The overall concept of phytomining of rare earth elements

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Abstract

The increasing demand for rare earth elements (REEs) for modern industry has led to a surge in mining activities and consequently has released these metals into the environment. Intensifying REEs in a habitat has impacts on its ecosystem, but on the other side, it also provides the opportunity to recover REEs from low-grade minerals. Phytomining has emerged as an ecologically sound technique to extract these valuable elements from contaminated soils where traditional mining is not competitive. This paper provides a glimpse of REE phytomining combined from three scientific areas. The accumulation of rare earth metals in plants is the first stage, referred to as the phytoextraction process. This is followed by elevating REE concentrations into bio-ores via the enrichment phase. Ultimately, extraction is the final step to complete the phytomining pathway for reclaiming REEs in brownfield land. In addition to the REE phytomining concept, an experimental system for the combustion of contaminated biomass is also introduced in this study, it is important to the success of the phytomining pathway.

1 Introduction

Rare earth elements (REEs) are a group of 17 chemically similar metallic elements in the periodic table, including scandium (Sc), yttrium (Y), and 15 "lanthanides" elements, from lanthanum (La) to lutetium (Lu). REEs are playing an increasingly vital role in industry, especially in green high-technology applications, such as wind turbines, hybrid cars, electric cars, batteries, etc. [1]. Moreover, these valuable elements are also widely utilized as fertilizers in agriculture to enhance the production and quality of crops [2], [3]. Despite high demand, the supply of REEs is limited and dominated by China, the source of up to 97% of global rare earth production [4]. Furthermore, the recycling rate of REEs is still extremely limited at only approximately 1% of end-products [1]. Because of the essential and provision risk, REEs are commonly considered critical strategic materials [5], [6].

The mounting demand for REEs in modern industry has stimulated a surge in mining activities, which has led to the release of these elements into the environment. Intensifying REE content in the environment adversely impacts the ecosystem and potentially threatens human health [7], [8]. Therefore, remediation of REEs contamination and recovery of REEs from secondary resources are globally crucial issues that have been receiving increasing attention recently.

Phytoextraction, using plants accumulating metals, is known as a feasible way to either remove metals from contaminated soils (a process called phytoremediation) or to extract valuable metals (referred to as phytomining) [9]–[11]. Phytomining is widely applied to recover nickel from brownfield land [12], [13]. Nevertheless, little attention has been paid to the procedure or to the prospect of REE phytomining. This study provides a glimpse of the REE phytomining pathway. Besides that, a suitable combustion and flue gas system for the combustion of contaminated biomass is also introduced.

2 Phytomining of rare earth elements

Phytomining of REEs offers a promising possibility of metal extraction at sites where traditional mining activities or recovering REEs from low-grade minerals are not competitive. In addition to conventional mining, producing REEs from secondary resources strengthening the circular economy has been paid worldwide attention. REE phytomining is a combination of three scientific areas of phytoextraction, enrichment, and extraction.

2.1 Phytoextraction of REEs

Phytoextraction is the first stage in the overall concept of REE phytomining. Phytoextraction refers to using plants to accumulate REEs from soils. Hyperaccumulators are usually chosen for phytomining; these plants accumulate vast quantities of REEs in their aerial parts without substantial adverse effects. The lower limit for hyperaccumulators has not been thoroughly defined. The suggested threshold concentration for REE hyperaccumulators could range from 100 to 1000 mg kg^{-1} [14]. During the phytoextraction process, plants accumulate REEs from soils and transport them in roots and other plant parts. Hyperaccumulators actively transfer REEs from roots to shoots, and storage of the metals in root parts is generally limited. The distribution of REEs within the major components of plants varies substantially, depending on the plant species and metals. Numerous investigations have indicated that concentrations of REEs in below-ground parts are greater than in the shoot following the decreasing sequence: root > leaf > stem (trunk) [15], [16]. This can be explained by the accumulation rate of REEs from the substrate to root being higher than the translocation rate from root to aerial tissues [17]. Contrarily, various studies have shown declining REEs concentrations in the order of leaf > root > stem due to substantial translocation of these metals from root to leaf [18]. Generally, the difference in REEs concentration among plants might reflect the disparate mobility of these elements in various plants.

The bioaccumulation factor (BF) and translocation factor (TF) are utilized to describe the bioaccumulative properties of hyperaccumulators. The bioaccumulation factor is the quotient of REEs concentration in aerial tissues to that in substrates. This index is used to depict the capability of plants to accumulate REEs from soil and translocate them into their shoots. The translocation factor is the ratio of metal concentration between above-ground and below-ground parts of plants. The higher the TF, the better the ability of the plant to transfer REEs from roots to shoots. This factor is vital for applying REE phytomining since typically only aerial plant parts are harvested. The two indices of BF and TF are usually recommended to be higher than one for accumulators [19]. Several ligneous plants are known as hyperaccumulators of REEs; among them, exceptional numbers were found within fern species [20].

In general, REEs are potential candidates for phytomining. *Phytolacca americana* (pokeweed) and fern species are commonly used for the phytoextraction of these elements. The BF and TF of those plants usually are higher than one, proving their ability to accumulate and translocate REEs. Presently the concept of REE phytomining is discussed on a rather theoretical basis.

2.2 Enrichment of REEs from contaminated biomass prior to REE extraction

During the phytoextraction process, plants accumulate REEs from contaminated soils and then translocate and store these metals into their roots and shoots. REEs accumulated in woody biomass can be recovered by applying extraction techniques. Prior to extracting REEs, the bulky contaminated plants should be lessened to a manageable amount and volume; the metal grade is then elevated in the solid residues called bio-ores. REE concentration heightening is crucial in the entire pathway of phytomining; it not only lowers the transportation costs but also minimizes the size of the downstream processing apparatus. Several enrichment approaches have been discussed, including thermal conversion (ashing, pyrolysis, gasification, combustion), composting, and compaction [21].

Thermal conversions are feasible approaches to elevate the concentration of metals contained in polluted woody biomass. The viability of these enrichment technologies has been demonstrated in terms of heavy metals [22]. The fate of heavy metals during the thermal conversion processes has been intensively studied [23], [24]. Several factors impact the metal flow, such as chemical speciation of metals, reactors, feedstock properties, and operating conditions including temperature, heating rate, pressure, resident time, etc. [25], [26]. To date, the information on heightening REEs of biomass used for phytoextraction is extremely sparse, with only a couple of investigations carried out so far. In one, the collected fern *Dicranopteris linearis* was ashed at 500 °C for two hours to remove organic matter and enrich metals in ash [27]. As a result, the total concentration of REEs was enhanced from 2032 mg kg^{-1} in the plant to 15956 mg kg^{-1} in the ash. Scandium was not detectable in biomass but could be found in the residual. The study also unveiled that 93% of rare earth metals in the fern were converted into its ash during the ashing process. Likewise, in another study, 92.3% weight of the harvested *Dicranopteris linearis* fern was reduced after incineration at 550 °C for three hours [28]. As a result, REEs were enriched into the solid remain at the level of 30000 mg kg^{-1}, which is roughly eleven times greater than the concentration of rare earths in the woody biomass (2700 mg kg^{-1}). Recently, an environmentally sound technique of vacuum-pyrolysis-condensation was proposed for the disposal of polluted biomass as well as for heightening these valuable metals in the solid remains [29]. It was observed that the pyrolytic product derived from *Dicranopteris linearis* containing 1948.67 mg kg^{-1} REEs reached 6160 mg kg^{-1} after treatment. The residues containing higher REE concentrations can be considered bio-ores that extraction technologies might further recover. On the whole, an enrichment process for lessening the contaminated plant material and elevating rare earth metals into solid remains is crucial for recovering REEs from biomass used for phytomining, but the available information is scanty.

2.3 Extraction of rare earth elements

Extraction is the eventual step in the phytoextraction-enrichment-extraction chain to recover REEs from brownfields. Traditional or emerging extraction methods can be applied to extract REEs from low-grade minerals. Conventional techniques of recycling REEs comprise pyro-metallurgical, hydro-metallurgical, and bio-metallurgical approaches. Meanwhile, emerging approaches consist of the ionic liquid method, mechanochemical technique, supercritical fluid pathway, and electrochemical technology applied to recycle REEs from waste materials containing valuable metals [30].

To our best knowledge, there is only one study aiming at reclaiming REEs in biomass ashes so far [28]. In this research, the collected plant *Dicranopteris linearis* was initially incinerated at 550 °C for three hours in a muffle furnace to secure complete oxidation. Then the fern ash was subjected to an extraction procedure consisting of two stages, namely pre-treatment and dissolution. The pre-processing step aimed to render rare earths available for extraction and eliminate aluminum as much as possible by using 6 M sodium hydroxide ($NaOH$) at an average temperature of 80 °C. Following that, the REEs were extracted by employing diluted nitric acid (HNO_3) at ambient temperature. The recovery rate of the extraction procedure was reported at 74% under optimal conditions.

Alternatively, a few approaches to extract REEs directly from polluted plants have been proposed. The first research based on the ion exchange leaching process was published in 2018 [31]. In this paper, harvested fern *Dicranopteris linearis* was initially leached in 0.5 M nitric acid solution with the presence of exchange resin.

Consequently, rare earth metals in the plants were dissolved and absorbed into the resin. This was followed by washing the resin with water and 0.75 M HNO_3. Ultimately, REEs are eluted using 3 M nitric acid, which provides a solution containing 81.4% REEs purity. This procedure resulted in an overall recovery rate of 78%. In another work, Laubie et al. (2018) reported a hydrometallurgical pathway to recycle REEs from natural fern growing on former mine tailings [32]. The manner includes a direct leaching step using an EDTA solution (Ethylenediaminetetraacetic acid), followed by precipitation with acid oxalic. The optimal conditions of the process can lead to an overall recovery yield of 70% REEs. More recently, a relatively comprehensive hydrometallurgical pathway for reclaiming REEs from a hyperaccumulator *Dicranopteris linearis* was revealed [33]. In the beginning, collected fern was leached in 0.25 M sulphuric acid at a solid-liquid ratio of 3:100 (g/mL). Following this, rare earth metals were precipitated by utilizing oxalic acid at a molar ratio of 8:0.37 after pH adjustment to 2.6. Eventually, the precipitate was calcinated at 700 °C for two hours in order to convert it to rare earth oxide as the final product of the procedure. As a result, 72% of REEs in the plant were reclaimed via this recovery route.

3 Experimental system for combustion of contaminated biomass

Combustion has been recognized as the most feasible pathway to concentrating REEs from contaminated biomass into solid remains [21], [34]. It is a crucial stage in the whole concept of REE phytomining. Therefore, it is important to develop a suitable combustion and flue gas system for the combustion of contaminated biomass. The schematic illustration of the experimental system is shown in Figure 1. The combustion experiments are carried out in a pilot-scale boiler located at the Department of Combustion Technology and Thermal Energy at the University of Miskolc. The boiler can be operated with solid biofuel in the form of pellets or chips. The biomass is supplied from the fuel storage of the boiler into the grate by a screw conveyor. The combustion air passes through the grate in the combustion chamber, where the biomass combustion process takes place. Solid fuels are combusted, and their products comprise hot flue gas and bottom ash. The bottom ash dropped down to the bottom of the boiler is sampled at the end of the combustion process. The high-temperature flue gas leaves the chamber and goes through the water heat exchanger and the air heat exchanger in sequence. In which, flue gas transfers thermal energy to the water and the cooling air moving between the pipes of the water heat exchanger and the air heat exchanger respectively. After the heat exchangers, flue gas with a lower temperature including gaseous components and particulate matter content (fly ash) is transported to the stack by a centrifugal fan. An isokinetic fly ash sampling system is used to separate and collect fly ash from the flue gas before it emits into the environment.

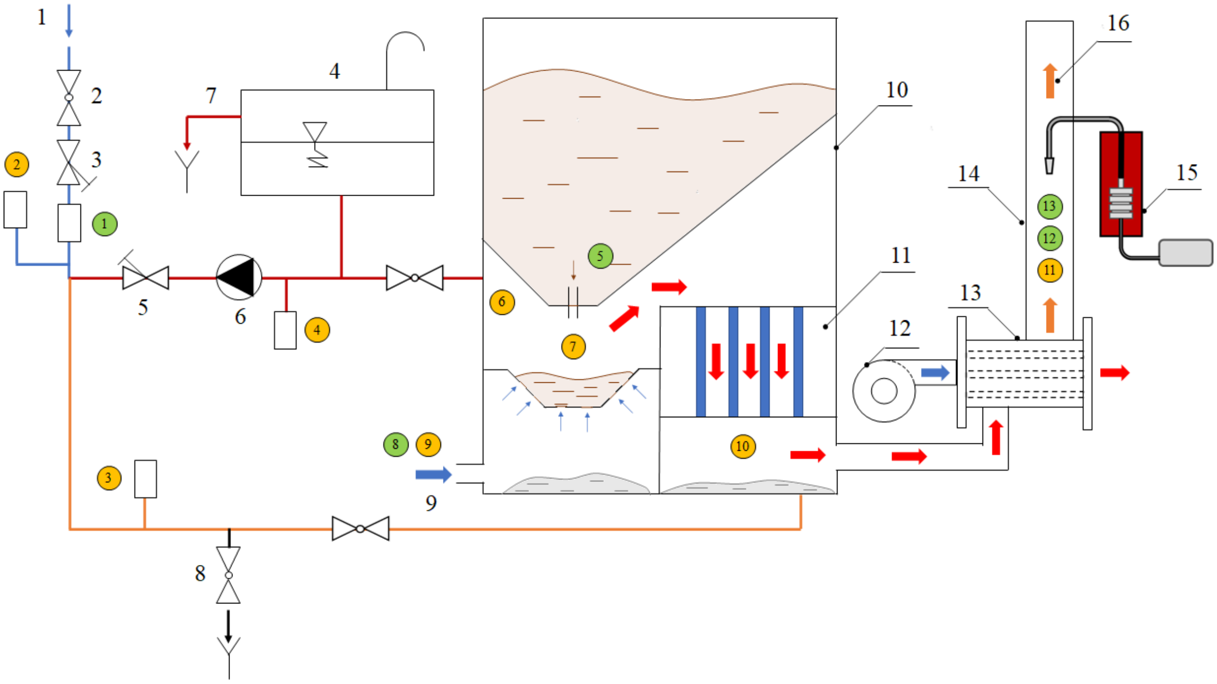

Figure 1. Schematic illustration of the experimental system with measurement points

Components: (1) Water inlet; (2) Ball valve; (3) Regulating valve for controlling the flow rate of water inlet; (4) Pump; (5) Regulating valve for setting water temperature difference; (6) Tank; (7) Water outlet; (8) Discharge valve; (9) Supplied air; (10) Boiler; (11) Water heat exchanger; (12) Fan; (13) Air heat exchanger; (14) Stack; (15) Isokinetic fly ash sampling system; (16) Flue gas.

Measurement points: (1) Water inlet volume flow rate; (2) Temperature upstream of the boiler; (3) Water inlet temperature; (4) Water outlet temperature; (5) Feed rate; (6) Temperature at the wall of the combustion chamber; (7) Temperature in the middle of the combustion chamber; (8) Supplied air volume flow rate; (9) Supplied air temperature; (10) Temperature of flue gas after the heat exchanger; (11) Temperature of flue gas in the stack (after the extra heat exchanger); (12) Velocity in the stack; (13) Pressure in the stack.

Solid combustion residuals are captured from preselected points as seen in Figure 2. After experiments, bottom ash and after water heat exchanger ash are respectively collected from the ashtray and in the chamber after the water heat exchanger. The deposited ash sample is taken from the surface of the tubes and the shell of the air heat exchanger at the end of the combustion process. The capture of fly ash is performed by an isokinetic fly ash sampling system employing a three-stage cascades impactor labeled Dekati® PM10. The fly ash sampling is started after the boiler reached steady-state operational conditions, and the collection method meets the regulations of the ISO23210 standard. Woody biomass together with combustion ashes will be taken for chemical analysis to investigate the behavior of REEs in the burning system during the combustion of contaminated biomass. The solid remains derived from biomass combustion would be subjected to a process of extraction process for reclaiming REEs, and they are a potential metal resource.

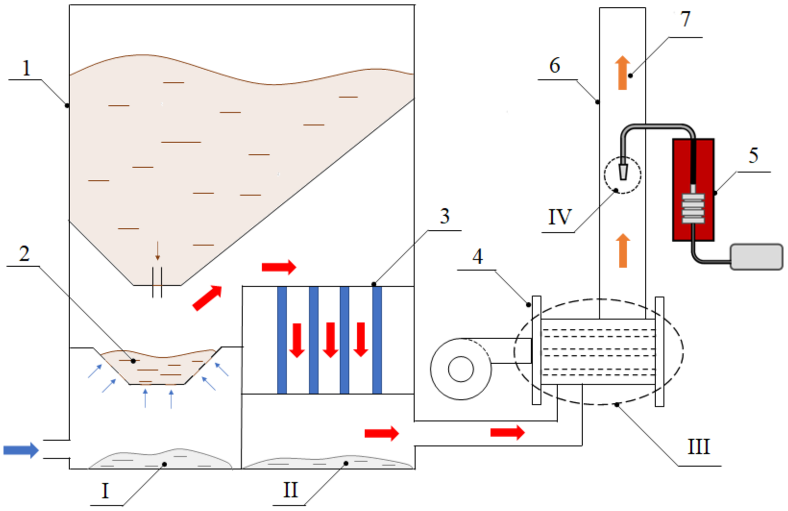

Figure 2. Sampling points of solid combustion residues

Main components: (1) Boiler, (2) Biomass, (3) Water heat exchanger, (4) Air heat exchanger, (5) Impactor, (6) Stack, (7) Flue gas

Solid remains: (I) Bottom ash, (II) After heat exchanger ash, (III) Deposited ash, (IV) Fly ash

4 Conclusion

Phytomining is an innovative method for recovering REEs from unconventional resources in which conventional mining is neither effective nor profitable. The novel technology has potential in this era of industrialization and metal reserve depletion. Despite its prospects and feasibility, the research regarding REE phytomining is still limited. The article provides a glimpse of the phytomining concept which links three scientific areas of phytoextraction, enrichment, and extraction. Phytoextraction is the first step in accumulating REEs from contaminated soils to plants. Afterward, the metals are concentrated in solid remains (bio-ores) through the enrichment phase. Eventually, extracting these valuable metals from bio-ores lays the last brick to finalize the route of REE phytomining. The recovery of REEs via the phytomining-enrichment-extraction pathway is just in its infancy, and it will require further multidisciplinary investigations encompassing botany, soil science, energy engineering, and chemistry. Also in this study, an experimental system for the combustion of contaminated biomass was developed to enrich REEs from biomass into solid remains. It is important to the overall concept of REE phytomining.

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