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

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17 **Abstract**

18 Bioleaching is considered to be a low-cost, eco-friendly technique for leaching valuable
19 metals from a variety of matrixes. However, the inherent slow dissolution kinetics and low
20 metal leaching yields have restricted its wider commercial applicability. Recent
21 advancements in bio-hydrometallurgy have suggested that these critical issues can be
22 successfully alleviated through the addition of a catalyst. The catalyzing properties of a
23 variety of metals ions (Ag^+ , Hg^{++} , Bi^{+++} , Cu^{++} , Co^{++} etc.) during bioleaching have been
24 successfully demonstrated. In this article, the role and mechanisms of these metal species in
25 catalyzing bioleaching from different minerals (chalcopyrite, complex sulfides, etc.) and

26 waste materials (spent batteries) are reviewed, techno-economic and environmental
27 challenges associated with the use of metals ions as catalysts are identified, and future
28 prospectives are discussed. Based on the analysis, it is suggested that metal ion-catalyzed
29 bioleaching will play a key role in the development of future industrial bio-
30 hydrometallurgical processes.

31

32 **Keywords:** Bioleaching; catalyst; metals; leaching; minerals

33

34 **1. Introduction**

35 Bioleaching is a low-cost, green technology for leaching metals from a variety of
36 minerals and waste materials (Zeng et al., 2016). Bioleaching has several advantages
37 compared to conventional hydrometallurgy (the leaching of metals with acids or bases) or
38 pyrometallurgy (the leaching of metals using thermal treatment), which have high energy
39 requirements, require a large amount of chemicals, and also produce high levels of
40 environmental pollution (Zeng et al., 2013). Currently, a significant portion of many
41 minerals/ores are processed at industrial scale using bioleaching (Walting, 2015). For
42 example, approximately 20-25% of the world's total copper (Cu) is produced using
43 bioleaching (Brierley, 2008). A number of successful commercial bioleaching operations
44 exist worldwide, and a Cu bioleaching plant (Morenci mine, USA) with a capacity of up to
45 230,000 tonnes/year is currently operational (Panda et al., 2015a).

46 Although bioleaching offers many advantages, the relatively slow dissolution
47 kinetics and low metal leaching yield are critical factors that hinder its large-scale
48 application. For example, laboratory bioleaching experiments may last for more than 300

49 days in order to obtain reasonable metal extraction efficiencies (Munoz et al., 2007), and in
50 large industrial operations such as Cu^{++} bioleaching, some researchers have taken up to 900
51 days to obtain a Cu yield of just 60% (Clark et al., 2006). Therefore, research efforts have
52 been directed towards improving the efficiency of the bioleaching process by improving
53 process dissolution kinetics and metal leaching yields.

54 The rate of reaction and bioleaching yield may be improved considerably by the
55 addition of suitable catalysts. A 'catalyst' is a substance that lowers the activation energy
56 and thereby increases the rate of reaction. A variety of metal ions (Ag^+ , Hg^{++} , Bi^{+++} , Cu^{++} ,
57 Co^{++} , etc.) and non-metallic catalysts (activated carbon, light illumination, waste
58 newspapers, polyethylene glycol, etc.) have been used to improve bioleaching efficiency
59 (Ballester et al., 1990; Liu et al., 2015; Niu et al., 2015; Panda et al., 2015a; Zhou et al.,
60 2015). However, the use of metal ions as a catalyst has gained most attention, as non-
61 metallic catalysts have produced relatively poor bioleaching yields of as low as 12.5%
62 (Zhang et al., 2016) and also require large amounts of catalysts of up to 2500 g/kg of ore
63 (Dong et al., 2013) to obtain significant leaching yields. In comparison, metal ions have
64 excellent catalytic properties and therefore it is expected that in future, metal ions will have
65 a significant influence on the development of a suitable bioleaching process at commercial
66 scale.

67 Previous review articles on bioleaching have primarily dealt with the fundamentals
68 and mechanism of bioleaching (Donati et al., 2016), the microorganisms involved and the
69 types of minerals bioleached (Das et al., 2011; Panda et al., 2015b; Donati et al., 2016), and
70 the mineral-microbial interaction (Diao et al., 2014). However, to date, the role and
71 potential of metal ions in promoting bioleaching efficiency has not been reported. Since the

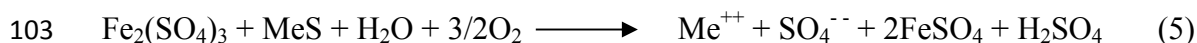
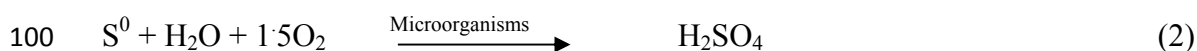
72 application of microbial-assisted bioleaching is emerging, and to date, no systematic review
73 has addressed the potential of metal ions as catalysts in bioleaching, the aim of this paper is
74 to (1) identify the metal ions which have the potential in catalyzing bioleaching of different
75 ores/minerals/waste/end-of-life materials (2) describe the role and catalytic mechanism of
76 these metal ions and how they improve the bioleaching efficiency of
77 minerals/ores/waste/end-of-life materials (3) select the most appropriate metal ion for
78 particular ores/minerals (4) evaluate the different techno-economic issues and
79 environmental challenges associated with the use of these metal ions, which need to be
80 overcome before the process may be applied on an industrial scale. This information will
81 assist metallurgists in understanding the catalytic properties of metal ions for improving the
82 efficiency of the bioleaching process.

83

84 **2. Bioleaching mechanisms and microorganisms involved**

85 Bioleaching involves extraction of metals from mineral ores using biological means
86 (Karthikeyan et al., 2015). A wide variety of microorganisms such as
87 chemolithoautotrophic bacteria, heterotrophic bacteria, archaea and fungi, play an important
88 role in bioleaching (Panda et al., 2015b). Chemoautotrophic bacteria such as
89 *Acidithiobacillus thiooxidans* (*At. thiooxidans*) and *Acidithiobacillus ferrooxidans* (*At.*
90 *ferrooxidans*) are the most dominant and industrially used microorganisms to extract the
91 metals from ore and minerals (Feng et al., 2016). Bioleaching microorganisms derive the
92 energy required for their growth from the oxidation of ferrous iron and reduced (inorganic)
93 sulfur compounds in acidic environments. During bioleaching, microorganisms catalyze the
94 oxidation of ferrous iron (Fe^{++}) and reduced sulfur compounds as per Eqs. (1-2). The

95 oxidation of Fe^{++} and reduced sulfur compounds lead to the generation of biologically
 96 produced ferric ion (Fe^{+++}) and sulfuric acid (H_2SO_4), respectively (Ma et al., 2017). The
 97 generated H_2SO_4 and/or Fe^{+++} act as oxidants and oxidize the metal sulphides (redoxolysis)
 98 and/or solubilize the metal sulfides and oxides as per Eqs. (3-5).



104 Species of *Acidithiobacilli* thrive in acidic conditions (pH 0.5-3) and are also
 105 tolerant of high concentrations of a variety of metal ions present in different leaching
 106 environments. Other microbial species may be used in bioleaching, including *Acidophilum*
 107 *cryptum*, *Thiobacillus thioparus* and *Halothiobacillus halophilus*. However, they are not
 108 widely studied, as they only grow at a relatively high pH range (2.5-8.0) in which efficient
 109 leaching does not take place (Chen and Lin, 2009; Xu et al., 2010; Vainshtein et al., 2015).

110 Besides chemoautotrophic bacteria, heterotrophic bacteria and fungi have also been
 111 used for the treatment of non-sulphides and oxide materials. However, in these cases, metal
 112 leaching is performed as a result of production of organic acids and complexing compounds
 113 secreted into the system (Vakilchap et al., 2016). A detailed overview of the different
 114 microorganisms involved in various bioleaching environment is provided by Krebs et al.
 115 (1997) and Panda et al. (2015b), amongst others.

116

117 **3. Bottlenecks in bioleaching process**

118 In recent years, the mining industry has made significant efforts to develop eco-
119 friendly and low cost bio-hydrometallurgical operations (Walting, 2015). However, certain
120 bottlenecks still exist which hinder its wider commercial applicability. The process kinetics
121 are currently much too slow for it to be economical. Longer periods of operation are
122 required compared to traditional methods of leaching to obtain reasonable yields (Clark et
123 al., 2006). For example, Cerda and Ohlbaum, 2008 reported 65–80% Cu recoveries from
124 chalcocite and covellite after a bioleaching time of up to 500 days in industrial operations.
125 Laboratory-scale experiments, performed in column reactors under mesophilic conditions,
126 also found that more than 300 days of bioleaching was required to obtain 7.3 to 27.1% of
127 Cu recovery from enargite and covellite-rich composites (Lee et al., 2015). Further, the
128 efficiency of the process is affected by atmospheric conditions and slight changes in
129 parameters such as temperature can adversely affect the process efficiency (Karimi et al.,
130 2010). In addition, with industrial wastes (such as spent batteries), bioleaching is mostly
131 conducted with low pulp density i.e. 1% w/v (Zeng et al., 2013). The process efficiency
132 decreases at higher pulp density due to the presence of alkaline wastes or metal toxicity to
133 leaching microorganisms (Niu et al., 2015). The maintenance of optimum particle size in
134 the reactor is another concern, as the presence of very fine particles (<25 μm) can
135 negatively impact the activity of cells due to attrition caused by increased particle-particle
136 collision (Nemati et al., 2000).

137

138 **4. Role and catalytic mechanism of metal ion in bioleaching**

139 Different materials have been reported to catalyze the bioleaching through varying
140 modes of action (Table 1). Generally, physical, chemical and electrochemical processes are

141 involved in the dissolution of minerals in aqueous solutions. In the case of physical
142 processes, there is no chemical transformation and salts are water soluble. The dissolution
143 of NaCl in water is such an example. In chemical processes, the crystalline solid is
144 insoluble in water, but becomes soluble in the presence of a certain ion in solution.
145 Chemical dissolution of minerals proceeds in two steps: (1) a physical process which
146 establishes an equilibrium between the aqueous phase and mineral solids, and (2) a
147 chemical reaction (in the vicinity of the solid) between the ions that just left the solid and
148 the reagent present in the aqueous phase. The third process involved in the dissolution of
149 minerals is electrochemical leaching. These are coupled redox reactions, which change the
150 oxidation state of the minerals and accelerates the dissolution in the leaching medium
151 (Habashi et al., 1983). Among these processes of mineral dissolution, the electrochemical
152 mechanism is well established and considered to be the most important. Habashi (1983)
153 postulated that the electrochemical mechanism of sulfide dissolution is affected by the (1)
154 presence of impurities in the crystalline structure that modify the conductivity of the
155 mineral solid (2) formation of galvanic couples on the basis of the various mineralogical
156 species present in the ore, and (3) presence of certain ions in solution, which, as they come
157 into contact with the surface of the solid, modify its electrochemical behavior. Most
158 research has been focused on this third factor i.e., the addition of suitable catalytic ions
159 which form a redox couple to influence the reactions between the metal sulphide and the
160 oxidizing medium. Using this mechanism, metal ions modify the electrochemical behavior
161 and catalyze the dissolution of sulfides in the leaching medium. Ballester et al. (1990, 1992)
162 also suggested that dissolution of different metals from mineral sulfides can be promoted
163 by the addition of soluble external ions. These metal ions cause the formation of a metal

164 sulfide, which dissolves the original sulfide mineral either by galvanic action or substitution
165 in crystal lattice. However, the catalyze effect of a particular metal ion during leaching will
166 be different for each mineral/ore. This is due to fact that different mineral sulfides have
167 different rest potentials (mV), which will impact the galvanic interaction between the metal
168 ion catalyst and mineral solids. In addition, each metal ion poses a unique ability to activate
169 the particular mineral sulfide surface, displacing the ions from the target mineral solid.

170 The first study on the catalytic effects of metal ions in the leaching medium
171 (without bacteria) was conducted by Scott and Dyson (1968), who studied the effect of
172 various metal ions on the dissolution kinetics of ZnS. Further studies were conducted by
173 Mulak (1987), who examined the catalytic effect of Cu^+ , Cu^{++} and Fe^{3+} during HNO_3
174 leaching of synthetic Ni_3S_2 , and observed that these metal ions catalyzed the dissolution of
175 mineral solids by several orders of magnitude. Since then, several studies on the catalytic
176 effect of metal ions on the dissolution of metals in the leaching medium have been reported
177 in the literature (both in the presence of microorganisms - bioleaching - and without
178 microorganisms). The first of these bioleaching studies was reported by Mcelroy and
179 Duncan (1974), who found that the addition of small quantities of Ag^+ during chalcopyrite
180 bioleaching with *At. ferrooxidans* dramatically enhanced the Cu leaching yield as opposed
181 to without Ag^+ .

182

183 **5. Catalytic role and mechanisms of different metal ions**

184 *5.1 Role of Ag^+*

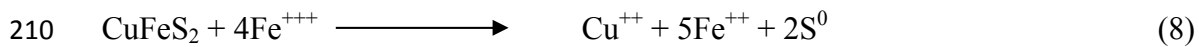
185 A variety of metal ions such as Ag^+ , Hg^{++} , Bi^{+++} , Cu^{++} , Co^{++} , etc. have been used
186 successfully as catalysts in various bioleaching studies (Table 2). Among these metal ions,

187 Ag^+ has received the most attention. Different Ag compounds such silver sulfate (Ag_2SO_4),
 188 silver nitrate (AgNO_3) and silver chloride (AgCl), have been used as a source of Ag^+ in the
 189 bioleaching medium. Although Ag^+ has been found to be efficient in enhancing the
 190 dissolution kinetics and leaching yields of metals from a wide variety of minerals and
 191 matrices, the majority of these bioleaching studies using Ag^+ have been reported for Cu-
 192 bearing ore and/or minerals such as chalcopyrite (Kuwazawa and Miura 2012; Abdollahi et
 193 al., 2015). Bioleaching of chalcopyrite (the principal source of Cu in the mining industry) is
 194 difficult due to the formation of secondary solid phases and jarosite-type precipitates,
 195 which contribute to surface passivation (Feng et. al., 2015; Panda et al., 2015b). The role of
 196 Ag^+ during chalcopyrite bioleaching is to form a film of silver sulfide (Ag_2S) on the
 197 chalcopyrite surface, which alleviates the surface passivation through the formation of a
 198 less tenacious and more porous layer of elemental sulfur (S^0). The new film, therefore,
 199 improves the semi-conductor properties of chalcopyrite, and facilitates the electronic
 200 transfer to the oxidant. The presence of Ag_2S in the bioleached chalcopyrite has been
 201 confirmed through X-ray diffraction by Hu et al. (2002) (Suppl. Fig. A1). Scanning
 202 Electron Microscopy (SEM) micrographs have shown the formation of Ag_2S precipitates
 203 on the chalcopyrite surface (Abdollahi et al., 2014) (Suppl. Fig. A2).

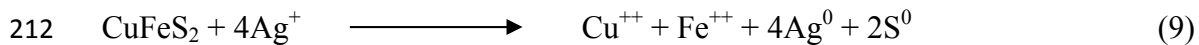
204 Ag^+ initially forms Ag_2S on the chalcopyrite surface, followed by Fe^{3+} mediated
 205 oxidation:



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



211 Elemental Ag can also form during the process:



213 The role of bioleaching bacteria in this process is to oxidize the Fe^{++} into Fe^{+++} , which
214 oxidizes the Ag_2S film.

215 The first report on the catalytic effect of Ag^+ during bioleaching was published as a
216 US patent developed by the researchers at the British Columbia Research Council (Mcelroy
217 and Duncan, 1974). In this patent, it was reported that during bioleaching with *At.*
218 *ferrooxidans*, the addition of only 0.5 g Ag^+ /kg of ore promoted the Cu yield to 88%
219 compared to 50% without Ag^+ . It was also found that instead of soluble silver salts,
220 insoluble salts such as Ag_2S can also be used. However, the quantity of Ag^+ required to
221 achieve a significant increase in bioleaching yield will be relatively higher using Ag_2S
222 (0.700-7.0 g Ag^+ /kg of chalcopyrite concentrate).

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

230 Most of these initial studies using Ag^+ as catalysts were conducted using mesophilic
231 bacteria such as *At. ferrooxidans*, *At. thiooxidans* and *Leptospirillum ferrooxidans* (*L.*
232 *ferrooxidans*). However, it has been reported that rate of bioleaching in different minerals

233 by thermophilic and moderate thermophiles is higher than mesophiles (Devecei et al., 2004)
234 due to faster reaction kinetics. Romano et al. (2001) reported that bioleaching yield of
235 chalcopyrite under mesophilic conditions was about 50%, whereas it increased to 100%
236 with thermophilic microorganism after three weeks of experiments. To harness the higher
237 kinetics, Ag^+ -catalyzed bioleaching was also explored with moderate thermophilic and
238 thermophilic microorganisms. Gomez et al. (1999) used shake flask bioleaching with mixed
239 moderate thermophilic bacteria, and reported that the Cu yield increased three-fold in the
240 presence of 0.1 to 0.5 g Ag^+ /kg compared to without the addition of Ag^+ . Moreover, the
241 catalyzing effects of Ag^+ were higher in moderate thermophilic bioleaching compared to
242 mesophilic bioleaching (Abdollahi et al., 2015). Gomez et al. (1999) reported that in the
243 presence of Ag^+ , it took only 5 days of moderate thermophilic bioleaching to obtain about 90%
244 Cu yield from chalcopyrite-molybdenite concentrate, whereas it took more than 10 days to
245 achieve a similar Cu yield with mesophilic bioleaching. In addition, relatively smaller
246 amounts of Ag^+ (0.77 g Ag^+ / kg of ore) were required to obtain a similar Cu yield using
247 moderate thermophilic bioleaching compared to mesophilic bioleaching (6.7 g Ag^+ / kg of
248 ore). Similar findings were observed by Abdollahi et al. (2014) in the case of Ag^+ -catalyzed
249 thermophilic bioleaching, who found that 75% Cu was leached from the concentrate
250 compared to only 27% with mesophilic temperatures. The reasons for the different effects
251 of catalyst at different temperatures were not explained in these bioleaching studies.
252 However, in the case of Ag^+ -catalyzed chemical leaching (without bacteria) a number of
253 factors such as higher solubility of silver complex, higher regeneration of Ag_2S by Fe^{3+} and
254 reduced jarosites precipitation, were found to be responsible for higher leaching yield (Guo

255 et al., 2011). Further studies are required to understand the mechanism and biochemical
256 aspects of catalyst-based bioleaching at different temperatures.

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

272 Although the majority of studies using Ag^+ as a catalyst were conducted with Cu-
273 bearing minerals and ore, researchers also exploited the catalytic properties of Ag^+ for
274 treating materials other than Cu. For instance, Guo et al. (2011) tested the process
275 effectiveness with the As-bearing mineral, realgar (As_2S_2), using both mesophilic (*At.*
276 *ferrooxidans*) and thermophilic *Sulfobacillus sibiricus* (*S.s*), and observed that in the
277 absence of Ag^+ , very little As_2S_2 was leached during bioleaching with either *At.*

278 *ferrooxidans* (0.2-0.5%) or *S.s* (1.5-2.2%). On the contrary, the addition of Ag^+ enhanced
279 the dissolution of As to 24.4% and 15.3% using *At. ferrooxidans* and *S.s*, respectively.

280 As Ag is a potentially toxic metal (David et al., 2008), the addition of Ag^+ during
281 bioleaching has been reported to cause a decrease in the bacterial growth rate and
282 subsequent iron-oxidation rate. To overcome this problem, a process in which corn steep
283 liquor (CSL) is added along with Ag^+ , was recently patented (Kuwazawa and Miura, 2012).
284 The authors reported that CSL acted as a source of organic nitrogen to the leaching media
285 and due to its addition, the iron-oxidizing capacity of iron-oxidizing bacteria was improved.
286 This caused a significant improvement in the leaching yield of Cu. It was found that the
287 addition of 10 mg/L of Ag^+ and 0.1 g/L of CSL led to dissolution of more than 80% of Cu
288 as compared to less than 10% in the absence of Ag^+ . They also observed that CSL can
289 either be added as an immersion solution or as powder.

290 However, until recently, the catalytic use of Ag^+ was limited to treat natural mineral
291 and ores. In a recent study, it was reported that the bioleaching yield of industrial waste
292 material and end-of-life products such as spent lithium batteries, can also be improved by
293 the addition of Ag^+ (Zeng et al., 2013). It was observed that the addition of only 2.0 g of
294 Ag^+ /kg of ore with *At. ferrooxidans*, led to dissolution of 98.4% Co. In the absence of Ag^+ ,
295 the leaching yield of Co was only 43.1%. Zeng et al. (2013) found that the catalytic role of
296 Ag^+ involved promoting the formation of the AgCoO_2 intermediate. This intermediate
297 AgCoO_2 was oxidized by bio-produced Fe^{3+} , resulting in higher yield of Co. The role of
298 the bacteria is to oxidize the Fe^{2+} back to Fe^{3+} . Chen and Lin (2009) also utilized the
299 catalyzing property of Ag^+ for decontamination of riverine sediments that were
300 contaminated with different metals (Cu, Ni, Zn, Pb and Mn). In this study, a higher pH

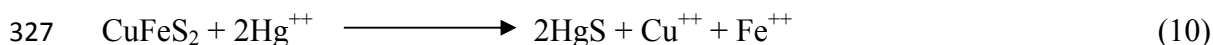
301 reduction rate was observed during bioleaching with Ag^+ . It was also observed that the Ag^+
302 added was incorporated into the lattice of the initial sulfide through a cationic interchange
303 reaction. This resulted in the short lag phase and high metal yield during bioleaching as
304 opposed to without Ag^+ . The best results were achieved by the addition of 1.5 g of Ag^+ / kg
305 of sediment, beyond which a decrease in leaching rate constant for these metals was
306 observed.

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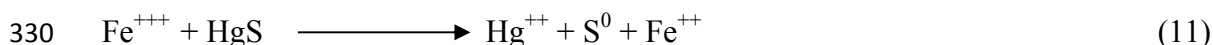
308 5.2 Role of Hg^{++}

309 Although Hg^{++} is considered to be extremely hazardous in the natural environment,
310 its catalytic properties have been exploited by many researchers to improve bioleaching
311 kinetics. Ballester et al. (1990) was perhaps one of the first researchers to report the
312 catalytic effects of Hg^{++} during bioleaching of the complex sulfide concentrate (FeS_2 ,
313 CuFeS_2 , ZnS and PbS) using *At. ferrooxidans*. Their study suggested that the addition of 2
314 g Hg^{++} /kg of concentrate (in the form of HgSO_4) during bioleaching enhanced the
315 dissolution of Cu to 80% compared to only 25% without Hg^{++} from the complex sulfide
316 concentrate. These authors speculated that the catalytic effect of Hg^{++} was due to its
317 tendency to replace the Cu from the sulfide lattice. The sulfide formed as a result of the
318 displacement reaction on the surface of the complex sulfide concentrate, acted as a cathode
319 with respect to the chalcopyrite, leading to the rapid dissolution of the mineral chalcopyrite.
320 The changes in chalcopyrite surface during Hg^{++} catalyzed bioleaching were examined
321 using SEM and auger electron spectroscopy (AES) (Gomez et al., 1997). They reported that
322 Hg^{++} were incorporated onto the mineral surface and formed a thin coating of HgS . The
323 standard Gibb's energy (ΔG^0_r) calculated for the reaction between chalcopyrite and Hg^{++}

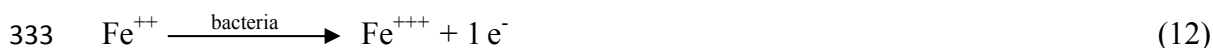
324 has also shown that the formation of HgS is thermodynamically possible. The mechanism
325 through which Hg^{++} catalyzes bioleaching is presented in Eqs. (10-12). As per reaction
326 mechanism, Hg^{++} first reacts with chalcopyrite and produces a thin coating of HgS.



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



331 The produced Fe^{++} is oxidized to Fe^{+++} by leaching bacteria, which is recirculated in the
332 leaching media.



334 Ballester et al. (1992) further argued that the concentration of Hg^{++} is an important
335 parameter that determines the efficiency of the bioleaching process. By employing different
336 concentrations of Hg^{++} ranging from 0.04 to 1 g Hg^{++}/kg of ore, they found that 0.2 g
337 Hg^{++}/kg of ore was the optimum Hg^{++} concentration for enhancing the bioleaching yields of
338 Cu and Zn from the complex sulfide. Moreover, using 0.2 g Hg^{++}/kg of ore, the bioleaching
339 period was also shortened to about 8 days compared to 21 days for the non- Hg^{++} inoculated
340 bioleaching experiment to achieve a similar Cu yield (20%). These authors also postulated
341 that a too low Hg^{++} concentration (0.04 g Hg^{++}/kg of ore) during bioleaching may not
342 induce desired changes, whereas a concentration beyond 0.2 g Hg^{++}/kg of ore may not
343 further improve the dissolution kinetics. This is due to the fact that at higher concentrations,
344 the Hg^{++} may impart toxicity to mesophilic *Acidithiobacilli*, which can suppress the
345 leaching. The toxic effects of Hg^{++} are more pronounced with thermophilic archaea
346 (*Sulfolobus sp.*), which poses less resistance to metal toxicity compared with mesophilic

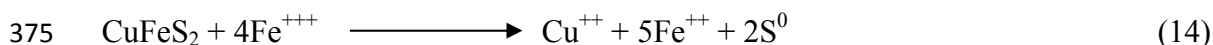
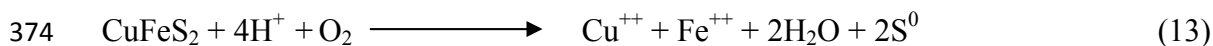
347 microorganisms. The toxic effect of Hg^{++} at higher concentration during bioleaching was
348 also highlighted by Escudro et al. (1993), who confirmed that 0.1 g Hg^{++} /kg of ore is the
349 optimum concentration at which Hg^{++} successfully enhanced the Cu yield from complex
350 sulfide to 58% compared to only 29% using 2.0 g Hg^{++} /kg of ore. Besides Cu leaching, the
351 addition of Hg^{++} has also been shown to promote the simultaneous dissolution of Zn from
352 complex sulfide, and about 85% of Zn was leached in the presence of 0.1 g Hg^{++} /kg of ore
353 compared to 65% without Hg^{++} . Moreover, the dissolution kinetics (250 hours instead of
354 400 hours) were greatly improved for achieving similar leaching of Zn (65%).

355

356 5.3 Role of Bi^{+++}

357 Along with Ag^{++} and Hg^+ , the catalytic properties of Bi^{+++} during bioleaching were
358 also first documented by Ballester et al. (1990). In their study on bioleaching of sphalerite
359 and complex sulfide concentrate using *At. ferrooxidans*, the authors observed that the
360 addition of Bi^{+++} as $\text{Bi}(\text{NO}_3)_3$ had an catalyzing effect on Zn dissolution from sphalerite and
361 about 78.4% of Zn was bioleached in the presence of Bi^{+++} compared to only 50% without
362 it. The catalytic effect of Bi^{+++} was explained on the basis of its tendency to influence
363 electrochemical dissolution process, so that it added the anodic behavior of the mineral. In
364 another study, Mier et al. (1994) observed that the role of Bi^{+++} during bioleaching was to
365 suppress the formation of phosphate compounds of Fe^{3+} , which otherwise precipitate in the
366 leaching medium. This results in higher availability of free Fe^{3+} and, therefore, higher
367 oxidizing properties during bioleaching, which are helpful in dissolution of Cu from
368 chalcopyrite. The mechanism through which Bi^{+++} catalyzes the chalcopyrite bioleaching is
369 presented in Eqs. (13-15) (Mier et al., 1994). Eq. (13) is purely a chemical reaction,

370 whereas Eq. (14) becomes prominent when bacterial growth takes place. The role of
371 bioleaching bacteria in this process is to oxidize the Fe^{++} and S^0 into Fe^{+++} and H_2SO_4 ,
372 respectively. The produced Fe^{+++} oxidizes the chalcopyrite, whereas H_2SO_4 maintains the
373 acidity of the leaching medium.



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



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

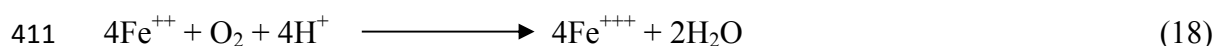
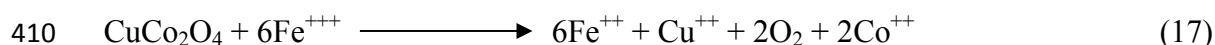
386

387 *5.4 Role of Cu^{++}*

388 Many researchers have tested the catalytic properties of Cu^{++} during bioleaching
389 due to its relatively cheaper cost and easy availability. Chen et al. (2008) used Cu^{++} as a
390 catalyst for treating a Zn containing mineral ‘marmatite’. It was reported that in the
391 presence of 5 g Cu^{++}/kg of ore, about 73% Zn was leached compared to 65% without Cu^{++} .
392 The enhanced leaching yield of Zn was attributed to the electrochemical effect of Cu^{++} on

393 bioleaching. It was postulated that during bioleaching, some Cu^{++} substitutes Zn^{++} and
 394 bonded the crystal lattice of marmatite. The CuS formed during bioleaching shows higher
 395 electrode potential and improves the conductivity of the mineral surface, so Zn dissolves
 396 preferentially as an anode. In addition, iron sulfide, elemental sulfur and jarosite were
 397 formed on the marmatite surface during bioleaching. These products formed a passivated
 398 layer, which suppressed the bioleaching process. The Cu^{++} catalyzed the bio-oxidation of S^0 ,
 399 which eliminated the barrier and led to the increased bioleaching of marmatite.

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



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

414 Besides spent lithium-ion batteries, spent Zn-Mn batteries have also been treated
 415 successfully in the presence of Cu^{++} . Niu et al. (2015) reported that the Cu^{++} has the ability

416 to enhance the dissolution kinetics of Zn and Mn from spent Zn-Mn batteries. Moreover,
417 this process can be performed at a higher pulp density (10%), which may enhance the
418 industrial application of the process. It was also reported that the leaching kinetics followed
419 the chemical reaction-controlled model. While conducting bioleaching in the presence of 8
420 g Cu^{++} /kg of ore, the leaching yield of Zn increased to 62.5% compared to 47.7% without
421 Cu^{++} . Similarly, the bioleaching yield of Mn also increased to 62.4% compared to 30.9%
422 without Cu^{++} . It was observed that the Cu^{++} formed a possible intermediate CuMn_2O_4 ,
423 which was oxidized by bio-produced Fe^{3+} .

424

425 5.5 Role of Co^{++}

426 Very few studies have used Co^{++} as catalytic ion in bioleaching operation, owing to
427 its higher cost compared to Cu^{++} and Bi^{+++} . Moreover, *At. ferrooxidans* is susceptible to
428 higher concentrations of Co^{++} (Mohseni et al., 2011). The catalytic properties of Co^{++} were
429 recognized in one of the earlier bioleaching studies conducted on the use of different metal
430 ions as a catalyst. Ballester et al. (1990) reported that the addition of Co^{++} in the form of
431 $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ significantly improved the bioleaching yield of Zn from the sphalerite
432 concentrate. After bioleaching for 400 hours with *At. ferrooxidans*, only 50% Zn could be
433 leached from the sphalerite concentrate. The addition of 2 g Co^{++} /kg of ore during
434 bioleaching enhanced the leaching yield of Zn from 50% to 68.4%. Similar findings were
435 made by Escudero et al. (1993), who conducted bioleaching of a complex sulfide
436 containing Cu, Pb and Zn. Bioleaching was conducted in a stirred glass reactor using a
437 mixed culture of bacteria (*At. ferrooxidans*, *At. thiooxidans*, *L. ferrooxidans*). The results
438 showed that the bioleaching yield of Cu was only 22% in the absence of a catalyst.

439 However, there was a drastic increase in the Cu recovery in the presence of Co^{++} and the
440 Cu leaching yield reached to 52% compared to 22% without Co^{++} . A similar increase was
441 also observed in the case of Zn, where about 92% of Zn was leached in the presence of
442 Co^{++} compared to 65% without it. The catalytic effect of Co^{++} was also attributed to its
443 electrochemical interaction with the mineral matrix, which favored the anodic behavior of
444 the sulfides during its reaction.

445

446 **6. Key challenges**

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

452

453 *6.1 Process economy*

454 Generally, the capital costs of bio-mining operations are less than those of smelting
455 operations. Dew et al. (1997) reported that the capital costs for a bio-oxidation plant of gold
456 ores was about two-fold lower than roasting or pressure oxidation, and that operating costs
457 were also lower. In the case of Cu bioleaching, the operating costs (in 2002) for leaching
458 dumps and in-place ore was calculated to be between US \$ 0.18 and US \$ 0.22/ pound of
459 cathode copper (Pradhan et al., 2008). These costs are competitive in comparison to the unit
460 costs of smelting/refining. However, operating costs of bioleaching operations may vary
461 depending on a number of factors such as plant location, cost of services at particular sites

462 etc. (Du Plessis et al., 2007). Cognizance of operating costs (such as addition of catalytic
463 ions) is therefore important, considering that most of the metal catalysts used during
464 bioleaching are precious or economically valuable commodities. Munoz et al. (2007)
465 concluded that Ag^+ -catalyzed bioleaching is economical and technically attractive. They
466 reported that the cost of Ag^+ addition per unit cost of Cu in the ore equates to only 6% of
467 the commercial price of Cu. Evaluating the effectiveness of this process in the current
468 scenario, the approximate price of Ag in the third quarter of 2016 (June-Sept 2016) is USD
469 \$ 670/kg (NASDAQ). Similarly, the average price of Cu in the third quarter of 2016 at the
470 London Metal Exchange (LME) is about USD \$4.85/kg. Therefore, the cost of Ag addition
471 (1g Ag/kg of Cu) per unit cost of Cu in the ore equates to 0.67 USD \$ /kg of Cu (1 g Ag \times
472 USD \$ 670/1000 g). This is equivalent to only 14% (USD \$0.67/ USD \$4.85 \times 100) of the
473 current international price of Cu. A detailed analysis involving the cost of different metal
474 catalyst added during bioleaching, their concentrations and their performance in increasing
475 the bioleaching yield, are provided in Table 4. The cost has been calculated by considering
476 price (in USD \$/kg) of metals catalyst (June-Sept 2016) as 670, 4.85, 26, 2.3, 0.018, 2.42
477 for Ag^+ , Cu^{++} , Co^{++} , Zn^{++} , Bi^{+++} and As^{+++} , respectively (NASDAQ, LME,
478 metalprices.com). The analyses suggest that considering the performance along with the
479 cost, Ag^+ and Cu^{++} are the most effective catalysts among all catalysts used. In comparison,
480 catalysts such as Co^{++} , Bi^{+++} and Hg^{++} are not so effective and, in addition, few studies
481 using them have been reported, which precludes a definitive conclusion to be made.
482 Between Cu^{++} and Ag^+ , Ag^+ is preferable, as it can be used for treating wide varieties of
483 minerals (Cu-bearing minerals, complex sulfide, spent batteries, Arsenopyrite etc.) as
484 opposed to Cu^{++} , which is primarily found to catalyze only spent batteries in bioleaching.

485 Moreover, the efficiency of Ag^+ is better compared to Cu^{++} . An increase of more than 40%
486 in the bioleaching yield of a target metal is routinely evident in most of these studies when
487 Ag^+ is used as a catalyst. Relatively few amounts of Ag^+ are required to induce the desired
488 catalytic effect. A concentration in the range of 0.5-1.0 g Ag^+ /kg of ore seems to be the
489 optimum concentration required to catalyze a wide variety of minerals and ore. Moreover,
490 in the case of a commercially important mineral such as chalcopyrite, the cost of Ag^+
491 addition can be as low as 4.42% of the current cost of Cu (Table 4). Therefore, Ag^+ seems
492 to be the best candidate among all catalysts, considering its cost of addition and
493 effectiveness. Future studies should explore its effectiveness for large-scale application.
494 However, considering its effectiveness in terms of the cost of the addition of metal ions, the
495 process seems attractive for large-scale application, but to drive a satisfactory cost analysis
496 of the overall process, the cost of safe disposal, recovery of metal ions from treated
497 residue/leachate, establishment of catalyst storage facilities, acclimatization of
498 microorganisms to metal ions etc., will have to be added to the total cost. Annual
499 maintenance and management costs will also be incurred. Hence, this process seems less
500 costly in terms of the cost of metal ion used, but could prove equally costly in terms of
501 overall cost of the process compared to traditional bioleaching. Unfortunately, inadequate
502 information is available in the literature on the economic aspects of metal ion-mediated
503 bioleaching processes, which limits the scope of a detailed cost-benefit analysis. Therefore,
504 the economic and commercial viability of this process remains a knowledge gap which
505 requires urgent attention.

506

507 *6.2 Toxicity to leaching microorganisms*

508 One of the major challenges associated with metal ion-catalyzed bioleaching is the
509 possible toxic/inhibitory effects of these metal ions to bioleaching microorganisms. It has
510 been observed that most of the metal ions used as catalysts are potentially toxic to
511 mesophilic *Acidithiobacilli* (David et al., 2008; Mohseni et al., 2011). However, the
512 concentration of particular metal ions at which it becomes toxic/inhibitory varies for each
513 microorganism species and strains. The inhibitory concentrations of various catalytic ions
514 to bioleaching microorganisms are shown in Table 5. It can be seen that the iron oxidation
515 rate of *At. ferrooxidans* was found to be inhibited at as low as 0.1 mg/L of $\text{Ag}^+/\text{Hg}^{++}$. In the
516 case of Ag^+ , the inhibition has been explained through a mixed mechanism in which Ag^+
517 replaces Fe^{++} in the active site of the oxidizing enzyme in the bacterial cell (De et al., 1996).
518 The accumulation of Ag on *At. ferrooxidans* cells has been confirmed during leaching of
519 sulfide ore mineral (Fang et al., 2014). Besides Ag^+ and Hg^{++} , other commonly used metal
520 ions such as Cu^{++} and Bi^{+++} are also known to inhibit the bacterial iron-oxidation capacity.
521 However, their inhibitory effects are observed at comparatively higher concentrations
522 compared to Ag^+ . The special ability of *Acidithiobacilli* to tolerate relatively higher Cu
523 concentrations during bioleaching is due to having in its genome several genes that are
524 related to Cu homeostasis, such as those coding for CopA efflux ATPases, Cus efflux
525 systems and copper chaperones (Latorre et al., 2016).

526 Considering these issues, the identification of an appropriate concentration of these
527 metal ions is very important in the development of a successful bioleaching process. A low
528 concentration of these metal ions may not necessarily induce desirable changes, whereas a
529 higher concentration may impart toxicity to these microorganisms. A possible solution to
530 overcome this problem is to screen and employ those microbial species which have higher

531 tolerance to these metal ions. Silver tolerant *Acidithiobacilli* sp. with the ability to grow in
532 relatively higher concentration of Ag^+ , have been reported (Wu et al., 2007). Another
533 method is to use the adapted culture which shows less inhibition in the presence of these
534 metal ions. This can be achieved through repeated sub-culturing in progressively higher
535 levels of these metal ions. Alternatively, the use of mutant strains produced through
536 microwave induced mutation can yield *Acidithiobacillus* sp. with higher tolerance to metal
537 ions (Wu et al., 2007).

538

539 *6.3 Recovery of metal ions*

540 As most of the metal ions used as catalysts during bioleaching are highly valuable
541 metal commodities, their recovery at the end of bioleaching process is an important
542 consideration for improving the cost-effectiveness of the process. There are different
543 processes through which these metal species can be recovered, depending on the type of
544 metal ions used and chemical state of that metal in the leaching system. The choice of
545 treatment technology also depends upon whether a metal species is left in solid residue or is
546 present as soluble species in solution.

547 The major process reported for recovery of different metal species from solid
548 residue is leaching in which a lixiviant is added to the metal-containing materials which
549 leach the metal. Thiourea leaching, leaching with thiosulfate, ozone leaching or bioleaching,
550 are the major leaching techniques which have been successfully reported for leaching
551 different metal ions ($\text{Ag}^+/\text{Hg}^{++}/\text{Cu}^{++}/\text{Co}^{+++}$) from a variety of primary minerals and spent
552 materials. For example, Li et al. (2012) employed a thiourea leaching process to recover Ag
553 from the printed circuit boards of waste mobile phones. A leaching solution having 24 g/L

554 thiourea and 0.6% of Fe^{3+} at room temperature was found to leach about 50% Ag within 2
555 hours. On the other hand, cementation, biosorption, ion exchange, electro-winning and
556 solvent extractions are the major techniques which have been reported for the recovery of
557 these metals from a variety of liquid streams. Theoretically, at the end of bioleaching
558 processes, metal ions used as catalysts may be present either in solution or left in solid
559 residue. However, most of the studies conducted, primarily with Ag^+ as a catalyst, have
560 reported that Ag^+ added during bioleaching remained in the solid residue (Romero et al.,
561 2003).

562 Relatively few studies have been conducted for recovery of metal ions either from
563 the actual leached solid residue or leachate. In one of these studies, Palencia et al. (1998)
564 developed a silver catalyzed IBES process (indirect bioleaching with effect separation) and
565 studied the recovery of the Ag^+ from the solid residue remaining after the Fe_2SO_4 leaching
566 of a chalcopyrite–sphalerite concentrate. Their study suggested that total recovery of the
567 Ag^+ added as a catalyst (2 mg/g concentrate) plus 93% of the Ag originally present in the
568 concentrate, can be obtained by leaching a leach residue (1 wt% of pulp density) with a 200
569 g/L NaCl–0.5 M H_2SO_4 at 90 °C and for 2 hours. Palencia et al. (1998) also found that to
570 achieve higher Ag recoveries, the previous removal of S^0 formed during bioleaching is
571 required. A similar acid-brine leaching process – the ‘BRISA process’ – has been
572 developed (Romero et al., 2003) in which the solid residue is leached in an acid-brine
573 medium with 200 g/L of NaCl and either HCl or H_2SO_4 . Romero et al. (2003) postulated
574 that it is possible to obtain total recovery of the Ag^+ added as a catalyst plus 75% of the Ag
575 originally present in concentrate (44 mg/kg) by leaching the residue with a 200 g/L NaCl–
576 0.5 M H_2SO_4 medium at 90 °C and 10% of pulp density in two stages of 2 hours each. Few

577 studies or processes have been developed to recover the catalytic metal ions from
578 bioleached residue. The reported process, developed by Palencia et al. (1998) and Romero
579 et al. (2003), also dealt primarily with recovery of Ag^+ from the chalcopyrite bioleaching.
580 The studies of other valuable ions (Hg^{++} , Cu^{++} , Bi^{+++} etc.) used as catalysts to recover
581 metals from other industrially important minerals and end-of-life industrial materials are
582 absent. Therefore, in order to develop a successful commercial process, more in-depth
583 studies using different metal ions have to be conducted under different process conditions.

584

585 *6.4 Environmental safety*

586 Large quantities of metal ions are going to be used as catalysts in order to develop
587 an industrial-scale bioleaching operation. Almost all metal ions employed as catalysts
588 during bioleaching are considered toxic, and their safe transport, storage and disposal at the
589 end of the bioleaching process, is a critical challenge to the mining industry. Meanwhile,
590 there are increasingly stringent regulations against environmental pollution of different
591 toxic metal ions, and many countries have banned the permanent storage and management
592 of surplus production of these metals. For example, the European Union (EU) implemented
593 an export ban on Hg in 2008 and enacted a further ban and policies for the permanent
594 storage and management of surplus Hg produced in EU countries in 2011 (The Zero
595 Mercury Working Group, 2007). Metallic ions such as Hg^{++} and Ag^+ are known for their
596 toxicity to marine, microbial, invertebrate and vertebrate communities (including humans)
597 including biomagnification via food chains, and have caused a number of public health
598 issues (Yang et al., 2012; O' Reily et al., 2016). The predominantly used Ag^+ are
599 biologically active and promptly interact with proteins, free anions and receptors on

600 mammalian, eukaryotic cell membranes, assimilated in the human body and enters the
601 systemic dissemination as a protein complex (Lansdown, 2006; Katharina, 2011). Similarly,
602 Hg is the most harmful metal known to humans (Tang et al., 2015) and divalent mercury
603 (Hg^{++}) is considered the most toxic form of Hg. Hg^{++} is highly reactive and binds to the
604 amino acid cysteine in proteins. Therefore, it has become a great concern to recover/remove
605 these species from the final effluent or residues and to ensure that they comply with the
606 stringent disposal standards. The US Environmental Protection Agency (USEPA) standards
607 for the disposal of hazardous wastes provide a disposal limit of Hg below 0.2 mg/L.
608 Similarly, the USEPA allowable disposal limit for safe disposal of Ag is 5 mg/L (USEPA,
609 2013). The EU (drinking water) regulation, 2014 (EU Regulations, 2014) also provides a
610 safe Hg limit of 0.001 mg/L for potable water. This regulation also prescribed a safe Cu
611 limit in potable water of 2 mg/L. Therefore, it's a challenge to the mining industry to
612 formulate a robust policy in order to recover these metal ions from bioleached residue,
613 maintain adequate storage facilities and safety procedures, and achieve safe disposal of the
614 treated residue.

615

616 **7.0 Future perspectives**

617 Although bioleaching is well understood, the commercial application of the process
618 is still limited in the extractive metal industry, owing to its slow kinetics. It is foreseen that
619 innovations such as the addition of metal ions as catalysts, may greatly improve the overall
620 bioleaching efficiency and economics of large-scale industrial operations by promoting
621 faster process kinetics and higher metal yields. Currently, studies on metal ion-catalyzed
622 bioleaching are mostly conducted at laboratory-scale, and have been conducted with

623 primary minerals and ores. Studies conducted with secondary resources (such as end-of-life
624 products, industrial waste materials, mining wastes, spent batteries etc.) are limited and
625 hence, research is needed to find out the process efficacy with these secondary resources. It
626 is important to note that most of these secondary resources contain a significant amount of
627 highly valuable metals and hence, their efficient processing through bioleaching will
628 achieve the goal of a “circular economy” (Ellen MacArthur Foundation, 2015). In terms of
629 catalytic ions, Ag^+ has proven to be the most exciting due to its positive effect on a wide
630 range of minerals (chalcopyrite, galena, complex sulfide, spent batteries etc.). There is
631 evidence that Cu-bearing minerals and ore are currently the most amenable for Ag^+
632 catalyzed bioleaching. Considering the fact that a significant amount of Cu is already
633 produced industrially using bioleaching (Panda et al., 2015b), Ag^+ -catalyzed bioleaching
634 (with *At. ferrooxidans*) offers the greatest potential to extract Cu from low-grade minerals
635 and concentrates in a more efficient and cost-effective manner. Moreover, Ag^+ can be
636 added to the leaching medium either as a finely divided metal or in the form of different
637 salts. However, types of salts used may affect the overall bioleaching process due to their
638 differential solubility in the leaching media and their toxicity towards bioleaching
639 microorganisms (Mcleroy et al., 1974). Silver salts such as AgCl , Ag_2SO_4 and AgNO_3 are
640 preferable as they are water soluble, although insoluble salts such as Ag_2S may also be used
641 but the quantity of Ag^+ required to achieve the same yield will be relatively higher using
642 insoluble salts (Mcleroy et al., 1974). Among water soluble silver salts, AgNO_3 may be
643 preferable to AgCl and Ag_2SO_4 , as the latter have a tendency to precipitate as
644 argentojarosite depending upon the media composition (Cordoba et al., 2009; Abdollahi et
645 al., 2014). In terms of toxicity, Ag_2SO_4 has been found to be more toxic to bioleaching

646 microorganisms compared to AgCl. This was attributed to its relatively higher solubility in
647 aqueous solution, which leads to higher bioavailability of soluble silver ion to bioleaching
648 microorganisms (Sato et al., 2000). However, there are currently criteria for choosing these
649 salts and the choice seems to be largely governed by its availability and cost. There is a
650 paucity of studies concerning the effect of different Ag⁺ salts on bioleaching process.
651 Studies with metal salts other than Ag⁺ (Hg⁺⁺, Bi⁺⁺⁺, Cu⁺⁺, Co⁺⁺) are also absent. Future
652 studies should explore this aspect. Moreover, studies on the combined use of metal ion
653 catalysts and non-metal catalysts or bi-metal ion catalyst are also absent. The simultaneous
654 use of metal ion (such as Ag⁺) and non-metal catalyst (such as activated carbon) compared
655 to a single catalyst, may have the potential to induce greater catalysis owing to synergistic
656 effect. Similarly, the use of bi-metallic catalysts, in combination or in series, may also
657 promote better bioleaching yields. Future studies should explore their possible efficacy and
658 reaction mechanisms during bioleaching.

659 It is also important to note that *At. ferrooxidans* is currently the most used
660 microorganism owing to its relatively higher tolerance to different metal ions generally
661 present in bioleaching media. However, as each mineral and ore have different chemical
662 compositions, other leaching microorganisms such as thermophilic bacteria, archaea, and
663 fungi, under different process conditions, may also prove to be useful agents for gaining
664 better efficiency. Issues with the safe usage of many metal ions have been a concern with
665 regulatory bodies and the public. Therefore, robust strategies for safe handling and disposal
666 need to be identified in accordance with the prevailing local and international laws.
667 Following this review, it is recommended that the focus of the future work should be on (1)
668 investigating the efficiency of processes with different secondary resources (2) evaluating

669 the use of different types of microorganisms (3) examining the process efficiency in larger
670 scale reactors, and (4) evaluating different cost-effective processes to recover metal ions
671 from treated bioleached residue and metal laden liquor.

672

673 **8. Conclusions**

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

683

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928 **Figure captions**

929 **Fig. A1:** XRD of the bioleached residue confirming the presence of Ag_2S (Hu et al., 2002)

930 **Fig. A2:** SEM micrographs (A and B) and EDAX mapping (C and D) showing Ag
931 precipitation on bioleached residues of molybdenite concentrate (Abdollahi et al.,
932 2014).

933 **Fig. A3:** SEM images of residues leached (A) without Cu^{++} (B) in the presence of Cu^{++}
934 (Zeng et al., 2012)

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951 **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)	Chalcopyrite concentrate	Nakazawa et al., 1998
Activated carbon	<i>At. ferrooxidans</i> , <i>At. thiooxidans</i>	12	25	79 (Cu)	Copper sulfide ores	Zhang et al., 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)	Chalcopyrite -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)	Chalcopyrite	Dong et al., 2013
Sodium chloride	<i>A. manzaensis</i> YN-25	66	10	82 (Cu)	Chalcopyrite	Chang et al., 2012
Waste newspaper	<i>At. ferrooxidans</i>	20	6	99.13 (Cu)	Chalcopyrite	Panda et al., 2015a
Polyethylene glycol	<i>At. ferrooxidans</i>	09	21	12.5 (Cu)	Chalcopyrite	Zhang et al., 2016

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954 **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	2.0	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	Escudro 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

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958 **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- Molybednite	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	Escudro 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	0.750	2.9	1	35	Spent lithium-ion batteries	Zeng et al., 2013
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

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963 **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)*100	Reference
Ag ⁺	Chalcopyrite	0.5	38 (Cu)	0.34	6.9	Mcelroy and Duncan, 1974
Ag ⁺	Complex sulphide	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

965 **Table 5:** Inhibitory concentration of catalytic ions to different bioleaching microorganisms

Catalytic ion	Salt	Toxic concentration (mg/L)	Affecting Microorganisms	Reference
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</i> , <i>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.

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