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RESEARCH ARTICLE

Bioleaching of available silicon from coal tailings using *Bacillus mucilaginosus*: a sustainable solution for soil improvement

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Abstract
In China, a large amount of soil lack available silicon, which leads to a decrease in crop yield. Furthermore, the solid waste coal tailings contain abundant minerals that are rich in silicon, which have not been fully utilized. In this work, we used *Bacillus mucilaginosus* as the leaching agent to convert insoluble silicon in coal tailings into available silicon for crop. After single-factor experiments, the optimal leaching conditions with bacterial dosage, coal tailings weight, initial pH, leaching temperature, and shaking speed were obtained. Kinetic analysis showed that the controlling process of the leaching was a chemical reaction. The leaching process was characterized by X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), Fourier transform infrared spectrometer (FT-IR), and high-performance liquid chromatography (HPLC). The results showed that bioleaching is a feasible and efficient method to extract silicon from coal tailings, with a maximum leaching amount of 260 mg L^{-1} after 16 days, which occupied 93% of the total effective silicon. In conclusion, this work demonstrates that bioleaching technology can effectively solve the problem of the environmental utilization of coal tailings by converting them into a soil improver that can provide beneficial nutrients for crop growth.

Keywords *Bacillus mucilaginosus* · Bioleaching · Coal tailings · Available silicon · Kinetics

Introduction

Coal tailings are byproduct generated from the coal preparation process, in which the high-ash coal and gangue are transformed into a mud-like substance that settles and undergoes dehydration (Liu and Liu 2010). Due to its high moisture content, large viscosity, high ash content, low heating value, and high processing cost, tailings are difficult to utilize directly. In 2019, China's raw coal production reached approximately 3.75 billion tons, of which coal tailings accounted for 6–8%. The environmental utilization of coal tailings remains a challenge due to the lack of effective treatment technology and facility. As a result, the majority of tailings have to be used for power generation in small power plants. However, this practice causes serious pollution to the environment due to the low calorific value and high content of harmful substances. Therefore, it is necessary to find a method that can utilize coal tailings environmentally.

Currently, the main utilization methods of coal tailings include using the coal content as fuel resources (Zhang et al. 1998), utilizing its abundant SiO_2, Al_2O_3, and other resources as chemical materials, and using its high viscosity (Tejada and Gonzalez 2007) as a soil amendment (Guo et al. 2014). However, most of these methods are based solely on the basic properties of coal tailings, such as its high coal content, high viscosity, and content of quartz and alumina. They fail to high-efficiently utilize the effective components in coal tailings and do not achieve the high-value resource utilization of coal tailings. Available silicon is an effective pesticide that can promote crop growth and development. However, more than 50% of farmland in China lacks effective silicon, and simple methods such as natural weathering and soil amendment are no longer sufficient to maintain Si balance in the soil (Gaur et al. 2020; Sommer et al. 2006). Therefore, measures need to be taken

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to supplement available silicon in the soil (Mitani-Ueno and Ma 2021). Coal tailings contain a large amount of silicate minerals that contain Si element that are beneficial to crops. By the effective utilization of Si in coal tailings, the available silicon in the soil can be replenished and coal tailings can be utilized environmentally (Azziz et al. 2012). Therefore, silicate minerals in coal tailings can serve as soil supplements, providing beneficial elements, while also realizing the resource utilization of coal tailings, solving environmental pollution problems, improving soil fertility, promoting crop growth and development, and increasing crop yields.

Biological leaching, also known as microbial leaching or bacterial leaching, refers to the technology of using microorganisms under certain conditions to extract target elements from minerals (Anguiano et al. 2018; Wang et al. 2018; Yin et al. 2021). During the growth process, the microbial activity and its metabolic products can convert the fixed-state elements in minerals into free states (Lv et al. 2019). Biological leaching technology has been widely welcomed in recent years because it has low development costs, high leaching efficiency, and is environmentally friendly (Sun et al. 2014).

Recently, many researchers have investigated silicon-activated bioleaching techniques, such as the treatment of magnesite, bauxite, nickel-bearing feedstock, and pyrolusite by silicate bacteria (Chaerun et al. 2017, Ghosh et al. 2016, Lian et al. 2008, Lv et al. 2021, Lv et al. 2020, Bhatti 2009, Srichandan et al. 2019).

Bacillus mucilaginosus, also known as silicate bacteria, is a gram-positive bacterium that belongs to the bacterial domain (Rahimzadeh 2015), Firmicutes phylum, Bacillaceae family, and Bacillus genus in taxonomy (Liu et al. 2017; Yang et al. 2010). Under the microscope, it appears as a rod-shaped structure, about 3–5 μm in length and 0.8–1.5 μm in width, with a capsule on its surface and oval spores (Nyanikova et al. 2002). In its metabolism, it can release organic acids such as acetic acid and butyric acid, and it has good abilities to dissolve silicon, potassium, and phosphorus. Its important characteristic is that through the substances produced during its growth process, such as amino acids, organic acids, and capsule polysaccharides, it can decompose potassium, silicon, and phosphorus in minerals such as feldspar and mica (Lian et al. 2001), transforming them from insoluble states to effective silicon that can be directly utilized by crops (Ehrlich et al. 2010).

The purpose of this study is to use the bioleaching of *Bacillus mucilaginosus* to convert the abundant insoluble Si in coal tailings into available Si that can be directly used by crops, thus supplementing soil nutrients. In this process, the optimal conditions (such as pH, agitation speed, temperature, bacterial inoculation amount, and leaching time) were obtained, the kinetic model was also explored, and the leaching mechanism was analyzed. This method not only high-efficient utilizes the available resources in coal tailings, but also effectively solves the problem of silicon deficiency in soil, thus improving soil quality. The transformation of coal tailings into a high-value Si-soil conditioner has important practical significance and broad application prospects.

Materials and methods

Coal tailings

The coal tailings used in this study was taken from the tailing filter cake of BinHu Coal Preparation Plant in Henan province of China. It appeared as black, moist, and chunky material. The elemental composition was determined by X-ray fluorescence spectroscopy (XRF), and the results are shown in the Table 1. The results indicate that SiO_2 and Al_2O_3 accounted for 60.78% and 23.92% of the total composition, respectively, indicating that Si and Al are the main elements in the coal tailings. The heavy metal content in the coal tailings was determined according to the detection methods specified in GB/T3058-2019, GB/T3058-2019, and "Rock and Mineral Analysis" (Fourth Edition, 2011), as shown in Table 2.

Microorganism and culture medium

The bacterial strain used in this study was purchased from YeShengWang Biotech Company, China. The silicate bacteria are heterotrophic microorganisms; therefore, an external source of organic carbon is required as a nutrient during their growth. The bacterial basal medium used in the experiment contained the following ingredients: sucrose of 10 g,

Table 1 Chemical composition analysis of coal tailings

Element	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO_2	P_2O_5
Content (%)	60.78	23.92	3.74	0.93	4.96	0.12	1.73	0.97	0.05	0.05

Table 2 Heavy metal content of coal tailing

Heavy metal	Cr	Li	Cu	Zn	Cd	Pb	As	Hg
Concentration (μg g^{-1})	120.57	35.775	88.845	338.46	0.285	128.46	34.62	0.135

yeast extract of 0.4 g, Na_2HPO_4 of 0.5 g, $MgSO_4$ of 0.2 g, $MgCl_2$ of 0.2 g, $CaCO_3$ of 1 g, and distilled water of 1 L. The mixture was then sterilized at 121 °C for 20 min in a sterilization pot (Lv et al. 2020; Teng et al. 2018).

Bioleaching experiments

The effects of factors such as the mass of bacteria, the amount of coal tailings, temperature, and pH on the leaching efficiency of coal tailings were tested via single-factor experiments. The experiments were performed in triplicate, varying the parameters as follows: bacteria 1–20 g, coal tailings 5–20 g, leaching temperature 20–35 °C, pH 5–9, shaking speed 150–240 rpm, and leaching time 6 days.

The experiment was conducted as follows: 90 mL of bacterial basal medium and 10 g of coal tailings were added into a 250-mL conical flask. The flask was then sterilized at 121 °C for 20 min. After sterilization, predetermined amount of *Bacillus mucilaginosus* was added under sterile conditions. The experiment was conducted at a temperature of 30 °C, pH of 7, with a shaking speed of 210 rpm and a leaching time of 6 days. The optimal amount of bacteria was determined by measuring the content of available silicon in the leaching solution and residue using the silicon-molybdenum blue spectrophotometric method.

Next, the optimized bacterial mass was fixed, and predetermined amount of coal tailings was added under the above-mentioned experimental conditions. The optimal amount of coal tailings was determined by measuring the content of available silicon in the leaching solution and residue using the silicon-molybdenum blue spectrophotometric method.

In addition, the optimal experimental conditions were fixed, and the pH and temperature were varied to determine the best leaching conditions. The content of available silicon in the leaching solution and residue was determined using the silicon-molybdenum blue spectrophotometric method. Each experiment was repeated three times. The experimental design is shown in Table 3.

To achieve the maximum leaching efficiency of effective silicon, leaching experiments were conducted under the optimized conditions. Leachate samples were taken over a period of 16 days, at 2-day intervals, respectively. After centrifugation and filtration, the amount of effective silicon in the supernatant was determined using the silicon-molybdic blue spectrophotometric method to analyze the kinetics of the leaching process (Fig. 1).

Table 3 Experimental design of optimum growth conditions for *B. mucilaginosus*

Test	Bacterial mass (g)	Tailings amount (g)	Initial pH	Temp. (°C)	Shaking speed (rpm)	Time (days)
1	1	10	7	30	210	6
2	5	10	7	30	210	6
3	10	10	7	30	210	6
4	15	10	7	30	210	6
5	20	10	7	30	210	6
6	m_1	5	7	30	210	6
7	m_1	10	7	30	210	6
8	m_1	15	7	30	210	6
9	m1	20	5	30	210	6
10	m_1	m_2	6	30	210	6
11	m_1	m_2	7	30	210	6
12	m_1	m_2	8	30	210	6
13	m_1	m_2	9	30	210	6
14	m_1	m_2	pH	20	210	6
15	m_1	m_2	pH	25	210	6
16	m_1	m_2	pH	30	210	6
17	m_1	m_2	pH	35	210	6
18	m_1	m_2	pH	40	210	6
19	m_1	m_2	pH	T	150	6
20	m_1	m_2	pH	T	180	6
21	m_1	m_2	pH	T	210	6
22	m_1	m_2	pH	T	240	6

m_1 is the optimal mass of bacteria, m_2 is the optimal amount of coal tailings, pH is the optimal initial pH, T is the optimal leaching temperature, and r is the optimal shaker speed.

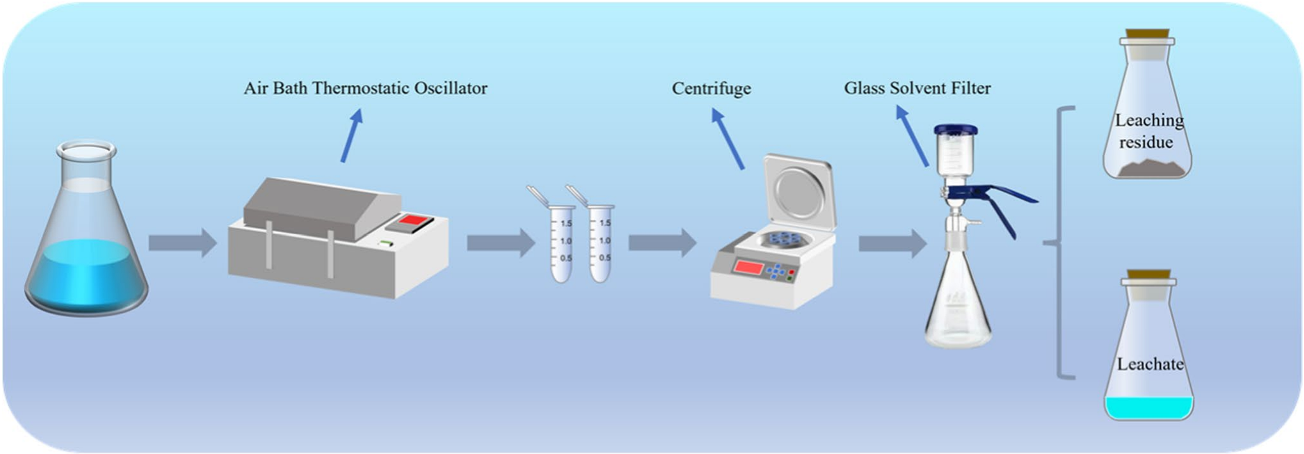


Fig. 1 Flowchart of bioleaching experiment

Analytical methods

Silicon content in solution was determined by silicon-molybdenum blue spectrophotometry (Chen et al. 2017). Accurately transfer 0.5 mL of the filtrate to a 100-mL volumetric flask, add 1 drop of p-nitrophenol indicator, and then add 3 drops of ammonia solution until a yellow color appears. Add 6 drops of sulfuric acid until the yellow color just disappears. Add 30 mL of water, 2 mL of sulfuric acid, and 5 mL of ammonium molybdate solution (80 g•L^{-1}), mixing well after each addition. Allow the solution to stand for 15–30 min, then add 2 mL of sulfuric acid and 10 mL of oxalic acid solution (50 g•L^{-1}), and immediately add 5 mL of ascorbic acid (20 g L^{-1}). Dilute the solution to the mark with water, mix well, and let it stand for 30 min. Measure its absorbance at a wavelength of 650 nm using the reagent blank solution as a reference.

Establishment of a standard curve: Accurately transfer 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 mL of a 100 mg•L^{-1} silicon working solution into a 100-mL volumetric flask. Add 1 drop of p-nitrophenol indicator and then add ammonia solution until a yellow color appears. Add sulfuric acid until the yellow color just disappears. Add 30 mL of water, 2 mL of sulfuric acid, and 5 mL of ammonium molybdate solution (80 g•L^{-1}), mixing well after each addition. Allow the solution to stand for 15–30 min, then add 2 mL of sulfuric acid and 10 mL of oxalic acid solution (50 g•L^{-1}), and immediately add 5 mL of ascorbic acid (20 g•L^{-1}). Dilute the solution to the mark with water, mix well, and let it stand for 30 min. Measure its absorbance at a wavelength of 650 nm using the reagent blank solution as a reference.

Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS, Talos F200 S/Talos F200S, JSM-IT300, Japan) was adopted to observe the micro-morphological characteristics of the samples surface. The samples were cleaned using absolute ethyl alcohol. After the surface cleaning, the samples were dried in air. Before SEM tests, the samples were sputter-coated with a layer of gold, and the surface composition of the leached residue was observed by a magnification of 8000 times.

X-ray diffraction (XRD, D8 ADVANCE, BRUKER, Germany) was used to analyze the phase changes of samples before and after the leaching experiments. The tailings in the leaching system was filtered, washed with deionized water, air-dried, and then the mineral powder was stacked on a sample platform, flattened and tested. The experimental conditions were set to a scanning angle of 10°–90° and a scanning speed of 10 mm min^{-1}.

Functional group distribution of leachate with different leaching times was determined by spectroscopy Vertex 80v, Bruker (Billerica, MA, USA), Germany, transform infrared spectrometer, using a liquid test module; a drop of the leached liquid was placed on the liquid analysis module and scanned 16 times in the range of 4000–400 cm^{-1} with a scanning resolution of 4 cm^{-1}.

The content of different kinds of organic acids in the leachate is measured by high-performance liquid chromatography (HPLC, Ultimate 3000DGLC, ThermoFisher, USA). An appropriate amount of homogenized sample was weighed and mixed with 5 mL of mobile phase (10 mm K_2HPO_4, pH = 2.55). Ultrasonic extraction was performed for 30 min, followed by a 1-h water bath at 60 °C. After centrifugation, the supernatant was filtered and injected into the machine. The instrument parameters were set as follows: a UV detector was used, with the column temperature maintained at 30 °C, an injection volume of 10 μL, a flow rate of 0.5 mL min^{-1}, and a wavelength of 210 nm.

Results and discussion

Optimization of experimental conditions

Effects of bacteria inoculum amount

Figure 2 shows the effect of inoculum mass on silicon leaching efficiency. As the amount of inoculum increased from 1 to 5 g, the ash content of coal decreased (coal mainly consists of organic and inorganic components, and the ash content is used to measure the inorganic content represented mainly by silicate minerals), and the content of available silicon increased. When the inoculum amount reached 5 g, the maximum leaching amount of 119.1 mg L^{-1} was obtained, and the content of available silicon decreased as the inoculum amount increased. This is because as the inoculum amount increased, the overall nutrient demand also increased significantly, but the amount of culture medium in the system was not sufficient to provide the necessary nutrients for coal greater than 5 g and the oxygen content in the system was not sufficient to maintain the bacterial cells' full aerobic respiration, leading to decreased bacterial activity and reduced silicon leaching efficiency. Therefore, 5 g was chosen as the optimal inoculum amount.

Effect of coal tailing amount

The appropriate concentration of coal tailings can enable the microbial strains and their metabolic products to come into contact with the coal tailings and react fully. First, the coal tailing concentration affects the concentration and exchange rate of O_2 and CO_2 in the system. When the coal tailing concentration is low, it does not affect the exchange rate of O_2 and CO_2 in the system. However, when the coal tailing concentration is higher than a certain value, the microbial consumption of O_2 is higher than the gas-liquid transfer rate, resulting in an accumulation of local CO_2, causing cell hypoxia, and reducing the reaction rate. Second, the slurry concentration also affects the biological activity. When the coal tailings are added in insufficient amounts, the active substances in the ore are decomposed by the microbial strains in the early stages of the experiment. When the ore sample is added in excessive amounts, the relative distance between mineral particles is insufficient, and the shear stress between solid particles and fluids will increase with the increase in slurry concentration. This will cause mechanical damage to the microbial cells, prevent the reproduction and metabolism of the microbial strains, change the structure of extracellular proteins, and even destroy the ecosystem of cells and shaking flasks, making it difficult for bacteria to adsorb onto the mineral surface and achieve the best mineral leaching effect. In addition, coal tailings contain heavy metal elements, and a high slurry concentration can increase the solubility of heavy metal elements in the system, thereby affecting the cell activity.

From Fig. 3, it can be observed that as the amount of coal tailings increased from 5 to 15 g, the concentration of effective silicon in the solution showed an increasing trend. This increase in coal tailings provided the system with more raw materials, resulting in a higher concentration of effective silicon. However, when the amount of coal tailings was increased from 15 to 20 g, the concentration of effective silicon sharply decreased. This could be due to the fact that the increase in coal tailings provided more raw materials to the system and also led to a decrease in dissolved O_2, an increase in fluid shear stress, and an increase in heavy metal elements (Gao et al. 2017; Song and 이계승 2010); the content of toxic metals in tailings exceeded the maximum tolerance of bacteria, as shown in Fig. 4, which reduced the cell activity and led to a decrease in the concentration of effective silicon. Therefore, the optimal amount of coal tailings was chosen to be 15 g.

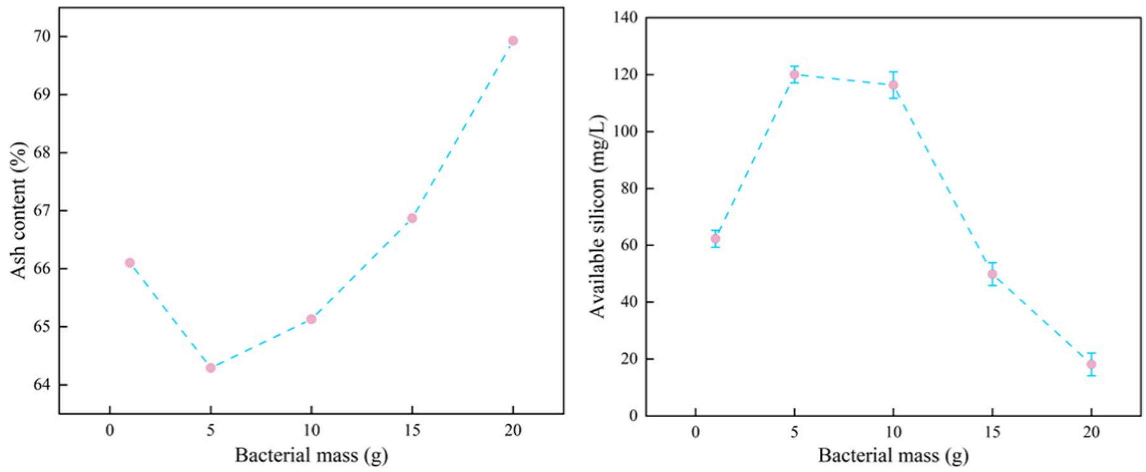


Fig. 2 Effect of bacterial mass on ash content of leaching residue (left) and available silicon leaching amount (right)

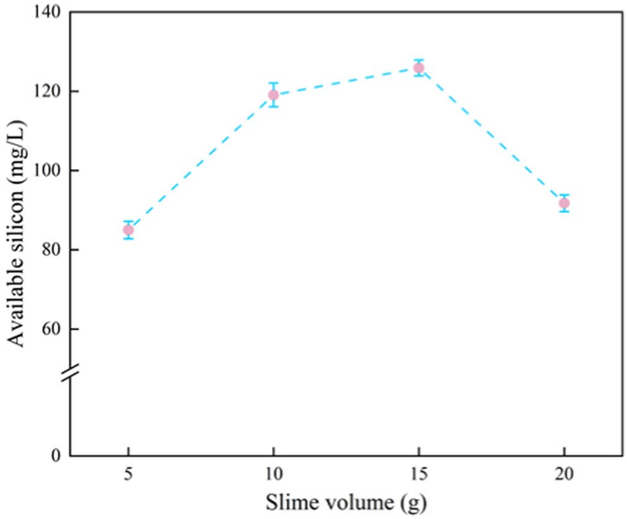


Fig. 3 Effect of tailing amount on available silicon leaching amount

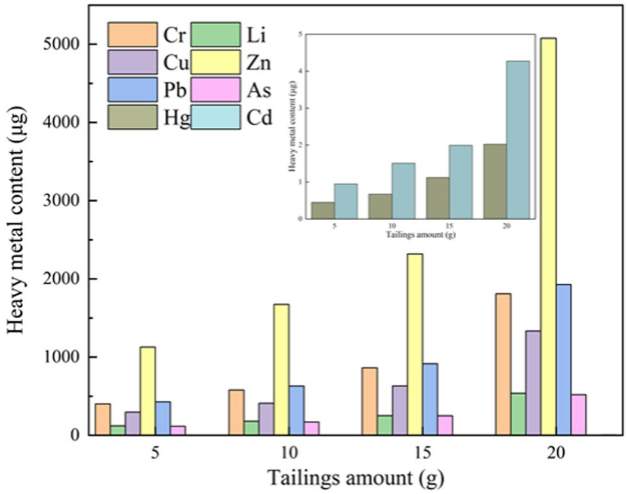


Fig. 4 Heavy metal content in leach residue with different coal tailings amount

Effect of initial pH

In the process of bioleaching, the initial pH value affects not only the metabolic activity and leaching efficiency of the microorganisms, but also the stability of the bioleaching system. If the initial pH value exceeds the range of bacterial growth, it may cause bacterial death, leading to a bottleneck in the bioleaching system and affecting its stability. In addition, the initial pH value may also affect the migration of elements during the bioleaching process, affecting the efficiency and quality of bioleaching. Therefore, appropriate initial pH values should be selected based on the actual situation to ensure the smooth progress of the bioleaching process and obtain higher leaching efficiency and quality.

Therefore, it is necessary to strictly control the pH of the reaction system to provide an appropriate environment to ensure the high reaction rate of enzymes and the growth rate of microorganisms. Figure 5 shows the significant effect of initial pH value on the leaching efficiency of silicon in bioleaching. It can be seen that the effective silicon content in the leachate was the highest at pH 7. As the pH decreased, the metabolic activity of *Bacillus mucilaginosus* was inhibited, resulting in a significant decrease in effective silicon content. When the pH increased from 7 to 8, the effective silicon content in the leachate slowly decreased. This is because organic acids are produced during bacterial metabolic activity, which can be neutralized by the alkalis in the system, maintaining a relatively mild pH. However, when the pH was between 8 and 9, the effective silicon content showed a sudden decrease. This is because the amount of organic acids produced by the bacteria is not enough to neutralize the alkalis in the system, resulting in a decrease in bacterial activity and effective silicon content. Therefore, in the process of bioleaching, the choice of initial pH value is very important, and a leachate with pH 7 should be chosen to obtain higher effective silicon content.

Effect of leaching temperature

Bacteria can achieve the best leaching effect within a certain temperature range. This can not only promote bacterial metabolism and proliferation, but also effectively increases the number of bacterial populations per unit time. However, low temperatures can reduce the activity of biological enzymes in bacteria, leading to a slower metabolism and growth rate. At the same time, high temperatures can cause protein denaturation and change the permeability of cell membranes, thereby causing biochemical reactions in

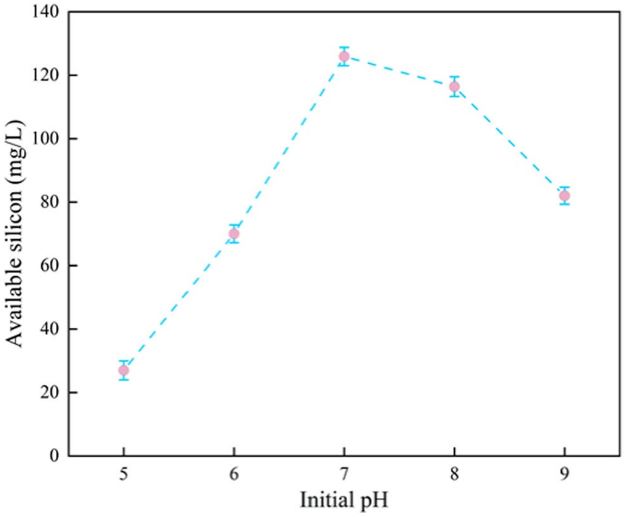


Fig. 5 Effect of pH on available silicon leaching amount

the cell to stop, ultimately leading to cell death. From the research results, it can be seen that 30 °C was the optimal temperature for *B. mucilaginosus* to leach silicon, and the effective silicon concentration was highest in this temperature range. When the temperature was lower than 30 °C, the bacteria have poor tolerance to low temperatures and the effective silicon content decreased greatly. Between 30 °C and 40 °C, the bacteria had good tolerance to high temperatures and the effective silicon content decreased less. Therefore, 30 °C was the optimal temperature for *B. mucilaginosus* to leach silicon (Fig. 6).

Effect of shaker speed

B. mucilaginosus is an aerobic bacterium that produces energy through respiration. In oxygen-rich environments, their metabolism and reproduction are more efficient. The adjustment of the shaking speed can control the amount of oxygen dissolved in the solution and the rate of carbon dioxide release. If the shaking speed is too low, the oxygen content in the culture medium may be insufficient to meet the needs of bacterial growth. If the shaking speed is too high, it will destroy the adhesion between bacteria and coal, and hinder the formation of the "capsule-bacteria-coal" complex. In addition, high shaking speed will increase the dissolved oxygen content in the solution, causing the bacteria to metabolize too quickly and consume a large amount of culture medium in a short time, wasting a large amount of formed "capsule-bacteria" system, thereby reducing the leaching efficiency.

The impact of rotation speed on leaching efficiency is not very strong, as shown in the Fig. 7. Effective silicon concentration gradually increased as the rotation speed increased from 150 to 210 rpm. When the rotation speed was 210 rpm, the leaching rate reached 125.9 mg L^{-1}, which was consistent with the beneficial effect of appropriate increase in oxygen concentration on leaching efficiency. However, when the rotation speed increased from 210 to 240 rpm, it caused significant mechanical damage to the bacteria, leading to a sharp decrease in leaching rate. Therefore, the optimal rotation speed was 210 rpm. Additionally, at lower rotation speeds, the leaching rate may be lower, but the damage to the bacteria is also smaller, which can reduce harm to the cells and ensure the quality of the leachate. On the other hand, higher rotation speeds may lead to higher leaching rates, but also greater damage to the bacteria, which can affect the quality of the leachate. Therefore, when selecting rotation speed, it is necessary to balance the trade-off between leaching rate and bacterial damage.

In this study, we determined the optimal leaching conditions for coal tailings using *B. mucilaginosus* through a single-factor experiment. The results showed that the maximum leaching amount of available silicon by *B. mucilaginosus* was 125.9 mg L^{-1} at 6 days under the following conditions: bacterial amount of 5 g, coal tailing amount of 15 g, initial pH of 7, leaching temperature of 30 °C, and shaking speed of 210 rpm. These results provide an important basis for further exploration of the mechanism of *B. mucilaginosus* leaching of coal tailings.

Leaching kinetics of coal tailing by *B. mucilaginosus*

In the process of leaching, not only the maximum leaching rate and the direction of leaching are important, but also the leaching rate is crucial in practical production (Pangayao et al. 2018). Therefore, leaching kinetics is the science that studies the leaching reaction rate and mechanism. By experimentally studying and analyzing the leaching reaction

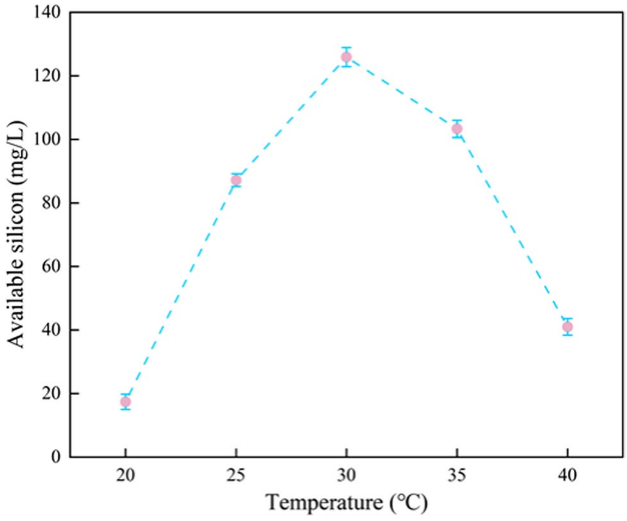


Fig. 6 Effect of temperature on available silicon leaching amount

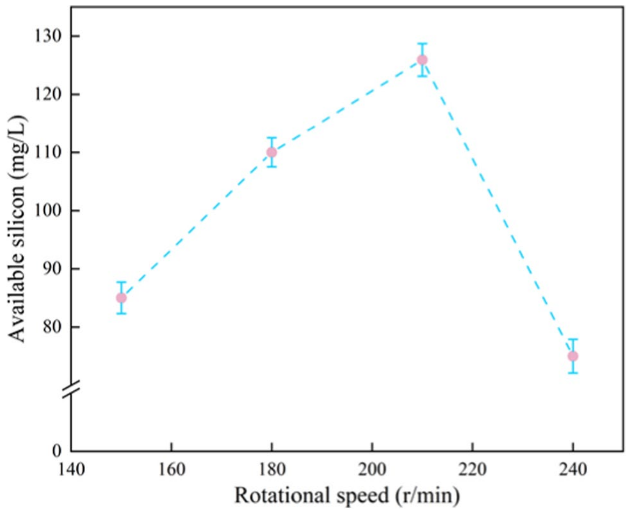


Fig. 7 Effect of rotational speed on available silicon leaching amount

mechanism and controlling steps, relevant mathematical models for the leaching process can be established, and leaching kinetic equations can be derived. These studies aim to promote the development of leaching processes, making them more easily applicable in engineering, design, scaling up, and automated control.

In order to better study the dynamic impact of different key factors on the available silicon conversion rate in coal tailings (where A is the total silicon content in coal tailings, a is the amount of available silicon extracted, and $\mu = a/A$ is the leaching rate of effective silicon), we designed experimental conditions with three bacterial masses (1 g, 5 g, and 10 g), three initial pH levels (6, 7, and 8), and three temperatures (25 °C, 30 °C, and 35 °C), based on confirmed experimental conditions such as tailing amount and shaking speed. The experimental results are shown in Figs. 8, 9, and 10. It can be observed that the increase of the leaching rate of effective silicon was relatively fast in the short term, but as time goes on, the growth rate became slower and there is no significant change in the leaching rate of effective silicon in the end, the final leaching concentration is about 260 mg L^{-1}, and the leaching rate is 93%.

The bioleaching process is a complex multiphase liquid-solid or gas-liquid-solid reaction process, which is generally in accord with the unreacted shrinking core model, also known as the shrinking core model. The shrinking core model considers that the leaching process is controlled by the following four sequential steps: (1) diffusion of leaching agents through the liquid film; (2) diffusion of reactants through the solid film shell; (3) the chemical reaction; and (4) the transfer of the resultant species to the bulk solution. Generally, the first and last steps are not the rate determining steps due to the vigorous shaking conditions during the bioleaching process (Shang et al. 2021).

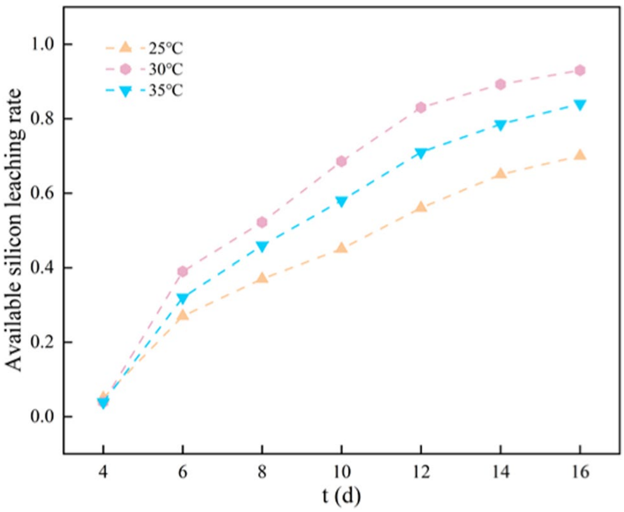


Fig. 8 Effect of temperature on available silicon leaching rate

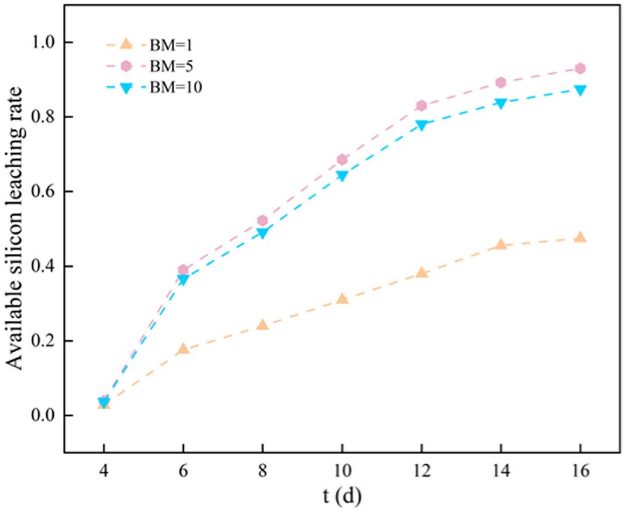


Fig. 9 Effect of bacterial mass on available silicon leaching rate

The kinetics of leaching process is controlled by chemical reaction is as follows:

$$1 - (1 - x)^{\frac{1}{3}} = k_a \times t$$

The kinetics of leaching process is controlled by diffusion as follows:

$$1 - 2x/3 - (1 - x)^{\frac{2}{3}} = k_b \times t$$

In the formula, k_a and k_b are rate constants, day^{-1}; x is the leaching efficiency of SiO_2, %; t is the leaching time, day.

Based on the above formula, we fit the experimental data in the graph and obtain the fitting curves of $1 - (1 - x)^{1/3}$ and $1 - 2x/3 - (1 - x)^{2/3}$ under different experimental conditions, as shown in the Fig. 11. Under all experimental conditions,

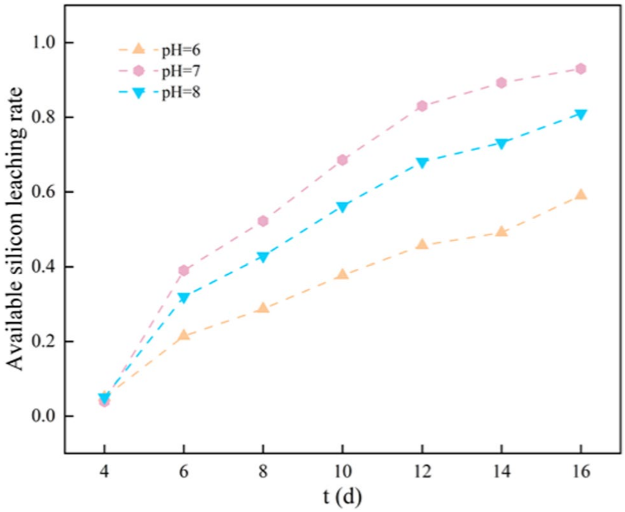


Fig. 10 Effect of pH on available silicon leaching rate

the leaching of available silicon in the coal tailings in the bioleaching system is controlled by chemical reactions.

In the leaching experiment, chemical reactions are an important factor that can be controlled by adjusting activation energy, reaction rate constant, and the concentration of reactants and products. Specifically, increasing the reaction temperature and increasing the concentration of reactants can reduce the activation energy and accelerate the reaction rate. However, excessively high temperature or excessively high concentration may cause the reaction unstable or reduce the quality of the products. Adjusting the pH value of the reaction can change the reaction rate constant.

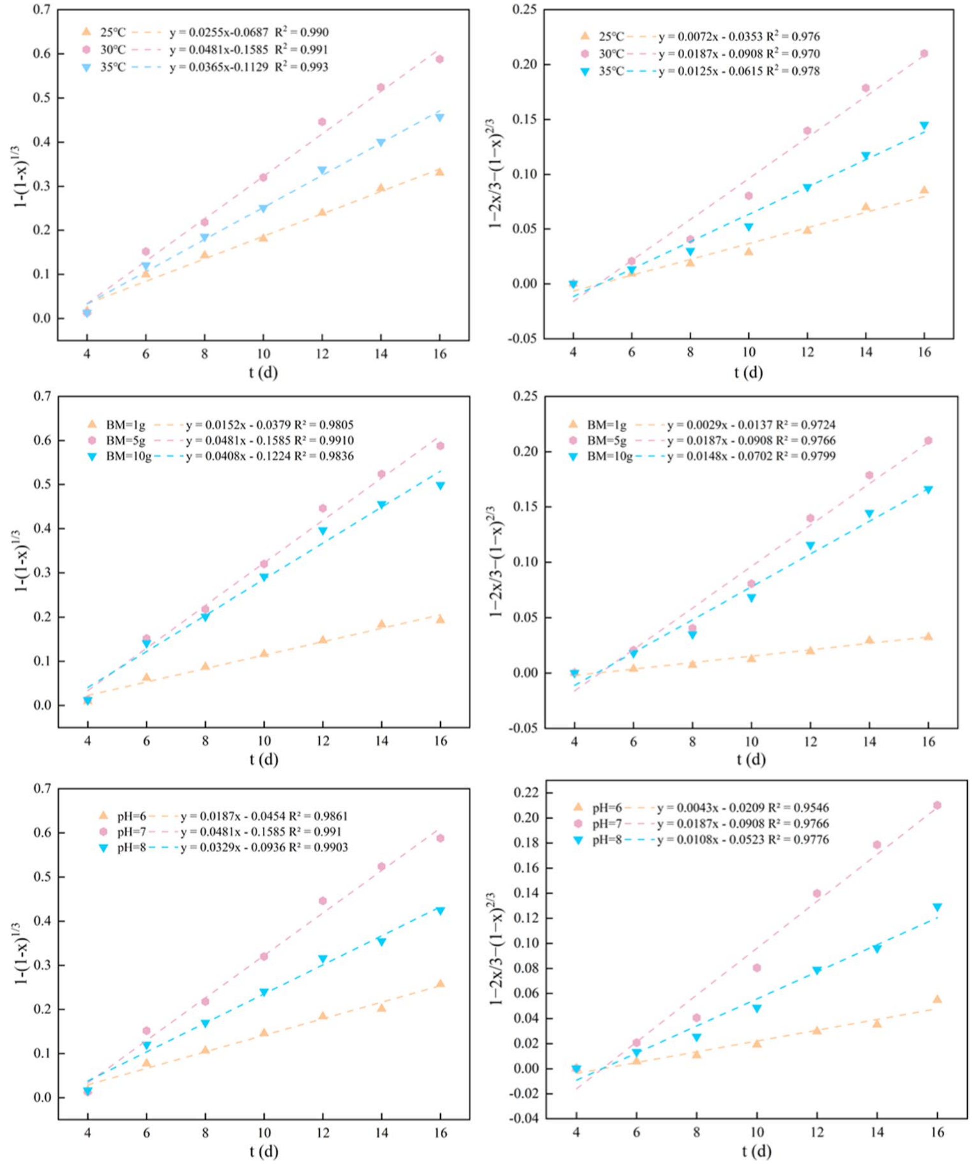
Therefore, by properly adjusting these factors, the chemical reaction in the leaching experiment can be effectively controlled to achieve the optimal leaching effect.

Phase transformations during bioleaching process

SEM-EDS analysis of coal tailings

The coal tailings were divided into four groups and subjected to bacterial erosion treatment for varying periods. Subsequently, the surface morphology and chemical composition of the samples were analyzed before and after treatment by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS).

Fig. 11 Linear-fitting data for kinetic studies during bioleaching: chemical reaction control (left) and diffusion control (right)



The SEM images revealed that the surface morphology and structure of the samples gradually changed with increasing leaching time. In the initial state (Fig. 12a), the sample surface exhibited a relatively flat and orderly block-like structure. However, as the bacterial treatment time increased, the sample surface began to show flaky peeling, gradually became rough, and finally formed holes and flocculent substances, indicating that the bacteria effectively eroded the sample surface, as shown in Fig. 12d.

EDS analysis showed that the chemical composition of the sample surface also changed over time. In the initial state (Fig. 12a), the surface Si content of the sample was 6.02%, which gradually decreased with increasing leaching time. When the bacterial leaching time reached 16 days (Fig. 12d), the surface Si content of the sample decreased to 0.15%, indicating that the bacteria could effectively extract the Si element on the coal surface into suspension.

XRD analysis of coal tailings

In this study, coal tailings that were not leached by *B. mucilaginosus* (i.e., raw coal tailings) and coal tailings that had been leached by *B. mucilaginosus* for 4, 8, and 16 days were analyzed using X-ray diffraction (XRD) technique (Fig. 13). After observation and comparison, we found that the peak areas of quartz and kaolinite in coal tailings changed after leaching by *B. mucilaginosus* Specifically, the peak area of quartz decreased significantly after leaching, while the peak area of kaolinite decreased slightly, and the peak area of sinnerite remained almost unchanged.

It is believed that this may be due to the fact that kaolinite is a layered silicate mineral with lower structural stability, which is easily eroded by *B. mucilaginosus*, while quartz is a framework structure mineral with higher structural stability (Xianzhe 2014). Although it is more difficult to leach, under optimized leaching conditions, the leaching efficiency of *B. mucilaginosus* for quartz is greatly improved, which is why we observed a decrease in the peak area of quartz after leaching. The crystal structure of quartz and kaolinite was altered, and the silicon in the crystals was released after leaching by *B. mucilaginosus*.

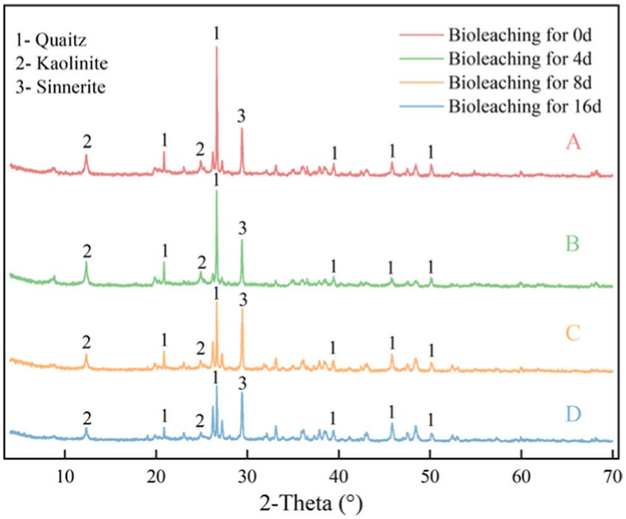


Fig. 13 The XRD spectra of coal tailings with different leaching times

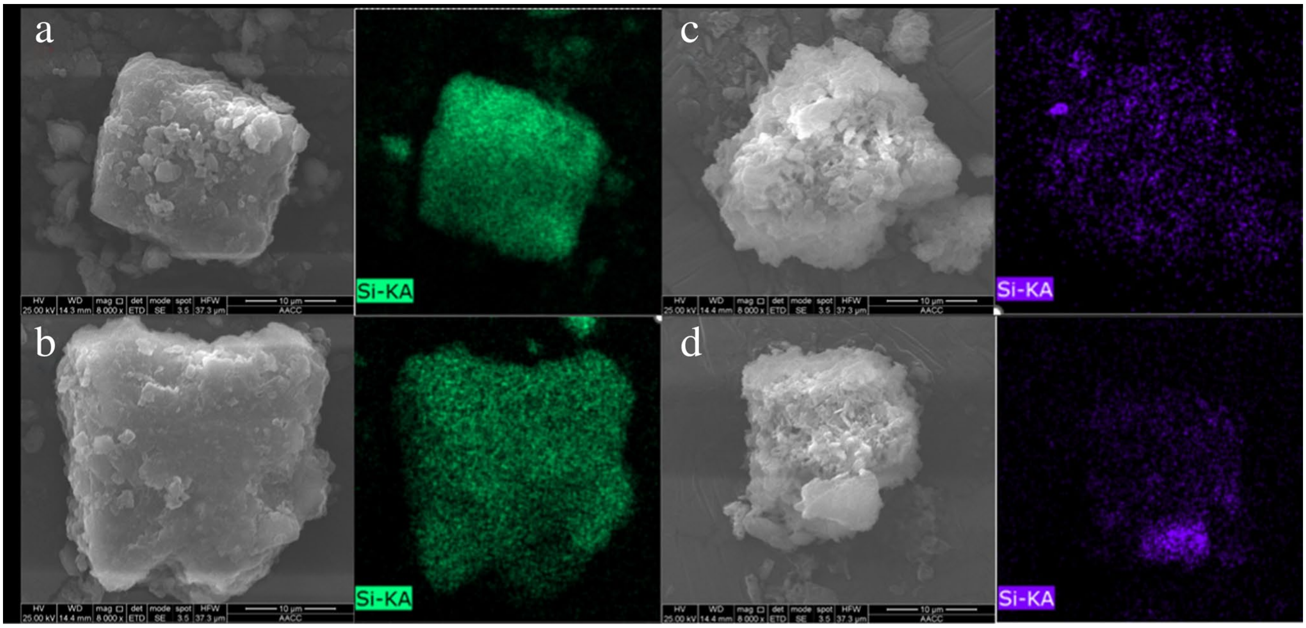


Fig. 12 The SEM-EDS spectrums of coal tailings with bacterial leaching for 0 day (**a**), 4 days (**b**), 8 days (**c**), and 16 days (**d**)

The conclusion that under optimized leaching conditions, *B. mucilaginosus* has a leaching effect on quartz and kaolinite in coal tailings, which releases silicon from the crystals, has been reached through this study. The XRD analysis results provide an important basis for further research on the application of *B. mucilaginosus* in the solid waste coal tailing field.

FT-IR analysis of liquid supernatant after bioleaching

The infrared analysis curves of coal tailings bacterial leaching solutions with different leaching times show that there were significant changes in functional groups under the action of bacteria (Fig. 14). The strong absorption peak at 1100 cm^{-1} in the graph represents the anti-symmetric stretching vibration peak of Si–O–Si in quartz, indicating the dissolution and release of silicon during the biologically leaching process. Combined with XRD spectrum analysis, it was found that quartz and kaolinite were leached into available silicon, which is the main source of available silicon. When the leaching time was 0, there was almost no characteristic peak of Si–O–Si in the leaching solution, and with the increase of leaching time, the integral area of the characteristic peak of Si–O–Si gradually increased, indicating that the leaching of silicon by bacteria has a good promoting effect. Except for the significant changes in the Si–O–Si characteristic peak, other characteristic peaks did not change much, indicating that the leaching of coal tailings by *B. mucilaginosus* does not produce other substances that may affect the performance of the product.

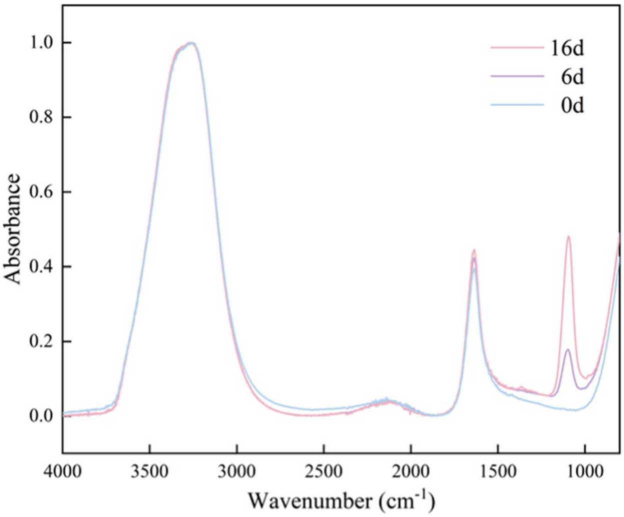


Fig. 14 The functional groups of leachate with different leaching times

HPLC analysis of liquid supernatant after bioleaching

Using the optimized factors as the leaching conditions, the content of organic acids in the leaching solution at fixed time intervals was quantitatively analyzed by high-performance liquid chromatography, and the effective silicon content at the same time interval was measured (Fig. 15). The leaching rate v_{μ} in a certain time period was calculated using the formula ($v_{\mu} = (\mu t_2 - \mu t_2) / (t_2 - t_1)$). Comparing v_{μ} with the concentration of organic acids, the results showed that within 4–6 days, the concentration of organic acids increased significantly, and the leaching rate in the leaching system was also high. Within 6–12 days, the organic acid content showed a gentle trend, and the leaching rate in the leaching system also showed a relatively gentle trend. Within 12–16 days, as the organic acid content in the system decreased, the leaching rate gradually decreased until it approached 0 and reached the maximum leaching rate. The results showed that there was a high correlation between the leaching rate of effective silicon and the concentration of organic acids.

The process of *B. mucilaginosus* leaching is shown in Fig. 16. First, the bacteria proliferate by taking up nutrients from the culture medium, producing small organic acids and capsule polysaccharides during their growth (Liu et al. 2006; Monib et al. 1984). Second, capsule polysaccharides, which contain polysaccharides and proteins, have side chains rich in –OH groups with strong adsorption capabilities, exerting strong adsorption on hydrophilic silicate minerals to form a bacterial-mineral complex. Third, the organic acids produced by the capsule polysaccharides and bacteria in the complex (as shown in Fig. 16) can strongly chelate and form a high-concentration

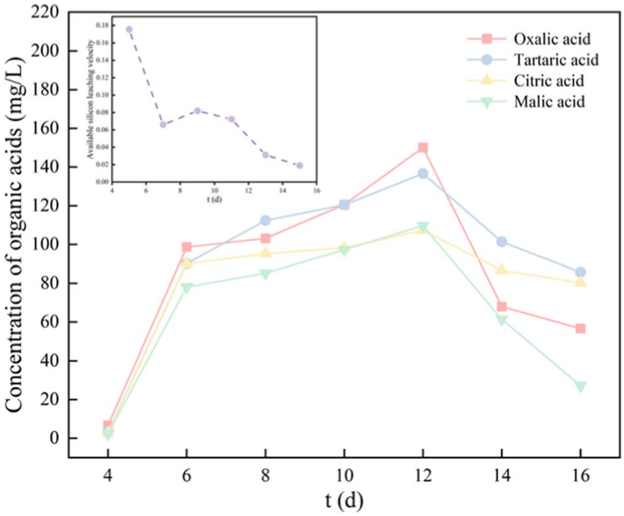


Fig. 15 The relationship between organic acid concentration and leaching rate

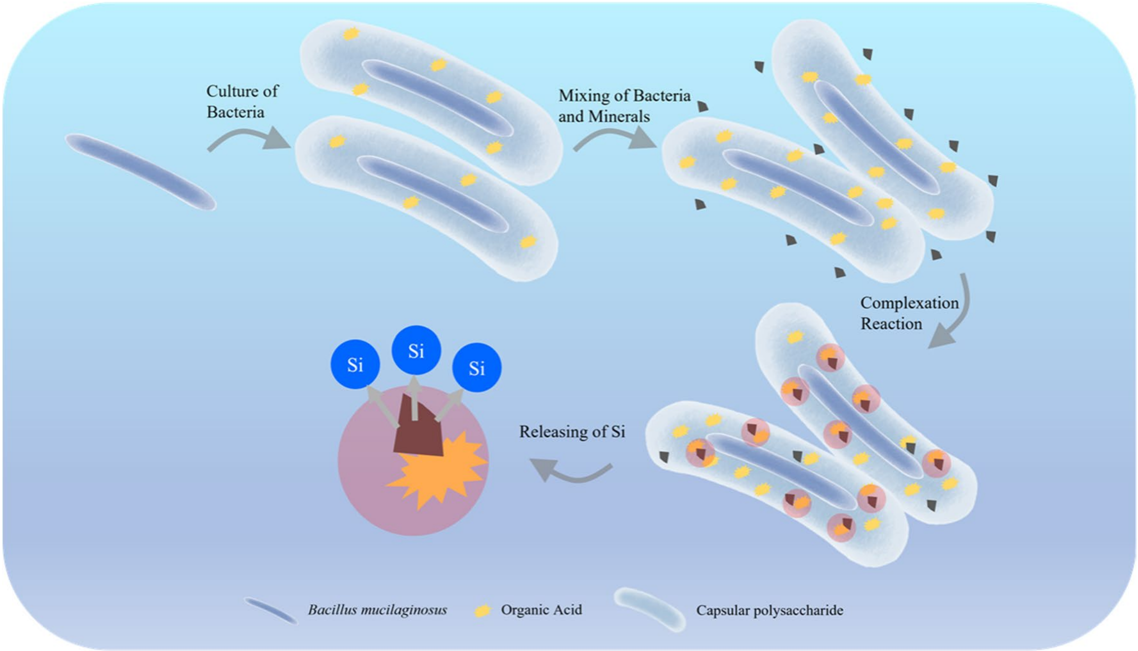


Fig. 16 Schematic diagram of the mechanism of bioleaching process

organic acid region (Sand and Gehrke 2006), causing etching of the mineral surface. Fourth, the etching action breaks the dynamic equilibrium of mineral dissolution and crystallization, promotes mineral degradation, and releases Si trapped in the crystal lattice, as shown in the Fig. 16.

Conclusions

In this study, the feasibility of using *B. mucilaginosus* through bioleaching technology to extract available silicon from coal tailings was evaluated. A maximum leaching amount of 125.9 mg L^{-1} was obtained at the optimal leaching conditions of 5 g of bacteria, 15 g of coal tailings, initial pH of 7, leaching temperature of 30 °C, shaking speed of 210 rpm, and a leaching time of 6 days. Kinetic analysis showed that the leaching process was controlled by chemical reactions. The maximum leaching amount of 260 mg L^{-1} was achieved after 16 days under the optimal conditions, with a leaching rate of 93%. Bacteria erode the surface of tailings by the various organic acids (oxalic acid, tartaric acid, citric acid, malic acid) produced through their own metabolic processes, leading to mineral phase transformations on the surface of tailing particles. This results in the decomposition of quartz and kaolinite, and the treated tailings exhibit irregular pores on the surface. The silicon (Si) content decreases, causing insoluble Si-containing minerals to convert into soluble and available silicon forms.

This efficient method addresses silicon deficiency in soil, utilizing coal tailings as a valuable silicon-soil improver.

Author Contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Qingshan Zhang, Long Liang, Mengjuan Jing, and Xinxin Yan. The first draft of the manuscript was written by Qingshan Zhang, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The authors declare no competing interests.

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