Microorganism Assisted Floatation of Spodumene: A review

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Abstract – This paper is a literature review aiming to critic the documented findings on how microorganism-aided spodumene concentration from hard rocks can be carried out efficiently and sustainably. Due to its high Lithium content and abundant occurrence of deposits, spodumene is the main Lithium bearing mineral currently being processed. Its beneficiation poses threats to the sustainability of the environment due to the extensive use of chemicals. The paper evaluates the use of microorganisms to enhance the floatability of spodumene, delineating how the reported spodumene recovery rates have been affected by fungi, bacteria and algae. The use of microorganisms in value extraction has mostly been reported limiting to bioleaching and bio-oxidation processes, however this paper will delve into challenging how microorganisms interact with spodumene surface bio-floatation. The review will close with the identification of key areas for future research including, the cloned novel microbial strains capable of enhancing lithium bearing mineral recoveries.

Keywords – Critical Literature Review, Energy Storage, Microorganisms, Spodumene.

I. Introduction

Application of biotechnology in the extraction of metals, mineral beneficiation and environmental control have been a major focus for many industries, and with the increased demands for metals and depletion of high grade ores, the role of microorganisms cannot be ignored. Microorganisms have been studied to provide cost effective alternatives for mineral processing, they provide the possibility for the beneficiation of low grade ores and sustainable environmental [1]. The investigation of microorganisms as floatation reagents has been extensively investigated and outlined in literature, the depth of knowledge that has been covered in this field is innumerable however there still remains a huge void for specific minerals such as spodumene.

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Many researchers have played a substantial role in the broadening of this field most of them relevant to this study, amongst these one may note the works of [1]-[6]. Key areas of study that were also extracted from by this paper included;

- The types of microorganisms that can be used in hydrometallurgical processes
- Their interactions with various metals
- Impact of use of microorganisms in floatation processes in terms of efficiency, conditions of operation and environmental impact.

II. Application of Microorganism in Mineral Beneficiation

Microbiologist and bacteriologist Box, 2022 in the article "*major microorganisms and their function,*" categorised microorganisms into various groups by not only using their morphological features, but also according to the conditions in which they thrive and their metabolic systems. The main groups in which microorganisms can be classified according to their structural characteristics include bacteria, fungus (yeasts and moulds), archaea, algae, protozoa and viruses [3].

In the literature for the various types of microorganisms that have been used for bio-hydrometallurgy, emphasis has been on bacteria and fungus, limited research has been conducted to investigate the use of archaea, protozoa and algae in mineral processing. The role of the later organisms in the environment and locations of their colonial habitats have been seen to contain extreme conditions including high heavy metal concentration, high temperature and low pH, however, they have not been comprehensively investigated in terms of their ability and efficiency to be used for beneficiation using hydrometallurgy later on floatation. Viruses have never been an option for investigation as they are classified as non-living organisms who come to live in the presence of a host organism [3]

The majority of collected documentation exhibited that advances and studies in the field of biotechnology and mineral processing have been centred on the bioleaching of metals and bioremediation of mineral wastes, many researchers have committed to the study of how microorganisms can be used to exploit low grade ores through microbial activity and mine waste treatment [5]. In an overview on *Application of microorganisms in the bio-mining of minerals,* S. Sana in 2021, gives a detailed outline on how the use of microbes in the bio-mining of lithium improved the recovery of lithium from 16% using chemical to 26% [7]. In the paper challenges of inhibition of microbial growth during metal leaching were

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identified, in a similar study by [8], lithium bioleaching proved complex in downstream processes where the low lithium concentrations attained during leaching presented extraction challenges using nanofiltration processes [2], [7], [8].

The knowledge passed from their work opened a new channel of possibility in the use of microorganisms in bio-floatation, the literature documented in these studies allow for other researchers to identify microorganisms that have been known to interact with specific minerals along with the working understanding of the metabolic action of these microorganisms . In this critical literature review, the link between bioleaching and biofloatation will be outlined by evaluating how common microbes can be manipulated to suite the two distinct applications. Thus one can study the bioleaching of lithium bearing hard rocks to have an understanding of the microorganisms that can be used for selective floatation of lithium bearing minerals like spodumene. Generally bioleaching is reported to be a time consuming process, days or even weeks are needed to dissolve minerals through bio-oxidation, but biomodification of mineral surfaces using microorganisms during floatation in principle requires a few minutes making it a more lucrative approach to concentration processes [4], [6].

III. Mechanism for Microbe-Mineral Interaction

Many of the collaborative and documented work of [1] shows the ability of microorganisms to enhance floatation processes, this is due to their ability to modify the surfaces of metals and this bio-modification alters the hydrophobicity or the hydrophilicity of minerals allowing for a complete separation between modified minerals and those that would not have been altered.

All studied literature confirm the complexities in understanding the mode of activity of microbes during bio-floatation, however a common concept has been thoroughly investigated on by many researchers working on biofloatation state that, interaction of microorganisms with minerals can either be direct due to the adhesion and attachment of the microorganism onto the surface of mineral particles, or it can be indirect due to the action of biological products from microbes, metabolites, acting as surface active agents which modify the surface of minerals [1], [9], [10], [11].

Christian Gram, a bacteriologist, investigated on the surface properties of bacteria and from his investigations, the cell walls of microorganisms is composed of different functional groups from strain to strain [12]. There are different types of proteins and polysaccharides that are responsible for the different surface properties, charge and floatation behaviour of microorganisms particularly bacteria. Many researchers agree that microorganisms with an overall gram-negative charge consist of a double layered membrane whose inner layer has a high concentration of peptidoglycan proteins on their surface and these are primarily responsible for the negative surface charge of the bacteria [9]. The lipids in the cell walls of many bacterial organisms produces their hydrophobic behaviour which play a crucial role in the formation of bio-flocculants, adhesion of bacteria to solid surfaces and air-bubbles and also biofilm formation around mineral surfaces in bio-floatation [9]. The cell surface charge for bacteria at any point and time is determined by the ambient micro-environmental conditions around the bacteria, thus the microbe is able to alter the charge on its surface to adapt to any forces of temperature, pH, ionic strength and chemical reagents around it [14]. For instance, the adhesion characteristics of bacteria like *Bacillus subtilis* and *Escherichia coli* are influenced by these surface modifications [1].

Various authors and researchers from literature have concluded on the use of the DLVO theory to explain the mechanisms of interactions that occur initially between microorganisms and minerals, this theory states that the interaction of electrostatic fields due to surface charges around mineral particles and microbes can cause repulsion or attraction to occur between the two entities. Goddard's work on *fundamentals of polymer adsorption* highlights that the DLVO theory attests to the presence of Van de Waals forces as the major force that attracts microorganisms to mineral surfaces [13]. The balance of these forces will determine whether the microbe and the mineral will attract or disperse. Other studies by P. Somasundaran, indicate that hydrophobic interactions play a significant role in the adhesion of microbes to mineral surfaces while others disagree on the significance of electrostatic forces of attraction in the adhesion of microbes to mineral surfaces [1].

In an investigation to evaluate *the effect of metal stress on microbe activity*, P. H. Zadeh, outlined in detail metabolic and physiochemical properties of microorganisms, he states in his paper that microorganisms release extracellular and intracellular components such as Extracellular polymeric substances (EPS) and Soluble Microbial Products (SMP) during their interaction with minerals in bio-floatation. The EPS and SMP are pools of organic matter – mainly polysaccharides, proteins, nucleic acids, lipids, humic substances, and some inorganic compounds that are secreted or released by microorganisms into the extracellular environment [10] and [15] goes on to explain that EPS substances once produced are bound to the surface of microbial cells where they play a crucial role in biofilm production, nutrient entrapment, stress protection and the provision of carbon sources to the microbe in cases of deficiency. Another author in the field. A. Ramesh added to this knowledge by concluding that SMP substances are purely a stress response mechanism by microorganisms or a cell-to-cell communication mechanism [11]. Both the EPS and the SMP components are made up of various but specific functional groups such as the carboxyl, hydroxyl and amino groups that play a substantial role in defining the surface properties of microorganisms [10].

Some EPS and SMP components, especially proteins, produced in response to metal stress have shown unique affinities for binding specific metals [10]. Hence, due to their high metal binding capacity, selectivity and specificity in binding different metals, SMP and EPS components can be harnessed to enhance biofloatation processes. EPS are categorized into two groups with respect to their association with the cell surface: i) tightly bound EPS (TB-EPS) and ii) loosely bound EPS (LB-EPS) while SMP are also broadly classified based on their formation into utilization-associated products (UAP) formed through substrate consumption and biomass growth and biomass-associated products (BAP) formed during the hydrolysis of biomass [16].

While there are still many academic debates with regards to how microorganisms first interact with mineral particles, the mutual theories amongst the considered literature emphasize that microbes come into contact with mineral surface during biofloatation initially by any one of the following including; hydrophobic interactions, chemisorption of microbes by formation of chemical bonds with the surface of minerals, electrostatic attraction and the use of Flagella, pili, fimbriae extensions on the surface of bacteria webbing around mineral particles [5], [6], [9], [16].

Attachment of bacterial cells to solid substrates is accompanied by the excretion of EPS and SMPs, they play a crucial role in the creation and stabilization of a biofilm around microorganisms and mineral particles that they have attached to [14]. This excretion of EPS and SMP activates adhesion of the microbes onto mineral surfaces by changing the charge of the bacterial envelope through the trapping of near surface or structural ions on the mineral surface [14]. The hydrophobic amino acids present in proteins of the EPS impart hydrophobicity to the mineral surface while polysaccharides present in EPS confer hydrophilicity. The amphipathic nature of the single stranded uronic acid (ssDNA) in the EPS allows this component to adhere and modify the surfaces of charged and uncharged mineral particles due to the presence of a hydrophilic phosphate backbone and hydrophobic lipid chains respectively [2].

Studies by J. Dubel show that it is crucial to measure the hydrophobicity of a specific mineral with respect to a specified microorganism by measuring the contact angle between a smooth mineral surface and a drop of the inoculum containing the microorganism. A Rame-Hart model A-100 contact angle goniometer, which is a specialized instrument designed for such measurements will then be used to assess the contact angle, a higher the contact angle indicates high hydrophobicity of a mineral [17].

IV. Use of Microorganisms as Biological Reagents in the Floatation of Lithium Bearing Rocks

In their collaborative work; *Biomodification of mineral surfaces and floatation,* M. Rao and Somasundaran settled that the conventional chemical reagents such as petroleum oils, Xanthates, cyanides, and amines, etc., used in mineral flotation are toxic, non-degradable and exorbitant in natural ecosystems, integration of microorganisms in floatation processes as modifiers has been noted to shift industries to adhere to the stricter legislations being imposed on them by several environmental organizations [18]. Microorganisms and their products have therefore been used as collectors, frothers and modifiers (activators, depressants, pH regulators, and flocculants), in biofloatation. Bio-flotation processes were initially developed by using bacterial strains of Rhodococcus opacus, Rhodococcus ruber, Staphylococcus carnosus, Stenotrophomonas and Escherichia coli, etc., as bio-collectors and Acidithiobacillus ferrooxidans, Ferroplasma acidiphilum, Leptosririllum ferrooxidans and Bacillus subtilis, etc., as depressant reagents. New authors of the current decade are also exploring the use of *P. polymyxa* to recover Lithium from its ores of hard pegmatic rocks [18]. A chemical analysis of the EPS produced from a microbial consortia showed the presence of bio-surfactants, compounds which tend to reduce the surface tension of liquid. Bio-surfactants have a higher surface-activity, lower toxicity, higher biodegradability and better environmental compatibility, in a floatation experiment conducted early 2010 by Fazaeloor, bio-surfactant molecules were seen to exhibit better froth characteristics in comparison to chemical frothers used in mineral flotation [20].

Numerous applications of biomodification of mineral surfaces in literature, have been intensely concentrated on the beneficiation processes of sulfide minerals, and the group of microorganisms that have been of economic significance in this field is *Thiobacillus Ferrooxidants.* These were studied to be chemolithotrophs that obtain their energy from the oxidation the ferrous and sulfur components in compounds. Amongst the other species widely used for surface alterations are *Thiobacillus thiooxidants*, *Leptospirullum ferrooxidants* and *Sulfolobus* acidocaidarios [4]. *Aspergillus niger and Penicillium simplicissimum* in a rare but insightful investigation by S. Sana are amongst some of the fungal microorganisms that have been used for metal solubilisation but not particularly in bio-floatation [7].

With regards to the biofloatation of lithium bearing ores, literature revealed that there is limited understanding and investigations that have been conducted to evaluate if lithium minerals like Spodumene can be concentrated by using microorganisms during floatation , and if so which microbes can be used to attain better recoveries than those made by the conventional process. The study of lithium particularly Spodumene containing hard rocks began a few decades ago and a few micro-floatation experiments have been conducted. In one study*, lithium recovery from lithium micas using sulphur oxidising microorganisms,* the author gave detail of how sulphur oxidising bacteria can used in lithium containing micas to produce sulphuric acid which in-turn dissolved lithium in the mica. There is no detail of the name of the bacterial but the investigation was more inclined to the bioleaching of lithium from mica ores [8]. The table below summarizes the major biological metabolites from microorganisms and how they have been used to enhance floatation of particular minerals.

TABLE I
MICROBIAL METABOLITES AND THEIR APPLICATIONS IN MINERAL PROCESSING AS FLOATATION REAGENTS [6]

Microbial biomolecules	Minerals/Ores	Highlights of Flotation Process
Protein and DNA of *Bacillus megaterium*	Sphalerite and Galena flotation conducted in Hallimond tube by using Protein and DNA of the bacterium as bio-collector	95% of sphalerite was floated in the presence of ssDNA and non-DNA fraction of the bacterium as a bio - collector
Bio-surfactant from *Pseudomonas aeruginosa*	Biosurfactant used as frother for coal flotation in a Denver cell at pH 7	About 72-79% of combustible matter was recovered from coal samples.
Extracellular polymeric substances (EPS). EPS isolated from mixed bacterial consortia	Cchalcopyrite and pyrite flotation conducted by using sodium isobutyl xanthate as a collector with bacterial EPS as an activator at pH 9.	EPS assisted flotation recovered 77% of chalcopyrite when chalcopyrite was floated alone and 70% chalcopyrite recovered from chalcopyrite and pyrite mixture.
Nucleic acid (Single stranded DNA)	Flotation of separate sphalerite galena mixture performed in Hallimond tube by using ssDNA as bio-collector at pH 8.	Up to 85% of sphalerite was selectively recovered from the sphalerite and galena mixture.
Bio-surfactants from *Bacillus circulans* and *Streptomyces* sp.	Quartz and Serpentinite separation by flotation in a Hallmond tube by using biosurfactant as a collector and Ni ions as activators	Highest recovery of quartz (68% w/w) was observed in the presence of biosurfactant producing broth of *Bacillus circulans* with an activator (Ni^{+})

V. FUTURE ASPIRATIONS IN THE USE OF MICROORGANISMS IN SPODUMENE FLOATATION

More contemporary techniques such as the use of biotechnology for mineral processing have developed to enhance the use of microorganisms in biofloatation. By conferring to the academic work of Hong in 2024, genetic modifications can improve the attachment of microorganism to mineral surfaces, for instance, the use of genetic engineering to create recombinant E. coli, the E coli is restructured so that it develops a protein on its surface that is able to bind complementarily to Lithium ions [19]. The findings of this investigation have created a foundation that researchers in this field can build upon to design or create new strains of microorganisms that selectively bind to Spodumene during floatation. Other bacteria like *Acidithiobacillus ferrooxidans* and *Leptospirillum ferriphilum* can be engineered to enhance their attachment to micaceous minerals. Bacteria adapted to specific minerals through genetic modification exhibit higher attachment efficiencies compared to those that would not have gone through the same pretreatment process [20]. Another pitch around this area of genetic modification would be to identify and culture microbes that are able to naturally mutate their genetic material and produce stress proteins that increase the selectivity of microbes towards spodumene minerals.

Another interesting study from the paper, *Utilization of P. polymyxa in the recovering of lithium bearing ores,*investigated the efficiency of a microorganism in the floatation enhancement of spodumene bearing minerals was conducted using Paenibacillus polymyxa bacterium. The researcher investigated if the pre-treatment of spodumene mineral with P. polymyxa could affect the settling velocity of the particles in a pulp, results showed that the microbe reduced the settling velocity of the mineral which translates to its ability to be used as a collector for spodumene minerals [21]. Although success of increased floatability of spodumene was noted, the author highlighted conducting further experiments of P. polymyxa with spodumene but in these experiments, include gangue materials like feldspar, mica and quartz that are usually associated with spodumene minerals [21]. Thus the study did not offer comparison of the floatability of spodumene minerals to its associated gangue material in the presence of the microorganism of choice.

VI. SHORTCOMINGS AROUND THE AREA OF THE USE OF MICROORGANISMS IN THE BIO-FLOATATION OF SPODUMENE

All the studied literature aided in the understanding of the use of microorganisms in bio-hydrometallurgy, common challenges were noted amongst all of the papers. One crucial challenge was the limited scope of bio-technology in the field of lithium bearing hard rocks [22], authors who managed to conduct investigations in this field lack the comparative analysis of the performance of microbes in biofloatation to the conventional use of chemical reagents. Experimentation on the various microbes that can be used for lithium ores has been limited to micro- and lab-scale tests and so there is room in this field to improve on the beneficiation of this energy element. Production costs and economic viability concerns have also been highlighted by researchers, as the use of microbes is associated with high handling and preparation costs, their integration into a chemo-physical process of floatation is also costly. Nonetheless, other students in this field strongly endorse the integration of the microbial and chemical processes in order to solve the case of slow kinetics that is associated with the use of biological components, a hybrid of the biochemical process can also improve the environmental sustainability of the system [23]. There has been a general understanding that microorganisms will have less devastating impacts on the environment but no detailed study has been conducted to critically analyse the effect of introducing a large population of foreign microorganisms in a new environment through tailings disposals.

Other authors have suggested and even investigated on the use of biological reagents such as microbial fat and biomass as floatation reagents in the case of non-sulphide or non-ferrous ore deposits however, these theories have not been extensively tested and applied even at laboratory scales [4].

The table below shows some of the applications of microbiology in mineral processing, it shows the specific microbes and the substrates they work on during separation by floatation processes.

VII. Conclusion

This critical literature review demonstrated that, while significant research has been conducted in the field of bio-floatation, several voids have been left unoccupied with regards to the concentration of lithium using biofloatation. The mandate of this paper was to outline the findings on the critical literature review of microorganism's interactions with lithium bearing hard rocks outlining the types and microbial interactions. Several techniques have been employed to accurately assess the mineralogy and crystallography of lithium bearing hard rocks, with a focus on spodumene which has significant economic importance. Considerable contributions with regards to the use of microorganisms in mineral processing have been made by scholars in the recovery of lithium from recycled lithium-ion batteries but a few researches delve into the comprehensive separation of spodumene from its associated gangue material using bio-floatation. Documented work reveal the use of P. polymyxa and genetically engineered E.coli as possible microbes that can alter the surface chemistry of spodumene ores, other organisms such as M. phlei have also proven efficient for biomodification of quartz and other gangue material associated with spodumene. Many researchers in this field agreed to a greater extent on the role of microorganisms in altering the surface of minerals either by direct adhesion of microbes onto the surface of minerals or by indirect surface modification using bio-reagents such as EPS and SMPs produced by the microorganisms. The conditions and mechanism for bio-floatation will largely depend on the type and amount of microorganism used for biomodification, however some scholars noted that chemical reagents used in flotation processes have the ability to inhibit microbial activity with minimum toxicity being noted for most Xanthates and pine oil reagents. Future studies in the area of bio-floatation of spodumene need to investigate the microorganisms that can be used for the biofloatation of spodumene minerals and its associated gangue material, outlining the techniques to be used in large scale industrial operations of lithium extraction for environmental sustainability.

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