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Leaching of rare earth elements from contaminated soils using saponin and rhamnolipid bio-surfactant

ZHOU Dan (周 丹)[1], LI Zhenzhen (李真真)[1], LUO Xianping (罗仙平)[1,2,*], SU Jia (苏 佳)[1]

(1. Jiangxi Key Laboratory of Mining & Metallurgy Environmental Pollution Control, Jiangxi University of Science and Technology, Ganzhou 341000, China; 2.Key Laboratory of Ionic-type Rare Earth Resources Development and Application, Ministry of Education, Ganzhou 341000, China)

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Abstract: The effective leaching of rare earth elements (La, Ce, Y and Eu) from simulated contaminated soil using bio-surfactant was investigated in a lab-scale column leaching experiment, where anionic biosurfactant rhamnolipid and non-ionic biosurfactant saponin were used as washing solutions. Soil properties and the rare earth element fractions were analysed to define the effect of leaching on soil and elemental speciation. Column leaching results showed that saponin solution was more effective than rhamnolipid in the removal of the four rare earth elements tested, with the accumulative removal efficiency of La, Ce, Y and Eu following flushing with 400 mL of 25 g/L saponin, reaching 35.258%, 26.072%, 31.476% and 30.849%, respectively. The change in REE speciation showed that REE removed from soils were mainly derived from the acid-soluble and residual fractions released when rhamnolipid solution was used as a leaching agent. However, for saponin leaching, removed REE amounts were derived from acid-soluble and reducible fractions. Complexation interactions were identified between saponin and REEs, according to infrared spectroscopy and ion exchange data, with saponin complexing with La, Ce, Y, and Eu at a complex ratio of 1:1.

Keywords: biosurfactant; saponin; rhamnolipid; rare earth; column leaching experiment; rare earths

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With the increase in demand in recent years for rare earth elements (REEs) as a new material[1,2], large scale resource mining has resulted in some serious environmental issues[3,4]. For example, in the ion-absorption REE mining regions of southern China, REEs have been found to accumulate in water, soil, and flora in mining areas[5,6], with REE concentrations reported ranging from 396 to 2314 μg/g and the lowest detected soil concentrations in the region being double the national average[7]. Recent publications have reported toxicity of REEs to both flora[8,9] and fauna[10,11], as well as establishing bioaccumulation of REEs in local communities, highlighting the human health risk due to multiple potential exposure pathways, in particular via dietary intake. Therefore, there is a crucial need for public health protection and remediation of contaminated soils from surrounding REE mining ore sites.

Removing metals from soil is a difficult process, involving high costs and time consuming processes due to the persistence of metal contamination and technical limitations[12,13]. Soil washing or leaching, is an effective method with potential for complete removal and recovery of metals[14,15]. At present, there are no reports of successful remediation of soils contaminated with rare earth elements, using leaching processes, so current technology for leaching of heavy metal contaminated soils, can only be used as a reference. In the leaching process, metals were extracted from soils into the wash solution using different chemical leaching agents such as acids, salts, chelants or surfactants, depending on the specific application. Acidic solutions have been found to be efficient leaching agents, but their damage to the physical-chemical structure of soil limits the potential applications of acidic agents, while chelating agents and synthetic surfactants persist in soils resulting in secondary pollution and causing an additional public health risk due to their slow rate of degradation[16]. Recently, increased attention has been focused on the use of bio-surfactants as leaching agents (both plant-derived surfactants and microbial surfactants), as they are eco-friendly, biodegradable and produced from renewable sources[17–19]. Saponin is a plant-derived non-ionic biosurfactant, that has been investigated due to its ability to remove metals from contaminated soils, with studies showing effective removal of Zn (95%), Cu (87%), Cd (51%), and As (71%)[20,21]. As an anionic microbe-derived biosurfactant, rhamnolipid has been shown to effectively remove Zn (70%), Cu (23%), Cd (73%), and Ni (68%) from con-

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* **Corresponding author:** LUO Xianping (**E-mail:** lxp9491@163.com; **Tel.:** +86-797-8312706)

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taminated soils[22–24]. These research has demonstrated that biosurfactants (rhamnolipid and saponin) can potentially be used to remedy contaminated soil; however, more research is needed as there are at present significant gaps in our understanding of the optimization of biosurfactant leaching systems for metal contaminated soil.

Therefore, the objective of this study was to evaluate the performance of biosurfactant leaching REEs using a laboratory column-leaching experiment, selecting a range of light REEs (La, Ce, and Eu) and a heavy REE (Y) as target pollutants and saponin and rhamnolipid as leaching agents. Furthermore the influence of the leaching process on the stabilization of La, Ce, Y and Eu in soils was investigated, with analysis of REE fractions performed in a sequential extraction procedure. The change of soil properties pre- and post-washing was also investigated to evaluate the effects of saponin and rhamnolipid on soil proprieties.

1 Materials and methods

1.1 Collection and treatment of soil samples

Samples of unpolluted surface soil (depth 0–30 cm) were collected from an agricultural area in Ganzhou City, China. Solutions of $La(NO_3)_3·6H_2O$, $Ce(NO_3)_3·6H_2O$, $Y(NO_3)_3·6H_2O$ and $Eu(NO_3)_3·6H_2O$ were combined with the soil and then air-dried and sieved (a 2 mm pore size), the synthetic "contaminated" soils were then aged for one month at room temperature and stored in plastic containers for subsequent experiments. The physical and chemical properties of soil samples, in addition to their REE content, are shown in Table 1.

1.2 Soil column washing experiment

1.2.1 Soil column equipment

Column leaching experiment were operated in a Plexiglas leaching column, with a height of 25 cm and inner diameter of 5 cm, where the inner column wall was processed as a rough surface to avoid preferential lateral flow pathways. 80 g of soil was poured into the column, stirring several times during filling to prevent soil layering, until a total length of 15 cm was achieved. A sheet of filter paper and 4-cm-deep layer of quartz sand were packed on top and bottom of each column for even distribution and filtration of the influent. The soil column inlet was connected to a peristaltic pump controlled inflow tube, with the outlet connected to the solution collector. The experimental setup of the soil column system is shown in Fig. 1.

1.2.2 Leaching method

Prior to the start of leaching experiments, the soil column was positioned vertically and slowly saturated with deionized water from the base of the column, with the column then kept at room temperature (25±2 ºC) for 24 h

Table 1 Physical-chemical properties and REE contents of simulated soil samples

Soil type	pH	Cation exchange capacity/(cmol/kg)	Organic matter (g/kg)	La/ (mg/kg)	Ce/ (mg/kg)	Y/ (mg/kg)	Eu/ (mg/kg)
Simulated contaminated soil	5.36	8.133	9.414	166.214	196.214	78.346	111.750

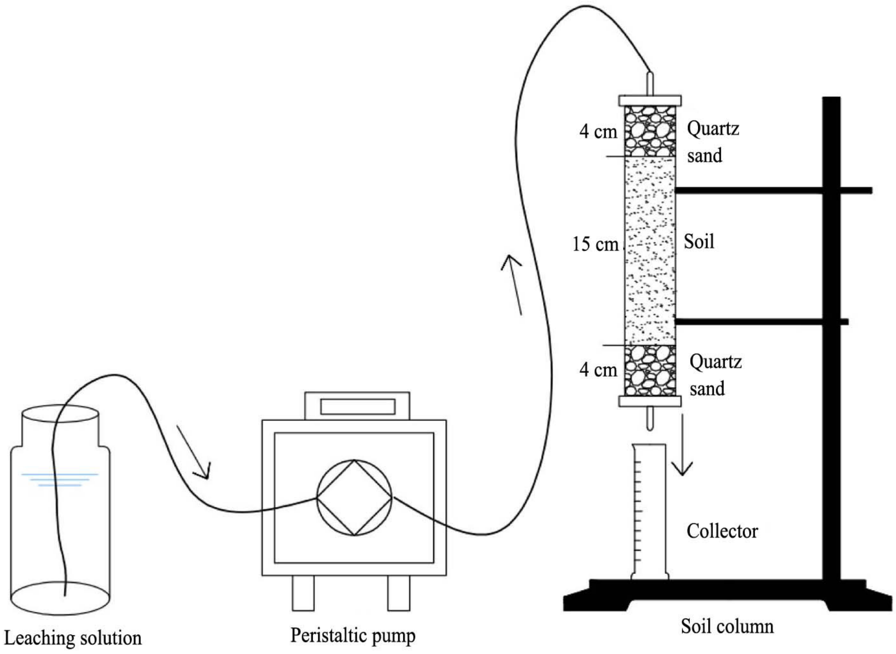

Fig. 1 Equipment of leaching experiment