UNIVERSITI TEKNOLOGI MARA

THE EFFECT OF HYDROLYZED HUMIC ACID ON RARE EARTH ELEMENTS LEACHING AND UPTAKE BY DICRANOPTERIS LINEARIS

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ABSTRACT

Rare earth elements (REEs) are essential for the manufacturing of smart electronics. Ion-adsorption clay (IAC) represents an alternative source of REEs, where these elements are weakly adsorbed on clay mineral surfaces and can be extracted through leaching processes. The effectiveness of leaching agents in enhancing REEs mobilization from IAC is crucial for the success of the *In-situ* extraction and subsequent bioavailability for plant uptake. However, the conventional use of ammonium sulfate $(NH_4)_2SO_4$ in REEs extraction generates high concentrations of ammonium (NH_4^+) and sulfate (SO_4^{2-}) ions, causing serious environmental risks. Humic acid (HA) may be an environmentally friendly alternative to $(NH_4)_2SO_4$. However, its low solubility and complex structure limit its effectiveness in acidic IAC. A hydrolysis process on HA may produce smaller compounds with greater solubility for further improve REE extraction from IAC. Furthermore, native REEs hyperaccumulator such as *Dicranopteris linearis* (*D. linearis*) can accumulate REEs and radionuclides with greater efficiency, especially when IAC is treated with a leaching agent such as hydrolyzed humic acid (FA). This study aims to investigate the uptake capacity of *D. linearis* and the potential of using FA at various pH (0.3 % w/w FA pH 2 and 0.3% w/w FA pH 6) for extracting REEs and radionuclides from IAC samples. The physicochemical properties of IAC samples, including soil texture, moisture content, organic matter content, pH, electrical conductivity (EC), and X-ray diffraction (XRD), were first analyzed. The characteristics of FA were also examined using Fourier Transform Infrared (FTIR) Spectroscopy, CHNS elemental analysis, and Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX) Spectroscopy. Leaching experiments were performed using batch and column setups with different leaching agents (0.3% FA pH 2, 0.3% FA pH 6, 0.3% $CaCl_2$, 0.3% $(NH_4)_2SO_4$ pH 2, and 0.3% $(NH_4)_2SO_4$ pH 6). In the plant uptake study, *D. linearis* was cultivated in IAC-amended soil for four months under different treatment conditions to assess its uptake of REEs and radionuclides. The REEs and radionuclide content were analyzed using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The IAC soil was characterized as acidic sandy loam (pH 4.51) with low water-holding capacity and enriched in REEs (Ce, La, Nd, Pr, Sc, and Yb) and radionuclides (Th and U), while FA contained abundant oxygen-containing functional groups (−COOH, −OH, aromatic), indicating strong metal complexation potential. FA pH 6 performed better in batch leaching and was able to leach REEs, i.e., Ce (11.59%), La (354.11%), Nd (24.89%), Th (453.64%), and U (1.35%) more optimally. Meanwhile, $(NH_4)_2SO_4$ pH 2 performed better in column leaching providing greater leaching efficiency for Ce (11.59%), La (95.56%), Nd (14.32%), and U (0.10%). The FA contains C, N, and Ca that support soil fertility, and the presence of oxygen-containing functional groups enhances REEs mobilization from IAC. The plant uptake study revealed roots preferentially accumulate radionuclides (Th and U) and Sc, while light rare earth elements (LREEs) including La, Nd, and Pr showed greater mobility and were more efficiently translocated to the shoots. These findings highlight the dual role of FA in improving REE extraction and nutrient supply, thereby supporting its application in phytoremediation.

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CHAPTER 1
INTRODUCTION

1.1 Research Background

Rare earth elements (REEs) have played a significant role in driving the advancement of modern industries toward a more sustainable and environmentally friendly economy. The discovery of REEs occurred in Sweden towards the end of the 18th century (Oladipo et al., 2023). According to the International Union of Pure and Applied Chemistry (IUPAC), REEs consists of 17 elements, including 15 lanthanides (La-Lu), Yttrium (Y), and Scandium (Sc). Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), and Gadolium (Gd) are classified as light rare earth elements (LREEs) meanwhile Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), Lutetium (Lu), and Yttrium (Y) are classified as heavy rare earth elements (HREEs) (Kim & Choi, 2023). Sc is formally classified as REEs by IUPAC, together with the 15 lanthanides and Y, due to their similar geochemical behavior, particularly their predominant occurrence as trivalent ions (Sc^{3+}). However, unlike the lanthanides, Sc is not typically categorized into both LREEs and HREEs. Furthermore, Sc is often excluded from discussions in economic geology because it is rarely enriched in significant concentrations in most REEs deposits (Qin et al., 2020). Other REEs is also found in the trivalent oxidation state. At the same time, Eu can also be found in the divalent state, and Ce in the tetravalent state (Dushyantha et al., 2020). REEs have extraordinary electromagnetic, catalytic, and optical properties, making them essential in the production and advancement of cutting-edge technologies, such as smart electronics (Opare et al., 2021).

Ion adsorption clay (IAC) is an alternative source of REEs, due to its low environmental impact compared to hard-rock sources such as monazite. IAC forms in weathered regolith, especially in tropical and subtropical regions, where REEs are weakly adsorbed onto the surface of clay minerals, especially kaolinite and halloysite, during long-term weathering of REEs-bearing rocks such as granite (Sobri et al., 2023). The IAC was easier to extract and lower cost than hard rock ores despite its low grade,