

MINIREVIEW

Microbial Leaching of Metals from Solid Industrial Wastes

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Biotechnological applications for metal recovery have played a greater role in recovery of valuable metals from low grade sulfide minerals from the beginning of the middle era till the end of the twentieth century. With depletion of ore/minerals and implementation of stricter environmental rules, microbiological applications for metal recovery have been shifted towards solid industrial wastes. Due to certain restrictions in conventional processes, use of microbes has garnered increased attention. The process is environmentally friendly, economical and cost-effective. The major microorganisms in recovery of heavy metals are acidophiles that thrive at acidic pH ranging from 2.0–4.0. These microbes aid in dissolving metals by secreting inorganic and organic acids into aqueous media. Some of the well-known acidophilic bacteria such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans* and *Sulfolobus* spp. are well-studied for bioleaching activity, whereas, fungal species like *Penicillium* spp. and *Aspergillus niger* have been thoroughly studied for the same process. This mini-review focuses on the acidophilic microbial diversity and application of those microorganisms toward solid industrial wastes.

Keywords: Acidophiles, solid waste, microbial leaching, metal recovery

Introduction

Environmental sustainability is vital due to progressive development of industrialized societies, declining natural resources and the detrimental consequences of climate change. Key areas of focus are the management and preservation of environmental resources, management of waste, prevention and treatment of pollution, and preservation of biodiversity (Verstraete, 2007). In this context, biotechnology has wide applications across many sectors including agriculture, industry, and medicine. Biotechnological processes are greener

compared to many traditional chemical-based technologies. Biological processes can contribute appreciably to future technologies, such as greenhouse gas reduction, biodegradable product synthesis, and, most importantly, management of reduced waste and pollution. Developing the ‘microbial resource management’ strategy, which mainly involves enhancement of the natural functional ability of the residing microbial communities, will promote an environmental-friendly use of biotechnology (Read *et al.*, 2011).

Microorganisms can play vital role by interacting with the inorganic compounds present in waste. Microorganisms are plentiful in nature and play vital roles in the weathering of rocks, mobilization of metals from minerals, and reduction and oxidation of metals. These microbial processes are also prominent in the geochemical cycling of inorganic compounds in nature. The main user-friendly advantages in these microbiological processes are their ease of operation and limited use of process controls. These microbiological principles and processes have the potential to be adapted for technical waste treatment applications. Lastly, the process is carried out in a closed loop that generates minimum effluents and thus is preferred as a green technology (Hoque and Philip, 2011).

Microbial leaching and mechanism

Biohydrometallurgy or so-called microbial leaching is the interaction between metals and microbes where the insoluble metal sulfides get converted to metal sulfate. The naturally occurring microorganisms do act upon the mineral sources in order to dissolve the metals in it or microorganisms can be externally added to the ore/mineral source to transform the solid metal-complex entity into solubilized solution form. Later, the dissolved metals can be recovered through conventional methods (Brandl and Faramarzi, 2006). For example, in the case of copper extraction, copper sulfide is microbially oxidized to copper sulfate and the metal ions are concentrated in the aqueous phase and the remaining solids are discarded. ‘Bio-oxidation’ is known as a closely related technology to bioleaching, but differ in certain way. In biooxidation process, the compounds of interest can be recovered from the solid material. Here the minerals first get oxidized microbially into the solution form in order to concentrate the required metal values in the solid material. Later the metals from the solid material get extracted by conventional way. For example, in the recovery of gold from arsenopyrite ores, the gold remains in the mineral after biooxidation and is then extracted via cyanidation in a subsequent step. The term bioleaching therefore, is clearly inappropriate when referring to gold recovery.

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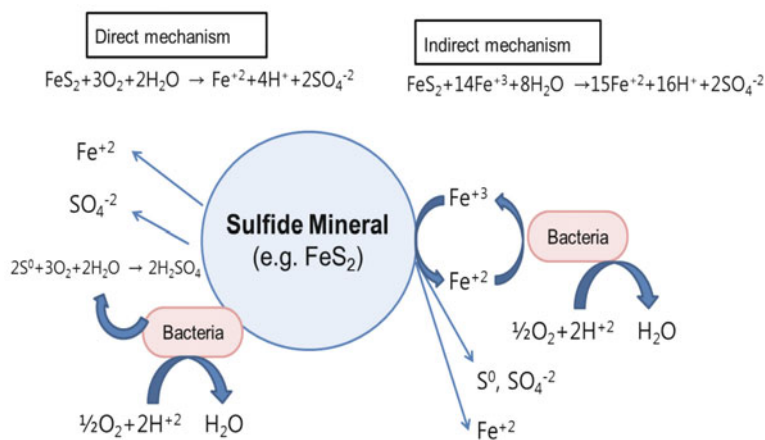


Fig. 1. Bacterial mechanism for metal sulfide dissolution. In the direct mechanism, bacteria attach directly to the sulfide mineral surface and, with aid of O_2 and CO_2 , bacteria dissolve metal ions to the solution phase and sulfide is changed to sulfate. In the indirect mechanism, bacteria take up O_2 and CO_2 and oxidize Fe^{+2} (energy source) to Fe^{+3} , which dissolve metal ions. After releasing metal ion, Fe^{+3} is again reduced to Fe^{+2} .

Bio-mining is a more general term that is used to refer to both processes and mainly relates to the application of microbial process in the mining industry for economic recovery on a large scale (Das *et al.*, 2011).

There are two major mechanisms involved in microbial metal solubilization of sulfide minerals (Fig. 1). One is a direct mechanism that involves physical contact of the organism with the insoluble sulfide. Microorganisms oxidize the metal sulfides obtaining electrons directly from the reduced minerals. An indirect mechanism involves the ferric-ferrous cycle. The oxidation of reduced metals is mediated by the ferric (III) ion and this is formed by microbial oxidation of ferrous (II) ion present in the minerals. Ferric (III) ion acts as an oxidant and oxidizes metal sulfides and is reduced to ferrous (II) ion that, in turn, can be microbially oxidized. In many cases, the direct mechanism dominates over the indirect one, mainly because the direct mechanism involves direct physical contact of bacteria to mineral surfaces. However, the surface attachment of microorganisms may not be an indication of the existence of a direct mechanism. Reflecting this, the term ‘contact leaching’ was introduced to indicate the importance of bacterial attachment to mineral surfaces (Tributsch, 2001). Indeed, the model of direct and indirect metal leaching does not have clear picture for the researchers and is still under discussion.

Depending on the metal composition in the solid waste or minerals or ores, different metabolic reactions can occur upon the microbe-metal interaction. Both prokaryotes and eukaryotes act on the metals based on (i) acidolysis, (ii) complexolysis, and (iii) redoxolysis (Brandl and Faramarzi, 2006). In acidolysis process, microorganisms are able to mobilize metals by the formation of organic or inorganic acids (e.g., citric acid, oxalic acid, sulfuric acid) and by oxidation and reduction reactions. The acid generation is a protonic reaction that weakens the metal ion bond and thus solubilize it. In the case of complexolysis process, the metal solubilization is by ligand-induced mechanism where microbial formation of complexing or chelating agents increases the metal mobility. For example, siderophore, an iron chelating agent, secreted by bacteria, strongly binds to the soluble ferric (III) iron. It occurs in common mineral phases of oxides and hydroxides in the environment, where siderophore actively binds to ferric (III) iron and helps in mobilization of metal

ions. Considering redoxolysis process, which takes place due to microbial action of either oxidation or reduction reaction. In this case the metal mobility increases based upon the type of metal, its mineral phase and oxidation state.

Besides acid generation, bacteria are able to produce catalytic compounds like ferric (III) iron, which acts as an oxidizing agent for the metal dissolution from waste or minerals. Ferric (III) iron is reduced during the reaction, but the effective microbes ensure continuous regeneration of ferric (III) irons. Also, many strains have the ability to anaerobically reduce ferric (III) irons to ferrous (II) irons (Rawlings, 2004). During interaction between microbes and metals, the role of the microorganisms is to generate the leaching chemicals and to create the space in which the leaching reactions take place. Microorganisms typically form an exo-polysaccharide (EPS) layer when they adhere to the surface of a mineral, but not when growing as floating (planktonic) cells (Ghauri *et al.*, 2007). It is within this EPS layer, rather than in the bulk solution, that the bio-oxidation reactions take place most rapidly and efficiently (Sand and Gehrke, 2006). The EPS serves as the reaction space.

From an industrial perspective, it is essential that these acidophiles are able to grow at low pH and tolerate high concentrations of acid. Two important reasons for this are to enable iron cycling and to permit reverse electron transport to take place. A low pH is required for the iron cycle whereby ferrous (II) iron serves as an electron donor under aerobic conditions and ferric (III) iron as an energetically favorable alternate electron acceptor if the concentration of oxygen falls. Ferric (III) iron as an alternate electron acceptor is therefore readily available to acidophiles, but is less available to aerobic neutrophiles or moderate acidophiles because ferric (III) iron is almost totally insoluble in neutral, aerobic environments (Baker-Austin and Dopson, 2007).

Microbiological leaching is relatively inexpensive, which has encouraged its use by environmental technologists for industrial waste treatment. Also, the process is quite flexible and microbes can easily adapt to varied conditions and metabolize/co-metabolize the substrates present in the medium. Most importantly, microbiological leaching is a green technology and there has been growing interest in the adoption of microbiological processes over conventional technologies for the treatment of industrial wastes to recover valuable

metals (Gadd, 2010).

Since most of the acidophilic microbes are prevalent in natural sites like mining area, they generate sulfuric acid (e.g., *Acidithiobacillus* species) or organic acids (in case of heterotrophic bacteria and fungi) as an occurrence of their metabolic process. All these processes are considered to be responsible for the microbial action upon the solid waste material in order to dissolve the metals. Previous reports have revealed successful application of the microbial dissolution of metals in industrial practices (Hoque and Philip, 2011; Asghari *et al.*, 2013). Application of microbial processes towards solid industrial wastes for metal dissolution is currently at preliminary state. This must be focused in the direction for sustainable environmental stewardship for industrialization of metal recovery from solid wastes in order to stabilize the global ecosystem (Rawlings, 2004).

Biodiversity of acidophilic microorganisms

The biodiversity of microbial communities involved in bio-processing is strongly correlated with the selected industrial approach. Experimental parameters such as temperature, pH, and substrate concentration are also important during the biooxidation process in different environments. The uniform conditions established in biooxidation tanks restrict biodiversity. The continuous flow nature of the process makes cell division time a crucial factor for prokaryotes to dominate the microbial community (Rawlings and Johnson, 2007). The most common microorganisms involved in the biomining processes are bacterial species of the genera *Acidithiobacillus* and *Leptospirillum*. Besides these, leaching archaeobacteria have been known for many years and all belong to the *Sulfolobales* group of extremely thermophilic, sulfur and iron oxidizers including the genera *Sulfolobus*, *Acidianus*, *Metallosphaera*, and *Sulfurisphaera* (Norris *et al.*, 2000). Recently, mesophilic and acidophilic iron oxidizing archaeobacteria have also been discovered. These belong to the genus *Ferroplasma*; two species, *F. acidiphilum* and *F. acidarmanus*, have been identified (Johnson, 2008). Most of these acidophiles live in naturally occurring acid mine drainage, mine effluents, mine ponds, and areas near mining excavations. Most abandoned mines generate acidic effluents through natural activities. The effluents often subsequently mix with other natural water bodies and can increase the microbial diversity. Due to development of advanced molecular biotechnological tools, the ecology of acidophilic bacteria in the acid mine drainage sites as well as in bioleaching reaction processes has been elucidated and published. Among the molecular tools, denaturing gradient gel electrophoresis is useful for the investigation of the microbiome composition and its evolution over time and space (He *et al.*, 2010; Mi *et al.*, 2011). The major bacteria those have been reported from environments affected by acid mine drainage are *Acidimicrobium* (*A. ferrooxidans*), *Acidisphaera*, *Acidithiobacillus* (*A. ferrooxidans*, *A. caldus*, *A. ferrivorans* and *A. thiooxidans*), *Acidobacterium* (*A. capsulatum*), *Acidocella*, *Acidiphilium* (*A. acidophilum*, *A. angustum*, *A. rubrum*, and *A. cryptum*), *Alicyclobacillus* (*A. disulfidooxidans*), *Ferrimicrobium* (*F. acidiphilum*), *Frauteuria*, *Leptospirillum* (*L. ferriphilum* and *L. ferrodiazotrophum*), *Sulfobacillus* (*S. acidophilus*, *S. thermotolerans* and *S. thermosulfidooxidans*), and *Thiomonas* (Edwards *et al.*, 2000;

Bruneel *et al.*, 2006, 2008). Acid-tolerant clones of *Gallionella* (*G. ferruginea*) that oxidize Fe above pH 4 were also documented from acid mine drainage-contaminated water and sediments (Bruneel *et al.*, 2005; Mohapatra *et al.*, 2011).

Knowing the bacterial identity in the mine-attached environment, some of the bacteria that could be of industrial importance can be isolated and adapted for further use in bioleaching processes of minerals or solid wastes. The mixed culture of bacteria from the natural habitat has been found to be more robust than pure culture while treating minerals or solid wastes. A pyrite biooxidation plant has been confirmed to contain of mixed culture of moderately thermophilic acidophiles. A consortium comprised of *Acidithiobacillus ferrooxidans*, *Acidithiobacillus caldus*, and *Leptospirillum ferriphilum* enhanced pyrite dissolution compared to pure bacterial cultures or mixed cultures comprising two of the three strains (Okibe and Johnson, 2004). Moreover, the study of ecological interactions within acidophilic mineral-oxidizing consortia showed that iron- and sulphur-oxidizing bacteria belonging to the genus *Sulfobacillus* likely play a secondary role in mineral oxidation, but are extremely important in the regulation of organic carbon compounds levels (Nanchucheo and Johnson, 2010). The ability of *Sulfobacillus* spp. to scavenge glycolic acid through their metabolism emphasized the relevance of ecological relationships established during bioleaching (Nanchucheo and Johnson, 2010). From a commercial point of view, biooxidation of heap for low grade minerals has been reported to contain many and diverse microhabitats due to a partial change in physico-chemical parameters (Rawlings and Johnson, 2007; Johnson, 2008). Moreover, the fitness of prokaryotes in heap leaching depends on their ability to adhere to the surface of the minerals and form biofilms (Sand and Gehrke, 2006). The presence of quorum sensing-signaling molecules involved in biofilm formation has been reported in *Acidithiobacillus* and *Leptospirillum* spp. (Rivas *et al.*, 2007; Ruiz *et al.*, 2008). In contrast, the quorum molecules could not be detected in the biofilm-forming acidophile archaeon *Ferroplasma acidarmanus* (Baker-Austin *et al.*, 2010).

The genome of the major prokaryote *Acidithiobacillus ferrooxidans* has been fully sequenced and it is the key acidophilic bacterium in almost all bio-mining applications. Available genomic information of this species is increasing daily. The future bioinformatics tool will exploit other key bacteria that could play significant roles in metal dissolution from low grade minerals and different kinds of solid industrial wastes, with the goal of unraveling their special properties and enhancing effectiveness during the dissolution process. Besides the application of these microbes towards metal dissolution from low grade minerals, a recent trend has shifted their application for a variety of solid industrial wastes. The naturally isolated bacteria as well as pure artificial cultures have significant roles in metal dissolution from solid wastes. However, the research is not yet at the commercial stage.

Metal-rich waste dissolution by microbes

The microbial leaching processing of solid waste allows the cycling of metals similar to biogeochemical metal cycles and diminishes the demand for resources such as ores, energy, or

landfill space. In recent decades, major solid wastes, such as electronic scrap, fly ash, galvanic sludge, spent petrochemical catalysts, and spent batteries have been explored for microbial leaching.

Among the major wastes, bioleaching has been considered as the key technology for fly ash treatment, electronic scrap, spent batteries, waste slag, and spent petro-chemical catalysts. *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*, and fungal species like *Aspergillus niger* have been used to recover Al, Ni, Zn, Cu, Cd, and Cr from coal fly ash (Seidel and Zimmels, 2001; Xu and Ting, 2009). Since the waste sample lacks key energy sources like iron and sulfur, both ferrous sulfate and elemental sulfur are added externally to permit bacterial activity. The alkaline nature of coal fly ash in general reduces the bacterial growth as well as leaching of metals. However, the proper adaptation with fly ash can help retain bacterial viability during the bioleaching process and enhances metal dissolution (Seidel and Zimmels, 2001). Fly ash treatment using *Aspergillus niger* using one-step and two-step processes have been described (Wu and Ting, 2006). Due to the alkaline nature of fly ash, pretreatment by water washing prior to bioleaching with *A. niger* can be done, which can significantly increase the metal leaching rate from fly ash (Wang *et al.*, 2009). Additionally, different waste sludge and river sediments have been examined in bioleaching recovery of metals (Pathak *et al.*, 2009). Among the examined bacteria, those in the genus *Acidithiobacillus* have proven particularly adept at leaching metals including Cu, Ni, Zn, and Cr, and more effectively remediating metal-contaminated sites. The waste sludge obtained after bioleaching can be safer for land applications (Wang *et al.*, 2007; Fang *et al.*, 2009).

Advancements in technological skill and industrial competitiveness have accelerated the appearance of new electronic items in the marketplace, which has increased the waste. These wastes contain harmful organic and inorganic metals that can affect the ecosphere if disposed outside. The recovery of harmful metals from the electronic waste or reduced toxicity of the disposed material has become an important research goal. Bioleaching using mesophilic and moderately thermophilic acidophiles may have a useful role to play. Ilyas *et al.* (2010) used *Sulfobacillus thermosulfidooxidans*, a moderate thermophile, to bioleach electronic scrap, and reported recovery of more than 80% of Ni, Cu, Zn, and Al. With proper adaptation and pretreatment, more than 90% of metal value could be recovered by a column leaching process in a pilot study (Ilyas *et al.*, 2013). The involved microbial consortia comprising acidophilic bacteria and fungi (*Aspergillus niger*, *Penicillium simplicissimum*) have been termed computer-munching microbes (Brandl *et al.*, 2001). The consortia are adept at dissolving heavy metals like Cu, Ni, and Zn in a single-step or a two-step bioleaching process. The latter is reportedly more effective for substantial metal dissolution (Yang *et al.*, 2009). Similarly, a recent study on bacterial leaching of metal concentrated printing circuit board with a mixed microbial consortium showed promising results for Cu extraction. Xiang *et al.* (2010) reported that the application of mixed bacteria isolated from an acid mine drainage site resulted in the leaching of 95% of the Cu in a two-step process using ferrous (II) iron as the major substrate for bacteria. The two-step process reduced the lea-

ching period from 12 days to 5 days. In another bioleaching study, the metallic and non-metallic components of the printing circuit board were separated first and the effect of the non-metallic component during metal bioleaching process was investigated (Zhu *et al.*, 2011). The authors concluded that the two-step process was very effective for bacterial leaching of Cu. Therefore, for industrial application, a two-step process is believed to be appropriate to increase leaching efficiency. In the two-step process, the bacterially generated acidic solution is treated as a lixiviant for metal dissolution. In general, the advantages of such processes are that independent lixiviant generation removes the link between the bioprocess and the chemical process and thus makes it possible to optimize each process independently to maximize productivity. This strategy can be used when the ore/waste does not contain the necessary mineral components in sufficient quantities to sustain a viable bacterial population. Furthermore, higher waste concentrations can be treated compared to the one-step process, which results in increased metal yields.

Apart from the electronic waste, another major solid waste is spent Li-ion and Ni-Cd batteries used in digital cameras, cellular phones, and laptop computers. Mishra *et al.* (2008a) studied Co and Li leaching from spent Li-ion battery waste using pure cultures of *Acidithiobacillus ferrooxidans*. A similar study was conducted by Xin *et al.* (2009), in which bioleaching of spent lithium-ion batteries with mixed cultures of acidophilic sulfur oxidizers and iron oxidizers was carried out. The spent batteries lacked iron or sulfur, and most of the components were present in the oxide form. These studies indicate that the mechanism of metal dissolution varies with different metal species and energy source types. With elemental sulfur as an energy source, the exclusive metal dissolution occurs through production of biogenic sulfuric acid by the bacteria (Zhao *et al.*, 2008). Recently, Zeng *et al.* (2012) studied the application of Cu-catalyzed bacteria for Co bioleaching from Li-ion batteries. Using Cu as a catalyst the leaching of Co reached 99% within 6 days of leaching in presence of ferrous (II) iron as the energy source. In this case, the catalytic mechanism was investigated to explain the enhancement of cobalt dissolution by Cu ions, in which LiCoO_2 underwent a cationic interchange reaction with Cu ions to form CuCo_2O_4 on the surface of the sample, which could be easily dissolved by ferric (III) iron. Other than Li-ion batteries, spent Ni-Cd batteries have also been treated in bioleaching processes where 100% Cd leaching has been reported by *Acidithiobacillus ferrooxidans* in the presence of $\text{Fe}_2(\text{SO}_4)_3$ solution. Comparing the leaching process with that H_2SO_4 solution, the latter showed reduction in Cd leaching due to the neutralization of the solution because of hydroxide samples present in the electrode of spent Ni-Cd batteries (Velgosa *et al.*, 2013).

Wastes generated from petrochemical sources have a significant detrimental effect on the environment. Spent petroleum catalyst is the major solid waste from petrochemical industries. In such industries, large quantities of catalysts are used in the purification or up-gradation of various petroleum streams or residues. The used catalysts lose their activity with time and when the activity decreased to acceptable level the catalyst is regenerated or reused. A number of

Table 1. Different Industrial wastes treated by bioleaching

Type of waste	Bioleaching efficiency	Microorganisms	Remark
Fly ash	Al:97%; Zn:98%; Fe:56%	<i>Aspergillus niger</i>	Xu and Ting (2009)
Sewage sludge	Cu:64%; Zn:76%; Ni:58%; Cr:52%	<i>Acidithiobacillus thiooxidans</i>	Pathak <i>et al.</i> (2009)
	Zn:89%; Cu:80%; Pb:50%; Cr:32%	Iron-oxidizing bacteria	Wen <i>et al.</i> (2013)
Electronic scrap	Cu:90%; Al:80%; Ni:82%; Zn:80%	<i>Thermoplasma acidophilum</i> & <i>Sulfobacillus thermosulfi dooxidans</i>	Ilyas <i>et al.</i> (2013)
	Cu & Sn:65%; Al, Ni, Pb & Zn:>95%	<i>Aspergillus niger</i> & <i>Penicillium simplicissimum</i>	Brandl <i>et al.</i> (2001)
	Cu:71%	<i>Acidithiobacillus ferrooxidans</i>	Yang <i>et al.</i> (2009)
Spent battery	Au:68.5%	<i>Chromobacterium violaceum</i>	Brandl <i>et al.</i> (2008)
	Co:99.9%	<i>Acidithiobacillus ferrooxidans</i>	Zeng <i>et al.</i> (2012);
	Co:100%	<i>Acidithiobacillus ferrooxidans</i>	Velgosova <i>et al.</i> (2013)
	Co:>90; Ni:>80%	<i>Acidithiobacillus</i> spp.	Xin <i>et al.</i> (2009);
Spent petroleum catalyst	Co:65%	<i>Acidithiobacillus ferrooxidans</i>	Mishra <i>et al.</i> (2008a)
	Fe, Ni & Mo:100%; Al:67%	<i>Acidianus brierleyi</i>	Bharadwaj and Ting (2013)
	Al:35%; Mo:83%; Ni:69%	<i>Acidianus brierleyi</i>	Gerayeli <i>et al.</i> (2013)
	Al:63%; Co:96%; Mo:84%; Ni:99%	<i>Acidithiobacillus</i> spp.	Gholami <i>et al.</i> (2011),
Spent fluid cracking catalyst	Ni:88%; Mo:46%; V:95%	<i>Acidithiobacillus thiooxidans</i>	Mishra <i>et al.</i> (2008b)
	Al:54.5%; Ni:58.2%; Mo:82.3%	<i>Aspergillus niger</i>	Saanthiya and Ting (2005)
	Mo:99.5%; Ni:45.8%; Al:13.9%	<i>Aspergillus niger</i>	Amiri <i>et al.</i> (2012)
	W:100%; Mo:92.7%; Ni:66.4%; Al:25%	<i>Penicillium simplicissimum</i>	Amiri <i>et al.</i> (2011b)
Waste electronic device	Au:11.3%	<i>Chromobacterium violaceum</i>	Chi <i>et al.</i> (2011)
Jewelry waste	Ag:5%	<i>Pseudomonas plecoglossicida</i>	Brandl <i>et al.</i> (2008)
Spent automobile catalytic converter	Pt:0.2%	<i>Pseudomonas plecoglossicida</i>	Brandl <i>et al.</i> (2008)

studies have investigated spent petroleum catalyst bioleaching (Mishra *et al.*, 2007; Beolchini *et al.*, 2010; Asghari *et al.*, 2013). The catalyst contains metals like Al, V, Mo, Fe, Sn, Sb, Co, and Ni, which facilitate different hydrocarbon transformations. The discarded spent catalysts usually contain 7–20% V+Ni, 15–25% coke, 7–15% sulfur, and 5–10% residual oil together with active metals (Mo and Co or Ni) and Al₂O₃ originally present in the catalyst. These metals contain a substantial amount of oil that could be harmful for bacteria. The waste catalysts need to be pretreated prior to bioleaching. Mishra *et al.* (2007) acetone washed the spent petroleum catalyst to remove the organic oil as well as hydrocarbon content and the pretreated catalyst showed efficient bioleaching with both iron and sulfur oxidizing bacteria (Mishra *et al.*, 2008b, 2009; Gholami *et al.*, 2011). A recent study reported the application of thermophilic bacteria on leaching of spent refinery catalyst (Bharadwaj and Ting, 2013). An optimization study by Gerayeli *et al.* (2013) reported 35% Al, 83% Mo, and 69% Ni bioleaching using the thermophilic acidophilic archaea *Acidianus brierleyi*. Additionally, *Aspergillus niger* was shown to be effective for the metal recovery from spent refinery catalyst where the oxalic acid secreted by the fungi could dissolve the valuable metals into aqueous media (Saanthiya and Ting, 2005; Amiri *et al.*, 2012). Fungi, such as *Aspergillus* and *Penicillium*, secrete organic acids like oxalic acid, citric acid, and maleic acid that selectively dissolve some of the metals from the spent catalyst sample (Amiri *et al.*, 2011a). Bioleaching of spent petroleum catalyst is effective with these microorganisms compared to individual acid treatment. However, most reports have been

bench scale studies; reactor studies have yet to be done.

Besides the role of acidophilic autotrophs in industrial waste bioleaching, several studies have explored the use of heterotrophic bacteria for recovery of valuable metals like gold, silver, nickel, and platinum from solid wastes (Faramarzi *et al.*, 2004). These heterotrophs, termed cyanogenic bacteria, produce cyanide in the aqueous medium, facilitating the formation of a cyanide complex of the respective metal ions. Well-known cyanogenic bacteria are *Chromobacterium violaceum*, *Pseudomonas fluorescens*, and *Bacillus megaterium*. Both nickel and gold form complexes like [Ni(CN)₄]²⁻ and [Au(CN)₂]⁻, respectively. Bioleaching studies have been conducted using nickel powder or electronic scraps using the aforementioned bacteria (Kita *et al.*, 2006; Chi *et al.*, 2011; Pradhan and Kumar, 2012). As well, these species have been used in attempts to dissolve silver from silver containing jewellery waste and platinum from automobile catalytic converters (Brandl *et al.*, 2008). Looking at the potential of cyanide complex formation by these consortia, a suitable term, bio-cyanidation, has been coined (Mishra and Rhee, 2010). Application of microorganisms in different industrial waste along with the bioleaching efficiency of metals is summarized in Table 1.

Conclusions and future prospectives

Solid waste generation is a global problem that demands environmental friendly treatment processing. A biotechnological approach is optimal in terms of maintaining the ecosystem in an economically feasible manner. Increased knowledge of the interaction between microbes and different types

of solid wastes is needed. Some of the solid wastes contain valuable metals. Their recovery through microbial and other assisted recovery technologies seems feasible. To improve the yield of metal obtained through bioleaching of solid waste, new microbial strains have to be identified that can withstand higher concentrations of potentially toxic metals. Microbial community composition using DNA and PCR techniques of different bio-heap systems, stirred tank reactors, and acid mine drainage sites will enrich knowledge of the potential of various autotrophs and heterotrophs. The dynamics of microbial populations are variable both spatially and temporally in the bioprocessing system. There is a need to define and understand the potential interactions among the components of microflora. For this purpose, strains that have been deliberately genetically modified or selected by mutation should be considered. Their use could reduce the residence time and simultaneously enhance the economy of the process. Most microbe-metal interactions that occur in solid waste processes remain unclear concerning the exact physiological mechanism of the microbes. Therefore, rapid, accurate and simple techniques are needed to gain greater control over microbial processes by plant operators. To date, biotechnological leaching is practiced in a small number of industrialized countries, but has great potential in developing countries. For the sustainable environmental protection, both developed and developing countries must adopt the emerging leaching biotechnology process.

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