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Health exposure risks and bioremediation of cyanide in cassava processing effluents: An overview

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ABSTRACT

Cassava (*Manihot esculenta* Crantz) and its by-products (cassava flour from the dry and water groups, *tapioca, tarubá, tucupi* and leaves) can bring risks to health and contamination of environmental compartments, due to the release of free cyanide (CN^-) and/or hydrocyanic acid (HCN) contents from cassava processing. However, the use of bioremediation with native microorganisms isolated from cassava wastewater is an alternative, economical and sustainable technology that could reduce health and environmental risks. Therefore, this work aimed to review the effects of ingesting cyanide-contaminated cassava and the main microorganisms that can bioremediate cyanide in cassava processing effluents.

1. Introduction

Cassava (*Manihot esculenta* Crantz) is important for traditional communities in some countries, including the Legal Amazon region in Brazil, due to its socioeconomic relationships linked to family farming, food security, practicality and simplicity in production even under adverse conditions [1,2]. In the different cassava varieties, cyanogenic glycosides are found, which may vary according to the variety, plant age and soil and climatic conditions, contaminating the environment and harming human health [3–7]. Human exposure and the risks generated by cyanide (CN^-) contained in cassava roots, occur mainly through inadequate consumption of cassava, without proper cooking [8–10], which can cause several clinical manifestations, from mild to severe, such as headache, nausea, vomiting, dizziness, mental confusion, hypertension, dyspnea, fixed and non-reactive pupils, difficulty breathing, cardiovascular problems, and loss of consciousness [3,9,11,12]. The effects of CN^- in the human organism are immediate such as the inhibition of the antioxidant defense against free radicals in the cells, the alteration of cellular ion homeostasis (alteration of the processes and reactions necessary for the maintenance of the living organism) and the inhibition of cellular respiration [13]. During the cassava processing the roots are crushed and pressed, in which, the solid part will serve for the production of flour and the liquid part (*manipueira*), will serve for *tucupi* production (obtained after spontaneous fermentation in environmental conditions and cooking) [14]. The *manipueira* when poured incorrectly, generates chemical and physical alterations, due to the bioavailability of the organic material and CN- contaminating the environmental compartments [15]. Thus, even containing toxic substances in cassava effluents, we can find microbial diversity such as *Bacillus* spp. and *Pseudomonas aeruginosa*, which may be beneficial in terms of

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Abbreviations: ATSDR, Agency for Toxic Substances and Disease Registry; $CaCN_2$, Calcium cyanide; Cu_2S, Chalcocite; $CuFeS_2$, Chalcopyrite; Co, Cobalt; CuCN, Copper cyanide; CN^-, Cyanide; EU, European Union; Fe^{3+}, Ferric ion; $Fe(CN)_6^{4-}$, Ferrocyanide; Fe^{2+}, Ferrous ion; FAO, Food and Agriculture Organization of the United Nations; CNO^-, Formation of cyanate; HCNO, Generate hydrogen cyanate; HCN, Hydrocyanic acid; H_2S, Hydrogen sulfide; SINAN, Information System for Notifiable Diseases; Fe, Iron; LD_{50}, Lethal dose; HgCN, Mercury cyanide; MS, Ministry of Health; $NiCN_2$, Nickel cyanide; PCR, Polymerase chain reaction; KCN, Potassium cyanide; FeS, Pyrrhotite; AgCN, Silver cyanide; NaCN, Sodium cyanide; SCN^-, Thiocyanate; hv, Ultraviolet radiation; WHO, World Health Organization; $ZnCN_2$, Zinc cyanide.

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bioremediating the CN^- present in these effluents [16,17]. Therefore, the objective of this review was to present the effects of the ingestion of CN^- by the consumption of cassava and its by-products, as well as the microorganisms used to reduce the cyanide present in the effluents of cassava processing.

2. Cyanide: Sources and toxic forms

The main sources of CN^- come from metal mining processes, organic chemical industries, pharmaceuticals, plastics, iron and steel plants, wastewater treatment, vehicle exhaust, burning of solid waste, landfills, pesticides, microorganisms (bacteria, fungi, and algae), and naturally in various foods and plants such as cassava [3]. Cyanide, is an easily bioavailable substance in different environmental compartments (soil, water and air) and therefore it is the subject of several socio-environmental discussions [3,6], as in the Amazon, with the extraction of gold by the Mining and illegal mining [18,19]. The availability of CN^- in the environment occurs through processes of complexation, precipitation, adsorption, formation of cyanate (CNO^-) and thiocyanate (SCN^-), volatilization, biodegradation, and hydrolysis [6,20]. In the soil, CN^- binds strongly to the organic and inorganic constituents of the soil (aluminum, iron and manganese oxides, certain types of clay, feldspar, and organic carbon) by adsorption, being able to form HCN, the most toxic form, and cyanate and thiocyanate less toxic forms [21]. Hydrogen cyanide in the soil evaporates and other cyanide compounds are formed, which in high concentrations are toxic to microorganisms [3]. Thiocyanate is formed in soil when CN^- binds to different species present such as free sulfur, mineral sulfides such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S) and pyrrhotite (FeS), polysulfides and thiosulfates [21]. The CN^- toxicity may vary due to intensity of sunlight radiation or ultraviolet radiation (hv), when bound to iron in the soil. In the absence of sunlight or ultraviolet radiation, ferrocyanide [$Fe(CN)_6^{4-}$] decomposes to form ferricyanide (a less toxic substance) in a slow process as can be seen in Eq. 1. In the presence of light, ferricyanide forms volatile and highly toxic hydrogen cyanide according to Eq. 2 [3,22].

$$\mathrm{Fe(CN)_6 3^- + 6H_2O + 3H^+ \leftrightarrow Fe(OH)_3(s) + 6HCN(aq)} \tag{1}$$

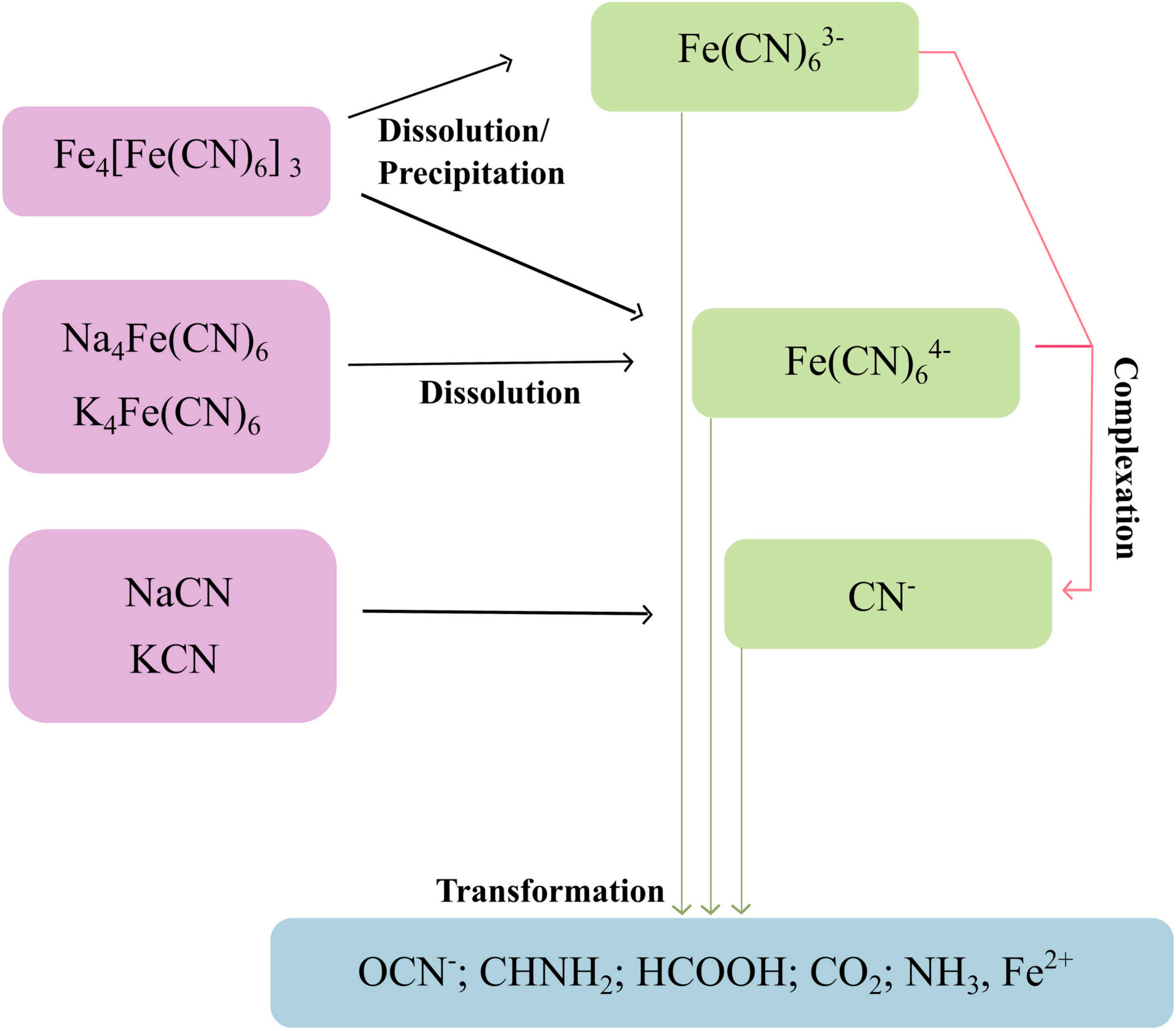

Fig. 1. Processes of cyanide transformation in water and soil.
Adapted from Jaszczak et al. [22] with adaptations.

$$\mathrm{Fe(CN)_6}4^- + hv \rightarrow \mathrm{Fe(CN)_6}3^- + \mathrm{CN}^- \tag{2}$$

In the environment, cyanide undergoes several transformations (Fig. 1), which result in processes that occur in water and soil [22]. Due to the abundance of iron in soils and sediments, complexed cyanide when exposed to sunlight releases free cyanide into the aquatic environment [6]. On aquatic surfaces, the toxic action of CN^- varies according to pH, and may be present in the form of various salts (more toxic complexes and more soluble in water) such as sodium cyanide (NaCN), potassium cyanide (KCN), calcium cyanide ($CaCN_2$) and mercury cyanide (HgCN) and less soluble forms such as copper cyanide (CuCN), zinc cyanide ($ZnCN_2$), nickel cyanide ($NiCN_2$) and silver cyanide (AgCN) [22]. In the atmosphere, CN^- is in the form of gas, HCN and fine dust particles, being removed in approximately 1 to 3 years [3].

3. Cyanide in cassava

Cassava is a weather-tolerant plant (droughts, pests, etc.) and has great nutritional potential (carbohydrates, proteins, sodium, lipids, minerals as magnesium, calcium, iron, and some vitamins) [23,24]. However, depending on the variety (*meek* or *brave*), linamarin and lotaustralin can be toxic since they are cyanogenic glycosides in the concentrations of 92 to 98 % and 2 to 8 %, respectively [7]. This toxicity depends on the conditions of climate, cultivation, growth, age, and consumed parts of cassava (leaves, stalks, and roots) [22,25]. Therefore, it is important to follow all stages of the cassava production chain, in order to obtain the correct processing of the roots and leaves in the artisanal manufacture of flour and other by-products (Fig. 2).

During the artisanal processing of dried cassava flour, in the phase of pressing the cassava mass, a liquid called *manipueira* is generated, which has a polluting power because it contains cyanogenic glycosides. After fermentation and boiling of the *manipueira*, it is possible to obtain the *tucupi*, yellow liquid containing catotenoids, fermented spontaneously by lactic bacteria that produces biogenic amines (tyramine and histamine), used in the preparation of regional foods and presents the potential of gas production [14,26–28]. The production steps of cassava flour, solid and liquid residues are generated, which can be expressed in mass balance, with utilization of these residues using clean technologies (Fig. 3).

According to the amount of kilograms of roots used for the production of cassava flour, the percentage of residues generated are about 18 % of peels, 30 % of *manipueira*, and 24 % of *crueira* (insoluble fraction retained on grid) and water loss through evaporation [29]. During root processing, the cyanogenic glycosides present in the vacuoles of plant tissue, when they suffer rupture, release HCN. This disruption occurs through the enzyme linamarase (β-glucosidase) for linamarin hydrolyses and initiates the chemical reaction to form glucose and cyanohydrin.

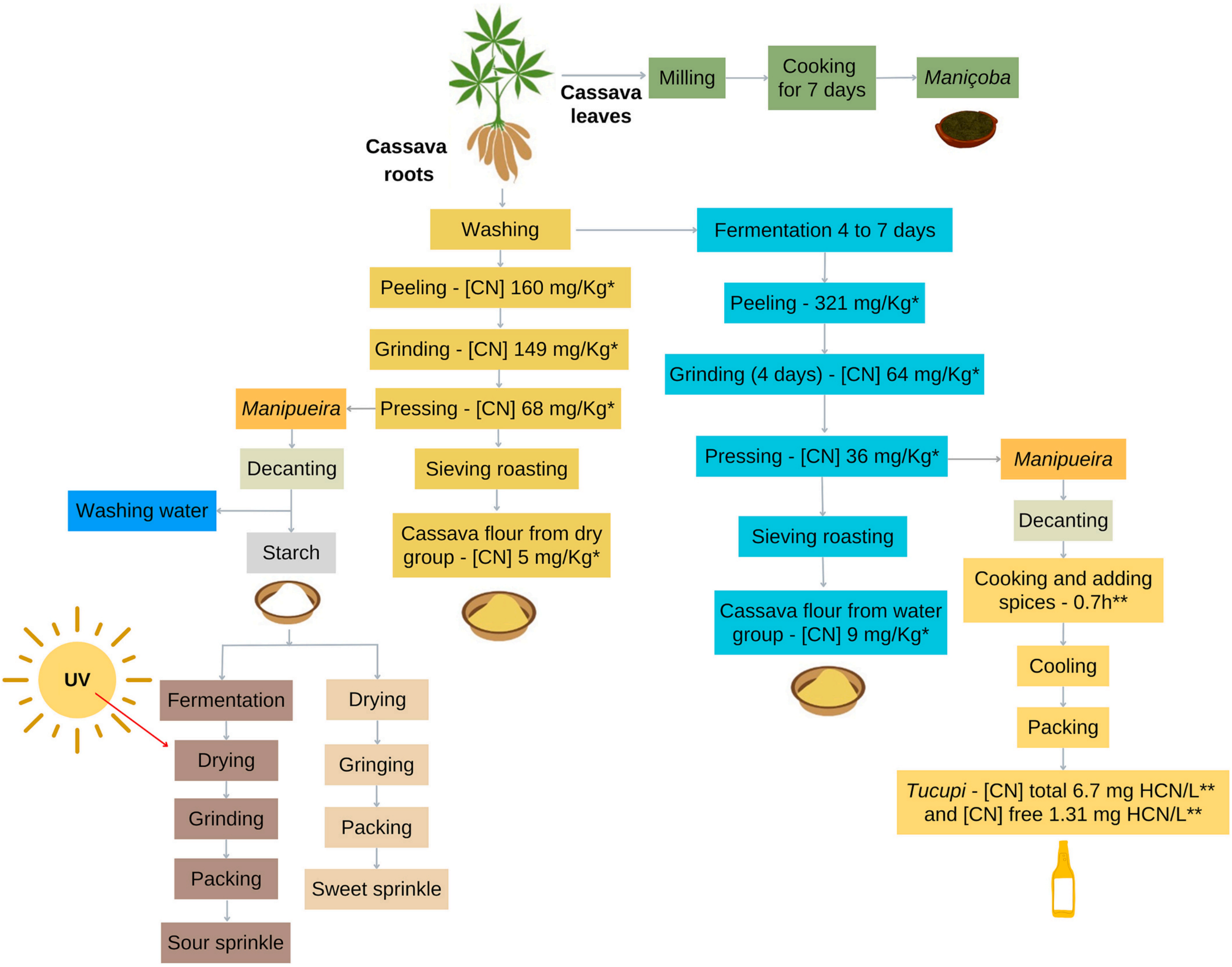

Fig. 2. Cassava production chain and its by-products in the Northern Brazil region.
Adapted from Chisté et al. [30]*, FAO and WHO [42], Cruz et al. [53], Campos et al. [54]** and Lima et al. [55].

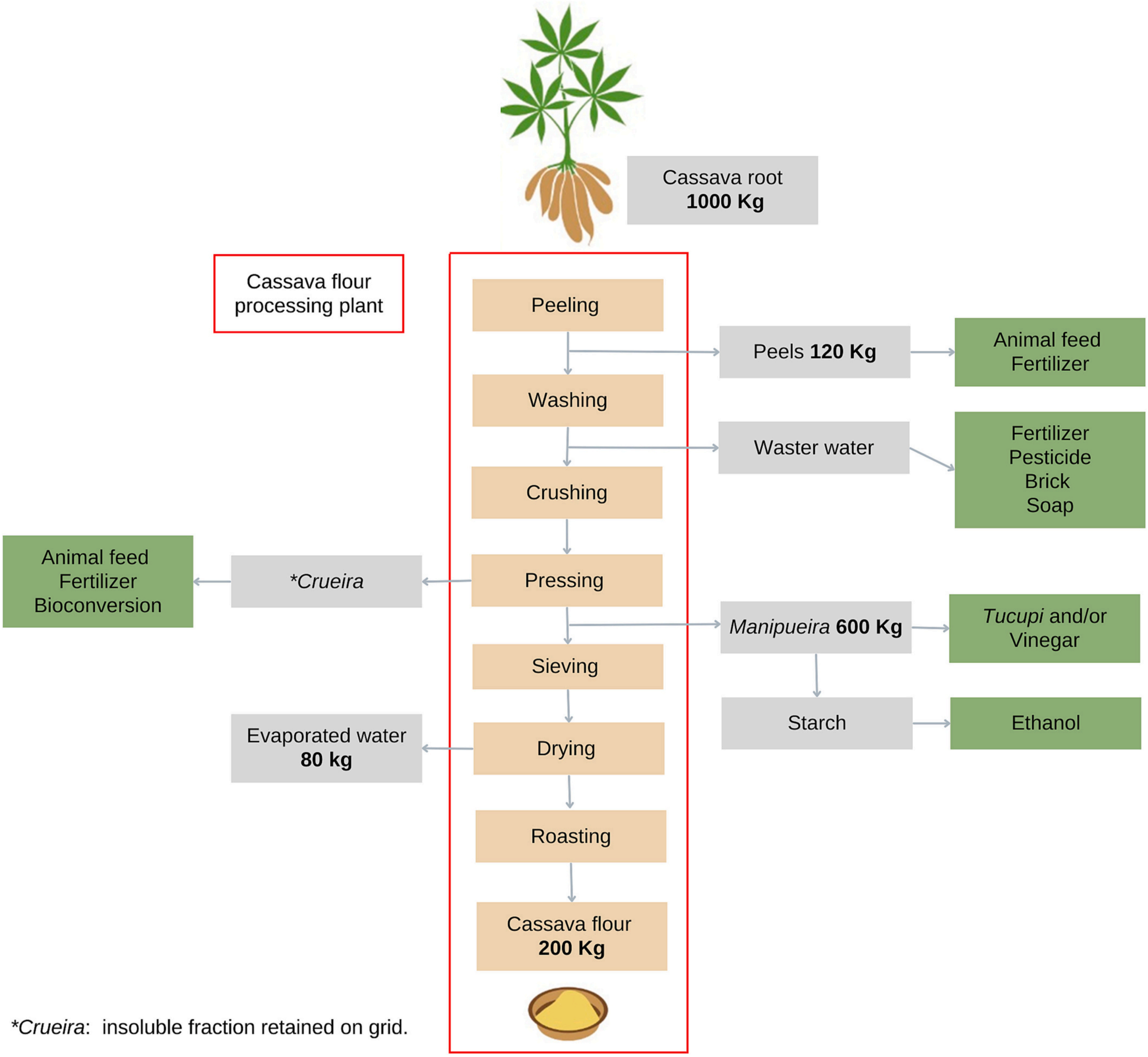

Fig. 3. Mass balance (kg) of the main steps in the production of cassava flour and the utilization of solid and liquid residues using clean technologies.
Adapted from Sebrae [29], Cruz et al. [53], Lima et al. [55] and Jekayinfa and Olajide [56].

The cyanohydrin can be dissociated by the enzyme hydroxynitrile lyase or by spontaneous processes that form hydrocyanic acid and acetone (Fig. 4) [30–32]. Table 1 shows previous studies that reported cyanide concentrations in edible parts of the cassava plant and its by-products.

Although cyanogenic glycosides have toxic effects, they are being used in mice for beneficial research, due to their biological properties (bioavailability, solubility and stability) that have antitumor effects such as amygdalin and linamarin/linamarase, being used to fight bladder, colorectal, liver, ovarian, breast and cervical adenocarcinoma cancers [33,34]. In the case of amygdalin, it acts in reducing glutathione reductase activity and elevates levels of reactive oxygen species (ROS), which at higher levels, suppresses cytochrome C oxidase activity in the electron transport chain, acting as a cytotoxic agent and leading to apoptosis of the cancer cell [34].

4. Cyanide in the human organism

HCN is a toxic and fast-acting substance and its acute (14 days or less), intermediate (15 to 364 days) or chronic exposure (365 days or more) will depend on the amount of the dose and the duration of time, when absorbed orally, dermally, ocularly or by inhalation [3]. The estimated minimum lethal oral exposure dose of HCN is 0.5 to 3.5 mg/kg per body weight [13]. Cyanide has great affinity for metalloproteins (about 40 enzyme systems) such as cobalt (Co) and ferric ion (Fe^{3+}) in methemoglobin, and cytochrome oxidase and ferrous ion (Fe^{2+}) in hemoglobin [3,28]. In addition to binding to cytochrome *c* oxidase, cyanide can contribute to signs of intoxication due to inhibition of catalase, peroxidase, hydroxocobalamin, phosphatase, tyrosinase, ascorbic acid oxidase, xanthine oxidase, and succinic dehydrogenase activities [3]. The inhibition effect of cellular respiration and the Fe atom interaction with CN^- can be demonstrated in Fig. 5. The cyanide, with a high affinity for the ferric ion (Fe^{3+}), binds strongly to the ferric ion of

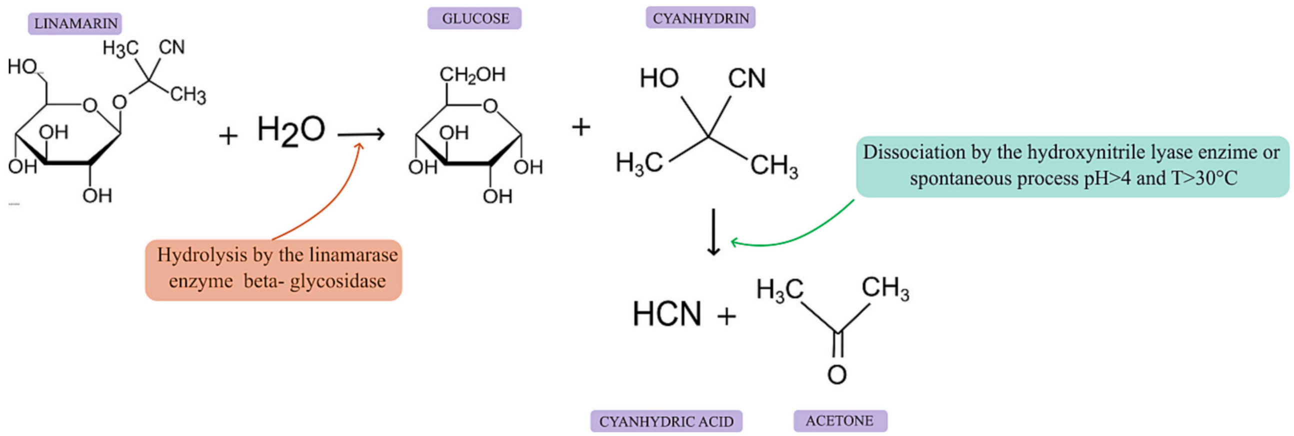

Fig. 4. The action of β-glucosidase and hydroxynitrile lyase enzymes on Linamarin (95 % of cyanogen glycoside present in cassava) responsible and the release of cyanide.
Adapted from Pereira et al. [57].

Table 1
Cyanide concentrations in edible parts of cassava and its by-products.

Cassava/by-products	Cyanide concentration range (mg/kg)	Reference
Bitter leaves	1067.8–2330.2	[25]
Cassava flour from dry group	7.7–20.6	[58]
	5.0	[30]
	16.0–27.0	[59]
Dry leaves	85.0	[60]
Cassava flour from water group	3.6–12.4	[58]
Fresh leaves	800–1600.0	[60]
	7.3–33.2 (after 10 months of cultivation)	
Roots	7.6–33.4 (after 12 months of cultivation)	[57]
	16.0–1212.0	[61]
Sheets	346.0–748.4	[61]
Sweet leaves	386.4–1317.6	[25]
Water flour	9.0	[58]
	6.0–10.0	[59]

(Source: summarized by the authors.)

cytochrome oxidase, forming a relatively stable mitochondrial complex called cyano-cytochrome oxidase, which blocks oxidative phosphorylization (interrupts the transport of electrons in the respiratory system by inhibiting the formation of oxygen, ATP and energy). Consequently, tissue anoxia occurs, which prevents hemoglobin oxygen from being used in cellular respiration [3,26].

Therefore, regardless of the different exposure routes, health is harmed (Fig. 6). The continuous ingestion of cassava and its by-products, when processed incorrectly (without cooking, drying or fermenting properly), brings a series of problems to human health, causing intoxications and the emergence of clinical signs such as mental confusion, muscle paralysis, difficulty breathing, headache, vertigo, blood disorders, thyroid gland enlargement, damage to the brain, central nervous system, heart and kidneys, nausea, vomiting, diarrhea, abdominal pain, acidemia, heart failure, pulmonary edema, dyspnea, bradycardia, hyperlactatemia, hypotension, apnea, seizures, coma, opisthotonos, trismus, mydriasis or even death [3,9,35,36].

An outbreak in Kasese county, Uganda in 2017 left 95 people intoxicated by ingesting cassava flour with a concentration of 88 mg / kg, corresponding to 8 times higher than the World Health Organization recommends (10 mg / kg). The main signs and symptoms detected were vomiting (95 %), diarrhea (87 %), malaise (60 %), dizziness (48 %), tachypnea (27 %), syncope (16 %), tachycardia (10 %) and fever (6 %), with two deaths [37]. Around 143 cases were reported from January 2017 to May 2018, due to intoxication by plants, of which 21 were due to the ingestion of cassava by children and adolescents, obtaining one death and the rest progressed to cure [38]. One child ingested a large amount of uncooked cassava, presenting hours later with acute encephalopathy with signs of mental confusion, drowsiness, vomiting, and cardiac arrest [20]. Healthy adults (12) consumed (acute exposure) pieces of fresh cassava roots (76–150 mg / kg) with an average of 113 mg / kg and the mass of cassava (90–45 g) with an average of 64 g. Consumption occurred in a single meal, where each piece of cassava contained 6.8 mg / kg of cyanide, obtaining an average blood concentration of 15.4 μM of cyanide after 37.5 min of ingestion. Only two subjects reached peaks of 21.5 μM and 31.9 μM after cassava consumption, but there were no clinical signs and symptoms of cyanide intoxication [8]. Workers involved in flour production were investigated for environmental and biological exposure to cyanide in the state of Alagoas, Brazil. Of the 36 workers analyzed, the concentration of CN in the air ranged from 0.235 to 7.77 mg HCN/ m^3, in which five samples were 50 % above the exposure limit of 5 mg /m^3 [39]. Regardless of the route of exposure, small amounts of cyanide (in the form of a gas or salts) can cause health problems (at levels of 0.05 mg / dL or higher) or death (at levels of 0.3 mg /dL or higher). The toxicity of CN depends on the amount, time (duration), the form of exposure, personal characteristics, and habits, in addition to the presence of other chemical substances. People exposed to 546 mg / kg HCN for ten minutes and 110 mg/kg HCN by 1 h died [3].

5. Cyanide exposure biomarkers

Biomarkers are classified as exposure, effect or susceptibility markers, they are indicators that are signaled by biological systems or through environmental samples [3]. In the human body, the amount of cyanide can be quantified by the internal dose of thiocyanate (Table 2) through blood, urine, saliva, tissues or plasma [3,40].

Exposure to cyanide in the human organism can be exacerbated due to the individual's genetic makeup, age, health and nutritional status, and exposure to other toxic substances. Populations most exposed to cyanide (CN^-) and thiocyanate (SCN^-) include active smokers and passive smokers, those who consume foods rich in cyanogenic glycosides, and people who live near industries and hazardous waste deposits, inhale gases from fires, apply pesticides, and work in research laboratories among others [3]. In 2014, the Information System for Notifiable Diseases (SINAN) of the Brazilian Ministry of Health registered around 90.000 cases of intoxication, which 3.4 % were related to intoxication by chemical products. Consequently, it was created a clinical protocol with therapeutic guidelines for the use and treatment of hydroxocobalamin in patients exposed to or intoxicated by cyanide in its acute form [11].

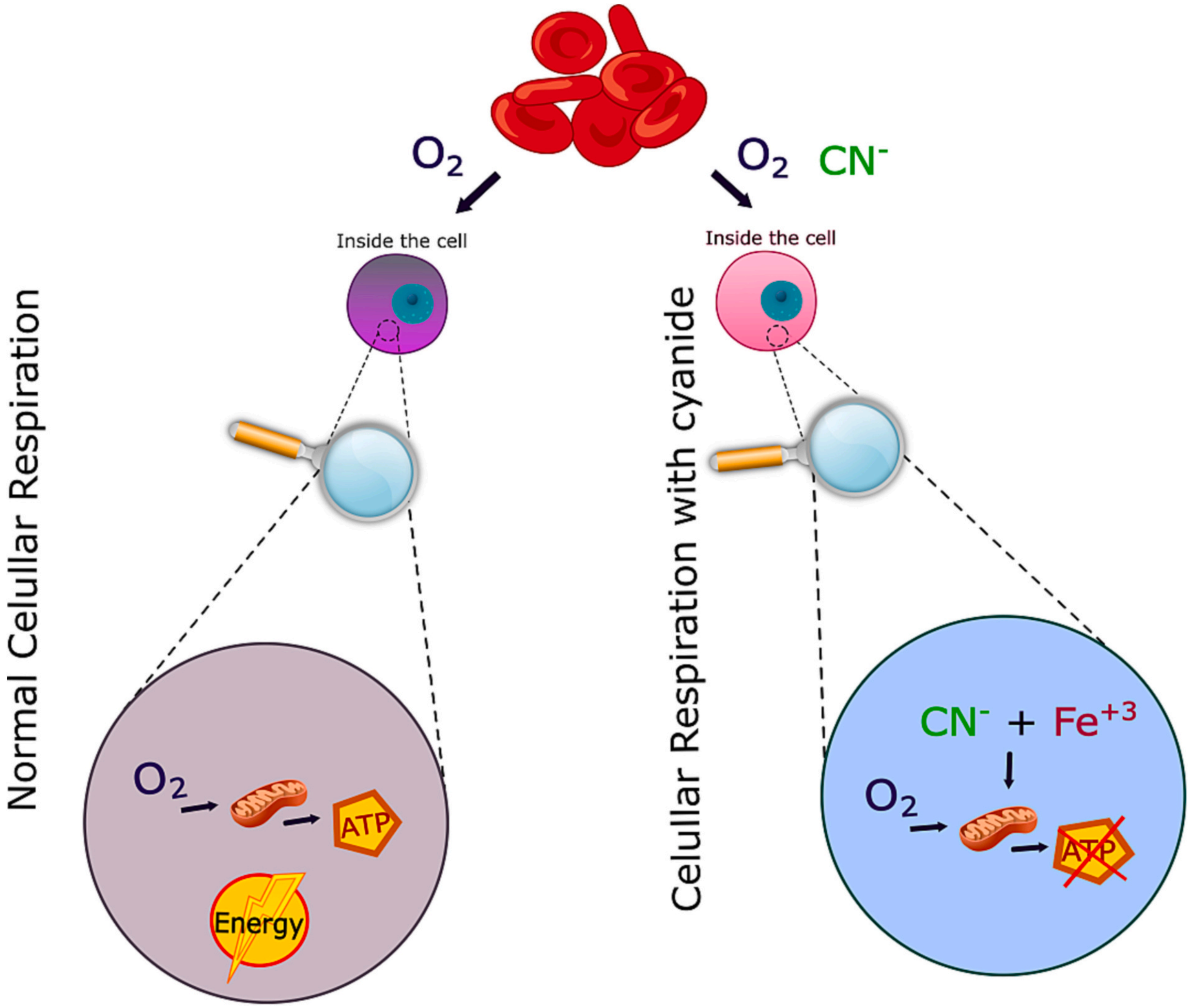

Fig. 5. Inhibition of cellular respiration by cyanide in the structure of the cytochrome C oxidase protein oxidase.
Adapted from Brazil [12].

6. Cyanide legislation

International agencies such as the Agency for Toxic Substances and Disease Registry (ATSDR), the WHO, and the Food and Agriculture Organization of the United Nations (FAO) conducted meetings to discuss and propose new solutions related to the safety, quality, and marketing of cassava and its by-products. Guidelines related to the prevention and reduction of hydrocyanic acid were also proposed [3,35]. The regulations in some countries as Brazil, Nigeria and some of the European Union (Table 3) show us that the precaution for the intoxication by cyanide is real and necessary.

For the European Union, the maximum permissible content of hydrocyanic acid, including hydrocyanic acid linked to cyanogenic glycosides, should be 50 mg / kg for cassava root (fresh, peeled) and 10 mg / kg for cassava flour and *tapioca* flour [41]. Regarding cassava flour, the WHO defined the level of 10 mg HCN/ kg as safe in relation to cyanide. Therefore, as there are no specific regulations in Brazil for cassava and its derivatives (roots, leaves, flour, *tucupi* and starch), which are ingested by the population, the same safety limit as the lethal dose (LD_{50}) recommended by the WHO is adopted [42]. The new Consolidation Ordinance of the Ministerial Office of the Brazilian Ministry of Health [43], which provides for the control, monitoring, quality and standard of potability of water for human consumption, did not include the substance cyanide, which was included in the former Consolidation Ordinance n° 5/2017, with a maximum allowed value of 0.07 mg / L [43,44]. Thus, the recommendations of the United States Environmental Protection Agency (EPA) and WHO must be adopted, for drinking water the maximum value for nitrate is 10 mg / L, for Nitrite is 1 mg / L and for cyanide (as free cyanide) it is of 0.2 mg / L, and for air we have cyanide (as CN) of 5 mg / m^3 and hydrogen cyanide of 11 g / m^3. In the case of inhalation, exposure concentrations will be expressed in mg /L for gases and volatiles and mg /m^3 for suspended particles. For oral ingestion, concentrations will be expressed in mg / kg / day as daily human doses, with a minimum risk level of 0.05 mg /kg/day [3]. Faced with the risk of cyanide poisoning, the Brazilian Ministry of Health approved the Ordinance of the Unified Health System [45].

7. Microbial diversity in cyanide removal in cassava effluents

Some microorganisms develop the skill to degrade nitriles (nitrilase, nitrile hydratase and amidase) and cyanides in contaminated environments, according to the Table 4.

The biodegradation of cyanide under aerobic conditions causes the microorganisms to consume HCN and generate hydrogen cyanate (HCNO), being transformed into ammonia and carbon dioxide through hydrolysis. The anaerobic biodegradation of cyanide and HCNO, it only occurs in the presence of hydrogen sulfide (H_2S) and at pH > 7.0 (dominant species) or pH < 7.0 (prevalent species), being slower [17].

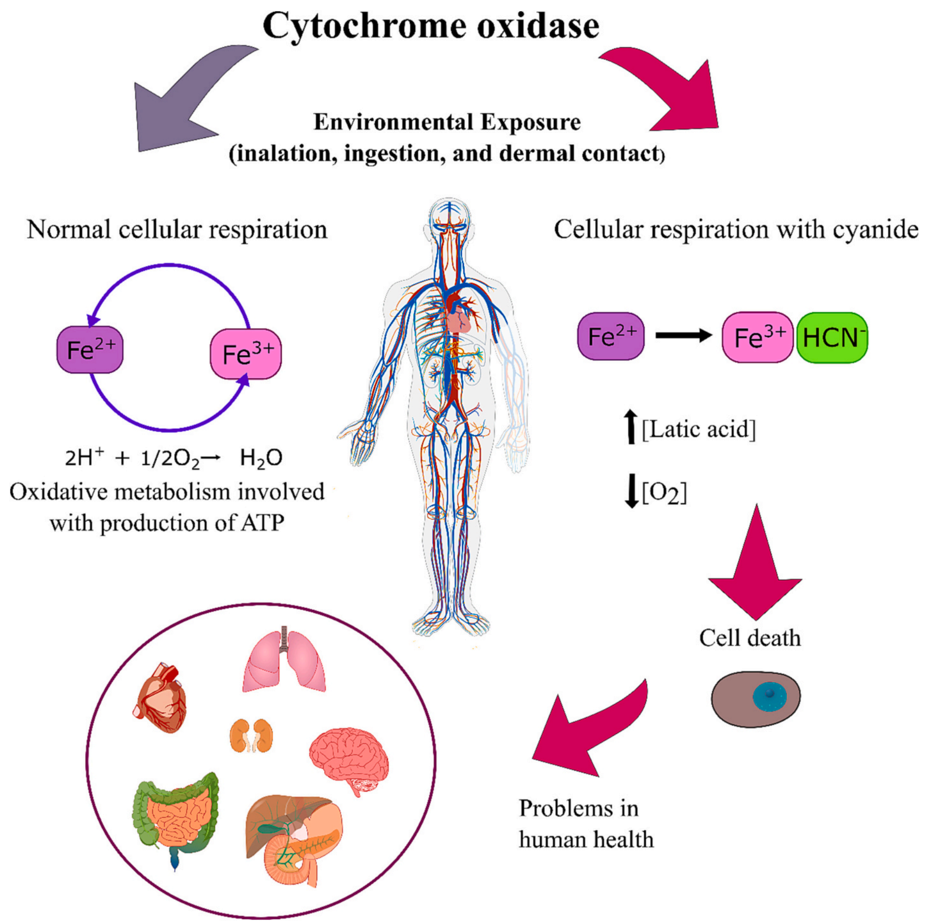

Fig. 6. Schematic of the impact of cyanide on the human body.
Adapted from Jaszczak et al. [22] with adaptations.

Table 2
Analytical methods in the determination of biomarkers for thiocyanate.

Biological material	Method analytical	Detection limit	Reference
Serum	Flame atomic absorption spectrometry	4 ng/mL	[62]
	Spectrometry	0.3 μg/mL	[63]
Spittle	Flame atomic absorption spectrometry	4 ng/mL	[62]
	Gas chromatography with electron detection	0.0115 nmol (in 0.2 mL)	[64]
	Chromatography using octadecyl silane on a column coated with cetyldimethylamine with detection of UV absorption (210 nm)	20 ng/mL	[65]
Urine	Flame atomic absorption spectrometry	4 ng/mL	[62]
	Gas chromatography with electron detection	0.0115 nmol (in 0.2 mL)	[64]
	Chromatography using octadecyl silane on a column coated with cetyldimethylamine with detection of UV absorption (210 nm)	20 ng/mL	[65]
	Spectrometry	0.3 μg/mL	[63]
	Suppressed ion chromatography with conductivity detection	200 nM	[66]

Source: ATSDR [3] with adaptations.

Luque-Almagro et al. [28] reported that, under anaerobic conditions, the residual effluents of cassava fermented in a fixed bed methanogenic reactor converted all the cyanide into organic nitrogen by the biomass. In a two-step reactor (equilibrium/pre-acidification reactor followed by methane reactor), cyanide was removed under ideal conditions (pH 6.0 to 7.5, temperature 25 to 37 °C) generating ammonia and formic acid. Razanamahandry et al. [46] showed that cyanide-degrading bacteria isolated from mining wastewater and wastewater containing thiocyanate, had satisfactory performances, with thiocyanate effluent bacteria showing higher biodegradation rates 2.114 g $CN^{-}.L^{-1}$ .O.D600nm $^{-1}$. h^{-1} compared to those isolated from mining effluent 1.209 g $CN^{-}.L^{-1}$. O.D600nm $^{-1}.h^{-1}$. Some bacteria species were identified as *Pseudomonas spp, Acinetobacter spp,* and *Proteus* sp. were capable of bioremediating cyanide contained in cassava effluents. Some techniques are used to identify the bacteria, such as the polymerase chain reaction (PCR), molecular identification technique and the staining technique, which allows separating of bacteria into Gram-positive and Gram-negative groups [47,48]. This last technique requires care, as there are different types of bacteria species with the same morphology and metabolism [48]. Vallenas-Arévalo et al. [49] isolated native cyanide-degrading bacteria in cassava effluents in Santa Maria da Serra city (Brazil), containing 305 mg/L of free cyanide with a reduction between 10 and 27.5 % after 72 h of incubation. In this study, there was no molecular identification of the studied strains. These same authors brought several studies that report the ability of different microorganisms to degrade from 60 to 100 % of cyanide. Nwakoby et al. [50] analyzed cassava effluent samples, obtaining a microbial population of *Staphylococcus aureus, Bacillus spp, Streptococcus spp, Pseudomonas aeruginosa, Aspergillus spp*, and *Candida* spp. Among these microorganisms, *Bacillus* spp. and *P. aeruginosa* had the ability to degrade cyanide. Table 5 shows some microorganisms capable of degrading cyanides.

In the case of bacteria, some have several metabolic pathways capable of cyanide degradation, in which, these routes are based on

Table 3
Regulations dealing with the maximum permissible limits of cyanide in environmental compartments in Brazil, Nigeria and the European Union.

Environmental compartments		Cyanide concentration [CN]	Country	Reference
Water	Superficial	Free cyanide 0.005 mg/L (Class 1 and 2 - sweets) Free cyanide 0.022 mg/L (Class 3 - sweets) Free cyanide 0.001 mg/L (Class 1 - salt flats) Free cyanide 0.001 mg/L (Class 2 - salt flats) Free cyanide 0.001 mg/L (Class 1 - brackish) Free cyanide 0.001 mg/L (Class 2 - brackish)	Brazil	[67]
		Cyanide (as CN) 0.2 mg/L	Nigeria	[68]
	–	Cyanides (expressed in total CN) 50 kg/year	European Union	[41]
Effluent	Human Release	Cyanide 50 μg/L Total cyanide 1.0 mg/L Free cyanide (distillable by weak acids) 0.2 mg/L	Brazil	[69]
		Cyanide (as CN) 2.0 mg/L - Public Sewer Cyanide (as CN) 0.2 mg/L - Marine Disposal Cyanide (as CN) 0.1 mg/L - mining and processing of coal, ores and industrial minerals) in surface water	Nigeria	[68]
		Cyanide and its compounds dissociable by weak acid 10 ppm	European Union	[41]
Soil		Cyanide 5 mg/kg (dry weight) - for chemicals, Pharmaceuticals, Soaps and Detergents Hydrogen Cyanide 2 mg/N/m^3 - Petroleum-based and chemical industries Cyanide and its compounds dissociable by weak acid 10 ppm	Nigeria	[68]
		Cyanide (expressed in total CN) 50 kg/year	European Union	[41]
Air	(Maximum degree of insalubrity)	Hydrocyanic acid 8 mg/L or 0.009 mg/L - up to 48 h/week (inhalation or skin absorption) Methyl Cyanide and Acetonitrile 30 mg/L or 0.055 mg/L Acrylonitrile and Vinyl Cyanide 16 mg/L or 0.035 mg/L - up to 48 h/week (inhalation or skin absorption) Cyanogen compounds 8 mg/L or 0.016 mg/L 2,4 Toluene diisocyanate and Toluene-2,4-diisocyanate 0,016 mg/L or 0.00011 mg/L	Brazil	[35]
Air	–	Cyanide 10 mg/N/m^3 - air emissions for textiles, clothing, leather and footwear industry	Nigeria	[68]
	–	Hydrogen cyanide 0.01 mg/m3 - long-term emissions of specific pollutants (24 h)		
	–	Hydrogen cyanide (HCN) 200 kg/year	European Union	[41]

Table 4
Nitrile and cyanide-degrading bacteria.

Degrades	Bacteria	Reference
Cyanide	*Pseudomonas pseudoalcaligenes* CECT5344	[70,71]
	Bacillus sp. EBE-2	[72]
	Acinetobacter courvalinii	[73]
	Bacillus pumilus and *Pseudomonas putida*	[74]
	Agrobacterium tumefaciens SUTS 1 and *Pseudomonas monteilii* SUTS 2	[75]
	Bacillus safensis PER-URP-08	[76]
Nitrile	*Rhodococcus rhodochrous BX2*	[77]
	Bacillus subtilis N4/pHTnha-ami	[78]
	Rhodococcus erythropolis ACN1, Variovorax boronicumulans ACN2 and *Pseudomonas konensis ACN4, Pseudomonas konensis ACN7, Pseudomonas* sp. *ACN5,* and *Pseudomonas* sp. *ACN8*	[79]

Table 5
Percentage of cyanide biodegradation by different microorganisms.

Microorganism	$[CN]_{start}$ (mg/L)	(%) Removal [CN]	$[CN]_{last}$ (mg/L)	Reference
Pseudomonas parafulva	200	94	12	[80]
Pseudomonas pseudoalcaligenes CECT 5344	0.6	100	0	[81]
Bacillus sp.	300	97	9	[82]
Bacillus sp., *Bacillus, Klebsiella, Providencia* and *Pseudomonas*	250	97	7.5	[83]
Bacterial consortia	80	95	4	[84]
Bacillus sp. *M01 PTCC 1908*	651	86.4	88.7	[85]
Pseudomona aeruginosa	1352	97.1	38.98	[86]
Escherichia coli	1352	75.95	325.1	[86]
Aneurinibacillus tyrosinisolvens JK-1	10	99.8	0.02	[87]
	20	97.9	0.42	
	30	96.6	1.02	
Bacillus subtilis	500	100	0	[88]

enzymatic processes such as hydrolytic, oxidative, reductive and substitution/transfer reactions (Fig. 7), e.g. *Pseudomonas pseudoalkaligenes* CECT5344 and *Pseudomonas aeruginosa* Rhodanese [51,52].

8. Final considerations

Understand that, in the artisanal processing of cassava, may cause risks to the environment and human health (ingestion of cassava and its derivatives containing cyanide), due to high affinity with metalloproteins that can be solubilized and/or bioavailable in different environmental compartments by processes of complexation, precipitation, adsorption, volatilization, biodegradation and hydrolysis. It is relevant the development of biotechnological researches that use alternative sustainable techniques capable of significantly reducing the risks of exposure and contamination by cyanide. Thus, this review pointed out new perspectives of biosustainable researches using different gram-positive bacteria (Bacillus sp. EBE-2, *Bacillus pumilus*, *Bacillus safensis* PER-URP-08, *Rhodococcus rhodochrous* BX2, *Bacillus subtilis* N4/pHTnha-ami and *Rhodococcus erythropolis* ACN1) and gram-negative (Acinetobacter courvalinii, *Pseudomonas pseudoalcaligenes* CECT5344, *Pseudomonas putida*, *Agrobacterium tumefaciens* SUTS 1, *Pseudomonas monteilii* SUTS 2, *Variovorax boronicumulans* ACN2, Pseudomonas konensis ACN4, Pseudomonas konensis ACN7, Pseudomonas sp. ACN5 and Pseudomonas sp. ACN8) cyanide bioremediators.

Compliance with ethical standards

This review article does not contain any studies with human or

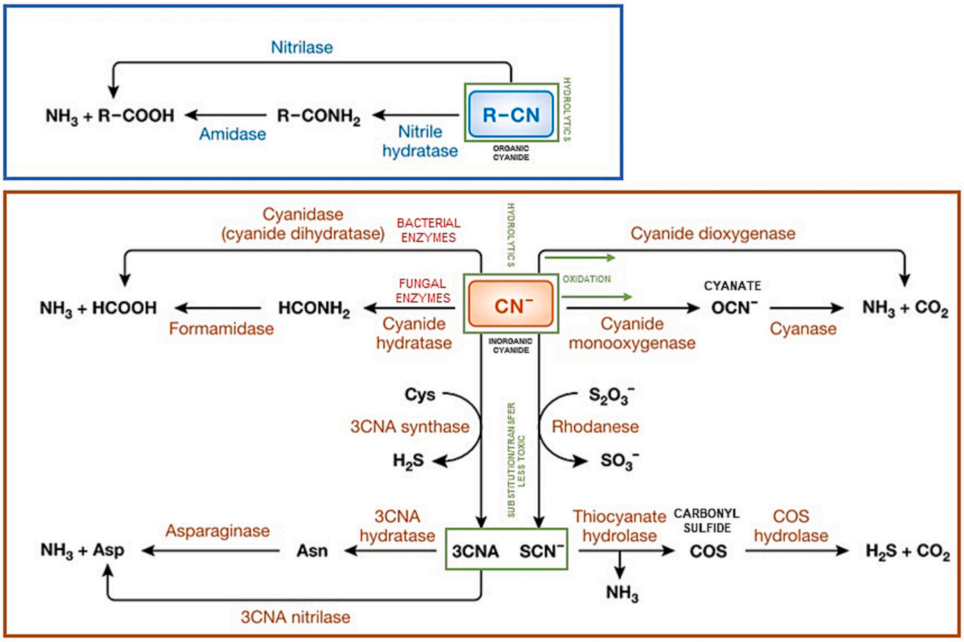

Fig. 7. General scheme of the metabolic pathways of cyanide degradation by microorganisms.
Adapted from Roldán et al. [52].

animal participants performed by any authors.

Submission statement and verification

This manuscript has not been published previously and is not being evaluated for publication elsewhere.

CRediT authorship contribution statement

Alana Coêlho Maciel: investigation, writing - review & editing; Taciane Almeida de Oliveira: conceptualization and considerations; Rosinelson da Silva Pena: table, conceptualization and considerations; Lidiane Diniz do Nascimento: figure and table; Gilson Celso Albuquerque Chagas Junior: conceptualization, considerations and validation; Alessandra Santos Lopes: validation, supervision and Financing Acquisition.

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Declaration of competing interest

The authors declare that they are unaware of competing financial interests or personal relationships that may have influenced the work reported in this manuscript.

Data availability

No data was used for the research described in the article.

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