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REVIEW PAPER

Recycling of platinum group metals from exhausted petroleum and automobile catalysts using bioleaching approach: a critical review on potential, challenges, and outlook

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Abstract Platinum group metals (PGMs) are essential in developing the modern high-tech industry. Spent petroleum and spent automobile catalysts are vital sources of PGMs, which have relatively higher concentrations of PGMs (0.1–1%) than those found in primary sources. Therefore, recycling these secondary PGMs sources is an integral element of the PGM supply policy of many countries. In recent years, 'bioleaching' has emerged as a sustainable technique to extract PGMs from the spent catalysts. Bioleaching processes are based on the capability of different microorganisms to mobilize PGMs through the production of different lixiviants (cyanide, organic acids, etc.). In this review article, we aimed to explore the potential of different microorganisms (cyanogenic bacteria and fungi) in leaching PGMs (Pt, Pd, Rh, and Re) from spent petroleum refinery catalysts and spent automobile catalysts. We also shed light on the role and mechanisms of these microorganisms in extracting PGMs from these spent catalysts. A detailed discussion is also being made on the effect of various process parameters concerning cyanogenic bioleaching. We also identified different technical and environmental challenges associated with bioleaching processes that need to be addressed before their scale-up at the commercial level. Our analysis suggests that cyanogenic bioleaching (biocyanidation) has exciting potential; however, specific challenges (slower kinetics and yield, toxicity) need to be addressed to scale the process from existing lab-scale to commercial application.

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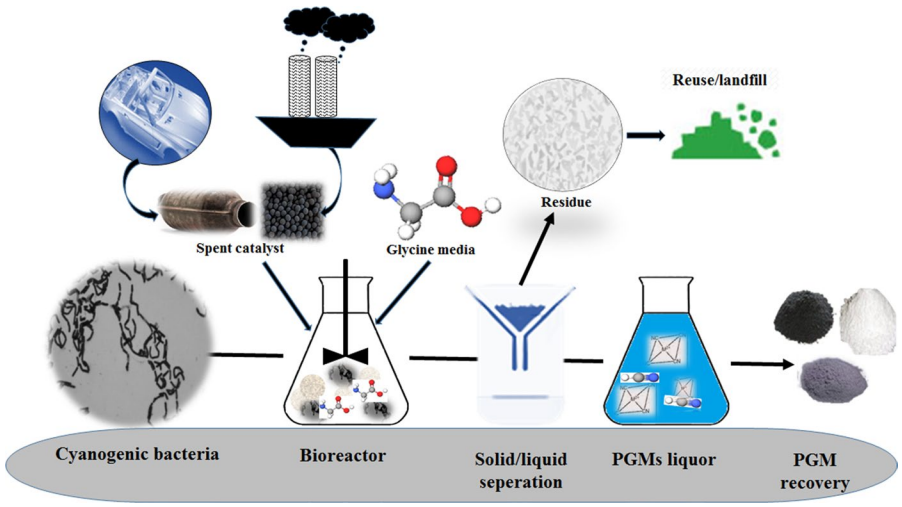
Graphical abstract



Keywords Biocyanidation · Bioleaching · Cyanide · Platinum group metals · Recycling

1 Introduction

Platinum group metals (PGMs) are six precious elements, namely platinum (Pt), palladium (Pd), iridium (Ir), osmium (Os), rhodium (Rh), and ruthenium (Ru). PGMs are a highly sought commodity in modern industries (Zheng et al. 2021) and, therefore, are also called 'First and foremost high-technology metal' (Dong et al. 2015). Among different PGMs, Pt, Pd, and Rh are the major PGMs consumed by industries (Fig. 1A). In catalysis, PGMs are used as the active components of a catalyst. The main PGMs-containing catalysts are employed in automobile emission control and the petroleum refining industry (Johnson Matthey 2021). The demand for cleaner fuel and stricter emission standards (Fig. 1B) force refineries and automobile makers to improve process efficiencies (Crown oil 2022). PGMs are unique in catalytic activities and thus play a vital role in improving the efficiency of refining processes and automobile emission control (Hughes et al. 2021). These two industries consumed about 41.7%, 84.7%, and 90.8% of the total Pt, Pd, and Rh, respectively, in 2021 (Fig. 2) (Johnson Matthey 2021). However, the PGMs containing catalysts employed in these industries deactivate with time and loss their activity. These deactivated catalysts, therefore, are discarded as spent catalysts. Nevertheless, due to the high content of PGMs, these spent catalysts are an excellent secondary source of PGMs. The typical concentration of PGMs in these spent catalysts is many times higher than their primary sources. For example, the PGMs content in the spent catalysts ranged from 0.01 to 1.3% w/w (Table 1), which is about 200–800 times more than the average grade (0.0005–0.0015%) of PGM ore deposits (Zientek et al. 2017). Thus, it can be safely assumed that recycling PGMs from spent catalysts is relatively more economical than primary mining.

Besides PGMs, these spent catalysts also contain various hazardous materials (e.g. metals, flame retardants, and organic substances) (Dong et al. 2015; Liu et al. 2021a, b). Due to uncontrolled disposal, these hazardous substances can cause potential air and groundwater pollution (Bahaloo-Horeh and Mousavi 2020). Therefore, PGMs containing spent catalysts must be appropriately recycled for their PGMs and to protect the environment. Ironically, the overall recycling rates (< 35%) of major PGMs (Pt, Pd, and Rh) from different secondary sources are still

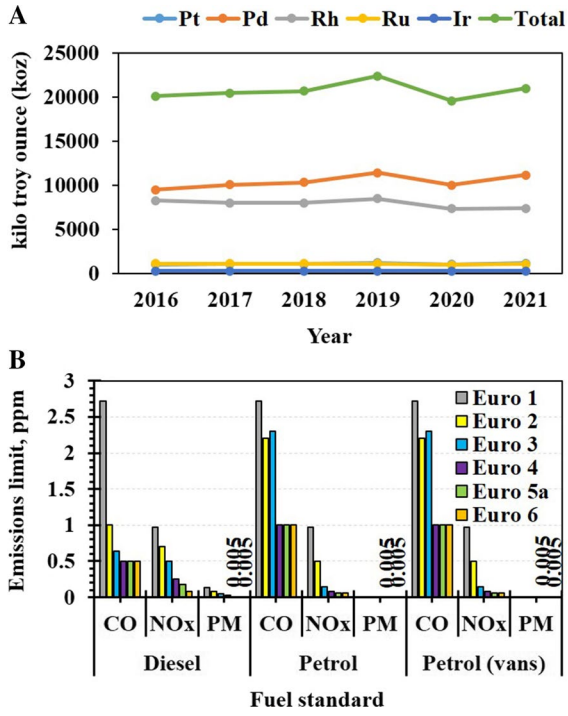


Fig. 1 **A** PGMs demand trend **B** Euro Fuel emission standards

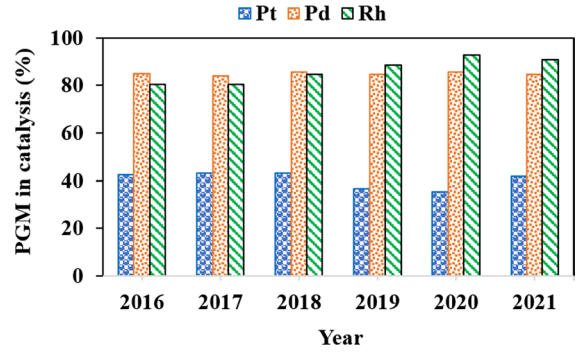


Fig. 2 Percentage PGMs consumption in refinery and auto-exhaust catalysts

low (Fig. 3A) (Johnson Matthey 2021). In contrast, the mining of PGMs from secondary sources results in lesser pollution. It was reported that the Pt production from spent automotive catalyst requires only 1/20th of the energy and global warming potential (Saidani et al. 2019) as compared to the primary production of Pt. Thus, due to the associated economic, and environmental benefits, efforts have been directed toward developing eco-friendly processes to recover PGMs from spent refinery and automotive catalysts (Yakoumis et al. 2021).

The conventional processes for PGMs recycling from these spent catalysts are mainly based on hydrometallurgy and pyrometallurgy (Yakoumis et al. 2021). However, these processes suffer from the requirement of high concentrations of the leaching agents, secondary pollution, high-energy cost, and emission of hazardous gases. An alternative to

Table 1 Chemical composition of PGMs spent catalysts

Si. No.	Catalyst type	Pt (%)	Pd (%)	Rh (%)	Re (%)	Total PGMs (%)	Major element (%)		References
							Al (as Al_2O_3)	Si (as SiO_2)	
1	Spent automobile	0.076	0.0368	0.0171	–	0.129	–	–	Ilyas et al. (2022)
2		0.201	0.453	0.637	–	0.718	27.140	–	Karim and Ting (2020)
3		0.090	0.16	0.012	–	0.262	40.000	34.000	Trinh et al. (2020)
4		0.220	0.540	–	–	0.760	47.800	28.200	Ilyas et al. (2020)
4		0.052	0.122	0.018	–	0.192	36.118	31.404	Wei et al. (2019)
6		0.087	0.367	0.033	–	0.487	3.695	–	Das et al. (2017)
7		0.068	1.150	0.702	–	1.288	53.459	0.400	Sucha et al. (2016)
8		0.069	0.045	0.016	–	0.130	37.800	34.570	Shin et al. (2015)
9	Spent refinery	0.307	–	–	–	0.307	92.150	0.120	Malekian et al. (2019)
10		0.212	–	–	–	0.212	89.970	0.970	Ding et al. (2019)
11		0.200	–	–	0.200	0.400	90.800	2.000	Asadzadeh and Sajadi et al. (2018)
12		0.230	–	–	–	0.230	88.594	–	Rui et al. (2015)
13		0.220	–	–	0.440	0.660	24.935	–	Motaghed et al. (2014)
15		0.200	–	–	0.430	0.630	95.500	1.300	Jafarifar et al. (2005)

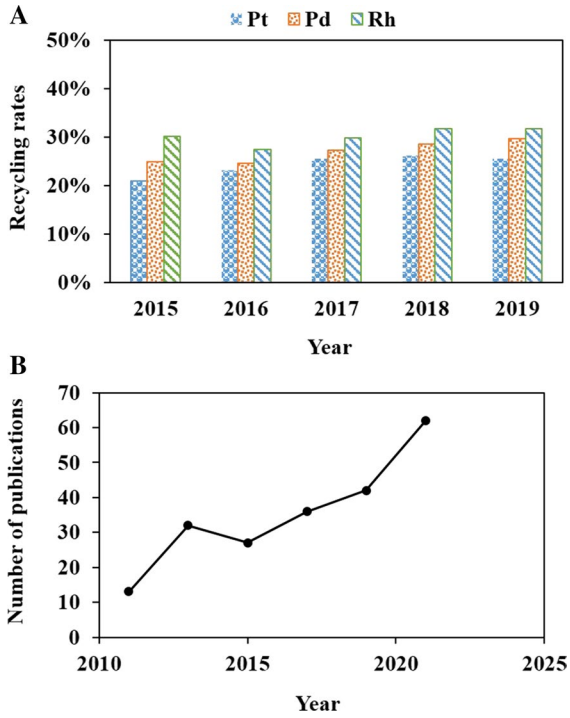


Fig. 3 **A** Recycling rates of Pt, Pd, and Rh from secondary sources **B** Number of articles published on Elsevier in the last decade (keyword "bioleaching of platinum group metals from spent catalyst")

conventional processes is the benign biometallurgical (bioleaching) process that extracts PGMs effectively, and it is eco-friendly (Karim and Ting 2021). Bioleaching processes do not use concentrated and corrosive chemicals, operate under ambient conditions, and don't emit harmful gases (Malekian et al. 2019; Karim and Ting 2020). Due to these characteristics, bioleaching has the potential to emerge as a viable alternative technique. Bioleaching processes employed for PGMs leaching from spent catalysts are based on the capability of different microorganisms (Rzelewska and Magdalena 2018). These processes are chiefly based on heterotrophic bioleaching, in which microorganisms (cyanogenic bacteria/fungi) utilize organic precursors to produce different lixiviants (cyanide, organic acids, etc.) in the leaching media (Malekian et al. 2019; Karim and Ting 2020). These lixiviate interact with PGMs and form soluble PGMs complexes (Rzelewska and Regel-Rosocka 2018; Padamata et al. 2020). However, despite their effectiveness and associated environmental benefits, they have not yet been commercialized and are limited mainly to lab-scale (Yakoumis et al. 2021). However, it is worth noting that bioleaching processes are eco-friendly and flexible. Moreover, the ever-increasing environmental regulations are likely to force recyclers to develop eco-friendly recycling technologies for PGMs (Directive 2000).

Previous reviews on PGMs recovery from petroleum and spent automobile catalysts have primarily discussed the hydrometallurgical and pyrometallurgical processes (Panda et al. 2018; Trinh et al. 2020; Yakoumis et al. 2021; Karim and Ting 2021). A detailed overview of different biological agents, their mode of action, reaction mechanisms, and leaching potential for spent petroleum refinery and automobile catalysts was mostly missing in the literature. Whereas, there has been a steady increase in the reported work in this research area over the past decade (Fig. 3B). Moreover, the research work is published in journals of varied research areas showing the multidisciplinary nature of the subject (Suppl. Figure 1). Keeping this in view, in this review article, we aimed at exploring the potential of different microorganisms to bioleach PGMs (Pt, Pd, Rh, and Re) from petroleum refinery-spent catalysts and spent automobile catalysts. A detailed discussion has also been made on various parameters affecting process efficiency. We also identified different techno-economic and environmental challenges associated with the bioleaching process that needs to be addressed before their scale-up at the commercial level.

2 Composition, deactivation, and environmental implications

Different PGMs catalysts are used in the petroleum refining and automobile industry (Dong et al. 2015). The fresh catalysts employed in these sectors pose different compositions (Fig. 4) regarding their support material, PGMs types, and PGMs concentrations (Dong et al. 2015). These catalysts get deactivated over time and thus discarded as spent catalysts (Birgersson 2006; Malekian et al. 2019). A primary discussion about these spent catalysts has been provided in the following section.

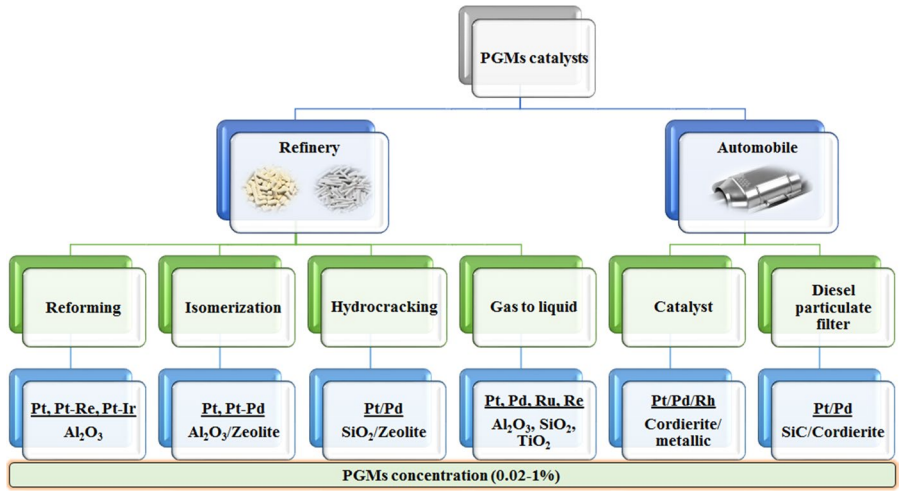


Fig. 4 Type of PGMs catalyst used in automobile and petroleum refining industry

2.1 Structure, composition, and deactivation of an automobile catalyst

The automobile exhaust catalysts are built from a ceramic or a metallic carrier (Fornalczyk et al. 2016). The carrier has a monolith honeycomb structure, usually with 1 mm × 1 mm large square cross-sections or channels (Rao and Sharma 2020). The honeycomb structure is coated with a highly porous washcoat (y-Al_2O_3), and various additives (CeO_2, NiO, BaO, CaO, and La_2O_3) for effective dispersion of PGMs (Serry et al. 2011). The market is dominated by the ceramic carrier (> 95% market share) as it is relatively cheaper to build and has reasonable efficiency (Kucharski 2010). The ceramic carrier is cordierite skeleton ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$), which is composed of magnesium oxide (3%–35% MgO), aluminum oxide (32%–35% Al_2O_3), silicon oxide (45%–51% SiO_2), and iron oxide (2%–12% Fe_2O_3) (Rzelewska and Regel-Rosocka 2018). The structures of different automobile catalyst carriers have been provided in the literature (Saternus et al. 2014).

During the lifetime of an automobile catalyst, it is exposed to extreme thermal and chemical conditions (fluctuations in temperature, gas velocity, and composition), which lead to its deactivation (Birgersson 2006). Among several mechanisms, chemical deactivation (poisoning and fouling), and thermal deactivation are the dominant mechanisms that can cause permanent deactivation (Birgersson 2006; Fernandes et al. 2009). The expected life of the automobile catalyst is 120,000–150,000 km, after which it requires replacement (Omrani et al. 2020). Thus, huge spent automobile catalysts are continuously generated and require treatment before disposal. However, these spent catalysts had significant quantities of PGM, making them a suitable candidate for recycling. For instance, spent light-duty vehicles (LDV) catalysts contain about 1000–3000 mg PGMs, while a spent heavy-duty vehicles (HDV) catalyst contains about 5–12 times (12,000–15,000 mg) higher PGMs (Yakoumis et al. 2021). A detailed description of the composition and morphology of the spent automobile catalyst is provided in Table 1, Figs. 5A, B, and 6A, respectively. Besides, PGMs, the spent automobile catalyst, also contain other metals. These metals are present in different fractions (Fig. 6B), affecting their environmental mobility and bioavailability.

2.2 Structure, composition, and deactivation of PGM containing refinery catalysts

Different refinery processes employ PGMs catalysts (Table 1; Fig. 4), among which catalytic reforming, isomerization, and catalytic cracking are the main processes that utilize a high portion of PGMs catalysts (Singerling 2017; Hasanova et al. 2019; Smith et al. 2022). The PGM loading in these fresh catalyst can be 0.02–1.0%. However, during the process, the activity of refinery catalysts decreases with time on stream due to the coke deposition, sulfur, and metals deposition on the active sites and pores of the catalyst (Tye 2019; Zhou et al. 2020; Vivas-Báez et al. 2021). The dominant deactivation mechanism can differ

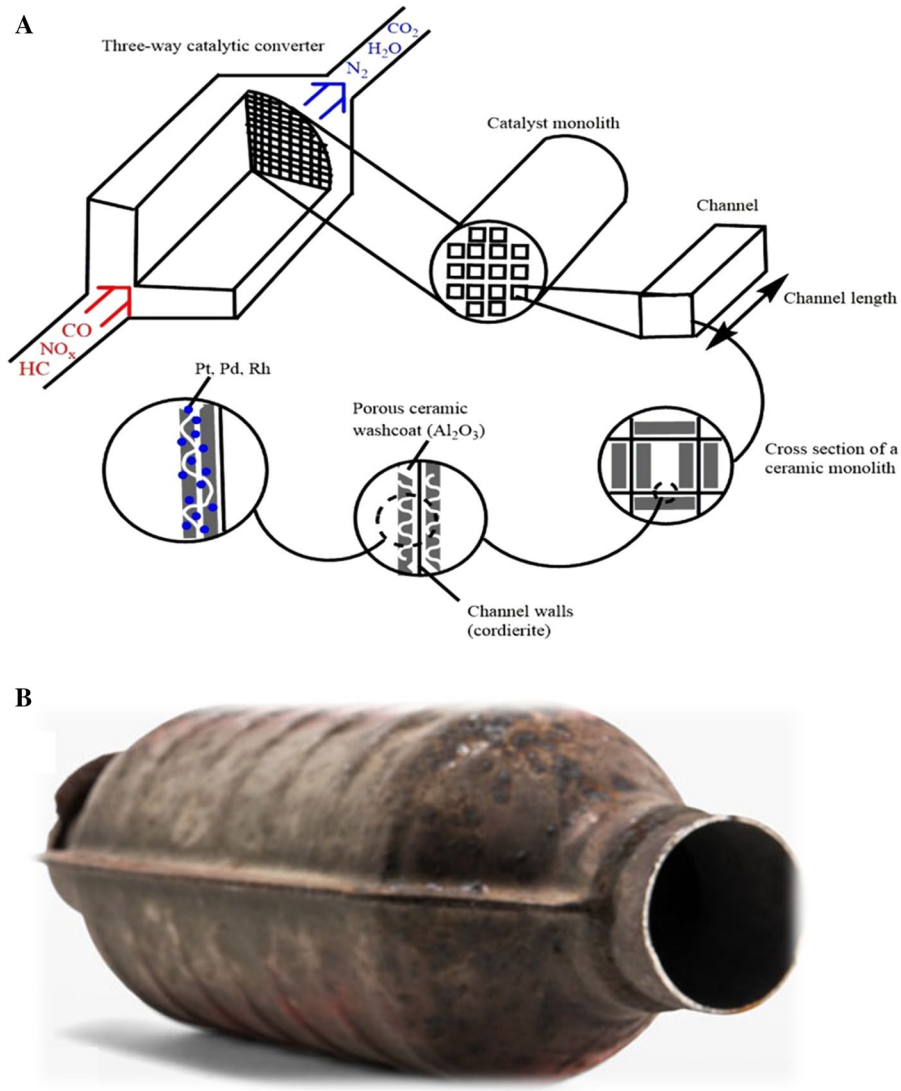


Fig. 5 **A** A three-way automobile catalytic converter (adapted from Karim and Ting 2021); **B** Spent automobile catalyst (adapted from Umicore 2022)

depending on the feed type, type of process, and operating conditions. For instance, in the reforming and isomerization process, coking may be the dominant mechanism (Sukkar et al. 2007; Ivanchina et al. 2021), whereas, for hydrocracking of heavier feeds, both coking and metal deposition play an important role in the deactivation of the catalyst (Vivas-Báez et al. 2021). Depending upon the type of feed, operating conditions, and catalyst composition, the expected life of these catalysts can range from 1 to 12 years (Hageluken 2008), after which they are disposed of as spent catalysts. The morphology of the fresh and spent catalysts is shown in Fig. 7A–D.

2.3 Environmental problems with PGM containing spent catalysts

The PGMs containing spent catalysts are a serious environmental concern due to their quantities and toxic materials (Bahaloo-Horeh and Mousavi 2020; Demarco et al. 2020). As an estimate, the global annual sale of catalytic converters was around 19 million units in 2012. The sale of catalytic converters is expected to increase to approximately 140 million units by 2019 (Kumar et al. 2018). As catalytic convertor has a certain life, vast quantities of spent automobile catalysts are expected to be generated (Saternus et al. 2020). Similarly, vast amounts of

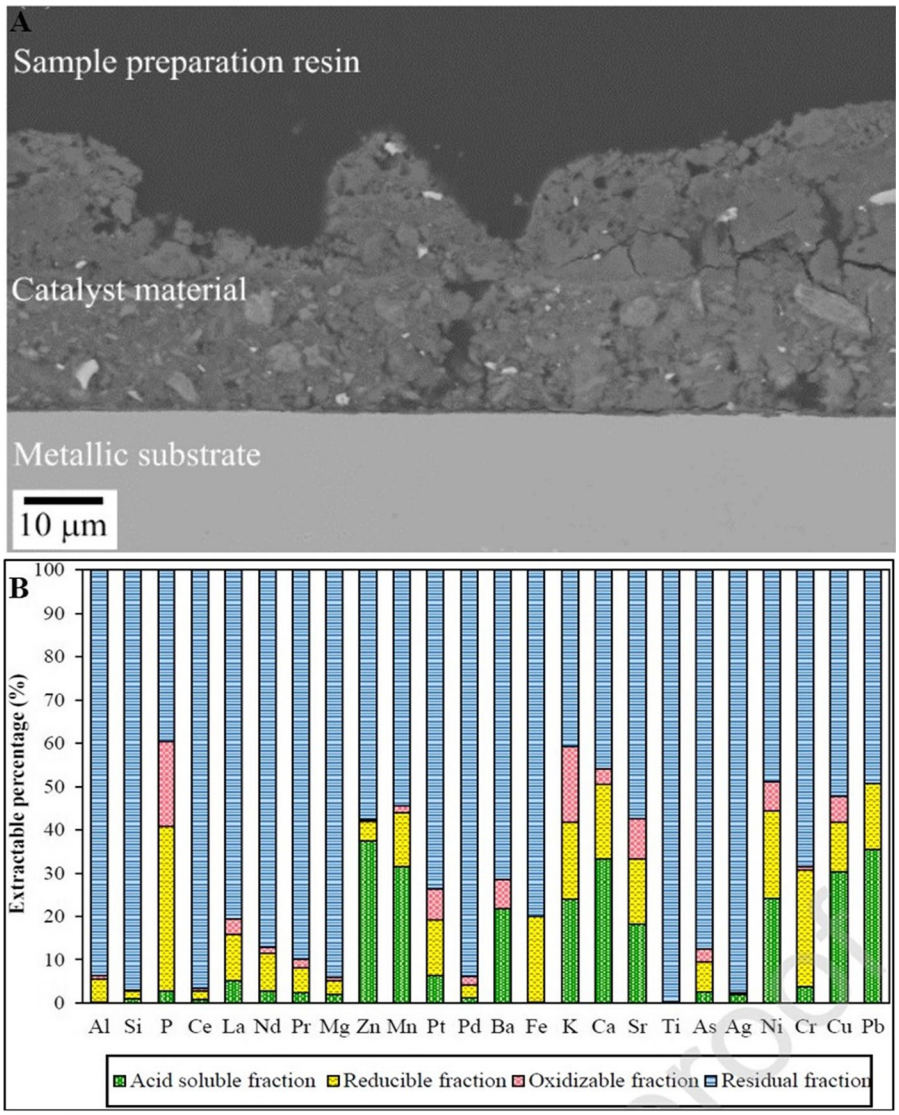


Fig. 6 **A** The cross-sectional SEM image of the spent diesel oxidation catalyst (adapted from Kanerva et al. 2019); **B** distribution profile of metals in spent automobile catalyst (adapted from Bahaloo-Horeh and Mousavi 2020)

PGMs spent catalysts are generated from the petroleum refineries. According to estimates, the fresh isomerization and reforming catalyst market in 2017 was about 40% (1.6 billion USD) of the total refinery market (4 billion USD) (Pulidindi and Prakash 2019). The refinery market demand is expected to increase by a compound annual growth rate CAGR of 3% from 2018 to 2025. The average lifetime of refinery catalysts can range from 2 to 10 years, and thus vast quantities of petroleum spent catalysts are also generated in refineries. The enormous quantities of spent catalysts can create handling and management challenges and pose hazardous environmental and health concerns (Wei et al. 2019). This is because the different PGMs and heavy metals present in these spent catalysts can pollute the environment if not disposed of properly (Bahaloo-Horeh et al. 2020). Once reached into the human, PGMs can cause respiratory sensitization, allergic reactions, dermatitis, lymphocyte proliferation, and possibly cancer (Kalavrouziotis and Koukoulakis 2009; Senthil et al. 2017). In the case of spent automobile catalysts, which contain various heavy metals (Zn, Mn, Ti, Zr, Ba, Ni, Cu, Pb, etc.), the probability of overall environmental contamination is higher (Bahaloo-Horeh and Mousavi 2020). A greenness ranking analysis on different PGMs in heterogeneous catalysts conducted by Bystrzanowska et al. (2019) also indicated that PGMs are potentially

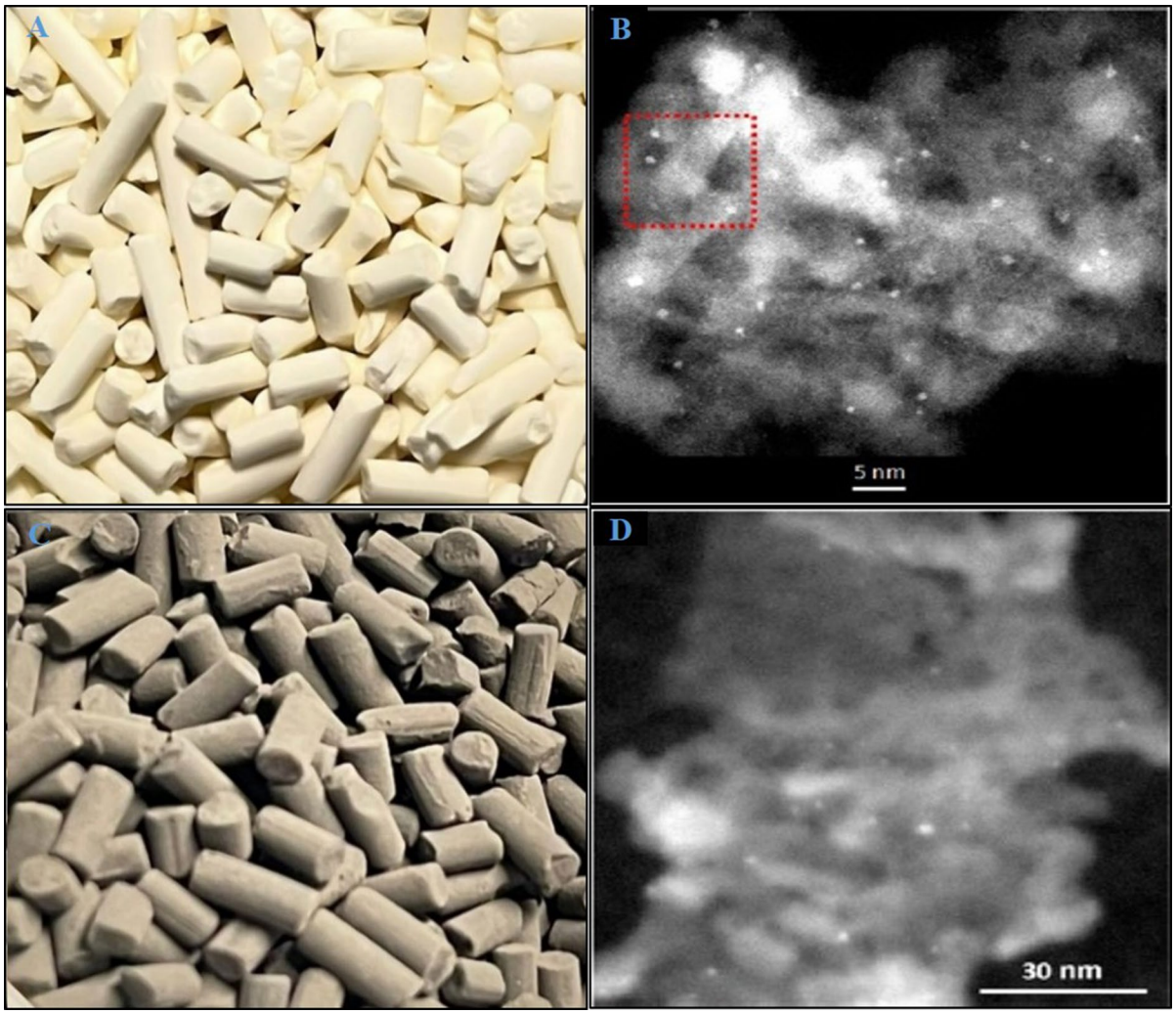


Fig. 7 **A** Fresh reforming catalyst **B** Scanning transmission electron micrograph of the fresh Pt-Re/γ-Al_2O_3 catalyst (Reprinted with permission from Sanchez et al. 2014, Copyright {2022} American Chemical Society; **C** spent reforming catalyst-extrudate shaped (D) Scanning transmission electron micrograph of the spent Pt-Re/γ-Al_2O_3 catalyst (Reprinted with permission from Sanchez et al. 2014, Copyright {2022} American Chemical Society

toxic to the environment. Their relative toxicity can be ranked as shown in Fig. 8. This analysis also revealed that Pd is the worst PGM based on the toxicity scenario ranking. In contrast, Ru is the greenest PGM according to toxicity scenario ranking. The life cycle assessment and endangered elements scenarios indicated that Ru was the best PGM, whereas Pt, Rh, or Pd are less environmentally friendly. The fractionation profiles of different metals in the spent autoexhaust catalyst (Fig. 6B) have also indicated that a significant portion of metals such as Zn, Ba, K, Ca, Sr, Ni, Cu, and Pb were present in the acid-soluble fraction (Bahaloo-Horeh et al. 2019). It is a common fact that the metals in the acid-soluble fractions exhibit the highest mobility and bioavailability. Thus, spent auto exhaust catalyst can be considered highly dangerous for the environment if not recycled/disposed of properly.

3 Bioleaching

Different processes such as hydrometallurgical, pyrometallurgical, and biometallurgical have been

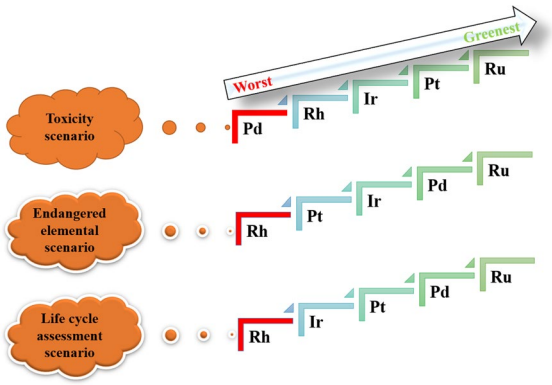


Fig. 8 Ranking of PGM metal in decreasing order based on toxicity scenario, endangered scenario, and life cycle analysis scenario

employed to extract PGMs and valuable metals from spent catalysts (Ding et al. 2020; Prasetyo and Anderson 2020; Yakoumis et al. 2021). However, hydrometallurgical and pyrometallurgical processes suffer with high capital cost, high energy requirement, harmfull gaseous emissions, etc. Due to the above disadvantages, research interest has now been shifted towards developing the eco-friendly bioleaching process. Bioleaching offers several advantages (lower carbon footprint, lesser energy, low emission, works at ambient conditions, and low downstream processing) compared to pyrometallurgical and hydrometallurgical processes. Bioleaching is a process in which the microbes extract valuable metals from primary and secondary sources by interaction with the minerals. Bioleaching is a commonly applied method in extracting base metals, precious metals, and PGMs from spent catalysts (Pathak et al. 2017; Karim and Ting 2021). The process utilizes different microorganisms that transform insoluble PGMs in the spent catalyst into a water-soluble form. Studies on bioleaching potential in the PGM extraction from spent autocatalysts and refinery catalysts have shown promising results (Motaghed et al. 2014; Karim and Ting 2020). Microorganisms such as bacteria (Shin et al. 2015), and fungus (Malekian et al. 2019) have been reported to bioleach the PGMs from spent catalyst.

Table 2 Bioleaching yield and operating conditions

Name of species	Domain	Leaching agent	Mode of operation	Reaction temperature	Medium pH	Solid conc. (w/v%)	Spent catalyst	Bioleaching yield (%)	References
P. plecoglossicida	Bacteria	CN^-	Batch	30	7.2	2.5	Spent automotive catalyst	Pt-0.2	Brandl et al. (2008)
C. violaceum DSM30191T	Bacteria	CN^-	Batch	150	11	20		Pt-92.1, Pd-99.5, Rh-96.5	Shin et al. (2015)
C. violaceum	Bacteria	CN^-	Batch	–	10.73	2		Pt-65.8, Pd-38.4,Rh-99.9	Das et al. (2017)
P. fluorescens	Bacteria	CN^-	Batch	30	9	1		Pt-38, Pd-44, Rh-91	Karim and Ting (2020)
B. megaterium	Bacteria	CN^-	Batch	30	9	1		Pt-35, Pd-41, Rh-82	Karim and Ting (2020)
A. niger	Fungi	Oxalic acid	batch	60	–	1.5		Pt- 60.9, Pd-73.7	Bahaloo-Horeh and Mousavi (2022)
A. niger	Fungi	Oxalic acid	Batch	70	0.5	1	Spent refinery catalyst	Pt-37	Malekian et al. (2019)
B. megaterium	Bacteria	CN^-	Batch	30	7	4.4		Pt-15.7, Re-98	Motaghed et al. (2014)

A detailed description of these microorganisms has been provided in Table 2. These microorganisms mediate bioleaching by producing different lixiviants (i.e. organic acids and cyanide) that can form soluble PGM complexes. This is a dominant biological process that has been reported for PGMs solubilization from the spent catalysts (Malekian et al. 2019; Karim and Ting 2020).

3.1 Role and mechanisms of bacterial leaching of PGMs from spent catalysts

Bacteria are single-celled microorganisms that are highly diverse, utilize different energy sources, and are adapted to survive under extreme environmental conditions (Weissenbach 2019). Due to their peculiar abilities, they interact with different minerals/solids and mediate redox reactions, leading to metal complexation/dissolution (Tanne and Schippers 2019; Zhang et al. 2021). The metal leaching through bacteria has a long history. The first reported miners of a metal (copper) using bacteria were probably the Romans who worked in the Rio Tinto copper mine in Spain (Nutter 2022). Over the years, the application of bioleaching for PGMs extraction from different primary and secondary sources has also gained attention. However, bacterial leaching for PGMs extraction from spent catalysts started gaining traction in early 2000. Several cyanogenic (cyanide generating) bacteria of the genus *Pseudomonas* (Brandl et al. 2008), *Bacillus (*Motaghed et al. 2014*),* and *Chromobacterium* (Karim and Ting 2020), have been reported

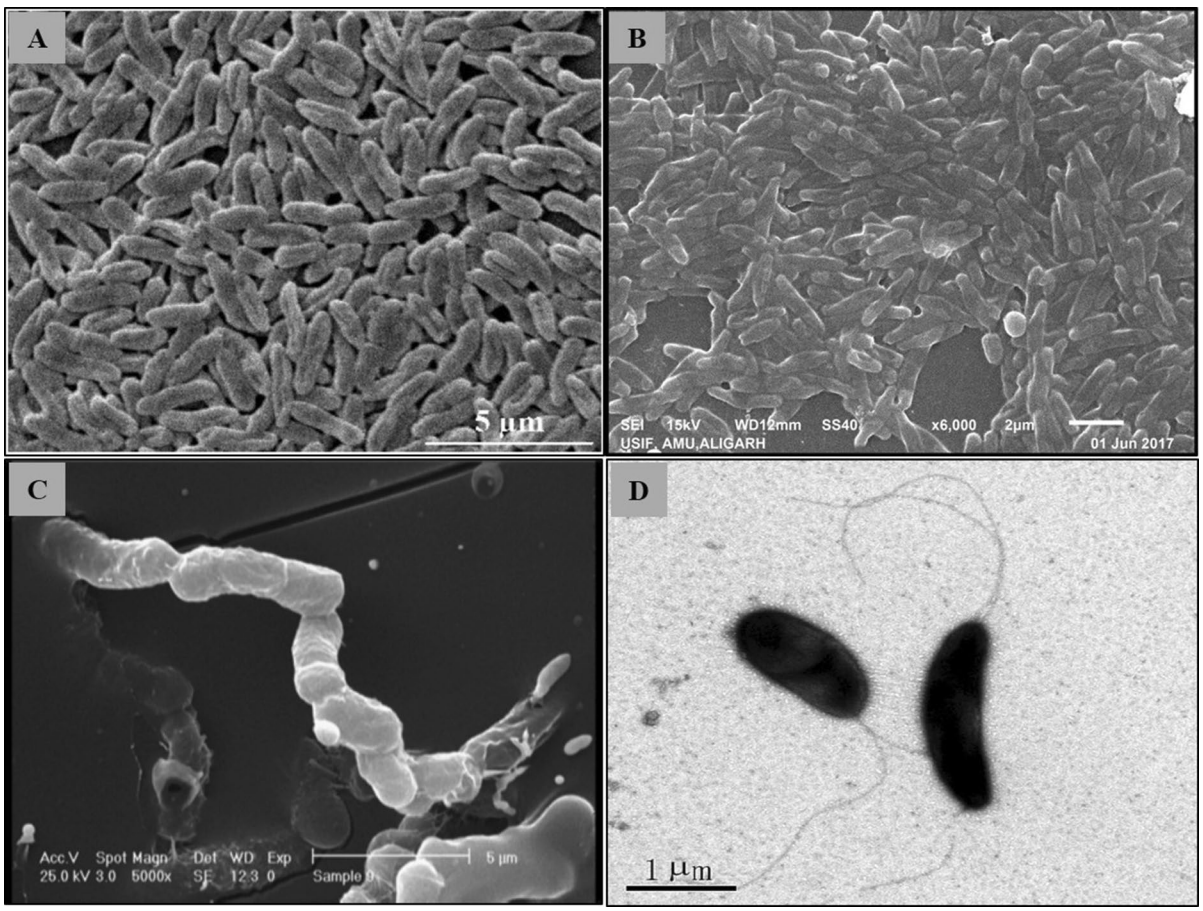


Fig. 9 Scanning electron micrographs of **A** *C. violaceum* (adapted from Poli et al. 2018); **B** *P. fluorescens* (adapted from Ansari and Ahmad 2019); **C** *B. megatirium* (adapted from Yazdani et al. 2009); **D** transmission electron micrograph of *P. plecoglossicida* (adapted from Zhang et al. 2014)

to bioleach PGMs from spent catalysts. Cyanogenic bacteria species such as *Pseudomonas fluorescens* (Karim and Ting 2020), *Pseudomonas plecoglossicida* (Brandl et al. 2008); *Bacillus megaterium (*Motaghed et al. 2014*), and Chromobacterium violaceum* (Shin et al. 2015; Das et al. 2017; Karim and Ting 2019), belonging to these genera have been employed to extract PGMs from spent catalysts. These cyanogenic bacterial species produce cyanide which interacts with PGMs and forms soluble complexes. Detailed information on the bioleaching potential of these species is provided in Table 2. Morphological details of *C. violaceum (*Poli et al. 2018), *P. fluorescens* (Ansari and Ahmad 2019), *P. plecoglossicida* (Zhang et al. 2014), and *B. megatirium* (Yazdini et al. 2009) have been provided in Fig. 9. Besides cyanogenic bacteria, several fungi, algae, and plants are also known to produce cyanide (Faramarzi et al. 2020); however, they have not been reported for the bioleaching of PGMs from spent catalysts. Cyanogenic bacteria are preferred as they produce sufficient cyanide to make soluble complexes with PGMs. Cyanide is a colorless liquid and one of the most toxic compounds known to humans (Motaghed et al. 2014). It boils close to room temperature (25.6 °C). It forms highly stable water-soluble PGMs complexes, and thus PGMs extraction using biological cyanide can be an excellent strategy to treat spent catalysts (Karim and Ting, 2022). Moreover, bioproduction of cyanide is advantageous as bacteria can produce sufficient cyanide and detoxify the cyanide (by metabolizing it) later (Vakilchap et al. 2020), thus reducing the risks and costs associated with the industrial synthesis. Cyanogenic bacteria (*C. violaceum, P. fluorescens, P aeruginosa, B. megaterium*), produce cyanide as a secondary metabolite from glycine (an amino acid) by an oxidative decarboxylation reaction (Knowles and Bunch 1986; Faramarzi et al. 2004). Two major metabolic pathways can undertake the biosynthesis of cyanide i. bacteria can either take up glycine from the culture (extracellular) medium, or it can synthesize from 3-phosphoglycerate (via serine decarboxylation (Garcıaa-Garcıa et al. 2016). In the cyanogenic bacteria (*C. violaecum*) genome, there is an operon for HCN synthase (hcnA, hcnB, and hcnC) that encode a formate dehydrogenase and two amino acid oxidases, respectively, which leads to cyanic acid synthesis. HCN synthase acts by transferring four electrons to the respiratory chain (Knowles and Bunch 1986). The metabolic pathway of cyanide production in cyanogenic bacteria and subsequent bioleaching mechanism are provided in Fig. 10 (Tay et al. 2013; Vakilchap et al. 2020). Cyanide is formed only for a short time during growth, typically in the early stationary phase by the enzyme HCN synthase. Afterward, cyanide concentration gradually decreases (sorption, consumption by cyanide-consuming compounds, utilization by organisms, and evaporation) for various reasons. Cyanide in solution occurs as free cyanide that includes cyanide anions (CN^-) and non-dissociated HCN (Faramarzi et al. 2004). The process

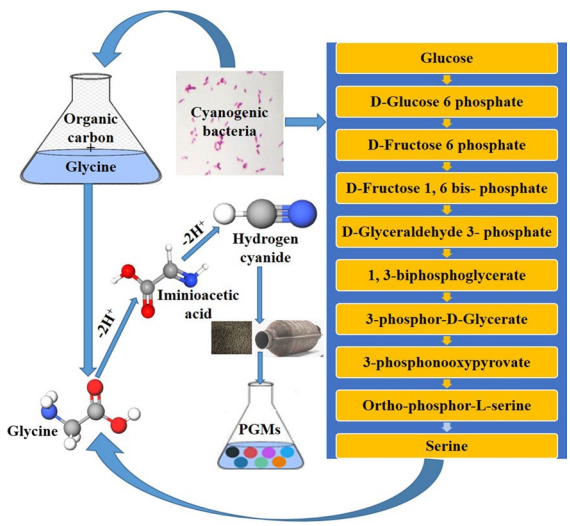


Fig. 10 Metabolic pathway of cyanogenesis and bioleaching mechanism

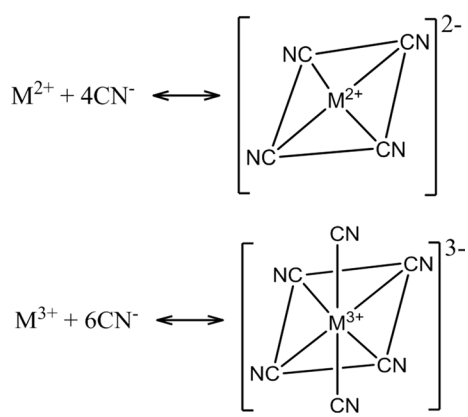


Fig. 11 PGM complexes with cyanide (M^{2+} represent Pt^{2+}/Pd^{2+}, whereas M^{3+} represent as Rh^{3+})

of cyanide production in bacteria is strongly regulated. The glycine can be converted to HCN and CO_2 through oxidative decarboxylation (Eq. 1) (Motaghed et al. 2014; Faraji et al. 2022).

$$C_2H_5NO_2 \xrightarrow{-2H^+} C_2H_3NO_2 \xrightarrow{-2H^+} HCN + CO_2 \quad (1)$$

The generated cyanide reacts with PGMs (Vakilchap et al. 2020) and produces highly soluble tetra and hexa-cyano PGM complexes (Fig. 11) under alkaline conditions (Sibrell et al. 1994). This is because, at close to neutral pH (pH = 7), molecular form (HCN) is dominant, while above neutral pH, ionic CN^- (pKa-9.3) is the predominant species. The formed Pt and Pd complexes pose square planar geometries, while the Rh complex is octahedral.

The earliest study on the bioleaching of PGMs from a spent catalyst was probably conducted by Brandl et al. (2008). In the above research, a cyanogenic bacteria *P. plecoglossicida* was used to bioleach the Pt from a spent automobile catalyst. The *P. plecoglossicida* were grown on the Luria–Bertani (LB) broth (pH 7.2) containing tryptone (10.0 g/L), yeast extract (5.0 g/L), and sodium chloride (10.0 g/L). Glycine (and metal-containing solids) was added to the medium to stimulate cyanide production. Bioleaching was conducted with a spent automobile catalyst (pulp density 25 g/L) at 30 °C. It was found that cyanogenic bacteria can solubilize minute amounts of Pt (0.2%) from spent automobile catalyst after ten days of bioleaching which was attributed to cyanide production (> 1.5 mg/L). The low bioleaching yield (0.2%) was attributed to the passivation of the spent catalyst surface by an oxide film. It was also confirmed that cyanogenic bioleaching proceeded under alkaline conditions (9–9.5) as opposed to conventional acidophilic bioleaching (pH < 3). This is highly important from an environmental point of view as the alkaline leachate might be less corrosive. Although bioleaching with *P. plecoglossicida* confirmed the potential of cyanogenic bacteria, the low Pt yield (0.2%) due to the passivation of spent catalyst surface made researchers explore different pre-treatment methods that can remove the competing metals and improve the PGMs recovery. It was reported that the pre-treatment of spent automobile catalysts using ultrasound-assisted nitric acid could drastically enhance the PGMs yield by cyanogenic bacteria (Karim and Ting 2020). The optimal pretreatment parameters were found to be ultrasound power (80%), nitric acid concentration (6 M), ultrasound duration (50 min), and ultrasound frequency (37 kHz). Using *P. fluorescens,* about 91% Rh, 44% Pd, and 38% Pt can be bioleached from the pretreated spent catalyst (pulp density 1% (w/v) and pH 9). The bioleaching yield of Rh (84%), Pt (33%), and Pd (24%) were lesser in the untreated spent catalyst. The improvement in PGM recovery was also observed in the case of *B. megaterium* where relatively higher Pt (35%), Pd (41%), and Rh (82%) were bioleached from the pretreated spent catalyst. The high PGMs recovery from the ultrasound-assisted pretreated spent catalyst was attributed to the removal of interfering metals (Cu and Zn), which tend to compete with PGMs for cyanide complex formation. Moreover, these metals can also exert toxicity on cyanogenic bacteria leading to decreased bacterial growth and subsequent cyanide production (Karim and Ting 2020). Similar findings were also obtained (Das et al. 2017) using a genetically modified bacteria, *C. violaceum* pBAD. The study indicated that about 99.9% Rh, 65.8% Pt, and 38.4% Pd can be bioleached under optimized bioleaching conditions (pulp density (2%), pH (10.73), glycine concentration (11.81 g/L), and agitation speed (150 rpm) using a genetically modified *C. violaceum*. Besides direct bioleaching, high pressure spent medium bioleaching has also been reported to achieve high PGM dissolution from the spent automobile catalyst. Ilyas et al. (2022) reported the pressure cyanide bioleaching of spent automobile catalyst using cyanide produced by *C. violaceum.* In this study, *C. violaceum* was grown in Yeast Peptone (YP) media and after 16 days of growth, about 5.8 g/L of biologically produced NaCN was collected in the solution. This NaCN was then used as a lixiviant for PGM bio-recovery. The study reported that under the optimized pressure leaching condition (150 °C, pO_2 200 psi, solution pH 11.6, and time 120 min) about 90% PGMs could be extracted using spent medium bioleaching. The use of spent medium bioleaching at ambient pressure to recover Pt, Pd, and Rh was also reported by Karim and Ting (2022). The study employed *P. fluorescenes* to produce cyanide as a secondary metabolite. It was reported that using spent medium leaching, high extraction of Pt (58%), Pd (65%), and Rh (97%) can be achieved from spent automotive catalysts within one day of bioleaching.

Although strategies such as pre-treatment, use of genetically modified bacteria, or pressure leaching of spent catalyst successfully improved the PGMs yield, the overall bioleaching yield of PGM in single-stage bioleaching was still low. It was reported that a two-stage process can overcome the drawbacks of the biological cyanidation process (such as low cyanide production, non-favorable pH for bacterial growth and cyanidation, and difficulty accessing lixiviant to the passivating surface). Shin et al. (2015) developed a two-stage bioleaching process for spent automobile catalysts. Cyanide was first biologically produced (1st stage) using a bacterium, *C. violaceum* DSM 30,191, and accumulated in a cyanide trap. Then the accumulated cyanide was used (in the second stage) to bioleach the different PGMs (Pt, Pd, and Rh) in a separate reactor. This process achieved a maximum cyanide accumulation of 954.8 and 6594.5 mg/L in the batch, and it is a continuous-type cyanide production system. Under this process, 99.5% Pd, 92.1% Pt, and 96.5% Rh can be bioleached (at 150 °C) within one h using a 1000 mg/L biogenic cyanide solution.

Besides spent automobile catalyst, cyanogenic bacteria have also been reported to bioleach the PGMs from a spent petroleum refinery catalyst. The earliest study on the bioleaching of PGMs from a spent refinery catalyst was conducted by Motaghed et al. (2014). They conducted bioleaching of Pt and Re from a spent naphtha reforming catalyst using *B. megaterium.* The study suggested that about 98% Re and 15.7% of Pt can be bioleached within seven days under optimum conditions (12.8 g/L initial glycine, 4% (w/v) pulp density). Moreover, operating parameters such as free cyanide concentration, medium pH, dissolved oxygen, glycine concentration, and pulp density affect the growth characteristics of *B. megaterium* and the bioleaching yield.

3.2 Role and mechanisms of fungal bioleaching of PGMs from spent catalysts

Over the years, fungi bioleaching has gained traction for recycling different valuable metals from secondary materials such as spent catalysts (Pathak et al. 2021), end-of-life printed circuit boards (Becci et al. 2020), electronic waste (Dusengemungu et al. 2021), etc. However, the application of fungi in PGMs leaching from the spent catalysts gained attention only recently, and there have been relatively lesser studies on the fungi bioleaching of PGMs (Malekian et al. 2019). This is perhaps due to the low solubility of non-chloride PGM complexes coupled with the high leaching of unwanted alumina in the liquor during fungal bioleaching (Bahaloo-Boreh and Mousavi 2022). Among different fungal species, *Aspergillus niger* (*A. niger*) of the genus *Aspergillus* have been reported to bioleach PGMs from refinery spent catalysts and spent automotive catalysts (Malekian et al. 2019; Bahaloo-Boreh and Mousavi 2022). The fungi employed for bioleaching utilize carbon as an energy source and produce different organic acids (oxalic, citric, gluconic, and keto-gluconic acids) as metabolites (White et al. 1997; Bahaloo-Boreh and Mousavi 2022). The organic acid type depends on the fungus type and operating conditions (medium pH, external agents, metal ions, etc.). The organic acids can mediate bioleaching reactions through different mechanisms (acidolysis, complexolysis, redoxolysis, and bioaccumulation), producing soluble PGM complexes. For example, citric acid produced during fungal bioleaching can directly form soluble complexes with PGMs such as Pt or Pd (Eq. 2–5) (Demarco et al. 2020).

$$Pt^{2+} + C_6H_5O_7^{3-} \rightarrow Pt(C_6H_5O_7)^{-} \quad (2)$$

$$Pt^{2+} + H^{+} + C_6H_5O_7^{3-} \rightarrow PtH(C_6H_5O_7) \quad (3)$$

$$Pd^{2+} + C_6H_5O_7^{3-} \rightarrow Pd(C_6H_5O_7)^{-} \quad (4)$$

$$Pd^{2+} + H^{+} + C_6H_5O_7^{3-} \rightarrow PdH(C_6H_5O_7) \quad (5)$$

Similarly, PGMs can form complexes with oxalate ions due to the fungal production of oxalic acid (Krishnamurty, and Harris 1961; Anderson and Lumetta 1985). The possible reaction of PGMs with oxalate ion can be written as follows (Eq. 6–7):

$$Pt^{2+} + C_2O_4^{2-} \rightarrow Pt(C_2O_4) \quad (6)$$

$$Rh^{3+} + 2C_2O_4^{2-} \rightarrow Rh(C_2O_4)_2^{-1} \quad (7)$$

The only probable study on the fungal bioleaching of PGMs from spent refinery catalysts reported by Malekian et al. (2019), in which *A. niger* was

used to bioleach the Pt from a spent decoked Sn-Pt/Al_2O_3 catalyst of a continuous catalytic reforming unit. Bioleaching was conducted under spent medium mode with a decoked spent catalyst at 30 °C and 180 rpm. It was found that *A. niger* can solubilize Pt, and under optimum leaching conditions (pulp density- 1%, spent medium pH- 0.5, and reaction temperature- 70 °C), about 37% Pt can be bioleached from the spent catalyst. The bioleaching was attributed to the production of fungal-produced oxalic acid, and blank leaching without oxalic acid under similar conditions yielded only 13% Pt. The study results strongly indicated that oxalic acid plays a vital role in Pt solubilization. This is largely because oxalic acid is a known complex-forming compound that can solubilize different metals, including PGMs (Eq. 6–7). The study also suggested that medium pH was an essential parameter for oxalic acid production. Pt recovery was significantly higher in the experiments with pH control due to the higher production of oxalic acid. This is because medium pH > 6 (optimum pH between 7 and 8) favors the fungal bioproduction of oxalic acid (Malekian et al. 2019; Pathak et al. 2021). The oxalic acid in fungus is synthesized through the activity of the cytoplasmic enzyme oxaloacetate hydrolase. This enzyme expression is optimal at higher pH, whereas its activity inhibits at lower pH (< 3) (Walaszczyk et al. 2018).

Besides spent refinery catalyst, the fungi have also been employed to bioleach the PGMs from a spent automotive catalyst. Bahaloo-Boreh and Mousavi (2022) conducted bioleaching of Pt and Pd from a spent automotive catalyst using a spent culture medium of *A. niger*. The study suggested that under optimum growth conditions *A. niger* produced a high concentration of oxalic acid (15.3 g/L). This bio-produced spent medium (containing 15.3 g/L of oxalic acid) can leach about 60.9% of Pt and 73.7% of Pd under optimum leaching conditions (pulp density of 15 g/L, temperature of 60 °C, and leaching time of 6 h).

The above discussion indicates cyanogenic bioleaching is currently the most utilized biological process for PGMs extraction from spent catalysts. Cyanogenic bioleaching offers high PGMs recovery due to the high cyanide-producing ability of the cyanogenic bacteria. However, besides PGMs, other non-PGM metals (Al, Si, Cu, Zn, Ni, etc.) are also present in high concentrations in the spent catalyst. Hence, a complete process scheme involving the recovery of PGMs, as well as other non-PGMs metals, needs to be formulated to develop a suitable industrial bioleaching process. A conceptual process flow scheme for bioleaching of PGMs is shown in Suppl. Fig. S2.

4 Key operating parameters

Bacterial cyanidation is currently the dominant bioleaching process for PGMs solubilization from spent catalysts. Therefore, the focus of this section will be to discuss the effect of different process parameters on the efficiency of bacterial cyanidation. Typically, biocyanidation involves using heterotrophic bacteria that produce HCN from glycine. CN^- is the main lixiviate that reacts with PGMs and produces soluble PGM-cyano complexes. However, operational parameters (such as bacterial growth, medium pH, glycine concentration, growth temperature, spent catalyst type, concentration, etc.) play a significant role in bacterial growth and cyanide production that can affect the biocyanidation efficiencies. A brief description of individual parameters is presented in the subsequent subsection.

4.1 Bacteria type

Cyanogenic bacteria have been reported to bioleach the PGMs with varying efficiency (Table 2). Typically, the ability of the cyanogenic bacteria to bioleach PGMs from the spent catalyst depends mainly on the quantity of HCN it produces. Thus, selecting an appropriate bacterial strain that can produce higher cyanide is important to developing a cost-effective bioleaching process. Theoretically, *C. violaceum* is better suited to produce higher cyanide than other cyanogenic bacteria. It contains six HCN synthase enzymes, while other bacteria lack one or more enzymes (Knowles and Bunch 1986; Liang et al. 2014). However, other species such *P. fluorescens, and B. megaterium* can also produce sufficient cyanide needed for PGMs solubilization. Between *P. fluorescens* and *B. megaterium,* the former produced higher cyanide (16 mg/L) than *B. megaterium* (13 mg/L) (Karim and Ting 2020). This increased cyanide by *P. fluorescens* was probably the reason which led to higher Pt (38%), Pd (44%), and Rh

(91%) solubilization from a spent automobile catalyst as compared to *B. megaterium* (Pt-35%, Pd-41%, and Rh-82%). Besides, genetically modified bacterial strains can produce higher cyanide than the wild type. This was confirmed by Das et al. (2017), who reported that the genetically modified bacteria (*C. violaceum pBAD*) could produce 68% more cyanide than the wild-type bacteria. Bioleaching with genetically modified bacteria caused 99.9% Rh, 65.8% Pt, and 38.4% Pd from the spent automobile catalyst. Furthermore, the selected cyanogenic bacteria also need to be resistant to the toxicity of the spent catalyst. *B. megaterium* seems more tolerant to high spent catalyst concentrations (4% w/v) as compared to *P. plecoglossicida* in which Pt solubilization efficiency decreased at > 2.5% (w/v) spent catalyst (Brandl et al. 2008).

4.2 pH

pH plays a vital role not only in PGMs solubilization but also in the growth of cyanogenic bacteria. Thus, finding an optimum pH is a balance between the optimal pH for bacterial growth and the chemical leaching of PGMs. Most of the cyanogenic bacteria reported for PGMs bioleaching from spent catalyst grow under neutral to alkaline conditions (Shin et al. 2015; Karim and Ting 2020). The optimal pH for growth of *P. fluorescens, B. megaterium*, and *C. violeaceum* is between 7 and 8, and any decrease in pH below neutral value negatively affects the growth. Therefore, most of the culture media employed for bacterial growth have neutral pH. During bioleaching, the medium pH tends to increase towards a more alkaline pH (pH > 9) either due to acid consumption or alkaline extracellular metabolites' production (Motaghed et al. 2014). Nevertheless, this increase in pH helps maintain the liquid cyanide concentration in the media due to the high pKa value of HCN (9.3). This is because, at neutral pH, cyanide exists as HCN gas and is highly volatile. An increase in pH during bioleaching thus reduces the volatility of cyanide due to the high pKa of HCN (9.3). Therefore, the concentration of soluble CN^- in solution is pH-dependent. The speciation study of cyanide during bioleaching of spent automotive catalyst also indicated that at pH 10.8, about 97.5% cyanide existed as ionic CN^- and only 2.5% was in the form of HCN (Shin et al. 2015). Also, due to its high pKa, the alkaline pH favors PGM-cyanide complexes and improves leaching.

4.3 Glycine concentration

In biocyanidation process, cyanide is the main lixivate responsible for the solubilization of PGMs. Cyanogenic bacteria can utilize different amino acids as precursors to produce HCN, among which glycine is the most preferred. Typically, glycine is produced by bacteria via serine decarboxylation (Garcia-Garcia et al. 2016). However, the concentration of bacterial-produced glycine (without externally added) is inadequate to generate a sufficient concentration of cyanide needed for effective PGMs bioleaching (Shin et al. 2015). Thus, in most bioleaching studies, glycine has been externally added to the culture media. The bacteria transform this externally added glycine into cyanide. The stoichiometric relationship between cyanide and glycine is 1:1 (Shin et al. 2015). Thus, maintaining an optimum glycine concentration in the culture media is vital as too low a concentration may not be adequate to produce sufficient cyanide needed for PGMs solubilization. In contrast, higher concentrations could be toxic to bacteria that can reduce intracellular Mg^{2+} ions essential for many metabolic processes (Eisenhut et al. 2007). Moreover, higher glycine concentrations in the media will also increase the process cost. Most bioleaching studies have used 1–12.8 g/L of glycine in the culture media. However, Shin et al. (2015) reported that 1 g/L of glycine was sufficient to produce adequate HCN, and there was not much difference in the final HCN concentration between 1 and 2 g/L of glycine. Moreover, glycine concentrations beyond 2 g/L (5 and 10 g/L), affects the growth of cyanogenic bacteria and subsequent HCN production was inhibited due to the possible toxicity of glycine.

4.4 Temperature

One of the most critical parameters in biocyanidation is the temperature, and any fluctuation in temperature below or above optima negatively affects bacterial growth and cyanide generation. Most of the cyanogenic bacteria employed for biocyanidation of PGMs from spent catalysts are mesophilic and grow at a temperature of about 30 °C (Table 2). Besides bacterial growth, temperature also plays a vital role

in the leaching of PGMs, and higher temperature (up to a certain temperature limit) is conducive to the leaching. The two-step bioleaching experiments conducted with a spent refinery catalyst with the bioprodcued HCN (using *C. violaceum)* showed that the higher leaching temperature up to 160 °C resulted in increased PGMs bioleaching yield. The bioleaching efficiency of Pt using bioprodcued HCN was almost 100% at 150 °C, as compared to < 10% at 50 °C (Shin et al. 2015). However, the leaching temperature > 150 °C negatively affects the PGMs solubilization as the O_2 level of the leaching solution decreases with an increasing temperature. Also, at a temperature above 100 °C, cyanide tends to hydrolyze, and the hydrolysis rate increases with increasing temperature. Furthermore, leaching temperature above 160 °C causes thermal decomposition of PGM-cyanide complexes to metals (Eq. 8–10), and thus leaching temperature up to 160 °C seems an optimum temperature for PGMs solubilization (Shin et al. 2015).

$$Pt(CN)_4^{2-} + 3/2O_2 + 7H_2O \rightarrow Pt + 4NH_3 + 4CO_2 + 2OH^- \quad (8)$$

$$Pd(CN)_4^{2-} + 3/2O_2 + 7H_2O \rightarrow Pd + 4NH_3 + 4CO_2 + 2OH^- \quad (9)$$

$$Rh(CN)_6^{3-} + 9/4O_2 + 21/2H_2O \rightarrow Rh + 6NH_3 + 6CO_2 + 3OH^- \quad (10)$$

4.5 Spent catalyst content

The content of spent catalysts in the leaching medium is a vital parameter during biocynadiation. Typically, an increase in spent catalyst content leads to a decrease in the bioleaching yield of PGMs (Motaghed et al., 2014). This is because spent catalyst content significantly influences bacterial growth and overall metabolic activity. Higher spent catalyst content increases the metal toxicity to the cyanogenic bacteria, which results in decreased cyanide generation. Brandl et al. (2008) reported that during bioleaching of spent automobile catalyst, the O_2 consumption (an indicator of metabolic activity) by *P. plecoglossicida* was significantly reduced at pulp densities of > 5%. Moreover, the Pt solubilization was also found to decrease at concentrations > 2.5% (w/v). Besides, the higher spent catalyst content in the leaching media may also lead to increased diffusion limitations. The negative effects of higher spent catalyst content were also reported by Karim and Ting (2019), who reported that Pt bioleaching efficiency decreased to 12% (at 4% solids concentration) from 52% (at 0.5% solids concentration). Similarly, the Pd bioleaching efficiency was decreased to 19% (at 4% solids concentration) from 59% (at 0.5% solids concentration). Hence, it is clear that an increase in the spent catalyst content decreases the PGM yield by bioleaching.

4.6 Presence of competing cations

The presence of undesired bulk (non-PGMs) metals in the spent catalyst significantly affect the PGM bioleaching efficiency due to their toxicity to the cyanogenic bacteria. Also, non-PGM metals such as Cu, Fe, and Zn tend to form water-soluble complexes with cyanide and thus compete for cyanide with PGMs (Karim and Ting 2020). This causes depletion of the available cyanide ions, decreasing PGMs biocyanidation efficiency. The presence of these base metals becomes essential in the case of spent automobile catalyst, which contains PGMs (in trace concentrations), along with the bulk concentration of base metals such as Si, Fe, Cu, Ni, Zn, Al, etc. The presence of these bulk metals in the spent catalyst reduces the overall recovery of PGMs. Thus, it is vital to pretreat the spent catalyst before bioleaching for maximum PGMs extraction. Pretreatment with nitric acid was an effective method to solubilize the non-PGMs (Das et al. 2017) from spent catalysts. Moreover, the pretreatment efficiency can be improved using ultrasound. Karim and Ting (2020) reported that the PGMs bioleaching (using *P. fluorescens*) efficiency of an untreated spent automobile catalyst was only 33%, 24%, and 84% for Pt, Pd, and Rh, respectively. Whereas bioleaching efficiency was relatively higher in ultrasound pretreated spent catalyst, and almost 38% Pt, 44% Pd, and 91% Rh were bioleached.

4.7 Oxygen

Oxygen is essential for the growth and respiration of cyanogenic bacteria and increasing dissolved O_2 during the growth phase results in enhanced cyanide production and PGMs dissolution. The O_2 consumption increases during the growth phase and decreases at the end of the log phase (onset of the death phase). Moreover, O_2 consumption is increased due to the

addition of spent catalyst since cyanogenic bacteria require higher O_2 to adapt to the new environment. Motaghed et al. (2014) also reported that the O_2 consumption by bacteria during bioleaching was substantially higher in the presence of a spent refinery catalyst than in the control sample. In the above study, the concentration of dissolved O_2 increased from 2 to 5 ppm as bacteria adapted to the new environment.

5 Technical challenges

The reported studies suggested that cyanogenic bioleaching is the most dominant method to be developed as an alternative to the conventional PGMs leaching processes. However, despite its potential, few studies have been reported, and the process has not been tested for larger-scale applications. Some bottlenecks persist, which need to be overcome to make the process viable for large-scale applications. These bottlenecks are discussed in subsequent subsections.

5.1 Efficiency, and economy

Cyanogenic bioleaching is effective, yet, the relatively slow kinetics of the process is one of the concerns that need to be addressed for developing the process for commercial-scale application. The typical biocyanidation reaction periods are 1–7 days (Motaghed et al. 2014; Das et al. 2017), slightly higher than the conventional hydrometallurgical operations (hrs). Thus, there is a scope to improve the reaction kinetics. Besides, the low bioleaching yield of PGMs in many instances is also an issue. The low bioleaching yield is attributed mainly to the oxide passivation layer on the spent catalyst surface (Brandl et al. 2008), competing ions (Karim and Ting 2020), and relatively less effective bacterial strain. However, the issue of low yield can be solved using either a pretreated spent catalyst or employing improved bacterial strains. It was reported that the pretreatment using ultrasonic-assisted nitric acid effectively improved the PGMs bioleaching from a spent automobile catalyst (Das et al. 2017). However, ultrasonication requires high energy and is thus likely to affect the process cost. Therefore, efforts should be made to develop less energy-intensive processes capable of PGMs bioleaching. Also, genetically modified bacterial strains capable of a higher reaction rate can be a plausible alternative. Das et al. (2017) employed a genetically modified *C. violaceum* pBAD for bioleaching of spent automobile catalyst and reported that it produced 68% more cyanide than the wild-type bacteria.

Besides process efficiency, establishing the economic feasibility of cyanogenic bioleaching is another vital concern that needs to be addressed. In cyanogenic bioleaching, one of the most important operating costs is the bacteria growth media's cost, which mainly contains a high purity carbon source (glycine) and inorganic nutrients (Table 3). Thus, a preliminary analysis of the nutrient media costs can provide a useful estimation of the unit cost of the process. The preliminary cost estimate of the bacteria-based bioleaching process is provided in Table 3. This analysis solely took into account the cost of nutrient media and is calculated for the unit treatment cost of spent catalyst only. The analysis indicated that in bacterial bioleaching, the cost of carbon source (glycine, peptone, etc.) constitutes the major portion of the total budget of nutrient media. Therefore, it can be assumed that the bioleaching cost can be significantly decreased by using cheaper alternatives to these carbon sources or the production of glycine from waste materials such as herbal medicine waste (Jouyandeh et al. 2022). As per the analysis (Table 3), the unit treatment cost/g spent on catalyst varies from € 0.16 to € 0.40 for cyanogenic bioleaching. These costs are slightly higher than conventional leaching based on hydrochloric acid and aqua-regia (0.08–0.34 €). Thus, considering the cost of chemicals only, cyanogenic bioleaching seems slightly expensive. However, to derive a detailed economy of the overall process, the capital cost, pretreatment costs, bioleaching yield, energy cost, downstream processing cost, environmental cost, workforce cost, maintenance, and management costs need to be added. Unfortunately, a comprehensive cost analysis is currently unavailable as inadequate information on the economic aspects of cyanogenic bioleaching of spent catalysts limits the scope of a detailed cost–benefit analysis.

5.2 Toxicity and environment

Typically, cyanogenic bacteria are well adapted to extreme environmental conditions. However, many cyanogenic bacterial species are known pathogens/opportunistic invaders and can cause severe infections

Table 3 Cost of media used for cyanogenic bioleaching (g/L)

Spent catalyst type	Leaching process	Bioleaching yield (%)	Quantity of chemicals and price (A)	Pulp density (g/L)-(B)	Treatment cost/g spent catalyst (€)-A/B	References
Spent reforming catalyst	Bioleaching (*B. megaterium*)	Pt-15.7, Re-98	Peptone (5 g/L) = €2.03; Yeast extract (2 g/L) = €0.14; Sodium chloride (5 g/L) = €0.23; Glycine (12.8 g/L) = € 5.17 *Total cost (€/L): 7.57*	44	0.17	Motaghed et al. (2014)
	Aqua regia (3 HCl: 1 HNO_3)	Pt- 98.3	HNO_3 = 69.60 HCl = 100.48 *Total cost (€/L): 170.08*	500	0.34	Jafarifar et al. (2005)
Spent automotive catalyst	Bioleaching (*C. violaceum* DSM30191T)	Pt-92.1, Pd-99.5, Rh-96.5	Peptone (10 g/L) = €4.06; Yeast extract (5 g/L) = €0.36; Magnesium sulphate heptahydrate (1 g/L) = 0.06; Glycine (1 g/L) = € 0.40 *Total cost (€/L): 4.89*	20	0.24	Shin et al. (2015)
	Bioleaching (*P. fluorescens)*	Pt-38, Pd-44, Rh-91	Tryptone (10 g/L) = €1.14; Yeast extract (5 g/L) = €0.36; Sodium chloride (10 g/L) = €0.45; Glycine (5 g/L) = € 2.02 *Total cost (€/L): 3.97*	10	0.40	Karim and Ting (2020)
	HCl leaching	Pt- 81; Pd- 87; Rh- 62	HCl (2 M) = €20.6 *Total cost (€/L):* 20.6	100	0.21	Trinh et al. (2017)
	Mixed reagent (HCl + NaCl + H_2O_2)	Pt- 100; Pd- 92; Rh- 61	HCl (3 M) = €30.94 NaCl (4.5 M) = €11.93 H_2O_2 (1% v/v) = €15.43 *Total cost (€/L): 58.31*	700	0.08	Yakoumis et al. (2020)

Table 4 Taxonomic, physical, growth, and pathogenic characteristics of microorganisms involved in PGMs bioleaching

Cyanogenic species	Taxonomy	Physical characteristics	Growth characteristics	Biological interaction	References
P. fluorescens	Bacteria, Proteobacteria, Gammaproteobacteria, Pseudomonadales, Pseudomonadaceae, *Pseudomonas*	Gram-negative, rod-shaped, motile via polar flagella, non-spore-forming	Obligate aerobes but can use nitrate instead of oxygen as an electron acceptor Growth temperature between 25 and 30 °C	Possible human pathogen	Liu et al. (2021a, b)
P. plecoglossicida	Bacteria, Proteobacteria, Gammaproteobacteria, Pseudomonadales, Pseudomonadaceae, *Pseudomonas, Pseudomonas putida group*	Gram-negative, non-fluorescent, rod-shaped, motile	Facultataive aerobes, Growth temperature between 28 and 30 °C	The opportunistic pathogen in fish	Tao et al. (2016)
C. violaeceum	Bacteria, Proteobacteria, Betaproteobacteria, Neisseriales, Neisseriaceae, *Chromobacterium*	Gram-negative, rod-shaped, non-sporing coccobacillus, motile via a single flagellum	Facultative anaerobic, Growth temperature between 35 and 37 °C	Human and animal pathogen	Martin and Martin (1998)
B. megaterium	Bacteria, Firmicutes, Bacilli, Bacillales, Bacillaceae, *Bacillus*	Gram-positive, rod-like, spore-forming, cell length up to 4 µm, the diameter of 1.5 µm	Aerobic, Can grow between 3 °C and 45 °C, with the optimum around 30 °C	Non-pathogenic in human	Environment and Climate Change Canada (2018)
A. niger	Fungi, Ascomycota, Eurotiomycetes, Eurotiales, Trichocomaceae, *Aspergillus*	Filamentous fungus forming filamented hyphae, colony-forming	Aerobic, Can grow between 20 and 45 °C	Human, animal, and plant pathogen	USEPA (1997)

in humans and animals if not handled properly. Detailed information on the taxonomy, growth characteristics and pathogenicity of these species have been provided in Table 4. The commonly used *C. violaceum*, is a known human pathogen (Durán and Menck 2001) that can cause fatal infections (Lang et al. 2021) by spreading rapidly to organs such as the liver, lungs, and spleen (Durán and Menck 2001). These infections can cause severe fever, abdominal pain, skin lesions, and the formation of metastatic abscesses (Duran and Menck 2001). Similarly, another cyanogenic bacterium, *B. megatarum* (although generally considered non-pathogenic), can act as an opportunistic pathogen in humans with pre-existing health conditions (Canada 2021). Besides their pathogenic ability, exposure to the bacterial-produced cyanide can also be fatal if not correctly handled. This is because cyanide is one of the most toxic substances known to humans (NIOSH). It has been cited as hazardous by different agencies such as the United States Occupational Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH) of United States, United States Department of Transportation (DOT), United States Environmental Protection Agency (USEPA), etc. (NJ Health 2021). NIOSH has recommended that workplace exposures to HCN should not exceed 4.7 ppm (as a 10-min ceiling). Besides, toxicity, the anhydrous and unstabilized HCN is an explosion hazard and can polymerize violently when exposed to high temperatures (> 50 °C). The sodium salt of cyanide (NaCN) has been classified as a dangerous substance by UN GHS. Therefore, adequate safety procedures in compliance with existing regulations and industrial practices should be adapted to avoid adverse health impacts and cyanide release into the environment. This can be achieved through implementing sound monitoring to monitor levels of cyanide in the environment. Notably, all possible sources of cyanide and discharges should be monitored to detect any excess cyanide in the background. The generated cyanide should be safely stored and handled to avoid any spillage. Besides, several various chemical, biological and physical methods can be employed for the treatment and recovery of cyanide (Dong et al. 2021). The treatment processes mainly transform the cyanide into a less toxic compound such as cyanate (OCN-). The sulfur dioxide and air process developed by INCO Limited, hydrogen peroxide-based process, use of Caro' acid, biological treatment, etc., are some of the prevalent methods that can be utilized to transform and degrade cyanide into less toxic forms. Similarly, several physicochemical (complexation, adsorption, etc.) methods can be employed to separate and recover the cyanide from the waste stream (Alvillo-Rivera et al. 2021).

6 Outlook

Recent laboratory studies have shown that cyanogenic bioleaching is the most effective biological process for PGMs extraction from spent automobile and spent refinery catalysts. These studies employed different cyanogenic bacteria, among which *B. megatarium* and *C. violaceum* seems to be the preferred choice due to their high bioleaching yield and cyanide-producing ability. However, the relatively slow kinetics, lack of pilot-scale studies, and high cost of growth media are still significant hindrances to scaling up the process on an industrial scale. It is therefore vital to identify bacterial strains with the highest cyanide synthesis capacity and low-cost glycine sources. For instance, using adapted culture (to spent catalyst) can result in less inhibition and thus can significantly enhance the leaching rate. The adapted culture can be produced through repeated subculturing of bacterial cells in progressively higher spent catalyst concentrations. Similarly, the production of genetically modified strains capable of generating higher cyanide can be a game-changer. Das et al. (2017) reported that it is possible to produce a genetically modified bacteria capable of producing 66% higher cyanide than wild bacteria. Using waste and cheap organic sources to produce glycine can be another feasible way to lower the media cost and valorization of waste materials. It would also be interesting to evaluate the possibility of a hybrid leaching system involving cyanogenic bioleaching (spent medium) and chemical cyanide leaching to improve the reaction kinetics and yield. Moreover, studies on cyanogenic microorganisms other than bacteria can also open new avenues as cyanide is produced by various organisms such as fungi, algae, and plants. Furthermore, most bioleaching studies are lab-scale studies, and there is a lack of intermediate scale-up studies. Thus, more in-depth studies on scale-up reactors are required to confirm the feasibility of the

process. Besides PGMs, spent catalysts also contain high concentrations of non-PGM metals (Al, Si, Cu, Zn, Ni, etc.). However, currently, no biological process is in operation that can completely extract PGMs as well as non-PGM metals. This is perhaps due to the lack of bioleaching studies and the heterogeneity of the different metals in the spent catalysts. Each metal present in the spent catalyst poses unique leaching chemistry and thus require a complex set of leaching process and conditions (Eh–pH) to enable its recovery. An ideal biocyandiation scheme, therefore, should incorporate processes that can recover both PGMs and non-PGMs metals effectively. This requires an in-depth study of the recycling process from an early lab scale to an intermediate pilot scale. The success of the pilot scale studies can pave the way for commercial operations. Based on our analysis, we recommended that the focus of future work should be on (1) exploring novel and improved bacterial species capable of high cyanide generation. This can be achieved by screening different cyanogenic bacterial strains and innovative approaches in metabolic engineering (Tay et al. 2013; Elahian et al. 2020). (2) studying a hybrid process that involves cyanogenic bioleaching as well as chemical cyanide leaching. It is expected that a hybrid process can result in higher yield kinetics owing to the flexibility provided by the chemical additions of cyanide. (3) study the feasibility of the process in larger-scale reactors to confirm the process's applicability for commercial applications, and (4) explore the use of organic solid waste and wastewater as a potential source for glycine production. This can improve the process economy and result in the sustainable valorization of waste. Based on this analysis, it can be suggested that the bioleaching of PGMs is an exciting alternative to the conventional leaching processes. Even though there are several bottlenecks and challenges, the potential for technological advancement and development is immense. This will lead to a good foundation for the future development of the PGMs bioleaching process.

7 Conclusion

The spent catalyst generated from petroleum refineries and the automobile industries is a hazardous and valuable material that should be recycled for its PGM value to ensure resource recovery and eco-friendliness. Therefore, it is crucial to investigate technologies capable of extracting PGMs sustainably. In this review, the potential of the bioleaching process in the extraction of PGMs from spent petroleum refineries and automotive catalysts has been explored. Our analysis has suggested that cyanogenic bioleaching is an emerging technology that can extract PGMs from the spent catalyst in an economical and eco-friendly manner. It has shown exciting potential (up to 100% PGMs efficiency) and offers numerous opportunities due to the emerging demand for an eco-friendly biological method for PGM extraction. However, this process is still in the early phase of laboratory research, and certain bottlenecks still have to be rectified to create a successful bioleaching process for PGM extraction. Consequently, future research should aim to alleviate these concerns and explore more integrated approaches and hybrid techniques that lead to developing a suitable industrial bioleaching process.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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