



Review

An Overview of Emerging Cyanide Bioremediation Methods

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Abstract: Cyanide compounds are hazardous compounds which are extremely toxic to living organisms, especially free cyanide in the form of hydrogen cyanide gas (HCN) and cyanide ion (CN⁻). These cyanide compounds are metabolic inhibitors since they can tightly bind to the metals of metalloenzymes. Anthropogenic sources contribute significantly to CN⁻ contamination in the environment, more specifically to surface and underground waters. The treatment processes, such as chemical and physical treatment processes, have been implemented. However, these processes have drawbacks since they generate additional contaminants which further exacerbates the environmental pollution. The biological treatment techniques are mostly overlooked as an alternative to the conventional physical and chemical methods. However, the recent research has focused substantially on this method, with different reactor configurations that were proposed. However, minimal attention was given to the emerging technologies that sought to accelerate the treatment with a subsequent resource recovery from the process. Hence, this review focuses on the recent emerging tools that can be used to accelerate cyanide biodegradation. These tools include, amongst others, electro-bioremediation, anaerobic biodegradation and the use of microbial fuel cell technology. These processes were demonstrated to have the possibility of producing value-added products, such as biogas, co-factors of neurotransmitters and electricity from the treatment process.

Keywords: anaerobic biodegradation; cyanide; electro-bioremediation; microbial fuel cell technology; omics



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1. Introduction

The contamination of soil, water sources and air with toxic chemicals, such as cyanide, recently became one of the largest global concerns for scientists and the general public [1]. Cyanide is a triatomic linear molecule and is widely known as a toxic chemical that has extreme toxicity to different living organisms, due to its natural characteristic of inactivating the respiration system by firmly attaching to the cytochrome C oxidase, which is a key enzyme in the electron transport chain [2]. There are several cyanide compounds, which amongst others include sodium cyanide (NaCN) and potassium cyanide (KCN), metal-cyanide complexes, thiocyanates and nitriles; all of these compounds are toxic and this toxicity is dependent on the chemical stability of each compound [3]. Their absorption in the respiratory system, digestive system or skin occurs easily and rapidly. There are three chief inhibition mechanisms of cyanides: (1) cyanide reaction with keto-compounds for cyanohydrin derivative formation; (2) cyanide reaction with Schiff-base intermediates for nitrile derivatives formation; (3) di- and trivalent metal ion chelating in metalloenzymes [3,4].

Cyanide is synthesized naturally through the utilization of cyanogenic microorganisms and plants [5]. However, the presence of the cyanide compounds in the environment emanates from anthropogenic sources, such as pesticides and plastics manufacturing, electroplating, metal and gold mining, amongst others [2,6–8]. The presence of the cyanide compounds in the environment has demonstrated ecological harm and direct threat to the

lives that feed from these water sources [9]. Therefore, it is prudent that the wastewaters that contain these compounds are treated before being discharged into the environment to mitigate against the ecological damage they pose [10]. There are processes which were developed to remediate these compounds and these include physical, chemical and biological remediation [11,12]. The physical and chemical methods have lost their popularity, due to the additional contaminants that these processes produce after remediating the cyanide compounds. Therefore, biological methods were explored and were observed to be environmentally benign, cheaper to operate and robust. This process uses organisms such as bacteria, fungi and algae, amongst others, where these organisms utilize a variety of enzymatic pathways to detoxify the cyanide compounds and these include: (1) hydrolytic; (2) oxidative; (3) reductive; (4) substitution/transfer and (5) synthesis pathway. The cyanide degradation pathway is influenced by the initial concentration of cyanide, pH, temperature, availability of oxygen, and the energy source for cell maintenance and growth, ammonia and various metals ions [6]. Although this process is characterized by high efficiencies and robustness, it is associated with microbial sludge formation which necessitates further processing, thus adding to the costs associated with the process. However, recent research has demonstrated that this sludge can be used to synthesize nanomaterials, which can be utilized in the process of polishing the wastewater for recycling to upstream units and/or disposal.

One of the major determinants of the performance of the biodegradation process is the type of the reactor system that is utilized. Numerous bioreactor configurations were explored, which include the use of a rotating biological contactor (RBC) [13], moving bed bioreactor system [13], stirred tank bioreactor system [14] and packed-bed bioreactors [15], to name a few. These reactor configurations result in satisfactory effluents after a particular period of operation, but are unable to recover value-added products from the processes. Therefore, newer, emerging and rapid technologies that can recover value-added products while treating the wastewaters need to be established [16]. Therefore, this review covers the techniques which can be utilized to recover value-added products from cyanide biodegradation and the application of genetic engineering or omics in accelerating cyanide biodegradation.

2. Emerging Cyanide Bioremediation Methods

2.1. Electro-Biodegradation of Cyanide Compounds

The numerous in situ and ex situ chemical, physical, biological and combinative techniques, such as adsorption, oxidation, electrolysis, simultaneous adsorption and biodegradation (SAB) and sequencing batch reactor (SBR), electro chemical oxidation, electro-coagulation (EC), electro-biodegradation and photo electrochemical degradation were recently assessed and also in the past for cyanide degradation [17–21]. These technologies are classified into two groups, in situ and ex situ techniques. The in situ technologies occur in the original site and they typically display a lower impact and economic cost [22]. In recent years, there has been increasing interest in the usage of electro-bioremediation, a hybrid and novel technique of bioremediation and electrokinetics to increase pollutant mobility, thereby maximizing the interaction among the microorganisms and pollutants in the contaminated soil and wastewater for improved remediation efficiency [23–28]. This technique relies on the application of a direct electric current to the contaminated habitat for pollutant degradation with the microorganisms that are responsible for the treatment of the contaminants, such as hydrocarbons, aromatic organics, inorganic substances (including nitrate, sulfate) and toxic metals [29–31]. The electro-bioremediation (EK-Bio) is a promising technique, especially for organic-contaminated habitats [32], and this technique is usually used for the in situ treatment of soils with low or low-medium permeability with low hydraulic conductivity values, such as clayey soil [22,30,33,34]. One of the most important advantages of in situ soil biological remediation is its independence for the removal of the polluted soil from its original site [26]. However, this technique is associated with high power inputs, which add to the costs of the system, since the electrical current needs to

be applied on the system. In addition, the electrodes which are normally utilized in this process are expensive and would need to be constantly replaced for long term experimental studies, thus adding to the cost of the process [35]. In the electro-bioremediation technique, the treatment of polluted soils occurs through the application of low intensity direct electric current (DC) (approximately $0.2\text{--}2\text{ V}\cdot\text{cm}^{-1}$) between electrodes placed directly into the contaminated soil. The migration of charged ions and many transport mechanisms occurs, such as electro-osmosis, electromigration and electrophoresis that could help the biological processes by collocating the charged species contained in the soil, such as contaminants, nutrients and microorganisms (Figure 1) [22,30,36,37]. During electro-bioremediation, the pollutants, nutrients, electron acceptors and soil microorganisms can move using various mechanisms in the soil and would allow biodegradation to occur [33,38]. The low-level alternating currents (AC) and DC electric fields stimulate the metabolic processes through the increasing activity of the microorganisms and increasing the possibility of interactions between the microorganisms and the pollutant. It also enhances the bioavailability of the contaminants or directly stimulates the microorganisms and finally increases the remediation rate [30,32,36]. The electrokinetic process in the electro-bioremediation technique and the well-known water electrolysis reactions (Equations (1) and (2)) occur at the electrodes. The hydrogen ions and the oxygen gas are produced on the surface of the anode, in an oxidation reaction, and the protons are transported towards the cathode (the negatively charged electrode), forming the so-called acid front. On the other hand, the hydroxyl ions and the hydrogen gas are produced on the surface of the cathode by reduction reactions at the cathode and they are transported towards the anode (the positively charged electrode), forming the basic front [23,39–43].

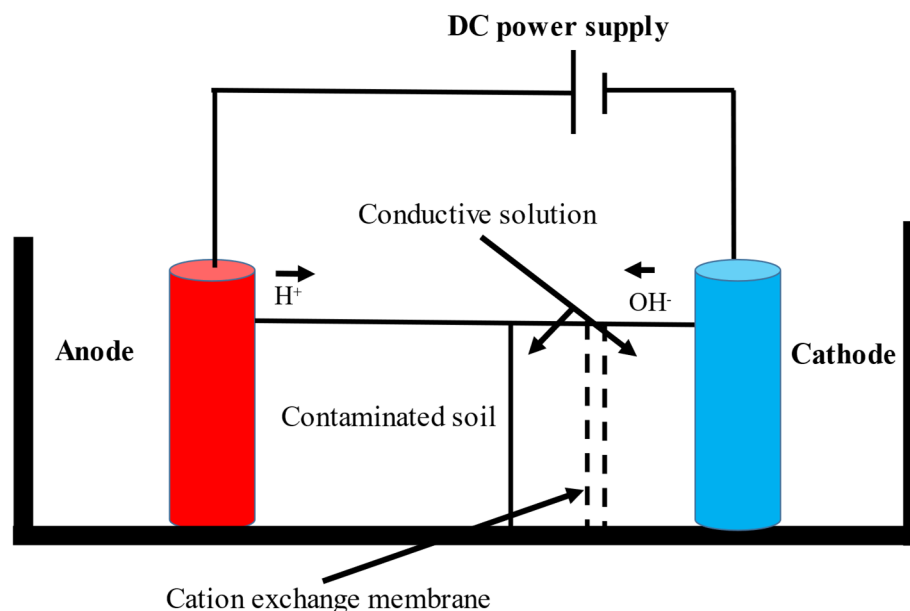


Figure 1. Electro-kinetic remediation process with ion selective membrane [23].

The DC fields and electroosmotic water will cause the microbes' movement towards the anode (as microbes are generally negatively charged) and the bacterial migration to the cathode, respectively [36]. In fact, the success of using electric fields depends on the specific conditions encountered in the field, such as the type and amount of the contaminant present, soil type, pH and organic content [36], including the viability of the microorganisms [40].

The EK-bioremediation can be affected by two main factors: Microorganism- and electrokinetic process-related factors. The microorganism-related factors include the capability

of surviving persistent changes in the soil pH, osmotic stress, temperature (cold or hot weather), UV exposure, dissolved oxygen (DO) and other geochemical conditions [23,44]. The water electrolysis reactions lead to the changes in the soil pH in EK remediation and the soil pH near the anode is in the range of 2–3.5 (organic degradation) and near the cathode, between 8–11 [24]. These changes of the soil pH near the anode and the cathode play a very important role in the outcome of the contaminants' electro-bioremediation. Most of the bacteria are viable at the optimum pH between 6 and 8, and the abrupt change in the pH gradient across the cell membrane has an adverse effect on the growth and metabolism of bacteria [40–43]. Several conventional and innovative techniques can be applied to control the pH during electrokinetic remediation, such as using an ion selective membrane which prevents the ions transport to the soil [45], adding chemical conditioning agents such as ethylene diamine tetra-acetic (EDTA), acetic acid and nitric acid [46–49], the constant changing/removing of the electrode compartments' solution [50], stepwise moving anode [51,52], polarity exchange [42,53], circulation of an electrolyte (anolyte and catholyte) solutions in the electrode compartments [54–56], the two anodes' technique (TAT) and the implementation of the circulation of the electrolyte solution [57]. The new technique is used to neutralize the hydroxyl ions and protons produced at the cathode and anode and water is formed with an anode and a cathode at the same water compartment [23]. In addition, an increase in the temperature between 5 and 20 °C, with the maximum increase in the soil near the anode during electrokinetic processes, was reported and the optimum temperature for the microorganism degradation was between 25 °C and 40 °C [37,58]. The increase in the temperature in EK-bioremediation may have a positive impact on microbial activities, but the high temperatures that result from high applied voltages for a prolonged duration have a detrimental effect on the viability of microorganisms [59].

It was found that the electric current had a detrimental effect on low initial cell densities, however, high cell densities survived despite the applied electric field intensities [60]. When the high electric field intensities are applied to low cell concentration setups, an overwhelming concentration of the cells is reduced, due to the applied current. This is explained by the delayed formation of the extracellular polymeric substances, which form a protective layer especially in high cell densities.

Another study showed that using the optimum electric field in electrokinetic bioremediation not only removed the pollutants but also retained most of the microorganisms [61]. Sub-lethal injuries, irreversible dielectric cell membrane breakdown or changes in the physicochemical surface properties can be observed in the EK bioremediation when DC is applied to living microbial cells; depending on the cell type and environmental characteristics, the treatment time is often maximized [27,62,63]. In addition, the migration of large volumes of charged ions to the oppositely charged electrodes and their accumulation in that location can affect the microbial activity and biodegradation efficiency [32]. In this technique, the production of toxic compounds (that is, those induced by the application of an electric field) led researchers to use bacteria that have the ability to tolerate stress environments [30]. Despite these changes in the environment of the process, some of the microorganisms protect themselves from external stresses by forming biofilms or producing spores [64].

The electrokinetic processes are affected by the following factors: electrolysis reactions; electric current and power for electrokinetics; the availability of power lines near the contamination sites; the cost of electricity; and the change in temperature [23]. The most important challenge for EK bioremediation is its high cost due to the high energy consumption. A renewable energy source, such as solar energy, to supply the electricity to the process can be a cost-effective and eco-friendly option and this source of energy has some benefits, which can enhance the remediation process [63,65–68].

Cyanide destruction using electrochemical oxidation was studied elsewhere, where the authors used the Ti/SnO₂-Sb-Ce anode under varying physicochemical conditions and observed a degradation efficiency of >98% in 4 h under alkaline conditions. However, it is worth noting that this process was not a biological process but rather an electrochemical

process [69]. To the authors' knowledge, there was only a single study that utilized a bacterium during an electro-biodegradation of cyanide, using *Bacillus pumilus* ATCC 7061, where the maximum cyanide concentration of 500 mg/L was degraded over a period of 301 h, with a degradation efficiency of 99.7% [70]. This demonstrated the robustness of this technique in the degradation of cyanide and therefore, more studies need to be undertaken to assess its efficacy. As such, the research needs to be conducted where the energy source to the system is renewable energy in comparison to the currently utilized energy sources, such that future studies can employ a more sustainable approach in conducting electro-bioremediation.

2.2. Microbial Fuel Cells in Cyanide Treatment

It was discovered that extracting energy from organic or inorganic matters by bacteria can provide an efficient method of solving the energy and environmental problems and produce electricity from the waste and renewable biomass [71–78]. The Microbial Fuel Cell (MFC) technology became one of the most attractive technologies for renewable energy production and simultaneous wastewater treatment. This bio-electrochemical transducer is capable of converting the chemical energy of organic or inorganic compounds originating from agricultural, dairy, municipal, food, industrial wastewater and many other sources into electric current, using microorganisms as the biocatalysts [79–82]. An MFC is a galvanic cell that generates electricity as a result of oxidation-reduction reactions and utilizing wastewater as a substrate (electron donor) [83,84]. A conventional two chambered MFC consists of two (anode and cathode) chambers which are separated by a proton or cation exchange membrane (PEM) and the protons produced at the anode pass through PEM to the cathode (Figure 2). The electrodes of both of the compartments are interconnected by an electrical circuit having an external resistor or load connected.

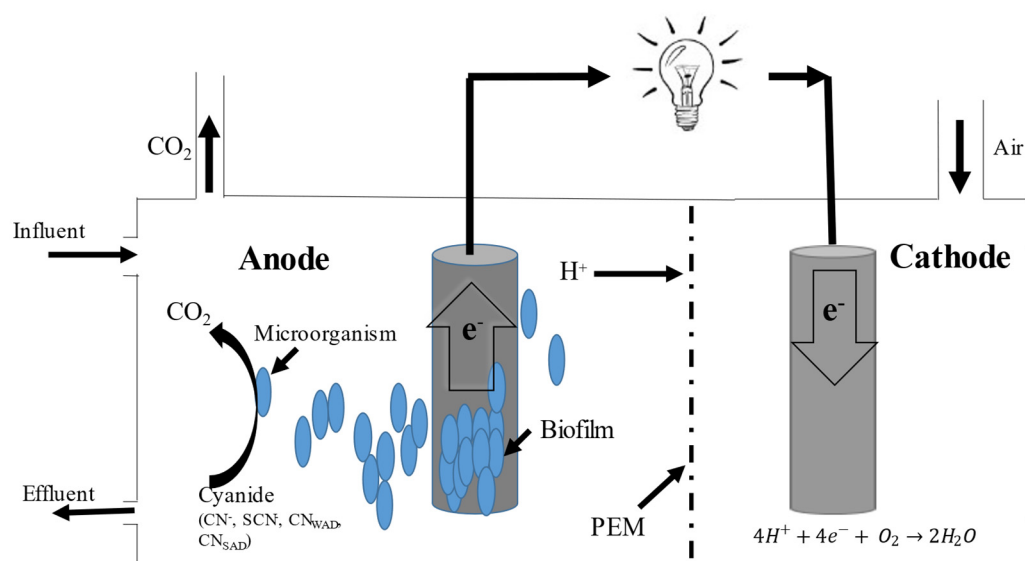


Figure 2. A general scheme of a two chambered microbial fuel cell [76].

At the anodic compartment, the microorganisms can catalyze the oxidative conversions and electrons, and protons and carbon dioxide are produced. After the electrons are produced from the microbial metabolic activity, they are transferred to the anode surface by redox-active proteins or cytochromes, and then passed to the cathode through the external circuit [85,86]. The cathode chamber is aerobic/anaerobic and contains an electrode, an electron acceptor (that is called a terminal electron acceptor (TEA), such as oxygen or ferricyanide, and a catalyst. The reduction in the electrons takes place at the cathode. Finally, the combination of electrons, protons and oxygen occurs in the cathode compartment and water is formed [83,87–91].

The MFC technology has several unique advantages including energy, environmental and operational benefits and it can utilize low-grade biomass or even wastewater to produce bioelectricity. This technology recovers much higher energy via electricity production from various substrates [74,92,93] and the transmission and utilization of electricity are convenient [94]. The MFCs are environmentally friendly technologies and the clean electricity is directly produced from the organic or inorganic matter in wastewater; additionally, some of the additional processes such as separation, purification and conversion of the energy products are not necessary. In comparison, methane and hydrogen can be produced from the anaerobic digestion process which requires separation and purification prior to their use. The power generation of MFCs varies depending on some of the factors that are categorized into two main factors including bacterial-related factors (bacterial metabolism, bacterial electron transfer, operating temperature, the nature of carbon source used, flow rate, sludge age and nature of inoculum used in the anode chamber) and MFCs system-related factors (performance of proton exchange membranes, internal resistance of electrolyte, efficiency of oxygen supply in cathodes, fuel cell configuration, dimensions and volume, nature and type of electrode, mediators present in the cathode chamber, electrolytes used, external resistance and the nature of the proton exchange membrane) [78,95].

The most important characteristics of the electrode material are the surface area, biocompatibility, conductivity, stability and non-corrosiveness [96,97]. A large number of substrates, such as various artificial and real wastewaters and lignocellulosic biomass, are considered as feed for the MFCs [74]. The anodic chamber is anaerobic and contains an electrode, microorganisms and an anolyte. [98]. The carbon-based materials of the anodes are carbon paper, cloth, felt or foam; reticulated vitreous carbon (RVC); graphite sheets, rods and granules; and graphite fiber brushes [99]. The electrons that are produced in the anodic chamber are sometimes transferred to the cathode by electron shuttles or mediators, such as methylene blue, neutral red, thionine, quinone, methyl viologen or humic acid [98,100–103]. The mediators become reduced inside the bacteria during microbial metabolism and the reduced mediator diffuses out of the cell and moves to the anode where it can be oxidized [104]. The electrons are absorbed by the anode and transferred to the cathode where they can reduce the electron acceptor [83,98]. The use of mediators in MFC adds to the cost of the process and they are also toxic compounds.

On the other hand, some of the microorganisms, such as *Shewanella* and *Geobacter*, have endogenous mediators or nanowires, c-type membrane proteins and pilli that can transfer the electrons from substrate to anode. In fact, using electrogenic bacteria is more beneficial [105,106]. In MFC technology, two kinds of microorganisms were used: microorganisms that need a mediator, such as *Saccharomyces cerevisiae* and *E. coli*, [101,103,107,108]; and the mediator-less ones, such as *Shewanella putrefaciens* and *Geobacter* species [72,107,109]. Pure or mixed cultures of microorganisms can be used in MFC, however microbial communities are preferred, due to their nutrient adaptability and stress resistance [110]. In addition, enzymes can also be used in this technology [105]. The oxygen reduction on the cathode is a very slow reaction and the catalysts existing in the cathode compartment is necessary. However, this does not improve the performance of the process since the anode compartment is responsible for performance. It is mainly meant to accelerate the oxygen reduction reaction at the cathode compartment. For improving MFC performance, anode surface modifications with nanomaterials and bacterial gene modifications are the most prevalent approaches [111–114]. For example, the bare electrodes with the low surface area can be easily modified with conductive nanomaterials of a higher surface area, such as graphene [115] and a catalyst such as platinum can be employed to the cathode electrode to increase the rate of oxygen reduction [81]. The best, most frequently used PEMs are Nafion and Ultrex CMI-7000 [81,98,116–120]. Various substrates, including simple and pure matters to a complex mixture of organic and inorganic compounds, can be applied in MFCs. On the other hand, the substrate concentration is one of the most important factors which affects MFC performance. Acetate, lactate, glucose, butyrate, proteins, urine,

cellulose, cysteine, glycine and glycerol, ammonia, metal and lignocellulosic materials are several examples of a simple substrate [90,121].

The different types of wastewater including agricultural, industrial, food, chemical and municipal wastewater are some examples of complex mixture of organic and inorganic compounds. Sulfide, nitrate, ammonium nitroaromatic compounds, chloroethane, pyridine, alkanes, indole, phenol, cellulose, chitin, landfill leachates, pentachlorophenol and hydrocarbon-contaminated wastewater can be used as the substrate in MFC [90,105,121]. The MFCs can also be used for the electricity generation of carbohydrates, such as monosaccharides (hexoses, pentoses) and sugar derivatives (galacturonic acid, glucuronic acid, gluconic acid), polyalcohols, protein-rich wastewater, acetic and butyric acids and volatile fatty acids (VFAs) [76,122]. The different configurations of MFCs are double-chamber MFCs, single-chamber MFCs (SCMFC) that have one side in the anodic solution and the other side is exposed to air and the air-cathode MFC, continuous flow MFCs or up-flow MFCs, integrated MFC systems (continuous flow MFC with multiple electrodes) or stacked MFCs [76,81,97,105]. Some of the recent developments of MFCs include the integration of the MFCs with existing beneficial processes from domestic levels (decentralized systems) to a community level (centralized and industrial systems) [123,124], the advanced treatment of toxic and micro-pollutants such as radioactive compounds and pharmaceutical products, overflow-type wetted-wall MFC (WWMFC), rotatable bio-electrochemical contactor (RBEC), self-stacked submersible MFCs (SSMFC), biocathode MFCs (usage of aerobic or anaerobic biofilms on cathodes for catalysis) [105,125], an air-cathode microbial fuel cell (AC-MFC) that has the capacity to directly use oxygen in the atmosphere as the terminal electron acceptor [126] and MFC system integration [74,127–129]. The basic parameters for the MFC operation are temperature, pH, pressure, salinity, organic loading, feed rate and shear stress [81]. The MFC operation has to occur in mild reaction conditions, such as ambient temperature, normal pressure and neutral pH [84]. The optimum pH for the growth of bacteria should be about neutral pH, but, in the anodic and cathodic compartment, pH will fluctuate between acidity and alkalinity during the course of the process and this affects the performance of the MFC [130]. In addition, power production is increased in high salinity through increasing conductivity [105].

Few studies were conducted on cyanide bioremediation using MFC technology to produce electric energy. A strain of *Klebsiella* sp. was isolated from a microbial fuel cell and designated as MC-1 where the organism was capable of generating electricity from degrading cyanide and exhibiting high electrochemical activity. This strain can use glucose–cyanide mixtures for electricity production in a microbial fuel cell (MFC). The maximum voltage and cyanide degradation efficiency was 412 mV and 99.51%, respectively [82]. In another study, sodium acetate and cyanide were used as the mixed substrates for cyanide degradation and electricity production using strain MC-1 in MFC technology. The cyanide degradation efficiency and the maximum output voltage of MFC were significantly increased. It was revealed that the growth cycle of the microorganism and the trend of electricity production were related to each other in an MFC [16]. In addition, the Haldane model was discovered to describe the degradation kinetics well while the SKIP model described the growth kinetics. A voltage stabilization at 0.55 V was established when the minimal concentrations of cyanide (1.64–20 mg/L sodium cyanide) were utilized, while higher concentrations produced lower voltages. It was proved that the cyanide treatment and electricity generation were feasible and cost-effective using the MFC technology. Due to large amounts of natural cyanoglycosides found in cassava, this results in the cassava mill wastewaters having high cyanide concentrations. The maximum power density of 1771 mW m⁻² was achieved during the treatment of the cassava mill wastewater (16000 mg-COD/L, 86 mg/L cyanide) using MFC [95]. These studies demonstrate the possibility of utilizing this technique for the production of electricity.

This technology was also shown to be applied at a commercial or pilot-scale, where Tota-Maharaj and Paul (2015) showed a power density of 96 mW/m² was achieved from the treatment of domestic wastewater with a 30 to 70% removal efficiency of chemical

oxygen demand [131]. The authors used sea water as their electrolyte in the cathode, while in the anode the domestic wastewater was treated using indigenous microbial communities within the wastewater. In addition, a 200 L MFC system treating municipal wastewater was used to produce 0.8–2.4 V where an energy harvesting device was attached to the system to convert the produced voltage to 5 V, such that ultra-capacitors and other components were charged using the energy produced from the system (Ge et al., 2015) [132]. In another study, Walter et al. (2018) assessed the capability of treating urine from a music festival using 12 MFC modules and it was observed that a cascade of four modules was producing 150 mW continuously for the treatment of the urine [133]. These studies, although only a few are mentioned herein, demonstrate the commercial viability of using MFC.

2.3. Anaerobic Cyanide Biodegradation

The anaerobic biological degradation of wastewaters has gained in popularity, where the microorganisms break down the biodegradable material under anaerobic environments for the treatment of wastewater [134]. This attractive technology has some benefits, which include biogas production, reduced biological oxygen demand (BOD) and these technologies are more cost-effective and energy-saving than aerobic processes. The anaerobiosis can also be a feasible and efficient removal technology for cyanide treatment [135,136]. This technology is used as a renewable energy source since it is able to produce methane (Figure 3) [134,137]. In addition, the digestate from the treatment process can serve as a fertilizer in the agricultural sector [137], thus ensuring a zero-carbon footprint from the process [138–143]. Different bacteria are involved in the breakdown of contaminants in wastewater and these organisms include acidogenic, fermentative and methanogenic bacteria [144,145].

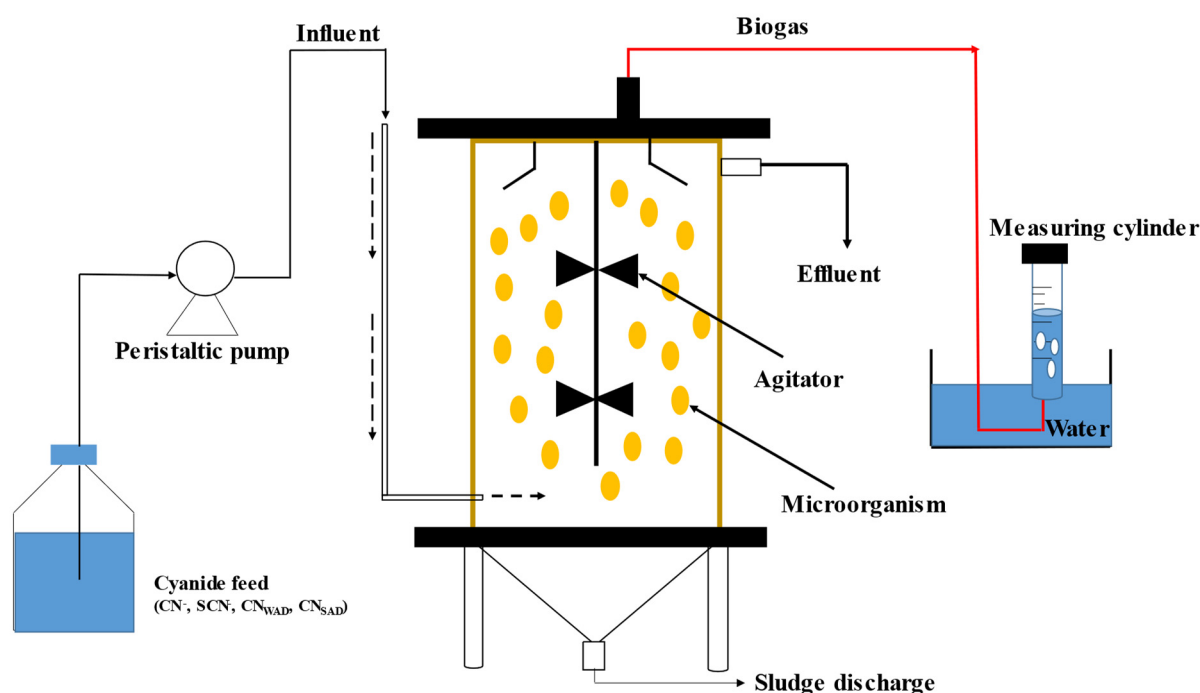


Figure 3. Anaerobic biodegradation of cyanide with biogas formation.

For an optimal anaerobic degradation process, hydrogenotrophic and acetotrophic methanogenesis are important and various processes were developed, such as the up-flow anaerobic sludge blanket (UASB) [146], the anaerobic fluidized bed reactor (AFBR) [147] and the anaerobic attached-film expanded-bed reactor (AAFEB) [137,148]. Several studies focused on the importance of anaerobic biodegradation of cyanide compounds using anaerobic reactors or a combination of both aerobic and anaerobic processes [12,149–153]. The first attempt for cyanide anaerobic biodegradation was carried out by Fedorak and

Hrudey (1989) in methanogenic semicontinuous batch cultures. Novak et al. (2013) and Gupta et al. (2016) reported the ability of Firmicutes with the archaeal genus *Methanosarcina* and anaerobic microorganisms in anaerobic cyanide degradation [151,153–155]. Because of the presence of many relevant metalloproteins in anaerobic microorganisms, especially methanogens, these microorganisms are even more sensitive to cyanide than aerobic microorganisms, and the cyanide toxicity threshold for some of the anaerobes is 2 ppm whereas it is about 200 ppm for most of the aerobic microorganisms [136,149,156–158].

Cyanide biodegradation in aerobic systems is more rapid than in anaerobic systems [141]. Thus, due to the slower growth rate and higher sensitivity to toxic compounds in anaerobic treatment, the aerobic degradation has been studied extensively compared to anaerobic treatment [155,159]. In a study for improving the cyanide biodegradation rate, the acclimatization of anaerobic microbes and identification of microorganisms that can produce methane in the presence of cyanide were carried out [155]. In another study, anaerobic sludge was well acclimatized to cyanide in the digester and the cyanide was successfully decomposed from cassava pulp. In fact, the cyanide anaerobic co-digestion in cassava pulp with pig manure as the co-substrate was successful without any inhibitory effect of the cyanide present in cassava pulp. The removal efficiency and methane yield was 82% and $0.38 \text{ m}^3/\text{kg}^{-1}\text{VSS}^{-1}$, respectively [160]. In addition, the successful cyanide removal, efficient COD removal and possible acclimatization of the biomass in the cyanide-contaminated waters was demonstrated in another study [149]. Among the five pathways for cyanide degradation in microorganisms, only the reductive or hydrolytic pathways are possible under anaerobic conditions [159]. The nitrogenase enzyme is involved in the reductive pathway that is required for biological nitrogen fixation and converts HCN into methane and ammonia as the end products [151]. This oxygen-sensitive enzyme is rarely found in living organisms, and thus, the cyanide degradation using this pathway is believed to be minimal [8,161,162]. Five different enzymes: (i) cyanide hydratase; (ii) nitrile hydratase; (iii) thiocyanate hydrolase; (iv) nitrilase and (v) cyanidase are involved in the hydrolytic pathway, which is the most commonly occurring pathway [8]. Table 1 summarizes the performances of the mentioned methods.

Table 1. The performance of the emerging methods for biodegradation of cyanide and related compounds.

Method		Performance Parameters							Reference
Reactor Type	Contaminant	Removal Efficiency (%)	Microbial Source	Anode	Cathode	pH	Temperature (°C)		
EBC	Free cyanide	99.7	<i>Bacillus pumilus</i> ATCC 7061	Aluminum	Aluminum	NM	30	[163]	
EK-BIO									
sMFC	Free cyanide	100	<i>Klebsiella</i> sp. (MC-1)	Disc graphite felt	Disc graphite felt with Pt	-	25	[16]	
dMFC	COD	88.34	<i>Klebsiella</i> sp.	-	-	-	25	[82]	
dMFC	Cyanide	99.51	<i>Klebsiella</i> sp.	-	-	-	25	[82]	
dMFC	Thiocyanate	100	<i>Thiobacillus</i> sp.	Graphite felt	Graphite felt	7	8	[164]	
sMFC	Phenol	88.9%	NM	Carbon felt	Carbon cloth with Pt	7	25	[165]	
sMFC	Ammonium	96.8%	WWTP sludge	Carbon cloth	Carbon Cloth	-	30	[166]	
ACMFC	COD	91%	Aerobic denitrifying sludge	Carbon fiber felts	Carbon fiber felts	8.0	-	[167]	
ACMFC	Ammonium	99%	Aerobic denitrifying sludge	Carbon fiber felts	Carbon fiber felts	8.0	-	[167]	
AB									
Serum bottles	Tetracyano nickelate	100	<i>Klebsiella oxytoca</i> NSYSU-011	-	-	7.0	30	[168]	
UASB	Free cyanide	100	UASB biomass	-	-	-	-	[151]	
Stirred conical reactor	Free cyanide	90-93%	UASB biomass	-	-	7.2-7.8	31	[160]	
Conical flasks	Free cyanide	100	Heap leach residue and water	-	-	8.5-9.5	22	[169]	
	Nitrate	≤ 40	Heap leach residue and water	-	-	8.5-9.5	22	[169]	
ABR	Potassium tetrahydroxy zinc(II)	100	Cow dung and wastewater sludge	-	-	6.8-8	37	[155]	
Bottle	Potassium cyanide	100	<i>Klebsiella oxytoca</i>	-	-	7.0	30	[170]	
	Phenol	100	<i>Klebsiella oxytoca</i>	-	-	7.0	30	[170]	
SGR	Cyanide	96	Sewage	-	-	8.0	27	[150]	
SGR	Thiocyanate	100	Sewage	-	-	8.0	27	[150]	

dMFC—Double Chamber Microbial Fuel cell; sMFC—Single Chamber microbial fuel cell; ACMFC Air-cathode microbial fuel cell; UFTMFC—Up-Flow Tubular Microbial Fuel Cell; UASB—Up-flow Anaerobic sludge blanket; ABR—Anaerobic batch reactor; SGR—Suspended Growth Reactor; EBC—Electro-Biodegradation Cell; NM—Not mentioned; COD—Chemical Oxygen Demand.

Pterin Production

Various compounds can be produced from the anaerobic remediation of cyanide and amongst these, is pterin. Pterins are ubiquitous compounds that are known as pteridines and they are heterocyclic nitrogen-containing compound made of fused pyrimidine and pyrazine rings [171,172]. Pteridines have the same nucleus of 2-amino-4-hydroxypteridine (pterin) which is a widely conserved biomolecule [173,174]. The pterins were identified as yellow pigments in butterflies and insects before their structures and functions were discovered. These compounds can be colored or colorless and there are three main classes of pteridines: lumazines; isoalloxazine and pterins [171]. Pterins can be classified into two major classes on the basis of the complexity of their side chains, conjugated (such as folic acid and methanopterin) and unconjugated (such as pterin, biopterin, molybdopterin, neopterin and pterin-containing glycosides) [175]. The pterins play essential roles in different organisms including eukaryotic and prokaryotic systems as enzymatic cofactors associated with growth and differentiation processes and antiviral, anticancer, antibacterial and diuretic drugs [174,176]. These compounds have key roles in immune system modulation, cellular signaling, coloration and metabolism regulation and in forming the backbone of several fundamental molecules, such as folic acid. They also mediate protection from UV damage [177]. Pterin has been proposed recently as a drug in neurological disorders and neurodegenerative diseases, such as Parkinson's and Alzheimer's diseases, depression, infantile autism and schizophrenia [175]. These compounds are the cofactor of cyanide monooxygenase (an enzyme involved in the oxygenolytic conversion of cyanide to carbon dioxide and ammonia) which allows bacteria to utilize alternate carbon and nitrogen sources, and the redox potential of pterins indicates that they may have an important role in cellular electron transport [172]. The cyanide oxidative degradation pathway depends on the presence of NADPH (nicotinamide adenine dinucleotide phosphate) and oxygen (O_2) and cyanide is converted into ammonia (NH_3) and carbon dioxide (CO_2) [138]. The immobilized cells of *P. putida* can degrade cyanide compounds (cyanides, cyanates, thiocyanates) and produce ammonia and carbon dioxide effectively using the oxidative pathway [21]. In addition, the strong oxidative enzymes of fungi have key roles in the treatment of xenobiotic chemicals [141].

The presence of cyanide-containing wastewater induces the production of cyanide-degrading enzymes and their necessary cofactors and enhancers in the cyanide-degrading microorganisms for utilizing cyanide as the carbon and nitrogen sources [175]. It was recently shown that cyanide oxygenase (CNO) is a pterin-dependent hydroxylase [176]. The pteridines are present in the prokaryotic system, green-sulfur bacteria and cyanobacteria species, including *Anacystis*, *Anabaena*, *Nostoc*, *Oscillatoria*, *Spirulina platensis* and *Synechococcus*. In addition, some of the anaerobic photosynthetic bacteria (*Chlorobium tepidum* and *C. limicola*) and a chemoautotrophic archaeobacterium (*Sulfolobus solfataricus*) were involved in pteridine production [175]. In a study, it was demonstrated that the main structure of pterins as a cofactor can be prebiotically formed from cyanide polymerizations [171]. The adjustment of the poisonous waste cyanide degradation, that is exploited in some of the industrial activities with the production of useful and therapeutic compounds in the microbial system, is a proven example of wealth from waste which is a promising and eco-friendly technology [175]. The natural production of pterin can be induced with its consecutive expression of cyanide monooxygenase enzyme during the bacterial degradation of cyanide. In a study, it was shown that *Bacillus pumilus* SVD06 is able to utilize cyanide and toxic metals for the efficient production of the pterin compound. The antioxidant properties and antimicrobial activities (against *Escherichia coli* and *Pseudomonas aeruginosa*) of the purified pterin compound were also shown and it was proved that the pterins inhibit the formation of biofilm [174]. Cyanide oxygenase is a cytoplasmic enzyme of *P. fluorescens* that needs a pterin cofactor in addition to oxygen and NADH for optimal activity [178]. Another study was completed for isolating the cyanate- and cyanide-utilizing bacteria, including actinomycetes, from the soil and water samples and their pteridine compounds were extracted [179].

A number of the cyanide-degrading bacteria isolated from an industrial area were screened for the presence of pterins in another work. The extraction and purification of pterins were carried out by an HPLC technique and the characterization of the purified compound was studied using ultraviolet/visible absorption spectrometry, infrared spectroscopy, excitation/emission properties, electrospray ionization mass spectrometry (ESI-MS) and nuclear magnetic resonance spectroscopy (NMR) [172]. The partial purification of CNO was carried out from *Pseudomonas fluorescens* NCIMB 11,764 and it was shown that the cyanide utilization and ammonia/formate production was a pterin-dependent conversion. In addition, it was revealed that there are several reduced pterin species capable of acting as natural cofactors for the enzyme, which were identified in the *P. fluorescens* NCIMB 11,764 cell extracts [180].

2.4. Application of Omics in Cyanide Bioremediation

Cyan-omics are a new generation of omics which develop our knowledge in cyanide biodegradation through applied genomics, transcriptomics and proteomics in bacterial cyanide detoxification. In Cyan-omics, there are three cyanide degrading bacteria which were studied extensively: *Pseudomonas pseudoalcaligenes* CECT5344; *Pseudomonas fluorescens* NCIMB 11,764 and *Azotobacter chroococcum* NCBIMB 8003. The genomes of these organisms were sequenced [143]. The transcriptomic analysis of the whole genome was carried out in *P. pseudoalcaligenes* CECT 5344 and *Nitrosomonas europaea*, using the DNA microarrays from the cells grown in different media, to identify the genes in the cyanide stress response [181,182]. At the proteomic level, some of the methods, such as the two-dimensional electrophoresis, have assisted in the identification of *Klebsiella oxytoca* responses to the presence of cyanide [183,184]. Nitrilase is one of the cyanide-degrading enzymes which can be used for cyanide bioremediation and new organisms containing nitrilase can be identified, using function-driven metagenomic analysis [185,186].

Genetic Engineering

The enhancement of enzyme production that is involved in bioremediation is through the genetic engineering approach, such as isolating the coding genes and the overexpression of enzymes by another expression host, and was successfully accomplished. This biotechnological technique is economic and the stability and activity of the enzymes are increased. The recombinant enzyme purification is easier than in the native strain [187,188]. The half-life, substrate specificity, pH and temperature stability of enzymes is increased by the genetic engineering approach [189]. REMI (restriction enzyme-mediated integration) is a new technique that is used for constructing mutant strains which can degrade cyanide faster than wild type and was recently applied for generating mutants of *Trichoderma koningii* T30, *T. atroviride* and *T. harzianum* and improve their cyanide biodegradability. The cyanide hydratase activity in the mutant strains of *T. koningii* and *T. harzianum* increased and the rhodanese activity in the mutant strains of *T. koningii* and *T. atroviride* increased [187]. A single copy of the cyanide hydratase gene is present in the *Leptosphaeria maculans* genome, although this gene poses as a promoter and contains four putative target sites for molecules such as GATA transcription factors, proteins that regulate nitrogen metabolism and other processes. Potassium cyanide induces the transcription of the cyanide hydratase in an aggressive *L. maculans* isolate [189]. A significant homology is detectable in comparison of the cyanide hydratase gene from *F. solani* and the corresponding gene from *Gloeocercospora sorghi*, *F. lateritium* and *Leptosphaeria maculans*. The expression and utilization of the cyanide hydratase (*chy*) gene could provide an important tool for cyanide biodegradation in activities that generate cyanide wastes [138].

3. Conclusions

The biological degradation of cyanide compounds was deemed as the most effective, robust and environmentally friendly technique for the remediation of these compounds. The recent research was aimed at accelerating the biodegradation process and to recover

resources that can be utilized in the energy and health professions through the treatment process. These techniques include electro-biodegradation and Microbial Fuel Cell technologies, including anaerobic biodegradation systems. These technologies are associated with the following:

- Accelerated cyanide biodegradation through electro-biodegradation;
- Electricity generation through the use of MFC technology;
- Methane production through anaerobic biodegradation systems;
- Production of bioactive compounds, such as pterins.

These techniques proved that cyanide biodegradation can be accelerated while other processes demonstrated the production of value-added products from cyanide treatment. The application of Cyan-omics has also increased our knowledge in cyanide degrading microorganisms through the use of genomics, transcriptomics and proteomics of the cyanide biodegrading strains. These processes demonstrate the economic value that can be attained from these new emerging processes that can be utilized. However, there have been no studies that have conducted a cost analysis of these processes; this needs to be considered for future studies.

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