



Review

Catalytic potential of selected metal ions for bioleaching, and potential techno-economic and environmental issues: A critical review



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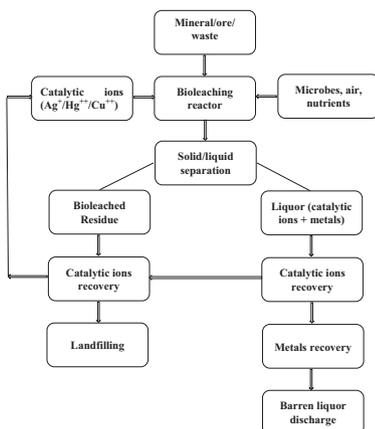
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HIGHLIGHTS

- Use of selected metal ions for promoting the bioleaching efficiency is summarized.
- The reaction mechanisms of each metal ion is described.
- Key techno-economic and environmental challenges are discussed.
- Future prospects for metal ion catalyzed bioleaching processes are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Bioleaching is considered to be a low-cost, eco-friendly technique for leaching valuable metals from a variety of matrices. However, the inherent slow dissolution kinetics and low metal leaching yields have restricted its wider commercial applicability. Recent advancements in bio-hydrometallurgy have suggested that these critical issues can be successfully alleviated through the addition of a catalyst. The catalyzing properties of a variety of metals ions (Ag^+ , Hg^{2+} , Bi^{3+} , Cu^{2+} , Co^{2+} etc.) during bioleaching have been successfully demonstrated. In this article, the role and mechanisms of these metal species in catalyzing bioleaching from different minerals (chalcopyrite, complex sulfides, etc.) and waste materials (spent batteries) are reviewed, techno-economic and environmental challenges associated with the use of metals ions as catalysts are identified, and future perspectives are discussed. Based on the analysis, it is suggested that metal ion-catalyzed bioleaching will play a key role in the development of future industrial bio-hydrometallurgical processes.

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1. Introduction

Bioleaching is a low-cost, green technology for leaching metals from a variety of minerals and waste materials (Zeng et al., 2016). Bioleaching has several advantages compared to conventional hydrometallurgy (the leaching of metals with acids or bases) or pyrometallurgy (the leaching of metals using thermal treatment), which have high energy requirements, require a large amount of chemicals, and also produce high levels of environmental pollution (Zeng et al., 2013). Currently, a significant portion of many minerals/ores are processed at industrial scale using bioleaching (Walting, 2015). For example, approximately 20–25% of the world's total copper (Cu) is produced using bioleaching (Brierley, 2008). A number of successful commercial bioleaching operations exist worldwide, and a Cu bioleaching plant (Morenci mine, USA) with a capacity of up to 230,000 tonnes/year is currently operational (Panda et al., 2015a).

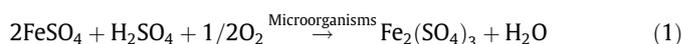
Although bioleaching offers many advantages, the relatively slow dissolution kinetics and low metal leaching yield are critical factors that hinder its large-scale application. For example, laboratory bioleaching experiments may last for more than 300 days in order to obtain reasonable metal extraction efficiencies (Munoz et al., 2007), and in large industrial operations such as Cu²⁺ bioleaching, some researchers have taken up to 900 days to obtain a Cu yield of just 60% (Clarke et al., 2006). Therefore, research efforts have been directed towards improving the efficiency of the bioleaching process by improving process dissolution kinetics and metal leaching yields.

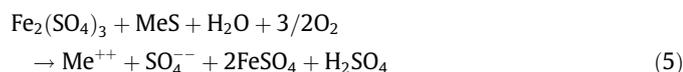
The rate of reaction and bioleaching yield may be improved considerably by the addition of suitable catalysts. A 'catalyst' is a substance that lowers the activation energy and thereby increases the rate of reaction. A variety of metal ions (Ag⁺, Hg²⁺, Bi³⁺, Cu²⁺, Co²⁺, etc.) and non-metallic catalysts (activated carbon, light illumination, waste newspapers, polyethylene glycol, etc.) have been used to improve bioleaching efficiency (Ballester et al., 1990; Liu et al., 2015; Niu et al., 2015; Panda et al., 2015a; Zhou et al., 2015). However, the use of metal ions as a catalyst has gained most attention, as non-metallic catalysts have produced relatively poor bioleaching yields of as low as 12.5% (Zhang et al., 2016) and also require large amounts of catalysts of up to 2500 g/kg of ore (Dong et al., 2013) to obtain significant leaching yields. In comparison, metal ions have excellent catalytic properties and therefore it is expected that in future, metal ions will have a significant influence on the development of a suitable bioleaching process at commercial scale.

Previous review articles on bioleaching have primarily dealt with the fundamentals and mechanism of bioleaching (Donati et al., 2016), the microorganisms involved and the types of minerals bioleached (Krebs et al., 1997; Panda et al., 2015b; Donati et al., 2016), and the mineral-microbial interaction (Diao et al., 2014). However, to date, the role and potential of metal ions in promoting bioleaching efficiency has not been reported. Since the application of microbial-assisted bioleaching is emerging, and to date, no systematic review has addressed the potential of metal ions as catalysts in bioleaching, the aim of this paper is to (1) identify the metal ions which have the potential in catalyzing bioleaching of different ores/minerals/waste/end-of-life materials (2) describe the role and catalytic mechanism of these metal ions and how they improve the bioleaching efficiency of minerals/ores/waste/end-of-life materials (3) select the most appropriate metal ion for particular ores/minerals (4) evaluate the different techno-economic issues and environmental challenges associated with the use of these metal ions, which need to be overcome before the process may be applied on an industrial scale. This information will assist metallurgists in understanding the catalytic properties of metal ions for improving the efficiency of the bioleaching process.

2. Bioleaching mechanisms and microorganisms involved

Bioleaching involves extraction of metals from mineral ores using biological means (Karthikeyan et al., 2015). A wide variety of microorganisms such as chemolithoautotrophic bacteria, heterotrophic bacteria, archaea and fungi, play an important role in bioleaching (Panda et al., 2015b). Chemoautotrophic bacteria such as *Acidithiobacillus thiooxidans* (*At. thiooxidans*) and *Acidithiobacillus ferrooxidans* (*At. ferrooxidans*) are the most dominant and industrially used microorganisms to extract the metals from ore and minerals (Feng et al., 2016). Bioleaching microorganisms derive the energy required for their growth from the oxidation of ferrous iron and reduced (inorganic) sulfur compounds in acidic environments. During bioleaching, microorganisms catalyze the oxidation of ferrous iron (Fe²⁺) and reduced sulfur compounds as per Eqs. (1) and (2). The oxidation of Fe²⁺ and reduced sulfur compounds lead to the generation of biologically produced ferric ion (Fe³⁺) and sulfuric acid (H₂SO₄), respectively (Ma et al., 2017). The generated H₂SO₄ and/or Fe³⁺ act as oxidants and oxidize the metal sulfides (redoxolysis) and/or solubilize the metal sulfides and oxides as per Eqs. (3–5).





Species of *Acidithiobacilli* thrive in acidic conditions (pH 0.5–3) and are also tolerant of high concentrations of a variety of metal ions present in different leaching environments. Besides chemoautotrophic bacteria, heterotrophic bacteria and fungi have also been used for the treatment of non-sulfides and oxide materials. However, in these cases, metal leaching is performed as a result of production of organic acids and complexing compounds secreted into the system (Vakilchah et al., 2016). A detailed overview of the different microorganisms involved in various bioleaching environment is provided by Krebs et al. (1997) and Panda et al. (2015b), amongst others.

3. Bottlenecks in bioleaching process

In recent years, the mining industry has made significant efforts to develop eco-friendly and low cost bio-hydrometallurgical operations (Walting, 2015). However, certain bottlenecks still exist which hinder its wider commercial applicability. The process kinetics are currently much too slow for it to be economical. Longer periods of operation are required compared to traditional methods of leaching to obtain reasonable yields (Clarke et al., 2006). For example, Cerda and Ohlbaum, (2008) reported 65–80% Cu recoveries from chalcocite and covellite after a bioleaching time of up to 500 days in industrial operations. Laboratory-scale experiments, performed in column reactors under mesophilic conditions, also found that more than 300 days of bioleaching was required to obtain 7.3–27.1% of Cu recovery from enargite and covellite-rich composites (Lee et al., 2015). Further, the efficiency of the process is affected by atmospheric conditions and slight changes in parameters such as temperature can adversely affect the process efficiency (Karimi et al., 2010). In addition, with industrial wastes

(such as spent batteries), bioleaching is mostly conducted with low pulp density i.e. 1% w/v (Zeng et al., 2013). The process efficiency decreases at higher pulp density due to the presence of alkaline wastes or metal toxicity to leaching microorganisms (Niu et al., 2015). The maintenance of optimum particle size in the reactor is another concern, as the presence of very fine particles (<25 μm) can negatively impact the activity of cells due to attrition caused by increased particle-particle collision (Nemati et al., 2000).

4. Role and catalytic mechanism of metal ion in bioleaching

Different materials have been reported to catalyze the bioleaching through varying modes of action (Table 1). Generally, physical, chemical and electrochemical processes are involved in the dissolution of minerals in aqueous solutions. In the case of physical processes, there is no chemical transformation and salts are water soluble. The dissolution of NaCl in water is such an example. In chemical processes, the crystalline solid is insoluble in water, but becomes soluble in the presence of a certain ion in solution. Chemical dissolution of minerals proceeds in two steps: (1) a physical process which establishes an equilibrium between the aqueous phase and mineral solids, and (2) a chemical reaction (in the vicinity of the solid) between the ions that just left the solid and the reagent present in the aqueous phase. The third process involved in the dissolution of minerals is electrochemical leaching. These are coupled redox reactions, which change the oxidation state of the minerals and accelerates the dissolution in the leaching medium (Habashi, 1983). Among these processes of mineral dissolution, the electrochemical mechanism is well established and considered to be the most important. Habashi (1983) postulated that the electrochemical mechanism of sulfide dissolution is affected by the presence of certain ions in solution, which, as they come into contact with the surface of the solid, modify its electrochemical behavior and catalyze the dissolution of sulfides in the leaching medium. Ballester et al. (1990, 1992) also suggested that dissolution of different metals from mineral sulfides can be promoted by the addition of soluble external ions. These metal ions cause the formation of a metal sulfide, which dissolves the original sulfide mineral either by galvanic action or substitution in crystal lattice. However, the catalyze effect of a particular metal ion during leaching will be different for each mineral/ore. This is due to fact

Table 1
Different catalytic agents reported for enhancing bioleaching efficiency.

Catalytic agents	Microorganisms	Conc. of the catalyst (g catalyst/kg of ore)	Reaction time (Day)	Yield (%)	Ore/Minerals	References
Activated carbon	<i>At. ferrooxidans</i>	0–625	19	42 (Cu)	Chalcocopyrite concentrate	Nakazawa et al. (1998)
Activated carbon	<i>At. ferrooxidans</i> , <i>At. thiooxidans</i>	12	25	79 (Cu)	Copper sulfide ores	Zhang and Gu (2007)
Activated charcoal	<i>At. thiooxidans</i> , <i>At. ferrooxidans</i>	80	16.7	86 (Cu)	Mine tailings	Nguyen and Lee (2014)
Activated carbon	<i>At. ferrooxidans</i> , <i>At. thiooxidans</i> , <i>L. ferrooxidans</i>	10	18	90.8 (Co)	Cobalt ore	Liu et al. (2015)
Ag ⁺	<i>At. ferrooxidans</i>	6.7	30	93 (Cu)	Chalcocopyrite-molybdenite	Abdollahi et al. (2015)
Cu ⁺⁺	<i>At. thiooxidans</i> , <i>L. ferriphilum</i>	8.0	13	62.5 (Zn), 62.4 (Mn)	Spent Zn-Mn batteries	Niu et al. (2015)
Cysteine	<i>A. caldus</i>	10	19	25 (Cu)	Ni-Cu sulfide	He et al. (2009)
Cysteine	<i>A. brierleyi</i> , <i>A. manzaensis</i> , <i>M. sedula</i> JCM, <i>S. metallicus</i> JCM	10	16	81.4 (Cu), 83.7 (Ni)	Ni-Cu sulfide	Li et al. (2014)
Quartz	<i>At. ferrooxidans</i> LD-1	2500	32	53.5 (Cu)	Chalcocopyrite	Dong et al. (2013)
Sodium chloride	<i>A. manzaensis</i> YN-25	66	10	82 (Cu)	Chalcocopyrite	Chang et al. (2012)
Waste newspaper	<i>At. ferrooxidans</i>	20	6	99.13 (Cu)	Chalcocopyrite	Panda et al. (2015a)
Polyethylene glycol	<i>At. ferrooxidans</i>	9	21	12.5 (Cu)	Chalcocopyrite	Zhang et al. (2016)

Table 2
Metal ions used as catalyst in different bioleaching studies.

Metal ion	Salt	Conc. (g catalyst/kg of ore)	Reaction time (Day)	Bioleaching yields (%)			Ore	References
				Cu	Zn	Co		
Ag ⁺	Ag ₂ SO ₄	2	16.7	90	84		Complex sulfide	Ballester et al. (1990)
Ag ⁺	Ag ₂ SO ₄	0.2	21	60			Complex sulfide	Ballester et al. (1992)
Ag ⁺	AgNO ₃	6.7	30	93			Chalcopyrite-molybdenite	Abdollahi et al. (2015)
Ag ⁺	Ag ₂ SO ₄	1.0	180	44.4			Low grade copper ore	Munoz et al. (2007)
Ag ⁺	AgNO ₃	2	7			98.4	Spent lithium batteries	Zeng et al. (2013)
Hg ⁺⁺	HgSO ₄	2	16.7	32.5	59		Sphalerite/complex sulfide	Ballester et al. (1990)
Hg ⁺⁺	HgSO ₄	0.2	21	23			Complex sulfide	Ballester et al. (1992)
Hg ⁺⁺	HgSO ₄	0.8	22	58	85		Complex sulfide	Escudero et al. (1993)
Bi ⁺⁺⁺	Bi(NO ₃) ₃	2.0	16.7	28	78.4		Sphalerite/complex sulfide	Ballester et al. (1990)
Bi ⁺⁺⁺	Bi(NO ₃) ₃ ·5H ₂ O	0.2	21	18			Complex sulfide	Ballester et al. (1992)
Cu ⁺⁺	CuSO ₄ ·5H ₂ O	75	10			99.9	Spent lithium ion batteries	Zeng et al. (2012)
Cu ⁺⁺	CuSO ₄ ·5H ₂ O	8.0	13		62.5		Spent Zn-Mn batteries	Niu et al. (2015)
Co ⁺⁺	CoSO ₄ ·7H ₂ O	2	16.7	55	90.5		Complex sulfide	Ballester et al. (1990)

that different mineral sulfides have different rest potentials (mV), which will impact the galvanic interaction between the metal ion catalyst and mineral solids. In addition, each metal ion poses a unique ability to activate the particular mineral sulfide surface, displacing the ions from the target mineral solid.

The first study on the catalytic effects of metal ions in the leaching medium (without bacteria) was conducted by Scott and Dyson (1968), who studied the effect of various metal ions on the dissolution kinetics of ZnS. Further studies were conducted by Mulak (1987), who examined the catalytic effect of Cu⁺, Cu⁺⁺ and Fe³⁺ during HNO₃ leaching of synthetic Ni₃S₂, and observed that these metal ions catalyzed the dissolution of mineral solids by several orders of magnitude. Since then, several studies on the catalytic effect of metal ions on the dissolution of metals in the leaching medium have been reported in the literature (both in the presence of microorganisms – bioleaching – and without microorganisms). The first of these bioleaching studies was reported by Mcelroy and Duncan (1974), who found that the addition of small quantities of Ag⁺ during chalcopyrite bioleaching with *At. ferrooxidans* dramatically enhanced the Cu leaching yield as opposed to without Ag⁺.

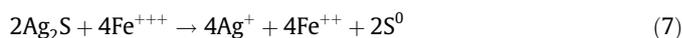
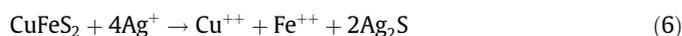
5. Catalytic role and mechanisms of different metal ions

5.1. Role of Ag⁺

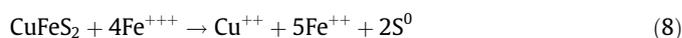
A variety of metal ions such as Ag⁺, Hg⁺⁺, Bi⁺⁺⁺, Cu⁺⁺, Co⁺⁺, etc. have been used successfully as catalysts in various bioleaching studies (Table 2). Among these metal ions, Ag⁺ has received the most attention. Different Ag compounds such silver sulfate (Ag₂SO₄), silver nitrate (AgNO₃) and silver chloride (AgCl), have been used as a source of Ag⁺ in the bioleaching medium. Although Ag⁺ has been found to be efficient in enhancing the dissolution kinetics and leaching yields of metals from a wide variety of minerals and matrices, the majority of these bioleaching studies using Ag⁺ have been reported for Cu-bearing ore and/or minerals such as chalcopyrite (Kuwazawa and Miura 2012; Abdollahi et al., 2015). Bioleaching of chalcopyrite (the principal source of Cu in the mining industry) is difficult due to the formation of secondary solid phases and jarosite-type precipitates, which contribute to surface passivation (Feng et al., 2015; Panda et al., 2015b). The role of Ag⁺ during chalcopyrite bioleaching is to form a film of silver sulfide (Ag₂S) on the chalcopyrite surface, which alleviates the surface passivation through the formation of a less tenacious and more porous layer of elemental sulfur (S⁰). The new film, therefore, improves the semi-conductor properties of chalcopyrite, and facilitates the electronic transfer to the oxidant. The presence of Ag₂S in

the bioleached chalcopyrite has been confirmed through X-ray diffraction by Hu et al. (2002) (Suppl. Fig. A1). Scanning Electron Microscopy (SEM) micrographs have shown the formation of Ag₂S precipitates on the chalcopyrite surface (Abdollahi et al., 2014) (Suppl. Fig. A2).

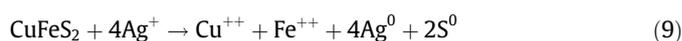
Ag⁺ initially forms Ag₂S on the chalcopyrite surface, followed by Fe⁺⁺⁺ mediated oxidation:



The silver ion recirculates between the solution and solid phase reactions, and the overall sum of the chalcopyrite reaction yields elemental S:



Elemental Ag can also form during the process:



The role of bioleaching bacteria in this process is to oxidize the Fe⁺⁺ into Fe⁺⁺⁺, which oxidizes the Ag₂S film.

The first report on the catalytic effect of Ag⁺ during bioleaching was published as a US patent developed by the researchers at the British Columbia Research Council (Mcelroy and Duncan, 1974). In this patent, it was reported that during bioleaching with *At. ferrooxidans*, the addition of only 0.5 g Ag⁺/kg of ore promoted the Cu yield to 88% compared to 50% without Ag⁺. It was also found that instead of soluble silver salts, insoluble salts such as Ag₂S can also be used. However, the quantity of Ag⁺ required to achieve a significant increase in bioleaching yield will be relatively higher using Ag₂S (0.700–7.0 g Ag⁺/kg of chalcopyrite concentrate).

Since, Ag⁺ salts are expensive, researchers also tried to use other forms of Ag in order to develop a cost-effective bioleaching process. Hu et al. (2002) conducted bioleaching using Ag-concentrate and found that addition of 20 g Ag-concentrate/kg of ore dramatically increased the Cu yield to 67% compared to only 24.3% without using Ag-concentrate. The promising results achieved using relatively cheaper Ag-bearing concentrates suggested that the industrial application of the Ag-catalyzed process can be enhanced using a cheaper source of Ag.

Most of these initial studies using Ag⁺ as catalysts were conducted using mesophilic bacteria such as *At. ferrooxidans*, *At. thiooxidans* and *Leptospirillum ferrooxidans* (*L. ferrooxidans*). However, it has been reported that rate of bioleaching in different minerals by thermophile and moderate thermophiles is higher than mesophiles due to faster reaction kinetics. To harness the higher

kinetics, Ag⁺-catalyzed bioleaching was also explored with moderate thermophilic and thermophilic microorganisms. Gomez et al. (1999) used shake flask bioleaching with mixed moderate thermophilic bacteria, and reported that the Cu yield increased three-fold in the presence of 0.1–0.5 g Ag⁺/kg compared to without the addition of Ag⁺. Moreover, the catalyzing effects of Ag⁺ were higher in moderate thermophilic bioleaching compared to mesophilic bioleaching (Abdollahi et al., 2015). Gomez et al. (1999) reported that in the presence of Ag⁺ it took only 5 days of moderate thermophilic bioleaching to obtain about 90% Cu yield from chalcopyrite-molybdenite concentrate, whereas it took more than 10 days to achieve a similar Cu yield with mesophilic bioleaching. In addition, relatively smaller amounts of Ag⁺ (0.77 g Ag⁺/kg of ore) were required to obtain a similar Cu yield using moderate thermophilic bioleaching compared to mesophilic bioleaching (6.7 g Ag⁺/kg of ore). Similar findings were observed by Abdollahi et al. (2014) in the case of Ag⁺-catalyzed thermophilic bioleaching, who found that 75% Cu was leached from the concentrate compared to only 27% with mesophilic temperatures. The reasons for the different effects of catalyst at different temperatures were not explained in these bioleaching studies. However, in the case of Ag⁺-catalyzed chemical leaching (without bacteria) a number of factors such as higher solubility of silver complex, higher regeneration of Ag₂S by Fe³⁺ and reduced jarosites precipitation, were found to be responsible for higher leaching yield (Guo et al., 2011). Further studies are required to understand the mechanism and biochemical aspects of catalyst-based bioleaching at different temperatures.

Most of the initial bioleaching studies using Ag⁺ were conducted in shake flasks. However, the type of reactor may play an important role, as process efficiency may suffer in large reactors such as columns due to the restriction of gas transfer in the columns (static system) compared to shake flasks and stirred reactors (agitated types) (Munoz et al., 2007). Nevertheless, column studies give useful information on the effect of different variables on bioleaching process for long periods of time and under conditions close to those found in heap leaching practice. Munoz et al. (2007) investigated the effectiveness of Ag⁺-catalyzed bioleaching process in a stirred reactor and column reactors for treating low-grade Cu ore. They found that the addition of 7.1 g of Ag⁺/kg of ore in the stirred tank yield 89.3% of Cu compared to 28% without Ag⁺. Similarly, in the column reactor, they found that at different concentrations of Ag⁺, the Cu recovery was at least double that in the absence of Ag⁺ (30%). Moreover, the particle size of ore was an important parameter and use of smaller ore size favors the higher bioleaching yield due to relatively higher surface area of the ore. Therefore, during silver-catalyzed bioleaching, the cost of crushing to finer size versus Cu yield have to be evaluated to determine an optimum particle size (Munoz et al., 2007).

Although the majority of studies using Ag⁺ as a catalyst were conducted with Cu-bearing minerals and ore, researchers also exploited the catalytic properties of Ag⁺ for treating materials other than Cu. For instance, Guo et al. (2011) tested the process effectiveness with the As-bearing mineral, realgar (As₂S₂), using both mesophilic (*At. ferrooxidans*) and thermophilic *Sulfobacillus sibiricus* (*S.s.*) and observed that in the absence of Ag⁺, very little As₂S₂ was leached during bioleaching with either *At. ferrooxidans* (0.2–0.5%) or *S.s.* (1.5–2.2%). On the contrary, the addition of Ag⁺ enhanced the dissolution of As to 24.4% and 15.3% using *At. ferrooxidans* and *S.s.*, respectively.

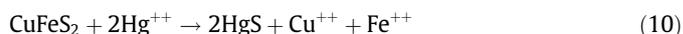
As Ag is a potentially toxic metal (David et al., 2008), the addition of Ag⁺ during bioleaching has been reported to cause a decrease in the bacterial growth rate and subsequent iron-oxidation rate. To overcome this problem, a process in which corn steep liquor (CSL) is added along with Ag⁺, was recently patented (Kuwazawa and Miura, 2012). The authors reported that CSL acted as a source of organic nitrogen to the leaching media and due to its

addition, the iron-oxidizing capacity of iron-oxidizing bacteria was improved. This caused a significant improvement in the leaching yield of Cu. It was found that the addition of 10 mg/L of Ag⁺ and 0.1 g/L of CSL led to dissolution of more than 80% of Cu as compared to less than 10% in the absence of Ag⁺. They also observed that CSL can either be added as an immersion solution or as powder.

However, until recently, the catalytic use of Ag⁺ was limited to treat natural mineral and ores. In a recent study, it was reported that the bioleaching yield of industrial waste material and end-of-life products such as spent lithium batteries, can also be improved by the addition of Ag⁺ (Zeng et al., 2013). It was observed that the addition of only 2.0 g of Ag⁺/kg of ore with *At. ferrooxidans*, led to dissolution of 98.4% Co. In the absence of Ag⁺, the leaching yield of Co was only 43.1%. Zeng et al. (2013) found that the catalytic role of Ag⁺ involved promoting the formation of the AgCoO₂ intermediate. This intermediate AgCoO₂ was oxidized by bioproduced Fe³⁺, resulting in higher yield of Co. The role of the bacteria is to oxidize the Fe²⁺ back to Fe³⁺. Chen and Lin (2009) also utilized the catalyzing property of Ag⁺ for decontamination of riverine sediments that were contaminated with different metals (Cu, Ni, Zn, Pb and Mn). In this study, a higher pH reduction rate was observed during bioleaching with Ag⁺. This resulted in the short lag phase and high metal yield during bioleaching as opposed to without Ag⁺. The best results were achieved by the addition of 1.5 g of Ag⁺/kg of sediment, beyond which a decrease in leaching rate constant for these metals was observed.

5.2. Role of Hg⁺⁺

Although Hg⁺⁺ is considered to be extremely hazardous in the natural environment, its catalytic properties have been exploited by many researchers to improve bioleaching kinetics. Ballester et al. (1990) was perhaps one of the first researchers to report the catalytic effects of Hg⁺⁺ during bioleaching of the complex sulfide concentrate (FeS₂, CuFeS₂, ZnS and PbS) using *At. ferrooxidans*. Their study suggested that the addition of 2 g Hg⁺⁺/kg of concentrate (in the form of HgSO₄) during bioleaching enhanced the dissolution of Cu to 80% compared to only 25% without Hg⁺⁺ from the complex sulfide concentrate. These authors speculated that the catalytic effect of Hg⁺⁺ was due to its tendency to replace the Cu from the sulfide lattice. The sulfide formed as a result of the displacement reaction on the surface of the complex sulfide concentrate, acted as a cathode with respect to the chalcopyrite, leading to the rapid dissolution of the mineral chalcopyrite. The changes in chalcopyrite surface during Hg⁺⁺ catalyzed bioleaching were examined using SEM and auger electron spectroscopy (AES) (Gomez et al., 1997). They reported that Hg⁺⁺ were incorporated onto the mineral surface and formed a thin coating of HgS. The standard Gibb's energy (ΔG⁰r) calculated for the reaction between chalcopyrite and Hg⁺⁺ has also shown that the formation of HgS is thermodynamically possible. The mechanism through which Hg⁺⁺ catalyzes bioleaching is presented in Eqs. (10)–(12). As per reaction mechanism, Hg⁺⁺ first reacts with chalcopyrite and produces a thin coating of HgS.



The produced HgS can be easily dissolved by bioproduced Fe⁺⁺⁺, which also leads to the regeneration of Hg⁺⁺.



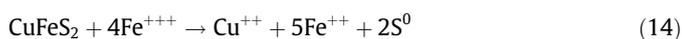
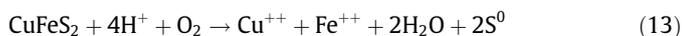
The produced Fe⁺⁺ is oxidized to Fe⁺⁺⁺ by leaching bacteria, which is recirculated in the leaching media.



Ballester et al. (1992) further argued that the concentration of Hg^{++} is an important parameter that determines the efficiency of the bioleaching process. By employing different concentrations of Hg^{++} ranging from 0.04 to 1 g Hg^{++}/kg of ore, they found that 0.2 g Hg^{++}/kg of ore was the optimum Hg^{++} concentration for enhancing the bioleaching yields of Cu and Zn from the complex sulfide. Moreover, using 0.2 g Hg^{++}/kg of ore, the bioleaching period was also shortened to about 8 days compared to 21 days for the non- Hg^{++} inoculated bioleaching experiment to achieve a similar Cu yield (20%). These authors also postulated that a too low Hg^{++} concentration (0.04 g Hg^{++}/kg of ore) during bioleaching may not induce desired changes, whereas a concentration beyond 0.2 g Hg^{++}/kg of ore may not further improve the dissolution kinetics. This is due to the fact that at higher concentrations, the Hg^{++} may impart toxicity to mesophilic *Acidithiobacilli*, which can suppress the leaching. The toxic effects of Hg^{++} are more pronounced with thermophilic archaea (*Sulfolobus* sp.), which poses less resistance to metal toxicity compared with mesophilic microorganisms. The toxic effect of Hg^{++} at higher concentration during bioleaching was also highlighted by Escudero et al. (1993), who confirmed that 0.1 g Hg^{++}/kg of ore is the optimum concentration at which Hg^{++} successfully enhanced the Cu yield from complex sulfide to 58% compared to only 29% using 2.0 g Hg^{++}/kg of ore. Besides Cu leaching, the addition of Hg^{++} has also been shown to promote the simultaneous dissolution of Zn from complex sulfide, and about 85% of Zn was leached in the presence of 0.1 g Hg^{++}/kg of ore compared to 65% without Hg^{++} . Moreover, the dissolution kinetics (250 h instead of 400 h) were greatly improved for achieving similar leaching of Zn (65%).

5.3. Role of Bi^{+++}

Along with Ag^{++} and Hg^{++} , the catalytic properties of Bi^{+++} during bioleaching were also first documented by Ballester et al. (1990). In their study on bioleaching of sphalerite and complex sulfide concentrate using *At. ferrooxidans*, the authors observed that the addition of Bi^{+++} as $\text{Bi}(\text{NO}_3)_3$ had an catalyzing effect on Zn dissolution from sphalerite and about 78.4% of Zn was bioleached in the presence of Bi^{+++} compared to only 50% without it. The catalytic effect of Bi^{+++} was explained on the basis of its tendency to influence electrochemical dissolution process, so that it added the anodic behavior of the mineral. In another study, Mier et al. (1994) observed that the role of Bi^{+++} during bioleaching was to suppress the formation of phosphate compounds of Fe^{3+} , which otherwise precipitate in the leaching medium. This results in higher availability of free Fe^{3+} and, therefore, higher oxidizing properties during bioleaching, which are helpful in dissolution of Cu from chalcopyrite. The mechanism through which Bi^{+++} catalyzes the chalcopyrite bioleaching is presented in Eqs. (13)–(15) (Mier et al., 1994). Eq. (13) is purely a chemical reaction, whereas Eq. (14) becomes prominent when bacterial growth takes place. The role of bioleaching bacteria in this process is to oxidize the Fe^{++} and S^0 into Fe^{+++} and H_2SO_4 , respectively. The produced Fe^{+++} oxidizes the chalcopyrite, whereas H_2SO_4 maintains the acidity of the leaching medium.



The role of Bi^{+++} is to combine with PO_4^{3-} and prevent the possible formation of ferric phosphate precipitates (FePO_4 , FeHPO_4 , etc.), which otherwise precipitate in the leaching medium and reduce the oxidation potential of $\text{Fe}^{+++}/\text{Fe}^{++}$ couple.

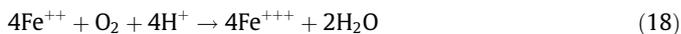
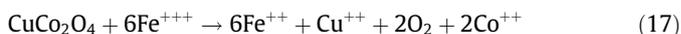
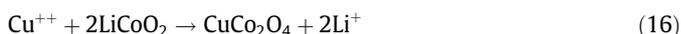


However, it has also been reported that the addition of Bi^{+++} during mesophilic bioleaching increased the bioleaching rate of both chalcopyrite and sphalerite, but not the final leaching yield (Ballester et al., 1992). The catalytic role of Bi^{+++} has also been investigated by these researchers during thermophilic bioleaching of chalcopyrite. It was reported that the addition of Bi^{+++} enhanced the Cu yield to 90% compared to 80% without it and that the presence of Bi^{+++} also promoted bacterial growth (Ballester et al., 1992).

5.4. Role of Cu^{++}

Many researchers have tested the catalytic properties of Cu^{++} during bioleaching due to its relatively cheaper cost and easy availability. Chen et al. (2008) used Cu^{++} as a catalyst for treating a Zn containing mineral 'marmatite'. It was reported that in the presence of 5 g Cu^{++}/kg of ore, about 73% Zn was leached compared to 65% without Cu^{++} . The enhanced leaching yield of Zn was attributed to the electrochemical effect of Cu^{++} on bioleaching. It was postulated that during bioleaching, some Cu^{++} substitutes Zn^{++} and bonded the crystal lattice of marmatite. The CuS formed during bioleaching shows higher electrode potential and improves the conductivity of the mineral surface, so Zn dissolves preferentially as an anode. In addition, iron sulfide, elemental sulfur and jarosite were formed on the marmatite surface during bioleaching. These products formed a passivated layer, which suppressed the bioleaching process. The Cu^{++} catalyzed the bio-oxidation of S^0 , which eliminated the barrier and led to the increased bioleaching of marmatite.

In addition to promoting the bioleaching efficiency of natural ores and minerals, Cu^{++} may also be effective in assisting the bioleaching of an industrial end-of-life waste material such as spent lithium-ion batteries (Zeng et al., 2012). Zeng et al. (2012) reported that almost 99.9% of Co present in a sample was bioleached in the presence of 75 g of Cu^{++}/kg of ore after 10 days of bioleaching, whereas only 43.1% of Co was bioleached in the same period of time without Cu^{++} . The catalytic action of Cu^{++} was due to the formation of an intermediate product (CuCo_2O_4) on the LiCoO_2 surface as a result of cationic exchange reactions. This intermediate CuCo_2O_4 was easily dissolved by bio-produced Fe^{+++} , leading to the higher bioleaching yield of Co as per Eqs. (16)–(18).



The changes in the particle size and morphology of bioleached residues in the presence of Cu^{++} are presented in Fig. A3 (suppl.).

Besides spent lithium-ion batteries, spent Zn-Mn batteries have also been treated successfully in the presence of Cu^{++} . Niu et al. (2015) reported that the Cu^{++} has the ability to enhance the dissolution kinetics of Zn and Mn from spent Zn-Mn batteries. Moreover, this process can be performed at a higher pulp density (10%), which may enhance the industrial application of the process. It was also reported that the leaching kinetics followed the chemical reaction-controlled model. While conducting bioleaching in the presence of 8 g Cu^{++}/kg of ore, the leaching yield of Zn increased to 62.5% compared to 47.7% without Cu^{++} . Similarly, the bioleaching yield of Mn also increased to 62.4% compared to 30.9% without Cu^{++} . It was observed that the Cu^{++} formed a possible intermediate CuMn_2O_4 , which was oxidized by bio-produced Fe^{3+} .

Table 3
Operating conditions reported for metal ion catalyzed bioleaching.

Metal ions	Salt	Conc. of the catalyst (g/kg)	Medium pH	Pulp density (%)	Temp. (°C)	Materials bioleached	References
Ag ⁺	AgNO ₃	0–1	2.5	10.67	35	Chalcopyrite	Mcelroy and Duncan (1974)
Ag ⁺	Ag ₂ SO ₄	2	2.0	5	35	Sphalerite/Complex sulfide	Ballester et al. (1990)
Ag ⁺	AgNO ₃	0.2–20	2.0	1	35	Spent lithium batteries	Zeng et al. (2013)
Ag ⁺		4	2.0	0.5	35	Realgar	Guo et al. (2011)
Ag ⁺		0.1	2.0	2	30	Arsenopyrite	Fang et al. (2014)
Ag ⁺	AgNO ₃	0–33.3	1.6	3.0	32	Chalcopyrite-Molybdenite	Abdollahi et al. (2015)
Hg ⁺⁺	HgSO ₄	2	2.0	5	35	Sphalerite and Complex sulfide	Ballester et al. (1990)
Hg ⁺⁺	HgSO ₄	0.8	2.0	5	35	Complex sulfide	Escudero et al. (1993)
Bi ⁺⁺⁺	Bi(NO ₃) ₃	2	2.0	5	35	Sphalerite and Complex sulfide	Ballester et al. (1990)
Bi ⁺⁺⁺	Bi(NO ₃) ₃ ·5H ₂ O	10		1	35	Copper-sulfide concentrate	Mier et al. (1994)
Cu ⁺⁺	CuSO ₄ ·5H ₂ O	75	2.9	1	35	Spent lithium-ion batteries	Zeng et al. (2012)
Cu ⁺⁺	CuSO ₄ ·5H ₂ O	8	1.0	10	35	Spent Zn-Mn batteries	Niu et al. (2015)
Co ⁺⁺	CoSO ₄ ·7H ₂ O	0.8	2.0	5	35	Complex sulfide	Escudero et al. (1993)

5.5. Role of Co⁺⁺

Very few studies have used Co⁺⁺ as catalytic ion in bioleaching operation, owing to its higher cost compared to Cu⁺⁺ and Bi⁺⁺⁺. Moreover, *At. ferrooxidans* is susceptible to higher concentrations of Co⁺⁺ (Mohseni et al., 2011). The catalytic properties of Co⁺⁺ were recognized in one of the earlier bioleaching studies conducted on the use of different metal ions as a catalyst. Ballester et al. (1990) reported that the addition of Co⁺⁺ in the form of CoSO₄·7H₂O significantly improved the bioleaching yield of Zn from the sphalerite concentrate. After bioleaching for 400 h with *At. ferrooxidans*, only 50% Zn could be leached from the sphalerite concentrate. The addition of 2 g Co⁺⁺/kg of ore during bioleaching enhanced the leaching yield of Zn from 50% to 68.4%. Similar findings were made by Escudero et al. (1993), who conducted bioleaching of a complex sulfide containing Cu, Pb and Zn. Bioleaching was conducted in a stirred glass reactor using a mixed culture of bacteria (*At. ferrooxidans*, *At. thiooxidans*, *L. ferrooxidans*). The results showed that the bioleaching yield of Cu was only 22% in the absence of a catalyst. However, there was a drastic increase in the Cu recovery in the presence of Co⁺⁺ and the Cu leaching yield reached to 52% compared to 22% without Co⁺⁺. A similar increase was also observed in the case of Zn, where about 92% of Zn was leached in the presence of Co⁺⁺ compared to 65% without it. The catalytic effect of Co⁺⁺ was also attributed to its electrochemical interaction with the mineral matrix, which favored the anodic behavior of the sulfides during its reaction.

6. Key challenges

Metal ion-catalyzed bioleaching offers great opportunities for the recovery of metals from a variety of minerals and ores. During bioleaching, these metal ions exhibit catalytic properties at wide range of operating conditions (Table 3). However, despite its high efficiency, to date, the process has not been developed for larger scale applications. Some of the key challenges which need to be overcome are now detailed.

6.1. Process economy

Generally, the capital costs of bio-mining operations are less than those of smelting operations. Dew et al. (1997) reported that the capital costs for a bio-oxidation plant of gold ores was about twofold lower than roasting or pressure oxidation, and that operating costs were also lower. However, operating costs of bioleaching

operations may vary depending on a number of factors such as plant location, cost of services at particular sites etc. (Du Plessis et al., 2007). Cognizance of operating costs (such as addition of catalytic ions) is therefore important, considering that most of the metal catalysts used during bioleaching are precious or economically valuable commodities. Munoz et al. (2007) concluded that Ag⁺-catalyzed bioleaching is economical and technically attractive. They reported that the cost of Ag⁺ addition per unit cost of Cu in the ore equates to only 6% of the commercial price of Cu. Evaluating the effectiveness of this process in the current scenario, the approximate price of Ag in the third quarter of 2016 (June–September 2016) is USD \$ 670/kg (NASDAQ). Similarly, the average price of Cu in the third quarter of 2016 at the London Metal Exchange (LME) is about USD \$ 4.85/kg. Therefore, the cost of Ag addition (1 g Ag/kg of Cu) per unit cost of Cu in the ore equates to 0.67 USD \$ /kg of Cu (1 g Ag × USD \$ 670/1000 g). This is equivalent to only 14% (USD \$ 0.67/USD \$ 4.85 × 100) of the current international price of Cu. A detailed analysis involving the cost of different metal catalyst added during bioleaching, their concentrations and their performance in increasing the bioleaching yield, are provided in Table 4. The cost has been calculated by considering price (in USD \$/kg) of metals catalyst (June–September 2016) as 670, 4.85, 26, 2.3, 0.018, 2.42 for Ag⁺, Cu⁺⁺, Co⁺⁺, Zn⁺⁺, Bi⁺⁺⁺ and As⁺⁺⁺, respectively (NASDAQ, LME, metalprices.com). The analyses suggest that considering the performance along with the cost, Ag⁺ and Cu⁺⁺ are the most effective catalysts among all catalysts used. Between Cu⁺⁺ and Ag⁺, Ag⁺ is preferable, as it can be used for treating wide varieties of minerals (Cu-bearing minerals, complex sulfide, spent batteries, Arsenopyrite etc.) as opposed to Cu⁺⁺, which is primarily found to catalyze only spent batteries in bioleaching. Moreover, the efficiency of Ag⁺ is better compared to Cu⁺⁺. An increase of more than 40% in the bioleaching yield of a target metal is routinely evident in most of these studies when Ag⁺ is used as a catalyst. Relatively few amounts of Ag⁺ are required to induce the desired catalytic effect. A concentration in the range of 0.5–1.0 g Ag⁺/kg of ore seems to be the optimum concentration required to catalyze a wide variety of minerals and ore. Therefore, Ag⁺ seems to be the best candidate among all catalysts, considering its cost of addition and effectiveness. Future studies should explore its effectiveness for large-scale application. However, considering its effectiveness in terms of the cost of the addition of metal ions, the process seems attractive for large-scale application, but to drive a satisfactory cost analysis of the overall process, the cost of safe disposal, recovery of metal ions from treated residue/leachate, establishment of catalyst storage facilities, acclimatization

Table 4
Comparative cost and performance of the metal ion catalysts during bioleaching.

Catalyst	Mineral/ore	Amount of catalyst (g catalyst/kg of ore)	Increment in bioleaching yield after catalyst addition (%)	Cost of catalyst addition to ore (A) in US \$ /kg of ore	Cost (%) wrt. to the price of target metal = (A/Current price of target metal in US \$ kg) x 100	References
Ag ⁺	Chalcopyrite	0.5	38 (Cu)	0.34	6.9	Mcelroy and Duncan (1974)
Ag ⁺	Complex sulfide	2.0	63.5 (Cu)	1.34	27.6	Ballester et al. (1990)
Ag ⁺	Chalcopyrite	0.32	50 (Cu)	0.21	4.42	Hu et al. (2002)
Ag ⁺	Chalcopyrite	1.0	44.4 (Cu)	0.67	13.8	Munoz et al. (2007)
Ag ⁺	Spent lithium ion batteries	2.0	55.3 (Co)	1.34	5.2	Zeng et al. (2013)
Ag ⁺	Chalcopyrite-molybdenite	6.7	40 (Cu)	4.49	92.5	Abdollahi et al. (2015)
Bi ⁺⁺⁺	Sphalerite	2.0	28.4 (Zn)	0.018	0.8	Ballester et al. (1990)
Bi ⁺⁺⁺	Chalcopyrite	10	10 (Cu)	0.09	1.9	Ballester et al. (1992)
Cu ⁺⁺	Marmatite	5.0	8 (Zn)	0.024	1.1	Chen et al. (2008)
Cu ⁺⁺	Spent lithium ion batteries	75	56 (Co)	0.36	1.4	Zeng et al. (2012)
Cu ⁺⁺	Spent zinc batteries	8.0	15 (Zn)	0.04	1.7	Niu et al. (2015)
Co ⁺⁺	Sphalerite	2.0	18.4 (Zn)	0.052	2.3	Ballester et al. (1990)
Co ⁺⁺	Complex sulfide	2.0	30 (Cu)	0.052	1.1	Escudero et al. (1993)
Co ⁺⁺	Complex sulfide	2.0	27 (Zn)	0.052	2.3	Escudero et al. (1993)

Table 5
Inhibitory concentration of catalytic ions to different bioleaching microorganisms.

Catalytic ion	Salt	Toxic concentration (mg/L)	Affecting Microorganisms	References
Ag ⁺	AgNO ₃	0.10	<i>At. ferrooxidans</i>	Tuovinen et al. (1985)
Ag ⁺	Ag ₂ SO ₄	0.2	<i>L. ferrooxidans</i>	Johnson et al. (1992)
Ag ⁺		0.9	<i>S. solfataricus</i>	Grogan (1989)
Ag ⁺	Ag ₂ SO ₄	20	<i>S. Bc</i>	Munoz et al. (1998)
Hg ⁺⁺		0.1	<i>At. ferrooxidans</i>	David et al. (2008)
Hg ⁺⁺		0.4	<i>S. solfataricus</i>	Grogan (1989)
Bi ⁺⁺⁺	Bi(NO ₃) ₃ ·5H ₂ O	9000	<i>S. BC</i>	Mier et al. (1996)
Cu ⁺⁺	CuSO ₄ ·5H ₂ O	5000	<i>At. thiooxidans, L.ferriphilum</i>	Niu et al. (2015)
Cu ⁺⁺	CuSO ₄	10,000	<i>At. ferrooxidans</i>	Das et al. (1997)
Cu ⁺⁺	CuSO ₄	3177	<i>Acidiphilum cryptum</i>	Johnson et al. (1992)
Co ⁺⁺	CoSO ₄ ·7H ₂ O	5300	<i>S. BC</i>	Mier et al. (1996)
Co ⁺⁺	CoSO ₄ ·7H ₂ O	2000	<i>L. ferrooxidans</i>	Sand et al. (1993)

of microorganisms to metal ions etc., will have to be added to the total cost. Annual maintenance and management costs will also be incurred. Hence, this process seems less costly in terms of the cost of metal ion used, but could prove equally costly in terms of overall cost of the process compared to traditional bioleaching. Unfortunately, inadequate information is available in the literature on the economic aspects of metal ion-mediated bioleaching processes, which limits the scope of a detailed cost-benefit analysis. Therefore, the economic and commercial viability of this process remains a knowledge gap which requires urgent attention.

6.2. Toxicity to leaching microorganisms

One of the major challenges associated with metal ion-catalyzed bioleaching is the possible toxic/inhibitory effects of these metal ions to bioleaching microorganisms. It has been observed that most of the metal ions used as catalysts are

potentially toxic to mesophilic *Acidithiobacilli* (David et al., 2008; Mohseni et al., 2011). The inhibitory concentrations of various catalytic ions to bioleaching microorganisms are shown in Table 5. It can be seen that the iron oxidation rate of *At. ferrooxidans* was found to be inhibited at as low as 0.1 mg/L of Ag⁺/Hg⁺⁺. In the case of Ag⁺, the inhibition has been explained through a mixed mechanism in which Ag⁺ replaces Fe⁺⁺ in the active site of the oxidizing enzyme in the bacterial cell (De et al., 1996). The accumulation of Ag on *At. ferrooxidans* cells has been confirmed during leaching of sulfide ore mineral (Fang et al., 2014). Besides Ag⁺ and Hg⁺⁺, other commonly used metal ions such as Cu⁺⁺ and Bi⁺⁺⁺ are also known to inhibit the bacterial iron-oxidation capacity (Table 5). However, their inhibitory effects are observed at comparatively higher concentrations compared to Ag⁺.

Considering these issues, the identification of an appropriate concentration of these metal ions is very important in the development of a successful bioleaching process. A low concentration of

these metal ions may not necessarily induce desirable changes, whereas a higher concentration may impart toxicity to these microorganisms. A possible solution to overcome this problem is to screen and employ those microbial species which have higher tolerance to these metal ions. Silver tolerant *Acidithiobacilli* sp. with the ability to grow in relatively higher concentration of Ag^+ , have been reported (Wu et al., 2007). Another method is to use the adapted culture which shows less inhibition in the presence of these metal ions. This can be achieved through repeated sub-culturing in progressively higher levels of these metal ions. Alternatively, the use of mutant strains produced through microwave induced mutation can yield *Acidithiobacillus* sp. with higher tolerance to metal ions (Wu et al., 2007).

6.3. Recovery of metal ions

As most of the metal ions used as catalysts during bioleaching are highly valuable commodities, their recovery at the end of bioleaching is an important consideration for improving the cost-effectiveness of the process. The major process reported for recovery of different metal species from solid residue is leaching in which a lixiviant is added to the metal-containing materials which leach the metal. On the other hand, cementation, biosorption, ion exchange, electro-winning and solvent extractions are the major techniques which have been reported for the recovery of these metals from a variety of liquid streams. Theoretically, at the end of bioleaching processes, metal ions used as catalysts may be present either in solution or left in solid residue. However, most of the studies conducted, primarily with Ag^+ have reported that Ag^+ added during bioleaching remained in the solid residue (Romero et al., 2003).

In one of these studies, Palencia et al. (1998) developed a silver catalyzed IBES process (indirect bioleaching with effect separation) and studied the recovery of the Ag^+ from the solid residue remaining after the Fe_2SO_4 leaching of a chalcopyrite–sphalerite concentrate. Their study suggested that total recovery of the Ag^+ added as a catalyst (2 mg/g concentrate) plus 93% of the Ag originally present in the concentrate, can be obtained by leaching a leach residue (1 wt% of pulp density) with a 200 g/L NaCl–0.5 M H_2SO_4 at 90 °C and for 2 h. A similar acid-brine leaching process – the ‘BRISA process’ – has been developed (Romero et al., 2003) in which the solid residue is leached in an acid-brine medium with 200 g/L of NaCl and either HCl or H_2SO_4 . Romero et al. (2003) postulated that it is possible to obtain total recovery of the Ag^+ added as a catalyst plus 75% of the Ag originally present in concentrate (44 mg/kg) by leaching the residue with a 200 g/L NaCl–0.5 M H_2SO_4 medium at 90 °C and 10% of pulp density in two stages of 2 h each. In general, few studies or processes have been developed to recover the catalytic metal ions from the actual bioleached residue. Moreover, the studies of other valuable ions (Hg^{++} , Cu^{++} , Bi^{+++} etc.) used as catalysts to recover metals from other industrially important minerals and end-of-life industrial materials are absent. Therefore, in order to develop a successful commercial process, more in-depth studies using different metal ions have to be conducted under different process conditions.

6.4. Environmental safety

Almost all metal ions employed as catalysts during bioleaching are considered toxic, and their safe transport, storage and disposal at the end of the bioleaching process, is a critical challenge to the mining industry. Meanwhile, there are increasingly stringent environmental regulations and many countries have banned the permanent storage and management of surplus production of these metals. For example, the European Union (EU) implemented an

export ban on Hg in 2008 and enacted a further ban and policies for the permanent storage and management of surplus Hg produced in EU countries in 2011 (The Zero Mercury Working Group, 2007). Metallic ions such as Hg^{++} and Ag^+ are known for their toxicity and have caused a number of public health issues (Lansdown, 2006; O’Reilly et al., 2016). The predominantly used Ag^+ are biologically active and promptly interact with proteins, free anions and receptors on mammalian, eukaryotic cell membranes, assimilated in the human body and enters the systemic dissemination as a protein complex (Lansdown, 2006). Similarly, Hg is the most harmful metal known to humans (Tang et al., 2015) and divalent mercury (Hg^{++}) is considered the most toxic form of Hg. Therefore, it has become a great concern to recover/remove these species from the final effluent or residues and to ensure that they comply with the stringent disposal standards. The US Environmental Protection Agency (USEPA) standards for the disposal of hazardous wastes provide a disposal limit of Hg below 0.2 mg/L. Similarly, the USEPA allowable disposal limit for safe disposal of Ag is 5 mg/L (USEPA, 2013). The EU (drinking water) regulation, 2014 (EU Regulations, 2014) also provides a safe Hg limit of 0.001 mg/L for potable water. This regulation also prescribed a safe Cu limit in potable water of 2 mg/L. Therefore, it’s a challenge to the mining industry to formulate a robust policy in order to recover these metal ions from bioleached residue, maintain adequate storage facilities and safety procedures, and achieve safe disposal of the treated residue.

6.5. Future perspectives

Although bioleaching is well understood, the commercial application of the process is still limited in the extractive metal industry, owing to its slow kinetics. It is foreseen that innovations such as the addition of metal ions as catalysts, may greatly improve the overall bioleaching efficiency and economics of large-scale industrial operations. Currently, studies on metal ion-catalyzed bioleaching are mostly conducted at laboratory-scale, and have been conducted with primary minerals and ores. Studies conducted with secondary resources (such as end-of-life products, industrial waste materials, mining wastes, spent batteries etc.) are limited and hence, research is needed to find out the process efficacy with these secondary resources. In terms of catalytic ions, Ag^+ has proven to be the most exciting due to its positive effect on a wide range of minerals (chalcopyrite, galena, complex sulfide, spent batteries etc.). There is evidence that Cu-bearing minerals and ore are currently the most amenable for Ag^+ catalyzed bioleaching. Considering the fact that a significant amount of Cu is already produced industrially using bioleaching (Panda et al., 2015b), Ag^+ -catalyzed bioleaching (with *At. ferrooxidans*) offers the greatest potential to extract Cu from low-grade minerals and concentrates in a more efficient and cost-effective manner. Moreover, Ag^+ can be added to the leaching medium either as a finely divided metal or in the form of different salts. However, types of salts used may affect the overall bioleaching process due to their differential solubility in the leaching media and their toxicity towards bioleaching microorganisms (Mcleroy and Duncan, 1974). Soluble silver salts such as AgCl , Ag_2SO_4 and AgNO_3 are preferable opposed to insoluble silver salts (Ag_2S) (Mcleroy and Duncan, 1974). Among water soluble silver salts, AgNO_3 may be preferable to AgCl and Ag_2SO_4 , as the latter have a tendency to precipitate as argentojarosite depending upon the media composition (Cordoba et al., 2009; Abdollahi et al., 2014). In terms of toxicity, Ag_2SO_4 has been found to be more toxic to bioleaching microorganisms compared to AgCl (Sato et al., 2000). However, there are currently criteria for choosing these salts and the choice seems to be largely governed by its availability and cost. There is a paucity

of studies concerning the effect of different Ag^+ salts on bioleaching process. Studies with metal salts other than Ag^+ (Hg^{++} , Bi^{+++} , Cu^{++} , Co^{++}) are also absent. Future studies should explore this aspect. Moreover, studies on the combined use of metal ion catalysts and non-metal catalysts or bi-metal ion catalyst are also absent. The simultaneous use of metal ion (such as Ag^+) and non-metal catalyst (such as activated carbon) compared to a single catalyst, may have the potential to induce greater catalysis owing to synergistic effect. Similarly, the use of bi-metallic catalysts, in combination or in series, may also promote better bioleaching yields. Future studies should explore their possible efficacy and reaction mechanisms during bioleaching.

It is also important to note that *At. ferrooxidans* is currently the most used microorganism in bioleaching. However, other leaching microorganisms such as thermophilic bacteria, archaea, and fungi, under different process conditions, may also prove to be useful agents for gaining better efficiency. Following this review, it is recommended that the focus of the future work should be on (1) investigating the efficiency of processes with different secondary resources (2) evaluating the use of different types of microorganisms (3) examining the process efficiency in larger scale reactors, and (4) evaluating different cost-effective processes to recover metal ions from treated bioleached residue and metal laden liquor.

7. Conclusions

The analysis suggests that addition of different metal ions (Ag^+ , Hg^{++} , Bi^{+++} , etc.) increases bioleaching efficiency remarkably. Although most of the metal ion-catalyzed bioleaching studies have obtained promising results, techno-economic challenges still exist and efforts are needed to overcome these challenges in order to make the technology feasible for large-scale application. Moreover, the feasibility and sustainability of these processes have not been demonstrated on a large-scale and there remains a need to scale-up investigations, which should include estimations of cost and environmental impact. This is a critical aspect in the development of future industrial metal ion-catalyzed bio-hydrometallurgical processes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.01.001>.

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