



Review

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



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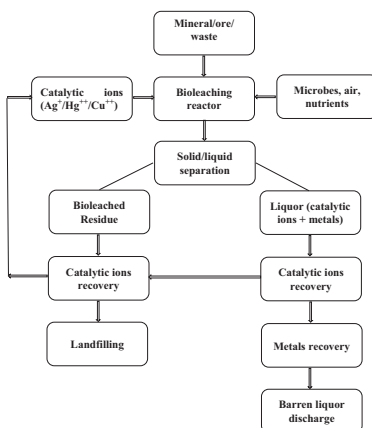
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HIGHLIGHTS

- 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).

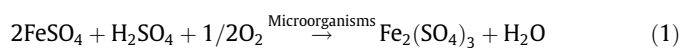
Although bioleaching offers many advantages, the relatively slow dissolution kinetics and low metal leaching yield are critical factors that hinder its large-scale application. For example, laboratory bioleaching experiments may last for more than 300 days in order to obtain reasonable metal extraction efficiencies (Munoz et al., 2007), and in large industrial operations such as Cu<sup>++</sup> 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<sup>+</sup>, Hg<sup>++</sup>, Bi<sup>+++</sup>, Cu<sup>++</sup>, Co<sup>++</sup>, 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 (Fe<sup>++</sup>) and reduced sulfur compounds as per Eqs. (1) and (2). The oxidation of Fe<sup>++</sup> and reduced sulfur compounds lead to the generation of biologically produced ferric ion (Fe<sup>+++</sup>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), respectively (Ma et al., 2017). The generated H<sub>2</sub>SO<sub>4</sub> and/or Fe<sup>+++</sup> act as oxidants and oxidize the metal sulfides (redoxolysis) and/or solubilize the metal sulfides and oxides as per Eqs. (3–5).



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