Review

Bioremediation of soil and water polluted by cyanide: A review

Lovasoa Christine Razanamahandry[1]*, Hela Karoui[1], Harinaivo Anderson Andrianisa[1] and Hamma Yacouba[2]

[1]Department of Water and Sanitary Engineering, Laboratory of Water, Decontamination, Ecosystem and Health (LEDES), International Institute for Water and Environmental Engineering (2iE), 01 Po Box 594, 01 Ouagadougou, Burkina Faso.
[2]Department of Research, International Institute for Water and Environmental Engineering (2iE), 01 Po Box 594, 01 Ouagadougou, Burkina Faso.

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 and fates, 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 on 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 nutriment availability. Bioremediation technologies were few applied in most of African Countries. Future works should focus on how to adapt the bioremediation technologies that already applied in other parts of the World in African context.

Key words: Biotreatment, chemical compound, environment, microorganism.

INTRODUCTION

Historically, cyanide has been used as chemical weapon in First World (Gupta et al., 2010). Actually, many industrial company and gold mining extraction sector use this compound. The leachate that released into the environment contains often residual cyanide. Cyanide is a chemical product that is universally recognized as

*Corresponding author. E-mail: c.razanamahandry@2ie-edu.org, tantely1989@gmail.com. Tel: +226 66691657.

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 (Patil and Paknikar, 2000; Young and Jordan, 1995) and acidification and/or destruction by chemical oxidation (Akcil, 2003; Young and Jordan, 1995). Among these technologies, the most used one is chemical oxidation (Botz, 2001; Dubey and Holmes, 1995; Parga et al., 2003; Roshan et al., 2009; Young and Jordan, 1995). But, the chemical oxidation processes are more expensive and could to produce other hazard compounds (Sharma, 2012; Vidali, 2001). Therefore, most of researches focused on the biological processes for destroying the cyanide compounds (Akinpelu et al., 2015; Fernandez et al., 2004; Huertas et al., 2010; Mekuto et al., 2013; Yamasaki et al., 2002; Wu et al., 2014). Microorganisms and/or plants could be transform cyanide on compounds less toxic. Cyanide is converted to carbon and nitrogen source by various enzymes present in microorganism (Ibrahim et al., 2015). The several researchers have been reviewed a bioremediation tests in different scale and conditions (Baxter and Cummings, 2006; Dash et al., 2009; Luque-Almagro et al., 2016). But, few of them show the applicability of the bioremediation technologies in the African countries. The objective of this paper is to thinking about the technology most adapted in Africa for remediating the natural environment polluted by cyanide, in which the sources, uses, behaviour and toxicity of cyanide are describe, and then different biodegradation test of cyanide by microorganism and plant and their efficiency are shown with the recent bioremediation technologies application in the world

CYANIDE

The term cyanide refers to all of the cyanide compounds that can be determined as the cyanide ion (CN−) (Donato et al. 2007; Franson 1992). 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. 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 (Stevens and Strobel, 1968; Ward and Lebeau, 1962). 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. Plants produce cyanide as a defence mechanism against herbivores (Jones, 1998; Nsimba, 2009; Randviir and Banks, 2015)

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 by-product 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 sulphide (H2S) and HCN. At US gas (work) sites it is typical to use 8 to 21 kg of gas purification material per 1000 m3 of gas produced (Theis et al., 1994; Kjeldsen, 1999). The spent iron ore contains high quantities of sulphide (typically 40 to 50%) and substantial quantities of cyanide (typically 1 to 2% by weight) (Kjeldsen, 1999; Theis et al., 1994; Young and Theis, 1991). During the electroplating process, the degreasing bath contains potassium or sodium cyanide and sodium hydroxide (Kjeldsen, 1999; Mohler, 1969). In gold mine extraction, tailing ponds containing gold mine wastes are sources of cyanide contamination (Alesii and Fuller, 1976; Boucabeille et al., 1994; Kjeldsen, 1999; Thompson and Gerteis, 1990).

INDUSTRIAL USE

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 (K4Fe(II)(CN)6) and sodium ferrocyanide (Na4Fe(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).
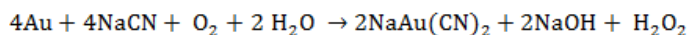
Gold mining use

Cyanide is also used in the chemical extraction of gold from low-grade ores by the heap leach process (Kjeldsen, 1999; White and Markwiese, 1994). This is the predominant process in the gold extraction industry that has been applied commercially since 1887 (Adams and Lloyd, 2008). Gold occurs in multi-phase mineralization including base-metal-rich mesothermal and base-metal-poor epithermal assemblages; it is recovered by a combination of amalgamation with mercury and leaching with cyanide (Carling et al., 2013).

The first recorded use of cyanide to extract gold from ores was in 1889 at the Crown Mine in New Zealand (Dorr, 1936; Johnson, 2014). A typical cyanide heap leach process has a series of steps (White and Markwiese, 1994). The gold-bearing ore is extracted, crushed to a nominal size, and piled on a constructed liner. An alkaline cyanide solution is sprayed on the pile. The cyanide solution is buffered to a pH of about 11 to keep cyanide from forming hydrogen cyanide, which can be lost through volatilization. The cyanide in solution complexes with gold (and other metals) extracting the metals from the ore. The cyanide solution is captured by the liner and is recirculated through the pile to further extract cyanide complexes metals (Kjeldsen, 1999). The stoichiometry by which this reaction occurs is known as the Elsner (1846) equation (Jeffrey, 2000):

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^-$$
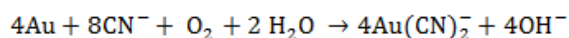
The fundamental process of gold extraction involves the formation of $Au(CN)_2^-$, a stable ion (Sadler, 1990) which brings gold into solution form and then be recovered by adsorption onto carbon. This aqueous ion is exploited by the gold industry most commonly through carbon in leach or carbon in pulp processes (Earls et al., 1995; Environment Australia, 1998; Minerals Council of Australia, 1996; Souren, 2000; Staunton and Jones, 1989). The current accepted mechanism describing gold dissolution in cyanide is shown in its simplest form by this equation (Donato et al., 2007):

$$4Au + 4NaCN + O_2 + 2H_2O \rightarrow 2NaAu(CN)_2 + 2NaOH + H_2O_2$$

After leaching, the crushed ore is either left on the pad or removed to another area for disposal (Kjeldsen, 1999). Therefore, artisanal gold mining is a substantial source of mercury and cyanide contamination in developing countries worldwide (Appleton et al. 1999; Carling et al. 2013; Cordy et al. 2011; Taylor et al., 2005).

War use

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).

CYANIDE BEHAVIOUR

In general, cyanide has three forms: CN_{free}, CN_{WAD} and CN_{SAD} (Botz et al., 2005). Free cyanide is the CN^- and HCN. Silver (Ag), Cadmium (Cd), Copper (Cu), Mercury (Hg), Nickel (Ni) and Zinc (Zn) are some examples of metals that form CN_{WAD} and while iron (Fe) forms C NSAD (Botz et al., 2005; Nsimba 2009). In nature, these forms of cyanide are present depending on the region.

In air

In air, cyanide is present mainly as gaseous hydrogen cyanide. A small amount of cyanide in air is present as fine dust particles. This dust eventually settles over land and water. Rain and snow help remove cyanide particles from air. The gaseous hydrogen cyanide is not easily removed from the air by settling, rain, or snow. The half-life (the time needed for half of the material to be removed) of hydrogen cyanide in the atmosphere is about 1 to 3 years. Most cyanide in surface water will form hydrogen cyanide and evaporate. However, the amount of hydrogen cyanide formed is generally not enough to be harmful to humans (U.S. Agency for Toxic Substances and Disease Registry (ATSDR) 2006).

In water

Cyanide in water

In water, there are various forms of cyanide such as:

CNfree (examples: CN- and HCN), CNWAD (examples: KCN, NaCN, cyanogen calcium (CaCN), cyanogen chloride (CNCl), cyanogen bromide (CNBr)) (ATSDR 1997; Xie and Hwang, 2000), CNSAD, cyanate (CNO-) and thiocyanate (SCN-).

In most natural waters, HCN is predominate (Doudoroff, 1976; Flynn and Haslem, 1995; Moran, 1998), but it is transported by rainwater in negligible quantities because of its solubility in water (ATSDR, 1997).

CNCl can be formed in drinking water during the interaction between humic substances and chloramines, occuring during chlorination of water (ATSDR, 1997; Boening and Chew, 1999). The half-life of cyanide in water is not known. Cyanide in water does not build up in the bodies of fish (ATSDR, 2006).

Physical properties

Cyanide in water takes gaseous and aqueous forms (Nsimba, 2009). Three gaseous forms of cyanide are present in water: HCN, CNCl, and CNBr (Nsimba, 2009; Xie and Hwang, 2000).

Thiocyanates are often present in the form of ferricomplexes, which can give a red coloration to water at concentrations of approximately 5 mg L-1 (Environmental Resources, 1987; Kjeldsen, 1999).

Chemical properties and reactivity

In water, free cyanide takes the form CN- and aqueous HCN (HCN(aq)). Carbon (C) is associated with nitrogen (N) by triple bond.

The CN- is a versatile ligand that reacts with many metal cations to form metal-cyanide complexes. These species, which are typically anionic, have a general formula $M(CN)_x$, where M is a metal and x is the number of cyano-groups, dependant on the valence number of M (Donato et al., 2007).

Dissociation

HCN (aq) is a weak acid and can dissociate into cyanide ion according to the following dissociation reaction (Sharpe, 1976; Smith and Mudder, 1991):

$$HCN(aq) \leftrightarrow H^+ + CN^- \quad pKa = 9.24 \text{ at } 25°C$$
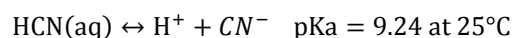
The distribution of HCN and CN- species is a function of pH for a simple aqueous solution at 25°C. At pH 9.2; CN- and HCN are in equilibrium. At pH 11; over 99% of the cyanide remains in solution as CN-. At pH 7; over 99% of the cyanide exists as HCN (Nsimba, 2009). The stability

of metal-cyanide complexes is variable and requires moderate to highly acidic pH conditions in order to dissociate. Weak metal-cyanide complexes dissociate under mildly acidic conditions (pH 4 to 6). Strong metal-cyanide complexes require strong acidic conditions pH < 2 to dissociate (Nsimba, 2009). Depending on the type of metal, some simple cyanides can dissolve in water, forming metal ions and cyanide ions (Donato et al., 2007; Klenk et al., 1996):

$$M_y(CN)_x \leftrightarrow M_y^+ + x(CN)^-$$
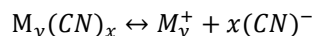
Dissolution

The gaseous forms of cyanide are soluble in water, but degrade by hydrolysis very rapidly at high pH. The hydrolysis degradation product is the cyanate ion (CNO-), which can subsequently hydrolyze to carbon dioxide (CO2) and ammonia (NH3) at alkaline pH conditions (CDC, 2005; IPCS/INCHEM 2005; Nsimba 2009). The solubility of metal-cyanide complexes is influenced by pH and temperature (Botz et al., 1995) and the presence of ammonia (Donato et al., 2007; Franson, 1992).

Thiocyanates are frequently quite soluble in water and can produce relatively high SCN- concentrations in groundwater. The potassium- and sodium ferrocyanides (which are added to road salt to prevent clumping) are readily soluble, but can re-precipitate in the presence of iron (III) (Kjeldsen, 1999).

Photo decomposition

If groundwater contaminated with ferrocyanide is exposed to daylight, iron-complexed cyanides may be transformed to free cyanide. Therefore, samples for cyanide analysis (total or weak acid dissociable cyanide) must be stored in dark containers (Kjeldsen, 1999).

Hydrolytic reactions

Cyanate hydrolyzes rapidly under acidic conditions to carbon dioxide and ammonia (FMC, 2005 in Nsimba, 2009)

$$CNO^- + 2H_2O \rightarrow CO_2 + NH_3 + OH^-$$
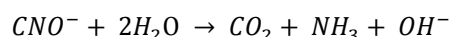
HCN is formed in solutions of cyanide by hydrolytic reaction of CN- in water (Doudoroff, 1976; Flynn and Haslem, 1995; Moran, 1998; Nsimba, 2009):

$$CN^- + H_2O \rightarrow HCN + OH^-$$
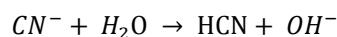
HCN is miscible with water, giving a weak acid. The CN

triple bond is readily hydrolyzed by strong alkali or acid giving formic acid and ammonia, with higher temperature favoring these reactions (Donato et al., 2007).

Hydrolytic reactions are catalyzed by some enzymes, such as cyanide hydratase, nitrile hydratase, cyanidase and nitrilase (Dash et al., 2008)

Oxidation

Free cyanide can be oxidized to form cyanate (CNO^-) or, depending on the pH, its protonated form fulminic acid (HOCN) (pKa=3.45 at 25°C) (Bard et al., 1985; Nsimba, 2009).

$$CN^- + H_2O \rightarrow CNO^- + 2H^+ + 2e^-$$
$$HCN + H_2O \rightarrow HCNO + 2H^+ + 2e^-$$

Volatilization

HCN is quite volatile with a vapor pressure of 84 000 Pa at 20°C. Henry's constant, (KH) is given as 1.7×10^{-3} (mg HCN (L air)$^{-1}$)$^{-1}$ (Gmelius Handbuch, 1977). Therefore if the concentration is 100 mg HCN L^{-1} in the pore water, and all the cyanide is assumed to be dissociated, then the equilibrium concentration in the gas phase in the pores will be 0.17 mg HCN (L air)$^{-1}$(Kjeldsen, 1999).

$$HCN\ (aq) \leftrightarrow HCN(g) \qquad LogK° = -2.8$$
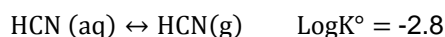
Sorption

The only significant cyanide sorption observed was for iron cyanides at low pH-values, where the total cyanide concentration in the water phase is low and thus insignificant (Kjeldsen, 1999).

Substitution/transfer

Free cyanide can react with various forms sulfur ($S_xS^{2-}, S_2O_3^{2-}$) to form thiocyanate, which is relatively less toxic than free cyanide. The reactions of polysulfide and thiosulfate with the CN$^-$ are as follows (Dash et al., 2009; Luthy and Bruce, 1979; Smith and Mudder, 1991; Zagury et al., 2004):

$$S_xS^{2-} + CN^- \rightarrow S_{x-1}S^{2-} + SCN^-$$
$$S_2O_3^{2-} + CN^- \rightarrow SO_2^{3-} + SCN^-$$
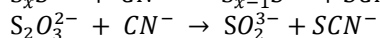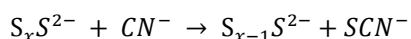
In soil and groundwater

Cyanide in soil and groundwater

The prevalent form of cyanide occurring in soils and groundwater are the following (Alesii, 1976; ATSDR, 1997; Shefchek et al., 1995):

1. HCN, also called cyanogen, hydrocyanic acid and prussic acid.
2. Simple cyanides (inorganic salts, for example NaCN, KCN).
3. Iron-complexed cyanides: Ferrocyanide (Fe(II)(CN)$_6^{3-}$), also called hexacyano- ferrate(II) and Ferricyanide (Fe(III)(CN)$_6^{4-}$), also called hexacyanoferrate(III).

An additional group is the so called nitriles, organic material with a R-CN composition where R refers to the organic radical. Various pesticides containing cyanides, as well as naturally occurring nitriles, originating from plants and microorganisms fall into this group (Fuller, 1984). A related group of compounds to the cyanides is the thiocyanates containing the (SCN) group (Kjeldsen, 1999).

Physical properties

The iron-complexed cyanides are often found as a Prussian blue colouration in the soil (ferri ferrocyanide Fe(III)$_4$(Fe(II)(CN)$_6$)$_3^{3-}$) and other similar iron-complexed cyanides. Cyanide concentrations of 100 to 500 mgCN kg^{-1} can produce bluish/greenish coloration in soils (Environmental Resources Ltd, 1987). Bog iron ore can also contain precipitated ferricyanides (Meeussen et al., 1990). Spent bog iron ore seems to contain very little free cyanide (Kjeldsen, 1999) SCN- are often present in the form of ferricomplexes, which can give a red coloration to soil. The red coloration is visible at concentrations of 50 mg kg^{-1} in soil (Environmental Resources Ltd. 1987; Kjeldsen, 1999)

In soils, cyanides are moderately mobile. The mobility depends on the pH condition and the percentage of iron oxides and the clay. They have a low mobility when pH is low and the percentage of iron oxides and the clay is high (ATSDR, 1997).

Chemical properties and reactivity

The behavior of cyanide compounds in soil and groundwater is governed by many interacting chemical and microbial processes (precipitation, dissolution, sorption and degradation). Therefore, cyanides in soil and groundwater have an extremely complex chemical behavior (Kjeldsen, 1999).

Dissolution and precipitation

If pH in soils is high, dissolution of iron cyanide can

result. And then, iron Fe (III) and $Fe(II)(CN)_6^{3-})$ are reform and they could be to raise to soil surface by capillary. On the surface, water is eliminated by evaporation and the ion could to precipitate, resulting in novel iron cyanide complexes (Bureau et al.,2011). Therefore, the rate of dissolution is affected by (1) buffer capacity of the soil, (2) transport of water through soils, and (3) alkalinity of water being transported through the soil (Kjeldsen, 1999; Meeussen et al., 1995).

Adsorption

Cyanide adsorption onto soils is dependent on cyanide speciation and soil mineralogy. Natural soils contain a mixture of many minerals varying greatly in physical characteristics. Aluminum oxides are ubiquitous soil components and important adsorbents in soil systems. Gibbsite $(Al(OH)_3(s))$ is the most common form of aluminum oxide found in soils (Sposito, 1984).

Sorption

Sorption of cyanide is limited, because most soil particles are also negatively charged. This limited sorption has been confirmed by column experiments with various cyanide compounds (Alesii, 1976; Zhang and Hendrix, 1991).

Retardation of cyanide due to sorption processes is generally of minor importance in most soils (Kjeldsen, 1999).

Solubility

The solubility of iron cyanide in soil is dependent on pH. Thus, reprecipitation of cyanide can occur if conditions change. Most near surface soils contain various iron hydroxides, which dissolve according to the following reaction (assuming that iron is in the $Fe(OH)_3$ form) (Kjeldsen, 1999):

$$Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O \quad \text{where} \quad \log K_s = 3.54$$
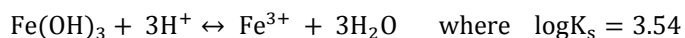
Transformation/mineralization

Biological oxidation and ultra-violet (UV) irradiation can be transformed CN_{SAD} or CN_{WAD} and SCN^- into NH_3, sulphate (SO_4), CO_2, metal ($Fe2+$, $Fe3+$, $Na+$,…) (Kjeldsen, 1999).

Complexation

This was done to obtain iron-cyanides like ferricyanide

(Fe III) and ferrocyanide (Fe II) (Kjeldsen, 1999)

In artisanal small scale gold mining catchment area

In general, three cyanide forms are observed in gold mining process waste solutions: CN_{free}, CN_{SAD} and CN_{WAD}. These forms are shown in Table 1. However, other compounds derived from cyanide are present such as cyanate (CNO^-), $CNCl$ and SCN^-(Souren, 2000; Donato et al., 2007). The main WAD cyanide complexes in mining tailings waste are $Cu(CN)_3^{1-}$, $Zn(CN)_4^{2-}$, $Ni(CN)_4^{2-}$ and $Fe(CN)_6^{3-}$ (Botz et al., 1995; Ou and Zaidi, 1995; Donato et al., 2008). Iron cyanides present in the metallurgical process are $Fe(II)(CN)_6^{3-}$ and $Fe(III)(CN)_6^{4-}$ (Donato et al., 2007; Franson, 1992; Klenk et al., 1996).

Transports and fate

In artisanal and small scale gold mining, cyanide can exist in tailings ponds, surface soil, surface water, atmosphere, soil and groundwater.

Water bearing cyanide in tailings pond is in contact with tailings solids and sediment, and the atmosphere. The fate and transport of aqueous cyanide is represented by a cyanide cycle encompassing a complex set of chemical reactions involving free cyanide radical and various metal-cyanide complexes. Biodegradation of free and WAD cyanide dominates in the tailings sediment, while metal-cyanide complexation, precipitation, biological oxidation (BO), photolysis, and volatilization are the primary fate mechanisms operating in the tailings pond water. Figure 1 shows that cyanide recycling occurs between the tailings pond water and the atmosphere (A → B →C → A). For example, a portion of free cyanide in the water column (A) can volatilize as gaseous HCN (B) into the atmosphere where it can be adsorbed into moisture droplets (C) and re-enter the ailings pound via precipitation. The other portion can be biologically degraded to ammonia, carbone dioxide, and nitrate (Donato et al., 2007; Smith and Mudder, 1991).

Cyanide can be transported into surface water. Both biological and physicochemical processes control the fate of cyanide in this zone. These include: Transport processes (advection and dispersion), photolysis (dissociation of iron/other metal-cyanid complexes to free cyanide via UV irradiation), volatilization of free cyanide into the atmosphere, microbiological degradation of free cyanide and weakly-complexed cyanide, plant uptake and assimilation of free and metal-complexed cyanide, rhizosphere mediated degradation of cyanide species, adsorption of free and metal-cyanide complexes onto sediments, precipitation/dissolution of iron and other metal-cyanide complexes (Bushey, 2003; Donalto et al., 2007).
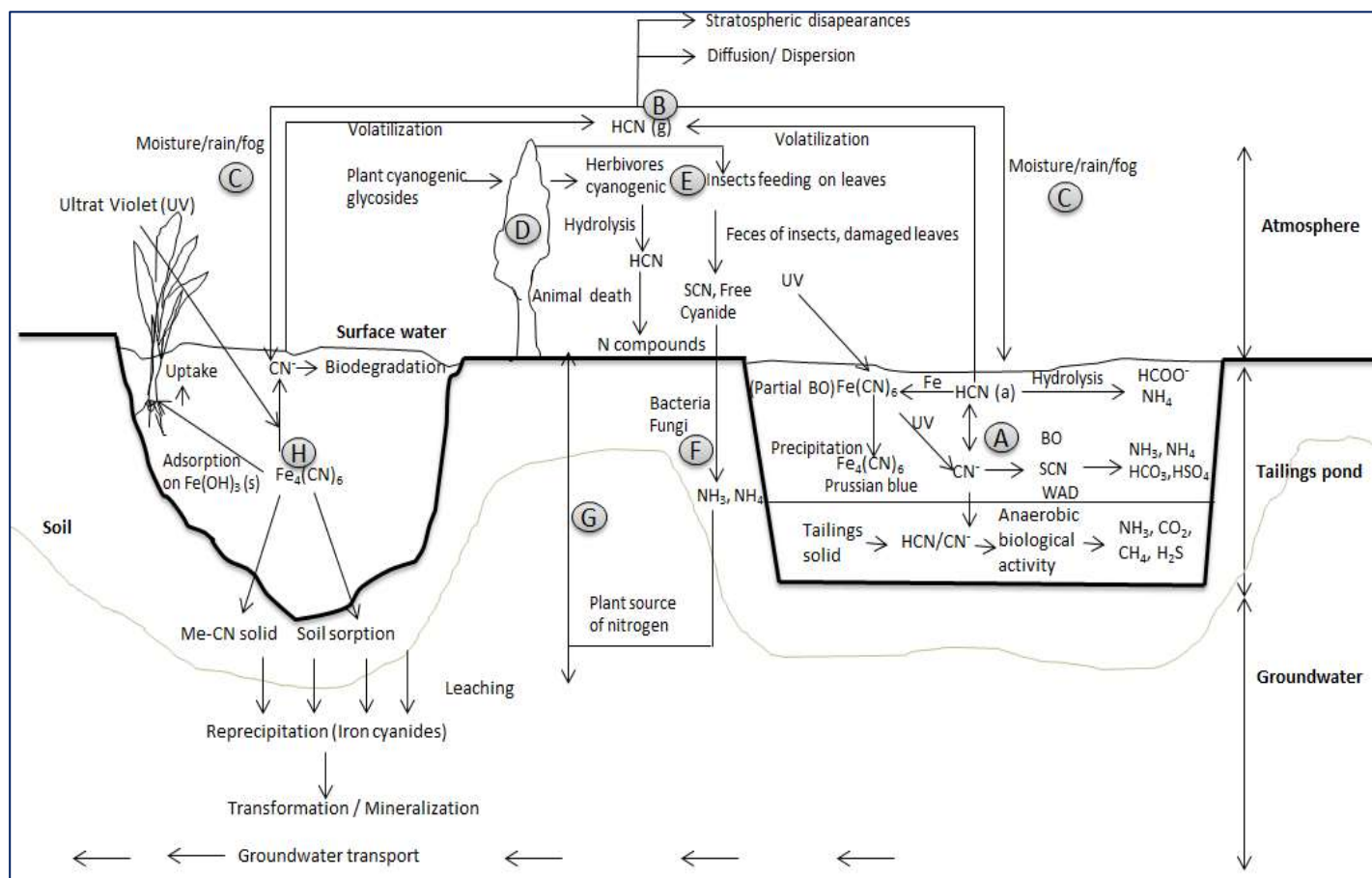
Figure 1. The different processes governing the behaviour of cyanide in nature and in a mine tailing pond (Bushey, 2003; Kjeldsen, 1999; Smith and Mudder, 1991).

Similar to the tailings pond, cyanide recycling occurring between the surface water and the atmosphere can be represented by:

H → B → C → H.

At the soil surface, cyanide can be present, if it was often land disposed on site during past mining exploitation. Leachates from this disposed material may contain iron-cyanide complexes and small amounts of other weak acid dissociable complexes depending on geochemical conditions. These soluble cyanide species can be taken up by plants or can be transported along with the groundwater as shown in Figure 1. Furthermore, cyanide in the plants can be transformed by animal metabolism (herbivores, insects). Residuals of these animals (feces, rest of animal death) and damaged leaves can be metabolized by soil microorganisms and taken up again by plants. Therefore, there is a cyanide recycling process between soil surface and groundwater following (Donato et al., 2007):

D → E → F → G → D

Physicochemical properties and reactivity

Cyanide, because of its high dielectric constant (Klenk et al., 1996), complexes readily in metallurgical circuits to dissolve other metals, preferentially gold from ores (Donato et al., 2007; Smith and Mudder, 1991; Staunton and Jones, 1989)..

Cyanide allows gold to be dissolved at a range of pH levels, although the stability of cyanide is greater at a higher pH. For gold mining metallurgical purposes, elevated pH levels of 9.5 to 10 maintain an appropriate cyanide-stability for gold dissolution (Donato et al., 2007; Souren, 2000).

Free cyanide is not persistent in the tailings environment (Botz et al., 1995; Resource Assessment Commission, 1991) and will degrade through physical, chemical and biological processes, into other less toxic chemicals (Environment Australia, 2003). Natural

Table 1. Cyanide compounds commonly present in gold mining tailings waste (Donato et al., 2007; Environment Australia, 1998; Klenk et al., 1996; Minerals Council of Australia, 1996; Sadler, 1990; Smith and Mudder, 1991; Souren, 2000).

Cyanide species	Examples
Free cyanide	CN^-, HCN
Weakly to moderately bound metal complexes (Weak-acid-dissociable) (WAD)	Zinc $Zn(CN)_4^{2-}$; Copper $Cu(CN)_2^{2-}$, $Cu(CN)_3^{2-}$; Including free cyanide
Strongly bound metal complexes (Strong-acid-dissociable) (SAD)	$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$

degradation, primarily by volatilization of cyanide in tailing storage facilities, is the most common method of removing cyanide in the gold mining waste (Botz et al., 1995; Donato et al., 2007; Environment Australia, 1998; John, 1988; Longe and Devries, 1988; Minerals Council of Australia, 1996; Ou and Zaidi, 1995; Sadler, 1990; Simovic et al., 1985; Smith and Mudder, 1995; Souren, 2000). A shallow pond with a large surface area increases the rate of conversion to gaseous HCN from the liquid phase (Environment Australia, 2003), although such spatial features attract wildlife (Donato, 1999). Aeration and mixing have a similar effect (Environment Australia, 2003). Once the pH of a tailings dam drops below 8 (Ou and Zaidi, 1995) or 9.2 (Staunton and Jones, 1989), the majority of cyanide is liberated via the gaseous state into the atmosphere (Donato et al., 2007). Unlike CN_{free}, WAD forms of cyanide, such as the copper complex, are resilient in the tailings dam environment (Brooks and McGlynn, 1987; Donato et al., 2007; Minerals Council of Australia, 1996; Sinclair et al., 1997; Staunton and Jones, 1989) and subsequently release cyanide ions under varying environmental conditions (Botz et al., 1995; Donato, 1999; Henny et al., 1994) and absorption by wildlife (Donato et al., 2007; Reece, 1997; Ryan and Shanks, 1996).

In addition the specific chemical profiles of metal cyanide complexes are important. Copper and zinc cyanide complexes are insoluble in water (Franson, 1992), but soluble in ammonia (Klenk et al., 1996).

Heavy-metal cyanide complexes are characterized by their stability, insolubility or being slightly soluble (Donato et al., 2007; Franson, 1992; Klenk et al., 1996).

The concentrations of bioavailable cyanide complexes to wildlife in the tailing environment depends strongly on the type and valence of the complex metal ion, as well as temperature, the pH of the solution, the pH of wildlife digestive tracts, dissociation rates and the concentration of the solution (Donato et al., 2007; Hallock ,1990; Klenk et al. 1996; Smith and Mudder, 1995).

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 (Donato et al., 2007; Henny et al., 1994). The most important exposure routes to humans are: ingestion and dermal contact, inhalation of volatilized cyanide, and groundwater exposure (Donato et al., 2007; Henny et al., 1994; Kjeldsen, 1999; Minerals Council of Australia, 1996; Ryan and Shanks, 1996; Wiemeyer et al., 1985).

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) (Donato et al., 2007; Henny et al., 1994; Kjeldsen, 1999). Hydrogen cyanide and other cyano-compounds that liberate free cyanide ions are highly toxic to almost all forms of fauna (Souren, 2000; Kumar et al., 2017). 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, b; Reece, 1997). Lethal limits varied between species (Table 2) (Donato et al., 2007)

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 3).

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

Table 2. Effects of free cyanide on some birds and other animals (Ballantyne, 1987; Bapat and Abhyankar, 1984; Christel and Eyer, 1977; Donato et al., 2007; Eisler, 1991a, b; Hagelstein 1997).

Species	Dose	Comment
Mallard Duck	0.53 mg CN kg^{-1} Bird Weight (BW);	No deaths
	1.43 mg CN kg^{-1} BW	Lethal dose (LD) 50 (C.I at 95% 2.2 to 3.2)
Turkey Vulture	36 mg NaCN kg^{-1} BW	Average time of death was 19 min
Rock Dove	1.6 mg CN kg^{-1} BW	Minimum LD
Black Vulture	2.54 mg CN kg^{-1} BW	Acute oral LD50
	3.7 mg CN kg^{-1} BW	All dead within 16 min
Japanese Quail	4.5 mg CN kg^{-1} BW	Acute oral LD50 for adult females
American Kestrel	2.12 mg CN kg^{-1} BW	Acute oral LD50
Domestic Chicken	11.1 mg CN kg^{-1} BW	Acute oral LD50
European starling	9.0 mg CN kg^{-1} BW	Acute oral LD50
Cattle	200 mg HCN kg^{-1} BW	Lethal
Dog	24 mg NaCN kg^{-1} BW	Lethal single dose
Mouse	8.5 mg CN kg^{-1} BW	LD 50 lethal single dose
Rat	5.1-5.7 mg NaCN kg^{-1} BW	LD 50 lethal single dose

Table 3. Lethal dose of cyanide for human depending on exposure way.

Exposure way	Lethal dose	Sources
Inhalation	200 - 314 mg HCN m^{-3}	Chaumont and Weil, 1960 ; Yacoub et al., 1974
Ingestion	0.56 - 1.52 mg CN kg^{-1}	Shete and Kapdnis, 2012; United State Environmental Protection Agency, 1987
Dermal contact	100 mg CN kg^{-1}	Rieders, 1971

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 (Botz 2001b; Dash et al., 2009; Dubey and Holmes, 1995; Parga et al., 2003; Young and Jordan, 1995), 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 reason, 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, 2006). In addition, various chlorinated organics may be produced if the wastewater contains organic substances (Dash et al., 2009).

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 entity polluted by cyanide

Cyanide is a chemical compound that microorganism 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).
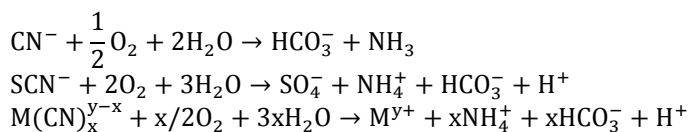
Biodegradation mechanism

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 (Bouari, 2012; Dursun et al., 1999).

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):

$$CN^- + \frac{1}{2}O_2 + 2H_2O \rightarrow HCO_3^- + NH_3$$
$$SCN^- + 2O_2 + 3H_2O \rightarrow SO_4^- + NH_4^+ + HCO_3^- + H^+$$
$$M(CN)_x^{y-x} + x/2O_2 + 3xH_2O \rightarrow M^{y+} + xNH_4^+ + xHCO_3^- + H^+$$

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

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + H^+ + H_2O$$
$$NO_2^{2-} + \frac{1}{2}O_2 \rightarrow NO_3^{3-}$$
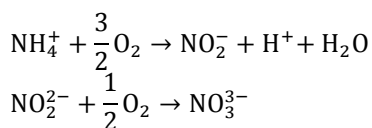
The ease of degradation of metal cyanides depends on their chemical stability: Free cyanide is the most readily degradable, followed by metal cyanide complexes of Zn, Ni, and Cu; iron cyanide the least degradable (Mudder et al., 1998).

Bioremediation capacity

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. Tables 4 and 5 show a comparison of studies evaluating cyanide biological transformation, respectively in water and in soil

In Tables 4 and 5, 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 and 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 microorganism as enzyme for degrading cyanide. *Pseudomonas Fluorescens* NCIMB 11764 was identified as the potential cyanide degrading bacteria, its performance is between 105 and 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 sorghi* is the most effective. Its maximal velocity is 4.4 mmol min^{-1} mg^{-1} (Basile, 2008; Jandhyala, 2002).

In the soil, the optimal condition was formed by a pH around 7 for bacteria and pH 4 for fungus. The cyanide degrading bacteria have a temperature between 30 and 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. *Pseudomonas putida.* was identified as the potential cyanide degrading bacteria (Bipinraj et al., 2003). The fungus, *F. oxysporum* N-10 is the most effective with a velocity 0.02 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.

Bioremediation technologies

More choice of bioremediation technologies were existed

Table 4. Comparison of potential cyanide bioremediation in water.

Microorganism	Enzyme	Origin	Compound to be removed	Optimum condition	Degradation efficiency	Final product
Bacteria						
Thiobacillus intermedius (Singleton and Smith 1988)	Rhodanese	Salt swamp Salt water	CN^- / 50 mM	Salt swamp : pH 8.1 Salt water : T 25°C	0.021 μmol min^{-1} (without enzyme) 0.042 μmol min^{-1} (with enzyme) 0.015 μmol min^{-1}	SCN^-Sulfite (SO_3^{2-})
a. *Klebsiella sp.* b. *Klebsiella pneumoniae* c. *Pseudomonas putida* (Silva-avalos et al., 1990)	Nhase	Creek water	Tetracyanonickelate (II){K2[Ni(CN)4] (TCN) KCN	0.25 - 16 mM TCN 0.25 mM KCN / T 41 °C		Ni(CN)$_2$
Pseudomonas fluorescens NCIMB 11764 (Kunz et al., 1992)			KCN/50 mM	20 - 50 mM pH 7 / T 31°C	85%/6 h (aerobic condition) 89%/12 h (anaerobic condition)	Formamide(HCNOH$_2$) or formate (HCOO$^-$)
P. fluorescens NCIMB 11764 (Kunz et al., 1998)	Cyanide oxygenase Keto-acid 23 mM		HCN	pH 7 T 30°C	760 μmol min^{-1} ml^{-1} (after 72 h) (without acid)	NH$_3$
P. fluorescens NCIMB 11764 (Fernandez et al., 2004)	cyanide oxygenase		KCN	10 - 50 μmol T 30 °C	90 - 100%	HCOO$^-$
a. *Neurospora crassa*, b. *Gibberella zeae*, c. *Aspergillus nidulans* (Basile 2008)	Cyanide hydratase	Waste water	KCN 20 mM Metal-cyanide complexes	pH: 5.2 - 9 (a) / 6 - 8.5 (b) 7,5 (c) / 6 - 7 (a), (b), (c) T 27- 43 °C	< 80% (a), (b), (c) (after 48 hours)	
Thiobacillus thioparus THI115 (Yamasaki et al., 2002)	thiocyanate hydrolase	Lake water	SCN$^-$	T 30°C	93% (in 38 h)	Carbonyl sulfide (COS)
Bacillus sp. (*Bacillus safensis, Bacillus lichenformis, and Bacillus tequilensis* (Mekuto et al., 2013)			Cyanide compounds	T 37°C	65.5% (200 mg CN L^{-1}) 44.3% (400 mg CN L^{-1})	
Micromonospora braunna (Shete and Kapdnis, 2012)	Cyanide hydratase	Garden soil	KCN (N source) : 10-1000 ppm Dextrose (C source)	T 30°C (aerobic condition)	98.79% (pour 100 ppm in 18 h)	HCOOH NH$_3$
B. safensis + B. lichenformis + Bacillus tequilensis (Mekuto et al., 2013)		Wastewater	KCN: 200 and 400 mg CN L^{-1}	T 37°C	65.5% (over 8 days) for 200 mg CN L^{-1} 44.3% (over 8 days) for 400 mg CN L^{-1}	

Table 4. Cont.

B. safensis + B. lichenformis + B. tequilensis + Agrowaste (Ananas comosus 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: 0.5% w/v) (Mekuto et al., 2013)		Wastewater	KCN: 200 and 400 mg CN L^{-1}	T 37°C pH = 9.5	89.5 % (over 8 days) for 200 mg CN L^{-1} 59.75 % (over 8 days) for 400 mg CN L^{-1}	
Burkholderia cepacia C-3(Adjei and Ohta, 2000)			Free cyanide 260 mg L^{-1} Fructose	T 30°C pH =10	80%	
Pseudomonas sp. (Kao et al., 2003)			Free cyanide 100 mg L^{-1} Lactate, sucrose	T 28-30°C pH 9-9.2	60%	
Pseudomonas sp. (Akcil et al., 2003)			Free cyanide 400 mg L^{-1} Whey	T 30°C pH 9-9.2	89%	
Klebsiella oxytoca (Kao et al., 2003)			Free cyanide 21 mg L^{-1} Glucose	T 30°C pH 7	99.9%	
Trametes versicolor			Free cyanide 400 mg L^{-1} Citrate	T 30°C pH 10.5	30% (Cabu et al., 2006) 100 % (after 42 h)(Akinpelu et al., 2015)	Ammonium Nitrogen (NH^{4+}-N)
Klebsiella oxytoca (Chen et al., 2008)	Nitrogenase		Free cyanide 157 mg L^{-1} Glucose	T 30°C pH 7	26%	
Pseudomonas pseudoalcaligenes CECT5344(Huertas et al., 2010)			Free cyanide 40 mg L^{-1} Acetate	T 30°C pH 9.5-10	99.9%	
Klebsiella pneumoniae + Ralstonia sp.(Chaudhari and Kodam, 2010)	Thiocyanate hydrolase	Wastewater (Effluent industrial sites)	KSCN (Thiocyanate)	T 37°C pH 6.0	500 - 2500 mg L^{-1} day^{-1}	H$_2$S
Bacillus sp. CN-22 (Wu et al., 2014)	Cyanide dihydratase	Wastewater (Electroplating effluent)	HCN 700 mg L^{-1}	T 31°C pH, 10.3	200 - 6.62 mg L^{-1} 72 h^{-1}	HCOOH NH$_3$
Bacteria + cassava peels (Siller and Winter, 1998)		Wastewater	KCN	T 25-37°C pH 6-7.5	400 mg L^{-1} day^{-1}	HCOO- (formate) NH$_3$
Enterobacter sakazakii (a) *Azotabacter sp* (b) *Rhizobium sp* (c) (Ninan et al., 2013)		Wastewater (effluent de Sago)	KCN	MIC 5000 ppm (a) MIC 50 ppm (b), (c)	99% (after 96 h)	

Table 4. Cont.

Pseudomonas fluorescens + *Chlorella vulgaris.* (Kiruthika, 2008)			Cyanide 0.5 mg + glucose 1 g (a) Cyanide 0.5 mg + glucose 1 g + NaCl 1 g (b) Cyanide 1 mg + glucose 1 g + NaCl 1 g (c) Cyanide 1 mg + glucose 1 g + NaCl 1g (d)	T 30°C pH 7.2 (a), (b) T 30°C pH 8.5 (c), (d)	60% (a) 58% (b) 54% (c) 51% (d)	
Fungus						
Fusarium solani (Barclay et al., 1998)	Cyanide hydratase		KCN 80 mM		Km: 4.7 mM Vmax : 1.7 microM min^{-1} mg^{-1},	
Gloeocercospora sorghi (Jandhyala, 2002)	Cyanide hydratase		KCN 30 mM		Km: 90 mM Vmax: 4.4 mmol min^{-1} mg^{-1}	
Gloeocercospora sorghi (Basile, 2008)	Cyanide hydratase	Wastewater	KCN 20 mM Metal-cyanide complexes	pH: 6 – 8.5 / T: 27- 43°C	< 80% (after 48 h)	
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		
Fusarium oxysporum + *Beta vulgaris(Agrowaste)* (Akinpelu et al., 2015)		Gold mining wastewater	Metal cyanide + KCN 500 mg CN L^{-1}		83 - 263 mg CN L^{-1}	120- 210 mg NH4 +-N L^{-1}
Plants						
Citrus sinensis (Santos et al., 2013)		Citrus sinensis solide waste	Free cyanide (F-CN) 100 mg L^{-1} + 0.1% (w/v) of unhydrolysed *Citrus sinensis* (a) Free cyanide (F-CN) 100 mg F-CN L^{-1} + 0.1% (w/v) of unhydrolysed *Citrus sinensis* (b) F-CN + heavy metals 10 mg L^{-1} (c)	T 50 °C pH 12 (a) et (b) T 40 °C pH12 (c)	17.82 % (a) 62.48 %, (b) 26.35 % (c)	

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 6, which summarize the advantages of the different technologies, and their conditions of application.

Bioremediation application in the world

Most of researches were focused on the

Table 5. Comparison of reports on cyanide biological transformation in soil.

Microorganism/plants	Enzyme	Source	Compounds to be removed	Optimum condition	Degradation efficiency	Final product
Bacteria						
a. *Pseudomonas putida* b. *Pseudomonas picketti* c. *Klebsiella pneumonia* (Silva-avalos et al., 1990)		Sewage sludge (a) Soil (b), (c)	TCN KCN	0.25 - 16 mM TCN 0.25 mM KCN T 41°C (with use of benzyl-amine for (a) ad		$Ni(CN)_2$
Thiobacillus thioparus THI115 (Yamasaki et al., 2002)	thiocyanate hydrolase	Soil	SCN^-	T 30°C	93% (in 38 h)	COS
P. putida (Bipinraj et al., 2003)		Wet soil	SCN^- 2 mM, KCN 0.2 mM, cyanocuprate (TCC) 0.5 mM, tetracyanonickelate (TCN) 0.5 mM Glucose 2 mM or Ferrous sulphide 1% or Thiosulphate 1 %	Alkali condition (4% Nacl) pH 7.5, T 30°C	With glucose : 99% TCC (in 109 cells/ml, 4 h) 92% TCN (in 109 cells/ml, 4 h) 95% KCN (in 109 cells/ml, 6 h) 96% SCN^- (in 109 cells/ml, 6 h) With ferrous sulphide : 81 % KCN (in 6 h) 91 % TC (in 9 h) With thiosulfate: 40 % TC (in 72 h)	
Alcaligenes xylosoxidans subsp (Ingvorsen and Godtfredsen, 1991)	cyanidase	soil	HCN	T 37°C	1% (in 55 h)	$HCOO^-$ NH_3
Fungus						
F. oxysporum N-10 (Yanase et al., 2000)	Hydratase Amidase	Soil	Tetracyanonickelate II (TCN) 0.5 mM and 20 mM	T 30°C	20-30 % (1 week) (for 0.5 mM TCN) 30 % (6 days) (for 20 mM TCN)	HCOOH, $HCOO^-$, NH_3
Fusarium solani + Trichoderma polysporum (Barclay et al., 1998)		Gasworks site soil	Tetracyanonickelate $K_2Ni(CN)_4$ 0.25 mM (a) Hexacyanoferrate $K_4Fe(CN)_6$ 0.5 mM (b) and $K_3Fe(CN)_6$ 0.5 mM (c)	pH 4	95% (b), (c): after 28 days 90% (a): after 28 days	
F. oxysporum + Scytalidium thermophilum + Penicillium miczynski (Barclay et al., 1998)		Gasworks site soil	Hexacyanoferrate $K_4Fe(CN)_6$ 0.5 mM	pH 4	32% after 28 days	

Table 6. Methods applied in bioremediation (Sharma, 2012; Shukla et al., 2010; Vidali, 2001).

Technique	Examples	Advantages	Conditions of application	References
In situ	Biosparging Bioventing Bioaugmentation	Most efficient Non Invasive Relative passive Naturally attenuated process, treat soil and water	Biodegradation abilities of indigenous microorganisms Presence of metals and inorganic compounds Environmental parameters Biodegradability of pollutants Chemical solubility Geological factors Distribution of pollutants	(Bouwer and Zehnder, 1993; Colberg and Young, 1995; Niu et al., 2009)
Ex-Situ	Land farming (Solid-phase treatment system) Composting (Anaerobic, converts solid organic wastes into humus-like material) Biopiles	Cost efficient ,Simple, Inexpensive ,self-heating Low cost Rapid reaction rate, Inexpensive, self-heating Can be done on site	Surface application, aerobic process, application of organic materials to natural soils followed by irrigation and tilling To make plants healthier good alternative to land filling or incinerating practical and convenient. Surface application, agricultural to municipal waste	(Antizar-Ladislao et al. 2007, Antizar-Ladislao et al. 2008)
Bioreactor	Slurry reactors Aqueous reactors	Rapid degradation kinetic optimized environmental parameters Enhances mass transfer Effective use of inoculants and surfactant	Bioaugmentat toxicity of amendments Toxic concentrations of contaminants	(Behkish et al., 2007)

bioremediation of water, soil and solid wastes in lab-scale. Application of bioremediation *in situ* or *ex-situ* is few limited. Figure 2 show the bioremediation applied on the entity polluted by cyanide in the World. Most of them were observed in America such as United States (Akcil and Mudder, 2003; Fernandez et al., 2004; Kunz et al., 1992; Kunz et al., 1998; Pinedo-Rivilla et al., 2009; Silva-avalos et al., 1990; Singleton et al., 1988; Wang et al., 1996), Mexico (Meehan et al., 1999), Ecuador (Diaz and Caizaguano, 1999); Europa such as France (Dumestre et al., 1997; Ferret, 2012), Germany (Ingvorsen en Godtfredsen, 1991), Switzerland (Brandl et al., 2003), Italy (Cipollone et al., 2007), Spain (Luque-Almagro et al., 2005; Luque-Almagro et al., 2008; Quesada et al., 2007), United Kingdom (Baxter and Cummings, 2006; Ezzi and Lynch, 2005), Ukraine (Podolska et al., 2003); Asia such as China (Zhou et al., 2007), India (Bipinraj et al., 2003; Shete and Kapdnis, 2012), Japan (Yamasaki et al., 2002), Iran (Mirizadeh et al., 2014; Naghavi et al., 2012), Malaysia (Maniyam et al., 2011), Taiwan (Kao et al., 2003), Thailand (Potivichayanon and Kitleartpornpairoat, 2010) and Oceania such as Australia (Markwiese and White 1991). Few Africans countries as Ghana (Adii,

2011), Nigeria (Oyedeji et al., 2013), South Africa (Akinpelu et al., 2015; Dent et al., 2009; Jandhyala et al., 2003; Mekuto et al., 2013; Ntwampe and Santos, 2013; Santos et al., 2014; Van Zyl et al., 2011) and Burkina Faso (Razanamahandry et al., 2016) have been applied bioremediation in laboratory scale. Only South Africa country had applied the cyanide bioremediation in field scale (Shumba, 2008). But, cyanide is widely used in the artisanal gold process extraction in African countries (Adii, 2011).

CONCLUSION

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
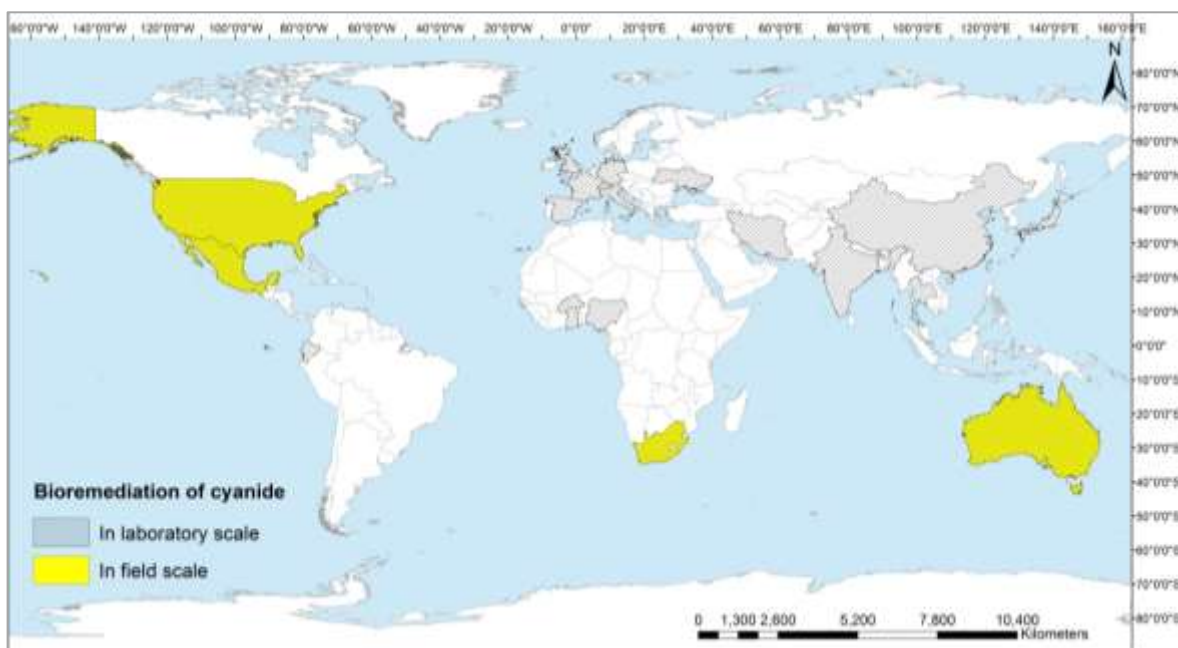
Figure 2. Bioremediation of cyanide in the world.

site. It is a cost effective process than the other conventional methods that are used for clean-up 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. Field scale of cyanide bioremediation is few applied in the World, especially the African countries. Future works should be focused on how to adapt the bioremediation technologies that have already applied in other parts of the world in African context.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

Aazam ES (2014). Environmental remediation of cyanide solutions by photocatalytic oxidation using Au/CdS nanoparticles. J. Ind. Eng. Chem. 20:2870-2875.

Adams M, Lloyd V (2008). Cyanide recovery by tailings washing and pond stripping Miner. Eng. 21:501-508.

Adii E (2011). Isolation of Acidithiobacillus ferrooxidans from sulphur treatment plant mine water and tailings of Anglogold Ashanti concessional area and their biooxidation potential of refractory ores Dissertation Submitted to the Department of Environmental Science College of Science Kwame Nkrumah University of Science and Technology In Partial Fulfillment of the Requirements for the Degree of Master of science in environmental science Faculty of Bioscience. P. 115.

Adjei M, Ohta Y (2000). Factors affecting the biodegradation of cyanide by Burkholderia cepacia strain C-3. J. Biosci. Bioeng. 89:274-277.

Akcil A, Mudder T (2003). Microbial destruction of cyanide wastes in gold mining: process review Biotechnol. Lett. 25:445-450.

Akcil A (2003). Destruction of cyanide in gold mill effluents: biological versus chem- ical treatments. Biotechnol. Biotechnol. Adv. 21:501-511.

Akcil A, Karahan AG, Ciftci H, Sagdic O (2003). Biological treatment of cyanide by natural isolated bacteria (Pseudomonas sp). Miner. Eng. 16:643-649.

Akinpelu EA, Amodu OS, Mpongwana N, Ntwampe SKO, Ojumu TV (2015). Utilization of Beta vulgaris Agrowaste in Biodegradation of Cyanide. Contam. Wastewater Biotechnol. 59-75.

Alesii BA, Fuller WH (1976). The mobility of three cyanide forms in soils. InResidual Management by Land Disposal Proceedings of the Hazardous Waste Research Symposium, US Environmental Protection Agency, Cincinnati, Ohio. p. 213.

Appleton JD, Williams TM, Breward N, Apostol A, Miguel J (1999). Mercury contamination associated with artisanal gold mining on the island of Mindanao, the Philippines. Sci. Total Environ. 228:95-109.

ATSDR (1997). Toxicological Profiles for Cyanide Agency for Toxic Substances and Disease Registry Atlanta GA: US department of Health and Human Services Public Health Services http://wwwatsdrcdcgov/toxprofiles/tp8html

Ballantyne B (1987). Toxicology of cyanides in: Marrs TC (Red) Clinical and experimental toxicology of cyanides Bristol UK: Wright.

Bapat JA, Abhyankar Y (1984). Cyanide poisoning in cattle due to feeding of sorghum. Indian J. Anim. Sci. 54:577-578.

Barclay M, Hart A, Knowles CJ, Meeussen JCL, Tetdl VA (1998). Biodegradation of metal cyanides bY mixed and pure cultures of fungi. Enzyme Microb. Technol. 22(4):223-231

Barcroft J (1931). The toxicity of atmosphere containing hydrocyanic acid gas. J. Hyg. (Lond) 31}1-34

Bard AJ Parsons R Jordan J (1985) Standard Potentials in Aqueous Solutions Marcel Dekker Inc New York

Baxter J Cummings SP (2006) The current and future applications of microorganism in the bioremediation of cyanide contamination Antonie Van Leeuwenhoek 90:1-17.

Behkish A Lemoine R Sehabiague L Oukaci R (2007) Gas holdup and bubble size behavior in a large-scale slurry bubble column reactor operating with an organic liquid under elevated pressures andtemperatures Chem. Eng. J. 128:69-84.

Bipinraj N Joshi N Paknikar K (2003) Biodegradation of cyanides under saline conditions by a mixotrophic Pseudomonas putida in: 15th International Biohydrometallurgy Symposium (IBS 2003) September 14-19 Athens Hellas"Biohydrometallurgy: a sustainable technology in evolution" Pp. 491-496

Boening DW, Chew MC (1999). A critical review: general toxicity and environmental fate of three aqueous cyanide ions and associated ligands Water Air Soil Pollut. 109:67-79.

Botz M, Mudder T, Akcil A (2015). Cyanide treatment: physical chemical and biological processes in: Adams M EL (Red) Advances in Gold Ore Processing pp. 1-28.

Botz M, Devuyst E, Mudder T, Norcross R, Ou B, Richins R (1995). Cyanide: an overview of cyanide treatment and recovery methods. Min. Env. Manag. 3:4-16.

Botz MM (2001). Overview of Cyanide Treatment Methods. Mining Environmental Management Min. J. pp. 28-30.

Bouari AR (2012). Bioremediation of cyanide contaminated water. These for obtaining the grade of master 2at the engineering internationale institute for water and environnement. Ouagadougou. Burkina Faso.

Boucabeille C, Bories A, Ollivier P, Michel G (1994). Microbial degradation of metal complexed cyanides and thiocyanate from mining wastewaters. Environ. Pollut. 84: 59–67.

Bouwer EJ, Zehnder AJB (1993). Bioremediation of organic compounds putting microbial metabolism to work. Trends Biotechnol. 11:287-318.

Brandl H, Stagars M, Faramarzi MA (2003). A novel type of microbial metal mobilization: cyanogenic bacteria and fungi solubilize metals as cyanide complexes in: 15th International Biohydrometallurgy Symposium (IBS 2003) September 14-19 Athens Hellas "Biohydrometallurgy: a sustainable technology in evolution" A. Pp. 457-463.

Brooks K, McGlynn J (1987). Cyanide in gold mining effluents: experiences in New South Wales in: Australia MCo Environmental Workshop Adelaide, Minerals Council of Australia Dickson ACT 1987.

Bureau MBJ, Lefevre SDJP , Gillet C (2011) Cyanures et dérivés. INERI S - Fiche de données toxicologiques et environnementales des substances chimiques.

Cabu A, Unal A, Kolankaya N (2006). Biodegradation of cyanide by a white rot fungus Trametes versicolor. Biotechnol. Lett. 28:1313-1317.

Carling GT, Diaz X , Ponce M, Perez L, Nasimba L , Pazmino E, Rudd A, Merugu S , Fernandez DP , Gale BK , Johnson WP (2013). Particulate and Dissolved Trace Element Concentrations in Three Southern Ecuador Rivers Impacted by Artisanal Gold Mining. Water Air Soil Pollut. Pp.224-1415.

Chaudhari AU , Kodam KM (2010). Biodegradation of thiocyanate using co-culture of Klebsiella pneumoniae and Ralstonia sp. Appl. Microbiol. Biotechnol. 85:1167-1174

Chaumont AJ, Weil E (1960). Intoxications mortelles par cyanures à l'atelier. Arch. Mal. Prof. 21:657.

Chen C, Kao C, Chen S (2008). Application of Klebsiella oxytoca immobilized cells on the treatment of cyanide wastewater. Chemosphere 71:133-139.

Christel D, Eyer P, Hegemann M, Kiese M, Lörcher W, Weger N (1977).

Pharmacokinetics of cyanide in poisoning of dogs, and the effect of 4-dimethylaminophenol or thiosulfate. Arch. Toxicol. 38:177-189.

Cipollone R, Frangipani E, Tiburzi F, Imperi F, Ascenzi P, Visca P (2007). Involvement of Pseudomonas aeruginosa rhodanese in protection from cyanide toxicity. Appl. Environ. Microbiol. 73:390-398.

Colberg PJS, Young LY (1995). Anaerobic Degradation of Nonhalogenated Homocyclic Aromatic Compounds Coupled with Nitrate Iron or Sulfate Reduction. Microb. Transform. Degr. Toxic Org. Chem. Pp.307-330.

Commission RA (1991). Kakadu Conservation Zone inquiry, final report volume 2 in: Commission RA editor Canberra: Australian Government Publishing Services.

Dash RR, Majumder CB KA (2008). A treatment of metal cyanide bearing wastewater by simultaneous adsorption biodegradation (SAB). J. Hazard. Mater. 152:387-396.

Dash RR, Gaur A, Balomajumder C (2009). Cyanide in industrial wastewaters and its removal : A review on biotreatment. J. Hazard. Mater. 163:1-11.

Davis R (1981) Cyanide detoxication in the domestic fowl in: Vennesland BE editor Cyanide in biology New York: Academic Press.

Dent KC, Weber BW, Benedik MJ, Sewell BT (2009). The cyanide hydratase from Neurospora crassa forms a helix which has a dimeric repeat. Appl. Microbiol. Biotechnol. 82:271-278.

Diaz X, Caizaguano R (1999). Biorememdiation of cyanide leaching residues. Process Metallurgy, 9:595-605.

Donato D (1999). Bird usage patterns on Northern Territory mining water tailings and their management to reduce mortalities public report department of mines and energy Vol (190) Darwin Northern Territory.

Donato D, Ricci PF, Noller B, Moore M, Possingham H, Nichols O (2008). The protection of wildlife from mortality: Hypothesis and results for risk assessment. Environ. Int. 34:727-736.

Donato DB, Nichols O, Possingham H, Moore M, Ricci PF, Noller BN (2007). A critical review of the effects of gold cyanide-bearing tailings solutions on wildlife. Environ. Int. 33:974-984.

Dorr JVN (1936). Cyanidation and Concentration of Gold and Silver Ores. McGraw- Hill New York.

Doudoroff P (1976). Toxicity to fish of Cyanides and Related Compounds, a review. US Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Duluth, Minn. 155pp.

Dubey SK, Holmes DS (1995). Biological cyanide destruction mediated by microor- ganisms.World J. Microbiol. Biotechnol. 11:257-265.

Dumestre A, Chone T, Portal J, Gerard M, Berthelin J , Dumestre A , Chone T, Portal J, Gerard M, Berthelin J (1997). Cyanide Degradation under Alkaline Conditions by a Strain of Fusarium solani Isolated from Contaminated Soils Cyanide Degradation under Alkaline Conditions by a Strain of Fusarium solani Isolated from Contaminated Soils . Appl. Environ. Microbiol. 63:2729-2734.

Dursun AY , Alık A C, Aksu Z (1999). Degradation of ferrous(II) cyanide complex ions by Pseudomonas fluorescens. Process Biochem. 34:901-908.

Eisler R (1991a). Cyanide hazards to fish wildlife and invertebrates: a synoptic review. US Fish Wildl. Serv. Biol. Report 85:1-55.

Eisler R (1991b). Cyanide hazard to fish. Biol. Report. a85

Environment Australia (2003). Cyanide management: a booklet in the series on best practice environmental management in mining. Canberra environment Australia Canberra.

Environmental Resources Limited, Great Britain Departement of the Environment (1988). Problems Arising from the Redevelopment of Gas Works and Similar Sites London United Kingdom. London: H.M.S.O.

Ezzi MI, Lynch JM (2005). Biodegradation of cyanide by Trichoderma spp and Fusarium spp. Enzym. Microb. Tech. 36:849-854.

Fernandez RF, Dolghih E, Kunz DA (2004). Enzymatic Assimilation of Cyanide via Pterin-Dependent Oxygenolytic Cleavage to Ammonia and Formate in Pseudomonas fluorescens NCIMB 11764. Appl. Environ. Microbiol. 70:121-128

Ferret C (2012). Rôle des Pseudomonas fluorescents dans la biodisponibilité des métaux contaminant les minéraux du sol :

application à la phytoremédiation Thèse pour obtenir le grade de docteur de l'université de Strasbourg. Ecole doctorale des sciences de la vie et de la santé. Université de Strasbourg.

Flynn CM, Haslem SM (1995). Cyanide Chemistry-Precious Metals Processing and Waste Treatment. US Department of the Interior, Bureau of Mines 9429, 282 pp.

Franson M (1992). Standard methods for the examination of water and wastewater 18th ed.

Fuller WH (1984). Cyanides in the environment with particular attention to soil in: Cyanide and the environment. Geochemical Engineering Program vol 1 Colorado State University Fort Collins 19 – 46.

Gupta N, Balomajumder C, Agarwal VK (2010). Enzymatic mechanism and biochemistry for cyanide degradation: a review. J. Hazard. Mater. 176:1-13.

Gurbuz F, Ciftci H, Akcil A (2009). Biodegradation of cyanide containing effluents by Scenedesmus obliquus. J. Hazard Mater. 162:74-79.

Hagelstein K (1997). The ecotoxicological properties of cyanide ACMRR Short course notes on management of cyanide mining Qld.

Hallock RJ (1990). Elimination of migratory bird mortality at gold and silver mines using cyanide extraction. In: Proceedings of Nevada wildlife/mining workshop Reno, pp. 9-17.

Handbuch G (1977). Der anorganichen chemie. Verlag Chemie GmbH,Weinheim, Germany.

Henny CJ, Hallock RJ, Hill E (1994). Cyanide and migratory birds at gold-mines in Nevada USA. Ecotoxicology, 3:45-58.

Huertas MJ, Sáez LP, Roldán MD, Martínez-Luque M, Blasco R, Castillo F, Moreno-Vivián C, García-García I (2010). An Alkaline cyanide degradation by Pseudomonas pseudoalcaligenes CECT5344 in a batch reactor Influence of pH. J. Hazard. Mater. 179:72-78.

Ibrahim KK, Syed MA, Shukor MY (2015). Biological remediation of cyanide: a review. Biotropia (Bogor) 22:151-163.

Ingvorsen K, Godtfredsen SE (1991). Novel Cyanide-Hydrolyzing Enzyme from Alcaligenes xylosoxidans subsp denitrificans. Appl. Environ. Microbiol. 57:1783-1789.

IPCS/INCHEM (2005). Cyanogen bromide. International Programme on Chemical Safety and the Commission of the European Communities.

Jandhyala D (2002). Cyanide degrading nitrilases for detoxification of cyanide containing waste waters. Biology and biochemistry. University of Houston, Houston, P.130.

Jandhyala D, Berman M, Meyers PR, Sewell T, Willson RC, Benedik MJ, Sewell BT (2003). CynD the Cyanide Dihydratase from Bacillus pumilus : Gene Cloning and Structural Studies CynD the Cyanide Dihydratase from Bacillus pumilus : Gene Cloning and Structural Studies. Appl. Environ. Microbiol. 69:4794-4805.

Jeffrey MI, Breuer PL (2000). The cyanide leaching of gold in solutions containing sulfide. Miner. Eng. 13(10):1097-1106.

John C (1988). Residue and cyanide management at the Boddington gold mine. AMIC Environmental workshop, Darwin. AMIC, Canberra 2:214-221.

Johnson CA (2014). The fate of cyanide in leach wastes at gold mines : An environmental perspective. Appl. Geochem. 57:194-205.

Jones DA (1998). Why are so many food plants cyanogenic. Phytochemistry, 47:155- 162.

Kao CM , Liu JK , Lou HR , Lin CS , Chen SC (2003). Biotransformation of cyanide to methane and ammonia by Klebsiella oxytoca. Chemosphere 50 :1055–1061.

Kao CM, Chen KF , Liu JK , Chou SM, Chen SC (2006). Enzymatic degradation of nitriles by Klebsiella oxytoca. Appl. Microbiol. Biotechnol. 71: 228–233.

Kao C, Liu J, Lou H, Lin C, Chen S (2003). Biotransformation of cyanide to methane and ammonia by Klebsiella oxytoca. Chemosphere, 50:1055-1061.

Kiruthika AJS (2008). Cyanide Detoxification and Recovery of Gold from Gold Effluent. Adv. Biotechnol. Pp. 20-26.

Kjeldsen P (1999). Behaviour of cyanides in soil and groundwater: a review. Water Air Soil Pollut. 115:279-307.

Klenk H, Griffiths A, Huthmacher K, Itzel H, Knorre H, Voight C, Weiberg O (1996). Cyano inorganics in: Gerhartz W Yamamoto YS Kaudy L Pfefferkorn R Rounsaville JF Ullmanns encyclopedia of industrial chemistry A8 VCH Pp.159-190.

Kumar R, Saha S, Dhaka S, Kurade MB, Kang CU, Baek SH, Jeon B (2017). Remediation of cyanide-contaminated environments through microbes and plants : a review of current knowledge and future perspectives. Geosystem. Eng. 20(1):28-40.

Kunz DA, Chen J, Pan G (1998). Accumulation of α -Keto Acids as Essential Components in Cyanide Assimilation by Pseudomonas fluorescens NCIMB 11764. Appl. Environ. Microbiol. 64:4452-4459.

Kunz DA, Nagappan O, Silva-avalos J, Delongt GT (1992). Utilization of Cyanide as a Nitrogenous Substrate by Pseudomonas fluorescens NCIMB 11764 : Evidence for Multiple Pathways of Metabolic Conversion. Appl. Environ. Microbiol. 58:2022-2029.

Li Q , Jacob DJ , Zhao Y, Kondo Y (2000). Atmospheric hydrogen cyanide (HCN): biomass burning source ocean sink. Geophys. Res. Lett. 27:357-360.

Longe GR, Devries F (1988). Some recent considerations on the natural degradation disappearance of cyanide. In Proceedings Economics and Practice of Heap Leaching in Gold Mining Symposium. Parkville, Victoria, Australia: Australasan Institute of Mining and Metallurgy. Pp. 67-70.

Luque-Almagro V, Huertas MJ, Martinez-Luque M, Moreno-Vivian M, Roldan LMD, Garcia-Gil J, Castillo F Blasco R (2005). Bacterial degradation of cyanide and its metal complexes under alkaline conditions. Appl. Environ. Microbiol. 71:940-947.

Luque-Almagro VM, Huertas M-J, Sáez LP, Luque-Romero MM, Moreno-Vivián C, Castillo F, Roldán MD, Blasco R (2008). Characterization of the Pseudomonas pseudoalcaligenes CECT5344 Cyanase an enzyme that is not essential for cyanide assimilation. Appl. Environ. Microbiol. 74:6280-6288.

Luque-Almagro VM, Moreno-Vivián C, Roldán MD (2016). Biodegradation of cyanide wastes from mining and jewellery industries. Curr. Opin. Biotechnol. 38:9-13.

Luthy RG, Bruce SG (1979). Kinetics of reaction of cyanide and reduced sulphur species in aqueous solution. Environ. Sci. Technol. 13:1481.

Maniyam MN, Sjahrir F, Ibrahim AL (2011). Biodegradation of Cyanide by Rhodococcus Strains Isolated in Malaysia. Int. Conf. Food Eng. Biotechnol. 9:21-25.

Markwiese JT, White CS (1991). Assessment of in situ Bioremediation of cyanide and nitrate at a heap leach mining operatiojn in new Mexico Agencies. Sci. Work Futur New Mex. Water Resour. Res. Inst. Pp. 52-56.

Meehan SME , Weaver TR, Lawrence CR (1999). The biodegradation of cyanide in groundwater at gasworks sites Australia: implications for site management. Environ. Manag. Health 10:64-71.

Meeussen JCL, Keizer MG, Van Reimsdijk WH (1990). The Solubility of Iron-Cyanide in Soils in: F Arendt M Hinsenveld and W J van den Brink (eds) Contaminated Soil 90 Kluwer Academic Publishers Dordrecht NL. p. 367.

Mekuto L, Jackson VA, Ntwampe KS, Obed (2013). Biodegradation of Free Cyanide Using Bacillus Sp Consortium Dominated by Bacillus Safensis   Lichenformis and Tequilensis Strains : A Bioprocess Supported Solely with Whey. Bioremediat. Biodegrad. Pp. 1-7.

Minerals Council of Australia (1996). Tailings storage facilities at Australia gold mines Submission to the senate environment recreation communication and the arts reference committee.

Mirizadeh S, Yaghmaei S, Ghobadi Nejad Z (2014). Biodegradation of cyanide by a new isolated strain under alkaline conditions and optimization by response surface methodology (RSM). J. Environ. Heal. Sci. Eng. 12(1):85.

Mohler JB (1969). Electroplating and Related Processes Chemical Publishing Company Chemical Publishing Company New York New York.

Moran RE (1998). Cyanide Uncertainties. Miner. Policy Cent 16.

Morocco AP (2005). Cyanides. Crit. Care Clin. 21:691-705.

Mudder T, Fox F, Whitlock J, Fero T, Smith G , Waterland R, Vietl J (1998). The Homestake wastewater treatment process. Part 2: Operation and performance cyanide. Monogr. London. Min. J. Books Pp. 365-388.

Naghavi N, Mazrouei B, Afsharzadeh S (2012). Analysis of cyanide

bioremediation using cyanobacterium, Chroococcus isolated from steel manufacturing industrial wastewater. Int. J. Biol. Chem. 6:113-121.

Ninan A, Bharathi S, Prabakaran JJ (2013). Molecular Characterization of Cyanide Degrading Bacterium- Enterobacter sakazakii Isolated from Sago Factory Effluent. Asia Pacific J. Res. 1:43-57.

Nsimba EB (2009). Cyanide and Cyanide Complexes in the Gold-mine polluted land i the East and Central Rand Goldfields South Africa Johannesburg 2009. P.195.

Ntwampe SKO, Santos BAQ (2013). Potential of Agro-Waste Extracts as Supplements for the Continuous Bioremediation of Free Cyanide Contaminated Wastewater .Int. J. Biol. Biomol. Agric. Food Biotechnol. Eng. 7:391-395.

Ohno T (1990). Levels of Total Cyanide and NaCl in Surface Waters Adjacent to Road Salt Storage Facilities. Environ. Pollut. 67:123-132.

Ou B, Zaidi A (1995). Natural degeneration. Min. Env. Manag. Pp. 5-6.

Oyedeji O, Awojobi KO, Okonji RE, Olusola OO (2013). Characterization of rhodanese produced by Pseudomonas aeruginosa and Bacillus brevis isolated from soil of cassava processing site. Afr. J. Biotechnol. 12:1104-1114.

Parga JR, Shukla SS, Carrillo-Pedroza FR (2003). Destruction of cyanidewaste solutions using chlorine dioxide ozone and titania. Sol Waste Manag. 23:183-191.

Patil YB, Paknikar KM (2000). Development of a process for biodetoxification of metal cyanides from wastewater. Process. Biochem. 35:1139-1151.

Pinedo-Rivilla C, Aleu J, Collado I (2009). Pollutants Biodegradation by Fungi. Curr. Org. Chem. 13:1194-1214.

Podolska V, Ulberg Z, Pertsov N, Yakubenko L, Imanakunov B (2003). An approach to cyanide degradation in wastewater of gold ore processing in: 15th International Biohydrometallurgy Symposium (IBS 2003) September 14-19 Athens Hellas "Biohydrometallurgy: a sustainable technology in evolution" Pp. 465-473.

Potivichayanon S, Kitleartpornpairoat R (2010). Biodegradation of Cyanide by a Novel Cyanide- degrading Bacterium. World Acad. Sci. Eng. Technol. 4:1093-1096.

Quesada A, Guijo MI, Merchán F, Blázquez B, Igeño MI, Blasco R (2007). Essential role of cytochrome bd-related oxidase in cyanide resistance of Pseudomonas pseudoalcaligenes CECT5344. Appl. Environ. Microbiol. 73:5118–5124.

Randviir EP, Banks CE (2014). The latest developments in quantifying cyanide and hydrogen cyanide. TrAC Trends Anal. Chem. 64:75-85.

Razanamahandry LC, Andrianisa HA , Karoui H, Kouakou KM, Yacouba H (2016). Biodegradation of free cyanide by bacterial species isolated from cyanide-contaminated artisanal gold mining catchment area in Burkina Faso. Chemosphere 157: 71-78.

Reece R (1997). Cyanide toxicity to birds in: ACMRR Short course notes on management of cyanide mining Perth: ACMRR.

Rieders F (1971). Noxious gases and vapors I: Carbon monoxide cyanides methemoglobin and sulfhemoglobin New York NY 4th McGraw-Hill Book Company.

Ryan P, Shanks R (1996). Tailings dams. Aust. Bird Watch. Pp. 7-11.

Sadler R (1990). The fate of cyanide in the gold processing industry. Aust. Sci. Mag. 1:51-52.

Santos BA, Ntwampe SK, Doughari JH (2014). Continuous Biotechnological Treatment of Cyanide Contaminated Waters by Using a Cyanide Resistant Species of Aspergillus awamori. Environ. Biotechnol. - New Approaches Prospect Appl. Pp. 123 -146.

Santos ABQ, Ntwampe KSO, Doughari JH (2013). Continuous Biotechnological Treatment of Cyanide Contaminated Waters by Using a Cyanide Resistant Species of Aspergillus awamori. Environ. Biotechnol. 24.

Santos BAQ, Ntwampe SKO, Doughari JH, Muchatibaya G (2013). Application of Citrus sinensis Solid Waste as a Pseudo- Catalyst for Free Cyanide Conversion under Alkaline Conditions. BioResources 8:3461-3467.

Sharma S (2012). Bioremediation : Features Strategies and applications. Asian J. Pharm. Life Sci. 2:202–213.

Sharpe AG (1976). Chemistry of Cyano Complexes of the Transition Metals. Acad. Press. London.

Shefchek J, Murarka I, Battaglia A (1995). Subsurface fate and transport of cyanide at MGP sites. Land Contame. Reclam. 3(2):18.

Shete HG, Kapdnis BP (2012). Production and Characterization of Cyanide Hydratase from Micromonospora braunna. Abstract : Univers. J. Environ. Res. Technol. 2:609-615.

Shumba T (2008). Removal of heavy metals from crud and slime dam material using soil washing and bioremediation Thesis submitted in partial fulfillment of the requirements of the degree of Master of Science in Extractive Metallurgical Engineering in the Departement of Process Engineering at Stellenbosch University. P. 131.

Siller J, Winter H (1998). Degradation of cyanide in agroindustrial or industrial wastewater in an acidification reactor or in a single-step methane reactor by bacteria enriched from soil and peels of cassava. Appl. Microbiol. Biotechnol. pp. 384-389.

Silva-avalos J, Richmond MG, Nagappan O, Kunz DA (1990). Degradation of the Metal-Cyano Complex Tetracyanonickelate (II) by Cyanide-Utilizing Bacterial Isolates. Appl. Environ. Microbiol. 56:3664-3670.

Simovic L, Snodgrass WJ, Murphy KL S (1985). Development of a model to describe the natural degradation of cyanide in gold milling effluents. In: Van Zyl, D (Ed.), Cyanide and the environment., vol. II. Colorado State University, USA, Pp. 413- 432.

Sinclair G, McMullen A, Peters R (1997). A case study of bird mortality and cyanide management at Northparkes in: ACMRR Short course notes on management of cyanide in mining: Australian Centre for Minesite Rehabilitation Research, Perth, Australia.

Singleton DR, Smith DW (1988). Improved Assay for Rhodanese in Thiobacillus spp Improved Assay for Rhodanese in Thiobacillus. Appl. Environ. Microbiol. 54:2866-2868.

Smith A, Mudder T (1995). Cyanide, dispelling the myth. Min. Env. Manag. Pp. 4-5.

Smith A , Mudder T (1991). The chemistry and treatment of cyanidation Wastes. Mining Journal Books London.

Souren A (2000). Living with cyanide. Geochem. News. 105:16-26.

Sposito G (1984). The Surface Chemistry of Soils Oxford. Univ. Press NewYork. p234

Staunton P, Jones K (1989). Disposal of cyanide containing tailings. AMIC. Environmental workshop. 1.Ballart: Australian Mining Industry Council.

Stevens DL, Strobel GA (1968). Origin of cyanide in culture of psychrophlic basidiomycetes. J. Bacteriol. 95(3):1094-1102.

Taylor H, Appleton J D, Lister R, Smith B, Chitamweba D, Mkumbo O et al (2005). Environmental assessment of mercury contamination from the Rwamagasa artisanal gold mining centre Geita District Tanzania. Sci. Total Environ. 343:111-133.

Theis TL, Young TC, Huang M, Knutsen KC (1994). Leachate characteristics and composition of cyanide-bearing wastes from manufactured gas plants. Environ. Sci. Technol. 28:99-106.

Thompson LC, Gerteis R (1990). New technologies for mining waste management biotreatment process for cyanide nitrates and heavy metals in: FM DOYLE (ed) Berkeley C (Red) Proceeding of the Western Regional Svmposium on mining and Mineral Processing Wastes. Berkeley California May 30 - June 1 1990 Pp. 271-278.

Van Zyl AW, Harrison STL, Hille RPV (2011). Biodegradation of thiocyanate by a mixed microbial population in: Mine Water - Managing the Challenges IMWA Aachen Germany. Pp. 119–124.

Vidali M (2001). Bioremediation: An overview. Pure Appl. Chem. 73:1163-1172.

Wang C, Kunz DA, Venables BJ, Wang C, Kunz DA (1996). Incorporation of Molecular Oxygen and Water during Enzymatic Oxidation of Cyanide by Pseudomonas fluorescens NCIMB 11764 These include : Incorporation of Molecular Oxygen and Water during Enzymatic Oxidation of Cyanide by Pseudomonas fluorescens NCIMB 1. Appl. Environ. Microbiol. 62:2195-2197.

Ward EWB, Lebeau JB (1962). Autocatalytic production of hydrogen cyanide by a certain snow mold fungi. Can. J. Bot. 40:85.

White CS, Markwiese JT (1994). Assessment of in situ Bioremediation of cyanide and nitrate at a heap leach mining operatiojn in new Mexico. J. Soil. Contam. 3(3): 271-283..

Wiemeyer ST, Hill FH, Carpenter JW, Krynitsky J (1985). Acute oral

toxicity of sodium cyanide in birds. J. Wildl. Discuss. 22:538–546.

Wild SR , Rudd T , Neller A (1994). Fate and effects of cyanide during wastewater treatment processes. Sci. Total Environ. 156: 93-107.

World Health Organization (2004). Hydrogen cyanide and cyanides: Human health aspects Geneva: Wo ed.

Wu CF, Xu XM, Zhu Q, Deng MC, Feng L, Peng J, Yuan JP, Wang JH (2014). An effective method for the detoxification of cyanide-rich wastewater by Bacillus sp CN-22. Appl. Microbiol. Biotechnol. 98:3801-3807.

Xie Y, Hwang CJ (2000). Cyanogen chlorid and cyanogen bromide analysis in drinking water in: John Wley & Sons Chichester UK P 2333 (Red) Encyclopedia of Analytical Chemistry Meyers.

Yacoub M, Faure J, Morena H, Vincent M, Faure H (1974). L'intoxication cyanhydrique aiguë Données actuelles sur le métabolisme du cyanure et le traitement par hydroxocobalamine. J. Eur. Toxicol. 7:22.

Yamasaki M, Matsushita Y, Nyunoya H, Katayama Y, Namura M (2002). Genetic and Immunochemical Characterization of Thiocyanate-Degrading Bacteria in Lake Water. Appl. Environ. Microbiol. 68:942-946.

Yanase H, Sakamoto A ,Okamoto K, Kita K, Sato Y (2000). Degradation of the metal-cyano complex tetracyanonickelate (II) by Fusarium oxysporum N-10. Appl. Microbiol. Biotechnol. 53:328-334.

Young CA, Jordan TS (1995). Cyanide remediation: current and past technologies in: Proceedings of the 10th Annual Conference on 1995 Pp. 104-129.

Young TC, Theis T (1991). Determination of cyanide in manufiictured gas plant purifier wastes. Environ. Technol. 12:1063-1069.

Zagury GJ, Oudjehani K, Deschenes L (2004). Characterization and availability of cyanide in solid mine tailings from gold extraction plants. Sci. Total Environ. 320:211-224.

Zhang J, Hendrix JL (1991). Attenuation of Cyanide in Soils' in: D R Gaskell (ed) EDP Congress Proc Symp Annual Meeting P.677.

Zhou X, Liu L, Chen Y, Xu S, Chen J (2007). Efficient biodegradation of cyanide and ferrocyanide by Na-alginate beads immobilized with fungal cells of Trichoderma koningii. Can. J. Microbiol. 53:033-1037.