Bioremediation of soil and water polluted by Cyanide: a review

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Abstract
Cyanide is a chemical that is widely distributed in the environment, mainly as a result of anthropogenic activities. Only small quantities are naturally produced. Most industrial activities use this chemical compound for manufacturing a product as electroplating or for extracting gold. Exposure to cyanide results in negative health impacts to the wildlife and humans. In nature, cyanide occurs in several species, of which the free cyanide forms are the most toxic ones. Cyanide can be removed by chemical or biological processes. Biological treatment called “bioremediation”, which is cost-effective and eco-friendly, is the most applied process to remove cyanide from contaminated environments. This technology focused by the use of microorganisms to remove pollutants. Many microorganisms have been reported to transform the cyanide in another less toxic compound, or to consume cyanide for their growth. The reactions are influenced by environmental parameters such as pH and temperature and by the nutrient availability.

Keywords: Biotreatment, chemical compound, environment, microorganism.

Introduction
Cyanide is a chemical product that is universally recognized as poison (Morocco 2005). It is highly toxic to living organisms (World Health Organization 2004). Many researches on the toxicity and the removal of cyanide have been published in the literature. Different technologies are available for cyanide removal. such as: alkaline chlorination or biological oxidation processes (Young and Jordan 1995; Patil and Paknikar 2000) and acidification and/or destruction by chemical oxidation (Young and Jordan 1995; Akcil 2003). Among these technologies, the most used one is chemical oxidation (Dubey and Holmes 1995, Young and Jordan 1995, Botz 2001, Pargh et al. 2003, Roshan et al. 2009)

However, only few articles have reported the potential for bioremediation of cyanide. The present work reviews these articles by comparing the efficiency of microorganisms that have high potential for the bioremediation of cyanide-contaminated environments. It will first discuss on the sources, uses, and toxicity of cyanide, and then will address the bioremediation technologies completed with the bioremediation potential of investigated microorganisms.
Cyanide

Cyanide is a group of compounds which contains a C≡N group: one atom of carbon linked with one atom of nitrogen by three molecular bounds. Cyanide compounds are usually categorized into 3 groups: the first group called free cyanide is related to the cyanide ion CN\(^{-}\) (produced by the dissolution of sodium or potassium cyanide in water) and the hydrogen cyanide gas (HCN); the second group is related to weak and moderately strong complexes formed between cyanide ion and some metals such as Zn, Ni, Ag, Cd, Hg; the third group is related to strong complexes formed between cyanide ion and Fe ion (Botz et al. 2005, Nsimba 2009). Other forms of cyanide include cyanates and nitriles.

1. Sources

The term cyanide refers to all of the cyanide compounds that can be determined as the cyanide ion (CN\(^{-}\)) (Franson 1992, Donato et al. 2007). Cyanide is produced by both natural and anthropogenic processes.

- **Natural processes**

Cyanide is produced naturally in the environment by various bacteria, algae, fungi and numerous species of plants including beans, fruits, vegetables and roots. Today, cyanogenic compounds can be found in more than 3000 species of plants, animals, microbes and fungi (Ward and Lebeau 1962, Stevens and Strobel 1968). Many common plants contain the natural form of cyanide, cyanic glucoside (Aazam 2014). Several plants produce cyanides, however in most cases; cyanide is present in extremely small quantities. Incomplete combustion during forest fires is believed to be a major environmental source of cyanide, and incomplete combustion of substances containing nylon produce cyanide through depolymerization (Li et al. 2000).

- **Anthropogenic processes**

Significant quantities of cyanide is a byproduct of various industrial processes, including coal coking, coal gasification and steel manufacturing as well as petroleum refining (Nsimba 2009). Cyanide also originates from metal finishing, ore extraction, and hydrometallurgical industries (Aazam 2014). The principal anthropogenic forms of cyanide are hydrogen cyanide (HCN), cyanogen sodium (NaCN) and cyanogen potassium (KCN). Anthropogenic inputs of cyanide into the environment are greater in quantity than natural inputs (Nsimba 2009). The process of degassing coal produces a raw gas containing hydrogen sulfide (H\(_2\)S) and HCN. At US gas (work) sites it is typical to use 8–21 kg of gas purification material per 1000 m\(^3\) of gas produced (Theis et al. 1994, Kjeldsen 1999). The spent iron ore contains high quantities of sulfur (typically 40–50%) and substantial quantities of cyanide (typically 1-2% by weight) (Young and Theis 1991, Theis et al. 1994, Kjeldsen 1999). During the electroplating process, the degreasing bath contains potassium or sodium cyanide and sodium hydroxide (Mohler 1969, Kjeldsen 1999). In gold mine extraction, tailing ponds containing gold mine wastes are sources of cyanide contamination (Alesii and Fuller 1976, Thompson and Gerteis 1990; Boucabeille et al. 1994, Kjeldsen 1999). Besides, in the artisanal small scale gold mining area, water and soil those have been analyzed were contaminated by the cyanide in all of sampling points that were heterogeneous distributed into a catchment area nerveless the few cyanidation ponds observed (Sawadogo 2015).

2. Uses

Plants produce cyanide as a defense mechanism against herbivores (Jones 1998, Nsimba 2009, Randviir and Banks 2015). Cyanide is used by humans in many cases. Every year, in industry, massive quantities of cyanides are used in metal extraction, electroplating, pesticides, metal hardening, photography, printing, dyeing, and many...
other manufacturing processes. It is also used in the production of organic chemicals such as nitrile, nylon, and acrylic plastics (Aazam 2014).

The use of cyanide also facilitates the storage of salt. Potassium ferrocyanide ($K_4Fe(II)(CN)_6$) and sodium ferrocyanide ($Na_4Fe(II)(CN)_6$) in maximum concentrations of 200 mg kg$^{-1}$ have been used as anti-clumping additives in road salt in order to facilitate handling and distribution (Ohno 1990, Kjeldsen 1999).

Cyanide is also used in the chemical extraction of gold from low-grade ores by the heap leach process (White and Markwiese 1994, Kjeldsen 1999). This is the predominant process in the gold extraction industry that has been applied commercially since 1887 (Adams and Lloyd 2008). Another use of cyanide is for war. Cyanide is a likely weapon for terrorists due to its notoriety, lethality, and availability. Battlefield use of cyanides was proposed by Napoleon III during the Franco-Prussian war, to improve the lethality of bayonets. The French introduced gaseous HCN to World War I in 1915, and used 4000 tons in battle (Morocco 2005). HCN gas was used in the gas chambers in the World War II holocaust, in prison for the execution of criminals with death sentences, and also as a chemical warfare agent (Nsimba 2009).

3. **Toxicity**

In nature, various forms of cyanide are present depending on the environment. The most toxic form is free cyanide.

Humans and the environment are highly affected by cyanide. Cyanide is the most significant contaminant that affects wildlife mortality (Henny et al. 1994, Donato et al. 2007). The most important exposure routes to humans are: ingestion and dermal contact, inhalation of volatilized cyanide, and groundwater exposure (Wiemeyer et al. 1985, Henny et al. 1994, Minerals Council of Australia 1996, Ryan and Shanks 1996, Kjeldsen 1999, Donato et al. 2007).

Other potential effects can occur on terrestrial species (plants and animals) and on surface water species (by recharge of cyanide containing groundwater to surface waters) (Henny et al. 1994, Kjeldsen 1999, Donato et al. 2007). Hydrogen cyanide and other cyano-compounds that liberate free cyanide ions are highly toxic to almost all forms of fauna (Souren 2000). The toxicity is related to the inverse of the bond strength of metal atoms and cyanide ligands (Klenk et al. 1996, Sadler 1990, Staunton and Jones 1989).

Many researchers have reported the lethal toxicity of several cyanide complexes to birds (Barcroft 1931, Davis 1981, Eisler 1991a, Eisler 1991b, Reese 1997). Lethal limits varied between species (Table 1) (Donato et al. 2007)

**Table 1: Effects of free cyanide on some birds and other animals** (Christel and Eyer 1977, Bapat and Abhyankar 1984, Ballantyne 1987, Eisler 1991a, Eisler 1991b, Hagelstein 1997, Donato et al. 2007)

<table>
<thead>
<tr>
<th>Species</th>
<th>Dose</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mallard Duck</td>
<td>0.53 mg CN/Kg BW</td>
<td>No deaths</td>
</tr>
<tr>
<td></td>
<td>1.43 mg CN/Kg BW</td>
<td>Lethal Dose (LD) 50 (C.I at 95% 2.2 to 3.2)</td>
</tr>
<tr>
<td>Turkey Vulture</td>
<td>36 mg NaCN/Kg BW</td>
<td>Average time of death was 19 min</td>
</tr>
<tr>
<td>Rock Dove</td>
<td>1.6 mg CN/Kg BW</td>
<td>Minimum LD</td>
</tr>
<tr>
<td>Black Vulture</td>
<td>2.54 mg CN/Kg BW</td>
<td>Acute oral LD50</td>
</tr>
<tr>
<td></td>
<td>3.7 mg CN/Kg BW</td>
<td>All dead within 16 min</td>
</tr>
<tr>
<td>Japanese Quail</td>
<td>4.5 mg CN/Kg BW</td>
<td>Acute oral LD50 for adult females</td>
</tr>
</tbody>
</table>
American Kestrel | 2.12 mg CN/Kg BW | Acute oral LD50
---|---|---
Domestic Chicken | 11.1 mg CN/Kg BW | Acute oral LD50
European starling | 9.0 mg CN/Kg BW | Acute oral LD50
Cattle | 200 mg HCN/kg BW | Lethal
Dog | 24 mg NaCN/Kg BW | Lethal single dose
Mouse | 8.5 mg CN/Kg BW | LD 50 lethal single dose
Rat | 5.1-5.7 mg NaCN/Kg BW | LD 50 lethal single dose

**Humans**

Human can be exposed to cyanides by breathing air and drinking water, touching soil or water containing cyanide, or eating foods that contain cyanide (ATSDR 2006), with potentially lethal results (table 2).

<table>
<thead>
<tr>
<th>Exposure way</th>
<th>Lethal dose</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhalation</td>
<td>200 – 314 mg HCN/m³</td>
<td>(Chaumont and Weil 1960, Yacoub et al. 1974)</td>
</tr>
<tr>
<td>Ingestion</td>
<td>0.56 – 1.52 mg CN-/kg</td>
<td>(Gettler and Baine 1938, United State Environmental Protection Agency 1987)</td>
</tr>
<tr>
<td>Dermal contact</td>
<td>100 mg CN-/kg</td>
<td>(Rieders 1971)</td>
</tr>
</tbody>
</table>

4. **Physical and chemical treatments of cyanide**

Cyanide could be removed by physical, chemical or biological treatments. Natural cyanide attenuation is also possible.

The physical and chemical treatments of cyanide operate on the principle of converting cyanide into a less toxic compound through an oxidation reaction. Several destruction processes are well proven to produce treated solutions or slurries with low levels of cyanide as well as many metals: alkaline chlorination process (Dubey and Holmes 1995, Young and Jordan 1995, Botz 2001b, Parga et al. 2003, Dash et al. 2009), sulfur dioxide and air process, copper-catalyzed hydrogen peroxide process, Caro’s acid process, the iron-cyanide precipitation, activated carbon polishing, ion exchange, reverse osmosis, ozonation, etc. (Ackil 2003).

Most of these methods are expensive and have several disadvantages (Wild et al. 1994). For example, alkaline chlorination process is not effective in the case of cyanide species complexed with metals such as nickel, silver, etc. due to slow reaction rates (Patil and Paknikar 2000). The process also produces sludge, which requires specific license for 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 (Kao et al. 2003, Kao et al. 2006). In addition, various chlorinated organics may be produced if the wastewater contains organic substances (Dash et al. 2009).

5. **Natural cyanide attenuation**

It is well reported that cyanide solutions placed in ponds or tailings impoundments undergo natural attenuation reactions, which result in the decrease of the cyanide concentration. These attenuation reactions are dominated by natural volatilization of hydrogen cyanide, but other reactions such as biological degradation, oxidation, hydrolysis, photolysis and precipitation also occur (Botz et al. 2005). At several sites, ponds or tailings impoundments are intentionally designed to maximize the rate of cyanide attenuation. Advantages of natural
attenuation include lower capital and operating costs when compared to chemical-oxidation processes. (Ackil 2003)

**Bioremediation of cyanide**

Cyanide is a chemical compound that microorganisms or plants can transform to another compound less toxic. Usually, microorganisms or plants are used for remediating environments polluted by cyanide. Bioremediation refers to the use of microorganism (Elkins 2013) and phytoremediation refers to the use of plants. Biological methods are preferred for cyanide removal because of their low operation cost, their ability to remove a wide range of cyanide compounds, and their ability to produce high quality effluents (Botz et al. 2005).

1. **Biodegradation mechanism**

There are many groups of microorganism discovered which can transform simple or complex cyanide compounds, including bacteria such as *Klebsiella oxytoca* (Chen et al. 2008), *Pseudomonas fluorescens* P70 (Dursun et al. 1999), fungus such as *Fusarium solani* (Barclay et al. 1998), *Fusarium oxysporum* (Akinpelu et al. 2015) and algae such as *Scenedesmus obliquus* (Gurbuz et al. 2009).

Cyanide is used as a nutrient by the bacteria for their growth, acting as nitrogen source. Some bacteria are able to use cyanide compounds as both a carbon and nitrogen source. Therefore, supply of external carbon source is no longer needed for these bacteria. Other bacteria need glucose as carbon source for survival in presence of cyanide (Dursun et al. 1999, Bouari 2012).

The biodegradation occurred into two steps:

The first step is the oxidative breakdown of cyanides, and subsequent sorption and precipitation of free metals into the biofilm. Cyanide and thiocyanate are then converted to ammonia, carbonate and sulfate (Ackil 2003)

\[
\text{CN}^- + \frac{1}{2} \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{NH}_3
\]

\[
\text{SCN}^- + 2\text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{SO}_4^- + \text{NH}_4^+ + \text{HCO}_3^- + \text{H}^+
\]

\[
\text{M(CN)}_{2-x}^- + x/2\text{O}_2 + 3x\text{H}_2\text{O} \rightarrow M^{3+} + x\text{NH}_4^+ + x\text{HCO}_3^- + \text{H}^+
\]

In the second step, ammonia is converted to nitrate through the conventional two step nitrification process shown below:

\[
\text{NH}_4^+ + \frac{3}{2} \text{O}_2 \rightarrow \text{NO}_3^- + \text{H}^+ + \text{H}_2\text{O}
\]

\[
\text{NO}_2^- + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_3^-
\]

The ease of degradation of metal cyanides depends on their chemical stability: free cyanide is the most readily degradable, followed by metal cyanide complexes of Zn, Ni, and Cu; iron cyanide the least degradable (Mudder et al. 1998).

2. **Bioremediation capacity**

Most of the reported studies on bioremediation have focused on: correlation of the growth kinetics of the bacteria and the rate of cyanide removed, evaluation of the environmental parameters on the degradation of different cyanide compounds or determination of the minimum inhibitory concentration (MIC) cyanide compounds for the microorganism. Table 3 and 4 below show a comparison of studies evaluating cyanide biological transformation, respectively in water and in soil.
In tables 3 and 4, the same bacteria were used for biological treatment of cyanide but the potential effectiveness varies depending on the composition of the medium, type and initial concentration of cyanide and organic matter, pH, and temperature.

In the water, the optimal condition is formed by a pH ranging from 5.2 to 10.5 for bacteria, from 6 to 8.5 for fungus and pH 12 for plant. Temperature is usually held between 25 – 50°C, with the majority around 30°C for bacteria, 43°C for fungus and 40°C for plants. Cyanide hydratase is often used by microorganisms as enzyme for degrading cyanide. The potential cyanide degrading bacteria is formed by *Pseudomonas Fluorescens* NCIMB 11764, its performance is between 105 – 706 µmol min⁻¹ for degrading free cyanide with or without enzyme as catalyzer (Kunz et al. 1992; Kunz et al. 1998). The mixed bacteria composed by *Klebsiella pneumoniae* and *Ralstonia sp.* have also a high potential with a velocity 1042 µg L⁻¹ min⁻¹ for degrading thiocyanate (Chaudhari and Kodam 2010). For Fungus, *Gloeocercospora sorgii* is the most effective. Its maximal velocity is 4.4 mmol min⁻¹ mg⁻¹ (Jandhyala 2002) (Basile 2008).

In the soil, the optimal condition is formed by a pH around 7 for bacteria and pH 4 for fungus. The cyanide degrading bacteria have a temperature between 30-37°C. But, for fungus, it stays around 30°C. For degrading cyanide, bacteria and fungus use various enzymes as: thiocyanate hydrolase, cyanidase and hydratase amidase. Microorganisms have a faculty to degrade strong acid dissociable cyanide in the soil than in the water. The potential cyanide degrading bacteria is formed by *Pseudomonas putida*. (Bipinraj et al. 2003). The fungus, *Fusarium oxysporum N-10* is the most effective with a velocity 0.02 mM Day⁻¹ and 1 mM Day⁻¹ respectively in the mixed (Barclay et al. 1998) and single culture (Yanase et al. 2000).

Glucose was often used as organic matter in water and soil and the final product of biodegradation is formed by ammonia or ammonium. While earlier studies only focused on the microorganism application, after the discovery of co-culture bacteria or fungus, many current studies are focused on the addition of agricultural wastes or wastes in the microorganism mixed culture.

Research about phytoremediation is not investigating deeply.
Table 3: Comparison of potential cyanide bioremediation in water

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Enzyme</th>
<th>Origin</th>
<th>Compound to be removed</th>
<th>Optimum condition</th>
<th>Degradation efficiency</th>
<th>Final Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Thiobacillus intermedius</em> (Singleton and Smith 1988)</td>
<td>Rhodanese</td>
<td>Salt swamp</td>
<td>CN⁻ / 50mM</td>
<td>Salt swamp: pH 8.1</td>
<td>0.021 µmol/min (without enzyme)</td>
<td>SCN⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Salt water</td>
<td></td>
<td>Salt water: T 25°C</td>
<td>0.042 µmol/min (with enzyme)</td>
<td>Sulfit (SO₃²⁻)</td>
</tr>
<tr>
<td>a. <em>Klebsiella sp.</em></td>
<td>Nhase</td>
<td>Creek water</td>
<td>Tetracyanonickelate (II) [K2[Ni(CN)₄] (TCN) KCN</td>
<td>0.25 – 16 mM TCN 0.25 mM KCN / T 41°C</td>
<td>0.015 µmol/min</td>
<td>Ni(CN)₂</td>
</tr>
<tr>
<td>b. <em>Klebsiella pneumoniae</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c. <em>Pseudomonas putida</em> (Silva-avalos et al. 1990)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Pseudomonas Flourescens NCIMB 11764</em> (Kunz et al. 1992)</td>
<td>Cyanide oxygenase</td>
<td>Waste water</td>
<td>KCN/20mM</td>
<td>pH: 5.2 – 9 (a) / 6 – 8.5 (b) 7.5 (c) / 6 – 7 (a), (b), (c) T 27-43°C</td>
<td>85%/6h (aerobic condition) 89%/12h (anaerobic condition)</td>
<td>Formamide (HCNOH₂) or formate (HCOO⁻)</td>
</tr>
<tr>
<td><em>Pseudomonas Flourescens NCIMB 11764</em> (Kunz et al. 1998)</td>
<td>Cyanide oxygenase</td>
<td>Keto-acid</td>
<td>KCN</td>
<td>pH 7 T 30°C</td>
<td>760 µmol/min/ml (after 72 hours) (without acid)</td>
<td>NH₃</td>
</tr>
<tr>
<td><em>Pseudomonas Flourescens NCIMB 11764</em> (Fernandez et al. 2004)</td>
<td>Cyanide oxygenase</td>
<td>Waste water</td>
<td>KCN</td>
<td>pH: 5.2 – 9 (a) / 6 – 8.5 (b) 7.5 (c) / 6 – 7 (a), (b), (c) T 27-43°C</td>
<td>&lt; 80% (a), (b), (c) (after 48 hours)</td>
<td></td>
</tr>
<tr>
<td>a. <em>Neurospora crassa</em>, b. <em>Gibberella zeae</em>, c. <em>Aspergillus nidulans</em>, (Basile 2008)</td>
<td>Cyanide hydrolase</td>
<td>Waste water</td>
<td>Metal-cyanide complexes</td>
<td>pH: 5.2 – 9 (a) / 6 – 8.5 (b) 7.5 (c) / 6 – 7 (a), (b), (c) T 27-43°C</td>
<td>&lt; 80% (a), (b), (c) (after 48 hours)</td>
<td></td>
</tr>
<tr>
<td><em>Thiobacillus thioparus THI115</em> (Yamasaki et al. 2002)</td>
<td>Thiocyanate hydrolase</td>
<td>Lake water</td>
<td>SCN⁻</td>
<td>T 30°C</td>
<td>93% (in 38 h)</td>
<td>Carbonyl sulfide (COS)</td>
</tr>
<tr>
<td><em>Bacille sp.</em> (Bacillus safensis, Bacillus licheniformis, et Bacille tequilensis) (Mekuto et al. 2013)</td>
<td>Cyanide compounds</td>
<td>Waste water</td>
<td>cyanide compounds</td>
<td>T 37°C</td>
<td>65.5% (200 mg CN⁻/L) 44.3% (400 mg CN⁻/L)</td>
<td></td>
</tr>
<tr>
<td><em>Micromonaspora braunna</em> (Shete and Kapdnis 2012)</td>
<td>Cyanide hydrolase</td>
<td>Garden soil</td>
<td>KCN (N source) : 10-1000ppm Dextrose (C source)</td>
<td>T 30°C (aerobic condition)</td>
<td>98.79% (pour 100ppm in 18 hours)</td>
<td>HCOOH NH₃</td>
</tr>
<tr>
<td><em>Bacillus safensis + Bacillus licheniformis + Bacillus tequilensis</em> (Mekuto et al. 2013)</td>
<td>Cyanide hydrolase</td>
<td>Wastewater</td>
<td>KCN: 200 and 400 mg CN⁻/L</td>
<td>T 37°C</td>
<td>65.5% (over 8 days) for 200 mg CN⁻/L 44.3% (over 8 days) for 400 mg CN⁻/L</td>
<td></td>
</tr>
<tr>
<td><em>Bacillus safensis + Bacillus licheniformis + Bacillus tequilensis + Agrowaste (Ananas comusus extract: 1% v/v, Beta vulgaris extract:1% v/v, Ipomea batatas extract: 1% v/v, spent brewer’s yeast: 1% v/v, and whey: 0.9% w/v) (Mekuto et al. 2013)</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>89.5% (over 8 days) for 200 mg CN⁻/L 59.75% (over 8 days) for 400 mg CN⁻/L</td>
<td></td>
</tr>
<tr>
<td>Organism/Strain</td>
<td>Medium/Conditions</td>
<td>Free Cyanide (mg/L)</td>
<td>Temperature (°C)</td>
<td>pH</td>
<td>Percentage</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>------------------</td>
<td>---------------------</td>
<td>-----------------</td>
<td>----</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td><em>Burkholderia cepacia C-3</em> (Adjei and Ohta 2000)</td>
<td>Fructose</td>
<td>260</td>
<td>T 30°C</td>
<td>pH 10</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td><em>Pseudomonas sp.</em> (Kao et al. 2003)</td>
<td>Lactate, Sucrose</td>
<td>100</td>
<td>T 28-30°C</td>
<td>pH 9-9.2</td>
<td>60%</td>
<td></td>
</tr>
<tr>
<td><em>Pseudomonas sp.</em> (Akcil et al. 2003)</td>
<td>Whey</td>
<td>400</td>
<td>T 30°C</td>
<td>pH 9-9.2</td>
<td>89%</td>
<td></td>
</tr>
<tr>
<td><em>Klebsiella oxytoca</em> (Kao et al. 2003)</td>
<td>Glucose</td>
<td>21</td>
<td>T 30°C</td>
<td>pH 7</td>
<td>99.9%</td>
<td></td>
</tr>
<tr>
<td><em>Trametes versicolor</em></td>
<td>Citrate</td>
<td>400</td>
<td>T 30°C</td>
<td>pH 10.5</td>
<td>30% (Cabu et al. 2006) 100% (after 42 hours) (Akinpelu et al. 2015)</td>
<td>Ammonium (NH₄⁺-N)</td>
</tr>
<tr>
<td><em>Klebsiella oxytoca</em> (Chen et al. 2008)</td>
<td>Nitrogenase</td>
<td>157</td>
<td>T 30°C</td>
<td>pH 7</td>
<td>26%</td>
<td></td>
</tr>
<tr>
<td><em>Pseudomonas pseudoalcaligenes</em> CECT5344 (Huertas et al. 2010)</td>
<td>Acetate</td>
<td>40</td>
<td>T 30°C</td>
<td>pH 9.5-10</td>
<td>99.9%</td>
<td></td>
</tr>
<tr>
<td><em>Klebsiella pneumoniae + Ralstonia sp.</em> (Chaudhari and Kodam 2010)</td>
<td>Thiocyanate hydrolase</td>
<td>KSCN (Thiocyanate)</td>
<td>T 37°C</td>
<td>pH 6.0</td>
<td>500 - 2500 mg/L/day</td>
<td>H₂S</td>
</tr>
<tr>
<td><em>Bacillus sp.</em> CN-22 (Wu et al. 2014)</td>
<td>Cyanide dihydratase</td>
<td>HCN 700 mg/L</td>
<td>T 31°C</td>
<td>pH 10.3</td>
<td>200 - 6.62 mg/L/72h</td>
<td>HCOOH NH₃</td>
</tr>
<tr>
<td><em>Bacteria + cassava peels</em> (Siller and Winter 1998)</td>
<td>Wastewater</td>
<td>KCN</td>
<td>T 25-37°C</td>
<td>pH 6-7.5</td>
<td>400 mg CN⁻/L/day</td>
<td>HCOO- (formate) NH₃</td>
</tr>
<tr>
<td><em>Enterobacter sakazakii</em> (a) Azotobacter sp (b) Rhizobium sp (c) (Ninan et al. 2013)</td>
<td>Cyanide dihydratase</td>
<td>KCN</td>
<td>MIC 5000ppm (a)</td>
<td>MIC 50 ppm (b), (c)</td>
<td>99% (after 96 hours)</td>
<td></td>
</tr>
<tr>
<td><em>Pseudomonas fluorescens + Chlorella vulgaris.</em> (Kiruthika 2008)</td>
<td>Cyanide 0.5mg + glucose 1g (a)</td>
<td>T 30°C</td>
<td>pH 7.2 (a), (b)</td>
<td>60% (a)</td>
<td>58% (b)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cyanide 0.5mg + glucose 1g + NaCl 1g (b)</td>
<td>T 30°C</td>
<td>pH 8.5 (c), (d)</td>
<td>54% (c)</td>
<td>51% (d)</td>
<td></td>
</tr>
</tbody>
</table>

**Fungus**

<table>
<thead>
<tr>
<th>Organism/Strain</th>
<th>Medium/Conditions</th>
<th>Free Cyanide (mg/L)</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Fusarium solani</em> (Barclay et al. 1998)</td>
<td>Cyanide dihydratase</td>
<td>KCN 80mM</td>
<td>Km: 4.7mM</td>
<td>Vmax: 1.7 microM min⁻¹ mg⁻¹</td>
<td></td>
</tr>
<tr>
<td><em>Gloeocercospora sorghi</em> (Jandhyala 2002)</td>
<td>Cyanide dihydratase</td>
<td>KCN 30mM</td>
<td>Km: 90mM</td>
<td>Vmax: 4.4 mmol min⁻¹ mg⁻¹</td>
<td></td>
</tr>
<tr>
<td><em>Gloeocercospora sorghi</em> (Basile 2008)</td>
<td>Cyanide dihydratase</td>
<td>Wastewater</td>
<td>KCN 20mM</td>
<td>Metal-cyanide complexes</td>
<td>pH: 6 – 8.5 / T: 27-43°C</td>
</tr>
</tbody>
</table>
Aspergillus awamori (Santos et al. 2013)  
Nitrilase  
Wastewater  
KCN 0-475 ppm  
Citrus peel, T: 45 - 50°C and pH: 4.0 to 5.5  
83 – 263 mg F-CN/L  
120- 210 mg NH4+-N/L

Fusarium oxysporum + Beta vulgaris (Agrowaste) (Akinpelu et al. 2015)  
Gold mining wastewater  
Metal cyanide + KCN 500 mg CN-/L  
83 – 263 mg F-CN/L  
120- 210 mg NH4+-N/L

Table 4: Comparison of reports on cyanide biological transformation in soil

<table>
<thead>
<tr>
<th>Microorganism/plants</th>
<th>Enzyme</th>
<th>Source</th>
<th>Compounds to be removed</th>
<th>Optimum condition</th>
<th>Degradation efficiency</th>
<th>Final Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bacteria</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a.Pseudomonas putida</td>
<td></td>
<td></td>
<td>TCN</td>
<td>0.25 – 16 mM TCN</td>
<td>93% (in 38 h)</td>
<td>Ni(CN)2</td>
</tr>
<tr>
<td>b.Pseudomonas picketti</td>
<td></td>
<td></td>
<td>KCN</td>
<td>0.25 mM KCN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c.Klebsiella pneumonia (Silva-avalos et al. 1990)</td>
<td></td>
<td>Sewage sludge (a)</td>
<td></td>
<td>T 41°C (with use of benzylamine for (a))</td>
<td>99% (in 109 cells/ml, 4 h)</td>
<td></td>
</tr>
<tr>
<td>Thiothrix thioparas (Yamasaki et al. 2002)</td>
<td>Thiocyanate hydrolase</td>
<td>Soil</td>
<td>SCN-</td>
<td>T 30°C</td>
<td>93% (in 109 cells/ml, 6h)</td>
<td></td>
</tr>
<tr>
<td>Thiothrix thioparas (Yamasaki et al. 2002)</td>
<td>Thiocyanate hydrolase</td>
<td>Wet soil</td>
<td>SCN- 2mM, KCN 0.2 mM, cyanocuprate (TCC) 0.5 mM, tetracyanonickelate (TCN) 0.5 mM</td>
<td>Alkali condition (4%) NaCl pH 7.5, T 30°C</td>
<td>99% (in 109 cells/ml, 4 h)</td>
<td></td>
</tr>
<tr>
<td>Alcaligenes xylosoxidans subsp (Ingvorsen et al. 1991)</td>
<td>cyanidase</td>
<td>soil</td>
<td>HCN</td>
<td>T 37°C</td>
<td>1% (in 55h)</td>
<td>HCOO- NH3</td>
</tr>
<tr>
<td><strong>Fungus</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fusarium oxysporum N-10 (Yanase et al. 2000)</td>
<td>Hydratase Amidase</td>
<td>Soil</td>
<td>Tetracyanonickelate H (TCN) 0.5mM and 20mM</td>
<td>T 30°C</td>
<td>20-30% (1 week) (for 0.5mM TCN) 30% (6 days) (for 20 mM TCN)</td>
<td></td>
</tr>
<tr>
<td>Fusarium solani + Trichoderma polysporum</td>
<td></td>
<td>Gasworks site soil</td>
<td>Tetracyanonickelate K2Ni(CN)4 0.25mM (a)</td>
<td>pH 4</td>
<td>95% (b), (c); after 28 days 90% (a); after 28 days</td>
<td>HCOO-, NH3</td>
</tr>
</tbody>
</table>
| (Barclay *et al.* 1998) | Hexacyanoferrate $K_4\text{Fe(CN)}_6$  
0.5mM (b) and $K_3\text{Fe(CN)}_6$  
0.5mM (c) |
|--------------------------|---------------------------------------------|
| *Fusarium oxysporum* +  
*Scytalidium thermophilum* +  
*Penicillium miczynski*  
(Barclay *et al.* 1998) | Gasworks site soil  
Hexacyanoferrate $K_4\text{Fe(CN)}_6$  
0.5mM  

pH 4  

32% after 28 days |
3. Bioremediation Technologies

More choice of bioremediation technologies are existed for removing cyanide. It could be conducted in-situ or ex-situ or by using bioreactors (Sharma 2012). Each method has its specificity and most of them are cost-effective as shown as in Table 5, which summarize the advantages of the different technologies, and their conditions of application.

Table 5: Methods applied in bioremediation (Vidali 2001, Shukla et al. 2010, Sharma 2012)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Examples</th>
<th>Advantages</th>
<th>Conditions of application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>In situ</strong></td>
<td>Biosparging</td>
<td>Most efficient</td>
<td>Biodegradation abilities of indigenous microorganisms</td>
<td>(Bouwer and Zehnder 1993, Colberg and Young 1995, Niu et al. 2009)</td>
</tr>
<tr>
<td></td>
<td>Bioventing</td>
<td>Relative passive</td>
<td>Presence of metals and inorganic compounds</td>
<td>Environmental parameters</td>
</tr>
<tr>
<td></td>
<td>Bioaugmentation</td>
<td>Naturally attenuated process, treat soil and water</td>
<td>Biodegradability of pollutants</td>
<td>Chemical solubility</td>
</tr>
<tr>
<td></td>
<td>Composting (Anaerobic, converts solid organic wastes into humus-like material)</td>
<td>Low cost Rapid reaction rate, Inexpensive, self-heating</td>
<td>To make plants healthier good alternative to land filling or incinerating practical and convenient.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Biopiles</td>
<td>Can be done on site</td>
<td>Surface application, agricultural to municipal waste</td>
<td></td>
</tr>
<tr>
<td><strong>Bioreactor</strong></td>
<td>Slurry reactors</td>
<td>Rapid degradation kinetic Optimized environmental parameters</td>
<td>Bioaugmentat Toxicity of amendments</td>
<td>(Behkish et al. 2007)</td>
</tr>
<tr>
<td></td>
<td>Aqueous reactors</td>
<td>Enhances mass transfer Effective use of inoculants and surfactant</td>
<td>Toxic concentrations of contaminants</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

This review summarizes the bioremediation technologies applied for cyanide decontamination. Potentiality of bioremediation technologies depends on the existence of cyanide degrading bacteria population; the availability of cyanide as contaminant and the environment factors. Bioremediation is a natural process; it takes a little time, as an acceptable waste treatment process for contaminating material such as soil. Bioremediation also requires a very less effort and can often be carried out on site. It is a cost effective process than the other conventional methods that are used for cleanup of hazardous waste and it does not use any dangerous chemicals. Bioremediation technologies could be applied in large scale and in different contaminated unit by cyanide as liquid, solid and gas industrial wastes. Nevertheless, the choice of single or mixed microorganism is very important for applying bioremediation.
References


