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Reduction of Hematite to Magnetite by Bacterial Transformation Process

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ABSTRACT

In this paper, two bacterial strains, namely W1b and W2, were isolated and identified from the tailings of Chadormalu iron ore mine. Both bacterial strains exhibited a remarkable ability to significantly increase the pH and regenerate the culture medium. This is particularly noteworthy given the challenging environmental conditions inherent to mine tailings. Based on the duration of bacterial activity, W1b and W2 were both able to maintain iron reduction conditions for 7 and 4 days, respectively, under similar conditions. With an initial amount of magnetite of 4.59%, through an examination of the granulation dimensions, it was found that smaller granulation dimensions and finer particles lead to an increase in the contact surface area, subsequently to an increase in magnetite recovery. The enhancement of contact surface area is crucial for optimizing the efficiency of biotechnological processes in mineral recovery. Based on the analysis results, it was determined that W1b bacteria exhibited the highest conversion efficiency of hematite to magnetite, achieving a significant 22% conversion in the Lb culture medium. Furthermore, W1b bacteria maintained alkaline environmental conditions and demonstrated regenerating properties, which are essential for sustainable bioremediation processes. The study indicates potential applications of these bacterial strains in the field of bioleaching and mineral processing, where improving recovery rates and maintaining stable conditions are of paramount importance.

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1. Introduction

The conversion of hematite to magnetite is facilitated by the activity of microorganisms, particularly dissimilatory iron reducing bacteria (DIRB). These bacteria possess a distinctive ability to convert iron oxide from Fe (III) to Fe (II), which is a crucial step in the process of biotransformation. The enzymatic activity of dissimilatory iron reducing bacteria accomplishes the reduction of Fe (III) to Fe (II) [1].

This process occurs under specific environmental conditions. These conditions comprise a neutral to alkaline pH, more negative Ehs, and the presence of food sources for bacteria [2]. As a result, the biotransformation of hematite to magnetite is a natural biotechnological process guided by the enzymatic activity of dissimilatory iron reducing bacteria. This process has significant implications across various scientific fields, ranging from the comprehension of geological processes to the advancement of new materials. The ability to control this biotransformation process presents innovative opportunities for scientific research and technological advancements. Iron, a chemical element with the symbol Fe and atomic number 26, is the sixth most abundant element globally, constituting approximately 5% of the Earth's crust. Common iron minerals, such as hematite and magnetite, contain approximately 70-72% iron.

Therefore, the economic significance of enriching hematite iron ore cannot be overstated [3]. For instance, several synthesis methods have been documented for the production of magnetite, including Sol-Gel, Thermal Decomposition, Co-Precipitation, Reverse Micelles, and Hydrothermal Synthesis. Furthermore, the rotary furnace method can be employed for magnetite regeneration using carbon or carbon oxide gas, or any other suitable regenerating gas. However, it is considered relatively costly compared to other methods. Nonetheless, magnetite can be efficiently refined with lower energy consumption in comparison to alternative refining techniques,

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such as biotransformation [4-9]. Additionally, with a relatively low investment, it can be purified and have impurities removed by a magnetic separator utilizing a weak magnetic field. Therefore, the conversion of other iron oxides to magnetite can be considered economically significant. On the other hand, in weathered ore, there are various types of minerals, each exhibiting distinct properties in terms of enrichment. Furthermore, the recovery of each mineral necessitates a unique method to enhance its quality. These minerals cannot be processed using a single method alone. In this case, converting all these minerals into magnetite can simplify the mineralization process, and by utilizing only one method (a magnetic separator with a weak magnetic field), weathered rock can be enriched.

The challenges in iron ore processing include the loss of iron in the form of hematite minerals. Additionally, the inability to effectively separate iron using high-intensity magnetic separators is another issue. High-intensity and gradient magnetic separators can be utilized to separate hematite from other waste materials. However, due to technological and economic limitations, alternative solutions like the utilization of regenerating and alkalizing bacteria are both cost-effective and efficient. For instance, the utilization of carbon monoxide gas as a hematite regenerator necessitates high temperatures, poses numerous environmental issues, and consumes substantial energy. Consequently, the bacterial method can serve as a viable alternative, offering a cost-effective and eco-friendly approach.

The biotransformation of hematite to magnetite through microorganisms has numerous applications in diverse industries and mines. Magnetite plays a crucial role in the production of high-quality steel [10]. The biotransformation of hematite to magnetite offers a sustainable and cost-effective method to acquire magnetite, which serves as a crucial material in the steel industry. The resulting magnetite enhances the strength, durability, and magnetic properties of steel, making it well-suited for a range of applications, such as iron construction, automobile manufacturing, and machinery production [11, 12].

Magnetite serves as a valuable iron ore in mining operations. The biotransformation of hematite to magnetite offers an alternative and beneficial approach to obtain ore rich in magnetite. This method reduces the reliance on conventional reclamation techniques, resulting in cost savings, minimizing environmental impact, and optimizing resource utilization [10, 13]. Owing to its distinctive properties, magnetite is widely employed as a highly sought-after material in diverse technological applications, such as data storage, magnetic resonance imaging (MRI), and magnetic sensors [14, 15].

The biotransformation of hematite into magnetite, as a means of synthesis, is regarded as an alternative, stable, and environmentally-friendly method in comparison to other transformation methods for magnetite [16]. The biotransformation of hematite to magnetite has revolutionized multiple industries, providing sustainable and innovative solutions. This process utilizes the unique abilities of microorganisms to produce magnetite, leading to advancements in steel production, environmental pollution reduction, mining and mineral processing, renewable energy, biomedicine, and electronics.[17-19].

One of the microorganisms involved in the biotransformation process of hematite to magnetite is bacteria. These bacteria play a crucial role in facilitating the conversion and have a wide range of applications [20]. Certain bacteria possess distinctive metabolic characteristics that allow them to interact with their environment and modify various substances, leading to transformation [21]. In the context of the biotransformation of hematite to magnetite, specific bacteria possess the capability to reduce the iron within hematite and facilitate its transformation into magnetite. The process initiates when these bacteria, known as dissimilatory iron reducing bacteria, come into contact with hematite under favorable conditions. These bacteria are capable of extracting electrons from organic materials or other sources and transferring them to iron ions in hematite. Then, bacteria utilize these electrons to reduce iron ions, resulting in the reduction of hematite to magnetite [22]. Additionally, dissimilatory iron reducing bacteria (DIRB) play a crucial role in the redox conversion of iron in the natural environment [23].

Geobacter and Shewanella strains are considered successful DIRB bacteria in biotransformation process. When cultivated in the presence of Fe(III) oxides, these bacteria usually form secondary minerals [24]. The validation of magnetite by

DIRB was initially performed by Lovley et al. [25]. Dissimilatory iron reducing bacteria (DIRB) are microorganisms that significantly contribute to the transformation of redox iron within the natural environment [23]. Notably, certain bacterial strains such as Geobacter and Shewanella have demonstrated success in biotransformation as DIRB. When these bacteria are cultivated in the presence of Fe (III) oxides, it is common to observe the formation of secondary minerals [24]. The pioneering work of Lovley, Stolz [25] reported the initial discovery of DIRB's ability to produce magnetite. According to a study conducted by Hansel, Benner [1], it was found that the size of magnetite crystals produced through non-biotransformation process is relatively smaller compared to the magnetite crystals generated through biotransformation experiments mediated by bacteria.

The present research focuses on the biotransformation of hematite to magnetite, aiming to provide the technical knowledge required for magnetite production from hematite. Additionally, this process has the potential to reduce high energy consumption costs and offer significant economic benefits to the country. Moreover, it can provide a competitive advantage to industrial owners who adopt this technology. One of the key advantages of this method is its ability to significantly reduce environmental damage and minimize the contribution of pyrometallurgical factories to greenhouse gas emissions. The objective of this study was to investigate and identify dissimilatory iron reducing bacteria, examine methods for converting hematite to magnetite, and conduct a technical-economic analysis of utilizing microorganisms in the biological reduction of iron. Additionally, this study aims to explore the potential of biological conversion as a novel and practical innovation for hematite mines.

2. Materials and Methods

The representative sample analyzed in this research was obtained from the dry tailings of the iron ore mine processing plant. The sampling process was carried out in accordance with the research objectives, wherein the desired tailings were selected and subsequently transferred to the research unit of Chadormalu mine. Following several steps of homogenization and division, the necessary representative samples were separated for further evaluation, adhering to the principles of laboratory and sampling. The representative sample was subjected to a magnetic field intensity of 1000 Gauss for 2 minutes using a high-intensity magnetic separator (Figure 1)in the laboratory to separate magnetite from hematite and other waste materials. In this research, the portion of the tailings devoid of the aforementioned magnetic materials holds significance as it contributes to the ongoing investigation.



Figure 1. The high-intensity magnetic separator device present in the ore processing laboratory at Tehran University.

Based on this, the final amount of tailings was analyzed by sieving, and granulation was performed. The grain size distribution curve of the tailings sample, d80, obtained after magnetic separation, is shown in Figure 2.

Due to the technical and practical limitations in this investigation, it is important to note that in Taylor's sieve series, the size difference between two consecutive sieve openings is very small, particularly in very small particle sizes. This small difference does not result in detectable changes in grain size for the purposes of this research. Therefore, in order to assess the impact of changes

in grain size and the distribution across three grain sizes intervals, the upper limit, middle limit, and lower limit were selected and tested. To carry out the biotransformation process of iron, dissimilatory iron reducing bacteria isolated from the soil of Chadormalu iron ore mine were used in order to multiply the desired bacteria.

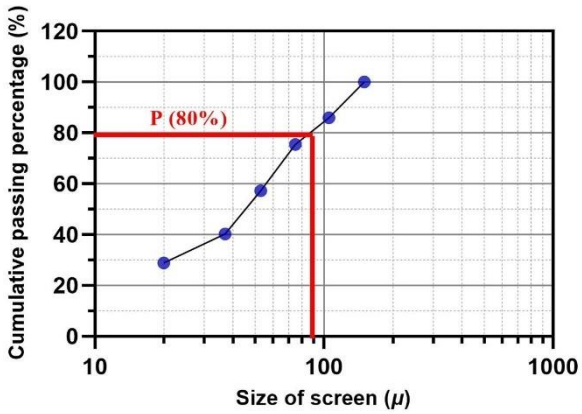


Figure 2. Grain size distribution curve of tailings samples obtained through magnetic separation.

The bacteria were transferred from the cultured plates to the liquid culture medium in the specified Erlens, as shown in Figure 3, for inoculation. The entire procedure was conducted under UV sterilization in a laminar hood, and all equipment and supplies were autoclaved at 121 degrees Celsius and 1 bar pressure for 20 minutes.

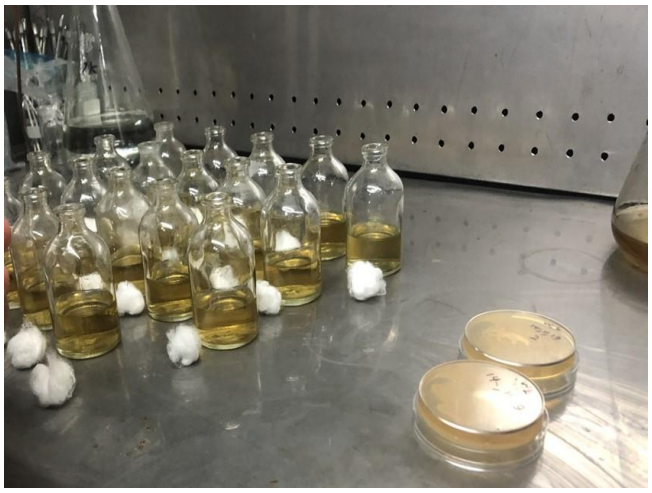


Figure 3. The transfer of bacteria from a solid culture medium to a liquid culture medium under a laminar hood.

3. Results and Discussion

Microbial or bacterial culture medium is a substrate that provides suitable conditions for the growth and multiplication of bacteria. To facilitate the growth of bacteria, liquid culture media can be utilized as given in Table 1.

The progression of bacteria in the culture medium is a crucial factor in microbiological studies. Within a culture medium, bacteria initiate reproduction during the log phase and, once acclimated to the new conditions, they enter the logarithmic growth phase. During this phase, the rate of bacterial division and population growth increases exponentially. However, over time, bacteria enter a phase of reduced growth rate, which could be attributed to a lack of nutrients, accumulation of metabolic waste, and changes in environmental conditions. Eventually, by enduring unfavorable conditions, bacteria enter the death and infection phase, resulting in a decline in their population. According to the findings, it was observed that the bacteria did not exhibit growth and multiplication in the culture medium of new media and entered the death phase. Additionally, the bacteria were cultivated in both Nb and Lb culture media simultaneously. However, due to the higher cost of raw materials in the Nb culture medium compared to the Lb one, the latter was chosen as it serves as an indicator and suitable medium for bacterial proliferation. The growth and development of bacteria in a culture medium are influenced by environmental factors and culture conditions, providing valuable insights into the behavior and properties of these microorganisms. This study contributes to a better understanding of the molecular and physiological mechanisms of bacteria, as well as advancements in bacterial culture methods and control.

In this research, bacteria were selected in a medium with the following characteristics: a) temperature ranging from 22 to 25 degrees Celsius (ambient temperature), b) neutral pH, c) Eh equals to zero, d) media sterilized by autoclave, and e) culture medium Lb, based on the provided proposal. Subsequently, the selected bacteria were examined in the designated culture medium, and

the results for pH and Eh are presented in Table 2 and Figure 4, respectively. Based on the results and characteristics of the bacteria, an increase in alkalinity of the media indicates enhanced bacterial activity. Similarly, a greater tendency of Eh towards more negative values suggests an ideal media for hematite regeneration in terms of favorable bacterial activity. Under such conditions, significant exponential growth of bacteria can be observed.

Culture media	Materials used	Consumption amount	References
Lb**	Sodium chloride	1% (w/v)*	[26]
	Tryptone	1% (w/v)	
	Yeast Extract	0.5% (w/v)	
Nb***	Peptone	0.5% (w/v)	[27]
	Beef Extract	0.3% (w/v)	
	Sodium chloride	0.8% (w/v)	
New media	$NaHCO_3$	30 mM****	[28]
	NH_4Cl	28 mM	
	$NaH_2PO.H_2O$	4.7 mM	
	NaCl	1.7 mM	
	KCl	1.3 mM	
	$CaCl_2.2H_2O$	0.68 mM	
	$MgCl_2.6H_2O$	0.49 mM	
	$MgSO_4.7H_2O$	0.41 mM	
	$MnCl2.4H_2O$	0.025mM	
	$Na2\ MoO_4.2H_2O$	0.004 mM	

* Weight / Volume (g/L)
** Luria-Bertani Broth
*** Nutrient Broth
**** millimolar

Table 1. The culture media investigated in the present study

Day	Sample	Eh	pH	Sample	Eh	pH
1	W1b	-20.01	7.72	W2	-113.8	6.68
2		-242	7.87		-92	6.77
4		-312.6	8.24		-52	8.27
7		-310	8.11		--	--

Table 2. The process of change in media conditions over time for regenerating hematite using bacteria

The Lb liquid medium was divided into two 250 cc Erlenmeyer flasks to determine the most efficient bacteria. Bacteria were added to each of the Erlens, and a tailings soil sample from the Chadormalu iron ore mine was added to the culture medium to achieve a pulp with a solid percentage of 20%. The samples were then placed in an incubator with a rotation speed of 160 rpm for 1, 2, 4, and 7 days aeration. This step was performed to assess the bacterial functionality. Samples mixed with bacteria were collected on the specified days. At the end of this stage, the concentration of iron in the samples was determined using the titration method. As a result, the efficiency of iron recovery by bacteria was evaluated.

The measurement of iron concentration was conducted following the instructions for the preparation and measurement of elements in iron ore using the titration method. W1b bacteria (The W1b strain belongs to the phylum Actinobacteria, class Actinomycetes, order Micrococcales, family

Micrococcaceae, and genus Glutamicibacter) showed a recovery rate of 21.67% for magnetite, while W2 (The W2 strain belongs to the phylum Firmicutes, class Bacilli, order Bacillales, family Bacillaceae, and genus Bacillus) bacteria showed a recovery rate of 6.9%. Based on these results, further research focused on investigating the potential of W1b bacteria

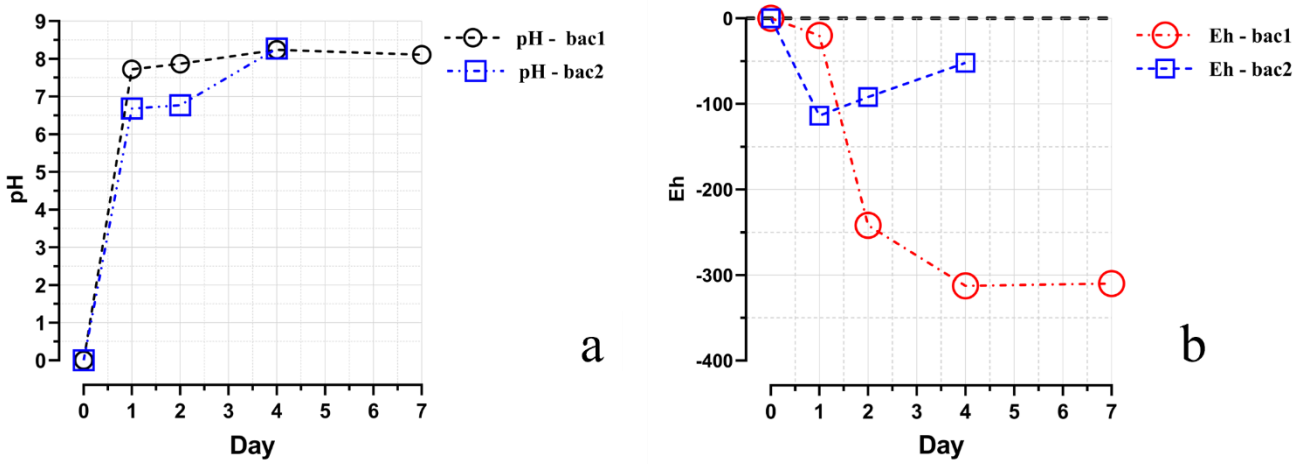


Figure 4. The trend of changes in media conditions with respect to time in hematite regeneration using bacterial strains: a) pH conditions and b) Eh conditions.

Table 3. The influence of the chosen granulation intervals on the changes in the media conditions during hematite biotransformation with the assistance of W1b bacteria.

Day	Sample	Eh	pH	Sample	Eh	pH	Sample	Eh	pH
1		-137	8.162		-137	8.162		-137	8.162
3	W1b-100	-41	9.338	W1b-270	-24	9.403	W1b-400	-33	9.293
6		-19	9.341		-146	9.61		-146	9.626

On the other hand, the granular dimensions in the Chadormalu iron ore tailings sample were divided into three intervals (maximum, median, and minimum) based on the grain size distribution. The selection of these intervals was made considering the weighting and the distribution of dimensions within each interval. During this step, an evaluation was conducted to assess the influence of granular dimensions on the biotransformation of hematite from the tailings sample. To achieve this goal, three specific dimensional ranges (53, 150, and 37 microns) were carefully chosen. Comprehensive evaluations were conducted on each of these ranges to obtain meaningful results. In Table 3, the variations in media conditions and their corresponding fractionations for W1b bacteria are presented. Figure 5 provides a visual representation of the diagram illustrating these changes. Table 4 displays the magnetite recovery percentages obtained from the granulation effect.

The results of this study highlight the successful biotransformation of hematite to magnetite using bacterial strains W1b and W2, with W1b demonstrating superior efficiency. The granulation process of the Chadormalu iron ore tailings revealed that finer particles resulted in a higher recovery rate of magnetite, with W1b achieving a maximum recovery of 30.93%. Additionally, the bacteria's activity was more effective under alkaline conditions, with W1b maintaining more negative Eh values, creating an optimal environment for iron reduction over a period of seven days. In contrast, W2 showed lower

recovery rates and less stable media conditions. The particle size played a crucial role, as smaller granules provided a larger contact surface area, which enhanced bacterial interaction and magnetite formation. These findings support the application of bacterial strains in biotransformation processes as a cost-effective and environmentally friendly alternative to traditional high-energy methods. The ability of W1b to maintain stable conditions over time demonstrates its potential for practical use in mineral processing and bioleaching operations, offering both economic advantages and a reduction in environmental impact.

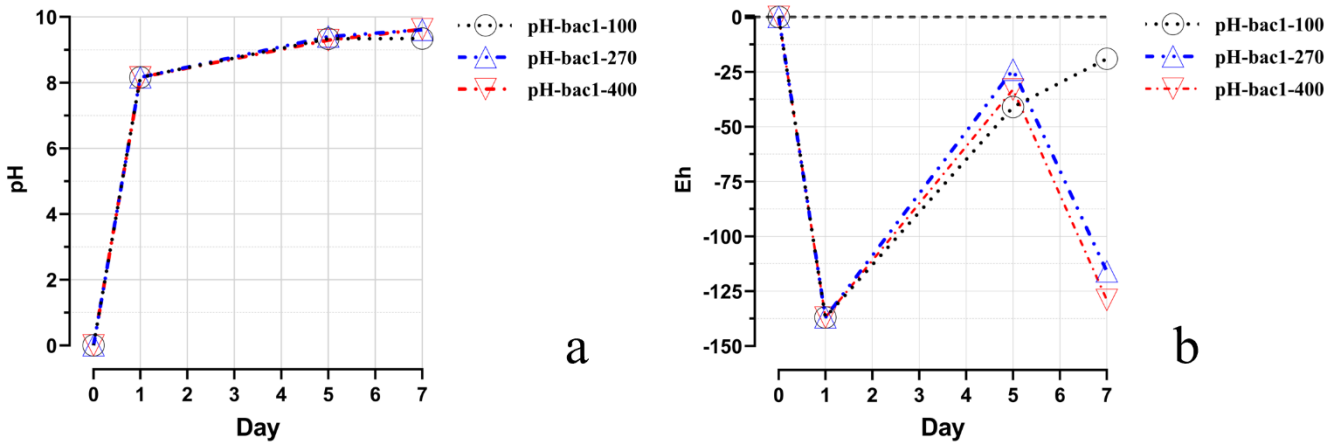


Figure 5. The effects of the chosen granulation intervals on the variations in media conditions during hematite biotransformation with W1b bacteria: a) pH changes and b) Eh changes

Table 4. The percentage of magnetite recovery using the selected bacterial strain W1b under various granulation conditions.

Sample	Magnetite recovery percentage	Sample	Magnetite recovery percentage	Sample	Magnetite recovery percentage
W1b-100	9.89	W1b-270	23.21	W1b-400	30.93

4. Conclusions

The evaluation of bacteria cultured in a liquid medium revealed that the bacteria caused the media to undergo alkalinization and reduction, providing evidence of their activity. The results demonstrated that the W1b bacteria exhibited the most optimal and stable media conditions for the bioreduction of trivalent to divalent iron in the Lb media, outperforming the W2 bacteria. The total bacterial activity showed that W2 bacteria achieved optimal media conditions for the biotransformation of hematite to magnetite within 4 days, while W1b bacteria required 7 days. Furthermore, the analysis of granulation dimensions revealed that smaller and finer particles led to increased contact surface area, resulting in higher magnetite recovery. Implementing the method of biotransformation process to convert hematite to magnetite in iron mines, following the completion of iron ore processing steps and prior to transferring the processing plant's tailings to the tailings dam, can provide economic benefits by preventing concentrate wastage and is also environmentally advantageous. The significant amount of tailings deposited in the tailings dam, with a high percentage of hematite particles, leads to substantial financial waste. Therefore, the importance of this research and its findings highlight that a considerable volume of hematite-containing tailings can be effectively utilized as

feedstock in the production process, without requiring extensive special conditions or equipment, thus emphasizing the valuable role and importance of biotransformation.

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