

Advanced Studies of Inert Landfill Fine Fraction Mass – Hunting for Values from Waste

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Abstract. The maintaining solution for keeping and storing waste over the last century has been landfilling as its costs are the lowest. A sustainable approach such as Landfill Mining (LFM) can be applied to recover Rare Earth Elements (REEs) and other valuable metals from waste that make fundamental assets in terms of economy and essential for developing industrial technologies. This study investigated concentrations of REEs and other metals in waste material. Samples from Ida-Virumaa (Estonia) landfilled waste fine fraction was taken to see the element concentration proceeded through sequential extraction. Additionally, the method of clay modification was developed that may serve as a sorbent to extract the REEs from the inert landfill fine fraction waste using hydroxyapatite modified clay. The amount of REEs might become of industrial interest if a feasible landfill mining approach for remediation of landfills and degraded industrial soils would be applied together with innovative recovery methods, e.g., sorption by modified clays.

Keywords: Landfill mining, modified clay sorbents, rare earth elements, resources recovery, waste valorization.

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1 Introduction

The maintaining solution for keeping and storing waste over the last century has been landfilling as its costs are the lowest. A kind of sustainable approach, called Landfill Mining (LFM) means "the excavation, processing, treatment and/or recycling of deposited materials" [1]. Landfills, dumpsites, and other contaminated sites are considered the main environmental problem areas worldwide [2, 3]. Active and former landfills contain mixed wastes that could be current or potential pollution problems. Waste can or does hold different contaminants with varying concentrations, chemical stability, and mobility [4, 5]. Waste could contain toxic chemical elements deeming it hazardous [6, 4]. Dumpsites and landfills are extensive resources – though end storage – for many metals that could prove to be viable opportunities. Former waste landfills can now be mined for valuable materials [7].

Technology advances at the highest level move on the electronic device market. More powerful, more efficient, and faster devices are released each year. As a result, thousands of tons of electronic devices are discarded annually as consumers upgrade to newer versions. These components are becoming one of the fastest-growing waste segments globally [8]. The price of minerals has been doubling in value since the beginning of the 21st century. It is expected to continue due to the global need for rare minerals. LFM is known as "planned actions to reduce and prevent environmental impacts and get extracted valuables from dumpsites" [4].

Macroelements like Ca, K, Mg, Na, and trace elements (*e.g.*, Cu, Fe, Mn, and Zn) are essential elements and compounds that affect vital functions of the human body – development, growth, and reproduction. Accumulation of these elements and compounds influences toxicity that could change flora, fauna, and human development [9, 10].

There are many sorption materials (raw as well as modified) that are used for the removal of Rare Earth Elements (REEs) from aqueous solutions, *e.g.*, carbonized polydopamine nano carbon shells, granular hybrid, modified clays and many other [11–17]. After the removal of REEs from aqueous solutions, clay sorbents can also be used to recover these valuable elements [18] as described in Figure 1.



Fig. 1. Clay modification with hydroxyapatite and possible usage in REEs recovery.

The work aimed to explore the concentration of various elements in the samples derived from a landfill site situated in Ida-Virumaa (Estonia), taken from a fine fraction of waste, as well as try to develop an innovative type of sorbent that can be used to recover lost REEs through the process of sorption.

2 Materials and methods

2.1 Materials, sampling, and preparation

The sampling of waste was done in the Ida-Virumaa landfill site, and preparation was done according to the methodology described in previous works [19, 20].

To develop a clay sorbent montmorillonite (Mt), the material with the trade name Montmorillonite K10 was purchased from Sigma-Aldrich (Germany). According to the product's specification, montmorillonite is a faint grey powder with pH 2.5 to 3.5, specific weight 300 kg m^{-3} to 370 kg m^{-3} and surface area $220 \text{ m}^2 \text{ g}^{-1}$ to $270 \text{ m}^2 \text{ g}^{-1}$. The Cation Exchange Capacity (CEC) of the Mt clay is $0.50 \text{ mmol g}^{-1} \pm 0.03 \text{ mmol g}^{-1}$ (determined by the methylene blue test). Lanthanum (III), neodymium (III), cerium (III) as model REEs were chosen for sorption experiments. All used chemicals were of analytical grade and used without further purification. All solutions were prepared using high purity deionized water ($10 \text{ M}\Omega \text{ cm}^{-1}$ to $15 \text{ M}\Omega \text{ cm}^{-1}$) obtained with a Millipore Elix 3 (Massachusetts, USA) purification system.

2.2 Sequential extraction

To obtain the results and analyze the bioavailability and mobility of metals fine fraction was performed by sequential extraction. These areas have future potential recovery materials [4]. The extraction procedure included three steps.

First, water-soluble fraction. A sample weighing $3.000 \text{ g} \pm 0.005 \text{ g}$ was placed in a 100 mL glass beaker. Deionized and heated ($40 \text{ }^\circ\text{C}$) water was added, and the beaker was left for 2 h on a mechanical shaker. To filter the extract, filter paper, and a $0.45 \text{ }\mu\text{m}$ membrane filter were used. The extract was filled into a polypropylene tube and acidified with 0.2 mL of HNO_3 (1:1) solution, left at $+4 \text{ }^\circ\text{C}$.

Second, acid-soluble fraction. The sediment left from the first step of fractionation was carefully collected into a 100 mL glass beaker, and 40 mL of 0.11 M CH_3COOH was added. Extraction was done after 16 h on a mechanical shaker. To filter the extract, filter paper, and a $0.45 \text{ }\mu\text{m}$ membrane filter were used. The extract was filled into a polypropylene tube and acidified with 0.2 mL of HNO_3 (1:1) solution, left at $+4 \text{ }^\circ\text{C}$.

Third, reducible fraction. The residue from the second step of fractionation was collected and poured into a 100 mL glass beaker. 20 mL of 0.5 M $\text{NH}_2\text{OH} \times \text{HCl}$ was added. The final step was done on a mechanical shaker for 16 h. To filter the extract, filter paper, and a $0.45 \text{ }\mu\text{m}$ membrane filter were used. The extract was filled into a polypropylene tube and acidified with 0.2 mL of HNO_3 (1:1) solution, left at $+4 \text{ }^\circ\text{C}$. At each step to analyze samples, blank samples were prepared.

2.3 Sorbent development and sorption experiments

Mt clay modification with synthetic hydroxyapatite (Hap, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) was prepared by the precipitation method under continuous mechanical stirring as described in previous research [21]. The amount of 20 g of clay sample was mixed with 100 mL 0.5 M CaCl_2 . Then 5 mL of 2 M KH_2PO_4 was slowly added to get 1.667 equimolar proportions of Ca/P. pH for

reactions was adjusted with 0.5 M NH₄OH to maintain in the range of pH 9 and 9.5. The reaction temperature was kept at 50 °C. After synthesis mixture was left overnight, then decanted and washed with deionized water until a neutral environment was achieved. In the end, obtained material was dried in oven Gallenkamp Plus II (London, UK) oven for 24 h at 40 °C. As a result; the composite material has increased sorption sites for positively charged elements, such as model rare earth elements, lanthanum (III), neodymium (III), and cerium (III).

Sorption experiments were carried out to investigate the sorption capacity of raw and modified clays for the removal of La(III), Ce(III), and Nd(III) from aqueous solutions. For the sorption-isotherm studies, 0.1 g of a prepared sorbent material (Mt-Hap) was placed in a 100 mL glass vessel and supplemented with 100 mL of La(III), Ce(III), or Nd(III) at a concentration ranging from 5 mg L⁻¹ to 1 000 mg L⁻¹. The mixture was agitated continuously on a multi-functional orbital shaker Biosan PSU-20i (Riga, Latvia) for 24 h at room temperature. After shaking, the mixture was centrifuged at 3 000 rad s⁻¹ (1 rad s⁻¹ = 1/60 Hz) for 12 min. and the supernatants were analyzed using an iCAP 7 000 coupled plasma-optical emission spectroscopy (ICP-OES) (Thermo Scientific). The quantity of the model REEs sorbed on the Mt-Hap sorbent was calculated using the following Equation (1):

$$qe = \frac{(C_i - C_e)}{m \times v} \quad (1)$$

Where,

- qe : The amount of La(III), Ce(III), or Nd(III) adsorbed on the sorbent mg g⁻¹
Ci and Ce : Initial and equilibrium liquid-phase concentrations of La(III), Ce(III) or Nd(III) mg L⁻¹, respectively
v : The volume of solution (mL)
m : Mass of sorbent used (g)

3 Results and discussion

Results from element fractionation analysis by sequential extraction and total content in Ida-Virumaa landfill have shown a wide range of macro and trace elements accumulated in the inert fine fraction. The highest average concentrations were detected for macro elements as Ca (> 55 %), Fe (> 20 %), Al (> 12 %), and Mg (> 5 %), followed by microelements that are in micro amounts. Seemingly one of the reasons of Ca, Fe, Al, and Mg come from the addition of construction and demolition waste in municipal masses as well as from dissipation of other inert municipal waste after the organic fractions are gone. REEs have also been detected in ranges from 1 mg L⁻¹ to 40 mg L⁻¹, which is not a high amount compared to average Clark numbers in geochemistry; however, with improved technologies of separation in the future, the latter's recovery additionally to macroelements might be of the particular interest.

Results of this study presented that municipal landfill in Ida-Virumaa has slight potential for recovery of metals, and certain REEs might be of interest as well. The second part of the study involved modification of the raw clay with hydroxyapatite to test theoretical opportunities to recover the REEs from the landfill leachate or other aquatic media linked to industrial wastewaters.

The initial concentration of La(III), Ce(III), and Nd(III) in the range of 5 mg L⁻¹ to 1 000 mg L⁻¹ influenced the sorption of chosen model REEs on the raw and modified Mt clay with hydroxyapatite. Increasing initial La(III), Ce(III), and Nd(III) concentration, the sorption capacity of clay samples improved (Figure 2). It can be explained by the number of occupied sorbent sites, *i.e.*, at lower concentrations, sorbent sites are vacant, but at higher concentrations, the sorbent sites are taken, thus resulting in increased sorption capacity regards La(III), Ce(III) and Nd(III) [22].

The sorption capacity increased more than two times after montmorillonite modification with hydroxyapatite, and the highest sorption capacity was 284 mg g^{-1} , 252 mg g^{-1} and 255 mg g^{-1} for La(III), Ce(III) and Nd(III) when the initial concentration of these elements was 1000 mg L^{-1} , 600 mg L^{-1} and 600 mg L^{-1} , respectively.

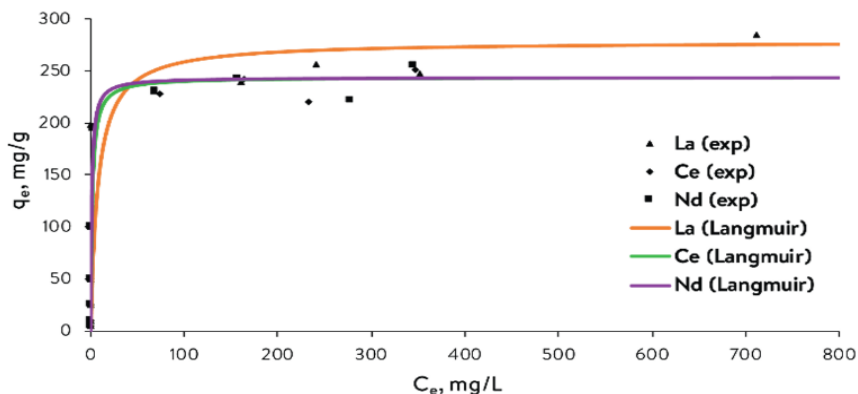


Fig 2. Effect of initial concentration on the removal of lanthanum (III), neodymium (III) and cerium (III) by modified montmorillonite with hydroxyapatite (experimental conditions: $C_i = 5 \text{ mg L}^{-1}$ to 1000 mg L^{-1} pH = 6, contact time = 24 h, T = 24 °C).

The LFM approach in former dumpsites might play an essential role in the recycling of so-called lost material – it can be called "hunting the valuables". The potential of fine-grained fractions from excavated waste is collecting considerably large amounts of valuable metals and REEs. Analytical screening studies are a part of the complete picture from a circular economy perspective, which in this paper is given as the sketch. On the other hand, new technologies, such as innovative sorbents, should be developed and elaborated to make this action feasible from an economic perspective.

Although the concentration of REEs is significantly lower than in mining areas, the concentration of elements such as Fe, Al, Cu, Pb, Ni, and others is interesting for extraction in nearest future. Studies on speciation and potential recovery approaches for the extraction of metals, metalloids, and REEs are to be continued. Some of the elements regard preliminary results might be called "reserves" as we are forced to remediate the land by the law anyway if the concern is about contamination. For environmental purposes, it is beneficial to handle potentially hazardous materials, including toxic metals and REEs that exist in landfills, and make sure these do not reenter the natural environment and are recycled.

4 Conclusion

Research provided the results on fine fraction elemental content for landfill waste containing potentially recoverable scarce metals and REEs resources. The amount of REEs might become of industrial interest if a feasible LFM approach for remediation of landfills and degraded industrial soils would be applied together with innovative recovery methods, *e.g.*, sorption by modified clays. The environmental value as itself might not be enough to cover the economic costs; however, other aspects such as ecosystem services restoration and real estate regain can add feasibility to the landfill mining projects in a circular economy perspective. The zero waste and the beyond the zero waste concept must be developed and improved, resulting in higher material standards, but it is not likely that the style of life and attitude of society will change significantly during the foreseeable future.

This study was supported by project No.1.1.1.2/VIAA/3/19/531 "Innovative technologies for stabilization of landfills – diminishing of environmental impact and resources potential in frames of circular economy", No. KIK-15401 "Humiinaineid sisaldava pinnase stabiliseerimine teemulletes põlevkivituha abil / Stabilization of soil containing humic substances inroads with the help of oil shale ash", No. SLTKT20427 and project SARASWATI 2.0.

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