feasibility of its extraction and recovery (Kuyucak and Akcil, 2013; Botz et al., 2016). Where recovery is not technically or economically justified, chemical or electrochemical destruction follows. For streams with low residual concentrations after the main treatment stage, deep polishing by adsorption and biological methods is more rational (Alvillo-Rivera et al., 2021; Vaca-Escobar et al., 2024).

For multicomponent effluents, a single technology is insufficient. The simultaneous presence of free cyanide, WAD cyanides, stable metal-cyanide complexes, thiocyanate and metals favours multistage schemes with distinct functions assigned to each stage (Dong et al., 2021; Mekuto et al., 2016). A recovery stage returns part of the cyanide, a destructive stage converts the residual cyanide compounds, and polishing lowers the residual pollutant concentration to the required level. The combination of methods is governed by the functional necessity of each stage rather than by the number of stages. The selection of a technology thus takes the form of a sequence of decisions: characterisation of the effluent, determination of the cyanide species and concentration, assessment of recovery potential, destruction where necessary, deep polishing, and reuse or discharge of the water.

The central question in comparing technologies is not which method delivers the highest cyanide removal, but which technology or sequence of processes is the more rational for the specific composition and purpose of the cyanide-containing stream. Direct comparison of the performance of individual processes thereby gives way to a technological strategy that accounts for the final fate of the cyanide, resource and energy costs, the secondary waste generated, and the scope for recovering valuable components (Dong et al., 2021; Vaca-Escobar et al., 2024).

ANALYTICAL DEFINITION OF TREATMENT PERFORMANCE

Reported treatment performance is inseparable from the cyanide fraction measured. Free cyanide methods target HCN and CN^- , whereas weak-acid-dissociable (WAD) cyanide procedures also

quantify cyanide released from relatively labile metal complexes. Total-cyanide methods additionally include strongly bound metal–cyanide species. Consequently, a decrease in free cyanide may coexist with persistent metal-cyanide complexes, while total-cyanide analysis may indicate a substantially higher residual concentration in the same sample (Jaszczak et al., 2017; Vaca-Escobar et al., 2024).

Analytically defined cyanide fractions are not directly interchangeable. Available approaches include distillation followed by colorimetric determination, ion-selective electrodes, flow-injection analysis, continuous-flow analysis, and chromatographic or electrochemical detection. The reported result depends on the separation procedure, detection technique, and operational definition of the cyanide fraction. Sulphide, thiocyanate, oxidants, suspended solids, and metal complexes may interfere with cyanide determination, while sample preservation, pH, and holding time may alter cyanide speciation before analysis (Jaszczak et al., 2017). These analytical differences can partly explain inconsistencies between treatment efficiencies reported for apparently similar wastewater matrices and processes (Dong et al., 2021; Vaca-Escobar et al., 2024).

Treatment studies should therefore report the analytical method, measured cyanide fraction, filtration status, preservation conditions, holding time, detection or quantification limit, and initial and final concentrations with their uncertainty. Free, WAD, and total cyanide should be measured in parallel whenever metal complexation or transfer to another phase is expected. A cyanide mass balance across the aqueous phase, solids, sorbents, concentrates, and potential gaseous emissions is also necessary to distinguish chemical destruction from physical separation or redistribution (Botz et al., 2016; Dong et al., 2021). Cyanate, thiocyanate, ammonia, nitrite, nitrate, and relevant dissolved metals should additionally be monitored so that disappearance of the initially measured cyanide fraction is not incorrectly interpreted as complete detoxification (Anning et al., 2020; Behnami et al., 2021; Vaca-Escobar et al., 2024).

TRANSFORMATION PRODUCTS, TOXICITY AND ENVIRONMENTAL FATE

Oxidation commonly converts CN^- first to cyanate (CNO^-), which is less acutely toxic than free cyanide but should not be regarded as the final

treatment endpoint unless its subsequent hydrolysis or oxidation is demonstrated. Further transformation may produce ammonia/ammonium, carbonate/bicarbonate, nitrite, and nitrate. Ammonia can impose an additional aquatic-toxicity and oxygen-demand burden, whereas nitrate may contribute to nutrient enrichment of receiving waters (Anning et al., 2020; Behnami et al., 2021; Vaca-Escobar et al., 2024). During alkaline chlorination, cyanogen chloride may occur as a transient intermediate when pH control is inadequate, while the process also increases the chloride and dissolved-salt content of the treated stream (Khodadad et al., 2008; Botz et al., 2016).

Biological degradation pathways may generate formamide, formate, and ammonia, followed under suitable aerobic conditions by nitrite and nitrate. Thiocyanate biodegradation or oxidation may additionally release sulphate and reduced or oxidised nitrogen species (Luque-Almagro et al., 2016; Anning et al., 2020; Mekuto et al., 2016). Other technologies do not necessarily destroy cyanide. Precipitation, coagulation, and electrocoagulation may transfer cyanide–metal complexes to sludge, whereas adsorption, ion exchange, and reverse osmosis transfer cyanide to spent sorbents, regeneration solutions, or membrane concentrates. These secondary streams remain potentially hazardous until they are regenerated, recycled, or subjected to further destruction (Botz et al., 2016; Dong et al., 2021; Vaca-Escobar et al., 2024). Moreover, photolysis of iron–cyanide complexes may regenerate free cyanide under sunlight, indicating that apparent environmental immobilisation should not automatically be considered permanent (Jaszczak et al., 2017; Vaca-Escobar et al., 2024).

Environmental performance should therefore be demonstrated using both chemical and toxicity-related endpoints. Post-treatment characterisation should include free, WAD, and total cyanide, together with cyanate, thiocyanate, ammonia, nitrite, nitrate, relevant metals, residual oxidants, and the leachability of generated sludge or concentrates. Whole-effluent toxicity testing or an appropriate aquatic bioassay is particularly useful for complex industrial wastewater because it can reveal the combined effects of residual cyanide species, transformation products, and other constituents that are not captured by measuring a single target compound (Jaszczak et al., 2017; Dong et al., 2021; Vaca-Escobar et al., 2024).

REGULATORY AND OPERATIONAL BENCHMARKS

Regulatory assessment of treated cyanide-bearing wastewater depends on the jurisdiction, discharge category, receiving environment and cyanide fraction specified by the applicable permit. Limits established for free, WAD, and total cyanide are not interchangeable because these fractions represent different groups of cyanide compounds and are determined using different analytical procedures (Jaszczak et al., 2017; Vaca-Escobar et al., 2024). Consequently, treatment performance should not be described as meeting regulatory requirements unless the regulated cyanide fraction, analytical method, and applicable national or site-specific discharge limit are explicitly stated.

ECONOMIC, ENVIRONMENTAL, AND TECHNOLOGY-READINESS ASSESSMENT

Published cyanide-treatment studies rarely report costs on a common functional basis. Capital and operating costs depend on wastewater flow, influent cyanide loading, the cyanide fraction targeted, reagent prices, electricity consumption, solids handling, and the potential economic credit from recovered cyanide or metals (Kuyucak and Akcil, 2013; Botz et al., 2016; Dong et al., 2021). Reported removal percentages, therefore, cannot be converted reliably into a universal cost ranking. Nevertheless, the literature identifies consistent cost drivers: oxidant and lime consumption together with sludge handling for chemical destruction; electricity, electrolyte addition and electrode replacement for electrochemical routes; ozone generation or UV irradiation and catalyst replacement for advanced oxidation; membrane pressure, pretreatment and concentrate management for reverse osmosis; and reactor volume, aeration, nutrient supply and biomass management for biological treatment (Betancourt-Buitrago et al., 2019; Dong et al., 2021; Vaca-Escobar et al., 2024).

Quantitative cost information remains limited. For sodium percarbonate treatment of gold-mine tailings, the operating cost was preliminarily estimated at US\$0.7–1.0 per tonne of tailings, including approximately US\$0.6 per tonne attributable

to the oxidant (Berkinbayeva et al., 2026). However, this estimate was derived from laboratory-scale results and requires validation under continuous pilot or industrial conditions. For most technologies included in Table 2, the original studies did not report capital expenditure, specific energy consumption, equipment lifetime, or the cost of managing secondary streams. Consequently, the available evidence supports the identification of major cost drivers but not a definitive numerical ranking of the technologies.

Environmental trade-offs follow the same mass-balance logic. Cyanide recovery can reduce the demand for newly produced NaCN and provide a reagent credit, but AVR transfers operational risk to enclosed HCN volatilisation, stripping, and absorption. Chlorination and INCO/SO₂-air oxidation are technologically mature but consume reagents and can generate dissolved salts and metal-bearing sludge. Membrane and sorption processes may require fewer direct chemical additions but transfer cyanide to a concentrate, spent sorbent, or regeneration stream, rather than destroying it (Kuyucak and Akcil, 2013; Botz et al., 2016; Dong et al., 2021). Photochemical and electrochemical processes may reduce some chemical inputs, although their environmental advantage depends on electricity consumption, grid carbon intensity, electrode or catalyst lifetime, and performance in complex real wastewater. Biological polishing generally avoids concentrated chemical oxidants but requires longer retention times, stable operating conditions, and larger reactor volumes (Alvillo-Rivera et al., 2021; Vaca-Escobar et al., 2024).

Future techno-economic assessments should report annualised capital expenditure and operating costs per cubic metre of treated wastewater and per kilogram of cyanide removed, together with pretreatment, monitoring, and secondary-stream management costs. Life-cycle assessments should apply the same treated-water target and system boundaries and should include reagent manufacture, electricity production, infrastructure, sludge or concentrate treatment, avoided NaCN production through cyanide recovery, and toxicity-related indicators. Until such harmonised data become available, Table 2 supports a conditional comparison based on wastewater characteristics, treatment objective, and technological readiness, rather than an absolute economic or environmental ranking (Dong et al., 2021; Vaca-Escobar et al., 2024).

CONCLUSIONS

Cyanide speciation changes both the apparent efficiency and the environmental meaning of treatment. Removal of free cyanide does not demonstrate the destruction of WAD cyanide or stable metal–cyanide complexes, and total-cyanide removal cannot distinguish destruction from transfer to sludge, sorbent or concentrate. Treatment studies should therefore pair a defined analytical fraction with initial and final concentrations, resource inputs, transformation products and a cyanide mass balance.

The standardised evidence comparison shows a clear trade-off. Mature oxidation processes provide rapid bulk detoxification but consume reagents and may create salts, ammonia or sludge; separation and recovery preserve cyanide value but require secure management of concentrated streams; biological treatment is attractive for polishing but needs longer residence time and robust loading control; and many advanced electrochemical and photochemical routes remain limited by energy reporting and low technological readiness. No method can be ranked based on percentage removal alone.

A defensible flowsheet begins with parallel measurement of free, WAD, and total cyanide, followed by recovery assessment for concentrated streams, bulk destruction where recovery is not justified, and polishing to the fraction-specific permit target. Verification must include cyanate, thiocyanate, ammonia, nitrogen species, metals, residual oxidant, and secondary-stream fate. The principal research need is not another isolated high-removal batch result, but continuous pilot evidence with harmonised cost, energy, waste, and life-cycle metrics on real wastewater.

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