Current Research Trends of Microbiological Leaching for Metal Recovery from Industrial Wastes

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The concept of microbiological leaching have played a greater role to recover valuable metals from various sulfide minerals or low grade ores during the middle era of twentieth century and that continued till the end of the century. Slowly, due to depletion of ore/minerals, and implementation of stricter environmental rules, microbiological leaching process has been shifted for its application to recover valuable metals from the different industrial wastes. Although there are conventional processes, physical and chemical methods, for treatment of industrial wastes, these technologies have certain limitation in practical applications. The microbial method is an efficient and cost-effective alternative to chemical and physical methods because of its low demand for energy, material and less generation of waste byproduct. There are several industrial wastes that possess toxic elements and thus when leached into atmosphere cause serious environmental problem. Among the wastes, spent petroleum catalysts, electronic scraps, lithium battery wastes, sewage sludge, fly ash etc. are some of the major industrially produced wastes. These solid wastes mostly contain Ni, V, Mo, Co, Cu, Pb, Zn, and Cr like heavy metals in it.

The major microorganisms those play the significant role in recovery of heavy metals from such wastes belong to acidophilic group. These acidophilic groups thrive in acidic pH ranges (pH 2.0 – 4.0) and help in dissolving the metals from solid phase of wastes into the aqueous phase. Among the bacteria *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans*, and *Sulfolobus* sp., are well known consortia for the bioleaching activity while *Penicillium*, and *Aspergillus niger* are some fungi those help in metal leaching process. The current chapter will be thoroughly studied about the application of these acidophilic microorganisms for the metal recovery from different industrial wastes. The key microorganisms and their bioleaching mechanism have been focused here.

Keywords: solid wastes; bioleaching; acidophilic microorganisms

1. Introduction

Due to invention of steam engine in the late 19th century there was tremendous growth of global industrial activities. This unexpected spurt in global industrial activities, which was in a way essential to sustain the phenomenal rise in population, resulted in progressive deterioration of the ecosystem due to discharge of highly polluted effluents in the forms of liquid, solid and gas. Technologists have been striving to develop eco-friendly and sustainable processes in order to arrest rapid degradation in the ecosystem. Therefore, concerted efforts are put to develop eco-friendly processes especially in the fields of mineral processing and extraction of metals, which have been the mainstay of world economy [1]. Usually, metal values are recovered from the respective ores through pyro- and hydro-metallurgical routes or a combination of both. But due to gradual depletion of high-grade ores, efforts are now being directed to recover metal values from wastes, complex and lean ores, which otherwise cannot be treated by conventional routes economically [2, 3]. The reuse of such materials not only conserves the non-renewable resources but also solve the problem of environmental degradation, which would otherwise have polluted the environment. The important technique that has been developed so far to treat the waste materials comes under the domain of hydrometallurgical processing. It involves aqueous media processing with the help of various acids, alkalis, organic solvents etc. in addition to employing conventional industrial process steps [4].

Bio-hydrometallurgy is a relatively new concept in which various microorganisms are employed to recover metal values. The technique is gaining importance due to its wide commercial application in the area of pharmaceutical, chemical and food processing industries. It is also relatively free from environmental concerns unlike conventional hydro-metallurgical steps [5]. The knowledge gained in these industries helped in its translation to mineral processing and metal extraction operations. The main advantage in the bio-hydro technique is the ease of operation as well as limited use of process controls thus making the operation more users friendly. The technique can also be applied to different types of materials, especially lean and so far unusable resources, by which metal values can be recovered. Lastly, the process is carried out in close loop generating minimum effluents and thus is preferred as green technology.

2. Major industrial wastes of 21st Century

With rapid increase of population along with industrialization, the waste generation fact sheet in the current century usually varies country wise. It is a cumbersome task to figure out an accurate map that how much waste in different industrial sectors being generated every day. Numerous industries (e.g., electroplating, metal-finishing, electronic, steel and nonferrous processes, petrochemical and pharmaceutical) discharge a variety of toxic heavy metals into the environment. These materials, if improperly dealt with, can threaten both public health and the environment [6]. Since the generated waste contains some valuable metals, therefore, suitable treatment process must be an appropriate approach to abate the toxicity. In general, the waste can be categorized into different section depending on the source type and presence of toxic elements in it. Before considering a waste to be toxic or not it must go through toxicity characteristic leaching procedure test where it can be determined whether the waste has toxicity characteristics in amount that meet or exceed the regulatory limits causing it to be a hazardous waste [7].

Most of the industrial wastes contain various metals like Zn, Cd, Cr, Cu, Ni, Pb, V, Mo, Co which are quite toxic for human health if inhaled beyond the limited concentration. Petrochemical or chemical refinery industries use different catalyst along upon certain base and after repeated use the catalysts lose their purity and finally get discarded. These catalysts contain various valuable metals like Ni, Mo, V, Co and their recycling is believed to be novel one [8]. Similarly, fly ash is another kind of waste that is commonly generated from coal-operated plants in world wide. It contains different heavy metals which can be recycled. Looking at our daily uses of electronic materials such as digital camera, television, computer, the old brands usually get outdated due to demand of new brands in the market. To procure the new asset, the old one becomes waste. However, such electronic components contain metals like Cu, Co, Au, Ag, which are valuable metals and recycling is the best option for such waste [9]. We can summarize these wastes into different category based upon their origin. Table 1 represents various wastes that come from different sources.

Table 1 Examples of hazardous waste generated by industries

Waste Generator	Waste Types
Chemical manufacturers	Acid and bases, spent solvents, organic constituents
Printing Industry	Heavy metal solutions, waste ink solvent
Petroleum refinery industry	Waste water containing benzene and other hydrocarbons, spent petroleum catalyst, waste sludge
Leather products manufacturing	Toluene and Benzene
Electronic industry	Electronic scrap, computer printer circuit board, waste battery
Metal manufacturing	Sludge containing heavy metal cyanide waste, paint waste

3. Why a biological process for waste treatment?

Conventional processes can be considered to treat the waste materials for recycling purpose. However, the overall process costs, both operational and capital, will be influenced by several criteria. The general cost of an operation depends on (i) the concentration of metal in solution, (ii) operational mode of equipment, (iii) the need of secondary treatment, and (iv) disposal of secondary waste such as sludge [10]. Industries need to invest huge sums of money in these sectors and therefore any new form of technology can significantly overcome such barriers in both economically and ecofriendly ways. So, biological techniques can be thought to be a suitable process over the comprehensive array of technologies for the treatment of heavy metals present in waste. Because microorganisms have the ability to accommodate a variety of pollutants, both organic and inorganic, it is important to appreciate from the outset that microorganisms cannot destroy metals. However, they can influence metals mobility in the environment by modifying their chemical and/or physical characteristics.

The way microbes interact with metals depends on whether the organisms are prokaryotic or eukaryotic. Figure 1 depicts a schematic feature regarding mechanism of microbe and metal interaction in environment. Microbes have the ability to bind metal ions present in the external environment at the cell surface or to transport them into the cell for various intracellular functions. The removal of metals from various aqueous streams by biosorption and bioaccumulation has received significant attention. These processes involve a typical ion-exchange process where the metal ion is exchanged for a counter-ion attached to biomass. Bioleaching is a similar process where microbes dissolve the metals present in the solid matrix of waste into soluble form. This process in general occurs in acidic medium where the metal ions can easily be mobilized in aqueous system. Most of the acidophilic microorganisms play key role for bioleaching process and previously these have been used in mineral dissolution from ores and concentrates for which these microbes are otherwise termed as biomining microbes. The fact that microbiological leaching is relatively inexpensive for which many environmental technologists rely on application of microorganisms for the industrial waste treatment. The second advantage is that the process is quite flexible and microbes can easily adapt the variations of conditions and metabolize or co-metabolize the substrates present in the concerned medium. The last and important aspect is that such process can be perceived as green technology. Therefore, there is continuous growing interest to adopt microbiological process over conventional technologies for the treatment of industrial wastes in order to recover valuable metals [11].

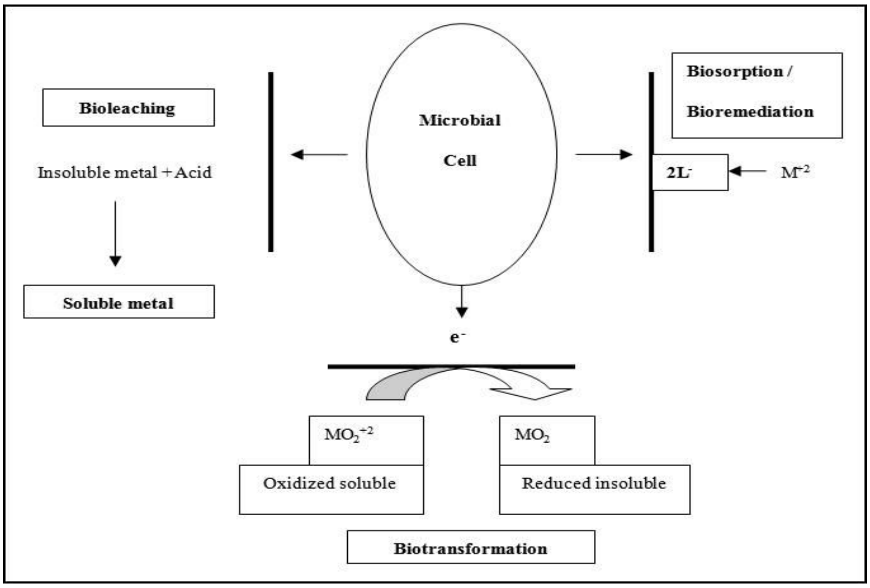

Fig. 1 Microbe-Metal interaction mechanism

4. Bioleaching of solid waste

For last several decades bioleaching was getting its priority in application for the metal recovery from ores/concentrates namely chalcopyrite, calcite, pyrite, arsenopyrite [12]. In the recent years, this process has shown its promising impact in treatment of infected wastes for the metal recovery. Among the major bacteria group those are involved in bioleaching process are chemolithotrophic acidophiles namely, *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Leptospirillum ferrooxidans* and heterotrophs like *Sulfolobus*. Besides, fungal species such as *Penicillium*, and *Aspergillus niger* are some of eukaryotic bioleaching microorganisms that applied in metal recovery from industrial wastes [13].

Among the major wastes, bioleaching has been considered as key technology for fly ash treatment, electronic scraps, spent batteries, spent petroleum catalysts during last several years. Different researchers have applied *Acidithiobacillus thiooxidans* as well as *Acidithiobacillus ferrooxidans* and fungal species like *Apsergillus niger* to recover metals such as Al, Ni, Zn, Cu, Cd, Cr from coal fly ash [14, 15]. Since the waste sample lacks the key energy sources i.e., iron and sulfur in it, both ferrous sulfate and elemental sulfur are added externally for the bacterial activity. The alkaline nature of coal fly ash in generally reduces the bacterial growth as well as leaching of metals. However, the proper adaptation with fly ash can help the bacteria in retaining their viability during bioleaching process and enhance the metal dissolution [14]. Additionally, different waste sludge and river sediments have also examined for bioleaching study to recover metals [15]. Among the bacteria *Acidithiobacillus* group are the key genus which have been used for such process to leach out metals like Cu, Ni, Zn, and Cr. By recovering the metal values from such sites, it has improved the contaminant sites. The waste sludge after bioleaching can be safer for land application [16-18].

Electronic waste or E-waste has been a major industrial waste in 21st century. Several reports have been published regarding the bioleaching of such waste recently. Mesophilic and moderately thermophilic acidophiles have been considered to be getting attention for leaching of metals from E-wastes. Ilyas et al. [19] have observed bioleaching of electronic scrap with *Sulfobacillus thermosulfidooxidans*, a moderately thermophile, that recovered more than 80% of Ni, Cu, Zn, and Al. Previously, Brandl et al., [20] have termed such consortia as computer-munching microbes, comprising acidophilic bacteria and fungi (*Aspergillus niger*, *Penicillium simplicissimum*), that appreciably dissolved heavy metals like Cu, Ni, and Zn. They have proposed the effect of single step as well as two-step bioleaching process for such waste and latter has been examined to be more effective for substantial metal dissolution [21]. For industrial application, a two-step process is believed to be appropriate to increase leaching efficiency. In the two-step process, bacterially generated acidic solution is treated as lixiviant for metal dissolution. In general, the advantages of two stage 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 E-waste, another major solid waste in the present society is spent battery which come from spent Li-ion battery or spent Ni-Cd battery sources, those specially used in digital camera, cellular phone or laptops. Mishra et al., [22] have studied Co and Li leaching from spent Li-ion battery waste by using pure culture of *Acidithiobacillus ferrooxidans*. Similar study has also been conducted by Xin et al., [23] where they have performed the bioleaching of spent lithium-ion battery with mixed culture of acidophilic sulfur oxidizers and iron oxidizers. These spent batteries have neither iron nor sulfur content within it and most of the components occur in oxide form. Therefore, bioleaching study of spent batteries has suggested 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 [24].

Wastes that generate from petrochemical sources are known to have serious impact upon environment. Spent petroleum catalyst is the major solid waste from petrochemical industries. In such industries large quantity of catalysts are used in order to purification or upgradation of various petroleum streams or residues. The used catalysts lose their activity with time and when the activity decreased to acceptable level; it is then regenerated or reused. A number of researches have been reported regarding the spent petroleum catalyst bioleaching [25-27]. The catalyst contains metals like Al, V, Mo, Fe, Sn, Sb, Co, 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 Al_2O_3 originally present in the catalyst. Since these metals contain substantial amount of oil that could be harmful for bacteria and therefore the waste catalysts need to be pre-treated prior to bioleaching experiment. Mishra et al., have conducted acetone washing of 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 [28, 29]. Additionally, *Aspergillus niger* is also found 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 [30, 31]. Bioleaching of spent petroleum catalyst has been found to be effective with these microorganisms compared to the individual acid treatment. However, most of the reports have been limited to bench scale study and reactor study has yet to be formulated.

Besides the role of acidophilic autotrophs in industrial waste bioleaching, several studies have been reported explaining some heterotrophic bacteria for recovery of valuable metals like gold, silver, nickel, platinum from solid wastes [32]. These heterotrophs are coined as cyanogenic bacteria that produce cyanide in the aqueous medium and hence cyanide complex of respective metal ions are formed. The well-known cyanogenic bacteria are *Chromobacterium violaceum*, *Pseudomonas fluorescens*, *Bacillus megaterium*. Both nickel and gold are found to form complexes like $[Ni(CN)_4^{2-}]$ and $[Au(CN)_2^-]$ respectively, while bioleaching studies are conducted from nickel powder or electronic scraps using the above mentioned bacteria [33]. Moreover, these bacteria have been attempted to dissolve silver from silver containing jewellery waste and platinum from automobile catalytic converters [34]. Looking at the potential of cyanide complex formation by these consortia, a suitable term, bio-cyanidation, has been coined. Hopefully this work would take certain attention in near future for the industrialists regarding its commercialization. Application of microorganisms in different industrial waste has been summarized in Table 2.

Table 2 Examples of industrial waste treated by bioleaching

Type of Waste	Metal values	Microorganisms	Remark
Fly ash	Al, Zn, Cu, Cd	*Acidithiobacillus* sp., *Aspergillus niger*	[14, 15]
Sewage sludge	Cu, Mn, Zn, Ni	*At. thiooxidans*	[16]
Sediment	Cr, Cu, Zn	*At. thiooxidans*	[17]
Tannery sludge	Cr	*At. thiooxidans*	[18]
Electronic scrap	Cu, Ni, Sn, Al, Zn	*Acidithiobacillus* sp., *Sulfobacillus*, *Aspergillus niger*	[19-21]
Spent battery	Co, Li, Ni, Cd	*Acidithiobacillus* sp.	[22-24]
Spent refinery catalyst	Co, Ni	*Acidithiobacillus* sp.	[25]
Spent petroleum catalyst	V, Ni, Mo	*Acidithiobacillus* sp.	[28, 29]
Spent fluid cracking catalyst	Al, Mo, V	*Aspergillus niger*	[30, 31]
Waste electric device	Au	*Chromobacterium violaceum*	[32, 33]
Jewelry waste/Automobile catalyst	Ag, Pt, Au	*Chromobacterium violaceum*, *Pseudomonas fluorescens*, *Bacillus megaterium*	[34]

5. Major bioleaching microorganisms

The acidophilic microorganisms that take part in dissolution of metals from the wastes are autotrophic in nature. They can grow in inorganic medium having low pH values. They can tolerate high metal ion concentrations. The two main functions of this type of bacteria are oxidation of Fe(II) to Fe(III) and S to H_2SO_4. These two reactions mainly control the reaction kinetics.

To understand the reaction kinetics, it is mandatory to know about the characterization of the microorganisms and conditions favorable to carry out the oxidation process. The acidophilic microorganisms that actively take part in oxidizing Fe(II) to Fe(III) and S to H_2SO_4 are *Acidithiobacillus*, *Sulfolobus*, *Acidianus* and *Leptospirillium* [35]. *Sulfobacillus* species are gram-positive, rod shaped with rounded or tapered ends and can grow at higher temperature [36]. *Acidianus* species are spherical with tetrahedron, pyramid disc or saucer shaped lobes [37]. *Leptospirillium* species are spiral shaped, non-spore forming and gram negative [38]. Depending on their tolerance to temperature the acidophilic micro-organisms are categorized into three sub-groups such as mesophiles, moderate thermoacidophiles and extreme thermoacidophiles.

5.1. Mesophiles

Mesophiles are those microorganisms which grow at a prevailing room temperature, i.e. 28-37^oC. Among the mesophiles, the most popular and widely used strain is *Acidithiobacillus ferrooxidans*. Although many strains of *Acidithiobacillus ferrooxidans* have been isolated from different sources, most of the strains showed the following optimum growth conditions, i.e. pH 1.5-2.5 and a temperature range of 28-37 ^oC. *Acidithiobacillus ferrooxidans* being a lithotroph, derives energy for its growth by oxidizing Fe(II) to Fe(III) and sulfur, sulfide and different oxyanion of sulfur to sulfate [39]. The assimilation of carbon dioxide by the microorganism is through Calvin Benson cycle catalyzed by the ribulose-biphosphate carboxylase enzyme. The nitrogen requirement is met through ammonium compounds present in the medium.

There is a poor resemblance of DNA homology between different strains of *Acidithiobacillus ferrooxidans*. *Leptospirillium ferrooxidans* is an acidophilic microorganism like *Acidithiobacillus ferrooxidans* [40]. The major drawback with *Leptospirillium ferrooxidans* is, it cannot oxidise sulfur to sulfate [41]. Therefore in order to oxidise Fe(II) and S it is essential to use a mixture of *Leptospirillium ferrooxidans* and *Acidithiobacillus ferrooxidans*. *Acidithiobacillus thiooxidans* has the same morphological characteristics as that of *Acidithiobacillus ferrooxidans*. The main difference between the two microorganisms is that the former cannot oxidize Fe(II). The bacterium gets its energy by oxidizing S and soluble sulfur compounds to sulfate.

5.2. Moderate thermophiles

Moderate thermophiles are able to grow at a temperature of around 50°C. There are number of thermophilic strains isolated from different geothermal environments and mine sites [42]. An important moderate thermophile is *Sulfobacillus thermosulfidooxidans* which has the ability to oxidize sulfur and iron [43]. The bioleaching kinetics by moderate thermophiles is more than mesophiles as the leaching experiments are carried out at higher temperature. The moderate thermophiles are usually available inside the core of the dump as the core temperature is 10-15 ^oC higher than the ambient.

5.3. Extreme thermophiles

Extreme thermophiles are those which can grow actively even at a temperature as high as 80^oC. The most important extreme thermophiles belong to the genus *Sulfolobus* [44]. A number of *Sulfolobus* species have been isolated such as *S. acidocaldarius*, *S. solfataricus*, *S. brierley*, *S. ambioalous* [45]. They show the following properties such as:

(i) anaerobic growth coupled with reduction of elemental sulfur.
(ii) aerobic growth coupled with oxidation of sulfur.
(iii) optimum growth temperature of 65-70 ^oC
(iv) able to oxidize both Fe(II) to Fe(III) and sulfur to sulfate.

Since the extreme thermophiles can grow at higher temperature, so oxidation kinetics is more than mesophiles and moderate thermophiles [45]. The bioleaching kinetics in presence of extreme thermophiles is higher than that of mesophiles and moderate thermophiles. The bioleaching dissolution reaction is exothermic therefore the temperature increases during the reaction. So if extreme thermophiles are used then heat exchanger may not be required to control the leaching temperature.

6. Mechanism of bioleaching

6.1. Bio-chemical reaction mechanism

Metal leaching is now recognized as being mainly a chemical process in which ferric iron and protons are responsible to carry out the leaching reactions. 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 exopolysaccharide (EPS) layer when they adhere to the surface of a mineral but not when growing as planktonic cells [46]. It is within this EPS layer rather than in the bulk solution that the bio-oxidation reactions take place most rapidly and efficiently and therefore the EPS serves as the reaction space [47, 48].

It has been previously established that the metal dissolution reaction is not identical for all metal sulfides and the oxidation of different metal sulfides proceeds via different intermediates [49]. Briefly, a thiosulfate mechanism has been proposed for the oxidation of acid insoluble metal sulfides such as pyrite (FeS_2) and molybdenite (MoS_2), and a polysulfide mechanism for acid soluble metal sulfides such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$) or galena (PbS). Since the industrial waste samples are mostly oxidic in nature, therefore for action of acidophiles, substrates are added externally.

In the thiosulfate mechanism, solubilization is through ferric iron attack on the acid-insoluble metal sulfides with thiosufate being the main intermediate and sulfate the main end-product. Using pyrite as an example of a mineral, the reactions may be represented as:

$$FeS_2 + 6\ Fe^{3+} + 3\ H_2O \rightarrow S_2O_3^{2-} + 7\ Fe^{2+} + 6\ H^+ \qquad (1)$$

$$S_2O_3^{2-} + 8\ Fe^{3+} + 5\ H_2O \rightarrow 2\ SO_4^{2-} + 8\ Fe^{2+} + 10\ H^+ \qquad (2)$$

In the case of the polysulfide mechanism, solubilization of the acid-soluble metal sulfide is through a combined attack by ferric iron and protons, with elemental sulfur as the main intermediate. This elemental sulfur is relatively stable but may be oxidized to sulfate by sulfur-oxidizing microbes such as *Acidithiobacillus thiooxidans* or *Acidithiobacillus caldus* (equation 5).

$$MS + Fe^{3+} + H^+ \rightarrow M^{2+} + 0.5\ H_2S_n + Fe^{2+}\ (n \geq 2) \qquad (3)$$

$$0.5\ H_2S_n + Fe^{3+} \rightarrow 0.125\ S_8 + Fe^{2+} + H^+ \qquad (4)$$

$$0.125\ S_8 + 1.5\ O_2 + H_2O \rightarrow SO_4^{2-} + 2\ H^+ \qquad (5)$$

The ferrous iron produced in equations (1) to (4) may be re-oxidized to ferric iron by iron oxidizing microorganisms such as *Acidithiobacillus ferrooxidans* or bacteria of the genera *Leptospirillum* or *Sulfobacillus*.

$$2\ Fe^{2+} + 0.5\ O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + H_2O \qquad (6)$$

The role of the microorganisms in the solubilization of metal sulfides is, therefore, to provide sulfuric acid (equation 5) for a proton attack and to keep the iron in the oxidized ferric state (equation 6) for an oxidative attack on the mineral.

6.2. Cellular mechanism

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 iron serves as an electron donor under aerobic conditions and ferric iron as an energetically favorable alternate electron acceptor if the concentration of oxygen falls. Ferric iron is almost insoluble at a neutral pH, whereas in acid solutions its solubility is increased. The possibility of using ferric iron as an alternate electron acceptor is therefore readily available to acidophiles but less available to aerobic neutrophiles or moderate acidophiles because ferric iron is almost totally insoluble in neutral, aerobic environments [50].

The external pH of the environment in which extreme acidophiles such as biomining microbes grow is low (e.g. pH 1.0-2.0), whereas the internal cellular pH remains close to neutral. This difference results in a steep pH gradient across the cell membrane. This pH gradient is important for nutritional purposes, especially when using a weak reductant such as ferrous iron as an electron donor. Autotrophic organisms have a high requirement for compounds such as NAD(P)H to reduce their carbon source (CO_2) to produce the sugars, nucleotides, amino acids and other molecules from which new cell mass is synthesized. Heterotrophic bacteria do not have as high a demand for NAD(P)H as their carbon source is more reduced than CO_2 and hydrogen atoms removed from their source of nutrition may be used to satisfy their lower NAD(P)H requirement. Chemolithotrophic autotrophs require a large transmembrane proton gradient to generate the required proton motive force to energise the synthesis of NAD(P)H. The process is known as reverse electron transport [51]. Although this phenomenon has not been studied in many iron-or sulfur-oxidizing chemolithotrophs, strong evidence has been presented that when grown on iron, *Acidithiobacillus ferrooxidans* contains a unique cytochrome *bc1* complex that functions differently from the bc1 complex used during the oxidation of sulfur in electron transport pathway [52]. One way of viewing this is that growth in acid solutions is a nutritional necessity as a large transmembrane pH gradient is required to produce the hydrogen atoms needed to reduce CO_2 to cell mass.

7. Conclusions

Bioleaching application for metal recovery from industrial wastes by acidophilic autotrophs and heterotrophs is a valuable process to recycle the waste along with detoxification of contaminated sites. Most of the acidophiles applied for bioleaching of solid waste are focused on recovery of metals like Cu, Ni, V, Zn, Cr, Cd, Fe, Al, and Co. But the concentration of solid waste material in the bioleaching process is a crucial matter as the former contains mixture of metals those can be toxic for cell growth.

Currently, most of the abandoned mine sites are recognized by the presence of acidophilic inhabitant which can be isolated and screened in bioleaching of waste materials. These abandoned mine pollution sites contain the microbes those can tolerate very high concentration of heavy metal ions. These cells can be considered as suitable catalyst for industrial application of bioleaching.

In future, to improve the yield of metal through bioleaching of solid waste, new strains have to be identified that should be capable of sustaining higher metal concentration. For this purpose, strains of genetically modified or selected by mutation can be considered. This can reduce the residence time and simultaneously enhance the economy of the process. In most of the bioleaching of industrial solid waste, the detail bacterial physiological role has not been established yet. Industrial waste containing different elements and how bacteria interact with individual elements need further research. Higher scale-up studies should be encouraged in this regard for industrial purpose.

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