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REVIEW ARTICLE

Phytoremediation of cyanide and iron cyanide complexes and the mechanisms involved

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Abstract: This paper reviewed the physical and chemical properties of cyanide species - free cyanide and iron-cyanide complexes, and the potential of cyanide phytoremediation with reference to the phytotoxicity of free cyanide and iron-cyanide complexes in plants. There are three possible pathways, which are β -cyanoalanine synthase, sulfur transferase and formamide hydrolase pathways, for transforming and assimilating endogenous free cyanide in plants. Iron-cyanide complexes are generally resistant to microbial and fungal degradation. It is suggested that there may be undiscovered degradation pathways involved in assimilating iron-cyanide complexes in plants; however the detailed pathways of assimilation of iron-cyanides are still unknown. While uptake of free cyanide is mainly by simple diffusion, as iron-cyanide complexes are membrane-impermeable, it is suggested that the complexes may be transported into the plants through the mode of protein mediated uptake. Upon uptake, biological fates of cyanide species vary with different species of cyanide, depending on their chemical properties and concentrations. Phytotoxicity of free cyanide in plants is much higher than that of iron-cyanide complexes as plants could generally withstand a higher concentration of iron-cyanide complexes comparing with free cyanide. However, it is still unsure if the iron-cyanide complexes are toxic themselves or if they disrupt the metabolism of plants indirectly. It is known that endogenous cyanogenic compounds play a role in providing sources of nitrogen and acting as precursors in some biochemical processes in plants. Studies suggested that exogenous cyanide species, to a certain extent, could benefit the plants through providing nutrition to them. However, there is still no study conclusively indicates that there is a direct acquisition of exogenous cyanide species by plants as their alternative source of nitrogen. Further investigations on the degradation pathways of iron-cyanide complexes and the essential enzymes involved in phyto-assimilation of iron-cyanide complexes are required for better understanding of the degradation and assimilation pathways of cyanogenic compounds in plants.

Keywords: phytoremediation; cyanide; iron cyanide complexes; cyanogenic compounds; phytotoxicity; assimilation; plants

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1 Introduction

Cyanide is used widely in industrial processes, such as mining, extracting, manufacturing processes of gold and other precious metals, chemical synthesis for synthesizing synthetic fibers and plastics, waste treatment processes, and electroplating (Ebbs et al., 2006). It is also produced as by-products during industrial processes such as chemical synthesis, iron and steel production, etc.. Cyanide species are common contaminants presented in former industrial locations that were primarily used for purposes of electroplating or as gashouses, such as some of the "Superfund Sites" in the USA (Boening and Chew, 1999; Meeussen et al., 1994). In the USA, since 1995, cyanide has been listed as one of the top 30 compounds on the CERCLA Priority List of Hazardous Substances (Ebbs et al., 2003). Ebel et al. (2007) has also shown that effluents generated from gold mining and extraction in the tailing ponds contained up to 400 mg/L of total cyanides; of the total cyanides, they included nearly 120 mg/L of free cyanide.

Mobility and speciation of cyanides are much affected by biotic and abiotic factors such as biological activities, redox potential, pH, presence of organic acids, etc. (Ebbs et al., 2008). In soil or sediment, it is believed that there are inter-conversions of different cyanide species (Yu, 2015). Realizing possible solutions for cyanide contamination requires the understanding of cyanide speciation and physical and chemical properties of different forms of cyanide species. In the following, physical and chemical properties, biological fates, specific transformation and assimilation pathways of free cyanide and iron cyanide complexes in plants will be discussed in detail.

2 Free Cyanide and Iron-cyanide Complexes

2.1 Physical and Chemical Properties of Free Cyanide

As the most toxic form of cyanide, free cyanide can exist as cyanide species - hydrogen cyanide (HCN) and cyanide anion (CN⁻). HCN exists as gaseous form under normal environmental conditions and has a very high solubility in water. Dissolution of HCN in water produces weak acid, HCN(aq) with pKa=9.24 at 25°C (Dzombak et al., 2006; Kjeldsen, 1999). Upon dissolution, when pH is lower than 7, free cyanide exists exclusively in the form of HCN(aq); at higher pH, HCN(aq) dissociates in water, forming soluble cyanide anion (CN⁻); and at pH higher than 11, HCN(aq) completely dissociates to form CN⁻ (Kjeldsen, 1999).

Endogenous free cyanide is presented in many vascular plants (Ebbs et al., 2010). The major source of endogenous free cyanide is from hydrolysis of cyanogenic glycosides, which then gives rise to hydrogen cyanide (Yu, 2015). Cyanogenic glycosides are organic cyanide species that present in more than 2650 cyanogenic plant species for self-defense mechanisms or as alternative forms of nitrogen for storage (Dzombak et al., 2006; Ebbs et al., 2006). Although free cyanide exhibits high toxicity, endogenous free cyanide is not likely to cause damage to the cyanogenic plants as the natural occurring level of endogenous free cyanide in plants is usually maintained to be very low (Ebbs et al., 2006). Cyanogenic plants possess high degradation capability to degrade and assimilate endogenous free cyanide (Ebbs et al., 2006), in which the rate of degradation and assimilation of endogenous free cyanide in the plants is higher comparing with that of the generation of endogenous free cyanide (Manning, 1988). There is thus not likely to be accumulation of endogenous free cyanide inside the cyanogenic plants.

2.2 Transformation and Assimilation Pathways of Free Cyanide in Plants

Free cyanide is not likely to be accumulated in plant tissues of healthy plants (Larsen et al., 2005). It is thus suggested that plants could possibly degrade both endogenous and exogenous forms of free cyanide through some defined degradable pathways. Previous studies have identified three possible degradation pathways, which are β -cyanoalanine synthase, sulfur transferase, and formamide hydrolase pathways to be involved in degradation of free cyanide in plants (Yu, 2015).

2.2.1 β-cyanoalanine Pathway

The first metabolic step of β -cyanoalanine pathway is being shown in Figure 1. The enzyme, β -cyanoalanine synthase, which is responsible in catalyzing precursors cysteine and hydrogen cyanide to products β -cyanoalanine and hydrogen sulfide, is a common enzyme found in all vascular plants (Yu, 2015). An enzyme which demonstrates the functions as both nitrile hydratase and nitrilase further catalyzes the conversion of β -cyanoalanine into asparagine or aspartate and ammonium (Ebbs et al., 2010). Asparagine can be converted into aspartate and ammonium by hydrolysis under the catalysis of asparaginase (Bruneau et al., 2006; Lea et al., 2007).



Figure 1. The first metabolic step for metabolism of cyanide through β -cyanoalanine synthase pathway; adapted from Yu (2015) with slight modification

2.2.2 Sulfur Transferase Pathway

The metabolism of cyanide through sulfur transferase pathway is being shown in Figure 2. The sulfur transferase pathway, also called the rhodanese pathway, converts cyanide (CN^{-}) to a less toxic cyanide form of thiocyanate (SCN^{-}) under catalysis of the enzyme rhodanese (Yu, 2015).

2.2.3 Formamide hydrolase pathway

$$CN^{-} + S_2O_3^{2^{-}} \xrightarrow{\text{rhodanese}} SCN^{-} + SO_3^{2^{-}}$$

Figure 2. Metabolism of cyanide through sulfur transferase pathway; adapted directly from Yu (2015)

The metabolism of cyanide through formamide hydrolase pathway is being shown in Figure 3. Cyanide in the pathway is first converted into formamide under catalysis of the enzyme formamide hydrolase, and then subsequently results in formation of formic acid and ammonia with formaldoxime as the intermediate compound (Yu, 2015). Formamide can also be converted into formate and ammonia through direct hydrolysis under catalysis of the enzyme formamide amidohydrolase (Shirai, 1978; Miller and Conn, 1980). Formamide hydrolase pathway was recorded in Japanese apricot (Prunus mume, Sieb. et Zucc.) and loquats (Eriobotrya japonica L.). However, it has not been any record or observation of the pathway in other plants other than the two species listed above (Srivastava and Duvvuru Muni, 2010), the actual significance of the pathway to the metabolism of cyanide in vascular plants therefore remains in doubt.



Figure 3. Metabolism of cyanide through formamide hydrolase pathway; adapted directly from Yu (2015)

2.3 Physical and Chemical Properties of Ironcyanide Complexes

General description of metal-cyanide complexes: various metal cations can form soluble metal-cyanide complexes upon reacting with cyanide anions (CN⁻). Weak metalcyanide complexes are the complexes that have relatively weaker bonds between metal cations and cyanide anions. They tend to dissociate readily upon slightly acidic environment and it causes the release free cyanide in the environment. It therefore raises greater concern with its toxicity in compare with strong metal-cyanide complexes. Copper cyanide species $(Cu(CN)_2^0, Cu(CN)_3^-, Cu(CN)_4^{3-})$, and zinc cyanide species $(Zn(CN)_2^0, Zn(CN)_3^-, Zn(CN)_4^{2-})$ are examples for weak metal-cyanide complexes. Strong metal-cyanide complexes, in contrast, are the complexes with a higher stability and are generally more resistant to dissociation under weak acidic conditions (for $pH \ge 2$) (Dzombak et al., 2006). They thus have lower toxicity in compare with weak metal-cyanide complexes.Gold cyanide complex $(Au(CN)_2^{-})$ is one of the examples. Iron-cyanide complexes such as ferrocyanide ($Fe(CN)_6^{4-}$) and ferricyanide (Fe(CN)63-) are also regarded as strong metalcyanide complexes. Iron-cyanide compounds can exist as more complex compound forms such as ferric-ferrocyanide $(Fe_4(Fe(CN)_6)_3)$, etc. Regarding biodegradation of ironcyanide complexes, they are generally rather resistant to microbial and fungal degradation (Ghosh et al., 1999; Meeussen et al., 1992).

2.4 Transformation and Assimilation of Ironcyanide Complexes in Plants

Although it is obvious that degradation of iron-cyanide complexes is taking place in plants, the exact degradation pathway of iron-cyanide complexes in plants is still not yet known (Yu, 2015). There were two proposed possible transformation and assimilation pathways of iron-cyanide complexes by plants. The first was direct assimilation of iron-cyanide complexes as substrates by plants through an undiscovered pathway (Yu, 2015). The second was dissociation of iron cyanide complexes back into ferric, ferrous and cyanide ions prior to metabolism and assimilation of free cyanide by plants through β -cyanoalanine pathway (Larsen and Trapp, 2006), the pathway as described above in Figure 1. There are studies demonstrated that upon uptake of iron-cyanides from the surrounding environment, iron-cyanide complexes likely maintain as their original complex forms inside the plant materials (Yu, 2015). Studies by Yu et al. (2011; 2012) also demonstrated that there were only slight changes in β -cyanoalanine synthase upon treating the plants with ironcyanides. Yu (2015) in his review commented that there is an indication that dissociation of iron cyanide complexes prior to assimilation may not be necessary and it is more likely that the iron cyanide complexes are transformed and assimilated in plants through an undiscovered pathway instead of β -cyanoalanine pathway.

2.5 Biological Fate and Uptake of Exogenous Free Cyanide and Iron-cyanide Complexes by Plants

Upon uptake by roots, the exogenous cyanide species can stay as unchanged original forms, bind to other compounds or be transformed through degradation, detoxification or assimilation (Bushey et al., 2006). The biological fate of different cyanide species is hugely dependent on the chemical properties and concentrations of the cyanide species (Yu, 2015). Phytotoxic effects to the plants will only appear when assimilation rates of the cyanide species are much slower than that of accumulation rates (Larsen et al., 2005). As aforementioned, the transformation and assimilation of free cyanide in plants are most likely through the defined pathways, such as β -cyanoalanine pathway in vascular plants; while the assimilation of iron-cyanide complexes in plants, as some studies suggested, may be through undiscovered degradation pathways. Exogenous free cyanide is believed to be taken by plants through simple diffusion while exogenous iron cyanide complexes are believed to be impermeable to membrane and therefore studies have suggested the uptake of iron cyanide complexes is through the mode of protein-mediated uptake (Yu, 2015).

3 Phytoremediation

Phytoremediation is commonly referred as the remediation method in utilizing vascular plants, algae and fungi for removing contaminants from the environment through metabolism or sequestration, or by inducing microorganisms to degrade contaminants in soil (McCutcheon and Schnoor, 2003). Polluted sites with low to medium contamination levels would be suitable for phytoremediation (Yu, 2015; Yu and Feng, 2016; Yu and Zhang, 2017). Phytoremediation is the technique that could simultaneously act on a wide variety of media and contaminants (Yu, 2015). It comprises of five technologies, which are phytoextraction, rhizofiltration, phytostabilization, phytovolatization and phytodegradation (Cunningham et al., 1995).

Phytoextraction is to extract contaminants from soil to the aerial tissues of the plants. Contaminants could then be eliminated from the polluted site through harvesting the aboveground plant tissues. This technology depends on factors such as bioavailability of the contaminants, possible concentration of contaminants to be accumulated in aerial tissues of the plants, and biomass production of the plants (Ebbs et al., 2006). Rhizofiltration is to eliminate contaminants from polluted waters through plant roots. The technology is effective in eliminating cationic contaminants (Ebbs et al., 2006). Examples of plants used for rhizofiltration include sunflower (*Helianthus annus* L.) and Indian mustard (*Brassica juncea* L.) (Dushenkov et al., 1995; Dushenkov et al., 1997).

Phytostabilization utilizes plants to modify the physicochemical conditions of the rhizosphere, and thereby stabilizing contaminants through making the contaminants, such as chromium and uranium become less soluble, mobile or toxic (Lytle et al., 1998). The technology can also be done through sequestration of contaminants in the roots of the contaminant-tolerant grasses (Ebbs et al., 2006).

Phytovolatilization is to utilize plants to convert contaminants to their volatile forms and then release the volatile forms to the air. The technology only applies to the contaminants in which their volatile forms are less toxic than their original forms (Ebbs et al., 2006). Examples of contaminants to be remediated include selenium (de Souza et al., 1998; Pilon-Smits et al., 1998) and volatile organic compounds (Meagher et al., 2000; Orchard et al., 2000).

Phytodegradation is to utilize plants to convert mutable contaminants to their other forms through metabolism. Degradation may be incomplete for some contaminants; the effectiveness of phytodegradation thus varies with different contaminants (Ebbs et al., 2006). The examples of mutable contaminants in which phytodegradation is effective include hydrocarbons, ammunition wastes and chlorinated solvents, etc. (Ebbs et al., 2006).

3.1 Cyanide Phytoremediation

Cyanide phytoremediation can utilize multiple phytoremediation technologies as stated above (Ebbs et al., 2006). It can be applied to both aqueous and terrestrial systems (Ebbs et al., 2006).

3.2 Phytotoxicity of Cyanide Species in Plants

The transport and assimilation capability of free cyanide and iron cyanide complexes of plants hugely depends on their genetic compositions (Yu, 2015). With regard to different exogenous species of cyanide with different levels of bioavailability, plants will show different physiological and biochemical responses, resulting in difference in the uptake, transport, assimilation and toxicity of different cyanide species (Yu, 2015).

Phytotoxicity of cyanide species is seen to have multiple effects on plants, ranging from reduction in growth rate (growth rate is dependent on transpiration rate, chlorophyll content, biomass, etc.), to inhibition of enzymatic pathways of plants (Yu, 2015). In terms of accumulation of cyanide species, although roots are in general the major site for accumulation of cyanides (2012), the fate for different cyanide species in plants is likely to be different as different species

of cyanide tend to have different distribution patterns in the plant materials (Yu, 2015). It is observed that the mitochondrial alternative oxidase that presents and activates when the plants are exposed to cyanide is partly responsible for the resistance of plants to cyanide toxicity (Ebbs et al., 2006).

In terms of phytotoxicity of free cyanide in plants, free cyanide is known to cause disruption to the metabolism of plants primarily through binding with sulfur, iron, coppercontaining enzymes and proteins (Ebbs et al., 2003; Schnepp, 2006; Barillo, 2009) or blocking the mitochondrial electron transport system through forming complex with iron in the terminal cytochrome (Cooper and Brown, 2008).

3.3 Phytotoxicity of Exogenous Free Cyanide in Plants

In response to different concentration of free cyanide, different species of plants exhibited different level of phytotoxicity to free cyanide. In general, plants could tolerate a much higher concentration of free cyanide when free cyanide is being applied to the soil rather than the hydroponic solution. The major reason may be due to some free cyanide will react with or bind to chemical substances in the soil to form complexes, causing immobilization or stabilization of some free cyanide in the soil; thus lessening the total free cyanide that is bioavailable to the plants in the soil.

With reference to previous studies, in hydroponic solution, mouse-ear cress (Arabidopsis thaliana) exhibited no toxic effects when exposed to 26 µg CN/L of free cyanide (McMahon-Smith and Arteca, 2000). For basket willows (Salix viminalis), the EC_{50} values were shown to be 1.5 mg CN/L (Trapp et al., 2001, cited in Ebbs et al., 2006). Basket willows exhibited toxic effects with reduction in transpiration by 50% when exposed to 2 mg CN/L of free cyanide for 3 days (Larsen and Pirandello, 2004) When being exposed to equal to greater than 20mg CN/L of free cyanide, it would result in immediate death (Larsen and Pirandello, 2004). For weeping willows (Salix bablylonica L.), the EC_{50} values were shown to be within the range of 3.27 to 8.34 mg CN/L of free cyanide, with the rate of transpiration as the sensitive indicator of toxicity (Yu et al., 2005). Diamond willows (Salix eriocephala var. Michaux), as compared with other willows, seem to have the ability to tolerate a relatively higher concentration of exogenous free cyanide. For basket willows, they already exhibited toxic effects when exposed to 2 mg CN/L of free cyanide for 3 days (Larsen and Pirandello, 2004); diamond willows, on the other hand, exhibited no negative effects on both the transpiration rates and growth rates when exposed to 2 mg CN/L of free cyanide for 20 days (Ebbs et al., 2003).

In soil, from the study by Wallace et al. (1977), bush bean (*Phaseolus vulgaris* L.) wilted after exposed to 25 mg NaCN/kg of soils (dried weight) for 3 days. There was pronounced growth reduction when the bush bean exposed to 100 mg NaCN/kg of soils (dried weight) (Wallace et al. 1977). When exposed to 100 mg NaCN/kg of soils (dried weight) for 9 days, it resulted in absolute lethality of the bush

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bean (Wallace et al. 1977).

From previous studies, positive effects were recorded from several species of plants when they were exposed to a certain concentration of exogenous free cyanide. For weeping willows (*Salix babylonica* L.), they exhibited positive growth when exposed to less than or equal to 4.74 mg CN/L of free cyanide (Yu et al., 2007). For Sorghum (*Sorghum bicolor*), no toxic effect but an increase in rate of transpiration was recorded when the plants were exposed to free cyanide concentration in the range of 20 to 50 mg CN/L in soil (Trapp et al., 2003).

3.4 Phytotoxicity of Exogenous Iron-cyanide Complexes in Plants

As aforementioned, the degradation and assimilation pathways of iron-cyanides in plants still remain questionable. Iron-cyanide complexes are considered to be less toxic to plants when comparing with free cyanide (Yu, 2015). Plants in general could withstand a much higher concentration of iron-cyanide complexes than free cyanide (Yu, 2015).

There were studies demonstrated that solid forms of ironcyanides, such as Prussian blue and Turnbull's blue, would be coated on the roots of plants when exposing the plants to ferrocyanide (Ebbs et al., 2006). Such plants include diamond willows (Salix eriocephala var. Michaux), tomato (Lycopersicum esculentum L.), indian mustard (Brassica juncea L.) and various grasses such as foxtail (Setaria sp.), barley (Hordeum vulgare L.) and wild cane (Sorghum bicolor L.) (Reeves, 2000; Samiotakis, 2002; Ebbs et al., 2006). Reeves (2000) has shown that when exposed to 8 mg/L of ferro-cyanide in hydroponic solution, the roots of diamond willows were coated with heavy precipitation of cyanide solids. With such thick coating, there was a decrease in water use, biomass and area of the leaves of diamond willows (Reeves, 2000). Ebbs et al. (2006) also demonstrated that when grasses including foxtail, barley and wild cane were exposed to ferro-cyanide with concentrations ranging from 30 to 143 mg/L, after 14 to 28 days of exposure, similar coatings with precipitation of cyanide solids on the roots of the plants as Reeves (2000) were observed and recorded. However, it is still not sure if the ferro-cyanide are themselves toxic to the plants, or if the negative impacts on plants such as loss of water use, biomass and leaves area with ferrocyanide exposure were simply due to the indirect effect of precipitation of cyanide solids on roots in blocking the movement of water and solutes across the cell walls of the roots (Ebbs et al., 2006).

With reference to previous studies, in hydroponic solutions, basket willows (*Salix viminalis*) did not show any sign of toxicity when exposed to 10 mg CN/L of ferro-cyanide or ferri-cyanide (Larsen and Trapp, 2006). When comparing with the results of basket willows under exposure of free cyanide in hydroponic solutions, under free cyanide concentration of 2 mg CN/L for 3 days, basket willows already exhibited phytotoxicity effects (Larsen and Pirandello, 2004). The results indicated that basket willows are likely to be more resistant to much higher concentration of iron-cyanide complexes than free cyanide. Other studies investigated on the phytotoxicity of iron-cyanide complexes on Balsam poplars (*Populus trichocarpa* L.). When exposed to 5.4 mg/L of Prussian blue, no toxic effect was observed in Balsam poplars (Larsen et al., 2005; Kang et al., 2007); there was a slight decrease in rate of transpiration when the plants were exposed to 27 mg CN/L of Prussian blue (Larsen et al., 2005; Kang et al., 2007); when exposed to even higher concentrations such as 1350 or even 2500 mg CN/L of Prussian blue, studies have shown that Balsam poplars would still be able to survive but there would be a significant reduction in the rates of growth and transpiration of the plants (Larsen et al., 2005; Kang et al., 2007; Wallace et al. 1977).

In soil, when exposed to 50 mg/L of ferro-cyanide, barley, oat and wild cane did not show any toxic effects or any loss of the biomass (Samiotakis and Ebbs, 2004).

3.5 Benefits of phytoremediation to plants

It is believed that endogenous cyanogenic compounds play a critical role in providing source of nitrogen and acting as a precursor for some biochemical processes in plants (Niedźwiedź-Siegień, 1988; Yu, 2015). For instance, endogenous cyanogenic glycosides are a source of nitrogen for cyanogenic plants and they also act as a precursor for synthesis of amino acids and proteins during the development of the seedlings (Niedźwiedź-Siegień, 1988). Both asparagine and aspartate generated from β -cyanoalanine pathway also act as an extra ammonium source to the plants (Yu, 2015).

For exogenous cyanide species that are the targets for phytoremediation, although there is still no study conclusively indicates that exogenous cyanide species can be directly assimilated by the plants to act as an alternative nitrogen source to the plants, studies have proven that to a certain extent, exogenous cyanide species does benefit plant nutrition (Yu, 2015). Machingura and Ebbs (2010) in their study suggested that under nitrogen-limiting conditions and non-toxic exogenous cyanide concentrations of, wheat can utilize exogenous cyanide to act as their alternate source of nitrogen.

4 Conclusions and Future Research Directions

In this review, physical and chemical properties of free cyanide and iron-cyanide complexes were discussed. Three transformation and assimilation pathways of free cyanide in plants were also reviewed. It is suggested that there are undiscovered degradation and assimilation pathways of ironcyanide complexes in plants. Phytotoxicity of free cyanide is higher than that of iron cyanide complexes, in which the plants could generally withstand much higher concentration of iron cyanide complexes when compared with free cyanide. This review also covered the possible benefits for plants in utilizing endogenous and exogenous cyanide as their sources of nitrogen. Although cyanide phytoremediation has been under intensive research in recent years, uncertainties still remain in a few of the study areas, including the physicochemical mechanisms of cyanide species in the environment, the biological mechanisms involved in transport and assimilation of free cyanide within the plants. It is also uncertain of the rule that governs the capacity for cyanogenic and non-cyanogenic plants to phytoremediate free cyanide, the fate of iron cyanide complexes in plants upon uptake, the contribution of exogenous cyanide species as an alternate source of nitrogen, and the factors that affect the uptake rates of cyanide by plants.

It is expected that for future research of phytoremediation, it should focus on these aspects: i) The detailed assimilation and degradation pathways of iron cyanide complexes in plants through utilizing N^{15} labeled ferro-cyanide and ferricyanide for quantitatively locating the fate and tracking the transport of iron cyanide complexes in plant tissues upon uptake; ii) The essential enzymes involved in phytoassimilation of iron cyanide complexes in plants and the respective DNA and proteomic expression of the enzymes, in order to have a better and a more complete understanding of the assimilation pathways of cyanogenic compounds in plants.

The recent momentum of biodegradation and transformation of pollutants has been obvious in developing countries, including Brazil, China, India as examples, but little innovation or breakthroughs have been discovered (Gu, 2016). It is important to keep in mind that new technological development will be based on new original research on new discoveries and such focus shall be made in future research.

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Conflict of Interest

All authors declare that they have no conflict of interest.

Ethical Approval

This article does not contain any studies with human participants or animals performed by any of the authors.

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