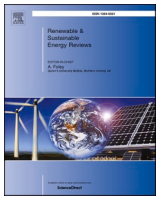
Renewable and Sustainable Energy Reviews 188 (2023) 113892

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Can microbial Bio-CN be a sustainable alternative to the chemical cyanidation of precious metals? An update and way forward

Anil Kumar [a,b], Alan Shemi [a,b], Liberty Chipise [a,b], Sanchia Moodley [a,b], Clarence S. Yah [b,c], Sehliselo Ndlovu [a,b,*]

[a] School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa
[b] DSI/NRF SARChI: Hydrometallurgy and Sustainable Development, University of the Witwatersrand, Johannesburg, South Africa
[c] Department of Internal Medicine, School of Clinical Medicine, Faculty of Health Sciences, University of the Witwatersrand, South Africa

ARTICLE INFO

Keywords:
Cyanogenic microorganisms
Bio-CN
Precious metals
PGMs
Bio-cyanidation
Resource recovery

ABSTRACT

The global demand for raw materials in technology, combined with environmental regulations and growing social awareness about the negative impacts of traditional metal extraction processes, has led to a shift towards green technology. Green technology has been defined as the use of science and technology to create less harmful products that protect the environment. Since biogenic cyanide (bio-CN) is naturally produced by microorganisms and is biodegradable, its use in precious metals (PMs) recovery from metal-bearing resources can be considered a viable and green alternative to chemical cyanidation. Several microorganisms are known to produce bio-CN, however, only a few such as *Chromobacterium violaceum* (*C. violaceum*), *Pseudomonas fluorescence* (*P. fluorescence*), *Bacillus megaterium* (*B. megaterium*), *Pseudomonas aeruginosa* (*P. aeruginosa*), *Pseudomonas chlororaphis* (*P. chlororaphis*) have been quantified. The present review summarizes research on cyanogenic microorganisms known to produce bio-CN, the mechanism and metabolic pathways involved in bio-CN production, and the genetics of cyanide production. This paper also discusses the factors influencing bio-CN production and the methods used for its quantification. The application of bio-CN in leaching PMs i.e., gold (Au), palladium (Pd), platinum (Pt), and rhodium (Rh) from primary and secondary resources, pre-treatment approaches used, and the mechanism of residual bio-CN detoxification are systematically and comprehensively reviewed and provided. Further, the review provides essential insights into challenges faced during bio-CN production and its application in PMs leaching and offers insight into new ways of thinking to move the process towards commercialization.

1. Introduction

Cyanide leaching was proposed in the 19th century, and since then it has been widely used in the extraction of PMs (gold, palladium, platinum, and rhodium) especially gold due to its advantages of strong complexation, technical simplicity, low cost, and high efficiency [1–3]. The Au cyanidation process works well under ambient conditions and can be accomplished in open dumps, vats, tanks, and heaps, based on the grade of the ore [4]. Globally, 90 % of gold extraction is carried out using the cyanide lixiviant and it is expected to dominate for a longer period well into the future [5,6]. Platinum group metals (PGMs) e.g., Pd, Pt, and Rh are the other important industrial commodities that belong to the PMs category, owing to their widespread applications in hydrogen fuel cells, biomedical devices, catalytic converters, jewellery, and space materials manufacturing [7–10]. The PGM cyanidation has been found to occur in a similar manner as that of the well-established Au leaching process. The Pd (II) and Pt (II) form a stable complex with cyanide, i.e., $[Pd(CN_4)]^{2-}$ and $[Pt(CN_4)]^{2-}$ [4,11]. The PGM cyanidation chemical reaction can occur under ambient conditions [4] and follows reaction kinetics described by the Elsner equations (1)–(3) [12]:

$$2Pt + 8NaCN + O_2 + 2H_2O \rightarrow 2Na_2\left[Pt(CN)_4\right] + 4NaOH \quad (1)$$

$$2Pd + 8NaCN + O_2 + 2H_2O \rightarrow 2Na_2\left[Pd(CN)_4\right] + 4NaOH \quad (2)$$

$$4Rh + 24NaCN + 3O_2 + 6H_2O \rightarrow 4Na_3\left[Rh(CN)_6\right] + 12NaOH \quad (3)$$

Cyanidation is a leading industrial process for the extraction of PMs from metal-bearing resources [13]. However, the chemical cyanidation process suffers from some disadvantages such as environmental and

* Corresponding author. School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa
E-mail address: Sehliselo.Ndlovu@wits.ac.za (S. Ndlovu).

https://doi.org/10.1016/j.rser.2023.113892
Received 14 March 2023; Received in revised form 2 August 2023; Accepted 11 October 2023
1364-0321/

Abbreviations

PMs	Precious Metals
PGMs	Platinum Group Metals
PGEs	Platinum Group Elements
CAS	Carbonaceous-argillaceous slate
Pd	Palladium
Rh	Rhodium
Pt	Platinum
Fe	Iron
Ni	Nickle
Cr	Chromium
Cd	Cadmium
Al	Aluminium
Zn	Zinc
Co	Cobalt
Cu	Copper
Mn	Manganese
Bio-CN	Biogenic cyanide
REEs	Rare earth elements
HCN	Hydrogen cyanide
H_2S	Hydrogen sulfide
mg/L	Milligram per Litre
w/v	Weight by volume
g/L	Gram per Litre
°C	Degree Celsius
μm	Micrometre
%	Percent
mg/Kg	Milligram per Kilogram
Kg	Kilogram
mg	Milligram
g/t	Gram per ton
M	Molar
μM	Micromolar
mM	Millimolar
rpm	Rotation per minute
h	hour
LB	Luria broth
YP	Yeast extract peptone
CN^-	Free cyanide
APHA	American Public Health Association
AGT	Alanine-glyoxylate transaminase
SGT	Serine-glyoxylate transaminase
BetA	Choline oxidase
BetB	Betaine aldehyde dehydrogenase
GbcAB	Glycine betaine demethylase
DgcAB	Dimethylglycine oxidase and dimethylglycine dehydrogenase
SoxBDAG	Sarcosine oxidase
ATP	Adenosine triphosphate
GacA	Global activator
ANR	"Anaerobic regulator of arginine deiminase and nitrate reductase"
FNR	"Fumarate and nitrate reductase regulator"
ISE	Ion-Selective Electrode
FeAsS	Arsenopyrite
PtS	Cooperite
$PtAs_2$	Sperrylite
Sb_2S_3	Stibnite
$CuFeS_2$	Chalcopyrite
FeS_2	Pyrite
WEEE	Waste Electrical and Electronics Equipment
PCB	Printed Circuit Board
MPCB	Mobile Printed Circuit Board
SIM	Subscriber Identity Module
CPCB	Computer Printed Circuit Board
ESM	Electronic Scrap Material
WPCB	Waste Printed Circuit Board
SAC	Spent Automobile Catalysts
PR	Primary Resource
SR	Secondary Resource
OSB	One-Step Bioleaching
TSB	Two-Step Bioleaching
SML	Spent Medium Leaching
PL	Pressure Leaching
PD	Pulp Density
PMS	Phenazine methosulfate
Na	Sodium
C	Carbon
N	Nitrogen
H_2	Hydrogen
O_2	Oxygen
CO	Carbon monoxide
CO_2	Carbon dioxide
NaOH	Sodium hydroxide
H_2SO_4	Sulphuric acid
NaCl	Sodium chloride
HCl	Hydrochloric acid
HNO_3	Nitric acid
$AlCl_3$	Aluminum chloride
$FeCl_3$	Ferric chloride
Na_2HPO_4	Sodium hydrogen phosphate
$MgSO_4$	Magnesium sulphate
$FeSO_4$	Ferrous sulphate
$AgNO_3$	Silver nitrate
$Pb(NO_3)_2$	Lead nitrate
$S_2O_3^{2-}$	Thiosulphate
UV	Ultraviolet
KCN	Potassium cyanide
NaCN	Sodium cyanide
WAD	Weak acid dissociable
DO	Dissolved oxygen
DCIP	2, 6-dichlorophenolindophenol
ATCC	American Type Culture Collection
pK_a	Acid dissociation constant

health risks associated with the extreme toxicity and leakage of cyanide. The potential leakage of chemical cyanide into groundwater and the surrounding environment necessitates an additional step of treatment of effluent leach solution prior to disposal [8,14–16]. On the contrary, the use of bio-CN requires no transportation as it is generated by microorganisms *in situ* [13], which lowers the associated transportation cost. Furthermore, bio-CN is biodegradable and therefore non-hazardous to the environment. Several other hydrometallurgical options such as acid leaching, chloride leaching, bromide leaching, thiourea, and thiosulphate leaching have been explored, however, these tend to suffer from low yield as well as environmental issues (Table 1). Moreover, with the declining grade of ores, these traditional processes are becoming uneconomical [17].

Biotechnological processes such as bio-CN leaching are seen as green, effective, and sustainable alternatives to traditional extractive metallurgical processes [18–20]. These processes are based on the natural biogeochemical cycling of minerals and metals [21]. Microorganisms promote metal mobilization using oxidation and reduction

Table 1
Comparison amongst bio-cyanidation and traditional PMs extraction processes.

Criteria/ Parameters	Cyanidation	Chloride leaching	Bromide leaching	Acid leaching			Thiourea leaching	Thiosulphate leaching	Bio-cyanidation		
Process conditions	Panton Process: Calcination at low temperature followed by cyanide (0.2 %) leaching at 60 °C and pH 9.2 for 100 h	Kell Process: a hybrid chloride/ sulphate-based technology. Firstly, pressure sulphuric acid leaching removes base metals, followed by PGM leaching post-roasting, with HCl/Cl_2.	PGM ore roasting followed by bromine leaching	Leaching using H_2SO_4 at pH 3 and 25 °C for 72 h	Leaching using HCl at pH 3 and 25 °C for 72 h	Leaching using 0.5 M HCl for 24 h, and then leaching with buffered siderophore i.e., Desferrioxamine B for 70–120 h at ambient temperature	Thiourea dissolves gold under process conditions of pH 1.4, redox potential 250 mV, thiourea concentration 1 %, and leach time of 10–15 min	Sodium and ammonium thiosulphate are generally used for gold leaching. Requires alkaline conditions. Ammoniacal leach solution having 2 M $S_2O_3^{2-}$, 4 M NH_3, 0.1 M $CuSO_4$ at 25 °C	Microbial contact leaching from spent automobile catalysts. Bioleaching from pretreated SAC using P. fluorescens at 0.5 % PD, pH 9, temperature 30 °C after day 1	Spent medium leaching: Cells (P. fluorescens) are removed after cyanide production and the cell-free medium was used to extract metals from pretreated SAC at 0.5 % PD, pH 10, temperature 30 °C after day 1	Microorganisms are cultured separately, and bio-CN is trapped in NaOH separately. The produced bio-CN was used for leaching PGM from SAC at pH 11, temperature 150 °C, pO_2 3000 psi, bio-CN 1000 mg/L for 1 h
Percent extraction	90.8 % of Pt, 94.4 % of Au, 91.9 % of Pd, 69 % of Cu, 32 % of Ni	80–85 % PGMs plus Au	95 % of Au, 85 % of Pt, 65 % of Rh	11.1 % of Pt, 13.8 % of Pd	18.9 % of Pt, 18.5 % of Pd	78 % of Pt	50–60 % Au extraction	80 % of Au	44 % of Pt, 54 % of Pd, 96 % of Rh	58 % of Pt, 65 % of Pd, 97 % of Rh	92.1 % of Pt, 99.5 % of Pd, 96.5 % of Rh
Salient aspects	High extraction High costs due to calcination and high-temperature leaching	Require specific material which increases the capital and operating costs due to the highly corrosive nature of Cl_2 gas	High extraction High equipment and operating costs	Low extraction Low reagent cost and high equipment cost because of H_2SO_4 corrosiveness	Low extraction High reagent costs and equipment costs because of acid corrosiveness	High extraction High reagent costs and high equipment costs	Large consumption, Requires stabilizing reagent High cost.	High selectivity Non-toxic Non-corrosive High reagent consumption makes it uneconomical	Technology is still under the lab scale. Efficient in case of low metallic concentrations Literature mentioned it as cost-economic however techno-economic analysis is required	Cost analysis is required	Efficient Cost-economic analysis is required.
Environmental concerns	Toxic to the environment and human health	Easy to leak, strong toxicity and corrosiveness	Volatile and difficult to transport	Generation of large amounts of metals and acid-laden wastewater.			Poor stability, strong corrosiveness, low toxicity	Environmentally Friendly	Environmentally friendly.	Environmentally friendly.	A greener and renewable approach to producing cyanide.
References	[44,45]	[45–47]	[48]				[49]	[45,50,51]	[35]		[52]

reactions or through the excretion of different bio-metabolites such as siderophores, organic acids, bio-CN, etc. [22]. Amongst all, bio-CN has been used widely and has shown promise to recover PMs from metal-bearing primary and secondary resources. The microorganisms produce bio-CN either as a defensive metabolite or for aggressive purposes [23]. Different bacteria (*C. violaceum, B. megaterium, P. fluorescens*, *Pseudomonas putida, Lysinibacillus sphaericus, P. aeruginosa, Rhizobium leguminosarum*, *Pseudomonas chlororaphis*, *Pseudomonas plecoglossicida*, *Pseudomonas aureofaciens*, and *Pseudomonas syringae*), fungi (*Marasmius oreades*, *Polysporus* sp., and *Clitocybe* sp.), and algae (*Chlorella vulgaris*) are known to produce bio-CN [24–26]. However, there is a lack of data on quantitative bio-CN production. Furthermore, there is limited information available on the physiology and mechanism of fungal cyanogenesis as compared to bacteria and algae, probably due to challenges in fungal growth and application [24,25].

The cyanide production reaction is catalyzed by HCN synthase [26,27]. The cyanogenic microorganisms produce bio-CN by metabolizing a non-toxic chemical (glycine) whereas chemical cyanide is generated by reacting ammonia and methane [28]. The process of bio-CN production generates smaller carbon footprints and consumes less energy compared to the corresponding chemical process. Moreover, bio-CN is generated *in situ* which eliminates the need for its transportation thus, making it much safer in terms of material handling [29]. The most notable advantage of cyanogenic microorganisms is their ability to detoxify or consume cyanide, hence can be used to remediate contaminated residues or leachate at the end of the bio-cyanidation process. For example, *C. violaceum* secretes β-cyanoalanine synthase and transforms cyanide into β-cyanoalanine. Similarly, *Pseudomonas* sp. uses cyanide as a sole source of nitrogen and carbon during nutrient-deficient conditions. Therefore, the use of such microorganisms in the metal extraction process can offer a sustainable route for the PMs mining industry [24].

Bio-cyanidation is a process that uses bio-CN to recover metals from solid metallic fractions [24,25,30–32]. Researchers have extracted PMs from primary and secondary resources using cyanogenic microorganisms like *C. violaceum*, *P. aeruginosa*, *B. megaterium*, *P. balearica,* and microbiomes including *Pseudomonas* and *Micrococcus* sp. indigenous to Carbonaceous-argillaceous slate (CAS), and pyrite [7,20,26–28]. Bio-cyanidation has been successfully applied to leach base metals (Co, Cu, Ni, Fe, Zn, Mn, and Cr) as well as PMs [33,34]. Amongst PMs, bio-cyanidation is largely exploited for the extraction of Au, but very limited studies are available on Pt, Pd, and Rh extraction [24–27,34–37]. The high chemical stability and water solubility of metal-cyanide complexes offer the advantage of applying cyanogenic microorganisms in industrial bioleaching operations. Other than PMs, bio-cyanidation has also been applied to extract rare earth elements (REEs) using *P. putida* WSC361, but showed no extractions [38], indicating that the extraction of REEs does not involve complexolysis [39]. Bio-cyanidation is a sustainable, eco-friendly, and cost-efficient alternate to chemical cyanidation for PMs extraction, particularly from lean-grade ores or secondary resources where conventional metallurgical methods are not economically feasible [29,40–43]. Since cyanide is an important lixiviant for the PMs extraction industry, it is believed that PMs leaching using bio-CN may offer significant environmental and economic benefits. Hence, bio-CN production and bio-cyanidation are the focal points of this review.

2. Cyanogenic microorganisms

More than half of the soil's microbial community consists of cyanogenic species [24]. However, the commonly exploited cyanogenic microorganisms for bioleaching of PMs are *C. violaceum*, *B. megaterium*, *P. aeruginosa*, *P. fluorescence*, and *P. balearica* [14,24,25,27,30,33,36,38,40,42,53–58]. The HCN produced by cyanogenic bacteria has characteristics of a usual secondary metabolite i.e., a) no evident role in primary metabolism and is produced under growth-limited conditions during the late log-phase or early stationary-phase, b) cyanogenic microorganisms are tolerant to bio-CN, and c) cyanogenesis serves an ecological function and may offer producing bacteria a selection advantage [59,60]. The cyanide-producing potential of cyanogenic microorganisms is not the same and varies with the type of bacterial strain used (Table 2). Further, HCN biosynthesis also depends on the growth medium, amount of bacterial biomass, and specific growth conditions [36,40,61]. Despite such large proportions of cyanide-producing microorganisms in the soil, it is evident from Table (2) that a very limited number of these microorganisms are quantified for cyanide production and the concentrations of cyanide produced tend to be very low i.e., in parts per million (ppm). Additionally, cyanide production has been carried using synthetic medium which might increase the cost during large-scale production. This warrants the need to explore novel microorganisms capable of producing higher bio-CN quantities as well as evaluation of media alternatives that might include the use of waste substrates in order to lower the production cost.

3. How do bacteria produce cyanide?

Cyanogenic microorganisms produce HCN as a secondary metabolite in the mid to late logarithmic growth phase using an enzyme called HCN synthase, also known as glycine dehydrogenase [60,74]. The HCN biosynthesis takes place in two steps in an oxidative decarboxylation reaction [60,75]. In the first step, cyanogenic microorganisms metabolize glycine into an unstable intermediate i.e., iminoacetate which is then converted to HCN in the second step (Equations (4) and (5)) [27,36,75–79]. Glycine serves as a direct precursor molecule in the biosynthesis of HCN. This has been proven by experiments conducted using radiolabelled [1–^{14}C] glycine or [2–^{14}C] glycine as a substrate where the carbon atom of HCN and CO_2 is acquired from glycine's methylene carbon and carboxyl group in *P. fluorescens, C. violaceum*, and *P. aeruginosa*. During the process, the C–N bond remains intact with exception for possible transamination/deamination reactions [14,80–83].

$$C_2H_5NO_2 + O_2 \rightarrow C_2H_3NO_2 + H_2 \rightarrow HCN + H_2 + CO_2 \quad (4)$$

$$C_2H_5NO_2 + O_2 \rightarrow C_2H_3NO_3 + H_2O \rightarrow C_2HNO_2 + 2H_2O \rightarrow HCN + CO_2 + 2H_2O \quad (5)$$

Since the reaction is oxidative, HCN synthase generates four electrons, necessitating an electron acceptor, which can be oxygen via the electron transport chain. Generally, aerobic conditions favour HCN production [84,85], however, the enzyme is sensitive to oxygen [60,86]. Although glycine protects the enzyme somewhat from oxygen toxicity, higher concentrations of glycine are inhibitory to bacterial growth [25,87]. Studies have also tested synthetic electron acceptors, among which phenazine methosulfate (PMS) has proven suitable for oxidizing glycine [82,88,89]. According to Castric [89], *in vivo,* oxygen is the natural electron acceptor. *In vitro,* the electron acceptor has yet to be identified; however, components of the membrane-bound respiratory system may be involved.

Cyanogenic microorganisms consume glycine from the extracellular medium, but when glycine fluxes away from cyanogenesis, it can be produced enzymatically from 3-phosphoglycerate [via serine decarboxylation] or extracellular choline [via glybetaine and sarcosine] (Fig. 1). The other alternative route of glycine synthesis is via the glyoxylate pathway, where bacteria secrete enzymes such as AGT (alanine glyoxylate transaminase) and SGT (serine glyoxylate transaminase) to utilize alanine-glyoxylate or serine-glyoxylate to make glycine and pyruvate or hydroxypyruvate, respectively [25,74]. Bacteria produce ATP using the glyoxylate pathway during heavy metal stress.

4. How is bacterial cyanogenesis regulated?

HCN synthase is a membrane-bound flavoprotein that is encoded by

Table 2
Cyanogenic Microorganisms and their cyanide-producing capabilities.

Sr. No.	Microorganism	Cyanide Concentration	Type of medium used	Quantitative Method	Reference
Bacteria					
1.	*Chromobacterium violaceum*	20–65 mg/L	Luria Bertani (Miller) media; Peptone broth 6 g/L Na_2HPO_4 and 0.5 g/L $FeSO_4$	Cyanide electrode coupled to an ion-selective electrode (ISE) meter; Picric acid assay method	[55,62]
2.	*Bacillus megaterium*	16–113 mg/L	Nutrient broth medium; Luria Broth medium	Picric acid colorimetricm ethod; Potentiometry titration against silver nitrate	[32,63]
3.	*Pseudomonas fluorescens*	5.27–15.5 mg/L	Cyanogenic medium composed of tryptone (6 g/L) and yeast extract (5 g/L); Nutrient broth	4-pyridinecarboxylic acid colour comparison method; Potentiometry titration against silver nitrate	[40,64]
4.	*Pseudomonas aeruginosa*	10–66.35 mg/L	Luria Bertani, Miller media; Nutrient broth	Cyanide electrode coupled to an ISE meter, Picric acid colorimetric method	[14,55]
5.	*Pseudomonas putida*	21.5 mg/L	Nutrient broth	Potentiometry titration against silver nitrate	[40]
6.	*Pseudomonas chlororaphis*	15.52 mg/L	Nutrient broth	Titration against silver nitrate	[58]
7.	*Acidovarax delafieldii* ATH2-2RS/1	8–34 μM	Tryptic soy broth	Colorimetric method	[65]
8.	*Pseudomonas balearica*	–	LB medium	Qualitative and APHA 4500 CN^-	[66]
9.	*Lysinibacillus sphaericus*	–	LB medium	Qualitative and APHA 4500 CN^-	[26]
10.	*Bacillus* sp.	–	LB medium	Qualitative and APHA 4500 CN^-	[26]
11.	*Pseudomonas* sp. WCS361	460 μM	Kings B medium	Isonicotinic acid-barbituric acid	[67]
Fungi					
12.	*Boletus satanas*	102 μM	Malt extract (g/L) (5); yeast-extract (15); D-glucose (15) and	Pyridine barbituric acid colorimetric method	[68]
13.	*Neurospora crassa*	18.8 μM	Fries basal medium	p-Nitrobenzaldehyde and o-Dinitrobenzene-based ultrasensitive and selective technique for cyanide determination	[69]
14.	*Pleurotus ostreatus*	429 μM	Malt extract (g/L) (5); yeast-extract (15); D-glucose (15)	Pyridine barbituric acid colorimetric method	[68]
Algae & Cyanobacteria					
15.	*Chlorella vulgaris*	15–155 μM	Mineral salts medium with nitrate; Nitrate/Mineral salts medium	Guilbault and Kramer method for cyanide determination using p-Nitrobenzaldehyde and o-Dinitrobenzene.	[69–71]
16.	*Anacystis nidulans* L1402–1	1.1 μM	Modified medium C of Kratz and Myers	Method to estimate microquantities of cyanide by Epstein	[72,73]
Mixed Culture					
17.	*C. violaceum* + *P. aeruginosa*	15 mg/L	LB medium	Cyanide electrode coupled to ISE meter	[55]
18.	*C. violaceum* + *P. fluorescens*	13 mg/L	LB medium		
19.	*P. aeruginosa* + *P. fluorescens*	11 mg/L	LB medium		
20.	*C. violaceum* + *P. fluorescens* + *P. aeruginosa*	14 mg/L	LB medium		

a cluster of *hcnABC* genes, which probably form an operon [90]. The expression of these genes (*hcnABC*) in *Escherichia coli* from the T7 promoter has been found to successfully induce cyanide production in the bacterium [91]. The nucleotide sequence analysis has revealed that in cyanogenic bacteria, *hcnA* encodes formate dehydrogenase, whereas *hcnB* and *hcnC* encode amino acid oxidases [85,91]. The HCN biosynthesis in cyanogenic bacteria i.e., *P. fluorescence* and *P. aeruginosa* is regulated/controlled by two regulatory proteins i.e., ANR (anaerobic regulator of arginine deiminase and nitrate reductase) and GacA (global activator) [14]. The mutants of *P. aeruginosa* affected in either GacA or ANR result in the production of very little HCN [91–93]. The ANR has its origin from the FNR (fumarate and nitrate reductase regulator) family of transcriptional regulators [94]. The *E. coli* FNR protein is an oxygen-sensing dimeric protein. When oxygen is present, the two $[4Fe–4S]^{2+}$ clusters of this protein are converted into $[2Fe–2S]^{2+}$ form, rendering the protein inactive. On the other hand, when the concentration of dissolved oxygen is below 5–10 μM, the FNR can attach to the conserved sequences (called the FNR box) in the promoter region of the target genes. The activation and repression of the target promoter depend on the FNR box position relative to the transcription start site [91,94–96]. Published information has revealed extensive structural and functional similarity among ANR and FNR proteins of *P. fluorescens* and *P. aeruginosa* [92,97]. Studies have also shown that the initiation of *a* gene expression by oxygen limitation chiefly depends upon the ANR protein and ANR box. Further, the oxygen tension controls the HCN synthase enzyme at two levels i.e., at the level of enzyme activity and during transcription via ANR [60,98].

Several researchers have reported that Fe stimulates cyanogenesis in *P. fluorescens*, *P. aeruginosa,* and *C. violaceum* [14,59,76,81,99,100]. The response to Fe in *P. fluorescens* CHA0 is induced by the ANR and is dependent on the presence of ANR box in the *hcn* promoter. When an artificial promoter that poorly responds to oxygen limitation replaces the natural strongly ANR-regulated *hcn* promoter, Fe regulation is lost. The limited Fe might inhibit the assembly of the Fe–S cluster on ANR apoprotein, favouring ANR inactivation even when oxygen is scarce [86].

The second regulator controlling cyanogenesis in *P. fluorescens* and *P. aeruginosa* is GacA. In *P. aeruginosa*, GacA triggers the LuxR-like transcriptional activator RhIR by positively controlling the expression of N-butyryl-homoserine lactone, thus inducing several exo-product coding genes including the *hcnABC* gene [93,101]. However, this induction needs a putative RhIR recognition site/lux box at about the −70 region in the *hcnA* promoter [60]. On the other hand, *P. fluorescence* CHA0 lacks a lux box in the *hcnA* promoter, and the N-acyl-homoserine lactone signal molecule was also not found in this bacterium. This means that there is a novel and distinct regulatory pathway functioning in this bacterium primarily at a posttranscriptional level [98].

5. Does the chemistry of cyanide matter?

Generally, cyanide is a triple-bonded negatively charged chemical compound that contains one carbon (C) and one nitrogen (N) atom. Cyanide is an anion, where carbon and nitrogen exist in +2 and −3 oxidation states. In solution, cyanide can occur as free cyanide, i.e., HCN and CN^-, or in the form of weak to moderately strong (Cu, Zn, Cd, Ni, and Ag) and strong metal-cyanide complexes (Au, Pd, Pt, and Fe) [102]. The occurrence or availability of free cyanide as CN^- or HCN in a solution/culture medium is pH-dependent (Fig. 2). It is reported that at

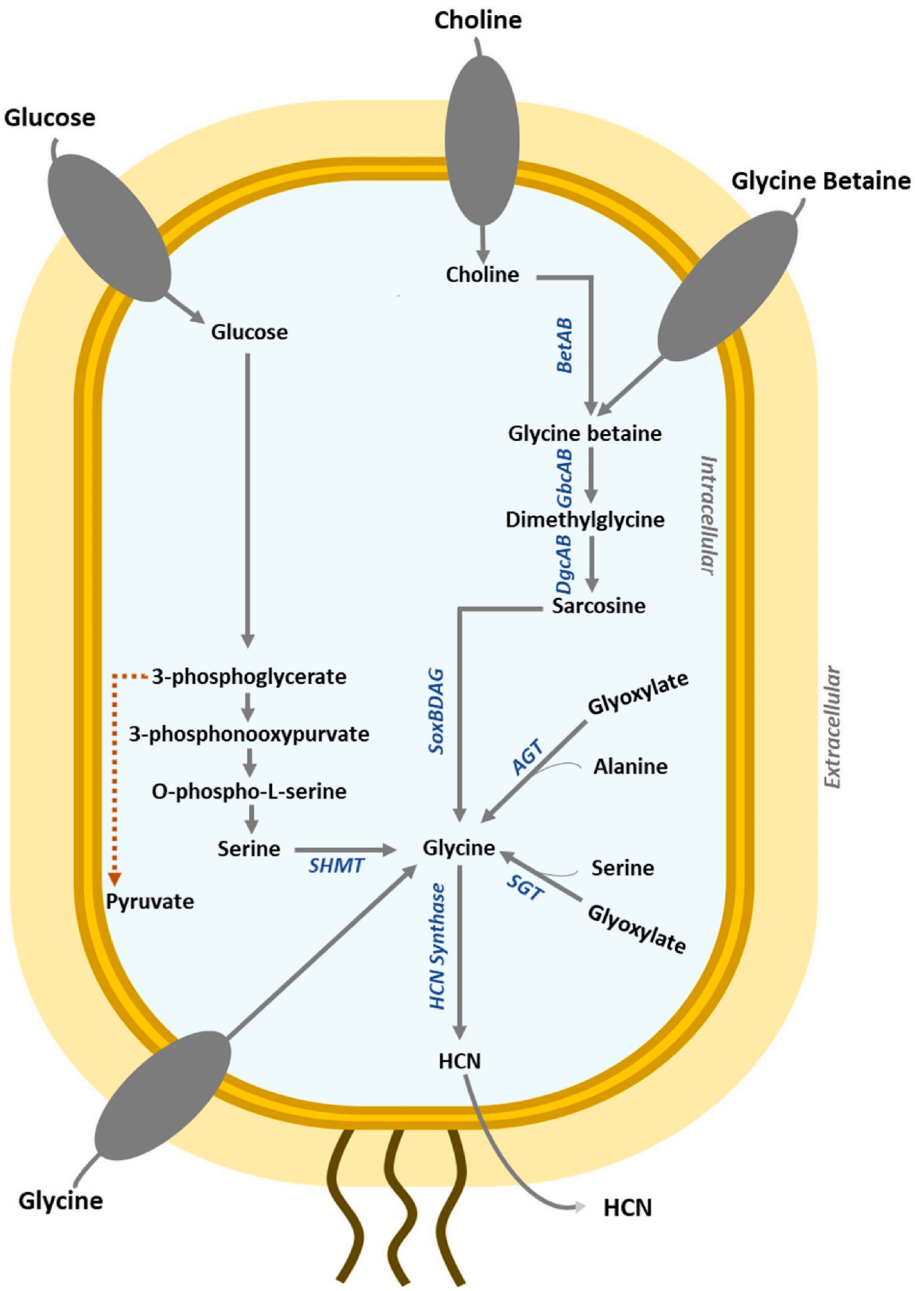


Fig. 1. Different metabolic routes followed by cyanogenic bacteria to produce bio-CN [Bet AB: choline oxidase (BetA) and betaine aldehyde dehydrogenase (BetB), GbcAB: glycine betaine demethylase, DgcAB: dimethylglycine oxidase and dimethylglycine dehydrogenase, SoxBDAG: Tetrameric sarcosine oxidase, SHMT: serine hydroxymethyltransferase, SGT: serine-glyoxylate transaminase, AGT alanine-glyoxylate transaminase. The ellipses represent the transporter, and the dotted arrow (————) route towards the glycolytic pathway (Drawn from information provided by Gracia et al. [74]; Tay et al. [90].

physiological pH ~7, cyanide is primarily present as HCN because of its pKa of 9.27, is volatile in nature, and can quickly disperse into the environment [54,55,58,63,103,104]. However, in the presence of metal ions and salts, the volatility is lessened due to the drop in the pKa value from 9.27 to approximately 8.3 [25,63,105]. The presence of free cyanide as CN^- in a solution is favoured under alkaline conditions due to an equilibrium shift towards CN^- at a pH of 10.5 or above (Equation (6)) [102,106] as shown in Fig. 2.

$$HCN \leftrightarrow H^+ + CN^- \quad (6)$$

This suggests the need to conduct bio-CN production activities as well as perform cyanogenic bioleaching operations under alkaline conditions otherwise loss of cyanide in the form of HCN gas may occur.

6. How is bio-CN detected and quantified?

Cyanide can be analysed as free cyanide (HCN and CN^-), in the form of weak acid dissociable (WAD) cyanide, strong complexed cyanide, and total cyanide. The term "total cyanide" includes WAD cyanide, strongly complexed cyanide, and free cyanide [108].

The detection of bio-CN can be performed by both qualitative as well as quantitative methods. The qualitative method indicates the absence or presence of HCN production through a change in colour. The organism (single isolate) to be tested was streak-plated on King's B agar medium containing 4.4 g/L of glycine [109]. A piece of filter paper (8.0 cm long and 0.5 cm wide) impregnated with 0.5 % of picric acid and 2.0 % of sodium carbonate was laid on the lid of the Petri plate. Thereafter, the Petri plate was closed airtight using parafilm followed by incubation

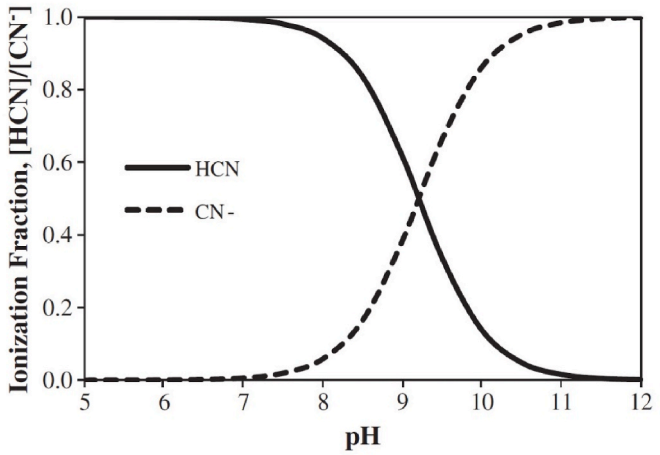


Fig. 2. Cyanide speciation distribution with respect to pH (adapted with permission from Estay et al. [107]).

at 28 °C for 48–96 h. After incubation, the discolouration in filter paper from yellow to orange brown is indicative of microbial HCN production [59,67,109]. To ascertain whether the colour change was due to HCN production or not, the filter paper was impregnated with 1 M NaOH instead of sodium carbonate and picric acid followed by estimation using the isonicotinic acid-barbituric acid protocol given by Nagashima and Ozawa [110].

Anning et al. [111] reviewed several methods to quantify the amount of cyanide present in a solution/medium. These methods include titrimetric, colorimetric, potentiometric (electrochemical), amperometry, polarographic, voltammetric technique, ion chromatography, gas chromatography, and ISE [29]. However, the commonly employed method to quantify bio-CN includes silver nitrate titration, picric acid colorimetry, pyridine barbituric acid colorimetry, 4-pyridinecarboxylic acid colour comparison, and ISE (Table 3). The choice of the method further depends upon levels of cyanide concentration as well as species of cyanide to be determined. Since microorganisms grow optimally at neutral pH, it is anticipated that they will produce HCN. However, there is a possibility of the formation of other species of cyanide such as thiocyanate, cyanate, NaCN, and WAD cyanide because of possible reactions with biometabolites like H_2S as well as components of the medium and bacterial cell wall. It is important to note that certain species such as sulfides, thiocyanate, and thiosulphate cause interferences and, therefore, must be removed while determining the levels of cyanide [112]. Therefore, in addition to quantifying bio-CN, a speciation analysis of bio-CN might be beneficial in determining the feasibility of bioleaching.

7. What can influence bio-CN production?

7.1. Incubation time/Growth

Cyanide production seems to be time/growth dependent as cyanogenic microorganism produces cyanide for a short period during their growth. Cyanogenic microbes produce cyanide between the mid to late log phase or in the early stationary phase and thereafter there is a decrease [40]. Therefore, the time of cyanide production may not be the same for all the bacteria because of variations in their doubling time. Wissing [121] using a strain of the genus *Pseudomonas* demonstrated that cyanide is produced just before the stationary phase (approximately at 7 h of bacterial growth) and thereafter, HCN production decreased. Yuan et al. [64] studied the kinetic relationship between cellular growth and bio-CN production at regular intervals of time using *P. fluorescens* P13 at 25 °C. The authors reported maximum cyanide production at 16 h of bacterial growth, and a further increase in incubation time resulted in

Table 3
Commonly employed methods to quantify CN^-/bio-CN concentration for precious metals leaching.

Method	Description	Bacteria tested	Reference
Sliver nitrate ($AgNO_3$) titration	• The method is based on $AgNO_3$ titration using p-dimethylaminobenzylidene ($C_{12}H_{12}N_2OS_2$) rhodamine indicator (lower detection range 0.1 ppm) or potentiometric endpoint to establish the free cyanide yield. • $AgNO_3$ titration using a potentiometric endpoint is recommended to quantify CN^- in gold leaching operations. • To quantify bio-CN, cell-free supernatant must be obtained by centrifugation and filtration prior to titration. • The presence of copper, zinc, and thiosulfate are the potential interferences.	*P. fluorescens* *P. putida* *C. violaceum* *P. plecoglossicida*	[29,40, 111,113, 114]
Colorimetric methods	• Several colorimetric methods have been documented and use reagents like picric acid, pyridine, barbituric acid, and 4-pyridine carboxylic acid. • Preferable for low cyanide concentrations like in the bio-CN process. • Time-consuming with possible interferences from sulfide, sulfur, thiosulfate, and thiocyanate species. • Picric acid is explosive in nature and therefore not applicable to the gold industry.	*B. megaterium* *P. fluorescens* P13 *P. plecoglossicida* *P. aeruginosa* *Pseudomonas* sp. *P. chlororaphis* *C. violaceum*	[14,27, 31,58,63, 105]
Ion-selective Electrode	• Potentiometric method using ISE coupled with pH and reference electrode. • The AgI or a mix AgS and AgI are the commonly used cyanide-selective membrane electrode (Orion 94-06) that liberate I^- by reaction with CN^- in solution. • Operates at a solution pH ranging from 0 to 14 with the optimal being 11–13. • Measures cyanide in a range from 0.26 to 2600 ppm. The detection limit of the method is 0.05 ppm. • No complicated sample processing, direct measurement of the sample is possible, convenient, quick, and reproducible tool for measuring bio-CN. • The ISE is very sensitive to interference from S, Ag, Zn, Cl, Ni, Cu, and Cd. • Affected by temperature which needs to be maintained above 10 °C.	*C. violaceum* *C. violaceum* DSM 30191^T **Mixed Culture** *P. aeruginosa* + *C. violaceum* *P. fluorescens* + *C. violaceum* *P. aeruginosa* + *P. fluorescens* *P. fluorescens* + *C. violaceum* + *P. aeruginosa*	[53–55, 90, 115–120]
Polarography	• This works on electro-analysis to determine electroactive species by their oxidation or reduction. • It uses three electrodes (working, counter, and reference) in an electric cell	*P. aeruginosa*	[29,111, 119]

(*continued on next page*)

Table 3 (*continued*)

Method	Description	Bacteria tested	Reference
	to generate electrical potential. • Used to measure bio-CN. • The technique is simple, rapid, highly sensitive, robust, reproducible, and inexpensive. • However, the method faces issues of toxic waste management (e.g., Hg) and is labour-intensive.		

a decreased cyanide concentration. Faraji et al. [29] reported maximum cyanide production at 24 h of bacterial growth using *B. megaterium*. Ruan et al. [58] investigated PMs leaching from electronic waste using the cyanogenic microorganism *P. chlororaphis*. The influence of pH on cyanide production with respect to culture time showed maximum cyanide production at 24 h of the culture time. In the same study, the researchers reported that the maximum cyanide production occurred at 72 h while testing the influence of amino acids i.e., glycine and methionine using *P. chlororaphis*. Merli et al. [36] while optimizing cyanide production using *P. aeruginosa* for PMs recovery reported an increase in cyanide production up to a peak value followed by a decrease with time. The *P. aeruginosa* was able to produce the highest cyanide (10 mg/L) in the shortest time of 20 h. The decrease in cyanide concentration after reaching a peak is attributed to cyanide degradation or utilization as a nitrogen and carbon source [36]. Other documented reasons for a decline in cyanide concentrations are reaction with metals, absorption on the cell surface, and evaporation as HCN [38,46].

7.2. pH

Initial pH of the growth media is a critical factor in influencing cyanide production. Alkaline pH favours the availability of more CN^- ions in the medium/solution because of the chemistry of cyanide. On the contrary, maximum bacterial growth and bio-CN production take place near a pH range between 7 and 8 [53,54]. However, cyanide at this pH is present in gaseous form (HCN) and is highly unstable and may leave the medium/solution [14,62,122]. Researchers reported different observations while testing the effect of pH on the bio–CN–producing ability of cyanogenic microorganisms. According to Chi et al. [53], cyanide concentration increased from pH 7.4–9 and thereafter decreased from pH 10–11 using *C. violaceum*. The concentration of cyanide was maximum at pH 9 (68 mg/L) whereas, the lowest (54 mg/L approx.) was reported at pH 11 in 5 days. Furthermore, incubation from day 5–7 resulted in a drop in cyanide concentration at pH 7 compared to alkaline pH because of its instability within a longer duration. Karim and Ting [35] reported higher cyanide production at 9.0 pH using *P. fluorescence* and *B. megaterium*. Yuan et al. [31] reported maximum cyanide production at 7.5 pH using *P. fluorescence* P13. Ruan et al. [58] reported a higher yield i.e., 7.1 mg/L at pH 7 than 10 (6.88 mg/L) using *P. chlororaphis* at a culture time of 24 h. However, the differences in cyanide production values between pH 7 and 10 were not significant.

In addition, researchers documented a decrease in pH during initial growth hours proceeded by a gradual increase in pH [14,36,76]. The drop in pH is attributed to the microbial conversion of glycine to iminoacetic acid and carbonocyanidic acid [14] or carboxylic acid i.e., oxamic acid [36]. The gradual increase in pH thereafter is because of the use of intermediate bioproducts to produce bio-CN. Furthermore, the increase in pH has also been attributed to the degradation of proteins into ammonium ions through the action of the protease enzyme [14].

7.3. Metabolic precursor molecules (amino acids)

Cyanogenesis can be induced by metabolic precursor molecules like amino acids. The most widely documented metabolic precursor for bio-CN is the amino acid glycine [14,24,27,33,36,53–55,64,66,76,104,104,123]. A bacterium produces different concentrations of cyanide on supplementation of medium with different amino acids, but, among all, glycine gives the highest concentrations of bio-CN (Table 4). The amount of glycine required to produce the highest cyanide concentrations varies with the type of bacterial strain used. According to Faramarzi et al. [105], glycine concentrations between 8 and 10 g/L produced the highest amount of cyanide using *C. violaceum*. Further, the authors reported that glycine concentration >10 g/L is inhibitory to bacteria. Brandl et al. [27] used 5 g/L of glycine while studying the bio-mobilization of metals using HCN-forming microorganisms. Their bacterial strain, *P. plecoglossicida,* produced approximately 11 mg/L of cyanide. Hu et al. [124], using the *Pseudomonas* strain, reported maximum cyanide production of 5 mg/L (approx.) at 4.4 g/L of glycine concentration. Merli et al. [36], using *P. aeruginosa*, reported 10 mg/L of cyanide at an optimal glycine concentration of 1 g/L. The study using *B. megaterium* reported an improvement in cyanide concentration from 20.0 to 36.7 mg/L when augmented with a glycine concentration of 0–5 g/L. Similarly, *P. aeruginosa* has also shown higher production of bio-CN, i.e., 46.9 mg/L, when supplemented with 5 g/L of glycine. However, increased glycine concentration (10 g/L) has been observed to have a negative impact on cell growth and cyanide concentration [14]. It can be seen from the above-mentioned studies that different researchers used different glycine concentrations; however, none of them tracked its consumption. The tracking of glycine consumption along with cyanide quantification is imperative and might be helpful during upscaling to manage cost as well as avoid toxicity issues.

Researchers have observed the combined effect of glycine and methionine on bio-CN production in a chemically synthesized medium [58,125]. The cyanide formation is stimulated by the presence of succinate, malate, and fumarate in a medium supplemented with glycine and methionine using glutamate-adapted cells, whereas the formation is depressed by azide and 2,4-dinitrophenol [125]. Ruan et al. [58] reported an improvement in cyanide production to 15.52 mg/L on supplementation of medium with 4.4 g/L of glycine and 2.0 g/L of methionine, when cultured for 72 h. They also reported higher cyanide production in the medium supplemented with methionine compared to that augmented with glycine. Though methionine exerted a positive influence on cyanide production and the presence of glycine boosted this influence, it is not a substitute for glycine [25,58]. Nevertheless, threonine can replace glycine for optimal production of cyanide because *P. aeruginosa* and *C. violaceum* can convert threonine to glycine without the formation of a C1 unit. Reciprocally, serine cannot be a precursor of cyanide as it is converted into glycine by serine hydroxymethyl transferase with the formation of a C1 unit [25,123]. Glutamate is another suggested substitute for glycine where bacterial cultures grow for a longer time, but the approach is not suitable because of the low cyanide yield [126]. Therefore, it is evident that the appropriate addition of glycine or other substitutes may promote bacterial cyanogenesis.

7.4. Temperature

Generally, bio-CN production is susceptible to temperature and occurs at very narrow temperature ranges compared to those required for bacterial cell growth [112]. For example, *C. violaceum* produces cyanide at a temperature range from 25 to 35 °C [127]. Ruan et al. [58] using *P. chloroaphis* investigated cyanide production at a temperature of 15, 25, and 30 °C and found maximum cyanide (7.56 mg/L) production at 25 °C. Comparable outcomes were reported by Yuan et al. [31] where optimum cyanide production occurred at 25 °C using *P. fluorescence* P13. The findings suggested that low temperature was conducive to cyanide production. A low temperature was conducive to HCN production as it

Table 4
Key factors influencing bio-CN production.

Bacteria	Factor	Conditions	Cyanide Concentration	Reference
Incubation Time				
P. aeruginosa 9-D2	Incubation Time	12 h	~0.23 μMoles HCN/mL of culture	[43]
P. aeruginosa	Incubation Time	6 h	~180 nMoles	[128]
P. fluorescens P13	Incubation Time	16 h	6.1 mg/L	[64]
B. megaterium	Incubation Time	24 h	113 mg/L	[32]
P. chlororaphis	Incubation Time	24 h	7.11 mg/L	[58]
P. aeruginosa	Incubation Time	20 h	10 mg/L	[36]
pH				
C. violaceum	pH	9	68 mg/L	[53]
P. fluorescens	pH	9	>20 mg/L (approx.)	[35]
B. megaterium	pH	9	>18 mg/L (approx.)	
P. chloroaphis	pH	7	7.1 mg/L	[58]
P. fluorescens P13	pH	7.5	5 mg/L (approx.)	[31]
Metabolic Precursors or Amino acids				
P. aeruginosa	Glycine (gly)	12.5 mM	1.091 μmol/mL	[31,131]
	Threonine (thr)	12.5 mM	0.981 μmol/mL	
	Phenylalanine (phe)	12.5 mM	0.666 μmol/mL	
	Valine (val)	12.5 mM	0.392 μmol/mL	
	Isoleucine (ile)	12.5 mM	0.348 μmol/mL	
	Leucine (leu)	12.5 mM	0.343 μmol/mL	
	Alanine (ala)	12.5 mM	0.294 μmol/mL	
	Serine (ser)	12.5 mM	0.266 μmol/mL	
	Glutamine (gln)	12.5 mM	0.225 μmol/mL	
	Proline (pro)	12.5 mM	0.206 μmol/mL	
	Arginine (arg)	12.5 mM	0.198 μmol/mL	
	Histidine (his)	12.5 mM	0.15 μmol/mL	
	Tryptophan (try)	12.5 mM	0.142 μmol/mL	
	Asparagine (asp)	12.5 mM	0.088 μmol/mL	
	Cystine (cys)	12.5 mM	.032 μmol/mL	
P. chloroaphis	Methionine	2.0 g/L	~12.5 mg/L	[58]
	Glycine + Methionine	4.4 + 2.0 g/L	15.52 mg/L	
C. violaceum	L-Glutamic acid	10 μmol/mL	4.0 μg/mL of Supernatant	[125]
	Alanine		3.8 μg/mL of Supernatant	
	L-Histidine		2.6 μg/mL of Supernatant	
	Aspartic acid		0 μg/mL of Supernatant	
	Hydroxyproline		0 μg/mL of Supernatant	
	Arginine		0 μg/mL of Supernatant	
Glutamate-adapted *C. violaceum*	L-Glutamic acid	Compounds were added to glutamate-adapted *C. violaceum* after 7 h in a final concentration of 10 μmol/mL	2.4 μg/mL of Supernatant	
	DL-Alanine		5 μg/mL of Supernatant	
	Glycine		4.9 μg/mL of Supernatant	
	DL-Methionine		6.5 μg/mL of Supernatant	
	Guanine		3.6 μg/mL of Supernatant	
	Glycine		4.0 μg/mL of Supernatant	
	Glycine ethyl ester		5.6 μg/mL of Supernatant	
	Glycine methyl ester		10.8 μg/mL of Supernatant	
	Glycine and methionine		21 μg/mL of Supernatant	
	Alanine and methionine		4.9 μg/mL of Supernatant	
	Serine and methionine		2.0 μg/mL of Supernatant	
	Arginine, glycine, and methionine		21 μg/mL of Supernatant	
	B12, glycine, and methionine		20 μg/mL of Supernatant	
	Glycine, methionine, and sarcosine		3.6 μg/mL of Supernatant	
P. plecoglossicida	Glycine	5 g/L	11 mg/L	[27]
P. fluorescens	Glycine	7.5 g/L	23 mg/L	[40]
P. putida	Glycine	10 g/L	15 mg/L	
B. megaterium	Glycine	12 g/L	4 mg/L	[77]
C. violaceum	Glycine	5 g/L	35 mg/L	[114]
P. aeruginosa	Glycine	1 g/L	10 mg/L	[36]
B. megaterium	Glycine	5 g/L	62 mg/L	[132]
B. megaterium	Glycine	5 g/L	36.7 mg/L	[14]
P. aeruginosa	Glycine	5 g/L	46.9 mg/L	
B. megaterium	Glycine	10 g/L	106 mg/L	[16]
B. megaterium	Glycine + Glutamine	2.84 g/L + 3 g/L	86 mg/L	[129]
Temperature				
P. chloroaphis	Temperature	25 °C	7.56 mg/L	[58]
P. fluorescens P13	Temperature	25 °C	5.5 mg/L (approx.)	[24]
Nutrients/Medium components and Metals ions				
P. aeruginosa 9-D2	Synthetic medium + $FeCl_3$	0.02 mM	0.328 μmol/mL	[59]
	Synthetic medium + $MnCl_2$	0.02 mM	.007 μmol/mL	

(*continued on next page*)

Table 4 (*continued*)

Bacteria	Factor	Conditions	Cyanide Concentration	Reference
	Synthetic medium + $ZnCl_2$	0.02 mM	.006 μmol/mL	
	Synthetic medium + $CuCl_2$	0.02 mM	0.004 μmol/mL	
	Synthetic medium + $Co(NO_3)_2$	0.02 mM	.007 μmol/mL	
P. aeruginosa 9-D2	Synthetic medium	-	7.07 nmol of HCN	[128]
	Synthetic medium + low phosphate	0.01 mM	1.23 nmol of HCN	
	Synthetic medium + high phosphate	250 mM	4.61 nmol of HCN	
P. fluorescens	Tryptone + Yeast extract	6 g/L + 5 g/L	12 mg/L	[24]
B. megaterium	Tryptone + Yeast extract + NaCl + Glycine	15 g/L + 5 g/L + 10 g/L + 5 g/L	90 mg/L	[16]
	Yeast extract + tryptone + NaCl + Glycine	5 g/L +15 g/L + 10 g/L + 5 g/L	79 mg/L	
	NaCl + Yeast extract + tryptone + Glycine	2.5 g/L + 5 g/L + 15 g/L + 5 g/L	108 mg/L	
	Corn steep + yeast extract + NaCl + Glycine	15 g/L + 5 g/L + 10 g/L + 5 g/L	118 mg/L	
C. violaceum	NaCl	0.17 mol/L	Approximately 39 mg/L	[76]
	$MgSO_4$	4.0×10^{-3} mol/L	59 mg/L	
	$FeSO_4$	1.8×10^{-3} mol/L	61 mg/L	
	Na_2HPO_4	1.0×10^{-2} mol/L	69 mg/L	
	$Pb(NO_3)_2$	3.0×10^{-6} mol/L	66 mg/L	
	NaCl + $FeSO_4$ + $MgSO_4$	$0.17 + 1.8 \times 10^{-3} + 4.0 \times 10^{-3}$ mol/L	~36 mg/L	
B. megaterium	$MgSO_4$ + $FeSO_4$ + Na_2HPO_4	0.5 + 0.25 +2.5 g/L	67.05 mg/L	[14]
P. aeruginosa	$MgSO_4$ + $FeSO_4$ + Na_2HPO_4	0.5 + 0.5 +5.0 g/L	65.7 mg/L	

resulted in decreased HCN volatilization and oxygen consumption. However, a decrease in oxygen consumption has a negative impact on Au [115] and other precious metals dissolution.

7.5. Nutrients and salts

Bio-CN production strongly depends upon the type of nutrients/growth medium used for bacterial growth. The carbon and nitrogen ratio significantly influences the biometabolite or bio-CN (in this case). Castric et al. [128] proved this by letting *P. aeruginosa* use L-glutamate as a source of carbon and energy, which resulted in prolonged cyanogenesis as well as postponed inactivation of cyanogenic enzymatic apparatus. Majorly, tryptone, and yeast extracts are complex sources of carbon and nitrogen [31]. Published reports have documented that media with different components like polypeptone, yeast extract, tryptone, meat extract, NaCl, and glycine (as a precursor) have been used for cyanide stimulation by cyanogenic bacteria (Table 4). Yuan et al. [31] investigated the impact of tryptone, yeast extract, and NaCl on the cyanide production of *Pseudomonas fluorescens* P13. Their results reported 1.5 times higher bio-CN production under optimized medium conditions (6 g/L tryptone and 2 g/L yeast extract) compared to the LB medium (10 g/L tryptone, 5 g/L yeast extract, and 10 g/L NaCl). Furthermore, it was revealed that cyanide concentration was maximum in the NaCl-deprived medium. NaCl is added to maintain the extracellular osmotic pressure during microbial growth. Faraji et al. [129] using *B. megaterium* studied the effect of growth medium components i.e., yeast extract, tryptone, and NaCl on bio-CN production through a one-factor-at-a-time optimization approach. The researchers varied tryptone concentrations from 0 to 20 g/L. A maximum of 90 mg/L bio-CN was produced at 15 g/L tryptone concentration, while 0 g/L and 20 g/L showed 51 and 66 mg/L of bio-CN, respectively. Likewise, 5 g/L yeast extract produced maximum bio-CN i.e., 79 mg/L. In the case of NaCl, the highest bio-CN concentration, i.e., 108 mg/L was obtained at a concentration of 2.5 g/L. However, with a further increase in NaCl concentration from 2.5 to 10 g/L, a decrease in bio-CN yield was observed. This is attributed to the fact that NaCl is not an energy source and does not have a role in bio-CN production, it only provides stability to bacteria causing cells to hold bio-CN inside. Additionally, Faraji et al. [16] investigated the potential of corn-steep waste on bio-CN production to make the process more economic and sustainable. The results showed that replacing 15 g/L tryptone with 15 g/L corn steep improved bio-CN production from 108 mg/L to 118 mg/L.

Besides organic components, some metallic salts like Na^+, Mg^{2+}, and Fe^{2+} can enhance cyanide production when added to the medium in small proportions (Table 4). These components act as catalysts because of the catalytic properties of their metallic parts [14,85]. According to reports, cyanogenesis was promoted by cultivating *C. violaceum* in a culture medium containing glycine and methionine, as well as ferrous and phosphate ions [24,99,130]. HCN-producing ability of *P. aeruginosa* was stimulated at an iron concentration above 1 μM but, was limited above 3×10^{-4} M. The same microorganism (*P. aeruginosa*) when grown in a medium containing inorganic phosphate showed a reduction in cyanide production above 10 mM of phosphate concentration. The addition of Cu, Zn, and Mn at a concentration of 20 μM had no effect on cyanogenesis [59]. In another study, Castric et al. [128] reported low levels of the cyanogenic enzyme under the conditions of limited Fe (1×10^{-6} M), limited phosphate (0.1 mM), and extra phosphate (250 mM). Tran et al. [76] investigated the effect of different salts (individual as well as mixed) on the bio-CN production of *C. violaceum*. Their study found Fe^{2+} and Mg^{2+} to beeffective in yielding a cyanide concentration of ~61 and 59 mg/L, respectively, in 5 days at an initial pH of 7.4. However, when a mixture of metallic salts was added to the culture medium, the cyanide yield after 7 days remained similar (~36 mg/L) to that attained without the addition of metal ions. Furthermore, they reported that bacterial growth was significantly reduced in the culture medium containing a combination of metal ions as compared to individual metal ions. This was linked to the possible toxicity and inhibition induced by the presence of metal ions. The bacterial growth was higher in the absence of metallic salts [76]. In another study, researchers examined the simultaneous impact of three metallic salts ($MgSO_4$ and $FeSO_4$/Na_2HPO_4) on the bio–CN–producing ability of *P. aeruginosa* and *B. megaterium*. According to their results, *B. megaterium* generated 67 mg/L of bio-CN on addition of 0.5 g/L of $MgSO_4$ and 0.25 g/L $FeSO_4$/2.5 g/L Na_2HPO_4 whereas, *P. aeruginosa* produced 65.7 mg/L of bio-CN on addition of 0.5 g/L of $MgSO_4$ and $FeSO_4$, and 5 g/L Na_2HPO_4 after 48 h. It should be noted that $FeSO_4$ cannot be applied alone as it may precipitate as iron hydroxide (at high pH~7.5) or can consume free cyanide ions by complexation. Therefore, the addition of sodium hydrogen phosphate (Na_2HPO_4) was recommended along with $FeSO_4$ to avoid precipitation and complexation with cyanide [14].

7.6. Other factors

Other factors such as oxygen/aeration and artificial electron acceptors have also been taken into consideration by some researchers. According to Wissing et al. [58], cyanide is not produced under anaerobic conditions. However, a change from anaerobic to aerobic conditions initiates cyanide production. It was reported that low levels of cyanide were detected when anaerobic equilibrium conditions were established. The cyanide levels remained unaffected even though extracellular glycine was present or absent. In *P. aeruginosa,* dissolved oxygen (DO) less than 20 μM in the growth medium induces cyanogenesis, and conversely, strong aeration of 180 μM of oxygen deactivates the HCN synthase enzyme with a half-life of 10 min [60,86]. Additionally, cyanogenesis was also induced anaerobically using an artificial electron acceptor such as methylene blue, phenazine methosulfate (PMS), ferricyanide, and 2, 6-dichlorophenolindophenol (DCIP). The cyanide production was high with PMS (4.1 HCN nmol/min/mg of protein) followed by methylene blue (2.7 HCN nmol/min/mg of protein), 2, 6-dichlorophenolindophenol [DCIP] (0.98 HCN nmol/min/mg of protein), and ferricyanide (0.02 HCN nmol/min/mg of protein) [75].

8. Can bio-cyanidation be an alternative to the cyanidation of precious metals?

Bio-cyanidation is a biomining process whereby cyanogenic microorganisms produce bio-CN, which is subsequently applied to leach metals from metal-bearing materials. Bio-cyanidation technique is based on complexolysis, i.e., complex formation between metals and bio-CN [13]. In terms of cost-effectiveness for gold recovery, bio-cyanidation is perceived to be better because it curtails costs for waste management, cyanide remediation, and the cost associated with safe usage and sourcing of the reagents [29,132]. Several studies are available on the bio-cyanidation of Au from gold-bearing primary ores and secondary metallic resources. However, very limited information is available on the bio-cyanidation of PMs, especially Pd, Pt, and Rh. The bio-cyanidation of PMs from PMs-bearing materials using cyanogenic microbes is discussed below.

8.1. Bio-cyanidation of Au

Gold occurs, in association with quartz, in minerals such as stibnite (Sb_2S_3), arsenopyrite (FeAsS), pyrite (FeS_2), and chalcopyrite ($CuFeS_2$). The association of gold with these minerals has an influence on its extraction efficiencies [43]. Usually, cyanide is employed to extract Au from mineral ores as the dicyanoaurate complex (Equation (7)), which has shown good chemical stability and solubility in water [133]:

$$2Au + 4CN^- + H_2O + 1/2O_2 \rightarrow 2Au(CN)^{2-} + 2OH^- \quad (7)$$

Au can also be extracted from mineral ores using microbial bio-CN. Several cyanogenic microbes have been isolated and characterized, but *C. violaceum* and species of the genus *Pseudomonas* are the most exploited for gold mobilization. *C. violaceum* has been considered effective in the solubilization of Au from mineral ores that are pre-oxidized and refractory [62,115]. Gold bioleaching using *C. violaceum* is not constant and depends on the ore type and heterogeneity of the metallic content. For example, using *C. violaceum* ATCC strain 12472, Campbell et al. [108] reported a gold extraction of 100 % from Au-coated glass slides [117], whereas Lawson et al. [62] after twenty days of leaching documented 53 % Au extraction from a low-grade Au ore with a gold content of 3.2 g/t.

Using *P. plecoglossicida*, Brandl and Faramarzi [134], reported a 68.5 % dissolution of gold as dicyanoaurate from shredded PCBs after an incubation of 80 h. In another study, Campbell et al. [117] conducted bioleaching of Au from two different gold-containing resources using *C. violaceum*. The authors reported that *C. violaceum* extracted 100 % Au within 4–7 days on glass test slides, whereas only 50 % of Au was extracted from bio-oxidized sulfidic-ore concentrate in 10 days. Shin et al. [114] also employed *C. violaceum* to recover gold from three different types of ore named H, R, and S. The Au contained in type H was 21.2 g/t; in type R, 1.14 g/t; and in type S, 1.34 g/t. The total available gold for direct cyanidation was 6.18 ± 1.49 mg/kg, 0.63 ± 0.00 mg/kg, and 1.21 ± 0.07 mg/kg for ores type H, R, and S, respectively. During the study, different strategies were employed, for example, pH, particle size, *C. violaceum* pre-growing conditions, and bio-oxidation pre-treatment. After 2 days of incubation in yeast extract peptone (YP) medium with 5 g/L of glycine added and a pH of 9.0, a maximum of 34.6 mg/L of bio-CN was produced. When pre-grown *C. violaceum* (overnight inoculation into the YP medium) was applied to the low-grade ground ore under laboratory conditions of 220 rpm and 30 °C for 5 days, Au extraction efficiencies improved to 40 %, 60 %, and 100 % compared to 5 %, 0 %, and 50 % for ores H, R, and S, respectively, when *C. violaceum* was employed without any pre-treatment [114].

Gorji et al. [14] used *B. megaterium* and *P. aeruginosa* to bioleach Au from pure Au particles as well as from an oxidized Au-bearing ore containing 6.2 g/t Au. The ore samples were procured from the Kalchuyeh mine located in Isfahan, Iran, and contained mainly 3.5 %, 0.5 %, and 0.5 % of Fe, Cu, and Al. In order to remove the cyanide-consuming interfering elements, the ore was pre-treated for 24 h using 6 M nitric acid at a temperature of 25 °C and pulp density of 25 % (*w/w*). All the bio-cyanidation experiments were conducted at 35 °C in a shaking incubator (150 rpm) for 108 h. The authors reported that 67.05 mg/L and 66.35 mg/L of bio-CN was produced by *B. megaterium* and *P. aeruginosa*, respectively. Furthermore, their results showed greater than 80 % Au extraction from pre-treated ore using *B. megaterium*, thus confirming that chemical pre-treatment had a positive impact on the process [14].

A summary of the raw material used, bacterial isolates employed, bioleaching conditions applied, cyanide concentration levels chosen, and recoveries obtained in some gold bio-cyanidation studies are presented in Table (5).

8.2. Bio-cyanidation of PGMs (Pt, Pd, and Rh)

Platinum, palladium, and rhodium are leachable from PGM mineral ores as water-soluble and chemically stable PGM-cyano-complexes as shown below in equations 8–10 [12,135,136].

$$2Pt + 8CN^- + 2H_2O + O_2 \leftrightarrow 2[Pt(CN)_4]^{2-} + 4OH^- \quad (8)$$

$$2Pd + 8CN^- + 2H_2O + O_2 \leftrightarrow 2[Pd(CN)_4]^{2-} + 4OH^- \quad (9)$$

$$4Rh + 24CN^- + 6H_2O + 3O_2 \leftrightarrow 4[Rh(CN)_6]^{3-} + 12OH^- \quad (10)$$

Documentation on the extraction of PGMs from ores or concentrates using cyanide-producing bacteria is limited (Table 5). However, some work has been reported on the recycling of PGMs from spent automobile catalytic converters using cyanogenic bacteria. Most likely, due to passivation, very little (0.2 %) platinum extractions as tetracyanoplatinate $[Pt(CN)_4]^{2-}$) were achieved from an automobile converter (1.06 g Pt/kg) after 10 days using *P. plecoglossicida*. Further, researchers reported that when a catalytic converter was present, the maximum cyanide recorded was 1.8 mg/L [27]. Another study conducted on the pressure bio-CN leaching of PGMs from an exhausted autocatalytic converter resulted in efficient dissolution of PGMs. During the process, *C. violaceum* was used to produce HCN gas, which was entrapped in NaOH to form a NaCN solution of biological origin. The pressure leaching was conducted in an autoclave using 5.82 g/L of captured bio-CN, which yielded >90 % PGMs dissolution under the conditions of 120 min, pO_2 of 200 psi, and a temperature of 150 °C [136].

Karim and Ting [35] investigated the potential of cyanogenic bacteria *B. megaterium* and *P. fluorescens* in the simultaneous bioleaching of

Table 5
Cyanogenic bioleaching of PMs from different metal-bearing primary and secondary resources. The leaching temperature is 30 °C unless otherwise specified.

Metals	Bacterium	Type of material*	Metals content (%)	Experimental conditions	Bio-CN conc. (mg/L)	% metals recovery	Reference
Au	*C. violaceum*	SR-WEEE	0.084	TSB: glycine 5 g/L, pH 7.2, 150 rpm, PD 10 g/L, 7 d	–	69.3	[33]
		SR-SIM cards	0.42	TSB: glycine 5 g/L, pH 9, 150 rpm, PD 10 g/L, 7 d	–	0.4	[34]
		SR-MPCBs	0.025	OSB: glycine 5 g/L, pH 11, $MgSO_4$ 0.5 g/L, 150 rpm, PD 15 g/L, 8 d	68	11.31	[53]
		SR-ESM	0.028	TSB: pH 7.5, 170 rpm, PD 5 g/L, 8 d	20	11.3	[54]
		SR-ESM	0.028	SML: pH 10, 170 rpm, PD 5 g/L, 8 d	20	30	[55]
		PR-Au ore	0.0003	OSB: pH 8.0, FeSO4 0.5 g/L, Na_2HPO_4 6 g/L, PD 100 g/L, 150 rpm, 20 d	45	53	[62]
		SR-Waste PCBs	0.025	OSB: glycine 5 g/L, pH 11, $MgSO_4$ 0.5 g/L, 150 rpm, PD 15 g/L, 8 d	54	11	[76]
		SR-WEEE	0.48	TSB: glycine 5 g/L, pH 7.2, 200 rpm, PD 5 g/L, 7 d	50	8	[139]
		PR-Low-grade ore	0.00012	TSB: glycine 5 g/L, pH 9, 220 rpm, PD 20 g/L, 5 d	35	60	[114]
		PR-Low-grade ore	0.00013	TSB: glycine 5 g/L, pH 9, 220 rpm, PD 20 g/L, 5 d	35	100	
		PR-Low-grade ore	0.0021	TSB: glycine 5 g/L, pH 9, 220 rpm, PD 20 g/L, 5 d	35	40	
	B. megaterium	PR-Cu-Au ore	0.00062	SML: pH 10, 35 °C, 150 rpm, PD 10 g/L, 4.5 d	67.1	81	[14]
		SR-CPCBs	0.021	TSB: glycine 0.5 g/L, pH 10, 170 rpm, PD 2 g/L, 6 d	16.3	63.8	[63]
	P. aeruginosa	PR-Cu-Au ore	0.00062	SML: pH 10, 35 °C, 150 rpm, PD 10 g/L, 4.5 d	66.4	69	[14]
		SR-WEEE	0.084	TSB: glycine 5 g/L, pH 7.2, 150 rpm, PD 10 g/L, 7 d	–	50	[33]
		SR-ESM	0.028	TSB: pH 7–7.5, 170 rpm, PD 5 g/L, 8 d	10	5.8	[55]
	P. fluorescens	SR-PCBs	0.0002–0.0032	TSB: glycine 7.5 g/L, pH 7.3–8.6, 150 rpm, PD 5 g/L, 2 d	15.5	22	[40]
		SR-WEEE	0.048	TSB: glycine 5 g/L, pH 7.2, 200 rpm, PD 5 g/L, 7 d	18	10.2	[139]
		SR-WPCBs	0.0035	OSB: glycine 10 g/L, pH 9, methionine198 g/L, 150 rpm, PD 3.3 g/L, 2.7 d	–	54	[140]
		PR-Au ore	–	OSB: pH 7.2, 180 rpm, PD 1 g/L, 7 d	34.5	20	[141]
	P. chlororaphis	SR-PCBs	0.0005	OSB: glycine 4.4 g/L, pH 7, 25 °C, methionine 2 g/L, 60 rpm, 3 d	15.5	8.2	[58]
	P. plecoglossicida	SR-PCB	0.002	OSB: glycine 5 g/L, pH 7.3, 150 rpm, 3 d	1.8	68.5	[134]
	P. putida	SR-PCB	0.0002–0.0032	TSB: glycine 10 g/L, pH 7.3–8.6, 150 rpm, PD 5 g/L, 2 d	21.5	44	[40]
		SR-WEEE shredding dust	0.00087	TSB: glycine 10 g/L, pH 7.2–8.4, 150 rpm, PD 10 g/L, 3 h	20	48	[38]
	P. balearica	SR-PCBs	0.008	TSB: glycine 6.8 g/L, pH 8.6, 31 °C, 150 rpm, PD 5 g/L, 7 d	–	73.9	[42]
		SR-PCBs	0.008	TSB: glycine 5 g/L, pH 9.0, 150 rpm, PD 10 g/L, 7d	–	68.5	[66]
	C. violaceum + *P. aeruginosa* + *P. fluorescens*	SR-ESM	.028	TSB: pH 7.5, 170 rpm, PD 5 g/L, 8 d	14.0	9.9	[55]
	C. violaceum + *P. aeruginosa*				15.0	10.2	
	P. aeruginosa + *P. fluorescens*				11.0	8.5	
	C. violaceum + *P. fluorescens*				13.0	9.1	
	P. putida + *B. megaterium*	SR-WPCBs	0.033	OSB: pH 10, 25 °C, 150 rpm, PD 5 g/L, 1.4 d	13.9	84	[61]
Pt	*B. megaterium*	SR-SAC	0.191	TSB: pH 9, 150 rpm, PD 5 g/L, 6 d	25	40	[35]
	P. fluorescens				27.5 (approx.)	44	
	B. megaterium			SML: pH 9, 150 rpm, PD 5 g/L, 1 d	–	52	
	P. fluorescens				–	56	
	P. plecoglossicida		0.0001	TSB: 7.2, 30 °C, 150 rpm, PD 25 g/L, 10 d	1.8	0.2	[27]
	C. violaceum		0.069	PL: pH 11, 150 °C, pressure 3000 psi, 200 rpm, PD 200 g/L, 1 h	1000	92.1	[52]
Pd	*B. megaterium*	SR-SAC	0.145	SB: pH 9, 150 rpm, PD 5 g/L, 6 d	25 (approx.)	51	[35]
	P. fluorescens				27.5 (approx.)	54	
	B. megaterium			SML: pH 9, 150 rpm, PD 5 g/L, 1 d	–	59	
	P. fluorescens				–	62	
	C. violaceum		.045	PL: pH 11, 150 °C, pressure 3000 psi, 200 rpm, PD 200 g/L, 1 h	1000	99.5	[52]
Rh	*B. megaterium*	SR-SAC	0.054	TSB: pH 9, 150 rpm, PD 5 g/L, 6 d	25 (approx.)	94	[35]
	P. fluorescens				27.5 (approx.)	96	
	B. megaterium			SML: pH 9, 150 rpm, PD 5 g/L, 1 d	–	95	
	P. fluorescens				–	97	
	C. violaceum		0.016	PL: pH 11, 150 °C, pressure 3000 psi, 200 rpm, PD 200 g/L, 1 h	1000	96.5	[52]

*PR-Primary Resource, SR- Secondary Resource, OSB-One-Step Bioleaching, TSB- Two-Step Bioleaching, SML- Spent Medium Leaching, PL- Pressure Leaching, PCB-Printed Circuit Board, MPCB- Mobile Printed Circuit Board, CPCB-Computer Printed Circuit Board, WEEE-Waste Electrical and Electronics Equipment, ESM-Electronic

Scrap Material; SAC-Spent Automobile Catalysts, PD-Pulp Density, SIM-Subscriber Identity Module, O1- low-grade free milling oxide ore, O2-semi-refractory sulfide ore.

Pd, Pt, and Rh from both untreated and pre-treated SAC. The parameters including pH, pulp density, and cyanide concentration were examined for their effect on the PGMs extraction. The leaching efficiencies of the spent medium and two-step bioleaching were also compared, which showed that the spent medium approach had a higher efficiency. Among the two cyanogenic bacteria used, *P. fluorescens* exhibited better extractions than *B. megaterium*, and the two species produced 27.5 mg/L and 25 mg/L of free cyanide, respectively. Highest extractions of 58% Pt, 65% Pd, and 97 % Rh were achieved from pre-treated SAC using spent medium of *P. fluorescens* after 24 h under the conditions of 0.5 % (*w/v*) pulp density and a pH of 10. It was found that pH and pulp density played a critical role in PGM extraction. Alkaline conditions were reported to favour the formation of bio-CN ions and consequently PGM extractions.

Shin and co-workers [52] used the two-stage approach to recover PGMs from spent automobile catalysts. They first produced the bio-CN using *C. violaceum* followed by 1 h of PGM leaching from the ground (<150 μm) SAC at 150 °C and 200 rpm. The maximum bio-CN concentrations obtained were 954.8 mg/L and 6594.5 mg/L using batch and continuous culture system, respectively. They limited the concentration of bio-CN to 1000 mg/L to prevent the occurrence of pH higher than required for PGM leaching. Since PGMs exhibit poor leaching kinetics at room temperature [12], the leaching efficiency was evaluated between temperature ranges of 50–200 °C. It has been demonstrated that PGMs leach at different rates during pressure cyanidation with Pd exhibiting the higher extraction efficiencies and Rh showing the least [12] Highest metal recoveries of 99.5 % Pd, 96.5 % Pt, and 92.1 % Rh were attained at 150 °C [12]. The higher extraction at elevated temperature corresponds to the effective breakage of the strong metallic bonds of PGMs. Mai et al. [137] reported that the metallic bonding energy of PMs has a high affinity with their melting points. The authors showed that the melting points of Rh, Pt, and Pd, in decreasing order, were 1966, 1772, and 1552 °C, respectively. However, if the solution's temperature exceeds 150 °C, the leaching efficiency decreases because of decreased oxygen solubility [52,138]. Chen and Huang [12] reported a decrease in the percentage of Pd leaching at a reaction temperature above 160 °C because the stability of $Pd(CN)_4^{2-}$ decreases at high temperatures, causing it to decompose easily to Pd metal. Conversely, the Rh and Pt cyanide complexes are stable in solution even up to 180 °C with a slight decomposition.

The high stability of $Rh(CN)_6^{3-}$ compared to $Pd(CN)_4^{2-}$ is attributed to its octahedral structure which implies the need to break Rh–CN bond prior to oxidation, whereas the Pd–CN bond is having a planar structure and would not necessitate the bonds breakdown prior to oxidation [12]. The PGM-cyanide complexes, up to a pH of 9.2, are dependent on pH, thereafter they become independent of pH. Additionally, oxygenated cyanide solutions are necessary for the formation of these complexes because they occur beneath the oxygen line.

9. Pre-treatment methods to enhance bio-cyanidation of PMs

Cyanide is non-selective to PGMs and easily forms complexes with base metals leading to increased consumption of lixiviant and poor leaching of PMs from both primary and secondary resources [4]. Iron presence in the feed material may result in co-complexation with PGMs in solution [142], leading to a need for additional steps to avoid loss of PGMs during recovery in downstream processes. Schouwstra and Kinloch [143] reported that if a large proportion of PGMs is locked inside the base metal's sulphide matrix, a base metal recovery process prior to cyanide leaching becomes essential. To accomplish this goal, several base metals extraction or pre-treatment processes have been applied such as bio-oxidation, chemical oxidation, high-temperature roasting, ultrasound-assisted nitric acid pre-treatment, calcination, and mechanochemical activation [9,43,144,145]. The pre-treatment technologies breakdown the ores to expose encapsulated precious metals and further remove base metals depending on the mineralogical profile of the material thereby reducing the consumption of lixiviant, and improving the PMs dissolution rate [4,8,146]. While selecting a pre-treatment technology to remove interfering elements, it should be noted that it must not co-dissolve the PMs.

9.1. Chemical pre-treatment

Chen et al. [147] used an acidic sodium chlorate solution to pre-treat spent auto-catalysts before subsequent leaching of Rh from spent auto-catalysts. They investigated the use of O_2 followed by H_2 and then CO (carbon monoxide). They also investigated the effect of treatment with O_2 proceeded by either CO or H_2. Best extractions of 82 % Rh were obtained after oxidative pre-treating with O_2 followed by reductive pre-treatment with H_2. The improved extractions were attributed to the formation of the more soluble metallic Rh that could be more easily chlorinated than the original Rh_2O_3.

The use of formic acid as a pre-treatment route prior to HCl leaching of PGMs from SAC was also investigated by Upadhyay et al. [144]. Since PGMs are more difficult to leach as oxides than as pure metals, using formic acid would probably reduce the PGM oxides according to the reactions presented in equations 11–13. The use of 20 % formic acid at room temperature resulted in improved subsequent PGM extractions by about 41 %, with Pt extractions of up to 90 % being achieved. In addition to formic acid, other alternative reducing agents including $AlCl_3$, Al powder, thiourea, NaOH, and sodium borohydride have been tested [8]. The main advantage of formic acid is that high extractions are achieved at low concentrations, minimizing environmental impact and reagent cost [148].

$$PtO + HCOOH \rightarrow Pt + H_2O + CO_2 \quad (11)$$

$$PdO + HCOOH \rightarrow Pd + H_2O + CO_2 \quad (12)$$

$$Rh_2O_3O + 3HCOOH \rightarrow 2Rh + 3H_2O + 3CO_2 \quad (13)$$

In another study [149] the use of Zn vapour prior to PGM leaching was reported to improve PGM recoveries. Sasaki and Maeda [149] attributed the improved extractions to the formation of highly soluble alloys between Zn and PGMs. Another possible reason for the improved PGM extractions was increased PGM surface area due to the preferential dissolution of Zn [150–153]. Tingle [154] and Sasaki and Maeda [153] also suggested that PGMs probably changed to chemically reactive states following Zn deposition. In addition to Zn, other metals proposed were Cu, Pb, Ni, and Al [154]. However, these alloying processes present a challenge of high energy demands associated with having to vaporise the alloying metals. Table 6 gives a detailed overview of some of the pre-treatment steps that have resulted in improved yields of PGMs.

9.2. Bio-oxidation

Bio-oxidation is preferred over traditional pre-treatment methods, since the latter have increased capital and operating costs, ineffective recovery of gold, and are non-eco-friendly in nature [156,157]. Bio-oxidation is seemingly more attractive because of its higher efficiency, environmental friendliness, and cost-effectiveness [156,158]. Bio-oxidation ensures microbial oxidation of metallic ores containing metallic compounds, with the target metal remaining in a concentrated form in the solid residues [159]. The bio-oxidation of minerals is predominantly utilized as a pre-treatment step, most notably in the

Table 6
Pre-treatment methods and subsequent recovery of PMs from primary and secondary resources.

Methods	Description	PMs dissolution approach	Yield		Advantages	Disadvantages	Reference
			Metal	Recovery (%)			
Oxidation followed by reduction	Oxygenation followed by the addition of hydrogen	Sodium chlorate	Rh	56 %	Increased dissolution rates	Use of high temperatures	[147]
Use of formic acid	PGMs were leached with electro-generated chlorine after pre-treatment of the SAC with formic acid that acted as a reducing agent for the PGM oxides.	Hydrochloric acid	Pt, Pd, and Rh	97 %, 94 %, and 90 %	High extractions are achieved at low concentrations of formic acid.	Use of high temperatures	[144]
Bio-oxidation	Removal of base metals from PGM concentrates using S and Fe oxidizing microorganisms.	*P. putida* WSC36, *B. megaterium*, *C. violaceum*	Au	48 %, 63.8 %, and 11 %	Results in the formation of a base metal-free residue Cost-effective Eco-friendly Low capital investment Low energy requirements	Poor leaching kinetics	[38,63, 139]
Ultrasound-assisted nitric acid pre-treatment	80 % ultrasonic power, 37 kHz ultrasonic frequency, 6 M HNO_3, 50 min	*P. fluorescens*	Pt, Pd, and Rh	38 %, 44 %, and 91 %	Accelerated leaching, improved recoveries, reduced reagent consumption, lower temperature requirements	Not effective below a critical particle size	[35]
		B. megaterium,	Pt, Pd, and Rh	35 %, 45 %, and 82 %			
Zn vapour deposition	Zn vapour treatment of spent automotive catalytic converters prior to acid leaching	Hydrochloric acid	Pt, Pd, and Rh	98 %, 97 %, and 65 %	Improved extractions	High energy demands associated with having to vaporise the alloying metals	[149]
Calcination	Formation of a $(Na,Li)_2PtO_3$ solid solution by heating Pt in the presence of Li_2CO_3 at 800 °C.	Hydrochloric acid	Pt	96–97 %	Increased dissolution in lixiviants such as HCl	High calcining temperatures	[155]
Mechanochemical activation	Done in the presence of an oxidizing agent – details still concealed	Hydrochloric acid	Pt, Pd, and Rh	77.2 %, 97.4 and 62.1 %	Improved recoveries	Activation of other mineral surfaces that might interact with target metals	[145]

pre-treatment of sulfidic gold ores [160]. The principal reason for gold ore bio-oxidative pre-treatment is to breakdown gold-associated minerals and to expose the molecular structure so that leaching reagents can subsequently access and extract the gold [161]. Bio-oxidative pre--treatment also eradicates, makes inert, or significantly decreases the occurrence of the gangue minerals which leads to refractoriness. The microorganisms used in the bio-oxidative pre-treatment process belong to the iron and sulfur-oxidizing group [156,162].

Sulfur- and iron-oxidizing bacteria (e.g., *Sulfolobus* sp. and *Acidithiobacillus* sp.) catalyse sulfide oxidation and release gold for the subsequent bio-cyanidation process. These bacteria oxidize Fe^{2+} into Fe^{3+} ions, thereby gaining energy. They also oxidize elemental sulfur to H_2SO_4 which aids the indirect in-situ dissolution of sulfides from the minerals-bearing ore. Thus, the main function of these microorganisms in bio-oxidation is to supply H_2SO_4 for a proton attack and Fe^{3+} ions for an oxidative attack on mineral ores in order to remove metallic impurities from refractory gold ores [43]. However, most of the bio-oxidizing microbes fulfil their carbon needs from the CO_2 in the gas phase, leaving a significant portion of preg-robbing carbonaceous residues that can limit the subsequent bio-cyanidation efficiency [163,164]. Few studies, on the other hand, have shown that fungi can be used to mitigate the negative impact of preg-robbing on bio-oxidation. For instance, Ofori-Sarpong et al. [164] made use of a fungal strain, *Phanerochaete chrysosporium*, that reduced the preg-robbing of anthracite-grade carbonaceous matter (CM) during gold extraction from the refractory gold ores. The strain's capacity to transform sulfides was studied to acquire an effective microbial process for the mining industry. The results illustrated a 15–35 % reduction of sulfide compounds in pyrite and arsenopyrite ores using *P. chrysosporium*. Consequently, this improved the bioleaching efficiency of Au during bio-cyanidation.

It has been documented that only bio-oxidation of gold containing sulfidic ores has been applied industrially, bio-oxidation of sulfidic low-grade Pt ores is still limited to lab-scale [165,166]. Using packed bed columns, bioleaching to recover base metals from low-grade ore flotation concentrate and coarse ore has been successfully applied at the laboratory scale using iron and sulfur-oxidizing thermophilic acidophiles. Subsequently, the residue containing PGEs was subjected to chemical cyanidation [4,165]. In another study, Heidrich et al. [166] conducted bio-oxidation of stockpiled oxidized PGE ore collected from Mokgalakwena Mine, Bushveld Complex, South Africa. The mineralogical composition showed the presence of >90 wt% silicates and trace amounts of Fe-(oxy)/hydroxides, both coupled with Cu, Ni, and Mn. PGMs were found in the form of native platinum, cooperite (PtS, low in Pd), sperrylite (PtAs2), and Pd-bismuth tellurides and were majorly amalgamated with silicates. To liberate PGEs, bio-oxidation was conducted by acidophilic sulfur and iron-oxidizing consortium dominated by *Sulfobacillus thermosulfidooxidans* and *Acidithiobacillus caldus*. The results of their study achieved an overall metal extraction of 96 % for Ni, Mn, Cu, and Co. The pre-treated residue was further subjected to chemical leaching (HNO_3/NaCl) leading to 89 and 96 % extraction of Pt and Pd, respectively.

Higher amounts of PMs are also found in secondary resources compared to natural ores/mines [9,29,167–170]. Like primary ores, the secondary resources also contain significant quantities of base metals which cause interference during the bio-cyanidation of PMs. A lot of effort has been vested in the research aiming at the base metals removal to enhance PMs leaching in the subsequent bio-cyanidation process [103,171]. Arshadi and Mousavi [63] conducted a study to enhance Au leaching from computer printed circuit boards (CPCB). Firstly, using *A. ferrooxidans,* the majority of Cu was extracted from CPCBs and, subsequently, the pre-treated residue was subjected to bioleach Au using *B. megaterium*. Under optimum conditions, 63.8% of Au was extracted from pre-treated CPCBs. Işıldar et al. [40] developed a two-stage process whereby autotrophic (a mixed culture of *A. ferrivorans* and *A. thiooxidans*) followed by heterotrophic bacteria (*P. putida*) were used for selective recovery of Cu and Au. First stage of the process recovered 98.4 % Cu using a mixture of autotrophic bacteria, while the second stage extracted 44.0 % Au using heterotrophic bacteria. Marra et al. [38]

conducted bioleaching of Au from the shredded dust of waste electrical and electronic equipment (WEEE) in a two-step process. These researchers first applied *A. thiooxidans* (DSM 9463) to completely leach the base metals out of the material. In the second step, cyanogenic microorganism *P. putida* WSC361 was applied to the pre-treated residue attaining 48 % solubilization of Au in 3 h. Regarding PGMs, there are no documented studies of a two-stage biobased process where bioleaching was used to remove interfering elements followed by bio-cyanidation to recover PGMs from both primary ores as well as secondary metallic resources.

10. What makes the bio-cyanidation process green and sustainable?

Cyanogenic microorganisms produce HCN/bio-CN which is a toxic bio-metabolite/bio-chemical. Interestingly, these microorganisms also have the capability of degrading or utilizing the free cyanide [25,29]. Literature has documented four major enzymatic pathways of cyanide degradation used by microorganisms i.e., oxidative pathway, hydrolytic, reductive, and substitution/transfer pathway (Fig. 3). Microorganisms can utilize one or more different pathways at a time. The pathway used is controlled by environmental factors like oxygen, pH, cyanide concentrations, and bioavailability and solubility in the soil-water system [172,173]. In the hydrolytic, oxidative, and reductive pathway, the cyanide is enzymatically catalyzed to simple inorganic and organic complexes which can be further transformed to carbon dioxide, methane, formic acid, ammonia ion, or carboxylic acid. However, during substitution or biosynthesis reaction, the microorganism assimilates cyanide as a nitrogen and carbon source [174–176]. Different enzymes involved in each pathway and the enzymatic reactions along with examples of microorganisms are shown in Fig. 3.

Different bacteria produce different enzymes (for example, β-cyanoalanine synthase, nitrilase, cyanidase, etc.) for the degradation or metabolization of cyanide. However, the enzyme β-cyanoalanine synthase is the dominant one among all [29]. Many bacteria including *C. violaceum*, *B. megaterium*, and *E. coli* produce the β-cyanoalanine synthase enzyme, which transforms cyanide to a non-proteinaceous amino acid β-cyanoalanine and H_2S. Further, these bacteria convert the β-cyanoalanine to asparagine or aspartate by using the enzyme cyanoalanine hydrolase or asparaginase [29,173,175–177]. Other microorganisms such as species of the genus *Pseudomonas* are also capable of producing cyanide and are extensively studied in the bio-cyanidation of metals. However, under appropriate conditions, these microorganisms metabolize cyanide to obtain nitrogen and carbon using an oxidative pathway [174,178]. For example, at low cyanide levels, *P. fluorescence* transforms cyanide into ammonia and carbon dioxide by producing cyanide monooxygenases. At higher cyanide levels, this organism can utilize two other pathways for cyanide metabolism: 1) cyanide hydratase-mediated catalysis of cyanide into formamide, and 2) cyanide dehydratase-assisted conversion of cyanide into formate and ammonia [29,179]. *P. putida* transforms cyanide into ammonia and CO_2 by secreting cyanide dioxygenase [175]. According to Ruan et al. [58], cyanogenic microorganism, *P. chlororaphis* can metabolize cyanide and even completely consume it before the stationary phase, albeit the mechanism is unknown. *P. aeruginosa* is reported to produce constitutive rhodanase (thiosulfate cyanide transsulfurase) activity, thus indicating the involvement of sulfur metabolism when species of sulfur are present. Researchers believe that cyanide toxicity is lowered by transforming it into thiocyanate [29,123].

Other than bacteria, a few species of fungus including *Scytalidium thermophilum*, *Fusarium oxysporum, Fusarium solani, Trichoderma polysporum,* and *Penicillin miczynski*, (either consortia or individual) are also known to possess cyanide degrading abilities [175]. Cyanide hydratase is predominantly a fungal enzyme that was initially identified from *Stemphylium loti*, a pathogenic fungus of the cyanogenic plant birdsfoot trefoil (*L. corniculatus* L.) [180,181]. Since then, it has been observed in

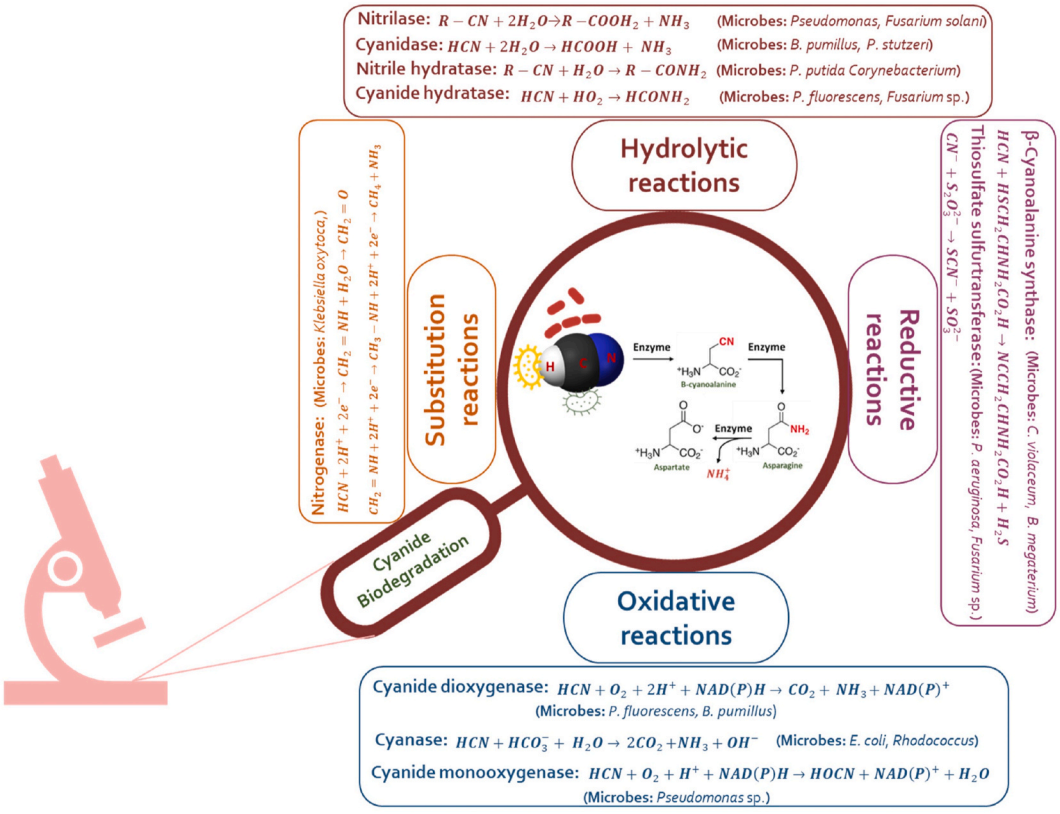


Fig. 3. Different routes of microbial degradation of cyanide (Drawn from information provided by Ebbs [173]; Gupta et al. [177]; Alvillo-Rivera et al. [176]).

several other fungi such as *Fusarium lateritium, Gloeocercospora sorghi*, *Leptosphaeria maculans,* and *Fusarium solani* [177].

The capability of these microorganisms i.e., both fungi and bacteria, to biodegrade cyanide under basic pH conditions, even at a sluggish rate, could be beneficial to a bioremediation process. Several examples of biological treatment of cyanide exist, for example, Barclay and Knowles [181] reported that the strain of *Fusarium* sp. can be used to remediate cyanide and metal-cyanide-containing soil and wastewater. Nazly et al. [182] reported that mycelia of *Stemphylium loti* can be immobilized and loaded into columns to bioremediate cyanide-containing wastes. Mudder and Whitlock [183] developed a process using the bacterium *P. paucimobilis* ATCC 39204 to treat wastes containing thiocyanate, cyanide, and metal-cyanide complexes at the lead operations plant of Homestake Mining Co. Richardson and Clarke [184] reported that ICI Biological Products generated dried *Fusarium lateritium* mycelia that can be sprinkled onto cyanide-containing waste. Thus, the bio-cyanidation process enables not only the extraction of critical metals but also a controlled release of cyanide into the environment. Subsequently, the cyanide-degrading capabilities of cyanogenic microorganisms have the potential to curtail effluent treatment expenses, which are quite high in the case of chemical cyanide effluent treatment [185].

11. Cost-economic analysis

The cost-economic analysis is imperative to guarantee the commercial viability of a process. Since bioleaching is dependent on microbial lixiviant production, it is important to compare chemical cyanidation and bio-cyanidation for metal leaching on the basis of the cyanide lixiviant, which is the key reagent input for PMs solubilization in the two processes. In the case of chemical cyanide production (Andrussow process), the cost of primary inputs, methane (USD 5.48 per 1000 Standard cubic foot), ammonia (USD 0.16/lb), NaOH (USD 0.16/lb), and air [186], is within reasonable margins. However, the unit cost of producing bio-CN seems to be relatively higher, comprising >90 % of the total cost, and this is attributed to the high reagent cost of primary inputs such as glycine (USD 70/lb) and LB medium (USD 82.9/lb) [price as at July 31, 2023]. The difference in primary input reagent prices, therefore, is the major differentiating factor for the economic viability of chemical cyanidation and bio-cyanidation. Nevertheless, the reagent costs should not be the final decider because, with a long-term outlook, the bio-cyanidation- cost could decrease, and both the product and process could provide several environmental cleaning benefits over their chemical counterparts. Thompson et al. [187] while performing a techno-economic analysis of bioleaching of rare earth elements (REEs) from waste materials found glucose as a major expense for the bioleach process comprising 44.3 % of the total cost. Although the profit was less, the authors concluded that the bioleaching plant was overall profitable. Economic analysis conducted on bioleaching of precious metals from waste PCBs by Ruan et al. [58] reported an improvement in price by almost USD 0.26/Kg of the mixed metallic particles. Since there is a dearth of techno-economic studies on bioleaching or bio-cyanidation of precious metals, it is generally difficult to predict the cost-economic effectiveness of the process. However, to make bio-cyanidation economically viable and attractive, cheaper alternative ingredients to glycine and LB medium such as corn steep waste [129], ought to be sought. Other additional efforts could be vested in optimizing process variables such as pulp density, cyanide concentrations, pH, and temperature for bio-cyanidation. Furthermore, more studies involving complete in-depth techno-economic analysis of large-scale bio-cyanidation followed by recovery to attain precious metals are highly recommended.

12. Challenges

The reviewed literature suggested that bio-cyanidation has potential to be developed as a green and sustainable alternative to traditional leaching processes. However, despite its potential, the process has been limited to lab-scale only. The commercial applicability is hindered by certain bottlenecks that need to be eliminated to make the process feasible for industrial-scale applications. The key bottlenecks are listed below.

12.1. Microbial Bio-CN producers

Even though 50 % of the soil microbial community belongs to cyanogenic microorganisms, only a few microorganisms have been quantified for bio-CN production and applied in PMs bio-cyanidation [24]. The dominant bacteria that are quantified and extensively investigated for PMs leaching are *C. violaceum*, *B. megaterium,* and species of the genus *Pseudomonas* [13,24,29,35]. This may be because the metallic components in the leaching environment pose toxicity to the microorganisms [188], affecting their growth and cyanide-producing ability- [26,66].

12.2. Analytical limitation

For all the analytical methods developed so far for determining cyanide concentration, interferences have been a challenge. Therefore, eliminating interferences is the crucial initial step prior to analysis [189]. The possible interferences include species such as sulfides, thiocyanate, thiosulphate, and some metal-cyanide complexes [111,190].

12.3. Stability of bio-CN

The stability of bio-CN is affected by the medium pH. When the pH is below 10.5, the gaseous form of cyanide, i.e., HCN, develops and reduces the quantity of bio-CN in the medium, and in turn, the bio-cyanidation of PMs [13,191]. The production of bio-CN under alkaline conditions is a challenge because at alkaline pH, most microorganisms fail to survive, which impacts the bio-CN yield and ultimately the bio-cyanidation of PMs [35,55]. Direct exposure to sunlight and air also reduces the amount of CN^- in the solution as UV radiations and gaseous oxygen naturally degrade cyanide to C and N compounds [102]. The stability of bio-CN is also impacted by the composition of the culture medium used for the growth of microorganisms. The presence of complexing agents such as metal ions and salts reduces the volatility of bio-CN, thereby, impacting the recovery of PMs [13].

12.4. Low yield and short duration of bio-CN production

Low bio-CN production by cyanogenic bacteria is another challenge hindering the industrial success of bio-cyanidation. Furthermore, the production of cyanide takes place within a limited period. Thereafter, the bio-CN exerts toxic effects on bacterial growth, and bacteria start utilizing it as a carbon and nitrogen source or convert it to other products like β-cyanoalanine [25,29]. Although self-degradation/consumption offers the advantages of eco-friendliness, it, however, limits the amount of cyanide produced and hence its application in the cyanidation process.

12.5. Mineralogy of material

The bio-recovery of PMs during bio-cyanidation also depends upon the type of material and the particle size used. For example, non-pretreated sulphidic ores present a challenge to the PGM cyanidation process due to the refractory nature of the ores caused by the locking of metals in the sulphidic matrix. The presence of base metals found in association with PGMs presents a second challenge because they compete with platinum group elements for cyanide, hence adversely affecting PGM recoveries as well as causing high cyanide consumption [146]. Similarly, it has also been found that secondary resources such as electronic waste and SAC also contain a higher level of interfering elements that interfere in PMs recovery [38]. Hence, sulphidic ores and PGM-bearing secondary material such as SAC require pre-treatment prior to bio-cyanidation to make the material amenable to bio-cyanide

leaching. In this context, pre-treatment via bio-oxidation or roasting is vital. Bio-oxidation is used as a pre-treatment step, for refractory gold ores and concentrates that contain sulphide minerals, to break down the sulfide mineral matrix and liberate the gold for subsequent cyanidation [13]. In the case of secondary resources such as e-waste or SAC, the pre-treatment is carried out to remove base metal interference in order to enhance precious metals leaching [9].

Mass transfer is another challenge in bioleaching. The particle size used in the leaching process influences the mass transfer. In general, reducing the particle size increases the overall contact surface area, therefore, reaction rate increases, and mass transfer occurs better. However, in a constant amount of sample, if the size reduction continues, the number of particles increases and can create tension between microbial cells and solid particles, leading to damage or lyses of the cells [63].

12.6. Low pulp densities and long leaching time

The bio-cyanidation of PMs is mainly carried out at lower pulp densities i.e., 10–20 g/L (1–2% *w/v*) for maximum recovery. At higher pulp densities, the efficiency of metal recovery decreases, which may be attributed to the inadequacy of air, a limited oxygen mass transfer rate, and the toxicity of metals beyond permissible limits, thereby inhibiting bacterial growth and lowering the recovery efficiencies. Additionally, long leaching time is another challenge that needs researchers' consideration. Documented investigations have reported that bio-cyanidation takes a long time i.e., 4.5–20 days for an agitated leaching approach compared to 24–72 h using KCN or NaCN in commercial gold tank cyanidation [13,132].

12.7. Scale-up limitation

The bioleaching of base metals ores and the bio-oxidation of gold ores have been applied successfully at the industrial scale, but the bio-cyanidation of PMs from both primary and secondary resources is still limited to shake flasks or laboratory scale owing to the low yield of bio-CN, use of lower pulp densities, long leaching time, and lower recovery efficiencies [192]. Additionally, to date, no biological process is in operation that can recover both PGM and non-PGM metals [193]. Therefore, if the process has to be scaled up the above-mentioned concerns need to be addressed. Furthermore, in-depth techno-economic analysis is required to evaluate the feasibility of the process for its commercialization.

13. Way forward

Based on our research experience and literature review analysis, future work should aim at (1) exploring novel cyanogenic microorganisms armed with properties such as the highest bio-CN producing capacity, alkalophilic in nature, and higher toxicity tolerance against metallic components in the leaching environment. Other than cyanogenic bacteria, studies on cyanogenic fungi, algae, and, plants may open new horizons in the bio-cyanidation of PMs (2) using innovative approaches in genetic and metabolic engineering to produce modified bacterial strains with high bio-CN synthesis capacity as well as high tolerance to wider pH ranges and metallic toxicity (3) development of a decoupled process i.e., growing microbial cells in a separate vessel and capturing and concentrating HCN in a separate vessel to improve bio-CN yield as well as eliminate cellular toxicity, HCN volatility, and bio-CN consumption/degradation. Culture-based (fed-batch and continuous culture approach) and medium-based (using organic waste resources as an alternative to glycine) amendments are required to prolong bio-CN production duration and to lower the process cost. Furthermore, it is expected that designing and developing a bioreactor for decoupled bio-CN production might confer positive impacts on bio-CN production (4) developing a repository/database for cyanogenic microorganisms (5) developing a new method or modifying the available cyanide quantifying methods to avoid sulphide based or other interference during quantification (6) necessitating studies on bio-cyanidation of PMs especially PGMs (Pd, Pt, and Rh) from both primary ores and secondary metallic resources (7) study process feasibility in large-scale reactors to confirm practical applicability of the process. While proceeding towards large-scale bioleaching operations, it is important to address the above-mentioned scale-up limitation that is hindering its (bioleaching) way to industry. In this context, using a decoupled process to produce bio-CN followed by its use in metal recovery may become a game changer for the mining industry. The decoupling process will not only solve issues such as lower bio-CN production and cyanide consumption but will also allow operation at higher pulp densities because microorganisms are already decoupled from the system, hence no microbial toxicity. (8) development of an ideal biological process that can completely extract precious and non-precious metals (9) techno-economic studies to guarantee commercial viability of the process.

14. Conclusion

The PMs are significant industrial commodities owing to their widespread applications and unique properties. The chemical cyanide leaching has certain limitations including expensive reagent cost, high health and safety risks, low recyclability, and adverse ecological and environmental impacts. Microbiological/biotechnological processes such as bio-cyanidation play a significant role since they offer ecological and environmentally friendly, cost-economic, and a green and sustainable alternative to traditional chemical cyanide leaching. The application of cyanogenic microorganisms to produce bio-CN *in situ* and its use in PMs bio-cyanidation has been successful from primary and secondary resources. Additionally, the inherent capability of cyanogenic microorganisms to detoxify/degrade/consume bio-CN raises its environmental acceptability. However, the technology is still limited to laboratory-scale use only. Thus, extensive research is needed to establish a thorough understanding of cyanogenic microorganisms and the bio-CN production process before its exploitation for upscaling.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Not applicable because the review article was prepared based on the information available in the literature.

Acknowledgements

The authors acknowledge the financial support from the EU Horizon 2020 BIORECOVER project (grant No. 821096). Two of the authors were funded by the National Research Foundation (NRF) and the Department of Science and Innovation (DSI) South Africa, through the SARChI chair in Hydrometallurgy and Sustainable Development (grant number 98350).

References

[1] Dong K, Xie F, Wang W, Chang Y, Lu D, Gu X, et al. The detoxification and utilization of cyanide tailings: a critical review. J Clean Prod 2021;302:126946.
[2] Li H, Long H, Zhang L, Yin S, Li S, Zhu F, et al. Effectiveness of microwave-assisted thermal treatment in the extraction of gold in cyanide tailings. J Hazard Mater 2020;384:121456.
[3] Altinkaya P, Wang Z, Korolev I, Hamuyuni J, Haapalainen M, Kolehmainen E, et al. Leaching and recovery of gold from ore in cyanide-free glycine media. Miner Eng 2020;158:106610.

[4] Mwase JM, Petersen J, Eksteen JJ. A conceptual flowsheet for heap leaching of platinum group metals (PGMs) from a low-grade ore concentrate. Hydrometallurgy 2012;111:129–35.

[5] Tu Y, Han P, Wei L, Zhang X, Yu B, Qian P, et al. Removal of cyanide adsorbed on pyrite by H2O2 oxidation under alkaline conditions. J Environ Sci 2019;78:287–92.

[6] Dong K, Xie F, Wang W, Chang Y, Chen C, Gu X. Calcination of calcium sulphoaluminate cement using pyrite-rich cyanide tailings. Crystals 2020;10. https://doi.org/10.3390/cryst10110971.

[7] Jha MK, Lee J, Kim M, Jeong J, Kim B-S, Kumar V. Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: a review. Hydrometallurgy 2013;133:23–32.

[8] Yakoumis I, Panou M, Moschovi AM, Panias D. Recovery of platinum group metals from spent automotive catalysts: a review. Cleaner Eng Technol 2021;3:100112.

[9] Karim S, Ting Y-P. Ultrasound-assisted nitric acid pretreatment for enhanced biorecovery of platinum group metals from spent automotive catalyst. J Clean Prod 2020;255:120199.

[10] Suoranta T, Zugazua O, Niemelä M, Perämäki P. Recovery of palladium, platinum, rhodium and ruthenium from catalyst materials using microwave-assisted leaching and cloud point extraction. Hydrometallurgy 2015;154:56–62. https://doi.org/10.1016/j.hydromet.2015.03.014.

[11] McInnes C, Sparrow G, Woodcock J. Extraction of platinum, palladium and gold by cyanidation of Coronation Hill ore. Hydrometallurgy 1994;35:141–59.

[12] Chen J, Huang K. A new technique for extraction of platinum group metals by pressure cyanidation. Hydrometallurgy 2006;82:164–71.

[13] Jorjani E, Sabzkoohi HA. Gold leaching from ores using biogenic lixiviants–A review. Current Res Biotechnol 2022;4:10–20.

[14] Gorji M, Hosseini MR, Ahmadi A. Comparison and optimization of the bio-cyanidation potentials of B. megaterium and P. aeruginosa for extracting gold from an oxidized copper-gold ore in the presence of residual glycine. Hydrometallurgy 2020;191:105218.

[15] Medina D, Anderson CG. A review of the cyanidation treatment of copper-gold ores and concentrates. Metals 2020;10:897.

[16] Faraji F, Mahandra H, Wang J, Ghahreman A. Evaluation of medium and applicability of corn steep waste for biogenic cyanide production by Bacillus megaterium for sustainable gold recovery. J Clean Prod 2022;372:133691.

[17] Chipise L, Ndlovu S, Shemi A. Towards the biobeneficiation of PGMs: reviewing the opportunities. Minerals 2021;12:57.

[18] Watling HR, Collinson DM, Corbett MK, Shiers DW, Kaksonen AH, Watkin EL. Saline-water bioleaching of chalcopyrite with thermophilic, iron (II)-and sulfur-oxidizing microorganisms. Res Microbiol 2016;167:546–54.

[19] Fathollahzadeh H, Eksteen JJ, Kaksonen AH, Watkin EL. Role of microorganisms in bioleaching of rare earth elements from primary and secondary resources. Appl Microbiol Biotechnol 2019;103:1043–57.

[20] Golmohammadzadeh R, Faraji F, Jong B, Pozo-Gonzalo C, Banerjee PC. Current challenges and future opportunities toward recycling of spent lithium-ion batteries. Renew Sustain Energy Rev 2022;159:112202. https://doi.org/10.1016/j.rser.2022.112202.

[21] Gadd GM. Microbial role in global biogeochemical cycling of metals and metalloids at the interfaces in the earth's critical zone. Springer; 2010. p. 5–7.

[22] Gavrilescu M. Microbial recovery of critical metals from secondary sources. Bioresour Technol 2022;344:126208.

[23] Utari PD, Quax WJ. Caenorhabditis elegans reveals novel Pseudomonas aeruginosa virulence mechanism. Trends Microbiol 2013;21:315–6.

[24] Faramarzi MA, Mogharabi-Manzari M, Brandl H. Bioleaching of metals from wastes and low-grade sources by HCN-forming microorganisms. Hydrometallurgy 2020;191:105228.

[25] Vakilchap F, Mousavi SM, Baniasadi M, Farnaud S. Development and evolution of biocyanidation in metal recovery from solid waste: a review. Rev Environ Sci Biotechnol 2020;19:509–30.

[26] Kumar A, Saini HS, Şengör S, Sani RK, Kumar S. Bioleaching of metals from waste printed circuit boards using bacterial isolates native to abandoned gold mine. Biometals 2021;34:1043–58.

[27] Brandl H, Lehmann S, Faramarzi MA, Martinelli D. Biomobilization of silver, gold, and platinum from solid waste materials by HCN-forming microorganisms. Hydrometallurgy 2008;94:14–7.

[28] Faraji F, Wang J, Mahandra H, Ghahreman A. A green and sustainable process for the recovery of gold from low-grade sources using biogenic cyanide generated by Bacillus megaterium: a comprehensive study. ACS Sust Chem Eng 2020;9:236–45.

[29] Wang J, Faraji F, Ramsay J, Ghahreman A. A review of biocyanidation as a sustainable route for gold recovery from primary and secondary low-grade resources. J Clean Prod 2021;296:126457.

[30] Brandl H, Bosshard R, Wegmann M. Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi. Hydrometallurgy 2001;59:319–26.

[31] Yuan Z, Ruan J, Li Y, Qiu R. A new model for simulating microbial cyanide production and optimizing the medium parameters for recovering precious metals from waste printed circuit boards. J Hazard Mater 2018;353:135–41.

[32] Faraji F, Mahandra H, Ghahreman A. An investigation for biogenic cyanide distillation for gold recovery and cyanide bioremediation by Bacillus megaterium. J Environ Chem Eng 2021;9:106030.

[33] Pradhan JK, Kumar S. Metals bioleaching from electronic waste by Chromobacterium violaceum and Pseudomonads sp. Waste Manag Res 2012;30:1151–9.

[34] Sahni A, Kumar A, Kumar S. Chemo-biohydrometallurgy—a hybrid technology to recover metals from obsolete mobile SIM cards. Environ Nanotechnol Monit Manag 2016;6:130–3.

[35] Karim S, Ting Y-P. Bioleaching of platinum, palladium, and rhodium from spent automotive catalyst using bacterial cyanogenesis. Bioresour Technol Rep 2022;18:101069.

[36] Merli G, Becci A, Amato A. Recovery of precious metals from printed circuit boards by cyanogenic bacteria: optimization of cyanide production by statistical analysis. J Environ Chem Eng 2022;10:107495.

[37] Cui J, Zhang L. Metallurgical recovery of metals from electronic waste: a review. J Hazard Mater 2008;158:228–56.

[38] Marra A, Cesaro A, Rene ER, Belgiorno V, Lens PN. Bioleaching of metals from WEEE shredding dust. J Environ Manag 2018;210:180–90.

[39] García-Balboa C, Martínez-Alesón García P, López-Rodas V, Costas E, Baselga-Cervera B. Microbial biominers: sequential bioleaching and biouptake of metals from electronic scraps. Microbiologyopen 2022;11:e1265.

[40] Işıldar A, van de Vossenberg J, Rene ER, van Hullebusch ED, Lens PN. Two-step bioleaching of copper and gold from discarded printed circuit boards (PCB). Waste Manag 2016;57:149–57.

[41] Işıldar A, van Hullebusch ED, Lenz M, Du Laing G, Marra A, Cesaro A, et al. Biotechnological strategies for the recovery of valuable and critical raw materials from waste electrical and electronic equipment (WEEE)–A review. J Hazard Mater 2019;362:467–81.

[42] Kumar A, Saini HS, Kumar S. Enhancement of gold and silver recovery from discarded computer printed circuit boards by Pseudomonas balearica SAE1 using response surface methodology (RSM). 3 Biotech 2018;8:100. https://doi.org/10.1007/s13205-018-1129-y.

[43] Karthikeyan OP, Rajasekar A, Balasubramanian R. Bio-oxidation and biocyanidation of refractory mineral ores for gold extraction: a review. Crit Rev Environ Sci Technol 2015;45:1611–43.

[44] Mpinga CN, Eksteen JJ, Aldrich C, Dyer L. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: a review. Miner Eng 2015;78:93–113. https://doi.org/10.1016/j.mineng.2015.04.015.

[45] Liu X, Wang Y, Xiao L, Ma L, Han P, Ye S. Eco-friendly and rapid extraction of gold by in-situ catalytic oxidation with N-bromosuccinimide. Heliyon 2022;8.

[46] Liddell K, Adams M. Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates. J S Afr Inst Min Metall 2012;112:31–6.

[47] Saguru C, Ndlovu S, Moropeng D. A review of recent studies into hydrometallurgical methods for recovering PGMs from used catalytic converters. Hydrometallurgy 2018;182:44–56.

[48] Sefako R, Sekgarametso K, Sibanda V. Potential processing routes for recovery of platinum group metals from Southern African oxidized PGM ores: a review. J Sust Metallurgy 2017;3:797–807.

[49] Prasad MS, Mensah-Biney R, Pizarro RS. Modern trends in gold processing — overview. Miner Eng 1991;4:1257–77. https://doi.org/10.1016/0892-6875(91)90171-Q.

[50] Zhang Y, Liu S, Xie H, Zeng X, Li J. Current status on leaching precious metals from waste printed circuit boards. Procedia Environ Sci 2012;16:560–8.

[51] Abbruzzese C, Fornari P, Massidda R, Veglio F, Ubaldini S. Thiosulphate leaching for gold hydrometallurgy. Hydrometallurgy 1995;39:265–76.

[52] Shin D, Park J, Jeong J, Kim B. A biological cyanide production and accumulation system and the recovery of platinum-group metals from spent automotive catalysts by biogenic cyanide. Hydrometallurgy 2015;158:10–8.

[53] Chi TD, Lee J, Pandey B, Yoo K, Jeong J. Bioleaching of gold and copper from waste mobile phone PCBs by using a cyanogenic bacterium. Miner Eng 2011;24:1219–22.

[54] Natarajan G, Ting Y-P. Pretreatment of e-waste and mutation of alkali-tolerant cyanogenic bacteria promote gold biorecovery. Bioresour Technol 2014;152:80–5. https://doi.org/10.1016/j.biortech.2013.10.108.

[55] Natarajan G, Ting Y-P. Gold biorecovery from e-waste: an improved strategy through spent medium leaching with pH modification. Chemosphere 2015;136:232–8. https://doi.org/10.1016/j.chemosphere.2015.05.046.

[56] Thakur P, Kumar S. Pretreatment of low-grade shredded dust e-waste to enhance silver recovery through biocyanidation by Pseudomonas balearica SAE1. 3 Biotech 2021;11:454. https://doi.org/10.1007/s13205-021-02977-4.

[57] Yaashikaa PR, Priyanka B, Senthil Kumar P, Karishma S, Jeevanantham S, Indraganti S. A review on recent advancements in recovery of valuable and toxic metals from e-waste using bioleaching approach. Chemosphere 2022;287:132230. https://doi.org/10.1016/j.chemosphere.2021.132230.

[58] Ruan J, Zhu X, Qian Y, Hu J. A new strain for recovering precious metals from waste printed circuit boards. Waste Manag 2014;34:901–7.

[59] Castric PA. Hydrogen cyanide, a secondary metabolite of Pseudomonas aeruginosa. Can J Microbiol 1975;21:613–8.

[60] Blumer C, Haas D. Mechanism, regulation, and ecological role of bacterial cyanide biosynthesis. Arch Microbiol 2000;173:170–7.

[61] Zhou Q, Ju W, Liu Y, Li J, Zhang Q. Influence of defects and dopants on the sensitivity of arsenene towards HCN. Appl Surf Sci 2020;506:144936.

[62] Lawson E, Barkhuizen M, Dew D. Gold solubilisation by the cyanide producing bacteria Chromobacterium violaceum. Process metallurgy, vol. 9. Elsevier; 1999. p. 239–46.

[63] Arshadi M, Mousavi S. Enhancement of simultaneous gold and copper extraction from computer printed circuit boards using Bacillus megaterium. Bioresour Technol 2015;175:315–24.

[64] Yuan Z, Yuan Y, Liu W, Ruan J, Li Y, Fan Y, et al. Heat evolution and energy analysis of cyanide bioproduction by a cyanogenic microorganism with the potential for bioleaching of precious metals. J Hazard Mater 2019;377:284–9.
[65] Owen A, Zdor R. Effect of cyanogenic rhizobacteria on the growth of velvetleaf (Abutilon theophrasti) and corn (Zea mays) in autoclaved soil and the influence of supplemental glycine. Soil Biol Biochem 2001;33:801–9.
[66] Kumar A, Saini HS, Kumar S. Bioleaching of gold and silver from waste printed circuit boards by Pseudomonas balearica SAE1 isolated from an e-waste recycling facility. Curr Microbiol 2018;75:194–201.
[67] Bakker AW, Schippers B. Microbial cyanide production in the rhizosphere in relation to potato yield reduction and Pseudomonas spp-mediated plant growth-stimulation. Soil Biol Biochem 1987;19:451–7.
[68] Brandl H, Faramarzi M, Stagars M. A novel type of microbial metal mobilization: cyanogenic bacteria and fungi solubilize metals as cyanide complexes. 2003. p. 13–8.
[69] Pistorius EK, Voss H. A D-amino acid oxidase from Chlorella vulgaris. Biochim Biophys Acta Enzymol 1977;481:395–406.
[70] Gewitz H-S, Pistorius EK, Voss H, Vennesland B. Cyanide formation in preparations from Chlorella vulgaris Beijerinck: effect of sonication and amygdalin addition. Planta 1976;131:145–8.
[71] Guilbault GG, Kramer DN. Ultra sensitive, specific method for cyanide using p-nitrobenzaldehyde and o-dinitrobenzene. Anal Chem 1966;38:834–6.
[72] Pistorius EK, Jetschmann K, Voss H, Vennesland B. The dark respiration of Anacystis nidulans: production of HCN from histidine and oxidation of basic amino acids. Biochim Biophys Acta Gen Subj 1979;585:630–42.
[73] Epstein J. Estimation of microquantities of cyanide. Anal Chem 1947;19:272–4.
[74] García-García JD, Sánchez-Thomas R, Moreno-Sánchez R. Bio-recovery of non-essential heavy metals by intra-and extracellular mechanisms in free-living microorganisms. Biotechnol Adv 2016;34:859–73.
[75] Wissing F. Cyanide formation from oxidation of glycine by a Pseudomonas species. J Bacteriol 1974;117:1289–94.
[76] Tran CD, Lee J-C, Pandey BD, Jeong J, Yoo K, Huynh TH. Bacterial cyanide generation in the presence of metal ions (Na+, Mg2+, Fe2+, Pb2+) and gold bioleaching from waste PCBs. J Chem Eng Jpn 2011;44:692–700.
[77] Motaghed M, Mousavi S, Rastegar S, Shojaosadati S. Platinum and rhenium extraction from a spent refinery catalyst using Bacillus megaterium as a cyanogenic bacterium: statistical modeling and process optimization. Bioresour Technol 2014;171:401–9.
[78] Li J, Qi X, Wei W, Liu Y, Xu X, Lin Q, et al. A "donor-two-acceptor" sensor for cyanide detection in aqueous solution. Sensor Actuator B Chem 2015;220:986–91.
[79] Ilyas S, Ilyas N. Microbial cyanidation of gold. Gold metallurgy and the environment. CRC Press; 2018. p. 157–83.
[80] Brysk MM, Lauinger C, Ressler C. Biosynthesis of cyanide from [2-14C15N] glycine in Chromobacterium violaceum. Biochim Biophys Acta Gen Subj 1969;184:583–8.
[81] Askeland RA, Morrison SM. Cyanide production by Pseudomonas fluorescens and Pseudomonas aeruginosa. Appl Environ Microbiol 1983;45:1802–7.
[82] Bunch AW, Knowles CJ. Production of the secondary metabolite cyanide by extracts of Chromobacterium violaceum. Microbiology 1982;128:2675–80.
[83] Anderson R, Roddam L, Bettiol S, Sanderson K, Reid D. Biosignificance of bacterial cyanogenesis in the CF lung. J Cyst Fibros 2010;9:158–64.
[84] Knowles CJ. Microorganisms and cyanide. Bacteriol Rev 1976;40:652–80.
[85] Liu R, Li J, Ge Z. Review on Chromobacterium violaceum for gold bioleaching from e-waste. Procedia Environ Sci 2016;31:947–53.
[86] Blumer C, Haas D. Iron regulation of the hcnABC genes encoding hydrogen cyanide synthase depends on the anaerobic regulator ANR rather than on the global activator GacA in Pseudomonas fluorescens CHA0. Microbiology 2000;146:2417–24.
[87] Harris RE, Bunch AW, Knowles CJ. Microbial cyanide and nitrile metabolism. Sci Prog 1987;1933:293–304.
[88] Wissing F. Cyanide production from glycine by a homogenate from a Pseudomonas species. J Bacteriol 1975;121:695–9.
[89] Castric KF, McDevitt DA, Castric PA. Influence of aeration on hydrogen cyanide biosynthesis by Pseudomonas aeruginosa. Curr Microbiol 1981;5:223–6.
[90] Tay SB, Natarajan G, Rahim MN bin A, Tan HT, Chung MCM, Ting YP, et al. Enhancing gold recovery from electronic waste via lixiviant metabolic engineering in Chromobacterium violaceum. Sci Rep 2013;3:1–7.
[91] Laville J, Blumer C, Von Schroetter C, Gaia V, Défago G, Keel C, et al. Characterization of the hcnABC gene cluster encoding hydrogen cyanide synthase and anaerobic regulation by ANR in the strictly aerobic biocontrol agent Pseudomonas fluorescens CHA0. J Bacteriol 1998;180:3187–96.
[92] Zimmermann A, Reimmann C, Galimand M, Haas D. Anaerobic growth and cyanide synthesis of Pseudomonas aeruginosa depend on anr, a regulatory gene homologous with fnr of Escherichia coli. Mol Microbiol 1991;5:1483–90.
[93] Reimmann C, Beyeler M, Latifi A, Winteler H, Foglino M, Lazdunski A, et al. The global activator GacA of Pseudomonas aeruginosa PAO positively controls the production of the autoinducer N-butyryl-homoserine lactone and the formation of the virulence factors pyocyanin, cyanide, and lipase. Mol Microbiol 1997;24:309–19.
[94] Spiro S. The FNR family of transcriptional regulators. Antonie Leeuwenhoek 1994;66:23–36.
[95] Becker S, Holighaus G, Gabrielczyk T, Unden G. O2 as the regulatory signal for FNR-dependent gene regulation in Escherichia coli. J Bacteriol 1996;178:4515–21.
[96] Rhodius VA, Busby SJ. Positive activation of gene expression. Curr Opin Microbiol 1998;1:152–9.
[97] Sawers R. Identification and molecular characterization of a transcriptional regulator from Pseudomonas aeruginosa PAO1 exhibiting structural and functional similarity to the FNR protein of Escherichia coli. Mol Microbiol 1991;5:1469–81.
[98] Blumer C, Heeb S, Pessi G, Haas D. Global GacA-steered control of cyanide and exoprotease production in Pseudomonas fluorescens involves specific ribosome binding sites. Proc Natl Acad Sci USA 1999;96:14073–8.
[99] Rodgers PB, Knowles CJ. Cyanide production and degradation during growth of Chromobacterium violaceum. Microbiology 1978;108:261–7.
[100] Voisard C, Keel C, Haas D, Dèfago G. Cyanide production by Pseudomonas fluorescens helps suppress black root rot of tobacco under gnotobiotic conditions. EMBO J 1989;8:351–8.
[101] Winson MK, Camara M, Latifi A, Foglino M, Chhabra SR, Daykin M, et al. Multiple N-acyl-L-homoserine lactone signal molecules regulate production of virulence determinants and secondary metabolites in Pseudomonas aeruginosa. Proc Natl Acad Sci USA 1995;92:9427–31.
[102] Kuyucak N, Akcil A. Cyanide and removal options from effluents in gold mining and metallurgical processes. Miner Eng 2013;50:13–29.
[103] Arshadi M, Mousavi S, Rasoulnia P. Enhancement of simultaneous gold and copper recovery from discarded mobile phone PCBs using Bacillus megaterium: RSM based optimization of effective factors and evaluation of their interactions. Waste Manag 2016;57:158–67.
[104] Arab B, Hassanpour F, Arshadi M, Yaghmaei S, Hamedi J. Optimized bioleaching of copper by indigenous cyanogenic bacteria isolated from the landfill of e-waste. J Environ Manag 2020;261:110124.
[105] Faramarzi MA, Stagars M, Pensini E, Krebs W, Brandl H. Metal solubilization from metal-containing solid materials by cyanogenic Chromobacterium violaceum. J Biotechnol 2004;113:321–6.
[106] Kyle JH, Hefter G. A critical review of the thermodynamics of hydrogen cyanide and copper (I)–cyanide complexes in aqueous solution. Hydrometallurgy 2015;154:78–87.
[107] Estay H, Becker J, Carvajal P, Arriagada F. Predicting HCN gas generation in the SART process. Hydrometallurgy 2012;113:131–42.
[108] Martínková L, Bojarová P, Sedova A, Křen V. Recent trends in the treatment of cyanide-containing effluents: comparison of different approaches. Crit Rev Environ Sci Technol 2023;53:416–34.
[109] Kumar A, Guleria S, Mehta P, Walia A, Chauhan A, Shirkot CK. Plant growth-promoting traits of phosphate solubilizing bacteria isolated from Hippophae rhamnoides L.(Sea-buckthorn) growing in cold desert Trans-Himalayan Lahul and Spiti regions of India. Acta Physiol Plant 2015;37:1–12.
[110] Nagashima S, Ozawa T. Spectrophotometric determination of cyanide with isonicotinic acid and barbituric acid. Int J Environ Anal Chem 1981;10:99–106.
[111] Anning C, Wang J, Chen P, Batmunkh I, Lyu X. Determination and detoxification of cyanide in gold mine tailings: a review. Waste Manag Res 2019;37:1117–26.
[112] Rocklin RD, Johnson EL. Determination of cyanide, sulfide, iodide, and bromide by ion chromatography with electrochemical detection. Anal Chem 1983;55:4–7.
[113] Dangton J, Leepowpanth Q. A study of gold recovery from E-waste by bioleaching using Chromobacterium violaceum, vol. 548. Trans Tech Publ; 2014. p. 280–3.
[114] Shin D, Jeong J, Lee S, Pandey B, Lee J. Evaluation of bioleaching factors on gold recovery from ore by cyanide-producing bacteria. Miner Eng 2013;48:20–4.
[115] Kita Y, Nishikawa H, Takemoto T. Effects of cyanide and dissolved oxygen concentration on biological Au recovery. J Biotechnol 2006;124:545–51.
[116] Kita Y, Nishikawa H, Ike M, Takemoto T. Enhancement of Au dissolution by microorganisms using an accelerating cathode reaction. Metall Mater Trans B 2009;40:39–44.
[117] Campbell SC, Olson G, Clark T, McFeters G. Biogenic production of cyanide and its application to gold recovery. J Ind Microbiol Biotechnol 2001;26:134–9.
[118] Das S, Ting Y. Improving gold (bio) leaching efficiency through pretreatment using hydrogen peroxide assisted sulfuric acid. Clean: Soil, Air, Water 2017;45:1500945.
[119] Blier A-S, Vieillard J, Gerault E, Dagorn A, Varacavoudin T, Le Derf F, et al. Quantification of Pseudomonas aeruginosa hydrogen cyanide production by a polarographic approach. J Microbiol Methods 2012;90:20–4.
[120] Christison TT, Rohrer JS. Direct determination of free cyanide in drinking water by ion chromatography with pulsed amperometric detection. J Chromatogr A 2007;1155:31–9.
[121] Wissing F. Growth curves and pH-optima for cyanide producing bacteria. Physiol Plantarum 1968;21:589–93.
[122] Kaksonen AH, Mudunuru BM, Hackl R. The role of microorganisms in gold processing and recovery—a review. Hydrometallurgy 2014;142:70–83.
[123] Liang CJ, Li JY, Ma CJ. Review on cyanogenic bacteria for gold recovery from E-waste, vol. 878. Trans Tech Publ; 2014. p. 355–67.
[124] Hu J, Tang Y, Ai F, Lin M, Ruan J. Biofilm for leaching precious metals from waste printed circuit boards using biocyanidation technology. J Hazard Mater 2021;403:123586.
[125] Michaels R, Corpe W. Cyanide formation by Chromobacterium violaceum. J Bacteriol 1965;89:106–12.
[126] Knowles CJ, Bunch AW. Microbial cyanide metabolism. Adv Microb Physiol 1986;27:73–111.
[127] Zoidakis J, Loaiza A, Vu K, Abu-Omar MM. Effect of temperature, pH, and metals on the stability and activity of phenylalanine hydroxylase from Chromobacterium violaceum. J Inorg Biochem 2005;99:771–5.
[128] Castric PA, Ebert RF, Castric KF. The relationship between growth phase and cyanogenesis in Pseudomonas aeruginosa. Curr Microbiol 1979;2:287–92.

[129] Faraji F, Mahandra H, Ghahreman A. Evaluation of different amino acids on growth and cyanide production by Bacillus megaterium for gold recovery. Sustainability 2022;14:9639.
[130] Shirazi-Beechey SP, Knowles CJ. Serine hydroxymethyltransferase and glycine cleavage enzyme from the cyanogenic bacterium Chromobacterium violaceum. Microbiology 1984;130:521–5.
[131] Castric PA. Glycine metabolism by Pseudomonas aeruginosa: hydrogen cyanide biosynthesis. J Bacteriol 1977;130:826–31.
[132] Faraji F. Bio-cyanidation of low-grade and refractory gold ores. 2022.
[133] Faramarzi MA, Brandl H. Formation of water-soluble metal cyanide complexes from solid minerals by Pseudomonas plecoglossicida. FEMS (Fed Eur Microbiol Soc) Microbiol Lett 2006;259:47–52.
[134] Brandl H, Faramarzi MA. Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste. China Particuol 2006;4:93–7.
[135] Chadwick BM, Sharpe AG. Transition metal cyanides and their complexes. In: Emeléus HJ, Sharpe AG, editors. Advances in inorganic chemistry and radiochemistry, vol. 8. Academic Press; 1966. p. 83–176. https://doi.org/10.1016/S0065-2792(08)60201-0.
[136] Ilyas S, Kim H. Recovery of platinum-group metals from an unconventional source of catalytic converter using pressure cyanide leaching and ionic liquid extraction. JOM 2022;74:1020–6.
[137] Mai S, Zhou G, Li W. Advanced inorganic structural chemistry. Beijing: Beijing University; 2001. p. 340–3.
[138] Karim S, Ting Y-P. Recycling pathways for platinum group metals from spent automotive catalyst: a review on conventional approaches and bio-processes. Resour Conserv Recycl 2021;170:105588.
[139] Pham V, Ting YP. Gold bioleaching of electronic waste by cyanogenic bacteria and its enhancement with bio-oxidation, vol. 71. Trans Tech Publ; 2009. p. 661–4.
[140] Li J, Wen J, Guo Y, An N, Liang C, Ge Z. Bioleaching of gold from waste printed circuit boards by alkali-tolerant Pseudomonas fluorescens. Hydrometallurgy 2020;194:105260.
[141] Salehi. Biomobilization of gold from mouteh gold ore by HCN-forming microorganisms: Pseudomonas fluorescens Migula ATCC 17386. Tehran, Iran: 15th International Congress of Microbiology; 2014.
[142] Gupta CK, Mukherjee T. Hydrometallurgy in extraction processes. CRC press; 2017.
[143] Schouwstra R, Kinloch E, Lee C. A short geological review of the Bushveld Complex. Platin Met Rev 2000;44:33–9.
[144] Upadhyay AK, Lee J, Kim E, Kim M, Kim B, Kumar V. Leaching of platinum group metals (PGMs) from spent automotive catalyst using electro-generated chlorine in HCl solution. J Chem Tech Biotechnol 2013;88:1991–9.
[145] Wei X, Liu C, Cao H, Ning P, Jin W, Yang Z, et al. Understanding the features of PGMs in spent ternary automobile catalysts for development of cleaner recovery technology. J Clean Prod 2019;239:118031.
[146] Nunan TO, Viana IL, Peixoto GC, Ernesto H, Verster DM, Pereira JH, et al. Improvements in gold ore cyanidation by pre-oxidation with hydrogen peroxide. Miner Eng 2017;108:67–70.
[147] Chen S, Shen S, Cheng Y, Wang H, Lv B, Wang F. Effect of O2, H2 and CO pretreatments on leaching Rh from spent auto-catalysts with acidic sodium chlorate solution. Hydrometallurgy 2014;144:69–76.
[148] Trinh HB, Lee J, Srivastava RR, Kim S, Ilyas S. Eco-threat minimization in HCl leaching of PGMs from spent automobile catalysts by formic acid prereduction. ACS Sust Chem Eng 2017;5:7302–9.
[149] Sasaki H, Maeda M. Zn-vapor pretreatment for acid leaching of platinum group metals from automotive catalytic converters. Hydrometallurgy 2014;147:59–67.
[150] Kayanuma Y, Okabe TH, Mitsuda Y, Maeda M. New recovery process for rhodium using metal vapor. J Alloys Compd 2004;365:211–20.
[151] Okabe TH, Yamamoto S, Kayanuma Y, Maedaaff M. Recovery of platinum using magnesium vapor. J Mater Res 2003;18:1960–7.
[152] Sasaki H, Maeda M. Enhanced dissolution of Rh from RhZn 3 formed through Zn vapor pretreatment. Metall Mater Trans B 2012;43:443–8.
[153] Sasaki H, Maeda M. Enhanced dissolution of Pt from Pt–Zn intermetallic compounds and underpotential dissolution from Zn-rich alloys. J Phys Chem C 2013;117:18457–63.
[154] Tingle W, Petit J, Frank W. Handbook of extractive metallurgy. 1997.
[155] Kasuya R, Miki T, Morikawa H, Tai Y. Synthesis of sodium platinates and their dissolution behaviors in hydrochloric acid: effects of lithium carbonate addition on platinate formation. Int J Miner Process 2014;128:33–9.
[156] Rawlings DE. Biomining (mineral bioleaching, mineral biooxidation). Encyclopedia of geobiology; 2011.
[157] Mxinwa S, Huberts R, Belaid M. Process parameters for bio-oxidation of sulphur in the pre-treatment of bioleaching residues destined for cyanide gold extraction, vol. 3; 2012. p. 1–5.
[158] Opare EO, Struhs E, Mirkouei A. A comparative state-of-technology review and future directions for rare earth element separation. Renew Sustain Energy Rev 2021;143:110917. https://doi.org/10.1016/j.rser.2021.110917.
[159] Mishra D, Kim D-J, Ahn J-G, Rhee Y-H. Bioleaching: a microbial process of metal recovery; a review. Met Mater Int 2005;11:249–56.
[160] Okibe N, Johnson DB. Biooxidation of pyrite by defined mixed cultures of moderately thermophilic acidophiles in pH-controlled bioreactors: significance of microbial interactions. Biotechnol Bioeng 2004;87:574–83.
[161] Xie X, Yuan X, Liu N, Chen X, Abdelgadir A, Liu J. Bioleaching of arsenic-rich gold concentrates by bacterial flora before and after mutation. BioMed Res Int 2013; 2013.
[162] Sutar AS, Awasare S. Bioleaching of ore using chemolithotrophic microorganisms (Acidithiobacillus ferrooxidans). Int J Res Environ Sci Technol 2015;5:14–21.
[163] Yen W-T, Amankwah RK, Choi Y. Microbial pre-treatment of double refractory gold ores. 2009.
[164] Ofori-Sarpong G, Osseo-Asare K, Tien M. Fungal pretreatment of sulfides in refractory gold ores. Miner Eng 2011;24:499–504.
[165] Mwase JM, Petersen J, Eksteen JJ. A novel sequential heap leach process for treating crushed Platreef ore. Hydrometallurgy 2014;141:97–104.
[166] Hedrich S, Kraemer D, Junge M, Marbler H, Bau M, Schippers A. Bioprocessing of oxidized platinum group element (PGE) ores as pre-treatment for efficient chemical extraction of PGE. Hydrometallurgy 2020;196:105419.
[167] Castro L, Blázquez ML, González F, Já Muñoz. Biohydrometallurgy for rare earth elements recovery from industrial wastes. Molecules 2021;26:6200.
[168] Reed DW, Fujita Y, Daubaras DL, Jiao Y, Thompson VS. Bioleaching of rare earth elements from waste phosphors and cracking catalysts. Hydrometallurgy 2016; 166:34–40.
[169] Zhuang W-Q, Fitts JP, Ajo-Franklin CM, Maes S, Alvarez-Cohen L, Hennebel T. Recovery of critical metals using biometallurgy. Curr Opin Biotechnol 2015;33: 327–35.
[170] Borra CR, Pontikes Y, Binnemans K, Van Gerven T. Leaching of rare earths from bauxite residue (red mud). Miner Eng 2015;76:20–7.
[171] Ruan J, Xu Z. Constructing environment-friendly return road of metals from e-waste: combination of physical separation technologies. Renew Sustain Energy Rev 2016;54:745–60. https://doi.org/10.1016/j.rser.2015.10.114.
[172] Raybuck SA. Microbes and microbial enzymes for cyanide degradation. Biodegradation 1992;3:3–18.
[173] Ebbs S. Biological degradation of cyanide compounds. Curr Opin Biotechnol 2004;15:231–6.
[174] Akcil A, Karahan A, Ciftci H, Sagdic O. Biological treatment of cyanide by natural isolated bacteria (Pseudomonas sp.). Miner Eng 2003;16:643–9.
[175] Sharma M, Akhter Y, Chatterjee S. A review on remediation of cyanide containing industrial wastes using biological systems with special reference to enzymatic degradation. World J Microbiol Biotechnol 2019;35:70.
[176] Alvillo-Rivera A, Garrido-Hoyos S, Buitrón G, Thangarasu-Sarasvathi P, Rosano-Ortega G. Biological treatment for the degradation of cyanide: a review. J Mater Res Technol 2021;12:1418–33.
[177] Gupta N, Balomajumder C, Agarwal V. Enzymatic mechanism and biochemistry for cyanide degradation: a review. J Hazard Mater 2010;176:1–13.
[178] Huertas M, Sáez L, Roldán M, Luque-Almagro V, Martínez-Luque M, Blasco R, et al. Alkaline cyanide degradation by Pseudomonas pseudoalcaligenes CECT5344 in a batch reactor. Influence of pH. J Hazard Mater 2010;179:72–8.
[179] Kunz DA, Nagappan O, Silva-Avalos J, Delong G. Utilization of cyanide as nitrogenous substrate by Pseudomonas fluorescens NCIMB 11764: evidence for multiple pathways of metabolic conversion. Appl Environ Microbiol 1992;58: 2022–9.
[180] Fry W, Millar R. Cyanide degradion by an enzyme from Stemphylium loti. Arch Biochem Biophys 1972;151:468–74.
[181] Barclay M, Day J, Thompson I, Knowles C, Bailey M. Substrate-regulated cyanide hydratase (chy) gene expression in Fusarium solani: the potential of a transcription-based assay for monitoring the biotransformation of cyanide complexes. Environ Microbiol 2002;4:183–9.
[182] Nazly N, Knowles CJ, Beardsmore AJ, Naylor WT, Corcoran EG. Detoxification of cyanide by immobilised fungi. J Chem Technol Biotechnol Biotechnol 1983;33: 119–26.
[183] Mudder TI, Whitlock J. Biological treatment of cyanidation waste waters. Miner Metall Process 1984;1:161–5.
[184] Richardson KR, Clarke PM. Production of cyanide hydratase. 1993.
[185] Srivastava RR, Ilyas S, Kim H, Choi S, Trinh HB, Ghauri MA, et al. Biotechnological recycling of critical metals from waste printed circuit boards. J Chem Tech Biotechnol 2020;95:2796–810.
[186] Baylis NA, Desai PN, Kuhns KJ. Sodium and specialty cyanides production facility. 2018.
[187] Thompson VS, Gupta M, Jin H, Vahidi E, Yim M, Jindra MA, et al. Techno-economic and life cycle analysis for bioleaching rare-earth elements from waste materials. ACS Sustainable Chem Eng 2018;6:1602–9.
[188] Priya A, Hait S. Comparative assessment of metallurgical recovery of metals from electronic waste with special emphasis on bioleaching. Environ Sci Pollut Control Ser 2017;24:6989–7008. https://doi.org/10.1007/s11356-016-8313-6.
[189] Rocklin RD, Johnson EL. Determination of cyanide, sulfide, iodide, and bromide by ion chromatography with electrochemical detection. Anal Chem 1983;55:4–7.
[190] Pohlandt C Jones EA, Lee AF. A critical evaluation of methods applicable to the determination of cyanides. J S Afr Inst Min Metall 1983;83:11–9.
[191] Logsdon MJ, Hagelstein K, Mudder T. The management of cyanide in gold extraction. Citeseer; 1999.
[192] Chauhan G, Jadhao PR, Pant KK, Nigam KDP. Novel technologies and conventional processes for recovery of metals from waste electrical and electronic equipment: challenges & opportunities – a review. J Environ Chem Eng 2018;6: 1288–304. https://doi.org/10.1016/j.jece.2018.01.032.
[193] Pathak A, Al-Sheeha H, Navvamani R, Kothari R, Marafi M, Rana MS. Recycling of platinum group metals from exhausted petroleum and automobile catalysts using bioleaching approach: a critical review on potential, challenges, and outlook. Rev Environ Sci Biotechnol 2022;21:1035–59. https://doi.org/10.1007/s11157-022-09636-x.