The effect of a new process on the environment of soil in ion adsorption rare earth ores

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Abstract: Rare earths are a kind of mineral resource with important strategic value, playing an irreplaceable key role in modern high-tech development and other fields. However, how to realize the efficient and green mining of rare earth resources has been a key issue that the rare earth industry has been trying to break through, because the rare earth mining process is prone to pollute ecological environments such as soil and water. Ion adsorption rare earth ore, mainly distributed in the south of China, is one of the rare earths, for which rare earth researchers have developed a new process leaching system with magnesium salt. In this study, the soil environmental problems as well as the microbial community structure underneath this new process heap-leaching demonstration site are evaluated. The results of the study showed that under the new process, there was a significant accumulation of sulfate content in the soil of the heap-leaching site and an imbalance in the soil calcium-magnesium ratio, which may disrupt the soil structure and reduce soil fertility. Meanwhile, the microbial community structure before and after the leaching site showed large differences at different points and depths, but didn't cause ecological risks. This study helps us to understand the environmental problems and impacts that may be caused by the new process of magnesium salt, and also helps to promote the application of the new process of magnesium salt leaching of ion adsorption rare earth ore, which lays the foundation for the exploitation of rare earth resources.

1. Introduction

Rare earth is one of the important strategic mineral resources [1, 2], especially in China [1, 3], among which ion adsorption rare earth ores are also known as weathered crust leaching rare earth ores [4]. This kind of mineral is characterized by easy mining and high economic value [5]. Due to their excellent physical properties such as photoelectricity and magnetism, ion adsorption rare earth ores are widely used in metallurgy, materials, petrochemicals, electronic information and other fields [6, 7]. China possesses about 23% of the global reserves of rare earths, which are mainly distributed in the southern provinces of Jiangxi, Fujian, Hunan, Guangdong, Guangxi, Yunnan and Zhejiang [8]. Among them, the share of rare earth reserves in the Gannan area of Jiangxi reaches more than 36%.

The mining process for ion adsorption rare earth ores has gone through three stages: pool leaching, heap-leaching and in situ leaching [9]. Currently, the heap-leaching process is mainly used, in which the topsoil of the rare-earth-containing section is stripped and transported to the leaching site for leaching treatment [10]. The heap-leaching process concentrates the collection and treatment of liquids by topographically constructing piles, but leaves the damage to vegetation and soil caused by mining largely unchanged [11]. The new process of heap-leaching can be based on the mineralization characteristics of rare earth ores, build a heap and leach on site, which can flexibly adjust the scale, make full use of the resources, and improve the recovery rate of rare earths and reduce the production cost [12, 13].

In the traditional extraction process of ion adsorption rare earth ores, ammonium sulfate is the most widely used leaching agent, followed by the use of ammonium bicarbonate for enrichment and recovery of rare earth elements [14]. However, this process causes irreversible pollution [15], such as ammonia-nitrogen pollution, to rivers, soil and groundwater in the vicinity of the mine [16]. With the increase in environmental requirements, the traditional ammonium extraction process is limited. To avoid ammonia-nitrogen pollution, researchers developed the magnesium salt leaching process [17]. Compared with the traditional ammonium salt leaching process, this process shortens the process flow, saves costs, improves rare earth recovery, and reduces the risk of environmental pollution and waste discharge [18]. However, the application of this process still needs to consider its

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impact on the environment. In this study, we analyzed the changes in soil physicochemical properties and microbial community structure at the demonstration site of the magnesium salt process heap-leaching to provided environmental protection support for the further promotion of the application of the magnesium salt process.

2. Materials and methods

2.1 Materials

The ion adsorption rare earth mine soil used in this work was from Guangxi Province, China. At the ion adsorption rare earth mine heap-leaching demonstration site, sampling points were selected according to the uniform distribution sampling method and sampled at different depths in the vertical direction, and the samples were split and transported to the laboratory for subsequent testing and analysis.

2.2 Methods

Indicators of soil nutrient content were tested through the Science Compass platform, and analysis of the microbial community structure and diversity of the soil was carried out through the Meggie Bioassay platform, utilizing the 16S rRNA analysis method. Table 1 shows the metrics and methods tested in this experiment.

Table 1. Indicators and methods of testing

Testing Indicators	Methods
organic matter	Potassium dichromate oxidation-volumetric method
Organic Carbon	Potassium dichromate oxidation-spectrophotometric method
Total Nitrogen	Kjeldahl Nitrogen Method
Phosphorus	Sulfuric Acid Extraction with Hydrochloric Acid-Colorimetric Method
Potassium	Flame Photometer Method
Exchangeable Calcium	Atomic Absorption Spectrophotometry
Magnesium exchange	Atomic Absorption Spectrophotometry
Sulfate	Chemical precipitation + turbidimetric method
Microorganisms	16s rRNA

Fig. 1. Some of the processes of the experiment
(a: Collection of experimental soil samples, b: Sieving of soil samples, c: Mixing of soil samples)

Figure 1a shows field sampling; Figure 1b shows laboratory sieving; and Figure 1c shows a diagram of the soil mixing process after sieving.

3. Results and discussion

3.1 Effect of the new process on the physicochemical properties of soil

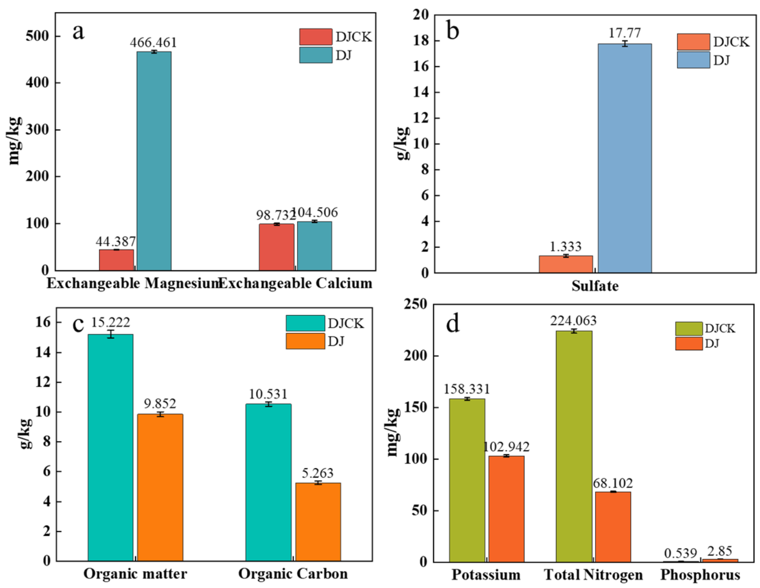

Fig. 2. Indicators of soil physical and chemical properties
(DJCK: heap-leaching control, DJ: heap-leaching,
a: Soil exchangeable calcium and magnesium content, b: Soil sulfate content, c: Soil organic matter and organic carbon content, d: Soil potassium, total nitrogen and phosphorus contents)

Calcium and magnesium ions are the major salt-based ions in soils and have important effects on plant growth and development, among other things. In ffigure 2a, in the soil of the ion adsorption rare earth heap-leaching site, the content of exchangeable calcium and magnesium is relatively low. After heap-leaching treatment, the magnesium content increased significantly from 44.387 g/kg to 466.461 g/kg due to the use of leaching agent under the magnesium salt leaching system, whereas the exchangeable calcium content was before and after the heap-leaching treatment, and the exchangeable calcium to magnesium ratio of the soil was 2.22:1, which was lower than the range of the calcium to magnesium ratio in normal soils (5:1-10:1). After the leaching treatment, the Ca/Mg ratio was out of balance with a ratio of 1:6.02. The decrease in soil Ca/Mg ratio further increased the acidity of the soil and adversely affected the soil texture.

Figure 2b shows that before heap-leaching, the concentration of sulfate in the soil is low, however, after heap-leaching treatment, the content increases significantly due to the cyclic reflux of leachate, which leads to the accumulation of sulfate. Long-term infiltration of soil and groundwater with high concentrations of sulfate wastewater will cause damage to soil structure, reduce soil fertility, and pose a threat to the ecological environment. At the same time, the high concentration of sulfate will corrode concrete materials and cause damage to buildings or underground facilities. Therefore, when using the new process of magnesium salt, it is necessary to pay attention to and solve the problem of high sulfate concentration.

The organic carbon and organic matter content of soils is an important indicator for assessing soil quality and is of key importance for increasing crop yields, regulating soil nutrient cycling and improving soil quality. Figure 2c shows that in the ion adsorption rare earth mining area, the organic carbon and organic matter contents of the soil without heap-leaching treatment were low. Specifically, the soil organic matter content is 15.222 g/kg, which is at the fourth level under the soil nutrient classification standard, and the organic carbon content is 10.531 g/kg, which is at the third level, which is medium level. However, after the heap-leaching extraction treatment, both the organic carbon and organic matter content of the soil decreased by one level.

Such changes may have implications for soil fertility and quality, as organic carbon and organic matter play an important role in increasing crop yields, regulating soil nutrient cycling and improving soil quality. Therefore, we need to further study and monitor these changes to develop effective soil remediation and management strategies to protect the health of soil ecosystems.

Figure 2d shows the variation in soil content of potassium, phosphorus and total nitrogen. The content of quick-acting potassium is abundant, which is more than 150 mg/kg. However, after the heap-leaching treatment, the content of quick-acting potassium has decreased, but it is still in the middle-upper level, and in general, the content of quick-acting potassium can satisfy the normal growth requirements of certain crops.

Nitrogen in soil is one of the essential nutrients for plant growth. Therefore, the total nitrogen content in soil is one of the important indicators for assessing soil fertility. Excessively high or low levels of total nitrogen can adversely affect plant growth. After the heap-leaching and leaching treatment, the total nitrogen content in the soil was reduced from 224.063 g/kg to 68.102 g/kg, which was at the tertiary level, and did not reach the nutrient standard of non-cultivated lands such as forest land and grassland.

The effective phosphorus content was extremely low. Although the effective phosphorus content increased slightly after the heap-leaching treatment, it was still less than 3 mg/kg, and the lack of effective phosphorus may limit the growth and development of plants.

3.2 Effect of new processes on soil microorganisms

3.2.1 Longitudinal microbial species analysis of the heap-leaching site

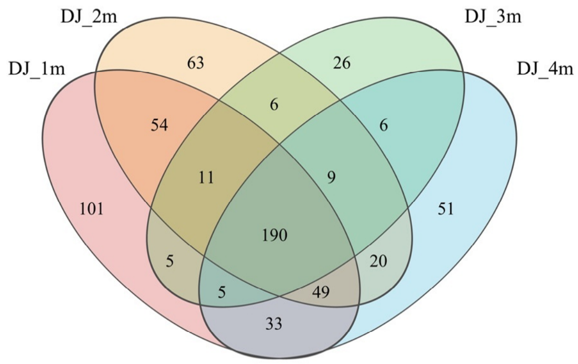

Fig. 3. Venn diagram of vertically oriented species at the heap leach site
(DJ_1m: heap leach 1m depth, DJ_2m: heap leach 2m depth, DJ_3m: heap leach 3m depth, DJ_4m: heap leach 4m depth)

The microbial Veen diagram at different depths of the soil is shown in figure 3. There were significant differences in the distribution of species under different depths in the soil of the heap-leaching site. According to the results of the study, the number of shared species (shared OUT) at different depths was 190. The endemic species (endemic OUT) showed the trend of DJ1m > DJ2m > DJ4m > DJ3m, i.e., the most endemic species were found in the soil at the depth of 1 meter, followed by the depth of 2 meters, then the depth of 4 meters, and finally the depth of 3 meters. This indicates that soil depth has a significant effect on species distribution.

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3.2.2 Effects of new processes on the structure of soil microbial communities

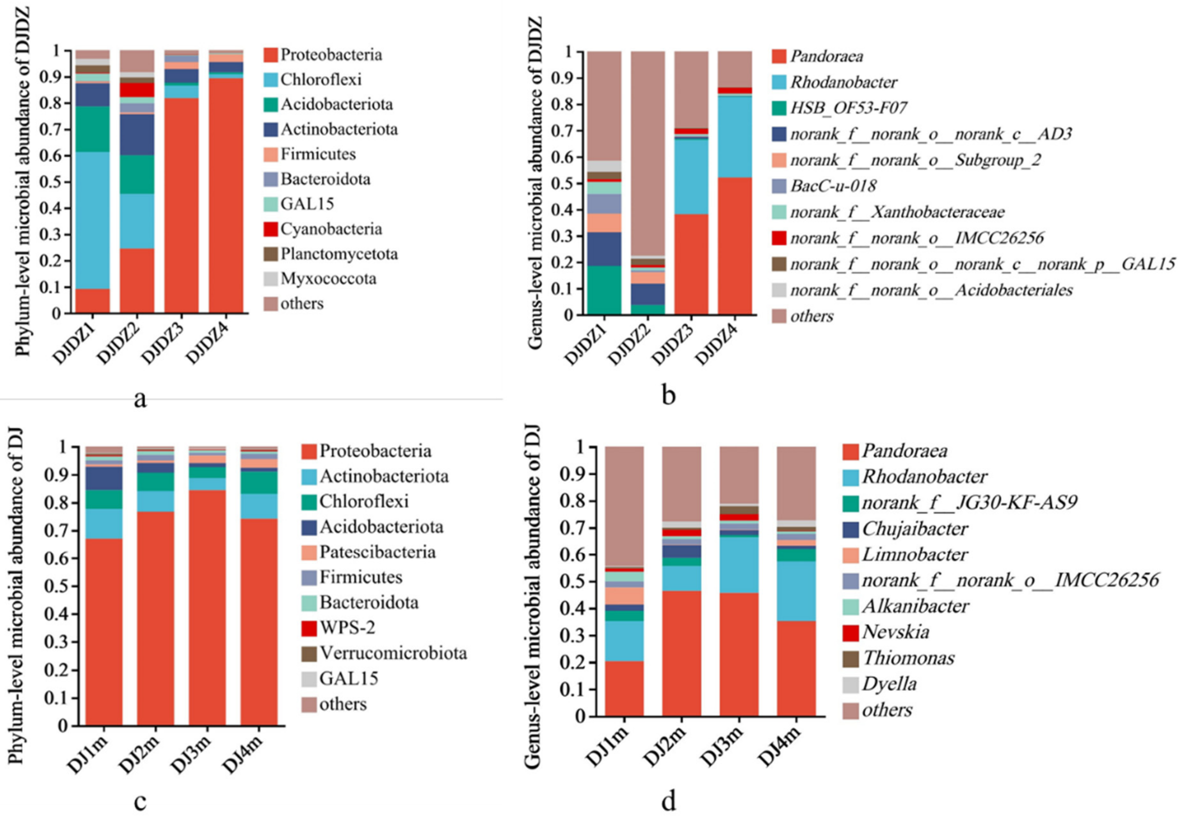

Fig. 4. Abundance of soil microbial structure
(DJDZ1-4: heap-leaching control site 1-4 m depth, DJ1m-DJ4m: heap-leaching site 1-4 m depth;
a: phylum-level abundance of microorganisms at the heap-leaching control site, b: genus-level abundance of microorganisms at the heap-leaching control site, c: phylum-level abundance of microorganisms at the heap-leaching site, d: genus-level abundance of microorganisms at the heap-leaching site)

As shown in figure 4a, significant changes in the levels of microbial phylum at different depths were observed in the soil of the heap-leaching control site. According to the results of the study, among the top five microbial phyla in terms of abundance, the abundance of Proteobacteria and Firmicutes increased significantly with depth, from 9.20% and 0.69% to 89.35% and 2.96%, respectively. The abundance of Chloroflexi and Acidobacteriota, on the other hand, gradually decreased with depth, from 52.10% and 17.29% to 1.46% and 0.76%, respectively. The change in the abundance of Actinobacteriota, on the other hand, was an increase followed by a decrease. At a depth of 1-2 m, the dominant phyla were mainly Chloroflexi, Acidobacteriota, Proteobacteria and Actinobacteriota, whereas the dominant phyla changed to Proteobacteria when the depth reached 3-4 m. In the heap-leaching control soil, the abundance of Actinobacteriota decreased from 1% to 0.5%.

In the heap-leaching control soil, Desulfobacterota, a sulfate-reducing phylum with sulfate-reducing ability, ranked 20th in abundance, with abundance percentages of 0.16%, 0.10%, <0.01%, and 0.01% at different depths (1-4 m), respectively.

As shown in figure 4b, among the horizontal microorganisms at the heap-leaching control site, we observed changes in the abundance of two bacterial genera, *Pandoraea* and *Rhodanobacter*, in soils at different depths. *Pandoraea* was the dominant genus in the top 1-2 m of soil, with abundance percentages of 32.94% and 62.32%, respectively, and remained as high as 17.94% even after reaching a depth of 3 m. *Pandoraea* has high metabolic capacity to degrade a wide range of organic matter, including fatty acids, sugars, and aromatic compounds. It is widely found in soil and water, helping to decompose, degrade and recycle organic wastes, and facilitating the recycling process.

While in the deeper 3-4 meters soil, *Rhodanobacter* became the main dominant genus with an abundance share of 28.11% and 30.62%. This group of microorganisms has a lower abundance in the surface soil, but has multiple metabolic pathways and abilities, and plays an important ecological role in the environment. *Rhodanobacter* has a strong biodegradation ability, and is able to degrade many organic substances, including volatile organic compounds (VOCs) such as benzene, toluene, xylene, and other organic pollutants such as polycyclic aromatic hydrocarbons (PAHs). Therefore, *Rhodanobacter* can be used as a bioremediation tool with great potential. At the same time, it can participate in a variety of material cycling processes, including the sulfur cycle, nitrogen cycle, and carbon cycle. As part of the microbial communities in soil and water, *Pandoraea*, *Rhodanobacter* interact with other microorganisms to maintain the balance of the ecosystem, participate in complex food webs and biotransformation processes, and play an important role in maintaining the biodiversity and function of soil and water.

The distribution of vertical phylum-level microorganisms under different depths showed a certain pattern. In the figure 4c, the most dominant phylum was Proteobacteria, with abundance percentages of 67.03%, 76.65%, 84.41%, and 74.19% under 1-4 m depth, respectively. The abundance of Proteobacteria increased and then decreased with increasing depth. In addition, the abundance percentage of Actinobacteriota was 10.66%, 7.44%, 4.31%, and 8.89%, and the abundance percentage of Chloroflexi was 6.73%, 6.56%, 3.88%, and 7.92%, respectively. In contrast, the abundance percentage of Acidobacteriota decreased with increasing depth with 8.38%, 3.52%, 1.50%, and 1.40%, respectively.The abundance percentage of Patescibacteria increased with increasing depth with 0.78%, 0.80%, 2.67%, and 3.10%, respectively. In addition, Firmicutes and Bacteroidota were present in some abundance at different depths in the longitudinal direction. These data reflect the trend of soil microbial community structure at different depths.

The level of microbial genera in soil was very rich and diverse in vertical distribution. In figure 4d, the abundance of *Pandoraea*, the dominant genus, is 20.39%, 46.37%, 45.65%, 35.21% at different depths and is significantly higher in the middle soil than in the surface and deep soils, respectively. In addition, the abundance of *Rhodanobacter spp.* is 14.83%, 9.18%, 20.71% and 22.14%, respectively, which is also higher in the deep soil than in the surface soil. In addition, the abundance of *Chujaibacter* at 2 m depth is 4.93%, which is significantly higher than the percentage at other depths, and its abundance gradually decreases with increasing depth. The abundance of *Limnobacter* at 1 m depth is 6.37%, which mainly grows in the surface soil. Among the top ten genera, *Alkanibacter*, *Nevskia*, *Thiomonas* and *Dyella* are present at different longitudinal depths with some abundance. These data demonstrated the complexity and diversity of microbial communities in soil and provided important clues to our understanding of the functioning of soil ecosystems.

4. Conclusions

In the new process system heap-leaching mining of ion adsorption rare earth ores, the treatment has a large impact on the changes of soil physicochemical properties and microbial community structure in the mining area. Due to the use of system leaching agents, it leads to the accumulation of sulfate content in the soil of the mining area, and the imbalance of soil calcium and magnesium ratio, which in turn destroys the soil structure and reduces the soil fertility. At the same time, the treatment also affected the horizontal and vertical distribution of the soil microbial community structure in the mining area to different degrees. It did not cause harmful effects on the environment despite the significant changes in the microbial community structure. Therefore, compared with the traditional ammonium salt process, the application of the new process system can not only reduce the production cost, but also reduce the risk of environmental pollution. However, we need to pay special attention to the accumulation of sulfate content and the imbalance of calcium to magnesium ratio. Microorganisms with sulfate-reducing ability can be screened from the microbial point of view and enriched to reduce the harm caused by sulfate accumulation to soil and groundwater.

We need further research and monitoring to assess the extent and persistence of such effects. Studying microbial functions and interactions can help to understand the diversity of microorganisms in soils at heap leach leaching sites and their ecological functions during the leaching process. Exploring the metabolic characteristics, interactions and responses of microorganisms to environmental factors can provided a more comprehensive understanding of their distribution patterns and functions in the ecosystem. It is hoped that the functions and interactions of these microorganisms in the ecosystem can be studied in depth in the future for better conservation and management of soil resources.

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