Review

Cyanide in industrial wastewaters and its removal: A review on biotreatment

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ABSTRACT

Cyanides are produced by certain bacteria, fungi, and algae, and may be found in plants and some foods, such as lima beans and almonds. Although cyanides are present in small concentrations in these plants and microorganisms, their large-scale presence in the environment is attributed to the human activities as cyanide compounds are extensively used in industries. Bulk of cyanide occurrence in environment is mainly due to metal finishing and mining industries. Although cyanide can be removed and recovered by several processes, it is still widely discussed and examined due to its potential toxicity and environmental impact. From an economic standpoint, the biological treatment method is cost-effective as compared to chemical and physical methods for cyanide removal. Several microbial species can effectively degrade cyanide into less toxic products. During metabolism, they use cyanide as a nitrogen and carbon source converting it to ammonia and carbonate, if appropriate conditions are maintained. Biological treatment of cyanide under anaerobic as well as aerobic conditions is possible. The present review describes the mechanism and advances in the use of biological treatment for the removal of cyanide compounds and its advantages over other treatment processes. It also includes various microbial pathways for their removal.

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Contents

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1. Introduction

Cyanide is a carbon–nitrogen radical, which may be found in a wide variety of organic and inorganic compounds. A common form, hydrogen cyanide is a colorless gas or liquid with a faint, bitter, almond-like odour [1]. Cyanide, in some forms, is a very powerful and fast acting toxin. When combined with metals and organic compounds forms simple and complex salts and compounds, the most commonly used forms being hydrogen cyanide, sodium cyanide, and potassium cyanide. Hydrogen cyanide can be a very dangerous fire hazard when exposed to heat, flame, or oxidizers. All forms of cyanide can be toxic at high levels, but hydrogen cyanide is the deadliest form of the toxins. At short-term exposure, cyanide causes rapid breathing, tremors, and other neurological effects and long-term exposure to cyanide cause weight loss, thyroid effects, nerve damage and death [1]. Skin contact with liquids containing cyanide may produce irritation and sores.

1.1. Sources of cyanide

In spite of its toxicity, cyanide is found in a wide range in the various life forms including photosynthetic bacteria, algae, fungi, plants and foods (such as beans, almonds and cashew nuts, etc.) and even in the animal kingdom such as in centipedes, beetles and in few species of butterflies, etc. [1,2]. Cyanide occurs naturally in cassava roots and potato-like tubers grown in tropical countries. Cyanide can enter surface water through releases from metal finishing industries, iron and steel mills, runoff from disposal of cyanide wastes in landfills, pesticides, and the use of cyanide-containing road salts. Most cyanide in surface water forms hydrogen cyanide and evaporates. Cyanide is commonly found as a contaminant in wastewaters from various industries including metal cleaning, plating, electroplating, metal processing, automobile parts manufacture, steel tempering, mining, photography, pharmaceuticals, coal coking, ore leaching, plastics, etc. [3,4].

Cyanide may be present in the environment in a variety of forms, including HCN, salts (such as NaCN or KCN) and various cyanide complexes (such as $Zn(CN)_2$ and potassium ferricyanide) [2–8]. Cyanides are not strongly adsorbed or retained within soils, so they remain in the aqueous phase and often form complexes with other, metallic contaminants of industrial effluents, such as Fe, Cu, Ni and Zn. Although KCN and NaCN readily dissociate to form CN^- and HCN at neutral pH, the metallo-cyanide complexes have a wide range of chemical and biological stabilities. Metal-complexed cyanides are classified according to the strength of the metal cyanide bond. Free cyanide refers to the most toxic forms of cyanide: cyanide anion and hydrogen cyanide. Weak-acid dissociable (WAD) [6,7] refer to cyanide complexes with metals such as cadmium, copper, nickel and zinc. Although thiocyanate (SCN) is a WAD, it is often considered in its own category. Strong-acid dissociable (SAD) [6,7] refer to cyanide-complexes with metals such as cobalt, gold, iron and silver. Cyanides also exist as organic cyanides in the form of nitriles like acrylonitrile, propinonitrile, etc. [9].

The industrial effluents generally contain between 0.01 and 10 mg/L of total cyanide [10,11]. However, some cyanide wastes from individual operations at electroplating and metal finishing plants can be stored for periods of years, after which the effluent may contain from 1% to 3% (10,000–30,000 mg/L) [10,11] of cyanide. In fact some industrial effluents from electroplating plants have been found to contain even higher cyanide levels of 100,000 mg/L [10,12]. These effluent cyanide concentrations of these industries are found very high as compared to cyanide levels of about 0.001–0.05 mg/L [10] found in unpolluted stream and lake water. Cyanide concentrations and speciation characteristics reported in the literature for various industrial wastewater effluents have been presented in Table 1.

Speciation investigations have found that the relationship between simple and complex cyanide species in industrial effluents is not consistent. For example, the complex forms of cyanide found in effluents from the chemical manufacturing plants can be either 0% or 100% of the total cyanide content. However, generally it appears that the cyanides in industrial effluents are found predominantly in complexed species. Thiocyanate (SCN) is one of the most important cyanide complex species present in industrial effluents, being found in some coal coking and coal conversion effluents in the concentration range 17–1500 mg/L SCN [14]. Thiocyanate concentrations ranging from 11 to 50 mg CN^-/L have been detected in effluents emanating from chemical manufacturing plants [30]. From this it is apparent that many industrial wastewater effluents contain elevated cyanide concentrations.

1.2. Effluent disposal standards of cyanide

To protect the environment and water bodies, effluents containing cyanide from various industries must be treated before discharging into the environment. Hence many countries and environmental protection agencies have imposed limiting standards for discharge of cyanide bearing wastewater to sewers. The US Environmental Protection Agency (USEPA) has proposed a limit for drinking and aquatic-biota waters regarding total cyanide are 200 and 50 ppb, respectively, where total cyanide refers to free and metal-complexed cyanides [31,32]. The German and Swiss regulations have set limit of 0.01 mg/L for cyanide for surface water and 0.5 mg/L [33] for sewers. In Mexico, disposal limit for cyanide has been set as 0.2 mg/L [33]. In India Central Pollution Control Board (CPCB) has set a minimal national standard (MINAS) limit for cyanide in effluent as 0.2 mg/L [31]. In view of these considerations cyanide recovery and/or removal is necessary for lowering the concentrations of cyanides to below regulatory limits.

2. Cyanide removal technologies

Because of the potential hazards associated with cyanide, control and remediation of cyanide-contaminated water is usually desired. Cyanide-contaminated water is often treated by alkaline chlorination or biological oxidation process [3,6]. These techniques are only effective for free cyanide (HCN, CN^-) and cyanide that is weakly bonded to metals. Cyanide that is strongly bonded or complexed with metals cannot be treated with these methods. To reduce the cyanide level for disposal of the effluent (<0.2 mg/L), several cyanide treatment systems have been developed. All these methods are based on cyanide recovery by acidification and/or destruction by chemical oxidation [5,6]. In many cases the process is burdened with high reagent costs and royalty payments. Table 2 presents the advantages and disadvantages of various cyanide treatment technologies commonly adopted. The type of cyanide compounds that can be removed or treated by a certain process has also been enlisted in that table.

The most commonly adopted method for cyanide-contaminated effluent treatment is the chemical oxidation techniques such as the alkaline-chlorination–oxidation process [2,33,6,7]. Here the cyanide containing waste is initially treated with chlorine or hypochlorite to produce cyanogen chloride, which then reacts to form the much less toxic sodium cyanate. Further, chlorination oxidizes the cyanate to carbon dioxide and nitrogen. Although this method of treatment can be very efficient in detoxifying free cyanide bearing wastes, it has several disadvantages [10]. Chlorination is not effective in the case of cyanide species complexed

Table 1
Concentration of cyanide emitted from various industries Industrial effluents reported (mg CN$^-$/L)

Industrial wastewater source	Simple	Complex	Total	Simple[c] (%)
Coke-oven wastewater [13]			54.8[b]	
Coke plant [14]			100–1000[b]	
Coke plant [14]			1.6–6.0[b]	
Coke plant [14]			0.1–0.6[b]	
Coke plant [14]			0.1–0.7[b]	
Coke plant [14]	0.3	25.4[a]	25.7[a]	1.17
Coke oven plant [15]			10–150[a]	
Coke plant waste [16]			10–38.1[b]	
Coke plant waste [17]			91–110[b]	
Coke plant waste streams [18]				
Coke oven liquor			0–8[b]	
Decantation tank			8[b]	
Final cooler condensate			196[b]	
Benzole separator			2736[b]	
Oil generation plant separator			104[b]	
Spent limed liquor			4[b]	
Coke plant ammonia liquor [19]			2–44.5[b]	
Coke plant ammonia liquor [17]			20–60	
Coal conversion (synthane) [17]			1–6	
Coal conversion wastes [17]			2–30	
Electroplating plants [10]	0.03–0.07	0.0–0.2[a]	0.03–0.27[a]	26–100
Electroplating plants [10,20]			0.01–14.24[b]	
Electroplating plants/PCB plants [21]			3.0–59.0[b]	
Electroplating plants [3]			3.6–6.6[b]	
Plating rinse [16]			0.3–4[b]	
Plating rinse [16]			32.5[b]	
Plating rinse [17]			25[b]	
Plating rinse [22]			60–80[b]	
Plating rinse [23]			30–50[b]	
Plating rinse [16]			1.4–256[b]	
Plating industries (rising waste) [12]			1.4–256[b]	
Plating industries (plating bath) [10]			4000–100,000[b]	
Plating bath [24]			30,000[b]	
Plating bath [25]			45,000–100,000[b]	
Plating bath [19,26,27]				
Brass			16,000–48,000[b]	
Bronze			40,000–50,000[b]	
Cadmium			20,000–67,000[b]	
Copper			15,000–67,000[b]	
Silver			12,000–60,000[b]	
Tin–zinc			40,000–50,000[b]	
Zinc			4000–64,000[b]	
Alkaline cleaning bath [23]			4000–8000[b]	
Blast furnace scrubber water [17]				
Steel making segment (range)			0.2–1.4[b]	
Steel making segment (max)			2.4[b]	
Blast furnace gas wash			48.5[b]	
Steel mill coke plant liquor [17]			7.5–396[b]	
Color film bleaching process [28,29]			71[b]	
Paint and ink formulation [17]			0–2[b]	
Bright dip [23]			15–20[b]	
Chemical industry [30]	0–0.03	10.4–50.9[a]	10.4–50.9[a]	0–0.3
Gold ore extraction [17]			18.2–22.3[b]	
Explosives manufacture [17]			0–2.6[b]	
Oil refinery [10]	0.0	2.25[a]	2.25[a]	0
Petroleum refining [17]			0–1.5[b]	

[a] Includes thiocyanate.
[b] Unspecified whether thiocyanate included.
[c] % of total cyanide concentration.

with metals such as nickel, silver, etc. due to slow reaction rates [3]. The process also produces sludge, which requires licensed disposal. Another disadvantage is that it is relatively expensive due to the quantity of chlorine required. Further, the addition of excess chlorine increases the total solids content of water, making it undesirable for recycling and reuses purposes and leaves a residue with a high chlorine content which is toxic to aquatic life [9,82]. In addition, various chlorinated organics may be produced if the wastewater contains organic substances.

In order to keep operational costs as low as possible, frequently effluents are only partially treated to the cyanate phase or in many cases the undecomposed metal cyanides containing effluents are directly discharged without treatment. Other methods for the treatment of cyanide containing wastes include copper-catalyzed hydrogen peroxide oxidation [83], ozonation [33], electrolytic decomposition [10,33,6,84], etc. However, these methods are also expensive and require special equipments and maintenance. Thus, there is an urgent need for the development of an alternative treat-

Table 2
Salient features of various cyanide removal technologies

Removal methods	Advantages	Disadvantages	Further treatment required?	Removes			
				Free CN	Thiocyanate	WAD metal complex	SAD metal complex
Biological oxidation/biodegradation [3,28,34–44]	Natural approach, received well publicity, and by regulators Use heaps as reactors reducing total washed volume, and possibly reach low flow areas of the heap more effectively Relatively inexpensive Biomass can be activated by aeration Can treat cyanides without generating another waste stream No chemical handling equipment or expensive control needed Cost is fixed with greater volumes of waste also Superior resistance to shock and upsets No toxic byproducts, hence environmental friendly	Technology is not well established Requires combination of metallurgy, biology and process engineering Tends to be very site specific with specific evaluation and study require for each type Can not treat high concentrations	No	Yes	Yes	Yes	Yes
Alkaline chlorination [3,6,35,45–48]	Technology well established The cyanate is relatively less toxic and further oxidized to carbon Dioxide and nitrogen at lower pH Remove metals through precipitation at elevated pH	Adds potentially objectionable cations/anions to water Excess hypo-chlorite is toxic Chlorine can react with organics to form chlorinated compounds Poor process control results in toxic intermediates Reacts preferentially with thiocyanate Many of the less expensive hypochlorite sources require special handing	Yes	Yes	Yes	Yes	No
Hydrogen peroxide [3,17,45,49–52]	Excess reagent decomposes to water and oxygen Relatively simple to operate Is not as reactive with thiocyanate	Reagent costly If precipitating ferrocyanides with copper, must dispose of precipitate Requires accurate measurement of chemical dose	Yes	Yes	No	Yes	Some
SO$_2$/air (INCO) process [3,17,45,49–52]	Reagent is very inexpensive For treating aqueous solutions and gold mine waste sludges Used over a wide pH range	At least some of reagent savings are offset by license/royalty payments Process adds sulfates to treated water If precipitating ferrocyanides with copper, must dispose of precipitate	Little	Yes	Some	Yes	Yes
Ozonation [6,17,33,45,49,50,53,54]	Some regeneration of cyanide possible	Produce ammonia Reagent cost and equipment	Yes	Yes	Yes	Yes	No
Anodic oxidation [6,55–61]	Treat all cyanide baths regardless of concentration	Require post treatment by a number of oxidation method	Yes	Yes	Yes	Yes	No
Electrodialysis [6,17,45,46,49,62]	Efficient in treatment	Costly Applicable to certain type of waste	No	Yes	Yes	Yes	Yes
Reverse osmosis [3,6,38,62,63]	Efficient in treatment	Costly External pressure and power require Applicable to certain type of waste	No	Yes	Yes	Yes	Yes

Method	Advantages	Disadvantages					
Electrowinning [6,38,45,64,65]	Performs well in concentrated solution Useful in gold processing	Proper controlled condition require Can not be directly used for removal Technology not properly established Thiocyanate does not respond Free cyanide liberated Not useful at low concentrations	Yes	No	No	Some	Some
Hydrolysis/distillation [5,6,45]	Simple methodology	High temperature, pressure and air requirement Production of hydrogen cyanide gas again difficult to be disposed of	Yes	Yes	No	No	No
AVR (acidification/volatilization and reneutralisation) [5,6,17,45,49,65]	Reduced energy consumption and increased volatilization	High acid consumption Sludge of gypsum is high Require specially designed reactor	Some	Yes	Some	Yes	Some
Flotation [6,66]	Separates SAD complexes by natural precipitation	Chances of decomposition and redissolution of precipitates	Most	Yes	Little	Most	Some
Iron cyanide precipitation [6,49,67,68]	Widely used as a polishing process Used suitably for mining industry	Limited to suitability to situations Works only with low concentrations of cyanide Maintaining pH is difficult Disposal of precipitate again a problem		Most	Some	Yes	Yes
Activated carbon [6,16,69–71]	Effective method Used as a polishing process	Cost is more Require good treated activated carbon Used only for low concentrations of cyanide Some times pretreatment required	Little	No	Some	Most	Yes
Resin [6,72,73]	Efficient	Pretreatment require Difficult to find suitable resin	Little	Some	Some	Yes	Yes
Catalytic oxidation [6,45,74–78]	Effective in presence of copper or other catalysts	Not a full treatment process Technology not well established	Yes	Yes	Yes	Yes	Some
Caro's acid [5,6,45]	Useful on site treatment Used where SO$_2$/air process is not suitable	Difficult to handle as it readily decompose to oxygen and sulfuric acid Not applicable to all type of site Limited application	Little	Yes	Yes	Yes	Some
Photolysis [6,45,79–81]	Effective process No undesirable by product Complete removal process	Requires high energy Difficult to operate Cost is more	Yes	Yes	Yes	Yes	Yes

ment process capable of achieving high degradation efficiency at low costs.

Although chemical and physical processes can be employed to degrade cyanide and its related compounds, they are often expensive and complex to operate. A proven alternative to these processes is biological treatment, which typically relies upon the acclimation and enhancement of indigenous microorganisms. Biological degradation of cyanide has often been offered as a potentially inexpensive and environmentally friendly alternative to conventional processes [31].

3. Bioremoval of cyanide compounds

Bioremoval/biotreatment can be less expensive than chemical and physical methods, but much faster than natural oxidation. The biodegradation of cyanide under anaerobic conditions has also recently demonstrated the feasibility for concomitant biogas generation, a possibly economic benefit of the process [8]. Significant advances have been reported in the use of plants for the phytoremediation [4] of cyanide compounds and evidence for the biodegradation of thiocyanate and metal–cyanide complexes has become available. Destruction of cyanide by microorganisms from tailings solutions and other process wastewaters is a proven alternative to traditional chemical and physical processes [3,9,82]. Although feasible, oxidation processes for cyanide degradation in settling ponds are expensive and can bring about environmental problems. The biological treatment methods have a higher capital cost, but a significantly lower operating cost, so that the present-worth cost is significantly lower for the biological method [35].

Biological processes, which might satisfy both the needs of extraction and environmental control, have been proven at large scale in well-understood and engineered systems in several countries [5]. In biological treatment of cyanide, bacteria convert free and metal-complexed cyanides to bicarbonate and ammonia, while the free metals are either adsorbed within the biofilm or precipitated from solution. The ease with which the metal cyanide complexes are degraded generally follows their order of chemical stability with free cyanide being the most readily degradable and iron cyanide the least. The degradability of the other metal cyanide complexes of Zn, Ni, and Cu are moderate [5–7]. Biodegradation as well as bioadsorption of iron cyanides are less as compared to Zn, Ni, and Cu cyanide complexes.

The microorganisms involved in the biological treatment of cyanide and thiocyanate usually include a heterogeneous mixture of commonly found indigenous soil bacteria which have through continuously extended exposure adapted to the treatment of these compounds [85]. Although cyanide is readily degraded by anaerobic bacteria, thiocyanate is not readily removed through anaerobic biological treatment. In addition, anaerobic biological treatment is slower and more susceptible to toxic upsets resulting from exposure to other constituents present in the solution being treated. As a result, the proper approach is to use an attached or suspended growth aerobic biological treatment process for thiocyanate removal. The most critical environmental factors associated with biological treatment include pH, temperature, oxygen levels, and nutrient availability [86].

The microorganisms responsible for cyanide degradation are generally divided into two classes as: Bacteria and Fungus. There are a variety of attached and suspended growth processes available for the aerobically biological treatment of cyanide and thiocyanate. These include rotating biological contactors, packed beds [87], biological filters, sequencing batch reactors [88], facultative lagoons, and activated sludge systems.

3.1. Factors affecting the environmental fate of cyanides biodegradation

The success of biodegradation depends upon the presence of microbes with the physiological and metabolic capabilities to degrade the pollutants in the contaminated environment. Cyanide compounds are found widely in nature and microbial metabolism of these compounds by various strains is also possible. However, the concentrations of cyanides within a soil or water can have a significant impact on biodegradation. For example, acetonitrile at high concentrations proved toxic to *Klebsiella oxytoca*, by causing damage to the nitrile degrading enzyme nitrile hydratase and inhibiting the biodegradation of the compound by the organism [9]. Also, the availability of nutrients may affect the biodegradation of cyanide compounds. Carbon has been identified as a limiting factor in the microbial degradation of metal–cyanides, which may prevent the bioremediation of industrially contaminated soils [86]. The availability of oxygen is a significant factor in the microbial mineralisation of cyanide, as oxygen is consumed during several of the cyanide degrading pathways [86]. Cyanide can be toxic to anaerobic bacteria, particularly methanogens. Additional pollutants present at contaminated sites may also affect biodegradation. The presence of high concentrations of co-contaminants can impact on cyanide degradation by influencing the indigenous microbial population, selecting for, or inhibiting, the growth of particular organisms [9,86].

Temperature is an important parameter for determination of biodegradation rate. Cyanide degrading enzymes are generally produced by mesophilic microorganisms, often isolated from soil, with temperature optima typically ranging between 20 and 40 °C [82,86,89–92]. The pH may be a particularly important factor in the bioremediation of cyanide-contaminated soils. The pH optima for bacterial and fungal growth are typically 6–8 and 4–5, respectively, and cyanide degrading enzymes generally have pH optima between 6 and 9, therefore, extremes of pH may have a significant effect on biodegradation. However, *Fusarium solani* and mixed cultures of fungi, including *F. solani*, *Fusarium oxysporum*, *Trichoderma polysporum*, *Scytalidium thermophilum* and *Penicillin miczynski*, were capable of degrading iron cyanides at pH 4 [93].
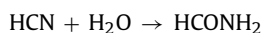
3.2. Degradation pathways of cyanide and nitriles

Several reports have described the common biodegradation pathways of cyanides. However, additional organisms with the capacity for cyanide biodegradation with new pathways [86,8] are continuously reported. There are four general pathways [94] for the biodegradation of cyanide: hydrolytic, oxidative, reductive, and substitution/transfer [8].
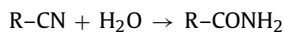
3.2.1. Hydrolytic reactions

Hydrolytic reactions are catalyzed by some enzymes, such as cyanide hydratase, nitrile hydratase, cyanidase and nitrilase [2,86,8]. Cyanide hydratase and cyanidase act on HCN whereas other two act on nitriles. These enzymes degrade the cyanide compounds through different reactions. These reactions are listed below as [8,35]:
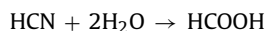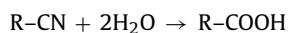
Cyanide hydratase

$$HCN + H_2O \rightarrow HCONH_2$$

Nitrile hydratase

$$R\text{–}CN + H_2O \rightarrow R\text{–}CONH_2$$

Cyanidase

$$HCN + 2H_2O \rightarrow HCOOH$$

Nitrilase
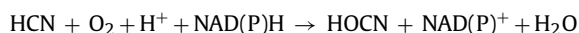
$$R–CN + 2H_2O \rightarrow R–COOH$$

Most frequently encountered cyanide conservation in fungal species is due to cyanide hydratase [8]. The cyanide hydratase activity is induced by low concentrations of cyanide in many fungi pathogenic to cyanogenic plants such as *Stemphylium loti* and *Gloeocercospora sorghi* [35]. *Fusarium* sp. uses cyanide hydratase to degrade cyanide [90]. This pathway results in irreversible conversion of cyanide into formamide and this ultimately gets converted into CO_2 and NH_3. This pathway has also been reported in the bacterium *Pseudomonas fluorescens* [95]. Cyanide hydratase and cyanidase are bacterial enzymes and have similarity at both the amino acid and structural levels to nitrilase and nitrile hydratase enzymes [8]. The biodegradation of organic cyanides (nitrites) has been reported by enzymes nitrilase or nitrile hydratase coupled with amidase [35]. Nitrilases and nitrile hydratases convert both aliphatic and aromatic nitriles to the corresponding acid or amide, respectively, but show less substrate specificity than cyanide hydratase and cyanidase [8]. Nitrile hydratase has been used by *K. oxytoca* for degradation of various nitrile compounds [9]. The presence of nitrile hydratase and amidase has also been shown in *Rhodococcus rhodochrous* Jl, *Rhodococcus* sp. N-774, *Brevibacterum* sp. R312, *Pseudomonas chlororaphis* B23 and several other bacteria [35].

3.2.2. Oxidative reactions

The oxidative reactions for the biodegradation of cyanide form ammonia and carbon dioxide. Cyanide monoxygenase [8,94] converts cyanide to cyanate. The cyanate is then catalyzed by cyanase resulting in the conversion of cyanate to ammonia and carbon dioxide. Cyanases have been identified in numerous bacteria, fungi, plants and animals. A second oxidative pathway utilizes cyanide dioxygenase to form ammonia and carbon dioxide directly [8].

Cyanide monoxygenase

$$HCN + O_2 + H^+ + NAD(P)H \rightarrow HOCN + NAD(P)^+ + H_2O$$

Cyanide dioxygenase

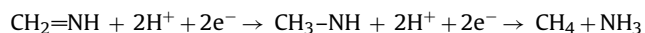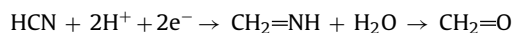$$HCN + O_2 + 2H^+ + NAD(P)H \rightarrow CO_2 + NH_3 + NAD(P)^+$$

Immobilized cells of *P. putida* can effectively use oxidative pathway to produce ammonia and carbon dioxide [96]. Various *Pseudomonas* species are responsible for complete oxidation of cyanide and thiocyanate [2,8]. Microorganisms like *Pseudomonas fluorescence*, utilize the cyanide as nitrogen source for their growth and catalyze the conversion of HCN with the consumption one mole of oxygen per mole of cyanide along with either NADH or NAD(P)H, using the enzyme cyanide oxygenase. It has also been reported that the enzyme responsible for the conversion of the cyanide into ammonia and carbon dioxide by cell free extracts of *P. fluorescens*, NCIMB 11764 was found to be cyanide monooxygenase with the formation of cyanate as a metabolic intermediate [35].

3.2.3. Reductive reactions

This is not much common and enzyme required for such pathway is found in rare species. These reactions follow a two step

mechanism [94] resulting in the formation of methane and ammonia [8,35].

$$HCN + 2H^+ + 2e^- \rightarrow CH_2=NH + H_2O \rightarrow CH_2=O$$

$$CH_2=NH + 2H^+ + 2e^- \rightarrow CH_3–NH + 2H^+ + 2e^- \rightarrow CH_4 + NH_3$$

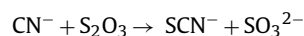*K. oxytoca* is able to degrade cyanide compounds to methane and ammonia [82].

3.2.4. Substitution/transfer reactions

Cyanide may be converted into β-cyanoalanine [94] or α-aminonitrile, catalyzed by β-cyanoalanine synthase, followed by hydrolysis of the products to release NH_3 and an acid. During this process there is no direct requirement for O_2 or NAD(P)H, nor is CO_2 released. Another pathway results in the conversion into thiocyanate which is less toxic than cyanide compounds. The thiocyanate produced from the above process by sulfurtransferase enzymes could then be biodegradaded either by carbonyl pathway or cyanate pathway. The biodegradation of thiocyanide by carbonyl pathway (in the presence of thiocyanate hydrolase) produces carbonyl sulfide (COS). The biodegradation of thiocyanate by cyanate pathway (in the presence of cyanase) resulted in the formation of sulfate and CO_2. Ammonia is produced in both the cases [8]. Cyanase has also been detected in *Flavobacterium* sp. and *Eschericia coli*. Cyanase from *E. coli* has been found to possess 156 amino acid residues [35]. The fungi *Acremonium strictum* produced ammonia and sulfate from thiocyanate. The degradation pathway for cyanide by sulfurtransferase enzymes has been shown below:

Cyanoalanine synthase

$$Cysteine + CN^- \rightarrow \beta\text{-cyanoalanine} + H_2S$$

$$OAS + CN^- \rightarrow \beta\text{-cyanoalanine} + CH_3COO^-$$
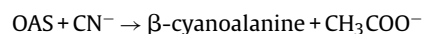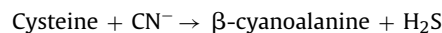
Thiosulfate:cyanide sulfurtransferase

$$CN^- + S_2O_3 \rightarrow SCN^- + SO_3^{2-}$$

3.3. Advances on biodegradation of cyanide

Dursan et al. investigated degradation of ferrous(II) cyanide complex (ferrocyanide) ions by free cells of *P. fluorescens*, in the presence of glucose and dissolved oxygen, as a function of initial pH, initial ferrocyanide and glucose concentrations and aeration rate in a batch fermenter [97]. The microorganism used the ferrocyanide ions as the sole source of nitrogen. They had found that 79% cyanide removal efficiency was achieved with maximum biodegradation rate at pH 5 and glucose concentration at 0.465 g/l. They used the substrate inhibition model [97] for kinetic study and for calculation of kinetic parameters. Dursan and Aksu further carried out degradation of ferrous(II) cyanide complex (ferrocyanide) ions by Ca-alginate immobilized *P. fluorescens* in a packed bed column reactor. In this study effect of flow rates was investigated and external film diffusion on degradation rate was studied [91].

Ackil et al. used two strains of *Pseudomonas* sp. isolated from a copper mine for biodegradation of cyanides at concentration range of 100–400 mg/L [89]. They compared their studies with chemical treatment methods and concluded that biological treatment methods are less expensive and environmental friendly but as effective as chemical method [89]. Kao et al. reported cyanide degradation by *K. oxytoca* [9]. They found that the resting cells could degrade, but cell free extract was not able to degrade which happened as a result of inactivation of nitrogenase (an oxygen-labial enzyme) caused

Table 3

Comparison of reports on bioremoval of cyanides

Sl no.	Compound to be removed	Microorganism	Type of reactor	Dependent parameters			
				Concentration	pH	Temperature (°C)	
1	(Cyanides)$_{WAD}$	*Pseudomonas* sp. (CM5, CMN2)	Batch	100–400 mg/L	9.2–11.4	30	[89]
2	Potassium cyanide	*Fusarium solani*	Batch	0.5–0.8 mM	9.2–10.7	30	[90]
3	Ferrous(II) cyanides complex	*Pseudomonas fluorescens* immobilized on Calcium Alginate	Packed Bed Reactor	–	4.0–7.0	25–35	[91]
4	Ferrous(II) cyanide complex	*P. fluorescens*	Batch	100 mg/L	5	25	[97]
5	Potassium cyanide	*Klebsiella oxytoca*	Batch	0.58 mM	7	30	[82]
6	Nitriles	*K. oxytoca*	Batch	25–100 mM	7	30	[9]
7	Cyanides	Mixed culture of bacteria	Continuous	20 mg/L	7	22	[88]
8	Sodium cyanide	*P.putida* immobilized on sodium alginate	Batch	100–400 mg/L	6.7	25	[92]
9	Sodium cyanide, cyanates and thiocyanates	*P.putida* immobilized on sodium alginate	Batch	4 mM	7.5	25	[96]
10	Cyanides + formamide	*Fusarium oxysporum* immobilized on Sodium alginate, *Methylobacterium* sp.	Packed bed reactor	1–7 mM	8	25–30	[87]
11	Metallo-cyanide	Strains of *Trichoderma* spp.	Batch	2000 mg/L	6.5	25	[99]
12	Phenol and cyanides	*P. putida* immobilized on Ultrafiltration membranes	Batch	–	–	27	[84]
13	Copper and zinc cyanide	*Citrobacter* sp., *Pseudomonas* sp.	Batch	52 mg/L	7.5	35	[3]
14	Tetra-cyano-nickelate(II)	*P. fluorescens* immobilized on zeolite	Batch	26 mg/L	–	30	[98]
15	Potassium cyanide	*Burkholderia Capita* stain C-3	Batch	10 mM	8.0–10.0	30	[103]
16	NaCN, NaHSO₃	*B. stearothermophilus* NCA 1503		5 mM, 50 mM	7.8	27 ± 2	[104]
17	Iron/nickel CN K₂Ni(CN)₄K₄Fe(CN)₆	Mix of (1) *F.Solani T.polysporum* (2) *F.oxyspoum, Scytalidium themophilum, Pencillium miczynski*	Batch	0.25–1.0 mM (Fe) 0.75 mM (Ni) 0.5 mM	4.0 and 7.0		[93]
18	Potassium cyanide	Granular Cyanidase	Fixed bed reactor	0–120 mg/L (70 mg/L)			[105]
19	Potassium cyanide	*Bacillus magaterium*	Batch				[106]
20	Potassium cyanide	*Eschericia coli* BCN6	Batch	50 mg/L, 100 mg/L, 200 mg/L	9.2	30	[36]
21	Potassium cyanide	*Stemphilium loti*	Batch	20 μM (2 mM)	6.5 7.5	25	[43]
22	Phenol, CN, Ni(CN)₄²⁻	*Pseudomonas fluorenscens* NCIB11764 (CN) *Pseudomonas* sp. (phenol)	Sequential continuous reactor	25 mM/dm³ 26 mg/dm³		30	[107]
23	Potassium cyanide	*S. loti, G. Sorgi*	Fixed bed batch	70 mM (7.5 ml/h)	7.0 5.3–5.7	28, 35	[108]
24	Tetra-cyano-nickelate potassium cyanide	*Pseudomonas putida* BCN3	Batch			30	[109]
25	Potassium cyanide	*Bacillus pumilis*	Batch	2.5 M	8.5– 9.0	40	[110]
26	Potassium cyanide	*Pseudomonas Acidovorans*	Continuous	31 mg/L (12,26,53,75 mg/L)	7.1, 7.9, 9.1	30	[40]
27	Potassium cyanide	*K. oxytoca* immobilized on alginate and cellulose triacetate	Batch	3 mM	7.0	30	[111]
28	Potassium cyanide	*Pseudomonas stutzeri* AK61	Batch	1 mM	7.6	30	[112]
29	Sodium cyanide	*Pseudomonas pseudoalcaligenes* CECT5344	Batch	2 mM	9.5	30	[101]
30	Tetra-cyano-nickelate(II)	*Cryptococcus humicolus* MCN2	Batch	51 mM	7.5	25	[113]

by the oxygen exposure after cell disruption. *K. oxytoca* also possessed enzymatic mechanisms to degrade nitriles [82]. Nitriles can also be degraded by *Nocardia rhodochrous, Arthrobacter Brevilbacterium, Pseudomonas putida, Pseudomonas marginalis, Pseudomonas aeruginosa, Rhodococcus erythropolis, R. rhodochrous* [82].

Chapatwala et al. studied the biodgradation of cyanides, cyanates and thiocyanates by *Pseudomonas putida* and found that cyanide compounds were used as sole source of carbon and nitrogen [92]. The end products of the degradation were NH_3 and CO_2 which caused reduction in pH of the medium. Immobilization has certain advantages. Immobilization of cells improves the degradation rate [84,87,91,92,98]. It prevents washing of cells and also it increases the cell density there by increasing degradation rate. The immobilization technique was also used by Kowalska et al. They used ultrafiltration membranes made of polyacronitrile [84] and carried out simultaneous degradation of cyanides and phenol using *Agrobacterium radiobacter, Staphylococcus seiuri* and *Pseudomonas diminuta*. The efficiency of phenol and cyanide biodegradation was dependent on transmembrane pressure. The immobilization technique was earlier studied by Babu et al. where immobilized cells of *P. putida* were able to degrade sodium cyanide as a sole source of carbon and nitrogen [92]. Various immobilization adsorbent are available like granular activated carbon (GAC), alginate beads, zeolite where they have shown very high efficiency and improved the degradation rate [92,96,97]. Simultaneous adsorption and biodegradation (SAB) is the latest development in cyanide removal [31]. Dash et al. (2008) reported high removal efficiency using *P. fluorescens* immobilized on Granular activated carbon in SAB process [31].

The degradation of cyanides has also been observed in sevaral fungal strains [93] *Fusarium solani, Trichoderma polysporum, F. oxysporum, Scytalidium thermophilum, Penicillium miczynski* have been isolated which are able to grow on metallocyanide complex as a source of nitrogen [31]. Dumestre et al. examined degradation by *Fusarium solani* under alkaline conditions, i.e. at high pH of 9.2–10.7 [90]. This could be of interest as it explored the ability of microorganisms to degrade cyanide under extreme conditions. Also at such high pH limits the volatilization of cyanohydric acid which is formed during the reaction is less. Another fungal strain *Trichoderma* spp. [99,93] has been isolated and studied for its degradation capabilities. Ezzi and Lynch found that this species could use cyanide as a sole source of carbon and nitrogen [99]. They also noticed that the inclusion of glucose could improve degradation rate by three times. *F. oxysporum* [87,93] was also found to possess good degrading capabilities for cyanide and formamide. Campos et al. studied on packed bed reactor using immobilized *F. oxysporum* on sodium alginate [87].

Apart from degradation there also exist biosorption [100] processes in which microorganisms adsorb the toxic compounds instead of degrading it. Sevaral fungal species are there (*Aspergillus fumigatus, Aspergillus niger, Aureobasidium pullulans, Cladosporium cladosporioides, Fusarium moniliforme, F. oxysporum, Mucor hiemalis*), which can act as biosorbents for cyanide compounds. Biodegradation and biosorption process can be used in combination for removal of cyanides as they can be very efficient as shown by Patil and Paknikar [100]. Iron(III) cyanide complex is known to get adsorb on *Rhizopus arrhizus* which is a filamentous fungus [4]. This fungus can adsorb the complex at very highly alkaline conditions at pH 13 with very high loading capacity of 612.2 mg/g of cyanide.

A strain, *Pseudomonas pseudoalcaligenes* CECT5344 [101], isolated from the Guadalquivir river (Córdoba), used several nitrogen sources including cyanide, cyanate, b-cyanoalanine, cyanacetamide and nitroferricyanide under alkaline conditions, which prevents volatile HCN (pK_a 9.2) formation. This bacterium was also grown on

heavy metal from cyanide containing wastewater generated by the jewellery industry. CECT5344 is a cyanide-resistant strain which induces an alternative oxidase and a siderophore-based mechanism for iron acquisition in the presence of cyanide [101].

Besides bacteria and fungi, algae could be used for the degradation of cyanides [102]. The detoxification of cyanide by algae was examined by exposing cultured suspensions of *Arthrospira maxima, Chlorella* sp. and *Scenedesmus obliquus* at pH of 10.3. The removal efficiency was 99%. This study has explored the use of algae in this field under extreme conditions with high removal efficiency. A novel study has confirmed the use of plants in the bioremediation of cyanide containing waste. A grass *Sorghum bicolour* [86] was tested for its ability to degrade cyanide in irrigation water during a lab scale study. Cyanide concentrations up to 125 mg/L were readily degraded by the plant.

Table 3 presents the summary of literatures on biodegradation of various cyanide compounds. It includes the details of pH, temperature, concentration of cyanides handled, details about type of reactor, type of microorganisms and compound they degraded.

3.4. Future scope of microorganisms and biological treatment of cyanides

Electroplating and mining industries are the major sources of cyanide bearing wastewater. With rapid growth in vehicle manufacture, ornamental work, utensil production, metallic material usage etc. the number of mining industries and metal plating shops are rising steeply all over the world. The continuous use of cyanide in the variety of industrial processes will require effective and economic remediation technologies. Continuous investigations are going on for testing the degrading abilities of new microorganism for a variety of cyanide compounds from waste, both under laboratory and field conditions. However, field applications of the cyanide biodegradation utilized only naturally occurring bacteria obtained by enrichment culture procedure developed in the laboratory or by natural selection in the field. However, bioremoval of cyanide from all type wastewaters is not amenable due to the extreme environmental conditions (low or high pH, toxicity of other pollutants) they present to microorganisms. A variety of pollutants other than cyanide compounds in wastewater cause inhibitory effect on the growth of microbes, which resulted in the decrease in biodegradation capabilities. Similarly, contaminated soils present a range of physicochemical conditions that may inhibit microbial growth. Therefore, organisms need to be selected not only on their ability to degrade cyanide compounds, but also to tolerate the additional stresses and compete effectively with indigenously microbial populations within the environment in which they will be operating [86]. The future of cyanide biodegradation technologies will focus on their ability to compete with the existing technologies with value added benefits or to fill specific needs associated with the treatment of industrial effluents [8].

4. Conclusion

The continuing generation of large volume of cyanide bearing wastes from various industries which resulted in contamination of soils and water suggests that novel processes are required to alleviate the serious environmental consequences of cyanide pollution. Most organisms capable of biodegrading cyanide are sensitive to cyanide concentration, with biodegradation and/or growth rate decreasing above specific thresholds for each organism. As effluents from some industries can have concentrations above the maximum range for most organisms, biological treatment may not be a viable option in all cases. The verities of catabolic activities by various microorganisms can be combined and modified to remedi-

ate inorganic cyanide and nitriles. The continued development and application of biotechnologies for cyanide biodegradation is limited primarily by physical and economic factors. However, optimization of the use of such biological systems both in wastewater and soil is required. Further, the development of microbial processes that is efficient in the extreme environmental conditions, such as low pH and contaminant toxicity, is required to ensure a technology that is competitive with the current chemical and physical remediation strategies currently practiced to reduce cyanide pollution. New microorganisms must be identified with respect to their degrading capabilities. The idea of recombinant strains which can degrade variety of compounds under extreme conditions must be developed. Further study is required in the field of genetic modification of microorganisms to meet the required recombinant strain.

Acknowledgements

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