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Bioleaching, a technology for metal extraction and remediation: Mitigating health consequences for metal exposure

Michael P. Okoh [1*], Ifeyomi W. Olobayetan [2], Salamatu S. Machunga-Mambula [2]

[1] *Department of Medical Biochemistry, Faculty of Basic Medical Sciences, College of Health Sciences, University of Abuja, FCT, P.M.B 117, Nigeria*
[2] *Department of Microbiology, Faculty of Science, University of Abuja, FCT, P.M.B 117, Nigeria*

Abstract

Bioleaching is a good technology for metal extraction from mineral ores and its concentrates. The high concentration of environmental metals is a major concern to environmentalists and health practitioners, as they constitute natural assaults on human health and the environment. Intracellular accumulations of metals are implicated for the generation of oxygen radical's e.g. reactive oxygen species (ROS). Exposures to arsenic (As), mercury (Hg) etc, are linked to different health effects and diseases. Several techniques could be used to remove heavy metals, however, recovery from minerals containing sulfide, are based on the activities of chemolithotrophic bacteria and fungi, as they convert insoluble metal sulfides residues into soluble metal sulfates. Bioleaching has potential for metal recovery, detoxification of industrial waste products, sewage sludge and can be used for soil remediation. Twelve (12) metals and minerals are being actively mined, processed and marketed in Nigeria, thus, bioleaching as a technology can be employed as an alternative means for metals mining/recovery. Recovery of metals from different wastes stream, as; industrial sludge, galvanic wastes, and electronics wastes using bioleaching technology will be a milestone. Moving forward, further research is required to establish this method of remediation bearing its potential to reduce environmental and human exposure to metal toxicants.

Keywords: Microbial; Metals; Bioremediation; Epigenetics; Bioleaching; Environment

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* Corresponding author. *E-mail address:* Michael.okoh@uniabuja.edu.ng

1. Introduction

The method of bioleaching was initially used in the recovery of metals using microorganisms to oxidize reduced iron and sulphur compounds. Most recently, bioleaching has emerged as a bioremediation tool for mopping heavy metal pollution, bearing, quantities of hazardous industrial waste, (fly ash, sooth, slag and filter dust), which are being produced worldwide. Due to the high concentration of environmental metals present in, such waste, they could be considered as 'artificial ores' and could serve as secondary raw materials, which in turn would reduce the demand for primary metals mining (Brandl, 2001). Using bioleaching to remove metals from these industrial wastes is detoxifying, and helps in improving environmental quality (Brombacher et al., 2007).

The mining of ores for metals produces waste, and it has added to the growing heavy metal pollution on the environment. Also, the recoveries of metal ions from low-grade ores, by conventional techniques are associated with environmental hazards (Devasia and Natarajan, 2004; Pradhan et al., 2006; Anjum et al., 2009). In aquatic ecosystem, there are presences of heavy metals, albeit in low concentrations (Abowei and Sikoki, 2005). The presence of metals in higher concentration in the environment is a serious issue to both environmentalists and health practitioners (Table 1 shows the effects of toxic metals on human health). These concerns are borne from the knowledge that metals like organic pollutants such as PolyChlorinated Biphynyl (PCB) can persist in the environment, and they bio-accumulate in the food chain (Okoh, 2015). Thus, the discharge of industrial effluent containing any metal pollutants into aquatic environment damage water body and make it unsuitable with concomitant health consequences to the immediate population (Nwuche and Ugoji, 2008).

Bioleaching is a promising (could be revolutionary) method that employs environmentally sound technologies that are useful for the mining industry and also for environmental detoxification. In bioleaching, the microorganisms produce, chemical by-product e.g. mineral acid, organic acids, polymers and enzymes, as a consequence of their metabolism (Anyakwo et al., 2011). It is these chemical by-products that attack the gangue minerals contained in the ore, dissolving them to illicit selective removal of the metals (Anyakwo et al., 2011). The same mechanism is also employed in decontamination and detoxification of soil and water (Jain and Sharma, 2004). This paper reviews the technology as an efficient bioremediation strategy and an alternative means that will conveniently deal with heavy-metal pollution.

2. Literature review

The method of bioleaching is a promising and effective alternative to usual treatments (chemical extraction or thermo stabilization), of heavy metal contaminated environment (Padmavathiamma and Li, 2007); Mulligan et al., 2001). Several techniques are used to treat heavy metals, such include; chemical precipitation, oxidation or reduction, filtration, ion exchange, reverse osmosis, membrane filtration technology, evaporation and electrochemical method. However, these techniques could become ineffective if concentrations of heavy metals are less than 100 mg/L (Ahluwalia and Goyal, 2007). Heavy metal as salts are water-soluble (in most cases), hence they get dissolved in wastewater, making it difficult to be separated by physical separation methods. However, physico-chemical methods on the other hand, are expensive and ineffective used in low concentration of heavy metals, whilst, biological methods like bio-absorption (a bioleaching mechanisms), for the removal of heavy metals could and can be effective in such circumstances (Hussein et al., 2004).

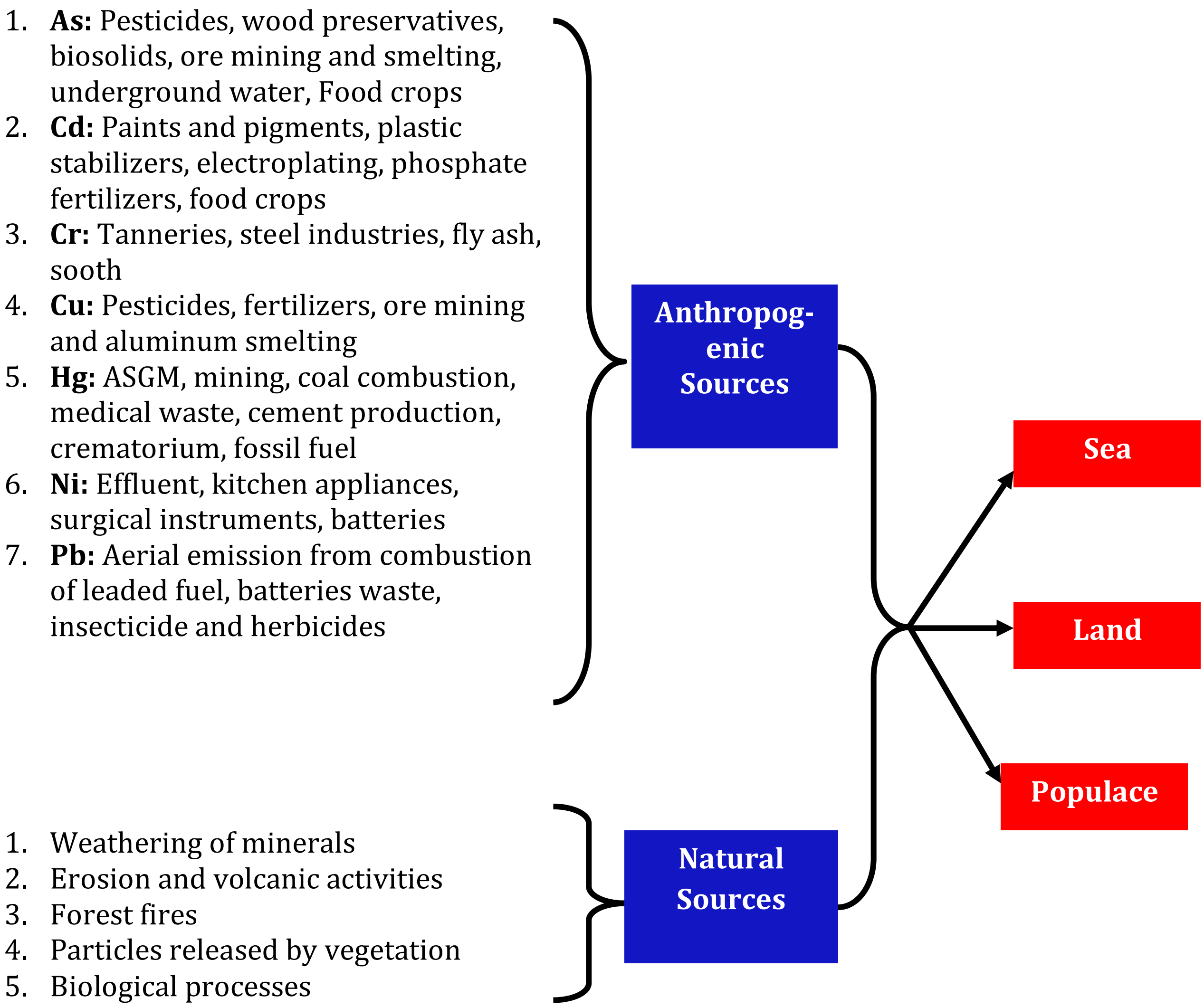

Figure 1. Sources of heavy metals in the environment

Heavy metals occur naturally in elemental form in the earth's crust. Metals such as mercury (Hg) for instance, are present in trace quantities or as impurity in many other economically valuable minerals most especially non-ferrous metals and in fossil fuels particularly coal. Some metals can naturally be released into the air as vapor during natural processes such as volcanic activity, forest fires, water body movement, weathering of rock, and biological processes. Anthropogenic sources (see Figure 1) remain one of the ways metals are released into the air, water and soil through industrial processes such as; mining operations, combustion of fossil fuels, cement production, incineration of hazardous wastes etc (Sabiha-Javied et al., 2009).

Widespread exposures to environmental metals are occurring due to human–generated sources and past practices that have left legacy of metals at landfills, mine tailings, contaminated sites, soils and sediments. Metals are persistent and cycles globally (Devasia and Natarajan, 2004; Pradhan et al., 2006; Anjum et al., 2009). This cycling can be more problematic in developing countries like Nigeria.

Metals such as Hg have effects on the environment that have over the years been recognized to be of global concern as a result of its nature and behavior in the environment including its abilities for long-range transport in the atmosphere, persistence in the environment, and more importantly its ability to bio-accumulate in nature leading to significant adverse effect on both human health and the environment (Okoh MP, 2015; Nwose et al., 2015).

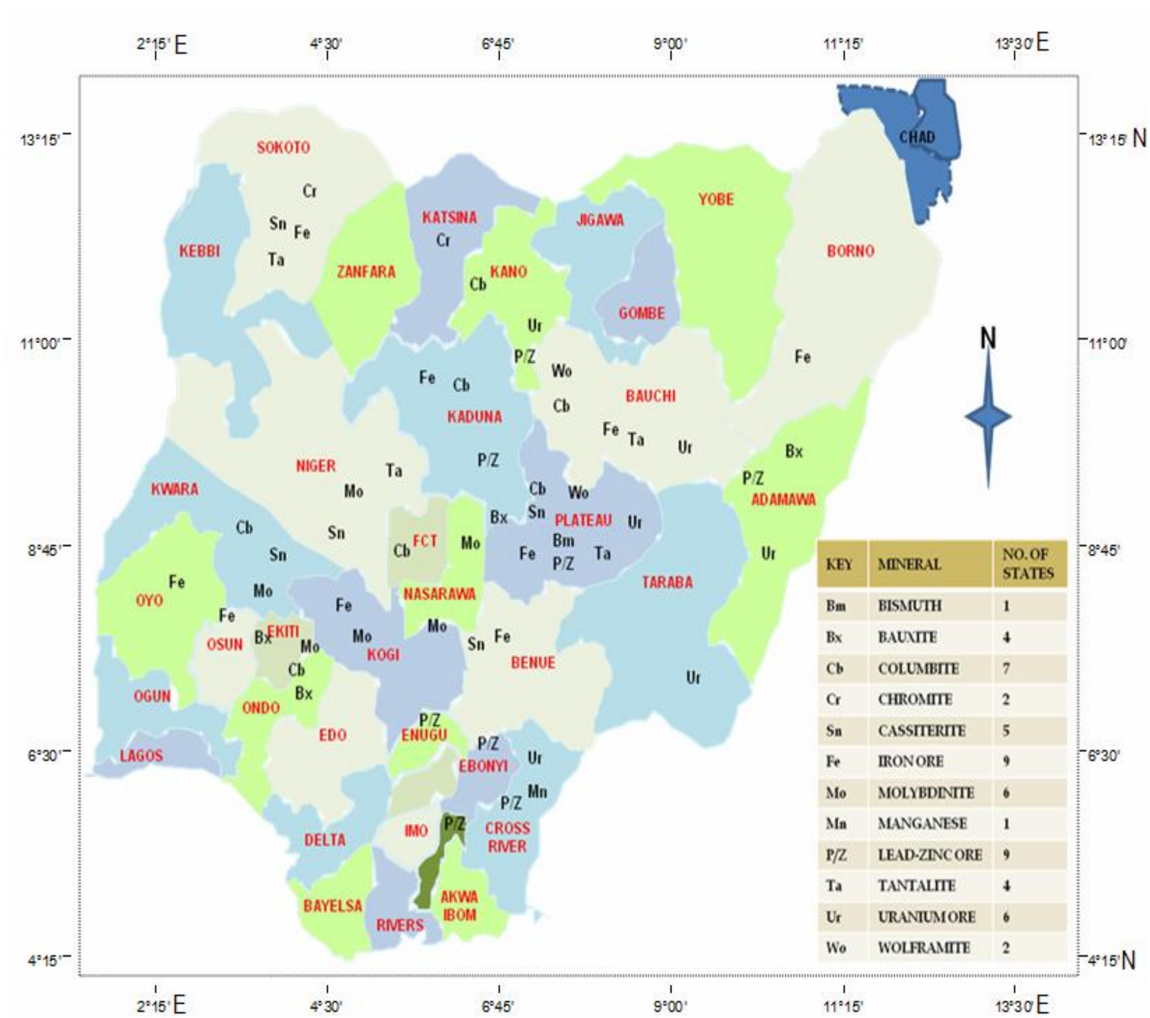

Figure 2. Identified Metallic Minerals in Nigeria (Adapted from Ruchita et al., 2015)

For releases that are due to anthropogenic activities a mass balance of heavy metals in the soil can be expressed using the Lombi and Gerzadek, formula of 1998 i.e.

$$M_{total} + (M_p + M_a + M_f + M_{ag} + M_{ow} + M_{ip}) - (M_{cr} + M_l) \quad (1)$$

Where; M is the heavy metal, *p* is the parent material, *a* is atmospheric deposition, *f* is fertilizer source, *ag* is agrochemical source, *ow* is organic waste source, *ip* is inorganic pollutant, *cr* is crop removal and *l* is losses by leaching, volatilization and other processes. Using such formula, it had earlier been estimated that emission of several heavy metals in atmosphere from anthropogenic sources is one to three orders higher than natural sources (D'Amore et al., 2005).

The effects of metals as epigenetics stressor was earlier discussed (Okoh 2018, submitted for publication). Specifically, the health effects of Arsenic (As) and mercury (Hg) are here further discussed due to their prevalence.

2.1. Health effects of arsenic and mercury

2.1.1. Effect of Arsenic (As)

Arsenic, is a metalloid and could hardly occur in nature as a free element. However, they are found most commonly as a component of sulphur- containing ores, where it occurs as metal arsenide. In natural waters it occurs in two oxidative states (iii) and (v). The first is in forms of arsenous acid (H_3AsO_3) with its salts, whilst the second is arsenic acid (H_3AsO_5) and its salt, respectively (Sawyer et al., 2003). Inorganic and most toxic forms of arsenic (arsenate and arsenite) are found in soils, crops and water, particularly in groundwater from deep wells, often used as drinking water (Solenkova et al., 2014).

Table 1. Summary of the toxic effects of heavy metals on human health (modified from: Ruchita et al., 2015)

Heavy Metal	EPA Regulatory Limit (ppm)	Toxic Effects	Reference(s)
Ag	0.10	Exposure may cause skin and other body tissues to turn gray or blue-gray, breathing problems, lung and throat irritation and stomach pain.	ASTDR, 1990
As	0.01	Affects essential cellular processes such as oxidative phosphorylation and ATP synthesis hence carcinogenic especially to the lung, kidney, bladder and skin	Tripathi et al., 2007 ASTDR, 2003
Ba	2.0	Cause cardiac arrhythmias, respiratory failure, gastrointestinal dysfunction, muscle twitching and elevated blood pressure	Acobs et al., 2002
Cd	5.0	Carcinogenic, mutagenic, endocrine disruptor, lung damage and fragile bones, affects calcium regulation in biological systems	Degraeve, 1981
Cr	0.1	Hair Loss	Das et al., 2008
Cu	1.3	Brain and kidney damage, elevated levels result in liver cirrhosis and chronic anemia, stomach and intestine irritation	Wuana and Okiemhen, 2011

Table 1. *Cont.*

Heavy Metal	EPA Regulatory Limit (ppm)	Toxic Effects	Reference(s)
Hg	2.0	Autoimmune diseases, depression, drowsiness, fatigue, hair loss, insomnia, loss of memory, restlessness, disturbance of vision, tremors, temper outbursts, brain damage, lung and kidney failure,	Ainza et al., 2010
Ni	0.2 (WHO permissible limit)	Allergic skin diseases such as itching, cancer of the lungs, nose, sinuses, throat through continuous inhalation, immunotoxic, neurotoxic, genotoxic, affects fertility, hair loss	Duda-Chodak and Baszczyk, 2008
Pb	15	Excess exposure in children causes impaired development, reduced intelligence, short-term memory loss, disabilities in learning and coordination problems, risk of cardiovascular disease	Padmavathiamma and Li, 2007
Se	50	Dietary exposure of around 300 μg/day affects endocrine function, impairment of natural killer cells activity, hepatotoxicity and gastrointestinal disturbances. Workers acutely exposed to high concentration of elemental selenium dust report symptom; as stomach pain and headache. Genotoxic effects of selenium had also been reported	Viceti et al., 2001 ASTDR, 2003
Zn	0.5	Dizziness and fatigue	Hess and Schmid, 2002: Ali et al., 2013

The toxic consequence of as are dependent on the oxidative state and the chemical species. For instance, inorganic arsenic (iAs) is thought to be carcinogenic especially to the lung, kidney, bladder and skin, (ATSDR, 2003). The toxicology of arsenic in its inorganic form has been established with manifestation as; acute toxicity, sub chronic toxicity, genetic toxicity, developmental and reproductive toxicity (Ali and Ali, 2010), immuno toxicity (Sakurai, 2003). The epigenetic alteration that can be induced by exposure to iAs had previously been covered (Ray et al., 2014). Moreover, Smeester et al., 2011; identified 183 promoters that were found to be methylated differentially due to iAs exposure in adult subjects from Mexico and, of the lots 17 tumors suppressor genes were identified to have their promoter's hypermethylated (Ray et al., 2014). Also, There had been correlation between iAs exposure and histone modulation with specific gender differences observed (Chervona and Costa, 2012). Drinking water is one of the primary sources of exposure to inorganic arsenic (Saha et al., 2011.).

2.1.2. Effect of mercury (Hg)

Input from Hg dose-response analyses (method that establishes relationship between exposure, severity and outcome of the adverse health consequences), shows clearly some of the dangers due to Hg poisoning as it had established that provisional tolerable weekly intake (PTWI) of 25000 $mgkg^{-1}$ body weight of Hg, is associated with a decrease of at least 3 Intelligent Quotient (IQ) points in children and an increase in systolic blood pressure of approximately 3 mmHg (0.4 kPa) in adults (Houston MC, 2011; Fillion et al., 2006; Noisel et al., 2011: Solenkova et al., 2014). The rate of absorption of mercury into the bloodstream ranges from 3% to

80% (WHO, 2010). Also, it is established that younger persons and fasting individuals tend to absorb higher amounts of Hg ingested or inhaled (WHO, 2010). The biological half-life of Hg varies depending on its chemical status and the tissue(s) in which it is stored. The average half-life of methyl mercury in human adults is 70 days (Jo et al., 2015). In oxidized form the biological half -life of Hg in human volunteers was about 58 days in the whole body, 64 days in kidneys, 21 days in the head region 27 and 3.3 days in the blood (ATSDR). The biological half-life of ingested mercuric salts was 29-41 days in women and 32-60 days in men suggesting a sex related difference (Tellez-Plaza et al., 2010; Camacho et al., 2017). It is likely that the half-life of mercury compounds is longer in the kidney than in the whole body due to the presence of mercury binding proteins (Camacho et al., 2017).

Table 1 (adapted from Ruchita et al., 2015) gives a general summary of the toxic effects of heavy metals on human health.

3. Bioleaching for bioremediation

Bioleaching as a process is "the dissolution of metals from their mineral source using certain naturally occurring microorganisms" or "the use of microorganisms to transform metal elements so that the elements can be extracted when water is filtered through it" (Mishra et al., 2005). It has been used to dissolve metals such as nickel, copper, zinc, cobalt, gold, lead, arsenic etc. The bacteria use to dissolve gold via bioleaching processes is *Acidithiobacillus spp*. As a technology, this method is good for accessing valuable metal compounds from solid substrates and for the detoxification of heavy metal contaminated waste such as ores, energy, or landfill space (Singh et al., 2015).

The industrial application of microbial leaching was facilitated via chemo-lithotrophic process, using iron-oxidizing bacteria such as, *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* (Aung and Ting, 2005). However, experiment have shown, industrial waste products, with high amounts of valuable metals cannot be treated using chemolithotropic methods. This is mainly, because most metals, such as fly ash and slag, are present as oxides rather than as sulfides. It is the metal oxides in such residues that can be leached by acid produced by *Thiobacillus thioxidans* (Bosecker, 1997). Moreover, this depends on the metal compounds in the residues, as vanadium, chromium, copper and zinc can be completely recovered (Blaise et al., 2010). Thiobacilli have also shows potential for the detoxification of sewage sludge, soil, sediment and water contaminated with heavy metals (Blaise et al., 2010).

The most important benefits of bioleaching used optimally, with best available technology, are the minimal damage it causes to the environment. Hence, it has potential to reduce the amount of greenhouse gasses in our atmosphere. The microorganisms used could be essential for the re-mineralization of organic matter, recycling living biomass, and contribute to the overall redox state of the surface of our planet and permanently bioengineered the environment. Moreover bioleaching has cost benefits especially when compared with the large-scale capital investment required for a chemical treatment plant.

3.1. Mechanism of bioleaching

The effects of bacteria and fungi on minerals are based on the ability for microorganisms to metabolize metals using three principles; acidolysis, complexolysis, and redoxolysis.

3.1.1. Acidolysis; formation of organic or inorganic acids (protons)

Microorganisms carry out metal solubilization through the formation of organic or inorganic acids for instance, in the production of citric acid by *Aspergillus niger* or gluconic acid by *Penicillium simplicissimum*, and sulphuric acid by *Acidithiobacillus ferrooxidans* and *A. thiooxidans* (Johnson, 2006). In these processes, protons, protonate the anion of the insoluble metal compounds e.g. the oxygen atoms covering the surface of the metal compound, when protons and oxygen combine with water the metal is detached from the surface (Mulligan et al., 2004). Equation 2 below shows acidolysis reactions were protons are obtained from the acids produced, with maximum enzyme amount available that determines the amount of metal oxides solubilized (Burgstaller et al., 1992). This process is usually fast and it is the most important mechanism for fungal bioleaching.

$$MeO + 2H^{+} \longrightarrow Me^{2+} + H_2O \quad (2)$$

In the above, MeO is the metal oxide.

3.1.2. Redoxolysis; oxidation and reduction reactions;

Redoxolysis is divided into the direct and the indirect mechanism. In the direct mechanism of redoxolysis, bacterial leaches metal via redox reaction, where metals are solubilized by enzymatic reactions through a physical contact between the microorganisms and the leaching materials, causing the destruction of the mineral. Microorganisms can oxidize metal sulfides via a direct mechanism with electrons obtained directly from the reduced minerals (Abdollahi et al., 2013), such mechanisms are best represented using the equation below:

Direct:

$$4FeS_2 + 14O_2 + 4H_2O \xrightarrow{\textit{Thiobacillus}} 4FeSO_4 + 4H_2SO_4 \quad (3)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \xrightarrow{\textit{Thiobacillus}} 2Fe_2(SO_4)_3 + 2H_2O \quad (4)$$

Further, with the equation below, direct bacterial leaching can be described:

$$MeS + 2O_2 \xrightarrow{\textit{bacteria}} MeSO_4 \quad (5)$$

where; MeS is the metal sulfide (Bosecker K, 1997).

In the ‘indirect’ mechanism, oxidation of reduced metals is mediated by ferric (III) ion and this ferric is formed by microbial oxidation of ferrous iron present in the minerals. Ferric iron acts as an oxidant and can oxidize metal sulfides and is reduced to ferrous iron, which can be oxidized through microbial formation (Hadi H, 2011; Bosecker K, 1997), in this case iron acts as an electron carrier. At low pH (2-3), bacteria oxidation of ferrous iron is shown to be more faster (>10^5) than chemical oxidation of ferrous iron (Bosecker K, 1997). Metal solubilization using indirect mechanism can best be repesented by the equation below:

Indirect:

$$MeS + Fe_2(SO_4)_3 \xrightarrow{bacteria} MeSO_4 + 2FeSO_4 + S^0 \quad (6)$$

The extraction of uranium from ores, is a good example of indirect bioleaching, this is captured in equation (7).

$$U^{IV}O_2 + Fe_2(SO_4)_3 \longrightarrow U^{VI}O_2SO_4 + 2FeSO_4 \quad (7)$$

Ultimately, this formation occurs when insoluble tetravalent uranium is oxidized to the water-soluble hexavalent stage of uranium (Bosecker K, 1997; Silverman, 2007).

3.1.3. Complexolysis; excretion of complexing agents

Complexolysis involves a procedure where an organic acid leaches metals through complex formation. Complexolysis is a slower mechanism compared to acidolysis. In complexolysis, solubilization of metal ions is based on the complexing capacity of a compound with, which a complex is formed. For instance, if the nexus between metal ions and ligands are stronger than the lattice bonding between metal ions with solid particles, the metal will be successfully leached out from the solid particles (IIyas et al., 2014; Ehrlich, 2001). Apart from organic acids, other metabolites, such as siderophores (low molecular weight chelating agent) can form complex, solubilize metals such as, ferric iron, magnesium, manganese and chromium (Gadd, 2000). Moreover, heavy metals, complexation can reduce the metal toxicity to the fungi when high concentrations of metals are present.

4. Potentials for bioleaching usage in the Nigerian mining sector

Nigeria as a developing country has a transition economy thus needs viable technology with less cumbersome operating mechanism to improve, revive its mining sector and remediate its legacy sites. Developing bioleaching technology would help the country to not only revive but also help to tackle heavy-metal pollution in the immediate environment. Properly thought through, bioleaching can be employed as an alternative and viable means of metal recovery in Nigeria, moving forward.

The acute Pb poisoning in Zamfara, Nigeria (Marcus, 2011), was due to the activities of artisanal small scale gold miners (ASGM) who were involved in crushing and grinding ores to extract gold and in the process release dust that is highly contaminated with Pb and mercury (Hg). Children in the affected areas were exposed to the dust and also through ingestion of contaminated water and food.

For ASGM activities, high concentration of metallic mercury, are usually in or in the vicinity of flowing water referred to as mining “HOTSPOTS” (Torres et al., 2017). They are major sources of Hg dispersion into aquatic system, which eventually result in methyl mercury contamination of aquatic animals especially fish, wildlife and communities living within the proximity of the mining areas, as mercury containing tailings are dumped into bodies of water and consequently the soil, streams, rivers, ponds and lakes are contaminated. Although, low mercury and mercury free methods are available for ASGM in Nigeria, prevailing socioeconomic factors, combined with other conditions, serve as a barrier to the adoption of such better practices. This problem is likely set to continue unabated for some time bearing the current mining laws and regulations in Nigeria, which although addresses ASGM activities with, most such laws mainly focusing on the provision of extension services.

Investigations have revealed that a total of twelve (12) metals and minerals are being actively mined, processed and marketed in Nigeria (MSMD,2003; Onyemaobi, 2002). Additionally, twenty-one (21) metals and minerals, including copper, uranium, manganese, are untapped (MSMD, 2003). Some of these minerals and their locations are shown in the Maps (Fig 4.0).

Moving forward, in Nigeria, bioleaching technology will provides an eco-friendly remedy to some of the mining issues especially as it relate to legacy sites. Hence, it should be given deserved attention.

5. Future perspective and conclusions

Bioleaching has been widely employed due to its ability to recover valuable metals whilst, for its decontamination mechanisms more study is required. Bioleaching will become even more relevant as there are increasing demands for less expensive and more environmentally friendly methods of metal solubilization. Therefore, further development of this technology is necessary to enhance both the technical and biological aspects of these processes. Enhancing the biological aspects, would involve increasing the rate of leaching and the tolerance of the microorganisms (via genetic improvement of bioleaching microbes to enhance adhesion of heavy metal contaminated soil, biochemical alteration in soil pH and sulfur ratio, usage of nanofiber technology with significant improvements in the oxygen reduction reaction (ORR), and oxygen evolution reaction (OER) processes) to heavy metals. Overall compared with smelting ore, the mechanism of bioleaching releases less harmful materials into the environment and causes less damage to the Earth. Moreover, this will offer an economic tool for recovery of valuable metals in the mining industry. Such recovery of metals from different wastes stream, as; industrial sludge, galvanic wastes, and electronics wastes using bioleaching technology will be a milestone. Therefore, in future development, there is the need to expand the role of biotechnology in the extraction and recovery of many metals.

Research in this area is essential as it could advance the science of bioleaching to the point where it will become economical for all applicable metals, to the extent it could be used for mining, and the microorganisms would take all the risk enabling the human workers to operate on safer surface. Research is needed to find microorganisms that are more suited to high temperature environments, as this would increase the speed of bioleaching. The release of acid via bioleaching into the local groundwater remains a major disadvantage of the mechanism. The genetic damage emanating from exposure to metal is irreversible with deleterious consequences on genome stability. The outcome of these mutagenic events is fundamental to understanding the extent of the toxicant' s pathogenesis on human health. Bearing also, the microbiological makeup of extreme environments could provide a new angle in understanding the emergence of pathogenesis, the role of adaptation and innovation in colonizing new environments, and the ecological dynamics within microbial communities. All this information may prove critical in the fight against diseases. Thus, there are needs to capitalize on the opportunities as provided by bioleaching, as the technology provides and integrate various disciplines spanning geology, microbiology, and molecular biology to biochemistry that could be harnessed, moving forward.

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