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Emergence of Bio-hydrometallurgy to Achieve Sustainable Process Development Goals in Extractive Metallurgy

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Abstract. The stringent environmental regulations and growing awareness of the low-carbon economy are presenting immense challenges to metallurgical operations, one of the major sectors with high emissions. Hydrometallurgy has been identified as a lower-emission technology in comparison to the high-temperature smelting and melt-refining processes. The close monitoring of traditional hydrometallurgical operations, however, does not fulfil the criteria for a sustainable, low-emission process. Recently, biotechnology has emerged as a green alternative within the hydrometallurgical domain, albeit significantly different from the basics involved in the process. Although the application of microbial activity has been successfully established in chalcopyrite leaching and bio-oxidation of gold-bearing minerals, the acceptability of bio-hydrometallurgy for other minerals and materials is still limited due to a wide research gap to connect solution chemistry, microbial activity, and extractive metallurgy. In general, a large portion of the total chemical consumption occurs in pre-treatment and/or leaching operations; hence, the primary application of microorganisms at the forefront can significantly minimize the overall consumption. Demonstrated applications in waste printed circuit boards and spent automobile catalysts have curtailed excessive acid usage, while the energy-intensive baking/roasting of monazite is successfully altered by microbial processing. Furthermore, the remarkable reduction in carbon footprints by the green biotechnology application in hydrometallurgy has been evaluated, which indicates sustainability in process metallurgy.

Keywords: Bio-hydro-metallurgy; Low-emission technology; Integrated process sustainability

1 Introduction

Metals are essential commodities for human lives and modern technology applications. Since the iron and copper ages, metallurgical processes have remained attractive to human civilization. Later on, different types of furnaces were innovated, while the advent of aqua-regia, cyanidation, and ammonia leaching gave rise to hydrometallurgical extraction of metals. Since then, these metallurgical processes gained their applications with necessary modifications time-to-time. However, in both metallurgical routes, one issue was very commonly identified, which was the generation of large quantity of secondary waste and effluents that resulting in environmental degradation [1-3]. After continuous progress in extractive metallurgy, the metal extraction routes are almost saturated. However, the indiscriminate exploration and fast depletion of metal contents, along with increasing impurities in primary reserves, have thrown serious challenges towards sustainable metallurgy [4,5]. The evaluation of a sustainable process mainly depends on various primary and secondary factors. Fig. 1 represents the prime objectives of a sustainable process that encompasses the features of cost-effectiveness, operational flexibility, and environmental friendliness with lower energy consumption and high extraction efficiency [6,7].

Compared to conventional smelting and chemical dissolution of metals, the use of microorganisms in metal extraction has been considered a green, low-cost, and less energy-consuming technique [8-10]. The microorganism encounters metal constituents in the environment, which commonly interact with single or multi-metal systems, depending on the type of microorganism (prokaryotic or eukaryotic) [11,12]. They act to bind metal species influencing the cell surface, carry them into the cell to produce various intercellular functions, and excrete metabolic products that lead

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to metal complexations. In contrast, the challenging growth of microbes in all weathers and different environments, their metabolic pathways, slow kinetics for their interactions with metal compounds, lower tolerance to metal toxicity, etc. have been identified as the great obstacles to the microbial process and susceptible to its sustainability [13-15].

With the growing confidence in bio-metallurgical processing, the practice extends to the knowledge base with innovative applications, newer techniques with divergent resources, and integrative processing routes [16-18]. An integrative process may consist of a sequence in which a primary or secondary source of metals can be treated by applying microbial activities for bio-oxidation, bio-leaching, bio-cyanidation, or bio-beneficiation as a pre-conditioning step with subsequent chemical processing, or vice versa. Such a typical process schematic can be presented in Fig. 2 [7,19], showing the plausible integration either at the forefront (for pretreatment) or at the backend (for separation, enrichment, and recovery) of the process.

Therefore, we assess the emergence of bio-hydrometallurgy towards achieving the sustainable process development goals in extractive metallurgy, either by alone application of microorganism or via a combination of bio and chemical techniques. Herein, we present an example of spent auto-catalysts showing the potential of microbial technology coupled with chemical technologies [20]. Not only the extraction efficiency but the first evaluation of circular economy values in such case has been evaluated, while the sustainable process index value and the environmental impact assessment has been determined in another processes.

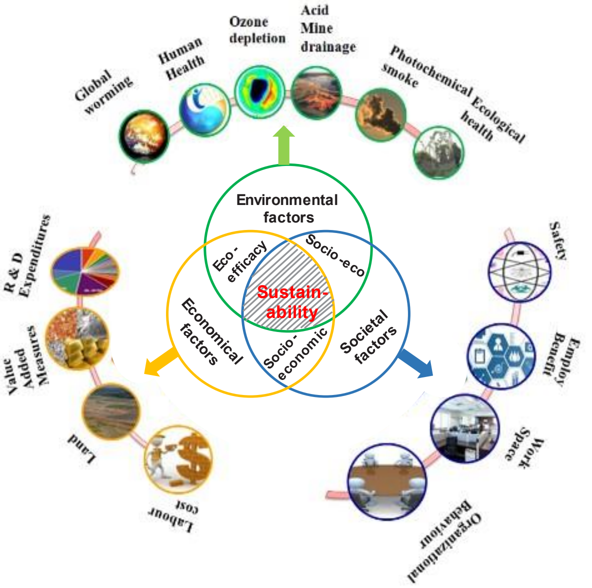

Fig. 1. Key factors attribution in sustainable metallurgy.

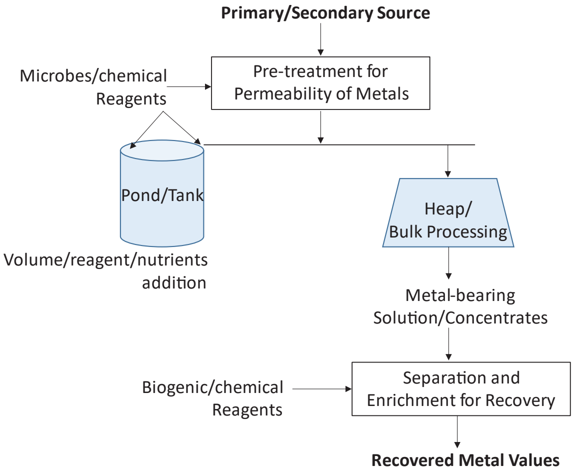

Fig. 2. Schematic representation of sustainable process development involving key factors attribution.

2 Metal-to-microbe interactions

A direct leaching process that involves electron transport from minerals, particularly the sulphides, to the cells attached to the material surface can be expressed as follows [21]:

$$2FeS_2 + 7O_2 + 2H_2O \xrightarrow{bacterial} 2FeSO_4 + 2H_2SO_4 \tag{1}$$

Whereas, indirect leaching proceeds by a metal sulphide oxidizing agent, Fe^{3+}, generated by Fe^{2+} oxidizing bacteria and can be given as follows [22]:

$$4FeSO_4 + O_2 + 2H_2SO_4 \xrightarrow{bacterial} 2Fe_2(SO_4)_3 + 2H_2O \tag{2}$$

$$FeS_2 + Fe_2(SO_4)_3 \xrightarrow{chemical} 3FeSO_4 + 2S^0 \tag{3}$$

$$2S^0 + 3O_2 + 2H_2O \xrightarrow{bacterial} 2H_2SO_4 \tag{4}$$

Metals (*m*) can also exist in zero-valent states (Cu, Zn, Ni, Al, Fe, Co, etc.) and/or in their oxide forms, which can be oxidized with ferric ions and undergo biogenic acid dissolution.

$$m + 2Fe^{3+} \xrightarrow{chemical} m^{2+} + 2Fe^{2+} \tag{5}$$

$$m + H_2SO_4 + 0.5O_2 \xrightarrow{chemical} mSO_4 + H_2O \tag{6}$$

$$mO + H_2SO_4 \xrightarrow{chemical} mSO_4 + H_2O \tag{7}$$

As the direct electron transfer between metal sulfide and attached cells via nanowires, enzymes, etc. has not been shown, the coupled cells instead supply an efficient extracellular polymeric substance, an EPS-filled reaction compartment exhibiting indirect leaching with ferric ions [23]. The terms contact and non-contact leaching are therefore suggested for the bioleaching by coupled and planktonic cells. Another term, of cooperative leaching, is suggested for dissolving sulphur colloids, sulphur intermediates, and mineral fragments by planktonic cells [24]. All these terms describe the physical behaviour of cells without giving information about their intrinsic chemical mechanisms.

For all-inclusive knowledge of chemical aspects of the microbial dissolution of metal sulfide, the thiosulfate and polysulfide mechanisms have been suggested [25]. Commonly, dissolution is attained with a composite protons attack and oxidation process, but the valence bonds of some metal sulfides (FeS_2, MoS_2, WS_2 etc.) do not require participation to bond the metal and sulphur, showing resistance against a proton attack. The bond can exclusively be broken by multistep electron transfers with oxidants, viz. Fe^{3+}. With the effect of the oxidant's attack, the sulphur moiety of metal sulfide can be oxidized, solubilizing the intermediate products of sulphur. The thiosulfate mechanism follows as [25]:

$$FeS_2 + 6Fe^{3+} + 3H_2O \xrightarrow{chemical} S_2O_3^{2-} + 7Fe^{2+} + 6H^+ \quad (8)$$

$$2\mathrm{Fe}^{2+} + \frac{1}{2}\mathrm{O}_2 + 2\mathrm{H}^+ \xrightarrow{bacterial} 2\mathrm{Fe}^{3+} + \mathrm{H_2O} \quad (9)$$

In the presence of sulphur, introducing an oxidant, viz. Fe^{3+}, electrons can be removed by the protons from the valence bond, causing a cleavage of bonds between the metal and sulphur moiety of the metal sulfides. Thus, these metal sulfides are relatively acid soluble, yielding the polysulfide as the main intermediate. The polysulfide mechanism can simply be given as [25,26]:

$$2mS + 2\mathrm{Fe}^{3+} + 2\mathrm{H}^+ \xrightarrow{chemical} 2m^{2+} + \mathrm{H_2S_n} + 2\mathrm{Fe}^{2+} \quad (\text{where}, n \geq 2) \quad (10)$$

$$\mathrm{H_2S_n} + 2\mathrm{Fe}^{3+} \xrightarrow{chemical} 0.25\mathrm{S_8} + 2\mathrm{Fe}^{2+} + 2\mathrm{H}^+ \quad (11)$$

The chemical inertness of elemental sulphur can be attacked by microbial oxidation to convert into sulfuric acid as following the reaction:

$$\frac{1}{8}\mathrm{S_8} + \frac{3}{2}\mathrm{O_2} + \mathrm{H_2O} \xrightarrow{bacterial} \mathrm{SO_4^{2-}} + 2\mathrm{H}^+ \quad (12)$$

Heterotrophic biological agents (bacteria or fungi) are able to produce organic metabolic end products that can solubilize metals from carbonates, phosphates, silicates, or fluoride-containing minerals by chelation, oxidation-reduction, and acid dissolution [27,28]. Similarly, some species of *Pseudomonas* and *Chromobacterium* can produce biogenic cyanide that can undergo complexation with gold and platinum group metals for their extraction. Both autotrophic and heterotrophic microorganisms can potentially accumulate metals and incorporate them into metalloenzymes like nitrogenase (Mo/Fe; V/F; Fe only), cytochrome oxidase (Cu, Fe), cytochromes (Fe), superoxide dismutase (Cu, Fe, Zn, or Mn), bacteriochlorophyll (Mg), etc. [29]. Enzymatic bacterial detoxification of hazardous and heavy metals and metalloids is another kind of interaction. Microbial oxidation of AsO^{2-} to AsO_4^{3-} by a strain of *Alcaligenes faecalis* and reduction of CrO_4^{2-} to $Cr(OH)_3$ by *Enterobacter cloacae* or *P. fluorescens* are examples of such redox reactions [11]. Various modes of microbial-to-metal interaction are shown in Fig. 3 [30].

3 Application in precious metals' recovery from spent auto-catalysts

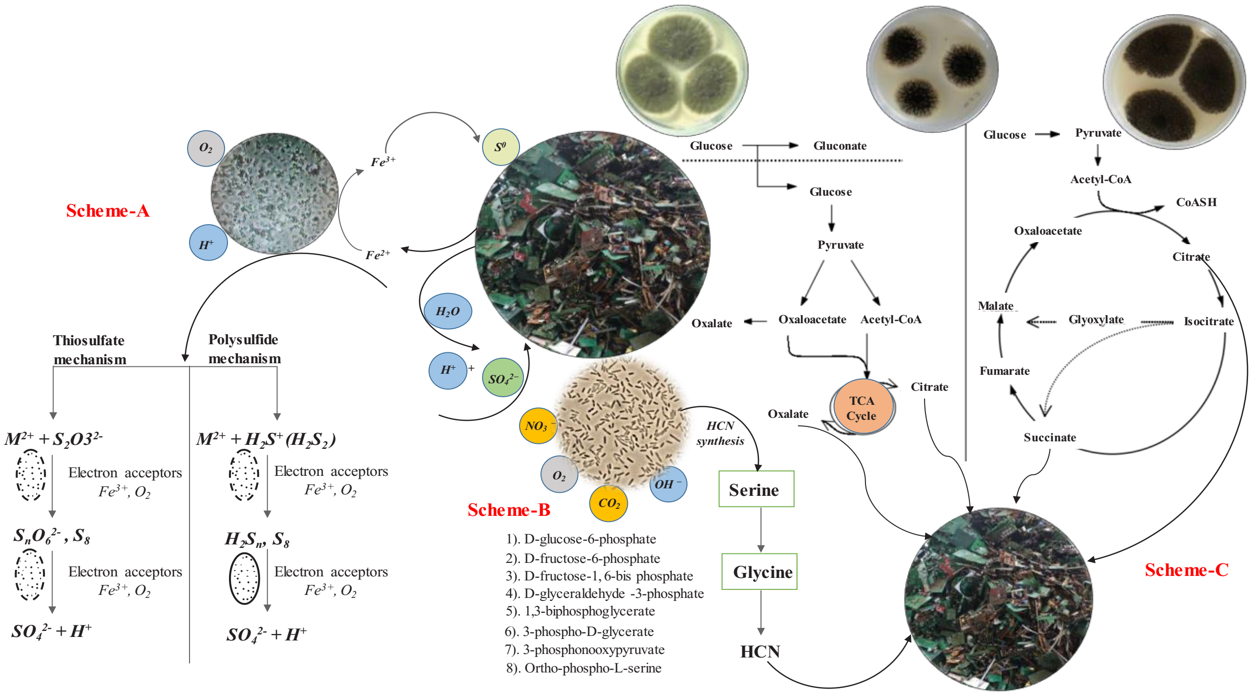

Fig. 3. Various metabolic pathways; **Scheme-A,** showing for thiosulfate and polysulfide mechanism using iron- and sulphur-oxidizing bacterial; **Scheme-B,** showing the bio-cyanidation via HCN synthase of cyanogenic microorganism; and **Scheme-C,** depicting the organic acid production via tricarboxylic acid (TCA) cycle driven by fungi.

To control the emissions from automobiles due to the burning of fossil fuels, the catalytic converters containing platinum and palladium made of cordierite substrate is commonly applied in the vehicles [31]. On average, about 2.0 $g \cdot kg^{-1}$ precious metals used in catalytic converter is quite a rich source to be extracted from spent catalysts [32,33]. The applied hydrometallurgical routes involving highly concentrated mineral acids generate significant quantity of environmental hazards. Hence, we applied the microbial technology clubbed with the advantage of pressure leaching and solvo-chemical extraction techniques for achieving the quantitative recovery of precious metals and used the added advantage of microorganism in effluent treatment [34].

The advantages of this work can be understood as: (i) replacing the highly concentrated acid solutions with biogenic cyanide solution as medium of Pt-Pd dissolution, (ii) bio-cyanide production using the oxidative decarboxylation of glycine for the HCN synthesis during the late exponential growth phase of *C. violaceum*, (iii) application of a green organic reagent, trihexyl(tetradecyl)phosphonium chloride ionic-liquid (P-IL) for the subsequent separation of Pt and Pd from cyanide leach solution, (iv) reutilized of ionic-liquid to control the processing cost-economy, (v) re-use of Pt-Pd depleted cyanide effluent (raffinate) for leaching in next batch after building-up the cyanide concentration that produced through the bio-cyanidation process, and (vi) breakdown of residual cyanide to less toxic products from the bleed solution before discharge in the latter stage of bacterial life-span itself that is used earlier in cyanogenesis (as depicted in Fig. 4) [20].

First, to overcome the short period of bio-cyanide production (1.48 $g \cdot L^{-1}$ CN^- after 48 h) in batch mode of bio-cyanogenesis [34], a continuous cyanide generation and accumulation system was developed. This yielded high CN^- in the solution, which was used as potential lixiviant for dissolving Pt and Pd [35].

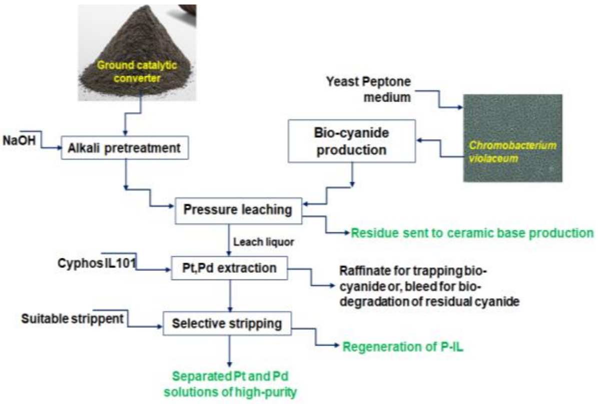

Fig. 4. Schematic for a green recycling of Pt and Pd from exhausted catalytic converter explored in this study.

3.1 Autoclave pressure leaching using bio-cyanide as lixiviant

The pressure cyanidation was studied at different temperatures (100–200 °C), while CN^- concentration = 2.9 $g \cdot L^{-1}$, pO_2 = 10.5 bar, solution pH = 11.2, and time = 1 h were kept constant. Results showed that at 100 °C, Pt and Pd dissolution was ~85%, which improved to be 91% Pt and 94% Pd at 150 °C. However, dissolution efficiency declined up to 87% Pt and 81% Pd at 250 °C, possibly due to cyanide destruction at higher temperatures through the increased hydrolysis rate.

Then, the variation in oxygen pressure (3.5–17.5 bar) at 150 °C was investigated that showed above 94% efficiency at a pO_2 = 17.5 bar (Fig. 5a). It depicts the catalytic role of oxygen in cyanidation process as Eq. (13). Since the maximum dissolution was achieved at pO_2 = 14 bars, it was maintained throughout the experimental sets.

$$m + 4\mathrm{CN}^- + \tfrac{1}{2}\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \leftrightarrow m(\mathrm{CN})_4^{2-} + 2\mathrm{OH}^- \quad (13)$$

3.2 Solvo-chemical separation and recovery of Pt and Pd from leach liquor

Further, the selective recovery of Pt and Pd was performed using a phosphonium-based ionic liquid (P-IL) at different concentrations (0.01–0.15 $mol \cdot L^{-1}$), while contacting both phases in unit phase ratio. The results elucidate that Pt and Pd extraction significantly increased with respect to increasing concentration of P-IL. Specifically, the extraction of Pt increased from only 12% to over 97%, while that of Pd surged from 5% to above 94%, as the concentration of P-IL molecules in the organic phase increased from 0.01 $mol \cdot L^{-1}$ to 0.15 $mol \cdot L^{-1}$, respectively. In a complementary investigation, a logarithmic plot of metals' distribution against P-IL concentration was executed, revealing a slope value approximately two. This finding implies that the extraction process at equilibrium can be expressed as follows [36]:

$$m(\mathrm{CN})_4^{2-} + 2\overline{[\mathrm{P}_{66614}]^+\mathrm{Cl}^-} \leftrightarrow \overline{[\mathrm{P}_{66614}]_2^+ . m(\mathrm{CN}_4)^{2-}} + 2\mathrm{Cl}^- \quad (14)$$

On the other side, the effect of pH, ranging from 9.6 to 11.2, was investigated. It revealed a consistent uptrend in extraction efficiency as pH levels decreased. Similarly, variations in temperature from 20 °C and 60 °C indicated a corresponding decline in extraction efficiency. Additionally, efforts were directed towards exploring the back-extraction of Pt and Pd from loaded-organic phase using investigated with NH_4SCN solution with concentrations ranging from 0.25−2.0 $mol \cdot L^{-1}$. The results illustrated in Fig. 5b show good selective stripping regardless of the reagent concentration. Pd-stripping increased from 68% to 94% by increasing NH_4SCN concentration from 0.25 mol·L^{-1} to 1.0 mol·L^{-1}, while a maximum of about 3% Pt stripping in the aqueous phase. Subsequently, Pt from the Pd-depleted organic phase was stripped in 1.5 mol·L^{-1} $S(CH_2CH_2OH)_2$ solution.

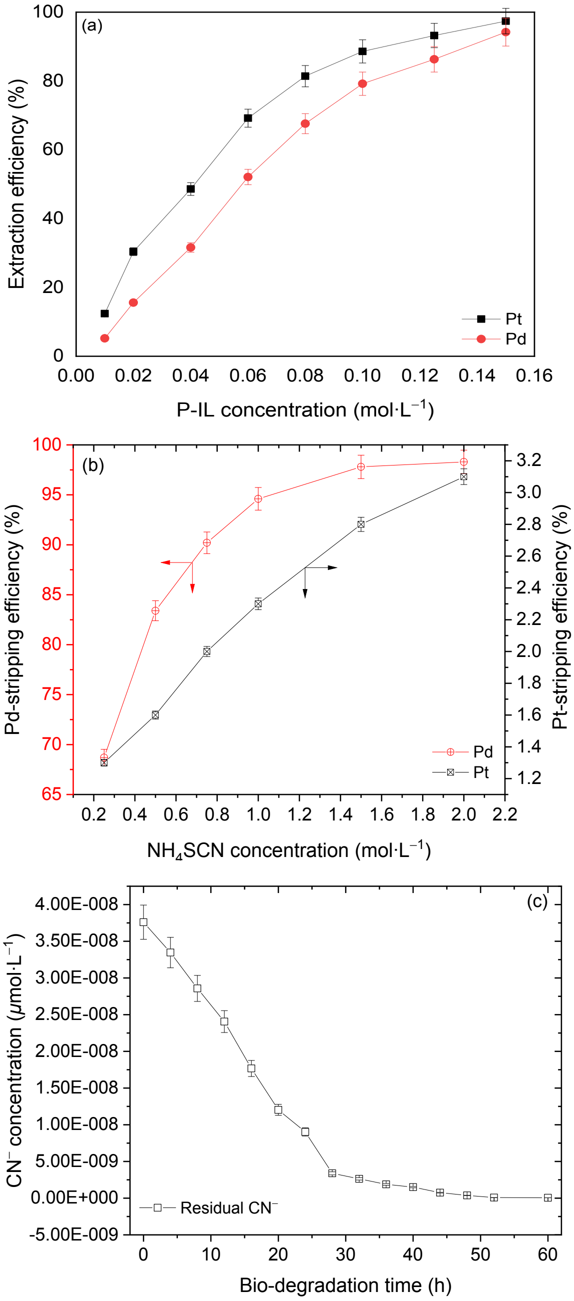

Fig. 5. Effect of P-IL concentration on Pt, Pd extraction from biocyanide leach liquor at an O:A ratio = 1, pH = 10.8, contact time = 10 min, and temperature = 25 °C **(a)**. Effect of NH_4SCN concentration on stripping of Pt and Pd from the loaded-organic phase at an O:A = 1, contact time = 10 min, and temperature = 25 °C **(b)**. Biodegradation of cyanide using the drained *C. violaceum* from bioreactor after their participation in bio-cyanide production **(c)**.

After that, the residual cyanide in raffinate was treated with the same *C. violaceum* used for cyanide production. It was observed that the bio-degradation of cyanide increased with time and reached >90% after 28 h (Fig. 5c). The maximum detoxification of CN^- was achieved after 60 h, getting the final CN^- concentration to be 5.64×10^{-11} µmol·L^{-1} from 3.76×10^{-8} µmol·L^{-1} in the raffinate. The involved proteinogenic amino acid and an α-amino acid in *C. violaceum* metabolism reaction with CN^- ions can be written as:

$$\mathrm{HSCH_2CH—(NH_2)—COOH + CN^- \leftrightarrow \beta - Cyanoalanine + H_2S} \qquad (15)$$

3.3 Process sustainability evaluation

The thus obtained results of this study was connected with the sustainable development goals and the reduction in greenhouse gases (GHGs, as CO_2-e) was evaluated in comparison to the primary production of PGMs [37] involving the mining and milling activities or ore that typically contains 3.112 Pt g·t^{-1} and 2.095 g·t^{-1} Pd. The results summarized in Table 1 revealed that the recycling of same quantity of PGMs as from the ore processing significantly reduced the emission potential.

As can be seen that the size reduction using Gyratory mill followed by fine grinding through the ball milling yielded a 1.63 t CO_2-e without any water use (refer Table 1). Moreover, considering the zero-reagent cost in bio-cyanide destruction process in comparison to a chemical process that consumes about 67−3202 kWh·kg^{-1} energy is found to be an added advantage of the present study. The reduction of a large GHGs to the environment demonstrates a direct benefit of the recycling process for PGMs' recovery from the exhausted catalysts.

Table 1. Comparing the energy and water consumption, and CO_2-e emission in the primary production of PGMs and their recycling from the quantity accumulated in catalysts waste.

PGMs' primary Production, Moz		Primary production standard data		
		g·t^{-1}	CO_2-*e*, t·kg^{-1} PGM	Water use, m^3·kg^{-1}
Pt	6.9	3.112	39.4	391.5
Pd	9.2	2.095		
PGMs' quantity in catalyst, Moz		PGMs' in ore	$^{a+b}$Total CO_2-*e*, t	^{a}Water use, million m^3
Pt	2.4	3.112	10.8×10^6	107.6
Pd	7.3	2.095		
Recycled PGMs' in ECC, Moz		PGMs' in ECC	$^{c+d}$Total CO_2-*e*, t	^{d}Water use, million m^3
Pt	2.4	756	1.63	0
Pd	7.3	367.5		

a = mining; *b* = milling; *c* = pulverization + ball milling; *d* = no mining activity involved; ECC = exhausted catalytic converter

4 Conclusions

The example herein used not only demonstrate the applicability of an eco-friendly microbial activity to bio-cyanide production followed by bio-destruction of residual cyanide but also the application of a phosphonium ionic-liquid in Pt-Pd separation with its regeneration and reuse potentials. Toxicity analysis of the leached residue and limiting GHGs' emission to a significantly low-value (1.63 t CO_2-*e*) in comparison to the primary PGMs' production (emitting 10.8×10^6 t CO_2-*e* for mining and milling activities) demonstrated the greener path of this recycling process. Consequently, the use of highly toxic chemicals (like cyanide and aqua-regia), a high-cost of CN^- destruction using traditional (chemical) treatment processes, high volume of effluent discharge, application of volatile and toxic organic solvents, and emission of GHGs from the mining activities of primary ores can be eliminated, which are essentially remained integral with the conventional metallurgy of precious metals.

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