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Review article

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Chemical, ecotoxicological characteristics, environmental fate, and treatment methods applied to cyanide-containing wastewater

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The main chemical, ecotoxicological, and environmental fate characteristics of cyanide, along with its treatment methods for cyanide-contaminated wastewater, were thoroughly examined. A global biogeochemical cycle of cyanide is proposed, covering the key physicochemical processes occurring in aqueous, soil, and atmospheric environments. The principles, advantages, and disadvantages of various treatment methods—including chemical, physicochemical, electrochemical, photochemical, and biological approaches—are evaluated. Finally, the feasibility of reusing cyanide waste is explored.

Cyanide has long been recognized as one of the deathliest poisons throughout human history[1]. It was not until Stewart and MacArthur discovered its potential as a gold ore leaching reagent[2] that cyanide found one of its most prevalent modern-day uses. For over a century, the anionic "free" form of cyanide (CN^-) has been employed in gold extraction due to its exceptional efficiency and low cost[2,3].

Despite this long history with cyanide in mining, the chemical industry is the largest consumer, utilizing over 80% of the cyanide produced annually[2]. It is used to produce organic materials such as nylon, nitrile, adhesives, plastics, paints, solvents, enamels, herbicides, pesticides, and fungicides[2,4]. Additionally, it is widely used in metallurgy, jewelry manufacturing, and certain pharmaceutical processes[4,5]. Only 20% of global cyanide production is allocated to the manufacture of sodium cyanide, of which 90% is consumed in gold mining operations, making up 18% of the world's cyanide production[2].

Unfortunately, all cyanide-consuming industries generate aqueous cyanide wastes because of incomplete cyanide consumption or production of cyanide derivatives. Furthermore, cyanide is often produced as a by-product in industries that do not intentionally utilize it, such as coal, coke, and petroleum production[6]. As a result, vast volumes of cyanide-containing wastewater are generated daily. Like many human-derived wastes, these effluents are ultimately discharged into the environment. Given cyanide's notorious toxicity for humans, plants, and animals—as well as its long-term persistence in the environment[7]—it is crucial that all wastewaters containing cyanide undergo treatment processes to minimize its environmental impact; particularly when it may enter potable water supplies.

In the early days of cyanide waste management, effluent dilution was widely practiced due to its simplicity and low cost[8]. However, as cyanide was not broken down into less toxic products, it remained prone to accumulating in ground and surface waters through natural processes. As a result, dilution was eventually replaced by chemical oxidation methods, such as alkaline chlorination and hydrogen peroxide (H_2O_2) degradation[8,9]. In time, more efficient, less polluting, and cost-effective methods emerged based on physicochemical, biological, and electrochemical principles[9]. Nevertheless, with each new method, unique constraints surfaced, requiring further refinement and adaptation. Consequently, research continues to this day in search of methods that offer the best balance between advantages and limitations.

Success in these efforts depends on a deep understanding of cyanide's chemistry, its environmental fate, and the core principles of wastewater treatment. While much of this knowledge is scattered across research papers and extensive book chapters, a consolidated and comprehensible overview remains absent.

Hence, this review presents cyanide's chemistry and ecotoxicological characteristics as starting points for understanding cyanides' behavior in wastewaters and nature, accompanied for the first time by an integral cyanide's biogeochemical cycle to assess its interactions while moving from wastewater sources to the different environmental matrices. Once underlying chemical processes have been addressed, an illustrative overview of the fundamental principles underpinning cyanide's wastewater treatment methods is presented for a feasible understanding, as these aspects comprehension is essential for the design of effective treatment strategies. Additionally, this review synthesizes the latest insights (5 years past) into cyanide wastewater treatment methods, highlighting their advantages and disadvantages.

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Cyanide's chemistry

Cyanides encompass a variety of compounds featuring a carbon atom triply bonded to the nitrogen atom (–C≡N) moiety in their structure[10,11], occurring either as an anion (i.e., inorganic cyanides) or as a covalent functional group (i.e., nitriles)[11].

Inorganic cyanides can generally be classified into free cyanide and complex cyanide. Free cyanide typically includes anionic cyanide (CN^-) and hydrogen cyanide (HCN), both of which are highly reactive towards various elements and molecules. Due to cyanide's filled "s" and "p" orbitals, and its empty "d" and "f" orbitals, it can share its triple bond electrons with oxygen and sulfur, forming cyanate (OCN^-) and thiocyanate (SCN^-) anions. Moreover, cyanide can establish π-acceptor bonds similarly to halides and can also act as a strong nucleophile in addition reactions, playing a critical role in many biological processes[12].

Both CN^- and HCN exist in an acid-base equilibrium. The HCN/CN^- pair has a pK_a of 9.24 at 25 °C, meaning that HCN will predominantly exist at a pH below 9.24, while anionic CN^- will prevail at pH values above 9.24[12,13]. This species distribution, however, can shift with temperature changes. Lower temperatures tend to hinder the dissociation of HCN into CN^-, thereby favoring the presence of HCN[12]. HCN is typically gaseous due to its poor solubility in water and high vapor pressure ($K_H = -2.8$ (Henry's constant))[14].

In its anionic form, cyanide can act as a ligand, often forming coordination complexes with transition metal cations. Cyanide establishes σ-bonds with the metal's empty d-orbitals by donating electron pairs, and it can also establish π-bonds by accepting electron density from the metal into its empty anti-bonding orbitals[12,15]. As a result, a variety of metal-cyanide complexes can form, exhibiting varying levels of stability.

These metal-cyanide complexes are commonly classified into weak and strong complexes. Weak metal-cyanide complexes, typically involving cadmium, zinc, silver, copper, nickel, and mercury cations, dissociate under mildly acidic conditions (pH 4–6)[12] due to their moderate stabilization constants (K_s)[16]. On the other hand, strong complexes, involving cobalt, platinum, gold, palladium, and iron cations, require strongly acidic conditions ($pH < 2$) for dissociation[12,17], owing to their higher K_s values[16].

Free and complexed cyanides are also prone to oxidation reactions. Under neutral to alkaline pH conditions and in the presence of an oxidizer, anionic cyanide can be converted to cyanate (OCN^-)[12]. Similarly, when cyanide dissociates from metal complexes, oxidation to cyanate can occur. However, due to the strong binding in certain metal-cyanide complexes, the cyanide ligands are less likely to undergo oxidation compared to their weak counterparts.

Whether free or complex, inorganic cyanide can be found in different aqueous and solid states in the environment[18], predominantly associated with anthropogenic activities. Even so, they also naturally occur primarily as HCN[19]. HCN is produced by certain bacteria, fungi, plants, and even insects[20,21], as part of their metabolic processes. Although the precise mechanism of HCN synthesis has not been elucidated for every organism, it is generally well understood in prokaryotes and cyanogenic plant species.

Particularly, when referring to bacteria, genera such as *Alcaligenes, Aeromonas, Bacillus, Pseudomonas*, and *Rhizobium* are known to have the ability to produce HCN[22,23]. These rhizosphere bacteria utilize the enzyme HCN synthase—encoded by the hcnABC gene cluster—to convert glycine found in soil pore water and root exudates into HCN and carbon dioxide[21,24].

In contrast, plants produce cyanide via the ethylene biosynthesis pathway. Ethylene, an important regulatory phytohormone, is derived from the oxidation of 1-aminocyclopropane-1-carboxylic acid (ACC) by the enzyme ACC oxidase (ACO). During this process, cyanide is released as a by-product[25,26]. Cyanide also exists in plants as cyanogenic glycosides[18,19]—sugar-bonded cyanides—which can release HCN through enzymatic action[27]. These secondary metabolites, commonly found in cyanogenic plants, are primarily derived from amino acids such as L-leucine, L-valine, L-tyrosine, L-isoleucine, L-phenylalanine, or cyclopentenyl-glycine[28,29]. The biosynthesis of cyanogenic glycosides involves a multi-step process catalyzed by two multi-functional cytochrome P450 enzymes, leading to the formation of unstable hydroxynitriles, which are subsequently glycosylated by soluble cytosolic glucosyltransferases[29].

The resulting concentration of plant cyanide compounds varies considerably depending on factors including plant section, maturity, time, and growing conditions[27]. Moreover, several commonly consumed plant goods have been found to contain cyanide molecules, including cassava, sorghum, corn, almonds, apricots, peaches, plums, bamboo shoots, sprouted beans, cherries, olives, potatoes, soybeans, nuts, and coffee beans[30,31].

Ecotoxicological characteristics

Cyanide's toxicity in nature depends on its chemical form. In aqueous or atmospheric media, cyanide is largely found as free cyanide, which is its most toxic form[32], particularly for humans and animals. This high toxicity is due to cyanide's ability to inhibit crucial metabolic processes[33].

In humans, free cyanide forms stable complexes with essential metalloenzymes[19,34], such as cytochrome oxidase, an enzyme involved in ATP synthesis. By inhibiting the function of cytochrome oxidase, cyanide disrupts cellular respiration[35,36], leading to central nervous system depression and respiratory failure[2,31]. Additionally, cyanide binds to iron in the blood, inhibiting oxygen transport, and causing asphyxiation[37].

In contrast, plants have evolved enzyme-meditated detoxification mechanisms to mitigate cyanide toxicity. These processes dampen cyanide's harmful effects by converting HCN to less toxic compounds[38–40]. For example, β-cyanoalanine synthases (β-CAS) convert HCN into β-cyanoalanine by combining it with cysteine. Alternatively, the enzyme rhodanese converts cyanide into thiocyanate[39,40]. Furthermore, when cyanide is found within organic molecules (e.g., cyanogenic glycosides, cyanolipids), it shows reduced toxicity[41].

Similarly, cyanide's oxidized derivatives, such as thiocyanate and cyanate, which are also present in aqueous environments, are significantly less toxic than free cyanide[41]. For example, thiocyanate is approximately seven times less toxic than cyanide[42], while cyanate's toxicity is reduced by a factor of 1000[43,44].

Further reductions in toxicity occur when cyanide forms coordination complexes with transition metals[41]. The toxicity of these complexes depends on their stability constants (K_s) and solubility product constants (K_{sp}). A higher K_s indicates stronger binding and reduced dissociation of cyanide, thereby lowering its inherent toxicity. Meanwhile, lower K_{sp} describes complexes with reduced solubility, which may precipitate out of solution and exhibit diminished toxicity. For example, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ complexes are 1000 times less toxic than free cyanide. When precipitation occurs, as with Prussian blue ($Fe_4[Fe(CN)_6]_3$), toxicity decreases by a factor of 1950[16].

Environmental fate: cyanide biogeochemical cycle

Cyanide fate in nature should not be regarded as a linear manner with a starting and ending point, but rather as an interconnected system of complex reactions and interactions involving various cyanide species in atmospheric, aqueous, and soil media. As such, the Cyanide biogeochemical cycle study approach is strongly recommended instead.

It was first described by Mudder in 1984 and has since been referenced consistently in more recent works[45]. Mudder's *Cyanide's Cycle* depicts the main physiochemical processes cyanide undergoes in the *Mining Tailings Model*, as illustrated in Fig. 1. Thus, this cycle focuses on cyanide's environmental fate as a by-product of mining activities; especially those involving gold extraction through cyanidation processes[46].

However, cyanide's fate extends beyond mining tailings, encompassing other researched scenarios such as the *Atmospheric Chemistry of Hydrogen Cyanide*, *Bushey's Cyanide's fate mechanisms on wetlands*, and *Cyanide's cycle in nature* itself. Therefore, this review aimed to integrate these three scenarios into a comprehensive discussion of cyanide's biogeochemical cycle. To the best of our knowledge, such a joint exploration of these scenarios has not been carried out yet.

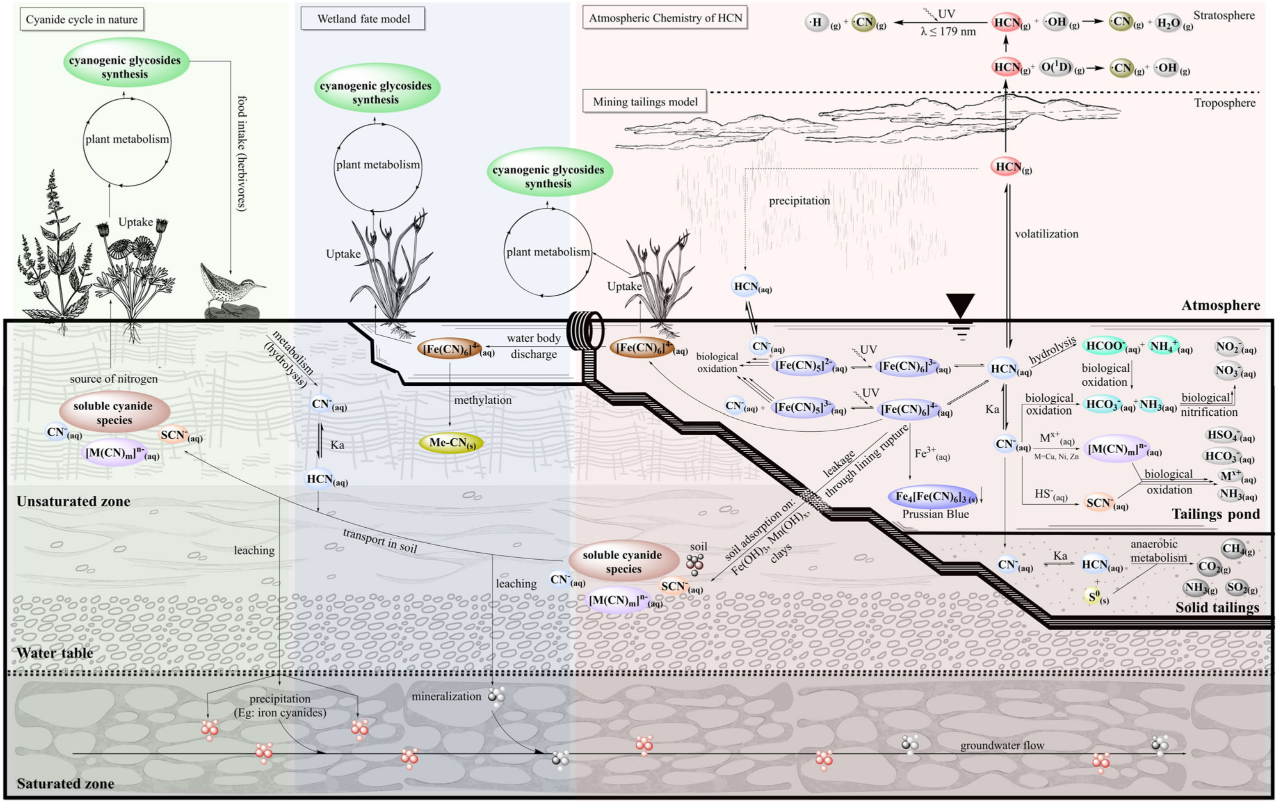


Fig. 1 | Cyanide's biogeochemical cycle[45,46,71,141].

Cyanide's biogeochemical cycle begins within the "mining tailings" segment (Fig. 1), where mining-derived cyanide-rich residues from extraction processes are produced (e.g., gold extraction)[2]. Once these residues are discharged in tailing ponds, they separate into two distinct phases: an upper aqueous phase and a lower phase comprising solid tailings in slurry form[47]. Between these two phases and the atmospheric one, cyanide undergoes one of eight processes: volatilization, oxidation, radical oxidation, photolysis, hydrolysis, precipitation, complexation, or sorption[48].

Cyanide's volatile nature derives from its low solubility in water and high vapor pressure (reaction 1), where it behaves as a weak acid (HCN) (reaction 2)[13,14]. Thus, cyanide's transport is facilitated throughout the atmosphere (Fig. 1), resulting in a lengthy atmospheric residence time (approximately five months)[49,50]. Particularly, HCN has no major role in tropospheric chemistry[49]; instead, in the stratosphere, HCN can undergo radical oxidation and/or photolysis reactions, which serve as principal sinks for atmospheric HCN[49]. Radical oxidation reactions include HCN oxidation by hydroxyl radicals (·OH) and singlet oxygen ($O(^1D)$)[49,51] (reactions 2 and 3, respectively), while photolysis reactions involve the ultraviolet-mediated photolysis of HCN, which only occur in the upper stratosphere (reaction 4)[49,51].

Volatilization	$HCN_{(aq)} \rightleftarrows HCN_{(g)}$	(1)
Radical oxidation	$HCN_{(g)} + \cdot OH_{(g)} \rightarrow \cdot CN_{(g)} + H_2O_{(g)}$	(2)
Radical oxidation	$HCN_{(g)} + O(^1D)_{(g)} \rightarrow \cdot CN_{(g)} + \cdot OH_{(g)}$	(3)
Photolysis	$HCN_{(g)} \xrightarrow{UV, \lambda \leq 179nm} \cdot CN_{(g)} + \cdot H_{(g)}$	(4)
Equilibria	$HCN_{(aq)} \rightleftarrows H^+_{(aq)} + CN^-{}_{(aq)}$	(5)

Despite HCN's limited water solubility, if dissolved by rainfall or in any body of water, including the tailings pond of its origin, it undergoes acid-base equilibria (reaction 5), leading to the formation of aqueous cyanide anions (CN^-). These anions gain mobility in water and have the potential to reach nearby land environments.

Within the aqueous phase of the tailings pond, cyanide chemistry is governed by several processes, including hydrolysis, thiocyanates formation, complexation, and biological oxidations[45]. The first two processes result in the less toxic formate and ammonium ion (reaction 6), as well as SCN^- (reaction 7). In terms of complexations, cyanide readily forms complexes with different metals (reaction 8), primarily with ferric (Fe^{3+}) or ferrous (Fe^{2+}) ions (reactions 9 and 10)[45].

Hydrolysis	$HCN_{(aq)} \xrightarrow{2H_2O} HCOO^-_{(aq)} + NH^+_{4(aq)}$	(6)
Thiocyanate formation	$CN^-_{(aq)} + HS^-_{(aq)} \leftrightharpoons SCN^-_{(aq)} + H^+_{(aq)} + 2e^-$	(7)
Complexation	$CN^-_{(aq)} \xrightarrow{M^{X+}} [M(CN)_m]^{n-}_{(aq)}$ Where, M = Cu, Ni, Zn	(8)
	$6HCN_{(aq)} + Fe^{3+}_{(aq)} \rightleftarrows [Fe(CN)_6]^{3-}_{(aq)} + 6H^+_{(aq)}$	(9)
	$6HCN_{(aq)} + Fe^{2+}_{(aq)} \rightleftarrows [Fe(CN)_6]^{4-}_{(aq)} + 6H^+_{(aq)}$	(10)

All the aforementioned cyanide species can undergo subsequent biological oxidation (reactions 11–13), including the anionic (CN^-) itself (reaction 14). In addition, secondary processes, such as biological nitrification (reaction 15), could occur as part of aerobic microorganisms' metabolic activity[14]. Similarly, aqueous CN^- or HCN in solid tailings can also be used by anaerobic microorganisms to fulfill metabolic requirements, resulting in additional reactions (reactions 16–21)[14].

Biological oxidation	$HCOO^-_{(aq)} + NH^+_{4(aq)} \rightarrow NH_{3(aq)} + HCO^-_{3(aq)}$	(11)
	$SCN^-_{(aq)} \rightarrow NH_{3(aq)} + HCO^-_{3\,(aq)} + HSO^-_{4\,(aq)}$	(12)
	$[M(CN)_m]^{n-}_{(aq)} \rightarrow NH_{3(aq)} + HCO^-_{3(aq)} + M^{x+}_{(aq)}$	(13)
	$CN^-_{(aq)} \rightarrow NH_{3(aq)} + HCO^-_{3(aq)}$	(14)
Nitrification	$NH_{3(aq)} + HCO^-_{3(aq)} \rightarrow NO^-_{3(aq)} + NO^-_{2(aq)}$	(15)
Anaerobic metabolism	$HCN_{(aq)} + S^0_{(s)} \rightarrow HSCN_{(aq)}$	(16)
	$HSCN_{(ac)} \overset{2H_2O}{\rightarrow} NH_{3(g)} + H_2S_{(g)} + CO_{2(g)}$	(17)
	$HCN_{(aq)} + 3H_{2(g)} \rightarrow CH_{4(g)} + NH_{3(g)}$	(18)
	$HCN_{(aq)} \overset{2H_2O}{\rightarrow} HCOO^-_{(aq)} + NH^+_{4(aq)}$	(19)
	$HCOO^-_{(aq)} + NH^+_{4(aq)} \rightarrow NH_{3(g)} + CO_{2(g)}$	(20)
	$CO_{2(g)} + 2H_{2(g)} \rightarrow CH_{4(g)} + O_{2(g)}$	(21)

Additional reactions involving cyanide species in aqueous solution include precipitation reactions. As mentioned, cyanide readily forms coordination complexes, particularly ferricyanide ($[Fe(CN)_6]^{3-}$) and ferrocyanide ($[Fe(CN)_6]^{4-}$) complexes. Under specific stoichiometric conditions, these complexes, previously discussed, can precipitate as insoluble salts of iron, copper, nickel, manganese, lead, zinc, cadmium, tin, or silver[45]. Most commonly, in the case of iron (II) ions, ferrocyanide complexes precipitate as the well-known coordination compound Prussian blue (reaction 22)[45].

If precipitation does not occur, aqueous ferric and ferrous complexes can undergo further reactions. Under the influence of incident ultraviolet light, typically coming from sunlight, these complexes can undergo photolytic reactions, leading to ligand loss. These reactions commonly yield iron-cyanide complexes with reduced oxidation states and free cyanide (reactions 23 and 24)[52], which can subsequently go through the rest of the processes.

Prussian blue precipitation	$3[Fe(CN)_6]^{4-}_{(aq)} + 4Fe^{3+}_{(aq)} \rightarrow\downarrow Fe_4[Fe(CN)_6]_{3(s)}$	(22)
UV−induced ligand loss	$[Fe(CN)_6]^{3-}_{(aq)} \overset{UV}{\rightarrow} [Fe(CN)_5]^{2-}_{(aq)} + CN^-_{(aq)}$	(23)
UV−induced ligand loss	$[Fe(CN)_6]^{4-}_{(aq)} \overset{UV}{\rightarrow} [Fe(CN)_5]^{3-}_{(aq)} + CN^-_{(aq)}$	(24)

Up to this point, this examination of cyanide's chemistry has been described within the limits of a tailings pond that has kept its integrity. However, tailings ponds' linings are prone to ruptures and thus may seep liquid tailings directly into the soil. Despite the frequency of such incidents, they have yet to be incorporated into existing cyanide cycle frameworks, even when they have been repeatedly reported[53–56]. Further, in addition to the aforementioned reactions, sorption processes can also occur with remaining aqueous cyanide species in tailings ponds. These species are commonly absorbed by ferric hydroxide and manganese hydroxide particles, as well as clays[46].

Similarly, cyanide's environmental fate beyond tailings ponds has been overlooked in previous cycles, neglecting the likely event that the pond's contents are discharged untreated into water bodies. Indeed, research has highlighted numerous cases of liquid tailings and associated wastewater being discharged without proper treatment, whether intentionally[57–61] or because of spill incidents[62,63]. Consequently, aqueous cyanide species are allowed to freely migrate into external aquatic environments.

The second segment of the biogeochemical cycle includes *Wetland section* (Fig. 1), reported by Bushey in 2003[46]. In this segment, free cyanide, ferric, and ferrous cyanide complexes are absorbed by plants and assimilated through their metabolism[46]. This process involves the biosynthesis of cyanogenic glycosides, secondary metabolites derived from amino acids, which plants employ in their defensive mechanisms against herbivores and other organisms[64,65]. Synthesized within the plant cytoplasm, these glycosides can undergo enzymatic hydrolysis into HCN, which is released as a chemical defense response[66]. Other processes that may occur in this segment include reactions between soil organic compounds and cyanide, resulting in the formation of compounds such as acetonitrile (Me-CN) or other nitrile solids[67].

Finally, the third segment of the cycle (Fig. 1) encompasses all processes and interactions involving cyanide with plant and animal species. As previously noted, cyanide is typically assimilated by plants to produce cyanogenic glycosides. These compounds can indirectly enter animal organisms through the consumption of cyanide-containing plants, as in the case of livestock[68–70]. Through this mechanism, animals metabolize plant cyanogenic glycosides, leading to the bioaccumulation of cyanide in their tissues. When they die, cyanide returns to the soil as free cyanide or various nitrogen-containing compounds[46]. Once in the soil, free cyanide and other soluble cyanide species may be transported through water-assisted leaching or react with metal ions and remain in the soil as insoluble salts (precipitates)[14]. Consequently, soluble cyanide species may continue their journey until reaching the water table through a very slow kinetic mobility process[14]. Cyanide that infiltrates groundwater may persist in soluble form and migrate within the groundwater or undergo precipitation and mineralization processes, depending upon existing ions[14,71].

Cyanide wastewater treatment methods

When cyanide is present in the primary environmental matrices, it poses a critical threat to human health, as well as to aquatic and terrestrial ecosystems. Therefore, cyanide's toxic nature calls for its removal from environmental matrices, particularly from water sources. Hence, environmental legislation across countries has established permissible levels of cyanide concentration in aqueous media. For instance, the US EPA has set a maximum level of cyanide concentration in water for human drinking purposes at 0.2 mg L^{-1} [72]. If cyanide is to be discharged into freshwater bodies, the maximum allowed concentration is capped at 22 μg L^{-1}, while for continuous discharge, it is 5.5 μg L^{-1} [73].

To comply with these quality standards, cyanide requires effective removal treatment processes whose selection depends on a series of factors. First, the type of wastewater must be considered, as cyanide concentration heavily depends on it. For instance, concentrations range from ≤100,000 mg mL^{-1} in electroplating baths[6], 10–1000 mg mL^{-1} coke plants[6,16], 50−500 mg L^{-1} in noble metal ore processing[16], 0.5–144 mg L^{-1} in petroleum refining[74], to 5–10 mg L^{-1} in coal gasification processes[75]. These variations determine the specific treatment approach. Conventional chemical and physicochemical methods are effective for high cyanide concentrations, whereas novel alternatives like biological treatments are better suited for lower cyanide concentrations (e.g., microbial degradation for 0–10 mg mL^{-1})[16]. Additionally, pretreatment may be necessary for certain wastewaters, such as stripping ammonia from coking plant waters[76].

Second, the composition of the effluents must be assessed, as not all treatment methods are effective for different cyanide species. For wastewaters primarily composed of free cyanide and weak acid dissociable complexes, conventional chemical and physicochemical treatments are appropriate. However, for effluents containing strong metal-cyanide complexes, physicochemical methods are preferred due to the complexes' resistance to oxidation[76]. The presence of other chemical entities also requires consideration. Free metal ions can mask and stabilize cyanide species, while dissolved organic matter increases the chemical oxygen demand, potentially competing with cyanide for oxidative treatments[77].

Third, the current technological readiness of treatment methods must be evaluated. While newer approaches such as phytoremediation, ozonation, UV-oxidation, or electrochemical advanced oxidation processes show promise, many remain in the research or pilot stage, with few reaching commercial scale like carbon adsorption processes[76].

Lastly, cost considerations are critical in selecting a treatment method. Historically, alkaline chlorination has been widely used for cyanide removal

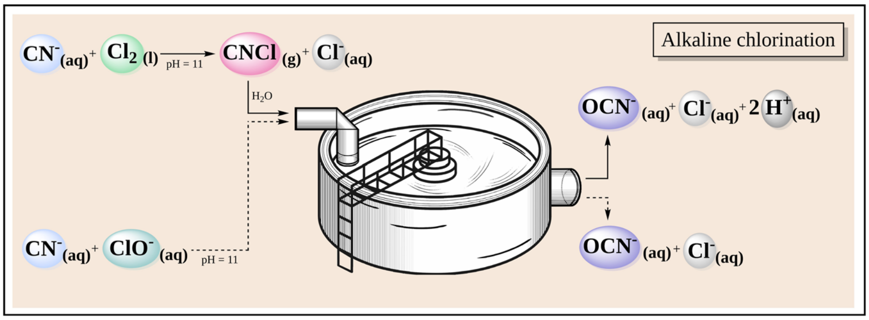


Fig. 2 | Alkaline chlorination process with the use of chlorine gas or hypochlorite ions as oxidants[80].

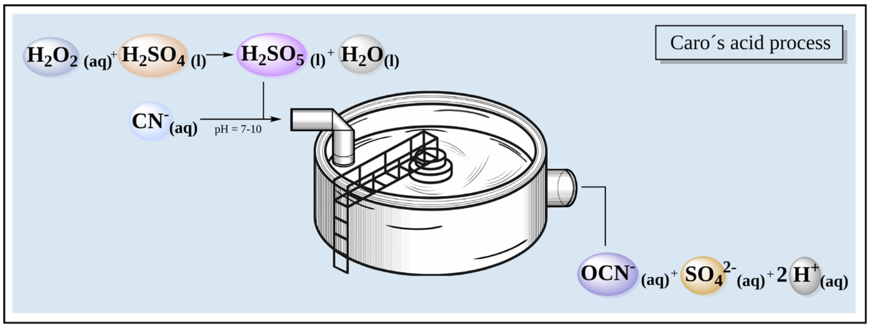


Fig. 3 | Main reactions involved in the Caro's acid process[48].

despite its high cost[9,78,79], which has driven the development of newer, more efficient, and cost-effective methods. A green approach has also emerged, emphasizing the reduction of toxic by-products, economization of reagents, and minimization of energy consumption as important factors when selecting the optimal treatment solution.

Methods principles

Cyanide removal from wastewater is generally achieved using five main treatment methods, each operating on distinct principles: chemical, physicochemical, electrochemical, photochemical, and biological. The following sections provide a concise yet comprehensive overview of these methods, aimed at enhancing clarity and understanding.

Chemical methods

Chemical treatment methods for cyanide wastewater involve reactions that convert cyanide into less toxic derivatives[48]. Among multiple reaction pathways, oxidation reactions are often preferred. As outlined in the biogeochemical cycle, while cyanide typically undergoes oxidation reactions through biological pathways, with the appropriate oxidizing agent, reactions can be performed without the intervention of living beings (i.e., microorganisms).

Conventionally, cyanide wastewater has been treated through alkaline chlorination[48]. At a pH of 11[80], this process involves the oxidation of aqueous cyanide by liquid chlorine (Cl_2) or hypochlorite ions (ClO^-) to form cyanogen chloride (CNCl), which subsequently hydrolyzes into the less toxic cyanate ion (OCN^-) (Fig. 2). Typically, an excess of chlorine is used to further oxidize cyanate[48]. While alkaline chlorination offers numerous advantages, such as its ability to treat a wide range of cyanide concentrations[48], important drawbacks include the high consumption of chlorine, resulting in high operational costs, hazardous chlorinated by-products (e.g., CNCl), and reduced oxidation efficacy for certain cyanide-metallic complexes[48]. Nevertheless, precipitation reactions present viable alternatives to oxidation methods. Notably, cyanide precipitation by iron (II) ions, as discussed in the biogeochemical cycle, stands out, as it can reduce cyanide concentration up to 1–5 mg L^{-1}. Furthermore, it does not require strong basic conditions; slightly acidic conditions (pH = 5–6) are preferred[48].

As the use of alkaline chlorination has declined over time, alternative oxidations reactions have gained prominence. Typically used ones employ H_2O_2 as an oxidizing agent, albeit in combination with other substances. In the Caro's acid process, before cyanide oxidation can take place, H_2O_2 needs to react with concentrated sulfuric acid (H_2SO_4) to form peroxymonosulfuric acid (H_2SO_5), also known as Caro's acid[48,81]. This compound is responsible for oxidizing cyanide into OCN^-[48,82] (Fig. 3). This process is frequently preferred for treating tailings slurry[48].

Alternatively, if H_2O_2 is used independently, metallic catalysis is required. By using aqueous copper (II) ions cyanide's oxidation by H_2O_2 is facilitated (Fig. 4). This catalytic process also applies to cyanide-metallic complexes, wherein metallic ions later precipitate as their corresponding hydroxides, typically at a pH of 9–9.5[48]. Similarly, copper (II) ions serve as catalysts when cyanide is oxidized by sulfur dioxide (SO_2)[48] or any reduced sulfur salt (i.e., metabisulfite)[82] in the presence of oxygen (O_2) gas (Fig. 4).

In general, Caro's acid process and SO_2 oxidation method are preferred for treating cyanide solid tailings, whereas H_2O_2 and SO_2 (to some extent) are commonly used to treat liquid tailings[48]. As in alkaline chlorination, their main disadvantages are the generation of toxic by-products, which is inherent to chemical treatment processes[83]; with some exceptions.

Namely, ozonation has recently gained attention in treating cyanide-containing wastewater. Specifically, it stands out based on cyanide intense reactivity with ozone and its complete degradation, without unwanted by-products generation[84]. In general, cyanide ozonation proceeds by hydroxyl radicals produced upon ozone hydroxide-ion catalyzed decomposition, in water[84,85]. Once these radicals are produced, they oxidize cyanide to cyanate, which can be degraded by further ozonation or additional hydrolysis reactions. Normally, a 90% removal is expected when ozone is administered in a 1–1.2 mol O_3/mol CN^- dose[84].

Physicochemical methods

In contrast to chemical methods for treating cyanide wastewater, physicochemical methods offer the advantage of avoiding the generation of toxic by-products. Among these methods, adsorption processes are notable for their ease of operation, high efficiency, and cost-effectiveness[86–88]. Nonetheless, as a major drawback, physicochemical methods do not eliminate

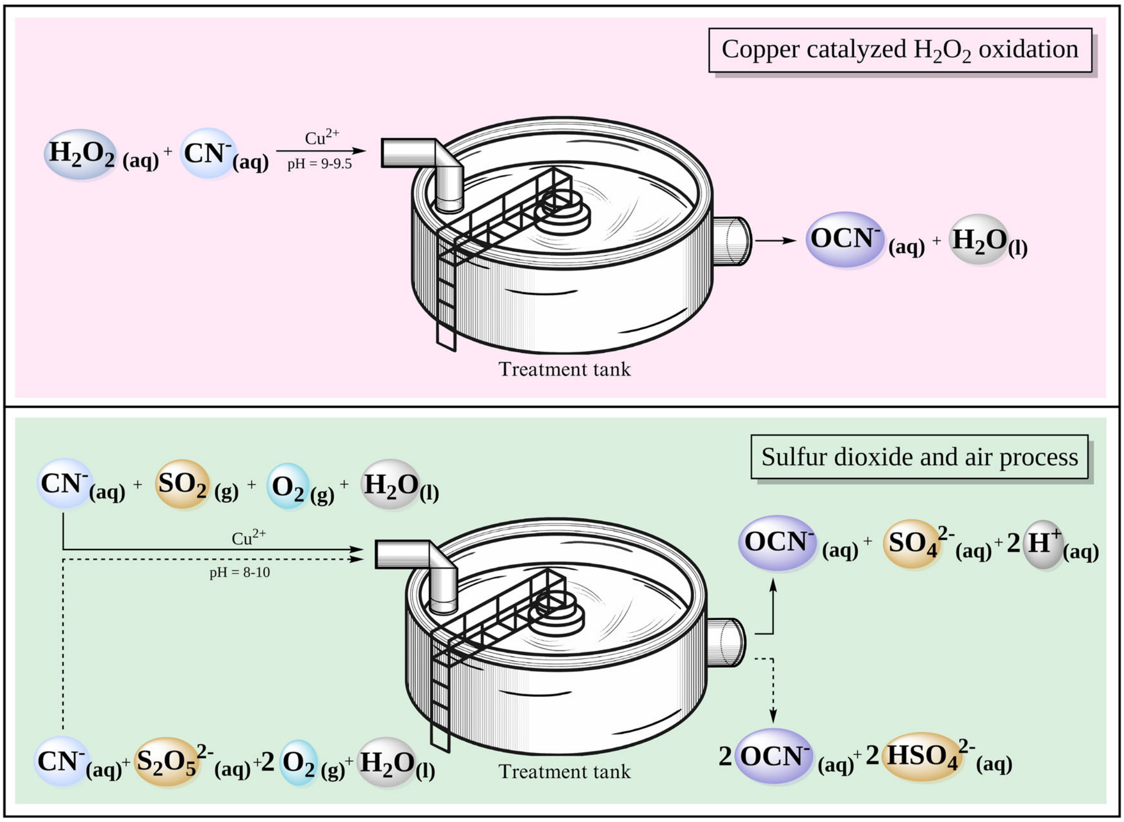


Fig. 4 | Cyanide oxidation reactions involved in the copper-catalyzed H_2O_2 process and the sulfur dioxide and air process[48].

contaminants from their original source. Instead, they simply transfer the pollutants to another medium for further treatment and eventual discharge[89].

In principle, adsorption occurs as a surface phenomenon in which an adsorbate (in this case, cyanide) interacts with an adsorbent or substrate, becoming attached to it[90]. If this interaction occurs via intermolecular forces, physisorption takes place; if chemical bonds are established, chemisorption occurs[90]. In either case, a wide variety of low-cost absorbent materials are available for this purpose, both natural or synthetic (organic or inorganic)[91].

Generally, in cyanide removal, physisorption is the preferred mechanism, as adsorbent recovery is desired; however, ongoing research is exploring chemisorption. Activated carbon (AC) is by far the most frequently used absorbent for cyanide removal, primarily because of its exceptional adsorptive and catalytic properties[92]. In addition to adsorbing cyanide species, AC can catalyze their oxidation to less toxic forms, such as OCN^-[92]. Nevertheless, studies have indicated that AC alone may not achieve optimal removal efficiency, necessitating surface modifications[92].

It has often been noted that AC removal efficiency can be improved by impregnating it with different metals[92,93]. The use of copper (i.e., Cu^{2+} ions) is typically favored over other metals due to its oxidizing effect on cyanide (i.e., catalytic oxidation). Briefly, when Cu^{2+} ions are impregnated on AC, free cyanide readily forms metallic complexes that get adsorbed on the AC surface. There, cyanide undergoes early oxidation to cyanogen, and subsequently to cyanate[94].

Similar results have been found for metallic oxides impregnated AC's surfaces[93]. Alternatively, surface modification can be achieved by incorporating organic moieties or functional groups that can enhance cyanide removal[92]. For instance, functional groups containing protonated carbonyl have been found to facilitate electrostatic anion complexation with cyanide[95]. Additionally, bacterial biofilms can be impregnated onto the AC surface; these absorb and biodegrade cyanide through metabolic/enzymatic process[20,92,96]. This aspect will be discussed in the context of biological methods for cyanide wastewater treatment.

In addition to AC, other commonly used absorbents include raw and modified zeolites[97–100], as well as new bioadsorbents. These alternatives offer similar advantages to AC in terms of low cost, effectiveness, and ease of use and are commonly found in food or plant waste/by-products[101–105].

Electrochemical methods

In general, the electrochemical degradation of cyanide wastewater relies on the use of an electrochemical cell, comprising an anode, cathode, and electric power source, wherein cyanide undergoes an oxidation process. This principle has spurred the development of multiple electrochemical techniques to effectively oxidize cyanide. While differing in approach, they all share the ability to remove pollutants from aqueous media, even at low concentrations, as has been reported for cyanide ($<500\ mg\ L^{-1}$)[106].

Overall, electrochemical techniques excel in generating less harmful by-products[107], particularly when compared with the toxicity and risk factors of the target pollutant. However, the exception is when by-products are of a halogen nature (i.e., Cl^- or Br^- oxidation by-products)[108]. Other advantages include their non-selective character and strong oxidizing capabilities[109]. Their primary limitation is their high energy consumption[110,111], especially when used at a large scale[110].

The simplest electrochemical techniques for cyanide degradation constitute direct and indirect electrooxidation methods. In direct oxidation, cyanide is oxidized at the anode, while in the cathode, heavy metals present in the cyanide wastewater are reduced[106,112] (Fig. 5). This process is usually preferred for treating cyanide in high concentrations ($>1000\ mg\ L^{-1}$)[106]. Conversely, indirect oxidation uses a "non-active" anode to generate strong oxidizing species[113], which facilitates the oxidation of cyanide in solution, particularly at low concentrations ($<500\ mg\ L^{-1}$)[106]. For instance, when sodium chloride is added to the electrolytic media as an electro-active supporting electrolyte, cyanide is oxidized by hypochlorite anions (ClO^-) generated in the anode[106,114] (Fig. 5).

In both scenarios, platinum or graphite electrodes are predominantly used as anodes[106]. However, when more reactive metals are used as anodes,

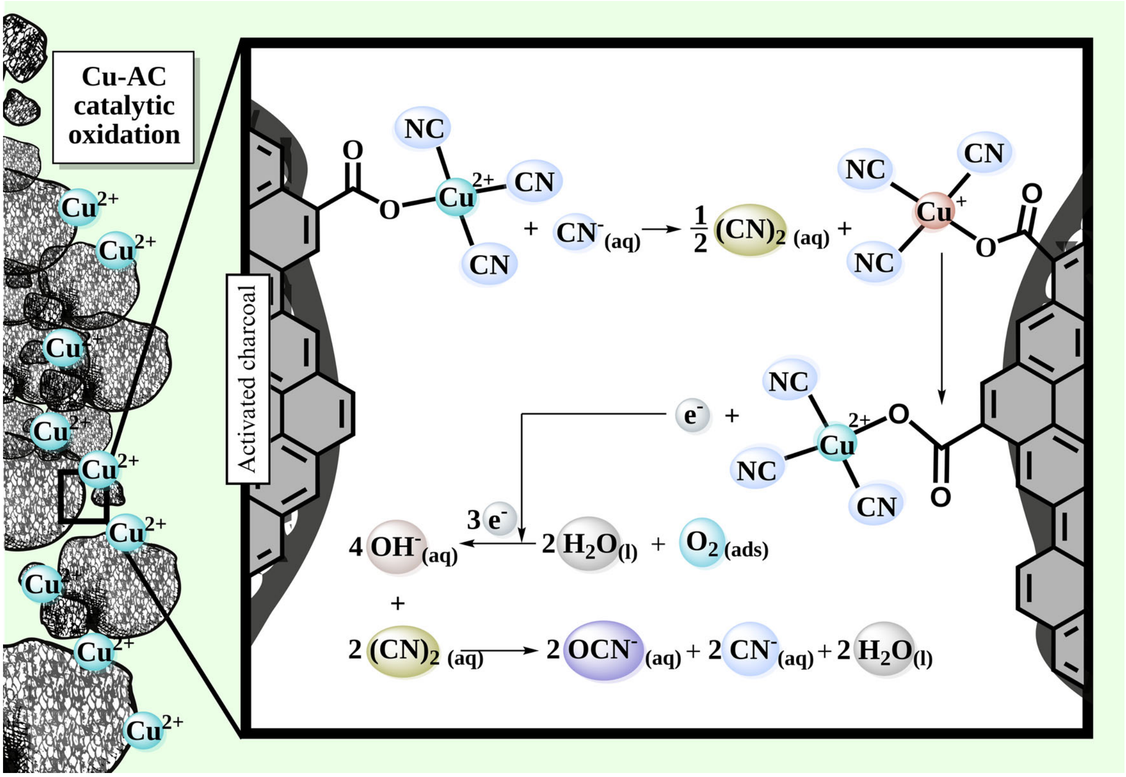


Fig. 5 | Catalytic reactions for cyanide oxidation using Cu-impregnated activated charcoal (Cu-AC)[94].

electrocoagulation is then possible. This technique involves the use of a cation-generating anode, typically iron or aluminum[115]. Once released into the solution, these cations facilitate the precipitation of cyanide as insoluble coordination complexes (e.g., Prussian blue) (Fig. 5).

Other novel alternatives have explored the possibility of reducing cyanide by electrocatalysis instead of the usual electrooxidation pathway. Although implausible, considering the strong electrostatic repulsion between anions (e.g., CN^-) and the negatively charged cathode, enhancing the binding ability of the cathode to overcome repulsion has been proposed. For instance, when transition metal oxides (e.g., Co_3O_4) are used as cathode, polarization under an electric field can foster the cathode's cyanide enrichment[116]. Consequently, cyanide reduction is made possible. After the reduction products have been generated, they can experience further oxidation processes.

In addition to the discussed techniques, contemporary research has shifted focus toward electrochemical advanced oxidation processes (EAOPs). This method involves the electric generation of hydroxyl radicals ($\cdot OH$)[117], primarily derived from water[108]. As one of the strongest known oxidizers (+2.8 V vs. standard calomel electrode, pH 0)[117,118], hydroxyl radicals play a crucial role in the oxidation processes. Owing to their rapid reactivity and non-selective behavior, they effectively degrade a wide range of contaminants[118,119], including cyanide. Typical mechanisms for generating hydroxyl radicals in EAOPs include water anodic oxidation, anodic oxidation with electrogenerated H_2O_2, and Electro-Fenton-related processes[120,121]. Among these, the first mechanism is particularly suitable for degrading cyanide, as it operates in alkaline conditions, thereby preventing HCN generation during cyanide oxidation (Fig. 6).

Even though cyanide requires high alkaline conditions to avoid HCN evolution, while it oxidizes to cyanate, low alkaline conditions are simultaneously desired to ensure efficient cyanate hydrolysis[122]. Although contradictory, Electro-Fenton-related processes can successfully overcome this obstacle. For instance, it has been reported cyanide can be directly mineralized to NO_3^- via heterogeneous Electro-Fenton generated $\cdot OH$ and $\cdot O_2^-$ radical oxidation[122].

Photochemical methods

Like the EAOPs, the photochemical approach to cyanide degradation also involves the generation of oxidizing radicals, but this only occurs because of incident electromagnetic radiation. Specifically, only ultraviolet radiation (UV light) can generate said radicals, either from oxidizing agents or catalysts[118]. When these oxidizing radicals, used to remove a particular pollutant, are produced by exposing oxidizers (e.g., H_2O_2, O_3, or Cl_2)[123] to incident UV light, the process is known as photooxidation.

Conversely, when oxidizing radicals are generated on the surface of a photo-activated catalyst, typically of a semiconducting nature, the corresponding process is referred to as photocatalysis. In this case, radicals can form from photogenerated electron-holes pairs ($h\nu^+_{vb}$), in the semiconductor valence band, which has oxidizing capacity, and from excited electrons (e^-_{cb}) in the respective conduction band, which have reductive capacity[118,124]. Through these mechanisms, several reactive oxygen species (ROS) are produced, such as superoxide ($^{\bullet}O^{2-}$), hydroxyl radicals ($^{\bullet}OH$), and singlet oxygen ($O(^1D)$)[89].

As previously mentioned, strongly oxidizing hydroxyl radicals are preferred for cyanide degradation, which is commonly produced using a titanium oxide (TiO_2) catalyst[124] (Fig. 7).

Whether employing a photooxidation or photocatalytic approach, cyanide undergoes oxidization to form cyanate. However, while the former involves a simple radical reaction[125], the latter entails a photocatalytic process utilizing electron-hole pairs within the photocatalyst[126].

Biological methods

In recent years, biological treatment of cyanide wastewater has gained popularity among other treatment alternatives, including physical or chemical processes. This approach utilizes microorganisms to remove pollutants from water in a simple, cost-effective, and robust manner[127]. In the case of cyanide, biological methods can reduce its concentration in wastewater to environmentally acceptable levels while also producing fewer harmful by-products[48]. Thus, biological treatment is regarded as an optimal alternative.

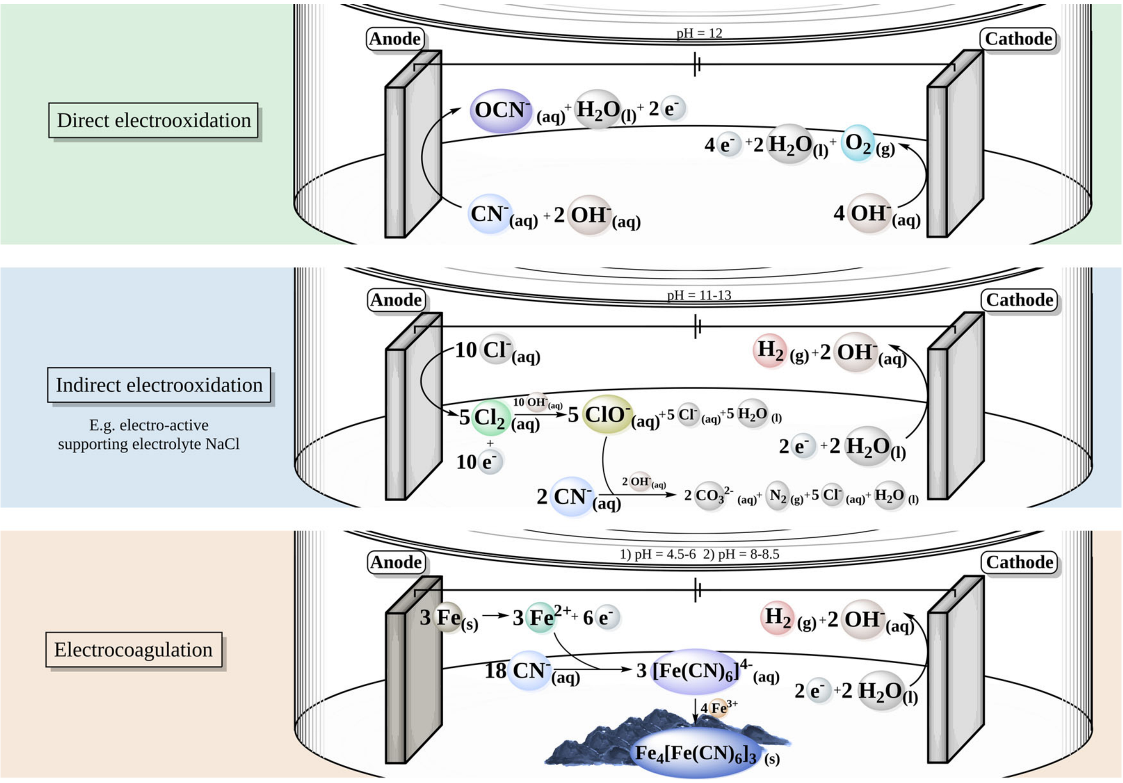


Fig. 6 | Main reactions occurring in conventional electrochemical techniques used for cyanide degradation[112,114].

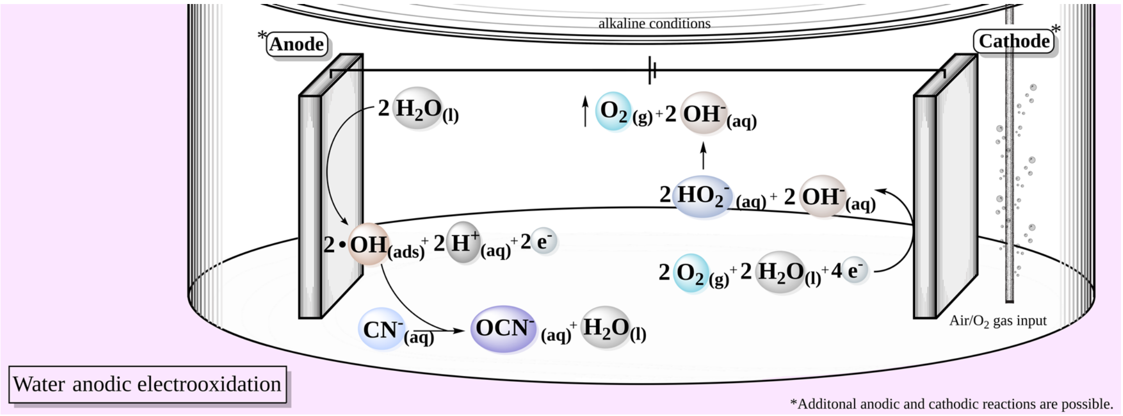


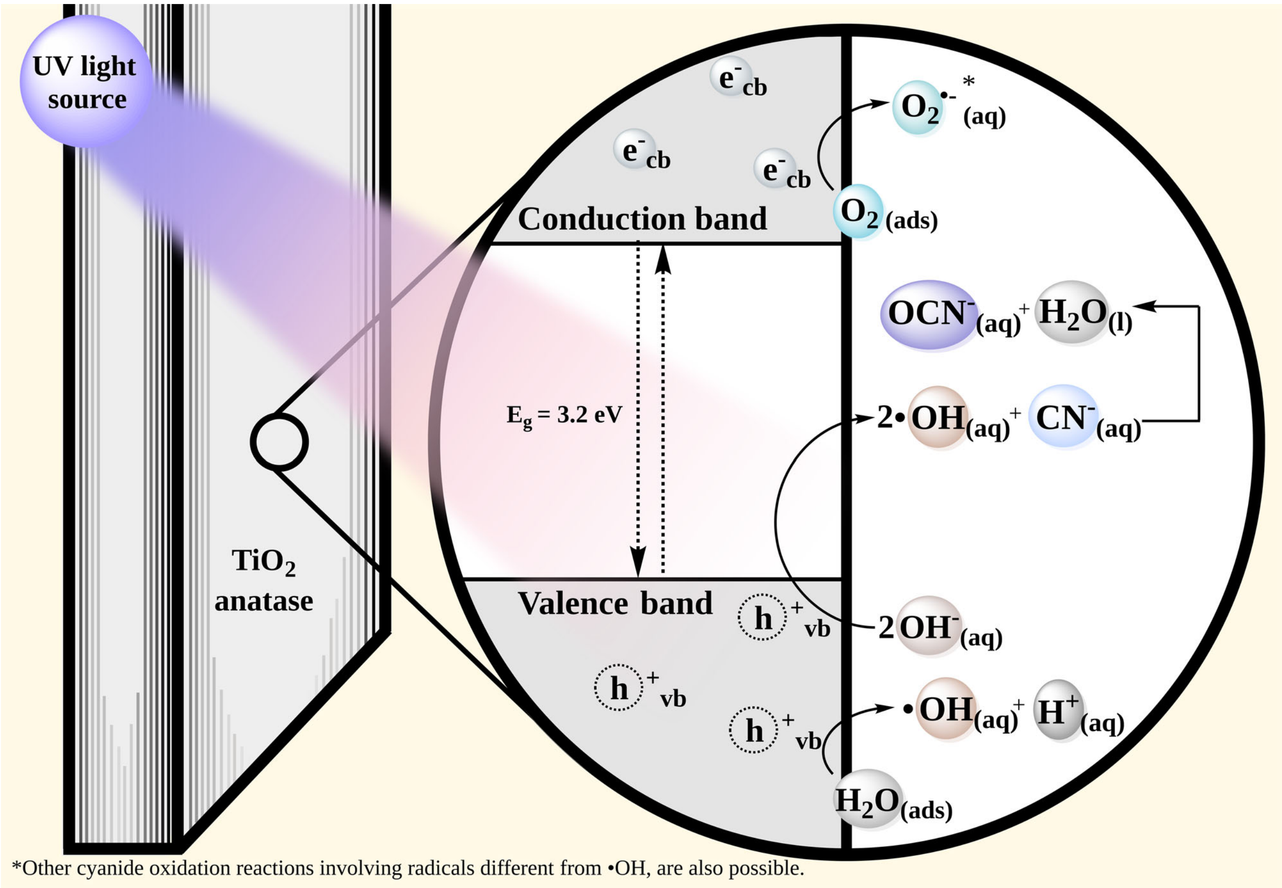
Fig. 7 | Main electrochemical advanced oxidation reaction for cyanide degradation[120,121].

Biological treatment methods range from phytoremediation to microbial bioremediation. Phytoremediation involves the use of plants to remove or reduce cyanide concentrations in water or soil, as plants can utilize cyanide to fulfill their nitrogen needs[128] (Figs. 9a). Conversely, microbial bioremediation relies on the metabolic activities of bacteria, fungi, or microalgae to degrade cyanide[129,130]. These microorganisms use cyanide as a source of nitrogen[131], thus breaking it down through one or more enzymatic pathways[83,131,132] (Fig. 9b). Bacterial strains from the genera *Pseudomonas, Bacillus*, and *Klebsiella*, among others, have been examined in the bioremediation of free cyanide and metallic-complexed cyanide[133].

Even though the above-mentioned bacteria are capable of degrading cyanide, they are still susceptible to its toxicity and that of their derivatives. In general, aerobic bacteria degrade active cyanide via nitrogen metabolism (ammonification−nitritation−nitrification) at the cost of free cyanide toxic inhibition[16,134]. If complexed with Fe^{2+} and Fe^{3+} ions, free cyanide toxic inhibition on aerobes can decrease[134]; nonetheless the metallic protection on cyanide can pose metabolic difficulties due to the complexes' stability[134]. On the other hand, anaerobic bacteria are more prone to degrade cyanide complexes (exhibiting lower toxicity) to cyanate and formamide via cyanide metabolic enzymes despite these complexes' chemical stability[16,134].

It has also been found that bimetallic binding on iron-cyanide complexes can foster cyanide release, and hence allow microbial metabolization. For example, $[Fe(CN)_6]^{4-}$ complex interaction energy (E_{int}) with Cu^+, Cu^{2+} or Ag^+ (i.e., respectively, −0.7, −0.59, −0.68 a.u.) suggests this metals can set free cyanide ligands for microbial degradation, on the contrary to Fe^{3+}, Co^{2+} and Ni^{2+} (i.e., respectively, −2.70, −1.55, −1.57 a.u.)[134].

In addition, research on bacterial-mediated bioremediation has expanded into the burgeoning field of environmental omics, particularly in the context of environmental pollution and remediation technologies, known as *cyanomics*. Like other omics technologies, research on *cyanomics* provides useful information on genes, mRNA, sRNA, and metabolites associated with microorganisms capable of removing



*Other cyanide oxidation reactions involving radicals different from •OH, are also possible.

Fig. 8 | Photochemical reactions behind cyanide's photocatalytic oxidation with TiO_2 catalyst[126].

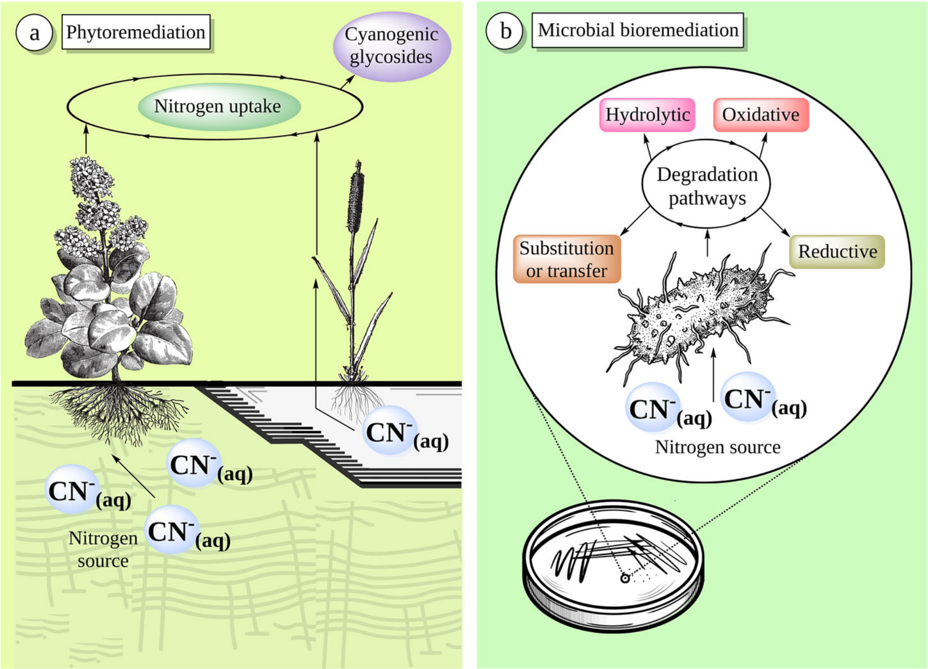


Fig. 9 | Primary biological treatment techniques for cyanide: phytoremediation and microbial bioremediation. a In phytoremediation, plants remove or reduce cyanide in water or soil by using it as a nitrogen source. **b** In microbial bioremediation, bacteria, fungi, or microalgae can metabolize cyanide, thereby degrading it[132].

cyanide from polluted media through their metabolic activities[135]. In terms of cyanotrophic bacteria, cyanomics has enabled the identification of genes and proteins involved in cyanide resistance, as well as those in cyanide degradation, opening possibilities of screening for cyanide-related genes in other bacterial genomes through comparative genome analysis[135].

Furthermore, its essential to emphasize that most state-of-the-art methods are centered on enzymatic processes involved in bacterial-

Table 1 | Latest cyanide wastewater treatments

Treatment type	Method	Overview	Principle	Strengths	Limitations	Ref.
Chemical	Precipitation	Ferrous sulfate-mediated cyanide precipitation	Cyanide is removed as a Prussian blue precipitate after addition of an aqueous ferrous sulfate solution.	Recovered cyanide as Prussian blue can be used for other purposes. Ferrous sulfate is a cost-effective precipitating agent.	Cyanide removal percentage of 58.74% after precipitation. Can increase to 92.42% after samples are filtered with activated charcoal. Low pH levels in samples after precipitation.	142
	Combined oxidation with adsorption	Combined O_3 and H_2O_2 cyanide oxidation with adsorption on activated charcoal	Cyanide is oxidized by hydroxyl radicals derived from O_3 alkaline decomposition through H_2O_2 and activated charcoal's basic surface groups.	H_2O_2 is a green, cost-effective, and commercially available oxidizer. Cyanide removal percentage as high as 99.98%.	Removal is only focused on free cyanide and not cyanide-metallic complexes. Requires an O_3 gas-generating source.	143
	Catalytic oxidation	CuO-catalyzed cyanide oxidation with H_2O_2	Hydroxyl and hydroperoxyl radicals, formed on the surface of CuO nanoparticles, oxidize cyanide in alkaline conditions.	CuO nanoparticles maintain catalyst activity up to four removal cycles. Reported cyanide removal up to 99.99%.	Cu^{2+} ions leach from CuO nanoparticles during cyanide removal at pH 11.	144
		$CuSO_4$-catalyzed cyanide decomposition with H_2O_2 and $Na_2S_2O_5$	Cyanide decomposition is achieved through the Cu^{2+}-catalyzed oxidizing action of H_2O_2 and $Na_2S_2O_5$ in alkaline conditions.	Could be applied to cyanide found in gold leach tailings, tailings, or leachates. Synergetic effect between H_2O_2 and $Na_2S_2O_5$ contributes to optimal cyanide oxidation	Cu^{2+} ions remain in treated water or leachates after cyanide removal. Cyanide removal is achieved through a seven-hour basis treatment.	7
Photochemical	Photochemical oxidation	Cyanide oxidation through UV-LED/ H_2O_2/Cu^{2+} system	Cyanide is oxidized by H_2O_2, and hydroxyl radicals derived from Fenton-like catalytic reactions of the latter and Cu^{2+} ions, under UV-LED (275 nm) irradiation.	Effective for free cyanide and cyanide complexes in presence of metallic ions such as Zn^{2+}. Complete cyanide removal after 30 min treatment.	Removal rate is reduced in presence of Ni^{2+} and Cr^{6+}. Removing cyanate by-products requires acidification. Once turned into ammonia, it may need further treatment to be mineralized.	145
Electrochemical	Electrochemical crystallization	Cyanide removal by electrochemical crystallization of Prussian and Turnbull's blue	Cyanide is removed as crystalized Prussian and Turnbull's blue via electrochemically generated Fe^{2+} ions, at a sacrificial iron electrode.	Cyanide content can be reduced further to < 1 mg L^{-1}. Recovered Prussian and Turnbull's blue can be reused.	Only acidic or neutral conditions favor cyanide removal. Prussian blue recovery is not favored at low or high dissolved oxygen levels.	146
	Ozonation-assisted electrocoagulation	Cyanide removal through ozonation-assisted electrocoagulation using an Al anode	A hydroxyl radical, generated from ozone decomposition in water, initially oxidizes cyanide content. Later, to further lower concentration, remaining cyanide is oxidized on an Al electrode, where by-products are coagulated.	After 40 min of ozonation and 30 min of electrocoagulation, 94.7% of cyanide is removed. Electrocoagulation products are generated in concentrations below maximum allowable limits.	Suitable for removal processes with previous biological oxidation treatment. Combined treatment with ozonation and electrocoagulation is required to reduce cyanide content below maximum allowable limits.	147
	Persulfate-enhanced electrochemical oxidation	Persulfate-enhanced electrochemical cyanide oxidation using boron-doped diamond anode	Cyanide content, under acidic conditions, is jointly oxidized by persulfate ions and hydroxyl radical generated on electrode's surface.	Cyanide removal percentage as high as 98.4% when initial concentration is 1280.15 mg L^{-1} and treatment time is fixed to 24 h. Addition of persulfate to the removal process reduces energy consumption.	Removal process is not optimized for alkaline conditions. Removal temperatures should not exceed 40 °C, as HCN quickly evolves from the acidic aqueous media.	148
	Electrolysis	Electrolysis-aided cyanide removal in hypochlorite media	Cyanide content is anodically oxidized on a graphite anode and further oxidized by hypochlorite and chlorate ions.	May be applied to remove cyanide from gold mining tailings. Applicable to both total and free cyanide.	Maximum allowable limits for Cl^- by-product might be exceeded. TC_4 cathode is required to fully apply the proposed cyanide removal method.	149
Physicochemical	Adsorption on activated charcoal	Adsorption on acid-treated activated charcoal	At pH 7, cyanide is removed by adsorption on the acid-activated charcoal surface, where faujasite and ascroftine content have a positive charge.	94.5% removal Is achieved under just 25 min of treatment and 30 g L^{-1} of activated charcoal. Complete cyanide removal is achieved when its initial concentration approaches 10 mg L^{-1}.	Cyanide adsorption on activated charcoal limited when removal temperature > 30 °C. To ensure maximum cyanide removal, aqueous media must be stirred (120 rpm) continuously.	150
		Cyanide catalytic oxidation by copper-loaded activated charcoal, enhanced by bimetallic synergy	Cu^{2+} ions loaded on activated charcoal, in the presence of Zn^{2+}, lead to cyanide species complexation and further degradation, under oxidative conditions.	Maximum removal capacity found at 24.78 mg/g, under acidic or weakly alkaline reaction conditions. Applicable for low-concentration and bio-refractory total cyanide.	Zn^{2+} secondary pollution is a direct outcome of the catalytic oxidation enhanced by bimetallic synergy.	77
	Adsorption on inorganic adsorbents	Cyanide adsorption on raw and iron-modified synthetic zeolites	Iron-modified zeolites remove cyanide content by surface adsorption and cyanide complex formation, in alkaline media.	Cyanide has a greater affinity to iron-modified zeolite than solely zeolite. Iron-modified zeolite reaches adsorption equilibrium after 24 h of treatment, after which it can be regenerated.	Modifying zeolite with iron reduces its surface area, reducing its adsorption capacity. Removal is hindered under acidic conditions. pH must be 10.5–11.	98
		Alkaline oxidation of adsorbed cyanide on pyrite, with H_2O_2	Cyanide is chemically adsorbed to the iron atoms in the pyrite crystals and subsequently desorbed with alkaline conditions and oxidized by H_2O_2.	May be applied to remove cyanide from mining tailings.	Several treatment by-products: thiocyanate, hexacyanoferrate, and sulfate.	151

Table 1 (continued) | Latest cyanide wastewater treatments

Treatment type	Method	Overview	Principle	Strengths	Limitations	Ref.
				Cyanide adsorption on pyrite is observed in a wide range of temperatures (25–85 °C)		
		Photocatalytic cyanide removal with green ZnO nanoparticles	Light-irradiated ZnO nanoparticles liberate electrons, which react with atmospheric oxygen to form H_2O_2. This later oxidizes cyanide.	ZnO nanoparticles are synthesized by green methods. 98% of cyanide is removed after 20 min treatment with 3 g L^{-1} of nanoparticles and UV-light irradiation.	Removal reaches only 45% when sunlight is used instead of UV light. Care must be taken when preparing nanoparticles with *Eucalyptus Globulus* extract, especially when experience with green nanoparticle synthesis is lacking.	152
	Adsorption on organic adsorbents	Cyanide adsorption on calcium alginate hydrogels	Cyanide removal is driven by adsorption on active sites of alginate sphere surface.	Applicable for free cyanide and metallic-cyanide complexes. No adsorption by-products.	Maximum cyanide removal of 85.02% achieved after two treatment cycles. Addition of activated charcoal or bioadsorbent to alginate spheres does not increase cyanide removal.	153
		Cyanide adsorption on coke breeze	Cyanide removal by adsorption is driven by cyanide's nitrogen atom interactions with superficial carbonyl groups.	Coke breeze, a by-product of steel production, is reused Considered a cost-effective treatment as adsorbent is not purchased.	Removal temperatures can only vary between 25 °C–45 °C basis. Removal improved in acidic or neutral conditions.	154
		Cyanide adsorption on thermal and acid-treated kaolin	Cyanide removal achieved through its adsorption on the acid-treated kaolin, facilitated by presence of SiO_2 and Al_2O_3 moieties.	Cost-effective removal method. Kaolin given new application beyond industrial uses.	Kaolin must be first converted into metakaolin via calcination (600 °C), before cyanide removal can start. During cyanide removal, aluminum ions leach from the kaolin.	155
		Cyanide adsorption on biochar	Cyanide removal driven by its adsorption on the biochar's surface.	Cost-effective removal method. Applicable cyanide and heavy metal removal from gold wastewater.	Maximum cyanide removal of 75%. For maximum removal, a 12 h treatment required.	156
	Adsorption on bioadsorbents	Cyanide adsorption on rice husks	At pH 7, cyanide is removed by its adsorption on rice husks' active surface sites.	Cyanide removal as high as 97%. An agricultural waste, rice husk is repurposed.	Removal process requires a pump system, and a column packed with the bioadsorbent.	157
		Cyanide adsorption on natural bitumen	Cyanide removed by surface adsorption on bitumen, facilitated by favorable interactions between cyanide and surface groups, e.g., phenol, carbonyl, amide, pyrrole.	Cost-effective removal method. Removal process is completed in just under 30 min.	Maximum cyanide removal reported as 61.64%. For optimal cyanide removal, gilsonite content in bitumen must be previously processed through flotation.	158
		Cyanide adsorption on pistachio shell waste	At pH 10, removal facilitated by cyanide chemical adsorption through intraparticle diffusion on pistachio shell.	Cost-effective removal method. Cyanide removal as high as 99%, after 60 min treatment.	Cyanide removal decreases beyond an initial cyanide concentration of 200 mg L^{-1}.	159
		Cyanide adsorption on lemon peel	At pH 8, surface carboxylic group in lemon peel removes cyanide by adsorption.	Cost-effective removal method. Cyanide removal as high as 99% after 25 min treatment.	Removal process requires a pump system, and a column packed with the bioadsorbent.	160
Biological	Phytoremediation	Water hyacinth (*Eichhornia crassipes*)-aided cyanide removal	Cyanide is adsorbed by the water hyacinth's extensive root system and is bioaccumulated in vegetal tissues.	Cyanide removal is achieved without any chemical substances or specialized equipment. A 92.66% cyanide removal rate can be achieved from an initial cyanide concentration of 20 mg L^{-1}.	13-day period required for maximum cyanide removal. Removal process poisons the water hyacinth, destroying its photosynthetic system.	161
		Mono and dicotyledon -aided cyanide removal	Mono and dicotyledon plants bioaccumulate cyanide in their roots, stems, and leaves.	Applicable for in situ treatment of gold mining tailings. Method can be further applied for Mn and As removal.	If monocotyledon plants are used, care must be taken as they are more susceptible to fungal infection, rendering them useless for phytoremediation.	162
	Microbial remediation	Cyanide biodegradation using *Aerococcus viridians* strain	Bacterial enzymes degrade cyanide into less or non-toxic products	High bacterial resistance to cyanide, up to a concentration of 550 mg L^{-1} Cyanide removal up to 84.1% and 86.7%, for initial free cyanide of 200 and 150 mg L^{-1} CN^- (pH 7–8, 34 °C), respectively.	Carbon and nitrogen sources for bacterial metabolic activities are needed for subsequent cyanide biodegradation. Prolonged growth time, up to 72 h, needed for bacterial biodegradation.	163
		Cyanide biodegradation using indigenous bacterial strains	Cyanide removal achieved by bacterial metabolic activities using cyanide as nitrogen source	Highest cyanide biodegradation achieved at alkaline conditions (pH 9), thus preventing cyanide volatilization	Ammonia is released as by-product of bacterial bioremediation. Prolonged bacterial growth periods (i.e., 4 days).	164
	Enzymatic remediation	Nitrilase-mediated biodegradation of cyanide	Nitrilase enzyme isolated from *Enterobacter* zs (PTCC 1909) degrades cyanide into ammonia and carbon dioxide	Highest removal rate was 73% with 650 mg L^{-1} of initial free cyanide	Costly separation techniques are required to isolate the desired enzyme. Enzyme's stability post-extraction not assessed.	165

mediated cyanide degradation[136]. Among these methods, preferred strategies often include the isolation of new bacterial strands from contaminated media that are capable of degrading cyanide, as well as the extraction of bacterial enzymes to use as catalysts in biodegradative reactions. Other related emerging cyanide bioremediation methods include electrochemical-based methods such as electro-bioremediation (EK-Bio) for in situ remediation, microbial fuel cell technologies, and anaerobic cyanide biodegradation in small reactor setups, with additional biogas formation[83].

Innovations in cyanide wastewater treatment

For a more comprehensive understanding of these treatment methods, this review examines the latest research pertaining to each technique, clarifying their fundamental principles and associated strengths and limitations (Table 1).

Future directions

Given the persistent threat posed by cyanide's high toxicity and ongoing use, research on mitigating its impact is being carried out in several scientific areas. The pursuit of the most efficient and cost-effective degradation methods remains paramount. Consequently, novel methodologies will continue to be developed with the aim of achieving maximum reduction of this pollutant in water, while ensuring economic viability.

While the removal of cyanide from wastewater remains the primary objective, it is worth considering the potential value of cyanide waste in different industries. For instance, cassava residues (which contain a significant amount of cyanide) from the agro-industry could be repurposed to produce biosurfactants or biogas[137,138], thereby offering products with lesser environmental impact. Similarly, cyanide residues produced in gold mining operations could be used for new extraction processes, presenting an economically viable alternative for purchasing cyanide for gold mines[139,140]. Numerous other scenarios wherein cyanide is produced as waste warrant further investigation.

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Author contributions

Conceived the project, K.V.-E. and P.J.E.-M.; visualization, K.V.-E. and P.J.E.-M.; supervision, K.V.-E. and P.J.E.-M.; investigation, D.A.-A., K.V.-E., and P.J.E.-M.; writing—original draft preparation, D.A.-A., K.V.-E., and P.J.E.-M.; writing—review and editing, D.A.-A., K.V.-E., and P.J.E.-M.; project administration, P.J.E.-M.; funding acquisition, P.J.E.-M. All authors have read and agreed to the published version of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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