Spectroscopic determination of selected rare earth elements (lanthanum, neodymium and dysprosium) in electronic waste samples

by

Martin Makombe

(*MSc Chemical Science – University of the Western Cape)*

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Supervisor: Prof. Vernon. S. Somerset

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Declaration

I, **Martin Makombe** , declare that the contents of this dissertation represent my own unaided work, and that the dissertation has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed Date 24/03/2023

Abstract

Rare Earth Elements (REEs) are nowadays critical elements required in technological accessories. Their presence in electronic waste leads to environmental pollution. Therefore, there is a constant necessity for accurate data and reliable fast analytical methods. The dumping of waste electrical and electronic equipment (WEEE) and its recycling, commonly known as "urban mining," has had negative environmental impacts. The fate of rare earth elements in the environment because of the disposal of electronic waste (e-waste) and urban mining poses a threat to human health and the aquatic ecosystem. The information regarding the abundance of rare earth elements (REEs) in electronic waste components (EWC) helps the recycling industry. However, after the end of use, improper disposal may be detrimental to the environment by releasing toxic substances. The e-waste can be both valuable as secondary raw materials source and toxic if not treated and discarded improperly.

Firstly, this study focuses on the development of a novel improved alkaline borate fusion application on e-waste determination. Due to the heterogeneous nature of e-waste, the composition of vast amounts of metals and the refractory nature of some elements, an improved and sensitive method was required. This study investigates the preparation, dissolution methods, optimisation of experimental particulars and instrumental techniques with a focus on selected rare earth elements (Lanthanum (La), Praseodymium (Pr), Neodymium (Nd), and Dysprosium (Dy) in electronic waste, soils and leachate derived from e-waste disposal. The optimum and safe fusion conditions for e-waste were achieved after slow thermal decomposition up to 550 ^{o}C, pulverisation to 90% of –53 µm, flux composition (90%$LiBO_2$ + 10% $Li_2B_4O_7$), 3:1 oxidant ratio of Na_2CO_3: $NaNO_3$, LiBr as the non-wetting agent. Also, a sample to flux ratio of 1:15 and a total fusion time of 10 minutes was optimised. The newly improved alkaline fusion results compared better to those obtained from classical mineral acid dissolution with at most 5% RSD on REEs studied. The alkaline borate fusion results in smartphones e-waste were at least 15% and 25% higher than in four acid digest and microwave-assisted digest techniques, respectively. The results indicated enrichment of REEs in smartphones followed by non-smartphones and computer waste.

Secondly, the study focuses on several microcosm studies using conditioned soil and crushed e-waste material to investigate the leaching of REEs in lab-scale experiments. For static column leaching, the H_2SO_4 lixiviant showed the highest accumulative recovery efficiency for Pr, Nd, and Dy, with 73.8%, 74.7%, and 52.2%, respectively. The total extractable REEs after 7 days were 73.91%, 45.79%, 16.85% and 10.55% for lixiviants H_2SO_4, H_3PO_4, $C_6H_8O_7$ and rainwater, respectively. The effects of major variables on REE batch leaching were analysed, including lixiviant type and concentration, time, stirring speed, pH, and solid-to-liquid ratio. In all batch leaching experiments, the temperature was kept constant at 23 ± 2 °C, and the agitation speed was maintained at 450 rpm. The leaching efficiency of La, Pr, Nd, and Dy was found to be significantly influenced by the lixiviant type, concentration, pH, and leaching time. The most efficient batch leaching was achieved using 1 M HNO_3, a leaching time of 10 minutes, a solid-to-liquid ratio of 50 g/L, and a strongly acidic pH. For La, Pr, Nd, and Dy, a leaching efficiency of 31.4%, 74.2%, 75.7%, and 75.2%, respectively, was observed.

Thirdly, In this study, we report the results of leachate quality and characterisation studies from simulated e-waste dump. The dump's physical and chemical properties were quantified using standard methods. The sediments and liquid leachate from the waste dumps were elemental quantified at different time intervals over a period of 4 years. The effect of leaching variables on rare earth elements were evaluated. The data obtained will help with a novel predictive modelling approach of REE leaching based on several leaching parameters and to be used on a large scale and in different natural environments. The novel approach is based on REEs' reactions to their disintegration, solubility, complexation/precipitation, and permeation in the natural environment. The outcome from this study suggests that the REEs hardly leached out in the first year of exposure but gradually increased in the second and third years. The order of leaching content was Nd > Pr > La > Dy, but this was largely due to the abundance of the elements in the original waste components. Also, the levels of the leached metals in the solid sediment samples were significantly higher than in liquid leachate.

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Dedication

This thesis is dedicated to my father, Phillip Makombe and my mother Josphine Makombe.

Research Outputs

Book Chapter

1. **Martin Makombe** and Vernon Somerset (**2019**). Chapter 1. Spectroscopic Determination and Evaluation of Rare Earth Elements in Electronic Waste and Wastewater. In **Elvis Fosso-Kankeu** (Ed.), *New Horizons in Wastewaters Management: Emerging Monitoring and Remediation Strategies*. (pp 3-34). New York, USA. Nova Science Publishers. ISBN: 978-1-53615-659-1. Book Chapter.

Publications

2. **Martin Makombe**, Charlton van der Horst, and Vernon Somerset. (**2021**). Improved borate fusion technique for rare earth elements analyses in electronic waste components. *Environmental Technology*. DOI: 10.1080/09593330.2021.1994017

3. **Martin Makombe**, Charlton van der Horst, and Vernon Somerset. (**2022**). The Leaching behaviour of Rare Earth Elements in Soil Derived from Electronic Waste: A Microcosm Study. International journal of Environmental Science and Technology. **(Submitted October 2022**).

4. **Martin Makombe,** Charlton van der Horst, and Vernon Somerset. (**2022**). Evaluation of the potential risk of rare earth element contamination from leachate originating from electronic waste disposal. **In preparation**.

Posters and presentations

1. **Martin Makombe** and Vernon Somerset. Evaluation of potential risk of rare earth element contamination from leachate originating from electronic waste disposal. Paper presented at the 28th SETAC Europe Annual Meeting, in Rome, Italy from 13 – 17 May 2018. [Poster presentation]

2. **Martin Makombe**, Charlton van der Horst and Vernon Somerset. Evaluation of potential risk of rare earth element contamination from leachate originating from electronic waste disposal. U6 Conference. Theme: Research, Innovation and Technology for African Development. CPUT, Cape Town Campus, Cape Town, South Africa. 4 – 6 September 2018. [Poster Presentation]

3. **Makombe, M**. and Somerset, V.S. Evaluation of potential risk of rare earth element contamination from leachate originating from electronic waste disposal. Paper presented at the at the Young Chemist Symposium (SACI), CPUT Campus, Bellville, South Africa. 17 May 2019. [Poster presentation]

4. **Makombe, M**. and Somerset, V.S. Spectroscopic determination of rare earth concentrations in environmental samples originating from electronic waste disposal. Paper presented at the Society for Risk Analysis (SRA), 5th World Congress on Risk in partnership with the Society of Environmental Toxicology and Chemistry (SETAC), 9th Biennial Meeting of SETAC Africa, CTICC, Cape Town, South Africa. 6 – 8 May 2019. [Oral presentation]

5. **Martin Makombe** and Vernon Somerset. Distribution of rare earth element concentrations in leachate originating from electronic waste disposal. Paper presented at the 29th SETAC Europe Annual Meeting in Helsinki, Finland. 26 – 30 May 2019. [Poster presentation]

6. **Martin Makombe**; Charlton van der Horst, Bongiwe Silwana; Emmanuel Iwuoha and Vernon Somerset. Application of an antimony film sensor for sensitive rare earth metal analysis in tap water samples. Paper presented at the 70th Annual Meeting of the International Society of Electrochemistry (ISE), Durban, South Africa. 4 – 9 August 2019. [Poster presentation]

7. **Martin Makombe**, Emmanuel Iwuoha and Vernon Somerset. Voltammetric and Spectroscopic Determination of Rare Earth Elements in Fresh and Surface Water Samples. Paper presented at the 5th International Symposium on Electrochemistry, University of the Western Cape, Bellville, South Africa. 11 – 14 August 2019. [Poster presentation]

8. **Martin Makombe** and Vernon Somerset. (**2021**). The Leaching and Speciation of Rare Earth Elements in Sediments Derived from Electronic Waste: Microcosm Study. Paper presented at the SETAC Europe 10th Young Environmental Scientists Meeting. A virtual meeting from 22 – 26 February 2021. https://yes2021.setac.org/ [Oral presentation]

9. **Martin Makombe**, Charlton van der Horst and Vernon Somerset**.** (**2021**). Rare Earth Elements in Soil Samples Derived from Electronic Waste: Microcosm Study. Paper presented at the SETAC Europe 31st Annual Meeting. A virtual conference from 3 – 6 May 2021. [Poster presentation]

10. Martin Makombe, Attendance of ICMGP2022 - International Conference on Mercury as Global Pollutant ICMGP). A virtual conference from 24-29 July 2022.

Other Journal and Book Chapter Publications

1. **Makombe, M**., Van der Horst, C., Silwana, B., Iwuoha, E. and Somerset, V. (**2016**). Antimony film sensor for sensitive rare earth metal analysis in environmental samples. Journal of Environmental Science and Health, Part A, 51(8): 597-606.

2. **Makombe, M.,** Van der Horst, C., Silwana, B., Iwuoha, E. and Somerset, V. (**2017**). Optimization of parameters for spectroscopic analysis of rare earth elements in sediment samples. In: Rare Earth Element: Chapter 3; Orjuela, J.E.A.; Ed.; INTECH: Croatia, 63-81.
3. **Makombe, M**., Van der Horst, C., Silwana, B., Iwuoha, E., & Somerset, V. (**2018**). Voltammetric and spectroscopic determination of rare earth elements in fresh and surface water samples. *Environments*, *5*(10), 112.

4. Van der Horst, C., Silwana, B., **Makombe, M.**, Iwuoha, E., Somerset, V. (**2021**). Application of a chitosan bimetallic nanocomposite for the simultaneous removal of cadmium, nickel, and lead from aqueous solution. DESALINATION AND WATER TREATMENT. 2021, 220: 168-81.

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Abbreviations

AAS	Atomic absorption spectrometric
AcOH	Acetic acid
BCR	Community Bereau of reference
BDL	Below detection limit
CCD	Charge coupled detectors
CF	Contamination factor
CiA	Citric acid
EC	Electrical conductivity
EDXRF	Energy dispersive x-ray fluoresence
EEE	Electrical and electronic equipment
EF	Enrichment factor
E-waste	Electronic waste
EWD	Electronic waste dump
FTIR	Fourier transformed infrared
HREE	Heavy rare earth element
ICP-MS	Inductive coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
LA-ICP-MS	laser ablation-inductively coupled plasma-mass spectrometry
ICP-SFS	ICP sector field mass spectrometer
LCD	Liquid crystal display
LED	Light emitting diode
LIBS	Laser induced breakdown spectroscopy
Ln	lanthanides
LOI	Loss on ignition
LOD	Limit of detection

LOQ	Limit of quantification
LREE	Light rare earth element
IPAA	Instrumental photon activation analysis
MREE	Middle rare earth element
NAA	Neutron activation analysis
PBTs	Bio- accumulative toxins
P b	Bulky density
PCB	Printed circuit board
PCD	Polychlorinated dioxins
PFA	Perfluoroalkyl
PPM	Parts per million
PSD	Particle size distribution
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
REE	Rare earth element
REEs	Rare earth elements
RSD	Relative standard deviatio
SEP	Sequential extraction procedure
SPL	Synthetic precipitation procedure
TCLP	Toxicity characteristic leaching procedure
TDS	Total dissolved solids
TGA	Themogravimetric analysis
TOC	Total organic content
TS	Treated soil
TXRF	Total reflection x-ray fluorescence
UV-VIS	Ultra violet visible spectrometer

WD	Wavelength x-ray fluorescence
WEEE	Waste electrical electronic equipment
WHO	World Health Organization
WPCB	Waste printed circuit boards
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X- ray fluorescence

CHAPTER 1

INTRODUCTION

1.1. Introduction

The chapter deals with the introduction to the study as presented in this thesis. The background briefly overviews rare earth elements (REEs) in electronic waste (e-waste); the origin, composition, uses and properties are discussed in section 1.2. The leaching chemistry of REEs from e-waste and soils derived from e-waste environments is also presented in section 1.2. Furthermore, the analytical determination of rare earth elements in electronic waste and in associated environments is discussed in section 1.3

Details of the problem statement, research questions, hypothesis, research aims, objectives, novelty, expectation of the study and delimitations are presented in this chapter sections 1.4 to 1.10. The chapter ends with a preview of the subsequent chapters in this thesis in section 1.11.

1.2. Background to study

1.2.1. The emergency of electronic waste onto the environment

Due to our ever increasing dependence on electrical and electronic equipment (EEEs) in today's life, the amount of e-waste generated worldwide is thriving at an alarming rate, while the management practices and policy-level initiatives are still at an infancy stage, especially in most of the developing countries (Borthakur, 2015). The REEs group are comprised of the lanthanide series plus scandium and yttrium. The REEs physicochemical properties are very close because of their close electronic configurations, and their most thermodynamically stable form is the trivalent, Ln(III) form (Galhoum et al., 2015).

The danger of improper disposal leads to contamination of soils, air, and water bodies because of leaching, toxic gas release, and runoff processes (Needhidasan et al., 2014). Although the mobility of REEs in natural environments is thought to be minimal (Brewer *et al.*, 2022), altered conditions can exacerbate REE dissolution and desorption, particularly at illegal e-waste dumping sites and recycling centers. These sites have a high concentration of potentially toxic metals. The composition of e-waste, landfill structure, age, and climate conditions all influence the leachates produced (Saha *et al.*, 2021). Because e-waste leachate is highly variable and heterogeneous, reliable quantification methods are required.

1.2.2. Abundance of rare earth elements in electronic waste.

Rare Earth Elements (REEs) are critical elements needed in the defense industry, green technology and most important advancement in technology. Therefore, the development of new sources of REEs is important to ensure a secure supply of these elements. This development affects the environment in two ways: First by extraction of natural raw materials including urban mining (recycling of e-waste) to supply the demand and secondly by pollution through the discarded electrical waste equipment. In general, the more classical metallic contaminants such as heavy and toxic elements to the environment are relatively well documented. However, knowledge gaps exist on rare earth elements on e-waste matrices and their speciation especially, on the environment. Rare earth elements (REEs) such as La, Pr, Nd, Gd and Dy are also present in significant amounts in smartphones (Kiegiel *et al*., 2018).

1.3 Spectroscopic determination of rare earth elements

Classical methods for rare earth determination in various matrices involve different digestion protocols from partial to near-complete dissolutions. Depending on the nature of the sample, complete dissolution can be a demanding task to achieve. The refractory nature of elements such as Cr, Ba, Sr, Ta, Ti, and Zr together with REEs require multiple severe acids or sophisticated methods for dissolution. Several solid-state techniques that do not require sample dissolution have been proposed such as laser ablation inductive coupled plasma mass spectrometry (LA-ICP-MS) (Stehrer *et al*., 2010), laser-induced breakdown spectroscopy (LIBS) (Costa *et al*., 2017; Aquino *et al*., 2015), pressed powder x-ray spectroscopy (XRF) (Schramm, 2016) or solid-state graphite furnace atomic absorption spectroscopy (Duarte *et al*., 2010). The major preference of solid-state over dissolution techniques lies in non-use of hazardous chemicals, non-destruction of the sample, environmentally friendly, cost-effective analysis and quick throughput. However, the lack of reaching low detection limits in sediments, soils and other environmental components deter the use of solid-state techniques in trace level analysis. Furthermore, to the above consideration, the scantiness of ideal reference materials for matrix-matched calibration impedes the quantification capabilities (Andrade *et al*., 2019).

The flux composition may differ with the type of sample, in fact, there is no universal flux for all sample types (Stephenson, 1969). The success of the applied analytical method is accompanied by appropriate sample preparation, decomposition, optimisation of parameters and matrix simplification techniques. In that respect, several studies concerning ion-exchange chromatographic methods for the determination of REE in geological materials have been reported (Zawisa *et al*., 2012), but the methodologies in electrical waste are yet to be explored fully.

1.4. Problem Statement

The emergency of rare earth metals through the disposal of electronic waste and urban mining into the environment has caused pollution to humans and the ecosystem. The characterisation and determination of these elements both in e-waste materials and in environmental matrices are essential in monitoring pollution levels and how leachable these elements are into the environment. The elemental determination of e-waste is complex because it contains an inhomogenity of materials requiring special end-of-life handling; mainly lead, mercury, arsenic, chromium, cadmium, and plastics that are capable of releasing toxic dioxins and furans, among other compounds. Accurate, fast and precise methods of determination are required to elucidate the problem.

1.5. Research questions

This study proposes to provide answers to the following questions:

1. Which analytical techniques are best suited for determining and quantifying the rare earth elements in electronic waste?
2. Which are the rare-earth elements present in smartphones e-waste and are they detectable by spectroscopic techniques?
3. Are these elements present in enough concentration to warrant re-cycling or to cause concern in any residue or effluent?
4. Are they highly soluble or insoluble and what is their environmental mobility?
5. Do the e-waste dumpsites activities increase REE contaminant transport in soils, or sediments and impact environmental and human health?

1.6. Hypothesis

Rare earth elements are found in electronic waste and may be determined by alkali borate fusion as the dissolution technique. These elements are leached into the environment when the e-waste is improperly discarded.

1.7. Aims

The overall aims of the study presented are firstly, the development and optimisation of an analytical procedure for the determination of REEs in e-waste. The research will focus mainly on the development of the novel borate fusion analytical method and the optimisation parameters for REEs analysis on ICP-OES. Secondly, the leaching behaviour of rare earth elements from electronic waste and environments polluted with e-waste. Thirdly, the quantification of REEs in electronic waste and the contaminated environment of the electronic waste dump. Additionally, it is hoped that the novel method will be applied to other environmental samples associated with REEs in South Africa.

1.8. The objectives of this study are:

1. To determine the analytical technique best suited for the accurate qualitative and quantitative determination of rare earth elements contained in e-waste from smartphones.
2. The development of the complete and safe decomposition technique for REEs in electronic waste and waste residue.
3. The analysis is limited to selected rare earth elements namely; La, Nd, and Dy.
4. Determine the impact of REEs leachates from e-waste which can be harmful to the environment if not properly managed.

5. To investigate the behaviour and mobility of selected REEs in e-waste dump where interaction with soil minerals and organic matter is likely to control their environmental behaviour.
6. Determination of the level of soil pollution and physiochemical parameters around the e-waste dumpsite.

1.9. Novelty and expectations of the research

The novelty and expectations of the study are highlighted below:

- The development and optimisation of alkaline borate fusion method for rare earth element analysis in electronic waste samples for the first time.
- To study the leachability of rare earth elements from electronic waste and contaminated soils and how they are released into the environment.
- To study the leaching trend of REEs exposed in dumps and evaluate how other physiochemical properties of exposed soils and leachate are affected by the presence of dumped electronic waste.

1.10. Delimitation

The electronic waste since it involves almost anything discarded that uses electrical power; however, in this study, focus was laid on smartphone and computer waste as it is a daily usage by almost everyone. The first step was the development of an improved borate fusion method involving the optimization of fusion decomposition techniques and the spectroscopic determination of selected rare earth elements (REE) in e-waste samples. The leaching behaviour of REEs from e-waste and soils containing residues of e-waste was evaluated through microcosm leaching studies. In most urban centers, including Cape Town, the electronic waste dumpsites are not properly defined and managed, so simulated dumps were constructed for this research. The study examined the impact of REE contaminants on surface water and soils using simulated dumps. The physiochemical parameters of the electrical waste dump, such as pH, electrical conductivity, total dissolved solids, and alkalinity, were investigated, as were the effects of rain quantity and composition. In terms of instrumentation, trace rare earth element analysis will be carried out using ICP-OES, ICP-MS, X-ray fluorescence (XRF) and X-ray diffraction (XRD) as the main elemental analysers. The limitation of this study was the inability to study all 15 elements of the rare-earth elements group; hence, at least 3 elements representing light rare earths (LREE) and heavy rare earths (HREE) were extensively studied

1.11. Layout of the Thesis

The introductory chapter of this thesis will end with a chapters outline as follows:

Chapter 1: Introduction

This chapter will provide the current information in the completed thesis.

Chapter 2: Literature review

Chapter two contains a review of literature focusing on the source, use, physical and chemical properties, and demand of REEs will be laid out. The theoretical background of REE sources and their impact on the environment are unveiled This chapter will also consist of the reviews of different literature associated with the nature, composition, disposal and environmental impact of e-waste. A review of different methodologies and the principles behind the analytical techniques on REE determination. This chapter is summarised in a book chapter.

Chapter 3: Experimental methods and analytical techniques

The outline of sampling protocol, analytical procedures and experimental methods used in this study to address the research objectives will be presented in chapter 3. The theory behind different experimental methods for e-waste is laid out. The spectroscopic techniques used for characterisation and quantification of REEs in e-waste are presented and discussed.

Chapter 4: Development of the alkaline borate fusion technique for e-waste determination.

New method development for REEs analysis in e-waste material is presented. Various optimised parameters such as type and composition of flux, solvent type, time and temperature of fusion will be covered in this chapter. The other analytical procedures, experimental methods and instrumental techniques will be laid out. A scientific paper will be published from the results obtained in this chapter.

Chapter 5: Microcosm set-up and e-waste exposure.

This chapter focuses on behaviour of REEs in e-waste and contaminated soils using a column and batch leaching microcosm setup. Detailed leachate chemistry on e-waste and contaminated soils, as well as the optimisation of major leaching variables are presented. Evaluation and spectroscopic analysis of samples collected in the microcosm study.

Chapter 6: This chapter focuses on the analysis of real sediment and leachate samples obtained from the e-waste dumps (simulated study). Different spectroscopic techniques will be employed to determine the leached content periodically including the speciation of REEs. The physiochemical parameters of the e-waste dumps and dumpsite rainfall will be analysed and presented.

Chapter 7: Conclusion and recommendations

The conclusions reached from the investigations of this thesis are presented. The knowledge and experience acquired from the study are used to make informed decisions on the environmental impact and appropriate recommendations for future work.

Chapter 8: References

This chapter will contain a list of all the research articles, books, chapters, internet material, and other sources consulted during the course of this study.

CHAPTER 2

LITERATURE REVIEW[∞]

2.1. Introduction

Chapter two contains a review of different literature focusing on the source, physical and chemical properties, disposal and environmental impact of rare earth elements in electronic waste. In this review, the focus is mainly on e-waste derived from mobile phones. This paper covers the following issues. Firstly, it covers the preliminary studies on the occurrence, nature, and uses of REEs. Secondly, the composition and impacts of e-waste are described. Thirdly, complementing other peer-reviewed publications on sample preparation procedures, dissolution methods and instrumental techniques with a focus on rare earth elements in WEEE will be discussed. The review chapter published and updated in this section.

[∞] **Martin Makombe** and Vernon Somerset (**2019**). Chapter 1. Spectroscopic Determination and Evaluation of Rare Earth Elements in Electronic Waste and Wastewater. In **Elvis Fosso-Kankeu** (Ed.), *New Horizons in Wastewaters Management: Emerging Monitoring and Remediation Strategies*. (pp 3-34). New York, USA. Nova Science Publishers. ISBN: 978-1-53615-659-1.

2.2. Overview

Rare Earth Elements (REEs) are critical elements required by technology vital accessories. Their presence in electronic waste gives rise to environmental pollution. Therefore, there is a constant necessity for accurate data and reliable fast analytical methods. Urban mining and electronic waste dump sites have negative impacts on the environment if not properly monitored. This review discusses the rare earth elements in electronic waste and their impact on the environment. The methods of quantification of rare earth elements in electronic waste and other associated environments are discussed. Classical methods such as wet acid dissolution, fused beads and alkaline fusion are commonly employed for rare earth metal analysis. Instrumental techniques that have been used recently include electrothermal vaporiser or laser ablation accessory connected to ICP-MS or ICP-OES, X-ray Fluorescence, Instrumental neutron activation analysis (INAA), Laser-induced breakdown spectroscopy (LIBS), Atomic Absorption Spectroscopy *(*AAS*)* and electro analytical techniques. These methods of analysis including accuracy, the limit of detection (LOD) and the limit of quantification (LOQ) are compared and discussed. This article summarises the preparation, dissolution methods and instrumental techniques with a focus on rare earth elements in electronic waste on work published in the last decade.

2.3. Emerging contaminants

Rare earth elements (REEs) are listed as critical materials by the European Union, and their demand will eventually outstrip supply (Zhou *et al.*, 2016). Rare earth elements are essential for modern electronics and meet global commitments for the usage of greener technologies such as renewable energy, defense machinery, audio and communication equipment, medical technology, computer hard disk drives and energy-efficient vehicles. Nowadays, REEs are found in many technologies, such as mobile cell phones, LED and compact fluorescent lights, laptops, and computers. This rapid technology development requires an abundant source of these critical elements, leading to economic concerns about the security of supply and an urgent requirement to find alternative sources (Zhou *et al*., 2016). More than 90% of the world's REE ore deposits are in Mongolia and China, which control the global market. Recently, China has cut several export quotas on REEs and this has led to global panic (Hurst, 2010; Xinhua, 2012). To avoid this scenario, alternative REEs need to be found and it may be worthwhile to recycle electronic waste so that it can be independent of expensive imports. The term e-waste or waste electrical and electronic equipment (WEEE) refers to any discarded electrical or electronic devices that mainly use electricity or are powered by batteries. Due to the increasing awareness of environmental protection, the recycling of REEs from e-waste is a global concern. Poor practices in China have led to significant environmental problems and the toxicological effects of REEs and their mechanisms of action are still poorly understood (Hurst, 2010). According to Amfo-Otu et al. (2013), Japan investigated fifty-five metals contained in WEEE during municipal waste treatment and the study revealed that some of the metals, such as copper (Cu) and aluminum (Al) were not recovered by the treatment process and ended up in landfills. Electrical and electronic equipment is in higher demand in the third and developing worlds than ever before. Many of these countries rely on second-hand equipment that is nearing the end of its useful life from developed nations. Many pieces of equipment have a limited life span before they are added to the stockpiles of e-waste. In addition, the adoption of western life through globalisation and modernisation has led to the saturation of e-waste comprising electrical and electronic equipment (WEEE) (Amfo-Otu *et al.*, 2013). The e-waste, if not properly discarded, presents a difficult environmental challenge. In the review by Sauve and

Desrosiers (2014), they defined emerging contaminants as those substances that pose harmful effects to the environment and to human health. These contaminants can be manmade, naturally occurring, or manufactured materials. The challenge to this is to understand their concentration in the environment and their toxic effects on animals and human health (Simonnot, 2012; Zhang *et al.,* 2012). In regard to these pollutants, large amounts of inorganic chemical reagents are essential in the production, purification and recycling of REEs.

Radioactive pollutants associated with REEs are also major environmental issues if they cannot be properly addressed (Zhou *et al.,* 2016). Nowadays, the recycling of e-waste has become popular and is normally termed "urban mining." The demands for some precious metals together with some rare earth metals of high economic value have also accelerated the rate of recycling (Amfo-Otu *et al.,* 2013). Recycling reduces the volume of total e-waste in dumps, but poor recycling procedures will lead to more pollution of the environment and expose humans to hazardous metals contained in e-waste. There is a great risk of letting electronic components decompose in the environment, releasing toxic elements. The broken parts of batteries contain toxic substances such as lead (Pb), cadmium (Cd), mercury (Hg), beryllium (Be) and arsenic (Ar). The precious metals and rare earth elements strongly add to the metallic composition of e-waste. Furthermore, inter elemental reactions and aqueous complexation of REEs at ambient temperature can cause unique effects on the environment. The extraction of REEs from ores usually involves decomposition with acidic or alkaline reagents, which can also be rampant in places of high acid rain (Kim *et al.,* 2016). Various reports within the past few years have indicated that some waste recycling from fluorescent equipment yielded rare earth metal phosphors (Binnemans and Jones, 2014). The existing processes for REEs recovery include acid leaching (Tian *et al.,* 2016), liquid-liquid extraction (Mei *et al.,* 2009), alkaline fusion (Wu *et al.,* 2014), ionic liquid extraction (Yang *et al.,* 2012), pre-concentration, and resin extraction (Amfo-Otu *et al.,* 2013). Although many researchers have studied REEs in different matrices using different techniques (*Zawisa et al., 2011*), there is still no unified conclusion on improved digestion procedures and techniques in e-waste analysis. During the last decade, the emphasis by many researchers has been placed on heavy metals and precious metals determination in e-waste with a little attempt on rare earth metals. Quantifying metal values in e-waste is valuable to the recycling industry and studies on environmental pollution (Golev and Corder, 2017).

2.4. Rare earth elements

2.4.1. Rare earth elements defined

The REEs are divided into two main groups consisting the light rare earth elements (LREEs) with lower atomic weight such as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu) and the heavy rare earth elements (HREEs) such as gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) (Figure 2.1).Two more elements occur with similar chemical and physical properties, which are scandium (Sc) and yttrium (Y). These REEs are members of the f-block in the periodic table which are highly electropositive and predominantly trivalent (Ln^{3+}) except for cerium (Ce^{4+}) and europium (Eu^{2+}) in certain environments.

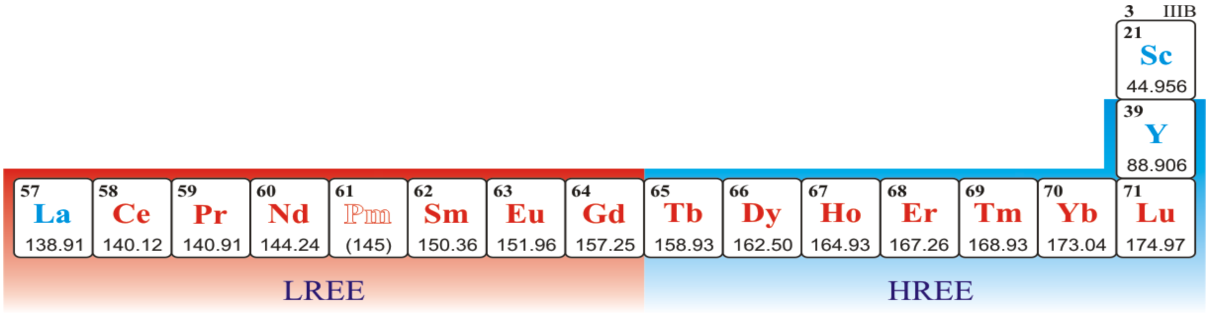


Figure 2. 1: **Periodic Table designating “light” and “heavy” rare earth elements (***Adapted from: https://www.periodni.com/rare_earth_elements.html*)

2.4.2. Occurrence of rare earth elements in nature

REEs have almost the same geochemical properties. They are mostly found as +3 cations that have a strong attraction to oxygen. Most of these elements are not actually rare in terms of their general abundance in the earth's crust, but they are rarely found in sufficient concentration in a single location for their mining to be economically viable. In nature, the REEs are most likely to be concentrated in phosphorites (PO_4) and argillaceous sediments.

Naturally, REEs are lithophiles, so they concentrate predominantly in the rocky part (laths) rather than the metal or sulphide phases where they co-exist (Albarede, 2011). The dominant REE minerals are thorium (Th)-bearing monazite PO_4 and are often presented as (Ce, La, Nd, Th) PO_4 (Kabata-Pendias, 2000; Cotton, 2013), bastnasite ($LnFCO_3$) and xenotime PO_4 with trace amounts of HREEs (Franz *et al.*, 1986). Coal fly ash is another source of REEs, especially LREEs (Franus *et al.*, 2015). Rare earth elements have many important applications in modern technology for which there is no equal substitute, but an increasing demand for these elements is straining supply.

2.4.3. Physical properties of rare earth elements

The physical characteristics of REEs show very diverse behaviors, which make them useful for a wide range of applications. In magnetism, Nd, Gd, Dy, Er and Sm show complex potentials that can be used for magnet manufacturing (Chakhmouradian and Wall, 2012). Some REEs provide sharply defined energy states, which can be efficiently used in lighting, colour and laser applications. REE ions can have electrons in f-orbitals and empty orbitals like the d-block elements. When a certain frequency of light is absorbed, it results in the formation of coloured ions through f-f electron transitions.

The different atomic structures and states of REEs lead to some unique properties that are essential in modern day technology gadgets (Henderson, 2013). The unpaired electrons contribute to ‘orbital magnetic moment’ and ‘spin magnetic moment'. Furthermore, there is a wide variety of similar and special characteristics inherent in the REEs that make them unique and well sought-after elements. Table 2.1 shows some of the physical properties of rare earth elements.

The LREE have a relatively large ionic radius, comparable to calcium (Ca^{2+}=1.12) and thorium (Th^{4+}=1.05), whereas the HREE have a smaller ionic radius, comparable to uranium ($U^{4+=}$1.00) and manganese ($Mn^{2+=}$0.96) (Shannon, 1976). Lanthanide contraction is the smooth decrease in ionic radius of lanthanides with increasing atomic number due to increased effective nuclear charge (Yoshida et al., 2004; Bounouira et al., 2007). Lanthanides are extremely dense metals with melting points even higher than d-block elements. They combine with other metals to form alloys. These are the f block elements, also known as the inner transition metals. The electrons in the inner transition elements/ions may be in the s, d, or f- orbitals.

Table 2. 1: Physical properties of rare earth elements.

Rare Earth Element	Atomic Number	Atomic Weight	Ionic radius (Å, CN8	Crustal abundance (ppm)	Density (g/cm^3)	Melting Point (^{o}C)	Hardness (Mohs)	Conductivity (W/m-1K-1)
Lanthanum (La)	57	138.905	1.16	31	6.15	920	2.5	13.4
Cerium (Ce)	58	140.116	1.143	63	6.77	795	2.5	11.3
Praseodymium (Pr)	59	140.908	1.126	7.1	6.77	935	1.41	12.5
Neodymium (Nd)	60	144.242	1.109	27	7.01	1024	1.23	16.5
Promethium (Pm)	61	145	1.093	-	7.26	1042	-	17.9
Samarium (Sm)	62	150.36	1.079	4.7	7.52	1072	1.44	13.3
Europium (Eu)	63	151.964	1.066	1	5.24	826	3.07	13.9
Gadolinium (Gd)	64	157.25	1.053	4	7.9	1312	5.13	10.6
Terbium (Tb)	65	158.925	1.04	0.7	8.23	1356	2.33	11.1
Dysprosium (Dy)	66	162.5	1.027	3.9	8.55	1407	1.8	10.7
Holmium (Ho)	67	164.93	1.015	0.83	8.79	1461	1.65	16.2
Erbium (Er)	68	167.259	1.004	2.3	9.07	1529	1.97	14.5
Thulium (Tm)	69	168.934	0.994	0.3	9.32	1545	1.77	16.9
Ytterbium (Yb)	70	173.045	0.985	1.96	6.9	824	N/A	38.5
Lutetium (Lu)	71	174.967	0.977	0.31	9.84	1652	2.6	16.4
Scandium (Sc)	21	44.956	0.87	14	2.99	1541	N/A	15.8
Yttrium (Y)	39	88.906	1.019	21	4.47	1526	N/A	17.2

Virginia Energy. https://energy.virginia.gov/geology/REE.shtml; *CN8 = coordination number VIII.*

2.4.4. Chemical Properties of Rare Earth Elements

The valence, or outer, electrons are most involved in reactions since they are exposed to the surrounding environment. All the lanthanides, from Ce to Lu, have a similar arrangement of their outer electrons. This explains why they are all found together in nature and why they all react similarly. When they react with other elements to form compounds, most lanthanides lose three of their outer electrons to form di-positive ions. Some lanthanides form ions with a +2 or +4 charge, but these are usually not so stable. A comparison of the sizes of the lanthanide atoms and their ions reveals a progressive decrease from lanthanum (La^{3+} = 0.115 nm) to lutetium (Lu^{3+} = 0.093 nm), which is referred to as the lanthanide contraction. Most ionic lanthanide compounds are soluble in water (Moeller, 2013). The lanthanides 4f valence orbitals have a limited radial extension. As a result, orbital factors do not affect the chemistry as much as in transition metal chemistry. This means that substrates can approach the metal center in a variety of orientations and reaction pathways are not orbital forbidden. The high reactivity of lanthanides in olefin polymerisation and hydrogenation may be related to the fact that there are no orbital limitations to slow down the reactions.

The lanthanides are quite electropositive and, as such, have a high affinity for oxygen and the halides that make them useful in catalytic converters of automobiles and in fuel cells (Anwander, 1999). The restricted radial extension of the f orbitals reduces the vibronic broadening of optical transitions which leads to sharp 4f-4f emission and absorption spectra. These sharp transitions lead to very specific and efficient optical processes, such that the lanthanides are often the components of choice in optical devices. One property of the lanthanides that affects how they will react with other elements is called their basicity. Basicity is a measure of the ease with which an atom will lose electrons. In another word, it would be the lack of attraction that a cation has for electrons or anions. The basicity decreases as the atomic number increases. For the lanthanides, the following is the basic series:

$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$

A significant property of the lanthanides is their magnetic characteristics. The major magnetic properties of any chemical species are a result of the fact that each moving electron is a micro-magnet. The species are either diamagnetic, meaning they have no unpaired electrons, or paramagnetic, meaning that they do have some unpaired electrons. The diamagnetic ions are the following ions: La^{3+}, Lu^{3+}, Yb^{2+} and Ce^{4+}. The rest of the elements are paramagnetic ions.

2.4.5. Chemical reactions of REEs

Reactions with water

Rare earth metals are quite electropositive and reacts slowly with cold water and quite quickly with hot water to produce the metal hydroxide and hydrogen gas:

$$2REE_{(s)} + 6H_2O_{(g)} \rightarrow 2REE(OH)_{3(aq)} + 3H_{2(g)} \qquad Eqn\ 2.1$$

The following is the reaction of neodymium with water:

$$2Nd_{(s)} + 6H_2O_{(g)} \rightarrow 2Nd(OH)_{3\,(aq)} + 3H_{2(g)} \qquad Eqn\ 2.2$$

Reactions with oxygen

REE reactions with air tarnish slowly in the air and burn readily to form REE oxides.

$$4REE_{(s)} + 3O_{2(g)} \rightarrow 2REE_2O_{3\,(s)} \qquad \text{Eqn 2.3}$$

The following are reactions of neodymium, praseodymium and dysprosium with oxygen:

$$4Nd_{(s)} + 3O_{2(g)} \rightarrow 2Nd_2O_{3(s)} \qquad Eqn\ 2.4$$

$$12Pr_{(s)} + 11O_{2(g)} \rightarrow 2Pr_6O_{11(s)} \qquad Eqn\ 2.5$$

$$4Dy_{(s)} + 3O_{2(g)} \rightarrow 2Dy_2O_{3(s)} \qquad Eqn\ 2.6$$

Reactions with halogens

REEs reacts with all the halogens to form REE(III) halides.

$$2REE_{(s)} + 3Cl_{2(g)} \rightarrow 2REECl_{3(g)} \qquad Eqn\ 2.7$$

The following are reactions of neodymium, praseodymium and dysprosium with chlorine, iodine and bromine respectively:

$$2Nd_{(s)} + 3cl_{2(g)} \rightarrow 2NdCl_{3(s)} \qquad Eqn\ 2.8$$

$$2Pr_{(s)} + 3I_{2(g)} \rightarrow 2PrI_{3(s)} \qquad Eqn\ 2.9$$

$$2Dy_{(s)} + 3Br_{2(g)} \rightarrow 2DyBr_{3(s)} \qquad Eqn\ 2.10$$

Reactions with acids

REEs dissolves readily in dilute sulphuric acid to form solutions containing the REE(III) ion together with hydrogen gas.

$$2REE_{(s)} + 3H_2SO_{4(aq)} \rightarrow 2REE^{3+}_{(aq)} + 3SO^{2-}_{4(aq)} + 3H_{2(g)} \qquad Eqn\ 2.11$$

The following are reactions of neodymium, praseodymium and dysprosium with sulphuric acid:

$$2Nd_{(s)} + 3H_2SO_{4(aq)} \rightarrow 2Nd^{3+}_{(aq)} + 3SO^{2-}_{4(aq)} + 3H_{2(g)} \qquad Eqn\ 2.12$$

$$2Pr_{(s)} + 3H_2SO_{4(aq)} \rightarrow 2Pr^{3+}_{(aq)} + 3SO^{2-}_{4(aq)} + 3H_{2(g)} \qquad Eqn\ 2.13$$

$$2Dy_{(s)} + 3H_2SO_{4(aq)} \rightarrow 2Dy^{3+}_{(aq)} + 3SO^{2-}_{4(aq)} + 3H_{2(g)} \qquad Eqn\ 2.14$$

2.4.6. Industrial Uses of Rare Earth Metals

The chemical and physical properties of REEs became so useful to modern-day technology equipment. Their unique optical and magnetic properties are being used to manufacture numerous industrial components. Table 2.2 reveals some of the uses of rare earth metals in various industrial applications.

Table 2. 2: Application and uses of rare earth elements in various devices and electronic equipment.

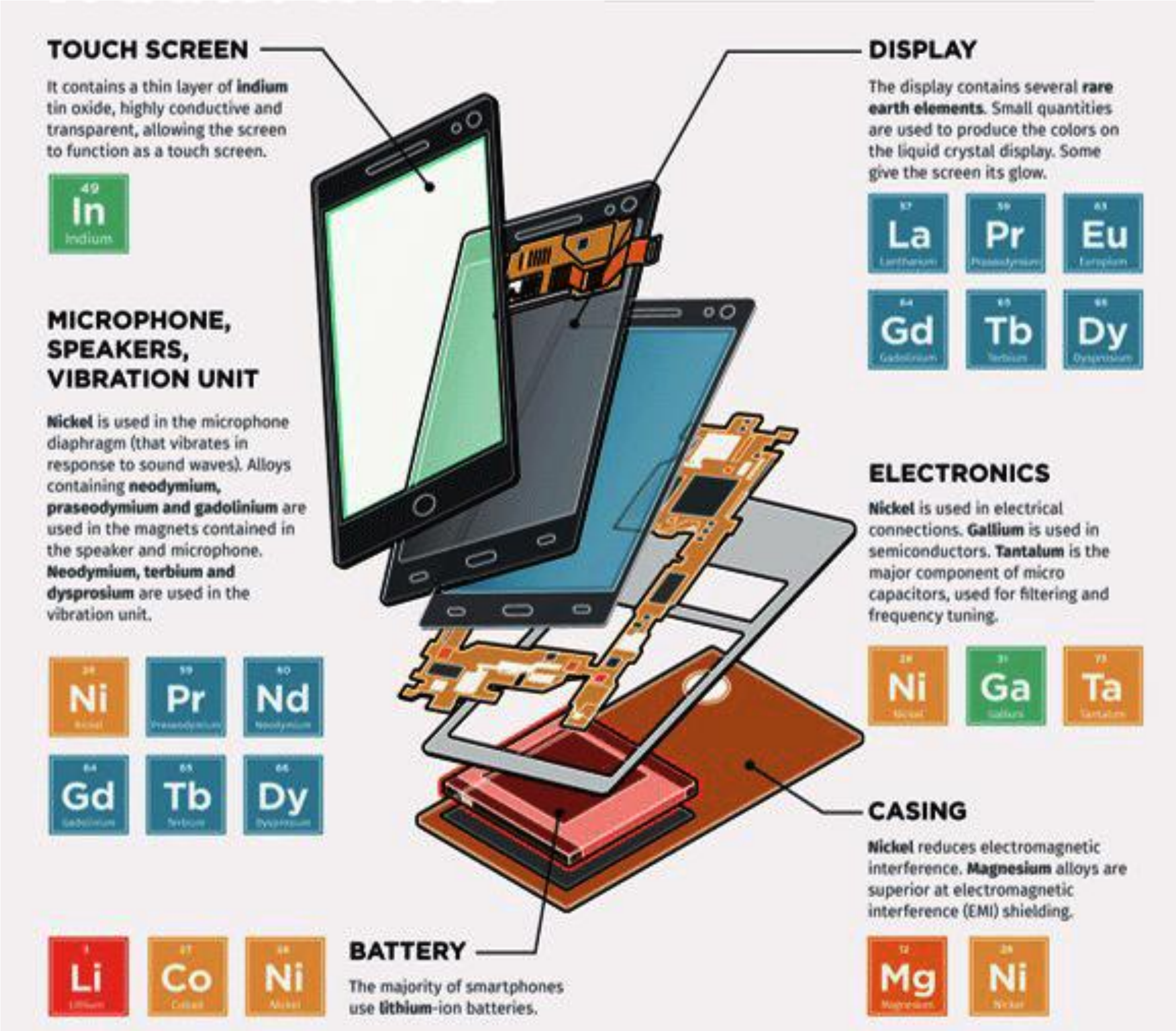
Application	**Uses**	**Rare Earth Metals**
Lightning and Electronics	Smartphones, cell phones display; colour TVs; LEDs lighting; fluorescent lamps; digital cameras; CDs and DVDs players; computers; lasers; flat screen displays	La, Ce, Pr, Dy, Nd, Eu, Gd, Tb, Tm, Y
Green energy	Electric motors; wind and hydro power turbines; batteries. fuel cells	La, Ce, Pr, Nd, Sm, Gd, Er, Ho
Medical Equipment	X-ray imaging; electron beam tubes; surgical lasers	
Chemicals and catalyst	Catalytic converters; fuel additives; petroleum refining. chemical processing	La, Ce, Pr, Nd, Lu
Glass and ceramics	Glass colouring; photo-optical glass; polishing powders. Refractories	La, Ce, Pr, Nd, Eu, Gd, Dy, Lu, Ho, Er, Y
Magnets	Microphones; speakers; computer hard drives; motors and generators; automotive parts; microwave power tubes	Pr, Nd, Sm, Eu, Tb, Dy
Defense	Satellite communications, Aircraft structures	La, Pr, Nd, Sm, Eu, Tb, Dy, Lu, Y

2.4.6.1. Critical elements in smarthones

The smartphones are rich with the lanthanides elements as well as other precious metals that makes them “smart”. The Table 2.3 and Figure 2.2 depicts the elements contained in smartphones and their technological uses.

Table 2. 3: Elements in smartphones

Smartphone Component	**Critical Metal**
Touch screen	In, Sn
Display	La, Pr, Dy, Gd, Eu, Tb
Speakers, Microphone, vibration unit	Nd, Pr, Gd, Tb, Dy, Ni
Electronics	Ga, Ni, Ta, Cu Ag, Au
Casing	Mg, Ni, Br, C
Battery	Li, Ni, Co, Al, C
Other non-conducting parts	As, O, P, Sb, Si



TOUCH SCREEN

It contains a thin layer of **indium** tin oxide, highly conductive and transparent, allowing the screen to function as a touch screen.

MICROPHONE, SPEAKERS, VIBRATION UNIT

Nickel is used in the microphone diaphragm (that vibrates in response to sound waves). Alloys containing **neodymium, praseodymium and gadolinium** are used in the magnets contained in the speaker and microphone. **Neodymium, terbium and dysprosium** are used in the vibration unit.

DISPLAY

The display contains several **rare earth elements**. Small quantities are used to produce the colors on the liquid crystal display. Some give the screen its glow.

ELECTRONICS

Nickel is used in electrical connections. **Gallium** is used in semiconductors. **Tantalum** is the major component of micro capacitors, used for filtering and frequency tuning.

CASING

Nickel reduces electromagnetic interference. **Magnesium** alloys are superior at electromagnetic interference (EMI) shielding.

BATTERY

The majority of smartphones use **lithium**-ion batteries.

Figure 2. 2: **Metals contained in smartphones (**University of Birmingham. https://www.visualcapitalist.com/visualizing-the-critical-metals-in-a-smartphone).

2.4.7. Environmental sources of REEs

Mining and exploration of REEs are a major source of REEs in the environment. Studies that have been carried out in China and Spain showed that the areas near mining activities are heavily polluted with REEs (Chunye *et al*., 2008; Liang *et al*., 2014; Zhenggui *et al*., 2001; Fernandez-Caliani *et al*., 2009). Huge amounts of mining wastewater and industrial waste carry a lot of radioactive elements, including REEs. Jinxial et al. (2010) showed in their study that the production of REEs in the Baotau region in China caused the surface and ground waters to be affected by radioactive substances and the accumulation of REEs, especially the LREEs.

The use of REE fertilizers has caused a lot of environmental pollution. The accumulation of REEs in soils, biota, and river water eventually affects the ecosystem as they are transferred to the food chain (Liu *et al.,* 2007). It has been found that the REEs improve the yields of the crops when applied correctly (Liu *et al.,* 2010; Peng *et al.*, 2007). The phosphate rock from which fertilizers are derived contains a lot of REEs and most of the REEs are eventually found in fertilizers and phosphogypsum waste (Tranchida *et al*., 2011).

The advancement of the use of electronics in homes and industry has resulted in environmental pollution from REEs if not properly handled and discharged. Products such as laptops, DVDs, rechargeable batteries, cellphones, phosphorous in color TVs, fluorescent light bulbs and many other components contain some REEs. Their disposal after use should be handled with care to avoid the accumulation of REEs in the environment (Humphuries, 2011).

2.4.8. Leaching of REEs

Many chemical engineering studies have been conducted successfully to leach out rare earth metals from their ores using a combination of multiacids and hydrometallurgy steps. Many times, this proved to be a daunting task as the separation and purification of individual REEs came at a huge cost and were time-consuming. In leaching, there are transport processes between the solvent and the surface of the element. Li et al. (2013) investigated different conditions for leaching REE concentrate. However, they optimised the conditions by using a $HCl–AlCl_3$ solution to obtain a leaching ratio of 76.5%. The recovery of the rare earths depends greatly on the type of acid used in the leaching system and the combination of leaching time, liquid-to-solid ratio and temperature. This has been exhibited by experiments using HCl, H_2SO_4 and HNO_3 acids, with the best recoveries obtained from H_2SO_4 (Meor, 2013). Leaching of REEs using HCl from Korean monazite concentrate (Panda *et al.,* 2014), leaching of total

REEs from the sea nodule was carried out using H_2SO_4 solution (Park *et al.*, 2013), HNO_3 leaching of LREEs from Sichuan bastnaesite (Shen *et al.*, 2017). The leaching and recovery of REEs from electronic waste are some of the studies that have been carried out in recent years (Peelman *et al.*, 2014; Binnemans *et al.*, 2014; Tan *et al.*, 2015). In a natural environment, the REEs are leached by rainfall and migrate through the soil into the groundwater aquifer.

2.4.9. Pathways for REE Migration in Soil

The migration of rare earth elements (REEs) from primary and secondary resources is affected by a number of mechanisms, including (1) REE solubility, (2) REE weathering and transformation, (3) erosion, (4) plant uptake, (5) REE adsorption by inorganic colloids, (6) leaching, and (7) complexation. (Zhaosheng *et al*., 1998; Jinxia *et al.*, 2010). Although the soil chemistry of the REEs is similar, there are slight variations in their hydrolysis and inorganic-organic complexation constants, as well as inherent variations in the susceptibilities of the different REE-bearing minerals to weathering. These variations allow fractionation and differential migration potential.

2.5. Electronic waste

2.5.1. Electronic waste defined

Typical e-waste originates from household equipment, communication gadgets, the office, audio, digital games, laboratories, medical devices, electric motors, green technology, lighting manufacturing and transport equipment. Cell phones have become an essential tool for our daily lives. Modern smartphones are multi-useful devices that are used as a calculator, navigator, watch, radio or music player, internet access, e-mailing, photography, etc. Many people purchase the latest technology in smart phones, which have a very short life span. In South Africa, mobile phones are estimated to have a life span between 18 and 24 months and are the most used device for internet access (Gutiérrez-Gutiérrez *et al.*, 2015). The characterisation of the e-waste is an important aspect that will inform the value addition of the e-waste and the recycling potential, leading to sustainable recycling of this waste and conserving space in landfills and saving the environment.

2.5.2. Presence of REEs in wastes

There are three main groups of wastes that might act as potential sources of REEs: industrial wastes, mining wastes, and electronic wastes. REE (fly ash) has been recovered by using wastes from processing minerals (phosphogypsum, red mud), processing coal, and other industries.Mine tailings and acid mine drainage are the primary sources of mining waste for REEs. Magnets, NiMH batteries, and phosphors—which are significant components of electronic display systems, hard drives, speakers, headphones, and spectrometers are significant sources of REE in electronic wastes (Dev *et al*., 2020).

2.5.3. Chemical composition of electronic waste

Many e-waste components, particularly printed circuit boards (PCBs), screens, speakers, and batteries, contain heavy metals such as Cd, Cu, Ni, Pb, Sb and precious metals such as Ag, Au, Pd and REEs such as La, Ce, Pr, Nd, Sm, Eu, Gd and Dy (Itoh, 2014). Many researchers have conducted studies on the determination of metallic components in e-waste and associated environmental pollution. Most of these studies have mainly leaned towards heavy metals and precious metals. Table 2.6 in section 2.4 illustrates the work done to date in terms of determining the metallic concentration of e-waste and pollution to the environment (Gutiérrez-Gutiérrez *et al.*, 2015).

2.5.4. Toxic elements in electronic waste

Electronic devices and products contain an array of toxic metals such as chromium, mercury, arsenic nickel, beryllium, barium, lead and Poly-Brominated Diphenyl Ethers (PBDEs), phthalates, and polyvinyl chloride (PVC) (Deval *et al*., 2015; Olubanjo *et al*., 2015). Lead, mercury, cadmium, and PBDEs are among the toxicants present in e-waste that are classified as persistent bio-accumulative toxins (PBTs) because of their tendency to integrate with the environment and accumulate in human tissues. A comprehensive review conducted by Sepulveda et al. (2010), where scientific data related to concentrations of Pb, PBDEs, polychlorinated dioxins (PCD) and furans were monitored around e-waste recycling areas in China and India. These organic constituents are mainly used in printed circuit boards, connectors, covers and cables

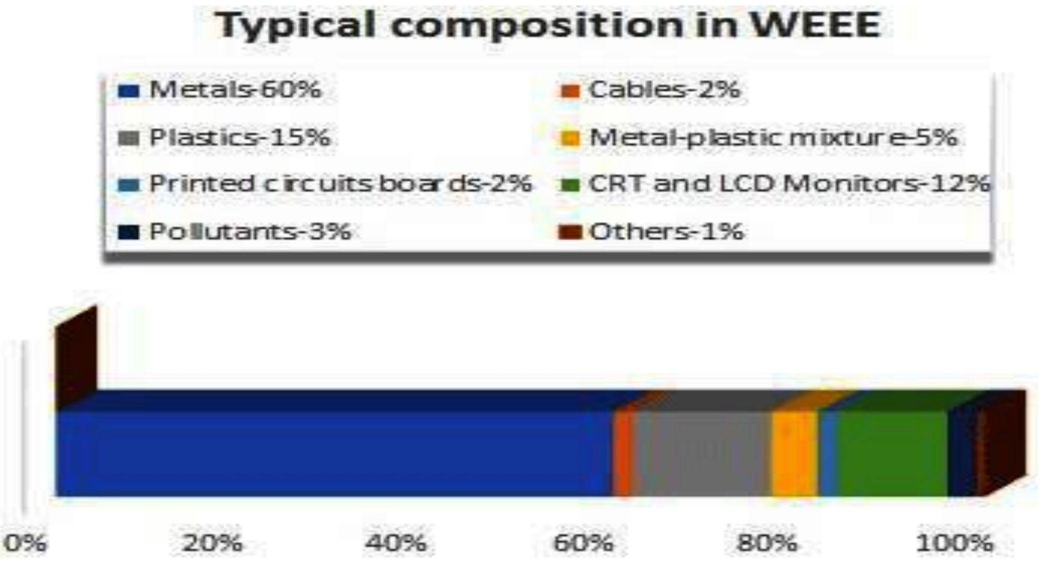


Figure 2. 3: General composition of e-waste illustration (*Adapted from (Ogondo* et al.*, 2011).*

2.5.5. Printed circuit boards

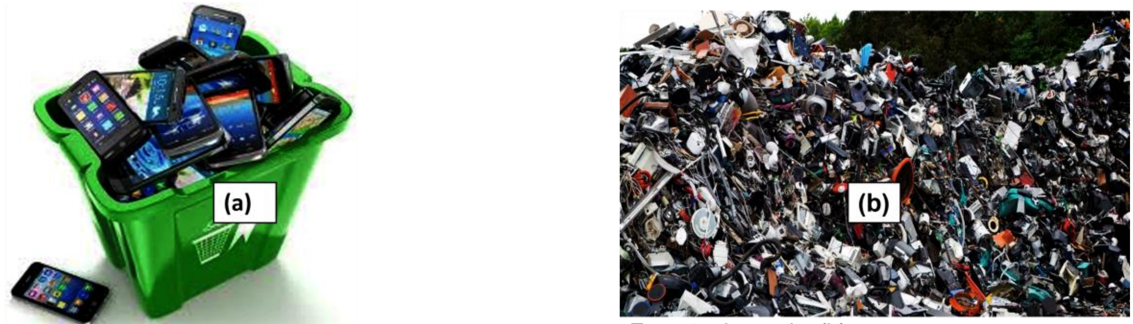
Printed circuit boards (PCBs) are flat, laminated hybrids composed of non-conductive substrate materials with layers of copper circuitry buried internally or on exterior surfaces. The board is then filled with electronic parts, and its surface is etched to let electricity flow through the copper from one part to the next. They are used in various electronic applications and are vital for today's technological applications. The electronic components include semiconductors, connections, resistors, diodes, and capacitors.

2.5.6. Thermal Behaviour of PCB

The thermal degradation of the printed electronic boards is an exothermic process. When heated to high temperatures, they decompose into smaller molecules. Pyrolysis is the process whereby a material decomposes into gases, oils and chars when it is heated to high temperatures under inert conditions. The boards typically consist of an insulating glass epoxy material with a thin layer of copper foil laminated to one or both sides. Phenol is the main product, together with brominated products recovered from the pyrolysis of PCBs (Barontini *et al*., 2006; Evangelopoulos *et al*., 2015). The thermogravimetric of pyrolysis is usually studied with thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), and gas chromatography-mass spectrometry (GC/MS).

2.5.7. Waste electrical and electronic equipment dilemma

The disposal of waste electrical and electronic equipment (WEEE) has caused serious environmental damage, especially in developing countries where proper environmental regulations are lacking (Olubanjo *et al*., 2015; Ofudje *et al*., 2015; Deval *et al*., 2015). Tonnes of e-waste not recycled in Europe are exported mainly to Asia and African countries where less stringent regulatory measures are in place for recycling purposes. China has become the largest dumping ground for e-waste (Chi *et al*., 2011; Guo *et al*., 2009; Leung *et al*., 2006). Many other countries, like Japan (Jang, 2010), Korea (Jang, 2010), Nigeria (Ofudje *et al*., 2014) and Ghana (Adaramodu *et al*., 2015; Amankwa *et al.*, 2017; Akortia *et al.*, 2017), have huge problems in dealing with the processing of e-waste. The e-waste that is not properly dismantled and recycled poses a great threat to environmental pollution, the loss of precious metal resources and a threat to human and aquatic life (Ofudje *et al*., 2015; Nnorom and Osibanjo, 2009; Nnorom *et al*., 2010; Wong *et al.*, 2007). Several countries around the world are now struggling to deal with this emerging threat.



Discarded smartphones (a)

E-waste dump site (b)

Sorted smartphone PCBs (C)

Burning e-waste (d)

Figure 2. 4: **Smartphone e-waste (a), e-waste dumpsite (b), Sorted smartphone PCBs and burning of e-waste at illegal recycling site (d).**

The movement of e-waste globally, coupled with high volumes, labour issues, financial incentives and poor regulations, is a threat to human health and the environment. Smith, (2015) discussed the economics of e-waste and the huge cost to the environment caused by the toxic nature of REEs and other metals. The variety of toxic metals and hazardous materials in WEEE in general requires proper care in the transportation, storage and recycling stages (Duan *et al*., 2008; Herat and Agamuthu, 2012; Robinson, 2009). Child labour and worker exposure at e-waste recycling sites, long-term effects on human health and the environment, unknown chemical concerns in e-waste and emissions from WEEE recycling are a global concern if not given attention. Seplveda et al. (2010) reviewed the effects of hazardous substances released from electrical and electronic equipment in China and India and showed how they affected human health.

2.5.8. Leachates from solid waste landfill

The co-disposal of e-waste with domestic waste in open dumps is a common practice in many developing countries, causing severe pollution to human health and the environment. Although the current focus is on end-of-life management of e-waste activities such as reuse, remanufacturing, servicing, recycling and disposal, reduction of e-waste generation through green design and cleaner production is gaining momentum. The degradation process involved in e-waste and solid municipal waste releases internal chemicals to the environment through leaching into groundwater and soil. According to the United Nations (UN), about 90% of the world's electronic waste is illegally traded or dumped (Nnorom and Osibanjo, 2009; Nichols, 2015). Computers and smartphones alone are estimated to be 41 million tonnes in 2017 and 50 million tonnes in 2018 (Balde *et al*., 2015; Nichols, 2015). According to the UN, e-waste represents 2% of America’s thrash in landfills, but it equates to 70% of gross toxic waste. South Africa is facing a waste crisis, but efforts can be made to reduce the negative environmental impacts. According to Douw 2022, approximately 54 million metric tons of waste are produced on a yearly basis in South Africa, the majority of which ends up in landfills (United Nations Waste Management).

According to Davranche et al. (2011) and Grybos et al. (2007), dissolved organic matter plays a critical role in REE release, while Fe-Mn oxides are the greatest source of released REEs, according to Mihajlovic et al. (2017). As a result, soil and sediment properties, as well as water factors, have an impact on REE mobilization. Du et al. (2021) investigated the geochemistry behaviour of rare earth elements on the topsoil of abandoned rare earth mine tailings with simulated rainfall leaching. Their results showed that mainly light rare earth elements migrated during the leaching, with the maximum migration value at a depth of 15 cm.

Wen et al. (2013) studied soil acidification and the leaching of rare earth elements from simulated soils. Their results showed that acid rainwater of pH below 3.5 promotes the transfer into soils. Locations around rare earth mining areas leaching REEs into soils and streams. Weathering has shown that REEs are leached into soils and streams (Liu *et al*., 2019). The REE mobility is strongly dependent on the soil solution acidity (Fernández-Caliani *et al*., 2009). The speciation of REEs usually determines the solubility and bioavailability of a substance (Khan *et al*., 2017).

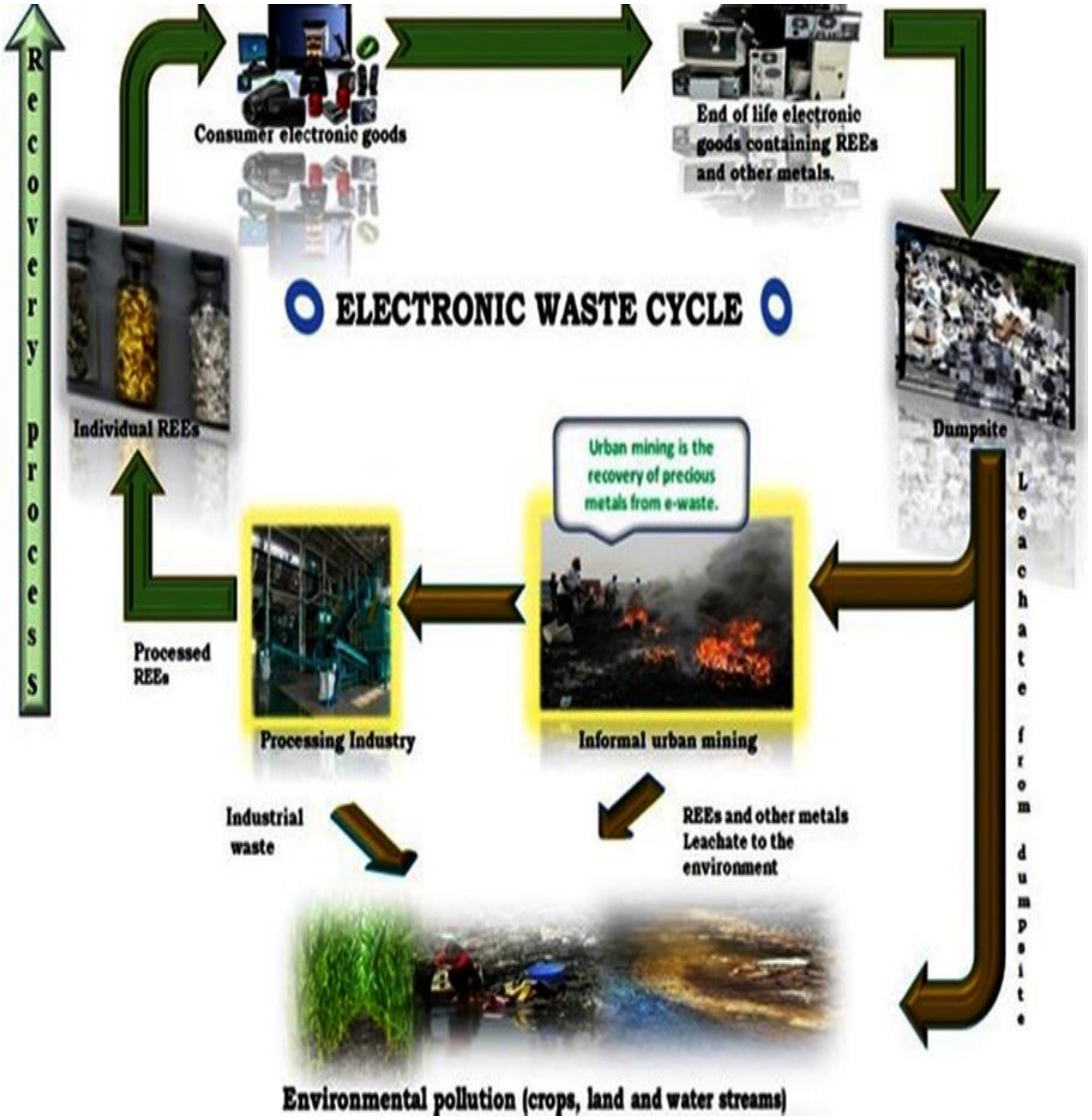


Figure 2. 5: **Electronic waste urban mining cycle.**

2.5.9. Electronic waste environmental pollution

2.5.9.1. Soil and sediments contamination by e-waste

Toxic heavy metal pollution is found naturally in the earth and becomes concentrated as a result of human activity and most of them can be toxic to all forms of life at high concentrations due to the formation of complex compounds. Sediments act as sinks for heavy metals and become an immediate source of heavy metal pollution in the water bodies (Goher *et al*., 2014).

Sediment analysis is a good proxy for the assessment of the geochemical status and environmental qualities. Soil and sediments are contaminated chiefly by landfill e-waste pollution from dumping sites and recycling sites (Kumar *et al*., 2018; Adesokan *et al*., 2016; Moeckel *et al*., 2020; Hoa *et al*., 2020 and Zhang *et al*., 2012). These studies have shown that the concentration of contaminated elements is highest in the topsoil and near the exposed site.

2.5.9.2. Aquatic Pollution from e-waste

The aquatic environment is at a potential high risk, because the piles of e-waste components are scattered and stored in waste dumps, which are routinely soaked or flooded by rainfall, producing run-off into local rivers. On the other hand, contamination of water and sediment can take place through infiltration or resuspension of the particles. In a study conducted by Amoyaw-Osei et al. (2011), water and sediment sample results showed that e-waste-related contaminants have entered Ghana's rivers and added to the pollutants from other sources migrating to the water bodies. Aquatic organisms may absorb metal pollutants directly from the water or indirectly via uptake from the food chain. Most metals exposed by e-waste are highly persistent, toxic in trace amounts and can potentially induce severe oxidative stress in aquatic organisms. Therefore, it is crucial to develop risk assessment methods to determine the degree of contamination of e-waste with the environment and then take effective measures to reduce the pollution.

2.5.9.3. Air pollution from e-waste

Even though exposure through ingestion of food is the obvious exposure route, contaminated air can still negatively impact the environment, including humans and wildlife (Julander *et al*., 2014). Song and Li (2014) showed that children inhale roughly twice as many toxic chemicals in the air compared to adults. Toxicological investigations and information on REE-associated health effects have been relatively thin up until recent years, but with the demand for these metals, it’s proving inexorable to ignore (Pagano *et al*., 2015).

2.5.10. Effects of electronic waste on human health

A study by Henríquez-Hernández et al. (2017) revealed that people with anaemia had higher levels of Pb, REEs and minority minerals that are widely used in the manufacture of consumer electronic devices. Table 2.4 illustrates some of the concerns about the impact of e-waste on human health and the environment. The e-waste can be both valuable as a secondary raw material source and toxic if not treated and discarded improperly. Tsydenova and Bengtsson (2011) classified e-waste as hazardous substances having adverse health and environmental implications.

Table 2. 4: Illustration of e-waste impact on human health and the environment.

Human Health	**Environment**
Asthmatic bronchitis	Ground and surface water pollution
Kidney and brain damage	Toxic chemicals in landfills
Bone and skin diseases	Acidification of soil
Central and peripheral nervous systems, damage to the reproductive system	Vegetation pollution through contaminated ground water
Heart, liver and spleen damage	Air pollution
Cancer	Aquatic life

Electronic devices contain an excess of components and parts, many of which contain portions of toxic chemicals that are harmful to humans and aquatic life once the more fragile exteriors begin to break down. Together with inorganic pollutants, e-waste components contain toxic compounds like PCBs and dioxins. Some of these components that contribute to the toxic waste include batteries, circuit boards, cathode-ray tubes, and lead capacitors (Perkins *et al.*, 2014). The toxic and harmful substances contained in mobile phones will cause severe effects to the environment and human health if disposed of improperly (Lim and Schoenung, 2010).

Naturally, the metals from e-waste can be leached into the environment by chemical or biological processes. Chemical leaching involves inorganic acids such as hydrochloric acid, sulphuric acid, nitric acid, a combination of various mineral acids, or ligand-assisted complexation. In places where acid rain is common, like Cape Town, South Africa, the leaching of metals is accelerated. Bioleaching is based on the natural ability of microbes to transform solid metallic compounds into their soluble and extractable forms. Oxidizing bacteria, including Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, Pseudomonas, Aspergillus, and Penicillium, are major microbes in metal bioleaching (Needhidasan *et al.*, 2014). Piles of e-waste that are exposed to extreme weather conditions, such as high temperatures, may explode and release toxic substances if they catch fire. The wet conditions created by rain may enable the devices to soak and break up, releasing enclosed metals. These devices will scatter, transport, and cause soil and surface water pollution where aquatic life exists (Basel Convention, 2009). Table 2.5 illustrates the relevant adverse effects of REEs, such as severe skin conditions, lung infections, and chest pains. For this reason, REEs have been included among the new and emerging occupational and environmental health risks by several international organizations (Pagano *et al.*, 2015). The toxicity studies done by Hirano and Suzuki (1996) on mice and rats showed that the REEs have moderate toxicity based on the different dosages administered. In another study by Bruce et al. (1963), the results of toxicity tests performed by intraperitoneal administration of the rare earth nitrates to female mice showed most of the mice poisoned got depressed after an hour, with those that remained in a depressed state for 8 hours eventually dying after 24 hours. Elsewhere, another study by Carpenter et al. (2015) revealed that elevated soil levels of REEs have an adverse effect on agricultural plants; therefore, monitoring of sites near REE mines and processing facilities is of great importance.

Table 2. 5: The toxicity of rare earth elements to humans and animals.

Z	Element	Symbol	Toxicological effects
21	Scandium	Sc	Considered non-toxic but dangerous when its gases are inhaled with air.
39	Yttrium	Y	Chest pains, shortness of breath, coughing and cyanosis. Caused lung and liver damage in experiments on animals, may cause lung disease to humans.
57	Lanthanum	La	Headache and nausea. In animal experiments it caused low blood pressure and hyperglycaemia.
58	Cerium	Ce	Powerful oxidising agent to react with combustible matter. Animals injected with cerium died of cardiovascular collapse. Pneumoconiosis to humans.
59	Praseodymium	Pr	Very low to moderate toxicity to humans.
60	Neodymium	Nd	Low to moderate toxicity, its dust and salts are irritant to eyes, mucous membranes and skin.
61	Promethium	Pm	Radioactive and unstable to be found in nature
62	Samarium	Sm	Low to moderate toxicity. Insoluble salts are non-toxic and the soluble ones slightly toxic.
63	Europium	Eu	Low toxicity compared to other REEs.
64	Gadolinium	Gd	Ulcers on abraded skin. A free ion of Gadolinium is highly toxic.
65	Terbium	Tb	Low to moderate toxicity. Skin irritant on contact.
66	Dysprosium	Dy	Insoluble salts are non-toxic and the soluble ones slightly toxic when ingested.
67	Holmium	Ho	Low acute toxicity.
68	Erbium	Er	Low to moderate toxicity.
69	Thulium	Tm	Low to moderate toxicity. Insoluble salts are non-toxic and the soluble ones slightly toxic. Thulium salts not absorbed by plants and hence does not get into the human food chain.

Continued

Z	Element	Symbol	Toxicological effects
70	Ytterbium	Yb	Compounds of Ytterbium are highly toxic and known to cause irritation to eyes and skin, and some might be teratogenic. Ytterbium dust causes fire and explosion hazard.
71	Lutetium	Lu	Low to moderate toxicity especially when powder is inhaled and upon contact with skin. May explode when heated.

2.5.11. Pollution indices for contamination assessment

Pollution indices are widely considered a useful tool for the comprehensive evaluation of the degree of metal contamination. The enrichment factor, the accumulation index, the potential ecological risk index factor and the potential environmental hazard index are common indices used in pollution assessment (Barbieri, 2016; Nowrouzi and Pourkhabbaz, 2014; Muzerengi, 2017).

2.5.11.1. Contamination factor (CF)

Contamination factor (CF) is used to indicate the level of contamination by metal and is calculated as:

$$CF = \frac{M_s}{M_b} \qquad Eqn\ 2.15$$

Ms and Mb are metal concentrations in the sediment analysed and the background concentration of the corresponding metal.

2.5.11.2. Geo-accumulation Index

Geo-accumulation index (I_{geo}) is a simple method used to quantify and assess the extent of trace elements contamination by comparing the actual metal concentrations in sediments with the geochemical background. It is calculated as:

$$Igeo = log2\left[\frac{Cn}{1.5Bn}\right] \qquad Eqn\ 2.16$$

where *Cn* is the concentration of metal analysed, *Bn* is the background level of the metal and 1.5 is the background matrix correction factor due to lithogenic effects.

2.5.11.3. Enrichment Factor

The Enrichment Factor (EF) may be theoretically described, and it can be approximated by comparing the examined element to a reference element in the sediments. Fe may be chosen as a reference element because it is abundant and mostly unaffected by anthropogenic activities. The following is the EF equation:

$$EF = \frac{\frac{E}{FE\ (sample)}}{\frac{E}{Fe\ (background)}} \qquad Eqn\ 2.17$$

where (E/Fe) sample is the ratio of a given element's absorption to the iron content of the sediment sample, and (E/Fe) Background is the ratio of a specific element's absorption to the iron content of the background value.

2.5.11.4. Potential ecological risk index

The potential ecological risk index method is used widely to assess the potential ecological risks posed by heavy metals. The monomial potential ecological risk index for each heavy metal (Eri) was calculated using the equation

$$Eri = T_{ri}\ x\ \frac{C_{ri}}{S_{ri}} \qquad Eqn\ 2.18$$

Where Tri is a factor of the toxic reaction of an individual toxic element, C_{ri} is the measured total concentration in soil and S_{ri} is the geochemical background value of the elements.

2.6. Review of methodology for REEs analysis

2.6.1. Sample Preparation

Sampling electronic waste is not a straightforward procedure because it depends on many factors, including the purpose of the sampling. A successful sampling strategy must begin with a meticulous plan and established protocols. In recent years, we have seen many studies concerned about e-waste and its surroundings. The studies in the literature include sampling direct and indirect e-waste matrices. These include e-waste components (Nnorom *et al.,* 2010), polluted soils by e-waste and dust (Bi *et al.,* 2011), contaminated water (Leung *et al.,* 2006), human blood and hair samples of exposed humans (Wang *et al.,* 2012; Li *et al.,* 2013), pregnant women (Zhang *et al.,* 2011), and vegetables (Li *et al.,* 2013). The heterogeneous nature of e-waste components makes sampling complicated; therefore, ideal sampling protocols must be followed. This involves procedures such as collection, cutting, shredding, sieving to 2 mm, crushing and milling e-waste components (Nnorom *et al.,* 2010). Each step is vital to increasing surface area, homogenisation and size reduction to the desired particle size, usually less than 50 µm. Other steps may include sieving, gravity or magnetic separation and ashing to concentrate or dilute specific elemental species in the original sample matrix. The sample preparation has been considered the most significant step before the determination by many instrumental techniques such as inductive coupled plasma-optical emission spectroscopy (ICP-OES), inductive coupled plasma-mass spectroscopy (ICP-MS) and atomic absorption spectroscopy (AAS) (Makombe *et al.,* 2017). Soil sampling is particularly complex because of the multitude of geological and biological materials resulting from weathering and degradation, including particles of different sizes with varying surface and chemical properties. For the determination of pollutants, the area needs to be illustrated into plots, soil samples taken at different profiles using a stainless steel shovel, and ground water samples taken and sent to the laboratory for analysis. Samples from a depth of 0–10 cm (topsoil) and 11–30 cm (subsoil) are normally collected for soil sampling (Olafisoye *et al.*, 2013; Adesokan *et al.*, 2016). After collection, it is necessary to remove stones, roots, course materials and any other foreign matter. Drying and sieving to 1 mm is strongly advisable. To avoid contamination, the samples should be stored in clean polyethylene bags (Ziploc).The case of sediment samples is kept in a freezer below 4 °C or freeze dried and kept in a desiccator after sampling and before analysis (Makombe *et al.*, 2017).

The surface water bodies are easily contaminated by run-off water and leaching from e-waste dumps, industrial processing plants and mining environments. Eventually, surface water finds its way into underground water resources. The shift in water chemistry affects humans and organisms that depend on this water. Proper sampling techniques are vital for the determination of both organic and inorganic particulates in water. These include using clean containers, rinsing containers to avoid contamination, using filtration to remove suspended particulates, acidification, and storing samples below 4 °C (Guo *et al.*, 2009; Makombe *et al.*, 2016; Yao *et al.*, 2008). Sampling water for rare earth metal analysis can be treated in the same manner as sampling water for inorganic and heavy metals.

2.6.2. Digestion procedures

The determination of analytes with reproducible and accurate results in routine analysis needs the complete digestion of the sample. Different methods of digestion have been employed to decompose REEs in different matrices with the focus on detection limit, accuracy, reproducibility and sample throughput. There are different ways to dissolve a sample, depending on its nature, origin, size, elements of interest, and concentration range. The wet digestion dissolution assembly includes the Parr bomb, the Kjeldahl flask, the crucible, quartz and aluminium vessels, PTFE containers, and specially designed apparatus. The use of inorganic acids in many decomposition applications, such as ashing, microwave and open vessel digestions, has been employed. Flux based fusion is widely used in many applications as a powerful digestion technique that includes digesting REEs in geological matter (Zawisa *et al.,* 2011; Whitty-Leveille *et al.*, 2017). The evaluation of different digestion conditions on printed circuit board combination fines was investigated by Ehi-Eromosele et al. (2012). According to the other group of researchers in Nigeria, dust was sampled at an e-waste recycling site and analysed for heavy metals using different digestion techniques (Ehi-Eromosele *et al*., 2012). The digestion methods were aqua regia and dry ashing, followed by aqua regia and nitric acid digestion, followed by extraction with hydrochloric acid. The aqua regia and nitric acid digestion produced better and comparable results for most elements.

The decomposition of e-waste rich in organic content requires oxidising acids, mostly nitric acid and hydrogen peroxide reagents. Plastic material in e-waste needs to be dehydrated in-situ by the addition of sulphuric acid. A wide range of digestion methods have been developed for the analysis of e-waste and related materials. Among them is the dissolution routinely attained by acid attack at atmospheric or elevated pressures, microwave-assisted digestion and alkaline fusion. Diverse digestion protocols have been developed to date, but unfortunately, the distinctive nature of the protocols and the e-waste material make comparison very difficult.

The dominant nature of e-waste is heterogeneous in composition; thereby, knowledge of the chemical forms of the metals available in the waste matrix is highly important to standardise the digestion protocols. Table 4 illustrates some of the main elements of the digestion protocols for e-waste. Different or combinations of acid conditions have been employed on a variety of e-waste materials; however, nitric acid is the most popularly used acid because of its oxidative capability and the dissolution of most salts (Whitty-Leveille *et al.*, 2017).

2.6.2.1. *Open Vessel Acid Digestions*

This is the most prevalent digestion method in analytical laboratories for the digestion of various matrices that include geological materials, sediments, soils and solid waste materials. This is carried out under atmospheric pressure, either in an open beaker or via reflux. The temperature attained is controlled by the boiling points of the acids, which are used either simultaneously or sequentially. The general acids used in wet chemical digestions are HCl, HNO_3, $HClO_4$, HF and H_2SO_4. Aqua-regia is a mixture of HCl and HNO3, and it is widely used because of its oxidising ability and the possibility that any free chlorine produced in the acid might enhance digestion. It is a highly corrosive, fuming yellow to red solution. The dissolution of cell phone and computer accessories such as liquid crystal displays (LCDs), plastic housing (PH), and printed circuit boards (PCBs) has been reported (Maragkos *et al.*, 2013; Nnorom *et al.*, 2010; Nnorom and Osibanjo, 2011).

2.6.2.2. Microwave Assisted Digestions

The microwave acid digestion system produces clear digestate from samples for elemental analysis by ICP, ICP-MS, or AAS. Rocks, sediments, plants, soil, foods, pharmaceuticals, plastics, metals, and more can be digested easily if a good combination of acids and heating conditions are employed. Microwave heating improves the imperfections of open vessel digestions as it can dissolve refractory elements and REEs with an easy but ideal combination of acids (Helmeczi *et al.*, 2016). The homogeneity and chemical form of the metals in the substrate are also vital. This is achieved by exposing a sample to a strong acid, in a closed vessel and ramping the temperature and pressure through microwave irradiation. Microwave heating is done through radiation with samples and only the sample and not the apparatus, which then improves the energy transfer and reduces digestion time. Table 2.6 illustrates WEEE samples digested with different acids and/or combinations of acids, including (i) conc. HNO_3, (ii) conc. HNO_3 + conc. HCl (aqua regia), (iii) conc. HCl, (iv) conc. HNO3 + Na_2O_2, (v) conc. HNO_3 + conc. HF, (vi) conc. HCl + conc. HF, (vii) conc. HNO_3 + conc. HCl + conc. Das and Ting (2017) evaluated various digestion protocols, which include microwave-assisted digestions with various acid combinations. Recent studies on polymeric e-waste (Iop *et al.*, 2017), computer keyboards (Oliveira *et al.*, 2017) and cell phone PCBs (Knoop *et al.*, 2014; Ogonori *et al.*, 2009) have utilised microwave digestion technique for heavy metals and REEs analysis.

2.6.2.3. Dry ashing

Dry ashing is a technique for determining the composition of a sample in its dry state. Normally, the sample is furnace heated in a crucible at 500-600 ^{o}C (Van Yken *et al.*, 2021). In this technique, water and other volatile materials present in the sample are vaporised upon heating. The full stages of dry ashing comprise sample drying, evaporation of volatile materials, and oxidation of the non-volatile residue to remove organic matter. Ashing acids are sometimes added to samples to accelerate the oxidative process, solubilise any residue, and/or prevent volatilization of the element of interest (Ehi-Eromosele *et al.*, 2012).

$$Ash\ content\ = \frac{M_{(ash)}}{M_{(dry)}}\ x\ 100 \qquad Eqn\ 2.19$$

Where, $M_{(ash)}$ is the weight of the sample after ashing, $M_{(dry)}$ is the weight of the sample before ashing.

Table 2. 6: Overview of the available analytical methods for the qualitative and quantitative analysis of selected parameters on waste electric and electronic equipment (WEEE).

Component	**Target analytes**	**Digestion condition**	**Instrumentation**	**Reference**
Mobile phone waste (PCBs, PHs, LCDs)	Cu	Digestion with inorganic acids with heating followed by filtration. PCBs: 1:3 HNO_3: HCl(aqua-regia); PHs: 1:1 H_2SO_4:HNO_3; LCDs: HCl	ICP-OES	Maragkos *et al.*, 2013
PCBs (Mobile phones and computers)	Cu	Aqua regia leaching, loss-on-ignition and chemical analysis	ICP-OES	Yamane *et al.*, 2011
Mobile phone PCBs	Al, As, Ba, Cd, Pb, Cu, Cr, Fe, Mn, Hg, Pd, Ag, Se, Na, Zn	1:3 HNO_3: HCl(aqua-regia) and H_2SO_4 digestion Qualitative analysis-ground material used.	ICP-OES (SEM/EDS), FT-IR,	Terena *et al.*, 2017
Mobile phones	Ag, Al, Ba, Cr, Cu, Mg, Si and Ti	Mobiles were dismounted, external and internal polymers were cut to 1 mm thickness.	LIBS	Aguirre *et al.*, 2013
PCBs (routers, mobile phones, smartphones)	Total of 41 elements that includes: Ag, As, Au, Be, Cd, Cr, Cu, Hg, Ni, Pb, Pd, Pt and Rh,	Aqua regia leaching, pyrolysis at 550◦C then leaching, fusion of the residual ash with $LiBO_2$ and subsequent dissolution in HCl	ICP-Sector Field Mass Spectrometer (ICP-SFS).	Holgersson *et al.*, 2017
Mobile phone, LCD, Circuit boards	REEs (La, Ce, Pr, Nd, Gd, Dy, Er, Y) and selected heavy metals	Microwave assisted digestion with HNO3 acid	ICP-OES	Knoop *et a*l., 2014
PCBs, LCDs (Mobile phones and comuters)	Multi elements that includes: Ag, Al, Au, Cu, Fe, Pd, Sn and Zn	Aqua regia, HNO_3 + HF + microwave and Na_2O_2 fusion + HCl dissolution	XRF, ICP-OES, SEM and energy-dispersive X-ray spectrometry (EDS)	Dervišević *et al.*, 2013

CONTINUED

Component	**Target analytes**	**Digestion condition**	**Instrumentation**	**Reference**
Computer accessories (PCBs, PHs, LCDs)	Al, Cu, Cr, Fe, Pb, Ni, Zn, As, Cd, Sn and Hg	Digestion and chemical analyses	ICP-MS	Kolias *et al*., 2014
Computer monitors	Cu, Cr, Pb, Ni	Computer monitor digested with sequential acids 1:1 HNO_3, concentrated HNO_3, H_2O_2 and HCl; Plastics digested with 1:1 (H_2SO_4 : HNO_3)	AAS	Nnorom *et al.*, 2010
Computer keyboard	As, Cd, Co, Cr, Cu, Ni, Pb, Sb, and Zn	HNO3 and HCl	ICP-OES and ICP-MS	Oliveira *et al*., 2017
Computer components	Cu and Pb	Refluxing with acids 1:1 HNO_3 and concentrated HNO_3 followed by heating with H_2O_2 and HCl	AAS	Olubanjo *et al*., 2015
PCBs (smartphone, mobile phone, laptop)	(Cu, Fe, Ni, Al, Zn, Pb, Cr, Mn, Co, Mo, Cd, Ag, Au, Pr, Dy, Pd, Pt, La, Ce	Open acid and/or Microwave digestion with HCl, HNO_3, H_2O_2.	ICP-OES	Tunali *et al.,* 2021

2.6.2.4. Alkaline Fusion Digestions

Alkali fusion is a process in which complex and other compounds in minerals are being destroyed into components by heating through a very high temperature with the aid of a fluxing agent, usually a basic material. Despite being effective, alkali fusion presents some disadvantages, such as the use of large amounts of fluxing agent, possible contamination, high blank levels, time consumption and tediousness. The application of this method requires complete dissolution of the sample matrix, which is difficult for samples containing refractory minerals that are commonly enriched in Zr, Hf, and REEs (Pinto *et al.,* 2012). The recoveries using partial dissolution procedures such as open acid and microwave-assisted digestion are low because of incomplete dissolutions (Navarro *et al*., 2008; Todand *et al.,* 1995). Table 2.6 reveals some existing methods for e-waste determination. However, no attempted research to date has been reported on using this dissolution procedure for the determination of REEs in WEEE. This has galvanised us to explore the advantages of this technique and apply it to e-waste determination.

2.7. Instrumental Techniques for REE Analysis

2.7.1. ICP-OES

ICP-OES is one of the most commonly used techniques with multi-element capability for the analysis of REEs. Due to its magnificently low detection limit, high precision and accuracy and rapidity, the ICP-OES technique is recognized as an effective technique for the quantitative determination of REEs in various matrices (Zawisa *et al.,* 2011). The REEs possess very narrow atomic emission lines, which require high-resolution detectors such as charge-coupled detectors (CCD). Tables 4 and 5 show the ICP-OES technique applied to multi-element e-waste analyses. Among the reporters are Knoop et al. (2014), who determined Ag, Al, Be, Co, Cr, Cu, Nb, Pb, Sb, Sn, Ti and Zn (non-REEs) and Ce, Dy, Er, La, Nd, Pr and Y (REEs) in mobile phones, LCDs, and circuit boards. They utilised the dilution technique to overcome high levels, while low level determination and detection limits were monitored by a low calibration standard. They carefully chose only 10 analytical lines from 280 lines for 7 REEs to achieve interference-free determination. Dealing with interferences in e-waste determination is critical since the matrix is rich with other elements, as graphically shown in Figure 2.6. A review by the same group, Puype et al. (2017), highlighted the use of ICP-OES in the detection of contaminants from WEEE in plastic food contact material. The ICP-OES has the capability to reach 10 ppb to sub-ppb depending on sample preparation technique and matrix effects within the sample.

Conventional analytical techniques in related studies reported the determination of REEs in natural water and wastewater by ICP-OES or ICP-MS (Zhu *et al.,* 2010; Bendakovská *et al.,* 2016; Makombe *et al*., 2016); geological materials (Pinto *et al.*, 2012; Helmeczi *et al.,* 2016; Zawisa *et al.,* 2011), spent catalyst from an oil refinery (Silva *et al.,* 2014), sediments (Makombe *et al.,* 2017) and contaminated soil (Gutiérrez-Gutiérrez et al., 2015). A comparison of plasma-based techniques compiled by Whitty-Leveille et al. (2017) showed that ICP-OES and ICP-MS, aided by proper digestion procedures, are effective for REEs analysis on geological matter. The physical and chemical similarities between the REEs complicate the accurate quantification due to spectral interferences and coincidences. The LREE oxides and hydroxides can cause polyatomic interferences on HREEs; therefore, a careful line free of interferences is essential.

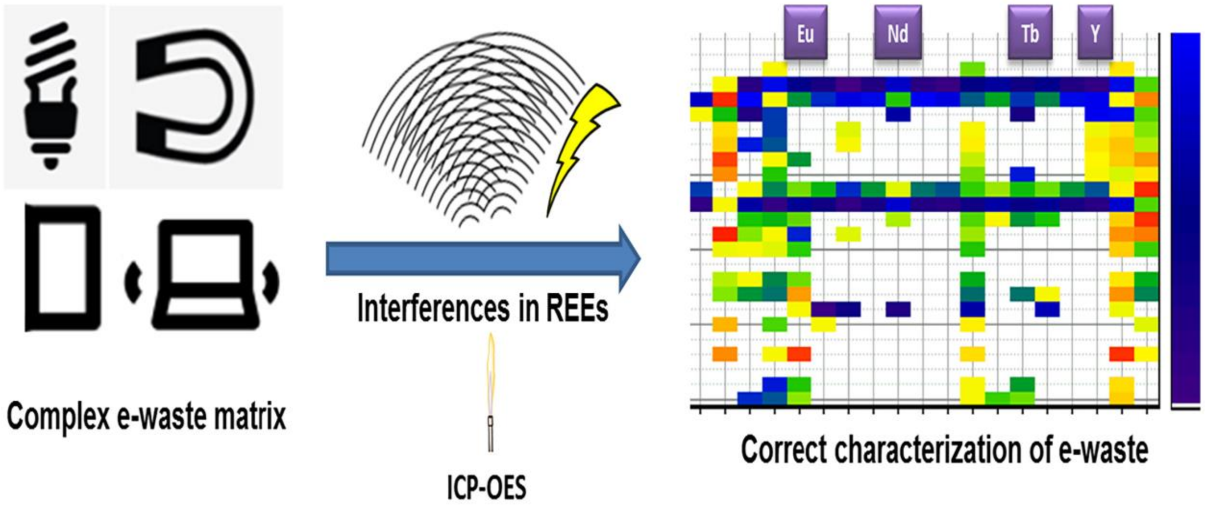


Figure 2. 6: Complex ICP-OES interferences in e-waste determination (adapted from (Patil *et al.*, 2022)).

2.7.2. ICP-MS

Among the reported techniques, inductively coupled plasma mass spectrometry (ICP-MS) is considered one of the most powerful techniques for this purpose due to its high sensitivity, specificity, isotopic measurements, multi-elemental capacity and a large linear working range. The main advantages of this technique are its extremely low detection limits, large dynamic range and detection of the isotopic composition of elements. The major barriers to ICP-MS detection are the occurrence of spectral and non-spectral interferences and the capital and operating costs. The formation of oxides and the refractory nature of REEs are some of the usual limitations of ICP-MS. Nevertheless, Silva et al. (2014) developed an ICP-MS method using ammonia in a reaction cell to overcome polyatomic interferences on the signal of Gd, Lu, Nd and Yb in spent catalyst samples.

The simultaneous quantification of 49 elements associated with e-waste in human blood by González-Antuña et al. (2017), demonstrated that the limit of quantification (LOQ) can be as low as 0.06 ng/mL for the REEs. Kolias et al. (2014), presented data on the determination of the toxic metal content of printed circuit boards, monitors, plastic housing of two cathode ray tube (CRT) monitors, three liquid crystal display (LCD) monitors, one LCD touch screen monitor and six motherboards. In general, except for Pb, higher metal concentrations were detected in motherboards in comparison with plastic housing and glass samples. Holgersson et al. (2017) analysed components of 30 mobile phones from different manufacturers using an ICP-Sector Field Mass Spectrometer (ICP-SFS). The metals determined included Ag, As, Al, Au, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Nb, P, Pb, Pd, Pt, Rh, Sc, Si, Sr, Sb, Sn, Ti, V, W, Y, Zr and Zn. Generally, most of these metals were found in mobile phones, with Pb being lower in modern phones than in older phones, which is a positive development credited to manufacturers. Studies on REEs have been carried out on people exposed to the e-waste environment, as shown in Table 2.7. Blood, urine and human hair were sampled and they showed positive values of REEs as compared to non-exposed human beings. Henriquez-Hernandez *et al.* (2017) reported REEs in the blood of exposed workers. Li *et al.* (2016) reported the concentration of REEs in urine from workers at manufacturing plant of cerium and lanthanum. They obtained limits of detection and quantification in the range of 0.009–0.010 mg L^{-1} and 0.029–0.037 mg L^{-1} by ICP-MS.

Table 2. 7: **Concentration of various REEs in WEEE and associated environments**

Sample matrices	**Instrument**	**Concentration**	**Reference**
Mobile phone LCD only Circuit boards	ICP-OES ICP-OES ICP-OES	Nd (1040), La (107), Pr (88.2), Dy (47.9), Y (4.58), Er (4.58), Ce (ND) (mg/kg) Nd (32.5), La (50.6), Pr (ND), Y (7.8), Er (ND), Ce (85.3) (mg/kg) Nd (ND), Lu (ND), Pr (ND), DY (ND), Er (ND), Y (1.02-4.37), Ce [6pcs(ND), 1 pc (32.4), 1 pc (25.1)] (mg/kg)	Knoop *et al*., 2014 Knoop *et al*., 2014 Knoop *et al*., 2014
Computer monitor powder	XRF, XRD, AAS	Ce (0.02), Nd (0.02), Eu (0.06), Y (17.0) (wt.%)	Resende and Morais, 2010
Polymeric food contact articles (FCAs)-Egg cutter	ICP-OES	La (2.40), Nd (2.51), Pr (4.54), Dy (0.42), Er (1207.12), Y (1.99) (mg/kg)	Puype *et a*l., 2015
Blood (exposed workers to e-waste)	ICP-MS	Ce (0.02), Eu (0.02), Er (0.01), Nd (0.05), Pr (0.01), Sm (0.02) (ng/ml).	Henriquez-Hernandez *et al*., 2017
Urine (exposed workers)	ICP-MS	La (1.07), Ce (1.13), Pr (0.02), Nd (0.01), Sm (0.01), Eu (0.01), Gd (0.02), Tb (0.01), Dy (0.01), HO (0.01), Er (0.01), Tm (0.01), Yb (0.01) Lu (0.01), Y (0.01) (µg/L).	Li *et al*., 2016
Human hair (Female residents)	ICP-MS	La (161.0), Ce (402.3), Pr (32.8), Nd (131.4), Sm (19.4), Eu (4.8), Gd (12.9), Tb (1.2), Dy (5.6), Ho (1.0), Er (17.1), Tm (0.3), Yb (2.1), Lu (0.3), Y (25.4) (ng/g)	Wei *et al*., 2013
Human hair (Male residents)	ICP-MS	La (194.7), Ce (483.5), Pr (40.0), Nd (158.8), Sm (24.9), Eu (4.3), Gd (14.9), Tb (1.6), Dy (6.5), Ho (1.0), Er (37.2), Tm (0.4), Yb (2.6), Lu (0.4), Y (30.3) (ng/g)	Wei *et a*l., 2013

2.7.3. Instrumental Neutron Activation Analysis (INAA)

Neutron activation analysis has been an analytical technique widely used for the determination of REEs in various matrices. However, even these powerful methods have several problems, like high costs, low throughput and inter-element interference, which makes their use toilsome. The major advantage of this application is that no sample digestion, extraction, volume loss, or dilution is required. Among the nuclear techniques, NAA is widely used in geological materials for REEs determination (Stosch, 2016; Silachyov, 2016), in heavy metals and REEs in phosphate fertiliser ingredients (Abdel-Haleem et al., 2001) and in plants and soils (Krafka *et al.*, 1999). Salvini et al. (2006) proclaimed good correlation results for REEs and Ir determination by NAA and ICP-MS in soil samples. The results showed good capability of NAA even at low detection limit levels. According to the documented studies to date, so far, no uses of NAA analysis in e-waste have been reported. The elemental analysis, including REEs, of shredded e-waste material by NAA yielded positive results that correlated with results from high-energy photons from instrumental photon activation analysis (IPAA) (Segebade *et al*., 2005). Cheraitia et al. (2018) detailed another procedure for neodymium recovery from e-waste and subsequent analysis by NAA.

2.7.4. X-Ray Fluorescence

X-ray fluorescence (XRF) spectroscopy is a powerful non-destructive technique used for routine chemical analyses of major, minor and trace elements in rocks, soils, sediments and fluids. The low cost of sample preparation, instrument stability and ease of use make XRF one of the most widely used radio-analytical techniques. Matrix affects quantification; careful optimisation of the parameters and reference samples that potentially match the unknowns should be used for precise calibration. Due to the wide range of matrix compositions and the lack of suitable reference materials in heterogeneous e-waste matrices, the quality of the results may be compromised. Sample preparation for XRF is mainly done with pressed powder pellets or lithium-borate fused beads (Willis and Duncan, 2008).

The XRF technique has been applied for the determination of REEs since about 1970 (Schramm, 2016). The two common XRF techniques are wavelength-dispersive x-ray fluorescence (WDXRF), which measures the wavelength of an element individually and energy-dispersive X-ray fluorescence (EDXRF), which gathers data for all elements in a sample at the same time (Willis *et al.*, 2014). The later technique is regularly used on handheld XRF spectrometers with better energy resolution (Willis *et al*., 2014). Portable XRF analysers are useful in REE recycling, including printed circuit board finishes, leads, terminations, solder and internal or external interconnects, to detect elemental compositions. When compared to EDXRF, WDXRF exhibits superior peak resolution of elements and sensitivity of trace elements.

Beccagutti et al. (2016) successfully determined the concentration of chlorine and bromine in mixed plastics from WEEE using EDXRF. In recent studies, total reflection X-ray fluorescence (TXRF) spectroscopy analysis has been gaining momentum for trace elemental determinations down to the ppb level. This can be achieved by adding even a drop of liquid to the sample carrier, drying it and then performing the measurement (Bilo *et al.*, 2015). Elaseer *et al.* (2015), quantitatively determined Fe, Cu, Pb, Ni and Cr in e-waste samples using TXRF spectroscopy in conjunction with microwave-assisted digestion. In their study, the average concentrations of metals in electronic circuit boards were quantified in the order of Fe (3.53%), Cu (2.11%), Pb (1.66%), Ni (1.60%) and Cr (0.11%). In a similar study, Fink et al. (2000) reported Ti, Zn, Br, Cd, Sn, Sb, and Pb in recycled thermoplastics from electronic waste by (TXRF).

2.7.5. X-Ray Diffraction

X-ray Diffraction (XRD) measures phases, components, and other structural factors such as grain size, crystallinity, and crystal defects (Mahaptra *et al.*, 2019). This technique is used for analysing a wide range of materials, including pharmaceuticals, plastics, minerals, metals, and waste materials, to determine the component phase. In e-waste, the technique has been used for the speciation and characterization (Lopez *et al.*, 2016) and the crystal structure of the magnetite particle (Iqbal *et al.*, 2022). Sharada et al. (2021) found that most of the waste PCBs were made up of metallic copper, tin, lead, aluminum, and iron using the XRD technique.

2.7.6. Laser-Induced Breakdown Spectroscopy (LIBS)

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopic technique which uses a focused pulsed laser beam to provoke optical sample excitation (Anabitarte *et al.*, 2012). The technique can provide quantitative chemical analysis for heavy metals, REEs and can also detect brominated flame retardants which make it versatile in a wide range of applications. The sensing technology of LIBS makes it useful for characterisation and identification of materials. More recently, it has been demonstrated that LIBS can be applicable in e-waste determinations. It's used in recycling of solid waste to identify material composition has been reported (Bakker and Xia, 2015). Analysis of metals in computer and mobile phone scrapes (Aquino *et al.,* 2015), identification and classification of polymer e-waste (Costa *et al.,* 2017), mobile phones (Aguirre *et al.*, 2013) have been reported recently. According to Aguirre *et al.* (2013), they developed a LIBS emission spectra technique using chemometric strategies which reveal identification of manufacturer and counterfeit products. Despite the challenges that involve calibration for accurate quantification by LIBS, its use in elemental quantification in scraps of computer and mobile phones is attractive due to minimum sample preparation, non-destructive, low running cost and fast response.

2.7.7. Atom Absorption Spectrometry

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements at a specific wavelength. The amount of light absorbed by the sample is proportional to the concentration of the element being measured. This technique has not been widely used for REEs analysis because of its inability to excite the refractory nature of the elements. The major limitation is the flame, which is not hot enough even with the addition of nitrous oxide flame for accurate determination of refractory nature elements. Additionally, the nebulisation system is inefficient as only a small fraction of the sample reaches the flame and has a shorter light path to the atomised sample (Makombe *et al.*, 2017). In the work by Nnorom et al. (2010), computer parts comprising printed wiring boards (PWB), cathode ray tubes (CRTs) and plastic housing units were dismantled, digested and analysed for heavy metals (Pb, Cr, Ni and Cu) using AAS. In the work done by Zhu et al. (2010), Pb and Cu concentrations were measured in waste computers by AAS after acid digestion. The parts disassembled were the printed wiring boards (PWB) of the CPUs and the cathode ray tube (CRT) of the monitor. High levels of Pb and Cu were obtained, which were above the toxicity threshold limit. In Lagos, Nigeria, the work reported by Ofudje et al. (2014), determined the concentration of heavy metals in dust and soils near e-waste dismantling sites using the AAS technique. Table 2.6 demonstrates some of the work done on e-waste analysis by AAS. However, according to the literature, no REEs determinations on e-waste by AAS have been reported.

2.7.8. Electroanalytical Techniques

Electrochemical techniques such as cyclic voltammetry (CV), square wave stripping voltammetry (SWSV), differential pulse stripping voltammetry (DPSV) and adsorptive stripping voltammetry (AdSV) have been developed for REEs analysis in various matrices (Li *et al.*, 2004; Li *et al.*, 2006; Liu *et al.*, 2005; Javanbakht *et al.*, 2008; Javanbakht *et al.*, 2009). In a previous study, Makombe et al. (2016) successfully determined LREEs, namely, La(III), Ce(III) and Pr(III) in water sampled near a REEs resource site. The electrochemical sensors combined selectivity, sensitivity, simplicity and rapidity for monitoring environmental sites. The development of sensors through electrochemical techniques has helped to rapidly analyse the REEs. However, most researchers still find it difficult to analyse all the REEs using electrochemical techniques because of their chemical complexity. In the literature to date, no REEs analyses by electroanalytical techniques have been reported on e-waste.

2.7.9. Spectroscopic Techniques Summary

In e-waste determination, the problem is exacerbated by the availability of a host of other metals with varying concentrations. When selecting a specific instrument, several factors must be considered, such as the matrices to be analysed, the elements to be determined, the detection limits required, and the measuring times. Table 2.8 illustrates some criteria used in choosing the ideal spectroscopic instrumentation. Among the instrumental technologies for the quantification of REEs, ICP-OES and ICP-MS plasma-based spectroscopy showed superior detection capabilities, a wide dynamic concentration range and better throughput. Critical comparisons of the results of e-waste determination are no easy task due to the heterogeneity of the samples and different methods of analysis (Zhu *et al.*, 2010).

Table 2. 8: **An illustration of the analytical criteria used in spectroscopic instrumentation.**

Analytical criteria	**Flame AAS**	**INAA**	**XRF**	**ICP-OES**	**ICP-MS**
Detection Limits	Not good for REEs La = <4000 ppb	Good for most elements La = <0.05 ppb	Not good for trace levels La = >10 ppm	Good for most elements La = <0.05 ppb	Excellent for most elements La= <0.005 ppb
Precision					
Short term	0.1-1%	1-5%	1-3%	0.3-2%	0.5-3%
Long term	2-5%	3-10%	2-5%	2-5%	2-5%
Sensitivity	Moderate	High	Low to Moderate	High	Excellent
Dynamic range	10^2	10^5	10^6	10^6	10^8
Sample throughput	10-15 secs per element	2-4 mins ± 30 elements	15-60 secs per element	± 60 elements per minute	± 60 elements per minute
Interferences					
Chemical	Present	Very few	None	Minimum	Periodically
Spectral	Minimum	Very few	High	Many	Few
Ionisation	Some	None	None	Many	Many
Sample volumes required	± 2 ml required per element	< 1 g	3 g – 10 g required	± 3 ml required	± 2 ml required
Isotopic analyses	No	Sometimes	No	No	Yes
Easy of use	Very easy	Ease to moderately easy	Easy	Ease to moderately easy	Moderately easy

2.7.10. Other Techniques

Alongside quantitative analyses, many other techniques have been useful in the qualitative determination of REEs and other elements in e-waste. Among the techniques that have been used for REEs analysis are Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), ultra-violet visible spectroscopy (UV-VIS) and pourbaix diagrams for thermodynamic study. SEM analysis provides images of sample surface topography, which provide valuable qualitative data (Das and Ting, 2017).

2.8. Summary

The review of data on REEs from e-waste revealed their effects on the environment and human health. The toxicity of the chemicals in e-waste causes harmful effects to humans and aquatic life. It was also observed that the combination of plastics, heavy metals, precious metals and REEs in e-waste increases the toxicity levels of air, water, and soil. The metals leach into the environment and the weather conditions may accelerate the leaching process. The information on heavy metals in e-waste have been investigated a couple of times by many researchers, but the data on REEs is very thin to date and this has allowed the current review to focus on REEs only. The sampling protocols for e-waste and its corresponding environment have been reviewed in this paper. It was also shown that sampling e-waste is a huge challenge because of the dissimilarity of the sample and the particle size fraction. Sampling is the backbone of accurate quantification of analytes in a sample and, hence, should be treated with high consideration. The sample dissolution procedures pertaining to REEs in e-waste have been explored. The vital part is to completely decompose the sample to liberate the REEs, which can then be accurately determined by an appropriate instrumental technique. According to the review, wet acid digestions using single or acid combinations such as aqua-regia are popular for e-waste dissolution. This can be achieved via open or closed vessel dissolutions. The microwave assisted digestions provide an excellent closed vessel technique by means of pressurised vessels with elevated temperatures attained in the process. The alkaline fusion processes for digesting REEs have been widely used in geological samples. This is an excellent complete dissolution technique that can be compatible with e-waste analyses if fully explored. To ensure better REEs dissolution, microwave digestion with a combination of acids and oxidizing agents has been the preferred dissolution approach over open-vessel acid digestions. Diverse instrumental techniques for e-waste quantification in recent years have been elaborated. The choice of the instrument is imperative for achieving the desired precision, sensitivity and accuracy of the result. The criteria for choosing the instrument have been revealed and this helps determine its applicability. Among the instruments, some are best for qualitative information only, such as FTIR, SEM, LIBS and XRD, as opposed to more quantitative techniques such as AAS, INAA, XRF, ICP-OES and ICP-MS. The dissolution method, limit of detection, limit of quantification, and interferences have a strong bearing on the preferred instrument. More recently, in e-waste analyses, it has been shown that ICP-OES and ICP-MS are the preferred instruments for REEs determination. Their simultaneous multi-element determination, low detection limits, wider dynamic range and isotope analyses make them more attractive. In addition, the ICP-MS boasts limited spectral interferences, good stability and low matrix effects. Therefore, it is recommended to explore studies for accurate REEs determination in WEEE using the available instrumental techniques. These findings, together with precise analytical data, will help environmentalists, municipalities, governments and any other organisations dealing with pollution of the environment.

CHAPTER 3

EXPERIMENTAL DESIGN

3.1. Introduction

This chapter describes the sampling methods and characterisation of e-waste materials used in this study. The main focus is rare earth elements determination and leachability from e-waste and in environments originating from electronic waste disposal. Furthermore, the chapter also outlines physico-chemical parameters that may affect leaching in e-waste landfills. The assimilated waste dumps from different e-waste materials are constructed, exposed to natural conditions, and studied for a period. The study design will also focus on developing and improving alkaline fusion as a dissolution technique for e-waste samples. The experimental and spectroscopic techniques used in this research study is outlined which includes an overview of instrument, principles and technique.

3.1.1. Graphical abstract of the experimental study

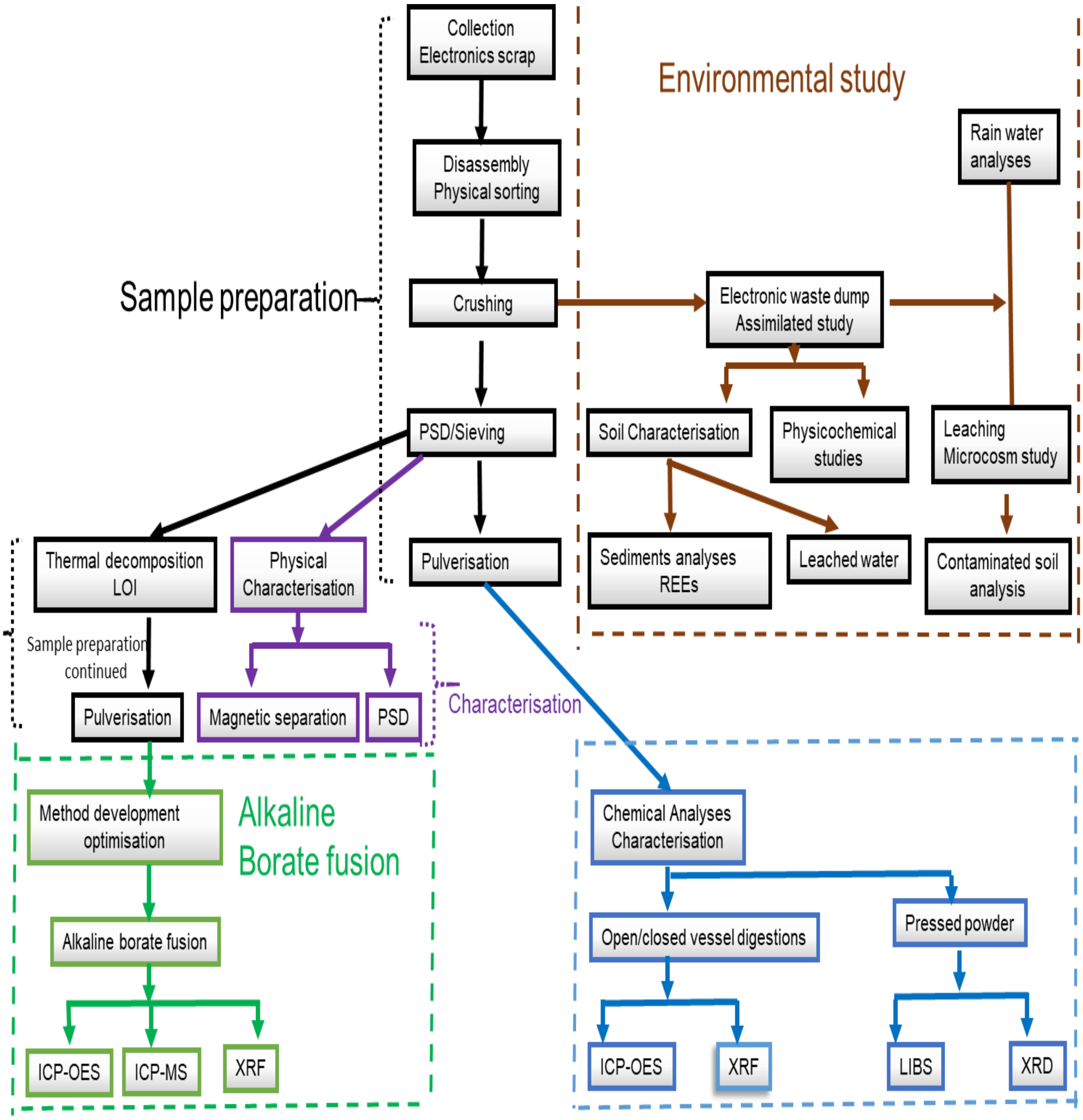


Figure 3. 1: Schematic layout of the experimental study.

3.2. Sample preparation

3.2.1. Collection and sampling of e-waste

The electronic waste components (EWC) utilised in this study emanated from mobile phones and printed circuit boards (PCBs) from computers, obtained from some electronics repair shops in Cape Town, South Africa. More than 50 mobile phones with the majority being smartphones all amounted to a weight of 10 kg and 6 PCBs with a total weight of approximately 5 kg were disassembled. The components came from different manufacturers, year models, and brands. The majority of feature phones were between 60 and 120 g in weight, while smartphones were between 110 and 200 g. Prior to pulverisation, printed circuit board (PCBs), speakers, mouthpieces, and liquid crystal displays (LCD), metals and aluminosilicate components weighing 60-80% of the total weight were crushed using a Boyd crusher provided by Rocklands (Johannesburg, South Africa). A composite mobile phone sample consisting of different smartphone models was chosen as representative of e-waste for optimising the alkali fusion procedure, leaching experiments and exposure to assimilated dumps. The particles, huge pieces, like metal, wires, plate, were cut, disintegrated and crushed. The computer boards were first cut with a hacksaw into small square pieces of 3 cm x 3 cm. The mobiles were dismounted and components such as batteries, plastic casings, and the glass were separated by physical sorting. The basic steps for e-waste preparation are laid out in Figure 3.2.

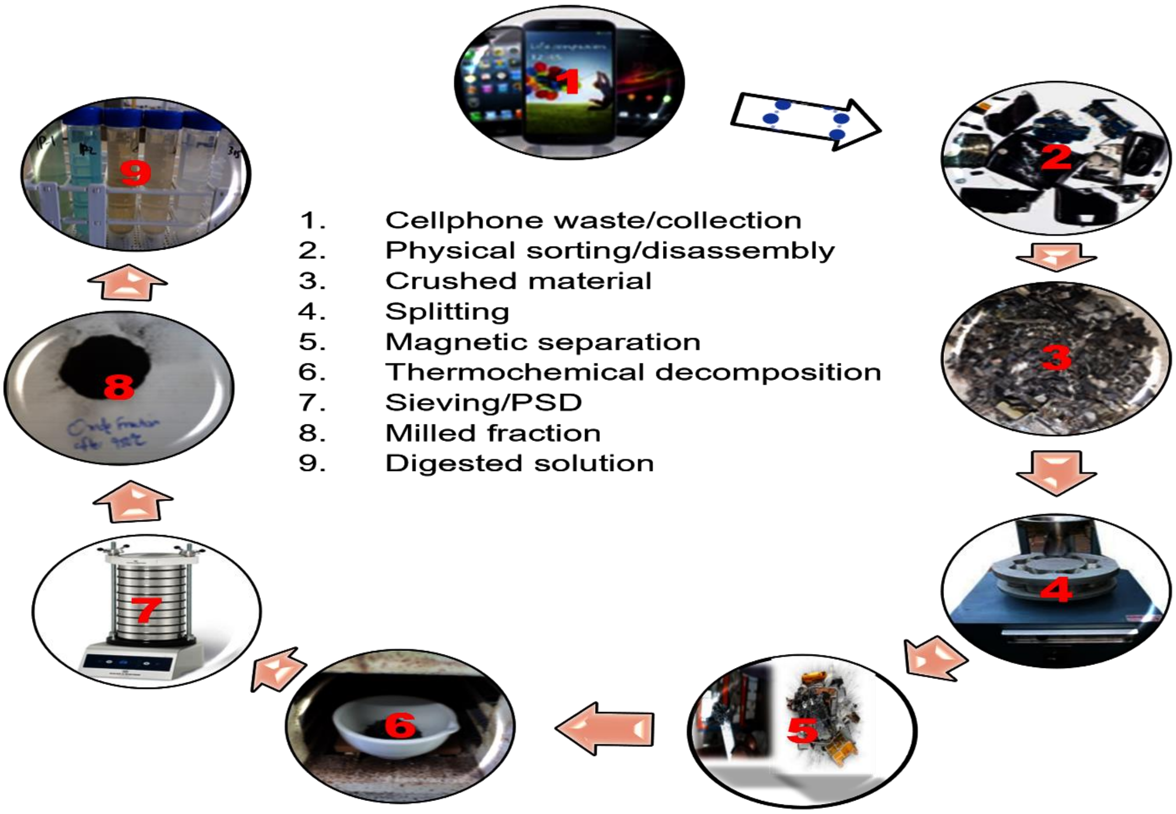


Figure 3. 2: **Electronic waste sample preparation stages.**

3.2.2. Crushing, splitting and milling

For the efficient size reduction process to liberate metals from the plastics the material is first broken into smaller pieces using a power hammer followed by two crushing processes. The e-waste samples were crushed into smaller particles (< 400 µm) with a Boyd crusher supplied by Rocklands (Johannesburg South Africa). After crushing, another physical sorting with the help of sieving was done to remove big metal pieces, plastics and wires. Wire mesh sieves king test supplied by Dick King Lab suppliers (Johannesburg, South Africa) with aperture size range from 20 mm to 53 µm and diameter of 200 mm was used in this study. The magnetic fraction was removed by a hand magnet on a small sample and larger samples by a magnetic separator supplied by (Carpco, Jacksonville Florida, USA) on bigger sample sizes. The pulverisation was performed in a cylindrical 100cc tungsten bowl containing puck and rings supplied by Dickie and Stockler (Johannesburg, South Africa). The jaw crusher and mill were cleaned with uncontaminated quartz after analysing each sample to avoid cross-contamination. The millable components were pulverised to a 90% passing pore size of 53 µm sieve in a 100 cm^2 tungsten pot size on a swing mill, all supplied by Dickie and Stockler (Johannesburg, South Africa). A small portion of samples was ground using ceramic motor and pestle to desired particle size and passed through 53 um sieve. A small amount of propylene glycol ($C_3H_8O_2$) was added to aid grinding to finer material. Cleaned glass pieces were used to clean the milling apparatus after each sample milling and served as blanks to assess cross-contamination. Milling for several minutes aided the homogeneity of the sample before a fraction is taken for analysis.

3.2.3. Soil preparation and treatment

Soil samples were collected from local sandy loam soil in the Ndabeni area in Cape Town (South Africa). The soil samples were collected from a depth of 0–15 cm below the surface and were then mixed to obtain a composite mixture. The soils consist mainly of medium and fine-grained sand with predominant particles smaller than 0.5 mm and greater than 0.125 mm and some proportions of organic matter. The soil was dried at 105 ^{o}C and sieved through a 2-mm sieve to homogenize the sample and remove large stones or organic debris.

The treated soil for microcosm studies was thoroughly mixed with the ground e-waste material at a 9-soil part to 1 e-waste part ratio, yielding a 10 percent e-waste in the soil. By combining 1.8 kg of soil and 0.2 kg of e-waste, a total of 2 kg of treated soil was obtained. The combined mixture was homogenised using the bottle-rolling technique. Before beginning the experimental analyses, the sample was left for three months without an airtight enclosure. This assisted the soil in regaining some of its natural forms after structural features and soil aggregation had been altered (Harvey *et al*., 2020).

3.2.4. Loss on Ignition (LOI) – Determining the Total Volatile Content

Loss on ignition describes the process of measuring the weight change of a sample after it has been heated to a high temperature causing some of its content to burn or to volatilise. Plastics are made of petrochemical hydrocarbons with additives such as flame-retardants, stabilisers, and oxidants (Miandad *et al*., 2019). Thermochemical decomposition of organic material at high temperatures in a limited amount of oxygen in a furnace was employed in this study. The furnace temperature was steadily increased up to 550 °C and maintain the temperature for at least 6 hours until all organics are burnt off. The gaseous emission produced were collected in a water jacket to avoid any atmospheric pollution. This process involves changes in chemical composition and physical phase of material to remain with metallic components. This process as described by Gurgul *et al*. (2017) is similar to pyrolysis where the thermal degradation of plastic waste at different temperatures (300–900 °C), in the absence of oxygen is done. The equation of loss of ingition (Equation 3.1) as expressed by Jock et al. (2013) is as follows:

$$\boldsymbol{LOI}, (\%) = \frac{W_i - W_f}{W_i} \ x \ 100 \qquad\qquad Eqn\ 3.1$$

where, W_i and W_f are initial and final weight respectively.

3.2.5. Storage of Samples

The dismantled e-waste material collected was stored in zip-seal plastic bags with labels written model, weight and component name. The crushed and milled content were stored in sealed air-tight plastic 50 ml vials and labeled accordingly. The prepared soil used for microcosm experiments was packed in airtight bags. The containers and bags were placed in a cupboard away from any direct sunlight, heat source, and fluctuating temperatures.

3.3. Size fraction characterisation

Particle size analyser and magnetic separation were used for particle size distribution and separations of magnetic particles from non-magnetic fractions. The resultant content obtained from the above procedures was subjected to elemental composition determination by spectroscopic techniques. The instrumental techniques divulge the content of REEs and other metals contained in e-waste.

3.3.1. Laser diffraction

Laser diffraction measures particle size distributions by measuring the angular variation in the intensity of light scattered as a laser beam passes through a dispersed particulate sample. The measuring technique is based on the diffraction and diffusion phenomenon and Fraunhofer and Mie's theory to obtain the particle size. This diffraction pattern gives the light scattering intensity as a function of the diffraction angle (Figure 3.3) (Horiba Scientific ,2010; Blott et al ., 2004).

The particle size affects several properties, from the accessibility of minerals during processing, to representative sampling, sample homogeneity and morphology. A wide range of techniques are available to determine particle size; however, the most broadly used technique is laser diffraction which was used in this study. A Horiba LA 960 particle analyser was used for the purpose of this study with an extremely wide measuring range from 10 nm to 5 mm. The e-waste soil samples are air dried ground gently and sieved through a 1-mm sieve, soil fines are then mixed thoroughly and sub-sampled via coning and quartering method and eventually subjected to analysis on a wet mode of analysis on a Laser Diffraction Particle Size.

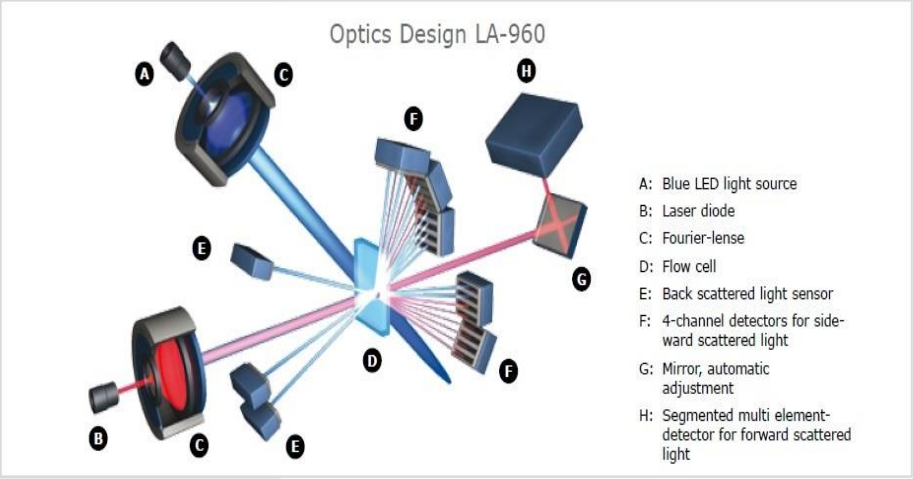


Figure 3. 3: **Schematic of the setup of typical laser light scattering spectrometer Horiba LA-960 (www.azom.com/article).**

3.3.2. Sieve particle size analysis

Sieve analysis is a method of determining the particle size distribution of material and it was useful for e-waste determination. The process separates fine particles from more coarse particles by passing the material through several sieves of different mesh sizes (Figure 3.4). This allows the mass fraction of particles within each size range to be measured and cumulative distribution constructed. The material was vibrated through a series of sequentially decreasing sieves using a single, or combination of horizontal, vertical or rotational motion. After the sieving process, the weight of the fractions sieved was recorded to give a cumulative mass distribution of the test sample. E-waste particles are known to contain a range of size fractions from very fine to larger particles even after being crushed. The large particles are comprised of large metallic sheets and wires that were removed after sieving. There are 2 types of sieve analysis that can be carried out; wet sieving and dry sieving. Wet sieving is normally suited for finer particles in the > 20 µm to 3 mm range. Dry sieving, which is suitable from >30 µm up to 125 mm was utilised in this study. The sieves used for the sieve analysis had sizes that ranged from 50 mm to 3550 mm.

Figure 3. 4: **Sieves of different mesh sizes on mechanical shaker.**

3.3.3. Magnetic Separation

Magnetic separation is the process of separating moderately or weakly magnetic (para-magnetic) materials from nonmagnetic components using magnets (Figure 3.5 a). This method has been used for quite a long time in treating magnetic mineral ores and for the removal of ferromagnetic impurities from mixtures. In this case, magnetic separation was used to remove the ferromagnetic iron impurities from electronic waste. The technique is designed to separate moderately or weakly magnetic (para-magnetic) materials from nonmagnetic components. The top-fed induced roll separator places all materials in contact with the highest magnetic field at the steepest magnetic gradient zones and utilises magnetic force and gravity to capture weakly magnetic particles. A turning-induced magnetic roll transports material through the active area and provides an opposing centrifugal force for the separation of magnetic and nonmagnetic materials. An illustration of the principle of operation is shown in Figure 3.5 b.

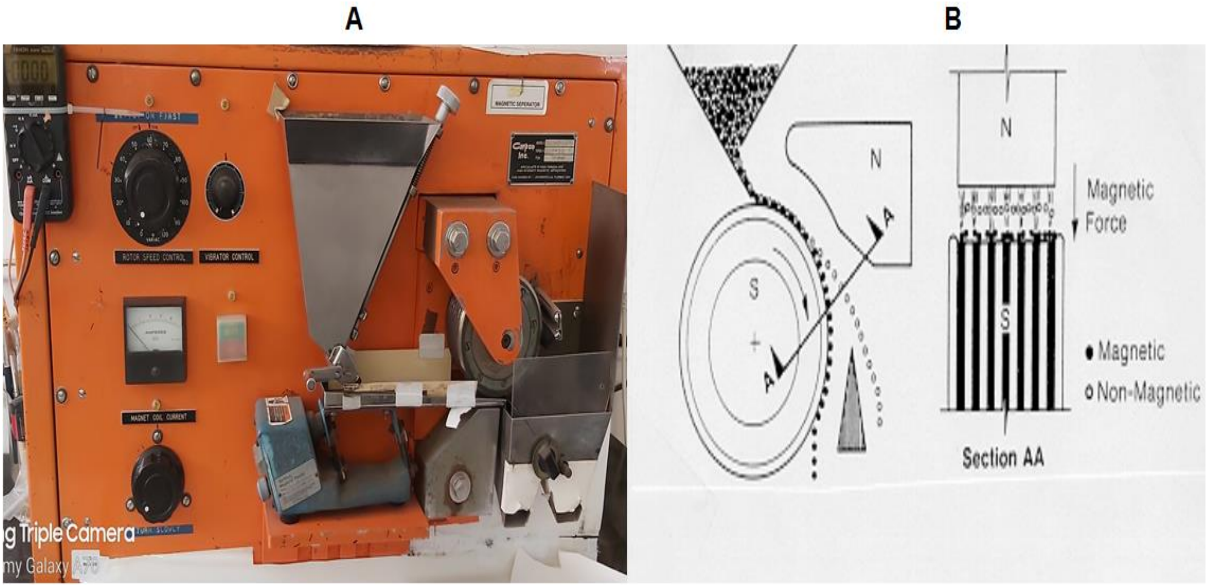


Figure 3. 5: **Carpco high intensity magnetic separator (A) and sketch diagram showing the principle of drum magnetic separator (B).**

3.4. Sampling of sediments and leachate from electronic waste dumps

Sediments/Soil sampling from e-waste dumps is incredibly complex because of divergent sizes with varying surface and chemical properties. Samples from a depth of 0-10 cm (topsoils) and 11-30 cm (subsoils) are normally collected for soil sampling (Ofudje *et al*., 2014; Olafisoye *et al*., 2013; Adesokan *et al*., 2016; Otache *et al*., 2014). However, for this study the sediment was taken from a depth of 15cm below the surface using a small stainless steel shovel. Figure 3.6 show the schematic assimilated e-waste dump. After collecting samples, unwanted material such as stones, roots, course materials and any other foreign matter was removed. Drying and sieving to less than 1 mm fractions are strongly advisable. The samples were stored in clean polyethene bags (ziploc) to minimise sample contamination. In the case of sediments, samples are kept in a freezer below 4 degrees Celsius or to be freeze-dried and kept in a desiccator after sampling and before analysis (Makombe *et al*., 2017).

The surface water bodies are easily contaminated by run-off water and leaching from e-waste dumps. Proper sampling techniques are vital for the determination of both organic and inorganic particulates in the water. The water was collected into clean containers, rinsing containers to avoid contamination, filtration to remove suspended particulates, acidification and storage of samples below 4°C (Guo *et al*., 2009; Makombe *et al*., 2016; Yao *et al*., 2008; Olafisoye *et al*., 2013). Sampling water for rare earth metal analysis was treated in the same manner as sampling water for inorganic and heavy metals.

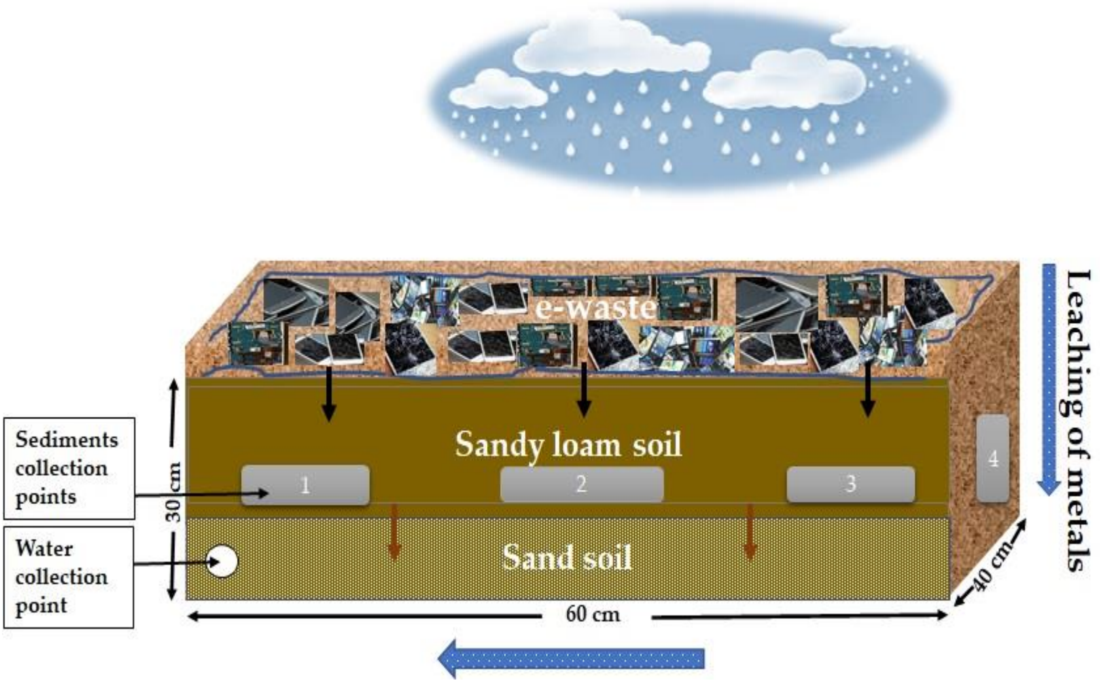


Figure 3. 6: **Simulated e-waste dumpsite design.**

3.5. Physio-chemical parameters of soil, sediments and leachate

3.5.1. Soil preparation for physicochemical analyses

The soil or sediment samples for the physiochemical test were oven-dried at 45 °C until the weight was constant and then sieved to pass a 1 mm sieve. The sieved portion was split and further ground to pass a 75 µm sieve for metals analysis. For pH, EC, alkalinity, TDS a 1:5

soil: water extract was prepared by shaking for 30 minutes on a mechanical shaker and the filtration using Whatman paper grade 42: 2.5 µm pore size.

3.5.2. Physio-chemical parameters measurements

The pH, electrical conductivity (EC), total dissolved solids measurements (TDS), temperature and total alkalinity, hardness are chemical parameters useful for water and sediment quality measurements. The physicochemical properties will also help in the identification of sources of pollution, for conducting further investigations on major environmental impacts. The pH, EC and TDS of the samples done in this study were measured by Hanna ion selective multi-meter model HI5522. The instrument was calibrated before use for each parameter. The pH was calibrated with buffer solutions 4.0, 7.0 and 10.0. The EC was calibrated with 12.88 mS/cm solution and TDS with 12.88 mS/cm all at room temperature. All the recordings were done in triplicate and the mean value with the standard error was calculated. The temperature was measured using a calibrated mercury thermometer and noted in °C. For the estimation of total hardness readings of magnesium (Mg) and Calcium (Ca) water were analysed on ICP-OES.

The alkalinity of dump leachate and rainwater was determined to gain an understanding of the ability to neutralise acids "buffering capacity." This parameter is very important for cation/anion which means without this acid neutralising capacity, any acid added to water would cause an immediate change in the pH. Alkalinity for natural water (in molar units) is normally defined as the sum of the carbonate, bicarbonate, hydroxide, and hydronium concentrations such that:

$$[Alkalinity] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H_3O^+] \qquad Eqn\ 3.2$$

The result is reported as milligrams per liter (mg L^{-1}) of calcium carbonate and is given by Equation 3.3:

$$mg.L^{-1}(HCO_3^-) = \frac{1000\ x\ 61.02\ x\ V(acid) x\ [HCL]}{V(sample)} \qquad Eqn\ 3.3$$

where V= mL and [ ] = mol/L

3.5.3. Bulk density measurement of soil

Bulk density is the weight of soil for a given volume. It is used to measure compaction. In general, the greater the density, the less pore space for water movement, root growth and penetration. The water was poured from the can into a graduated cylinder and the volume was measured in mL. The weighted soil was poured into the measuring cylinder and the new volume was recorded. The bulk density was estimated by dividing the dry weight of the soil material (Wd) by the volume of soil (V) (Equation 3.4).

$$Bulky\ density\ (gcm^3) = \frac{Wd}{V} \qquad Eqn\ 3.4$$

3.6. Sampling and analysis of rainwater

Acid rainwater and air quality composition has gained great importance in the recent years on environmental monitoring (Grandi and Szpyrkowicz, 1991). Salty rain water is common in Cape Town because of being surrounded by the Atlantic and Indian Ocean nearby. The main objective of this study was to determine the impact of acid rain on the mobility of metals, such rare earth elements (Wen *et al.*, 2013).

Rain water was collected by putting a graduated rain funnel on its mouth and decant the water in a clean plastic bottle. The top part of the rain funnel was inserted with a filter to capture any debris or impurity particles. The rain funnel was inserted at the top end of the building free from obstruction. The pH was measured soon after collection with minimum volume of 15 ml for a single reading repeat. The remaining volume was stored in a refrigerator below 4 ^{o}C.

3.7. Digestion procedures

3.7.1. An overview of inorganic acids used in digestions procedures

The oxidizing ability of nitric acid decreases (reduction potential decreases) as the concentration decreases. Nitric acid and its oxidising ability is a strong mineral acid that produces soluble salts, useful for keeping the elements of interest in solution until they reach the plasma of the ICP or flame of the AAS. It is also good on its chemical compatibility, purity and available at low cost. However, nitrate is generally considered to be a 'poor ligand' in that its coordination ability is not enough to keep hydrolysis from occurring. The most popular 'good ligands' used in combination with nitric acid are HCl and HF.

Nitric acid was mixed with HCl in the ratio of 3:1 as aqua regia to make a better ligard, this was because the products of this combination are nitrosyl chloride and chlorine which are strong oxidixing agent. The oxidizing properties of the acid anion, for example as shown in Equation 3.5

$$Ln + 6HNO_3 \rightarrow Ln(NO_3)3 + 3NO_2 + 3H_2O \qquad Eqn\ 3.5$$

Hydrochloric acid is the salt of hydronium ion, H_3O^+ and chloride. It is the monoprotic acid least likely to undergo an interfering oxidation-reduction reaction. These attributes, plus the fact that it is available as a pure reagent, make hydrochloric acid an excellent acidifying reagent. Roth *et al*. (2017) showed that HCl is good on leaching rare earth elements singular or in combination with other acids and NaOH.

Perchloric acid should never be used alone and allowed to go to dryness. Hot perchloric acid is very dangerous especially when added to organic matter. It is very useful in digestion in that it raises the temperature of the solution because of its high boiling point. Perchloric acid is very useful when used in conjunction with nitric acid. These acids were carefully prepared in singular or combination for the digestion purpose.

The samples prepared using hydrofluoric acid (HF) in the acid combination formed insoluble fluorides with many elements including alkali earth metals and rare earth elements. The microwave digestate with HF produced a clear solution but the insoluble fluorides still forms and was minimised by using at least 4% boric solution which bind with the HF to liberate the elements.

3.7.2. Open vessel digestion

Samples and reagents were heated on sand baths, hot plates in open beakers or flasks, made of glass, quartz, teflon (PTFE, PFA) or glassy carbon. Acid fumes were evaporated or (partially) condensed in reflux coolers. Volatilization loss of analytes in open-vessel digestion is a concern for only volatile elements but not REEs. The work was carried out in the fume hoods with good extraction system. Typical sample weight was 0.2 to 1 g depending on the concentration of analytes. Single or multi acids were added simultaneously or sequential. The most common acids used for the e-waste digestions were HCl, HNO_3, H_2O_2, $HClO_3$, and HF. The maximum reaction temperature depends on the acids used. For REEs determination on e-waste the addition of multiple of acids sequentially was highly regarded as best.

3.7.3. Closed vessel microwave assisted digestion

Samples and reagents are treated in closed pressurized vessels, made of mainly fluoroplastics (PTFE, PFA). Mars 6 iWave used in this study uses CEM's PowerMax technology to automatically maximize the amount of microwave energy to the reaction for a complete digest regardless of the number of vessels and sample size. The system adjusts the power throughout the run, providing the control necessary for complete digests, while preventing exothermic reactions. The system also uses integrated sensor technology to recognize the vessel type as well as the sample number then apply the appropriate amount of power to ensure the highest quality digest. Figure 3.7 displays the components of the microwave system. Typical sample weight is 0.1 g to 1.0 g depending on the nature of sample and volume of reagents used. The reaction temperature is easily raised high due to the pressurized vessels even with using low boiling point acids such as HCl and HNO_3.

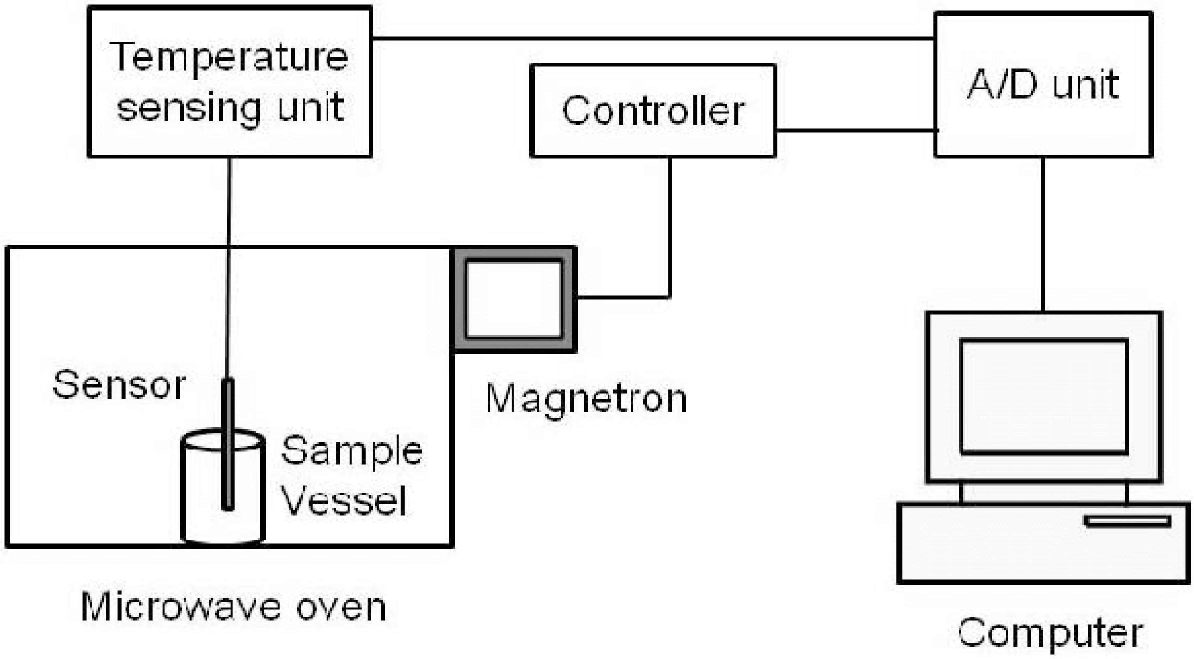


Figure 3. 7: Schematic diagram showing microwave oven system.

3.7.4. Fusion digestion

The alkali borate fusion is a technique was used to prepare various types of samples for subsequent XRF analysis, ICP analysis or AA analysis. The alkali fusion technique consisted finely ground sample mixed with a borate flux inside a 95% Pt - 5% Au crucible, heated to 1000 °C with agitation until the oxidiser and flux melted. The agitation made sure the sample dissolved homogeneously in the flux. For X-ray fluorescence (XRF analysis), the melt was then cast into a mould and cooled, resulting in a glass disk Figure 3.8. For liquid solutions the melt was poured into diluted acid for subsequent inductively coupled plasma (ICP analysis) or atomic absorption (AA analysis) in teflon beakers with dilute acid concentration Figure 3.8. The benefits of this method is the minimum use of strong acids (conc HNO_3, HCl or HF) and whilst the Si bonds are completely broken.

The automatic claisse M4 gas fusion used have parameters that can be modified: gas flow, mixing speed and amplitude, function duration, crucible angle and cooling air flow. The crucibles rotate while inclined for efficient agitation and superior homogenization of the melt in less time.

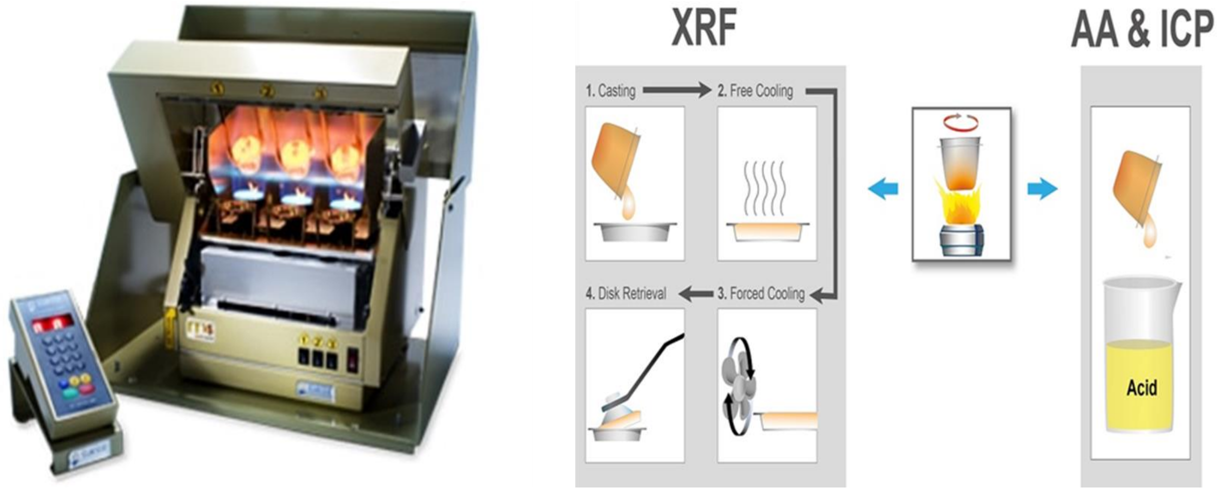


Figure 3. 8: **Gas fluxer showing fusion steps for glass beads for XRF and solutions for ICP or AAS.**

3.8. Leaching and speciation protocols

3.8.1. Laboratory Leaching (Microcosm) studies

Several parameters influence leachability, and these were evaluated at lab-scale experiments. In terms of e-waste, these are particle sizes, temperature, the concentrations of the solvents used, contact time between the solid and the liquid, solid to liquid ratio, pH and agitation of the mixture. Figure 3.9 demonstrate the recovery of REEs from solid e-waste components exposed to chemical leaching.

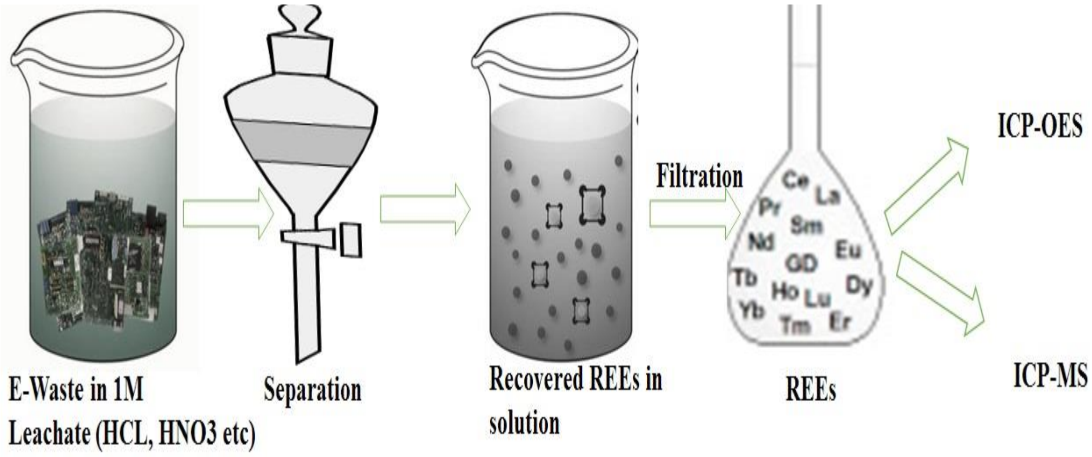


Figure 3. 9: Stages of leaching solid e-waste.

3.8.1.1. Column leaching setup

To model the dissolution of contaminants (REEs) from contaminated soil, leaching tests were performed as column and batch tests. Column tests were carried out by passing a leaching solution through stationary simulated solid waste in a polythene column with an internal diameter of 20 mm and a height of 300 mm (Figure. 3.10(a)). To preserve the structure of the soil under test, a layer of 4 cm of clean sand with particle sizes greater than 1000 μm was packed and separated by a layer of glass fibre before and after the 15 cm layer of 40 g treated soil (Figure 3.10(b)). To obtain a clear filtrate for elemental analysis, the outflow leachate was further filtered with a 0.45 µm filter. Before a volume of the lixiviant was poured into each column, pure distilled water was injected to saturate the solid waste. A peristaltic pump with a speed of 0.8 mL/minute carefully pumped a total amount of 150 mL lixiviant solution onto each column once every 24 hours.

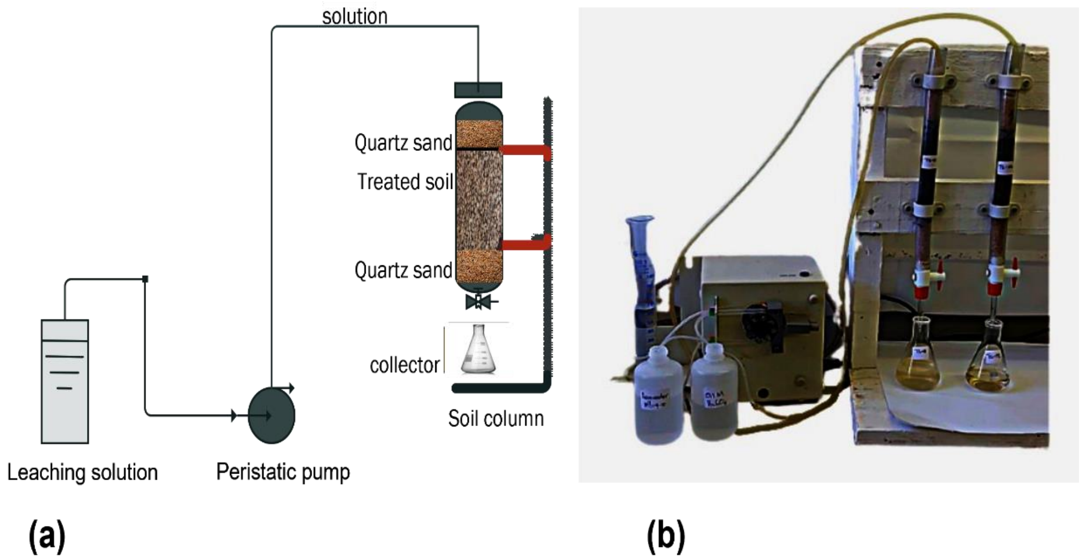


Figure 3. 10: **Schematic diagram of column leaching experimental setup (a) and picture image of experiment setup (b).**

3.8.1.2. Batch leaching

A given mass of solid sample was placed in a container with a specific volume of liquid leaching solution. Water, salt buffers, acidic solutions, basic solutions, or organic solvents can all be used as leaching solutions. For all batch leaching tests, the following lixiviants were used: distilled water, rainwater, 1 M H_2SO_4, 1 M HNO_3, 1 M HCl, 1 M $C_6H_8O_7$, and 1 M CH_3COOH. The mixture was stirred for a set period. The agitator stirring speed was set to 450 rpm, and the temperature was kept constant at 25 ± 1 ^{o}C for all experiments. The mixture was filtered with a 0.45 µm filter after stirring on a magnetic stirrer. Figure 3.11 demonstrates the batch leaching procedure for the crushed and milled e-waste and soil contaminated with e-waste.

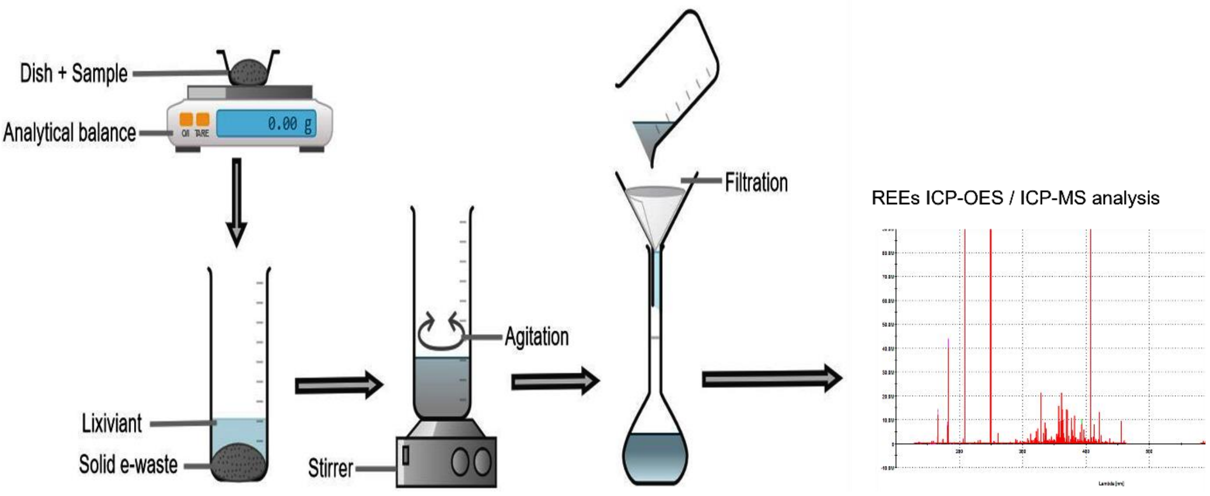


Figure 3. 11: **Schematic diagram of batch leaching experimental setup.**

3.8.2. Sequential extraction analysis

For the fractionation and mobilisation of REEs in soils, sequential extraction procedures (SEPs) was adopted from the two extensively used SEPs, namely, the four-step SEP proposed by Tessier et al. (1979) or the three-step BCR (Community Bureau of Reference) procedure developed in the framework of the Standards, Measurements and Testing Program of the European Commission (Liu *et al.*, 2018). Duplicate runs were made for each sample and the averaged results were used for yield calculations. Following each extraction, the mixture was filtered to separate the liquid and the residues. In this work a five-stage extraction procedure was employed as detailed by the extraction processes given in Table 3.1.

Table 3. 1: Sequential extraction procedure conditions.

Step	**Fraction**	**Extractant conditions**	**Duration (Hrs)**
1	Ion-exchangeable	The initial solid sample of 1.0 g was treated with 30 mL of 1 M ammonium acetate (NH_4OAc) at neutral pH with agitation.	2
2	Carbonate bound	To residue of step 1 add 1 M NaOAC pH 5.0 adjusted with acetic acid at 23 ± 2 ºC.	6
3	Fe-Mn oxide bound	To residue of step 2 add 0.1 M $NH_2OH.HCl$ (adjust to pH 2 with HNO3) with occasional stirring.	12
4	Oxidisable (Organic)	To residue of step 3, add 5 mL 30 % H_2O_2, adjusted to pH 2 with HNO_3, heat at 85 ºC for 1 h; occasionally shake; add 5 mL 30 % H_2O_2, 85°C, 1 h; add 1 M NH_4OAc (pH 2 with HNO_3) 25 mL	12
5	Residual	To the residue of step 4 add HNO_3+HF, 11 mL, under high pressure, 200°C	1

3.9. Spectroscopic techniques

3.9.1. ICP-OES Spectroscopy

The determination of rare earth elements requires sensitive instrument capable of detecting at trace elemental levels. The complexity of separating the REEs requires a high-resolution instrument, sensitive and good selectivity. The spectro arcos ICP-OES shown in Figure 3.12 equiped with CCD detectors was used in this study for the elemental determination. The Spectro Arcos ICP-OES (SPECTRO Analytical Instruments, Germany) is equipped with smart analyser software. The instrument has been developed with rich library that makes analysis of rare earth elements attractive. Components of the ICP-OES instrument include the peristaltic pump, the nebuliser, the spray chamber, the RF generator, the torch, the optical systems, the detectors and the data processing system (Ross and Fredeen, 1997).

Sample solutions include digested soil or other solid material or natural water. The aqueous samples taken in this study were filtered through a 0.45 μm membrane filter to remove suspended solids and acidified with to 2-3% in HNO_3 to prevent adsorption of metals onto polypropylene sample bottle or onto instrument tubing or glassware prior to introduction into the plasma. For the purpose of this study the water samples were acidified at 2% HNO_3.The sample through a peristaltic pump was introduced to a cyclone spray chamber and through a high sensitivity glass, single-pass cyclone spray chamber and nebulizer using argon gas. It was then passed through axially oriented plasma.

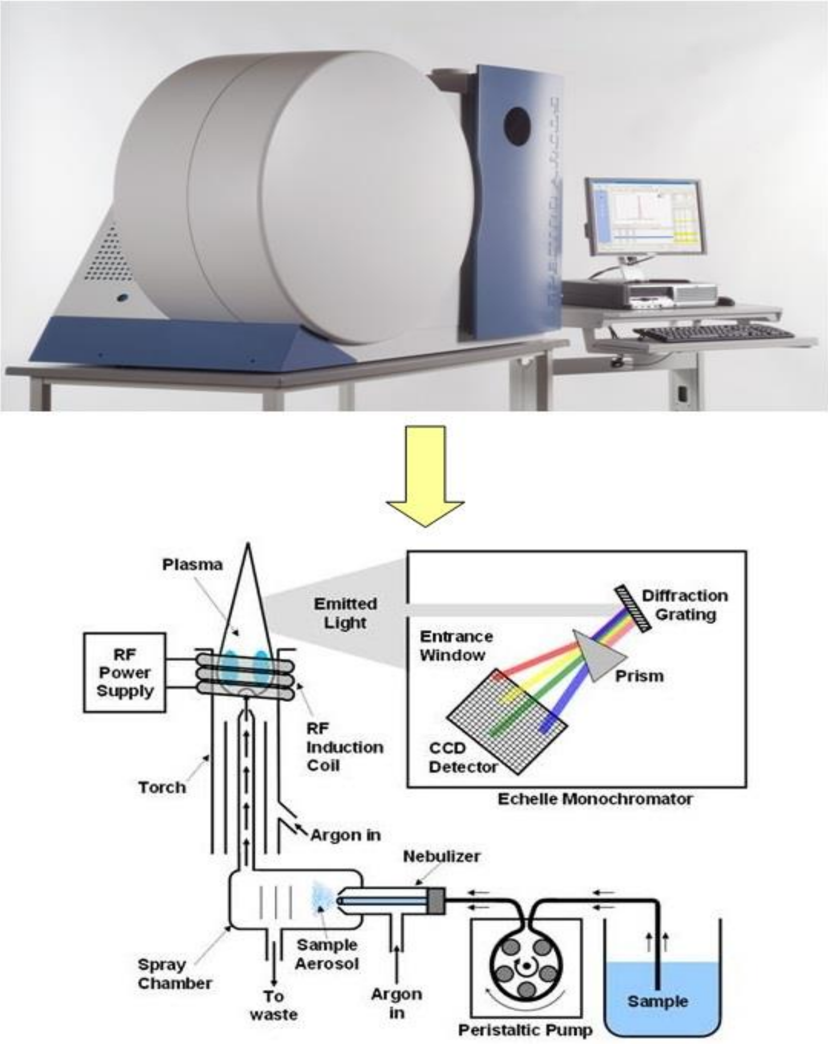


Figure 3. 12: **The Spectro Arcos ICP-OES and the Schematic diagram (Spectro, Ametek).**

3.9.2. ICP-MS Spectroscopy

The ICP-MS is a quantitative analysis that accurately determines how much of a specific element is in the material. The ICP-MS instrument used is a Thermo-Fisher X-Series II quadrupole ICP-MS with a New Wave UP213 solid-state laser ablation system. The X-series II instrument is equipped with a 48-sample auto sampler for automated solution analysis. The shematic representation is shown on Figure 3.13. The concentration of each element is determined by comparing the counts measured for a selected isotope to an external calibration curve that was generated for that element. Liquid calibration standards are prepared in the same manner as used in ICP-OES analysis. These standards are analysed to establish the calibration curve. The unknown samples were then run, and the signal intensities were compared to the calibration curve to determine the concentration of the unknown.

The most essential components of ICP-MS are the vacuum system that provides high vacuum for ion optics, quadrupole, and detector. The Ion optics guides the desired ions into the quadrupole while assuring that neutral species and photons are discarded from the ion beam. The mass spectrometer acts as a mass filter to sort ions by their mass-to-charge ratio (m/z) and the detector counts individual ions exiting the quadrupole.

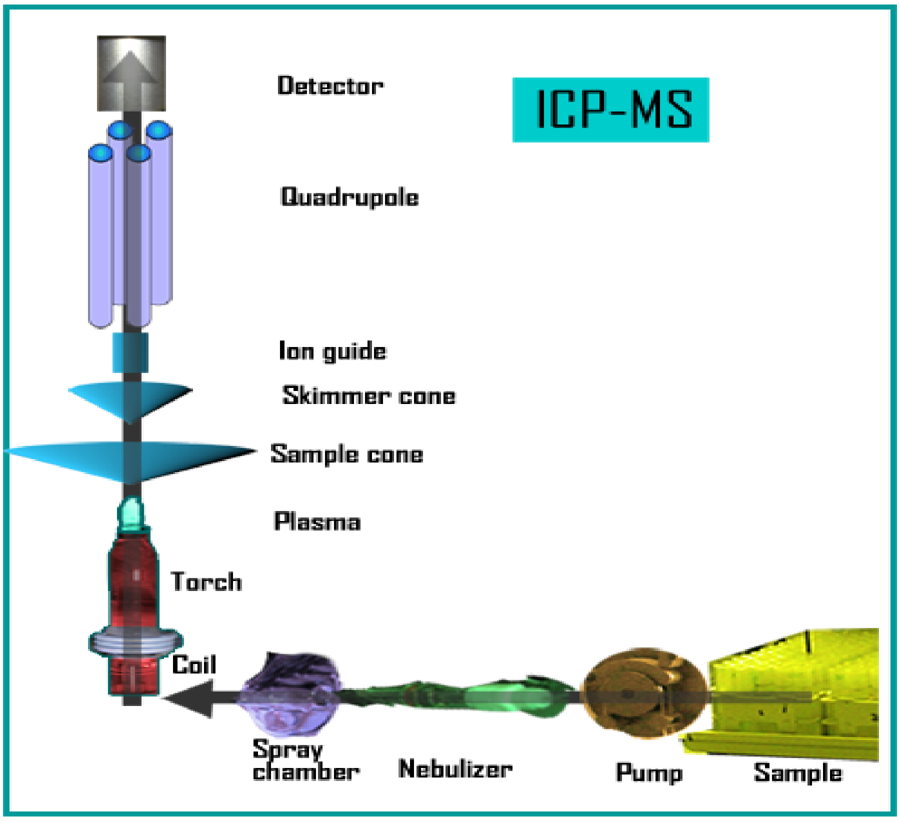


Figure 3. 13: **ICP-MS schematic diagram** (www.ru.nl/science/gi/facilities-activities/elemental-analysis/icp-ms/).

3.9.3. X-Ray Fluorescence

X-ray spectroscopic techniques include X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS), both providing simple and accurate methods for determining the elemental composition of a material. Energy dispersive (EDXRF) and wavelength dispersive (WDXRF) XRF spectrometers are available, as well as handheld/portable devices. The new Supermini200 which was utilised has improved software capabilities, shorter measurement times and lower detection limits. Combined with Rigaku's SQX fundamental parameters software the EZ Scan allow unknown samples to be measured without any prior setup. Supermini200 WDXRF spectrometer is equipped with parameter as shown in Table 3.1. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured. Control standards that were used in the calibration procedures. The XRF technique reports concentration as % oxides for major elements and ppm (mg/kg) for minor and trace elements.

Table 3. 2: Parameters for Supermini200.

Condition	**Feature**
Atmosphere	Vacuum
X-ray tube	Palladium
Power (W)	200
Detectors	Scintillation and F-PC
Crystals	3- position changer (LiF-200)
Primary beam filter	Zirconium (Zr)

3.9.4. LIBS

Laser induced breakdown spectroscopy (LIBS) is a quantitative atomic emission spectroscopy technique which uses highly energetic laser pulses to provoke optical sample excitation. Laser pulse strikes the surface of the sample and ablates an amount of material (Anabitarte *et al*., 2012). In this plasma, the matter constituting the samples is dissociated into atoms and partially ionized. Figure 3.14 illustrates the handheld LIBS spectrometer that was used and the schematic process of the laser system. LIBS is fast, easy and in situ chemical analysis with reasonable detection limits and more so minimum sample preparation (Costa *et al*., 2017). The main component of LIBS is the laser that generates the energy and the main parameter is the pulse time. In order to promote cleanliness of the LIBS nozzle, the sample powders were encapsulated in clear tape or pressed to avoid dispersion of particulates. The sample was then placed onto the LIBS nozzle for analysis. The cleaning shots were performed to ablate through the tape before directly hitting the sample.

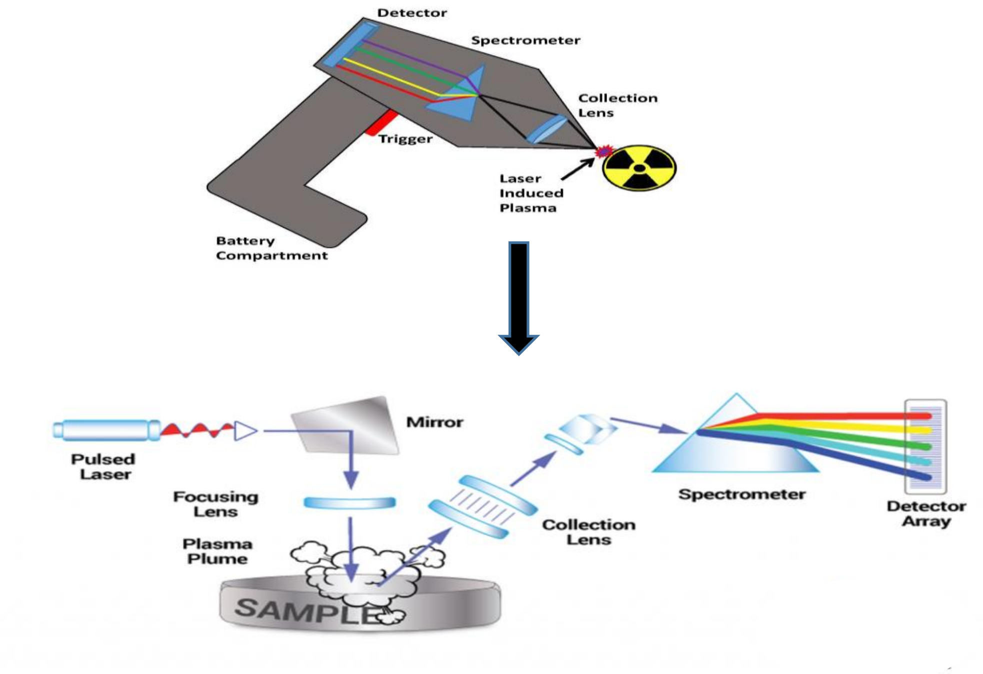


Figure 3. 14: LIBS schematic diagram.

3.9.5. X-ray diffraction (XRD)

X-ray diffraction (XRD) is a technique commonly used to identify crystalline substances, such as minerals or inorganic compounds. However, for this research, the qualitative analysis was performed to determine the elemental phases of e-waste material, solid residue recovered from leaching, contaminated e-waste sediment and uncontaminated soil. The samples were prepared for analysis using a back-loading method (Guinier, 1994). Diffractograms were obtained using a Malvern Panalytical Aeris diffractometer equipped with a PIXcel detector and fixed slits that were exposed to Fe-filtered Co-K radiation. X'Pert Highscore plus software was used to identify the phases. The Rietveld method was used to calculate the relative phase amounts (weight%). It requires that the structure model be adjusted to be as close to the true structure as possible (Zhao *et al.*, 2018). In an X-ray diffractometer, the sample rotates at an angle θ in the path of the collimated X-ray beam, while the X-ray detector, which collects the diffracted X-rays, is mounted on an arm and rotates at an angle of 2θ as shown on Figure 3.15 below. Bragg's Law describes the general relationship between the wavelength of the X-rays that hit a material, the angle at which they hit, and the distance between the crystal lattice planes of atoms. It can be written as:

$$n\lambda = 2d\ sin\theta \qquad Eqn\ 3.6$$

where n (an integer) is the "order" of reflection, λ is the wavelength of the incident X-rays, d is the interplanar spacing of the crystal and θ is the angle of incidence.

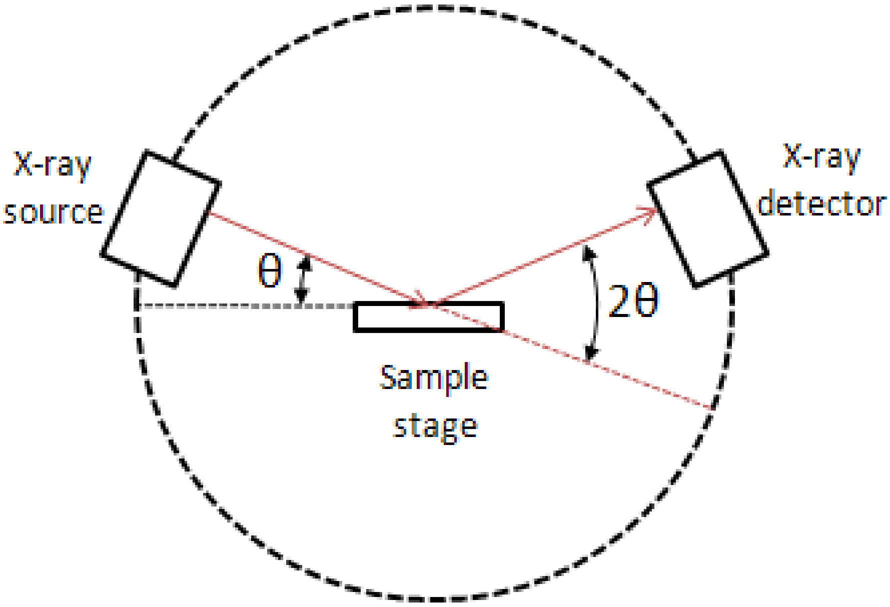


Figure 3. 15: **Schematic representation of the X-ray diffractometer consists of an X-ray source, a sample stage, a detector and a way to vary angle θ.**

3.10. Summary

This chapter focused on the scientific techniques used to complete this research investigation successfully. It started with characterisation and sample preparation techniques for solid e-waste. The methodologies came next, with an emphasis on the new, improved fusion alkali approach for e-waste determination. The leaching of rare earth elements in various mediums and conditions was studied using macrocosm procedures in the laboratory that included batch and column experiments.

After that, the amount of metals in the soil and leachate was measured in order to assess the leaching of rare earth elements from assimilated e-waste dumps. Additionally, assessed were the physicochemical factors that affect leaching capability. The physicochemical parameters of the monthly rainwater sampling at e-waste dump locations were measured. Quantitative measurement of the trend of leaching over three years is provided by further mineralogical characterisation of the dump sediments and leachates. It is possible to comprehend the pollution model by comparing the contaminated and uncontaminated e-waste landfills. The chapter concludes by highlighting the principles and spectroscopic techniques used in this research.

CHAPTER 4

IMPROVED BORATE FUSION TECHNIQUE FOR DETERMINATION OF RARE EARTH ELEMENTS IN ELECTRONIC WASTE COMPONENTS[∞]

4.1. Introduction

This chapter presents and discusses the development and optimisation of the alkaline borate fusion method for REE determination in electronic waste for the first time. Firstly, the sample preparation stages that were investigated in section 4.3 are presented and explained based on the data obtained from the analytical protocols explained in Chapter 3. Secondly, the optimisation of experimental particulars comprises the choice of oxidiser, flux composition, non-wetting agents, fusion time, and sample to flux ratio in section 4.4. The third phase, at the end of section 4.4, consists of spectroscopic determination by inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray fluorescence (XRF) spectroscopy. This chapter will end with a comparison of results from two spectroscopic techniques: ICP-OES and XRF.

[∞] **Makombe, M.**, van der Horst, C., & Somerset, V. (**2021**). Improved borate fusion technique for determination of rare earth elements in electronic waste components. *Environmental Technology*, 1-14. DOI: 10.1080/09593330.2021.1994017

4.2. Overview

The electronic waste rich with a plethora of elements ranging from base metals, precious metals, rare earth metals, and refractory elements proves to be cumbersome to fully digest a sample. The use of open acid digestions has been utilised in other approaches (Maragkos *et a*l., 2013; Nnorom *et al*., 2010) as well as microwave (closed vessel) digestions (Das and Ting., 2017, Knoop *et al*., 2014; Oliveira *et al*., 2017). The limitations of acid digestions, with both open and closed vessel approaches, on refractory elements are well documented (Adams *et al*., 2003; Ishak *et al*., 2015). The wet chemical degradation of the sample into solution is usually by a single or combination of acids. The solvent nature of the acids such as the oxidizing nature of the acid anion, reduction of the hydrogen ion by the metal and the ability of the acid anion to form soluble complexes with the sample cation (Kuboyama *et al*., 2005) is considered. The near-total dissolution is achieved by a combination of hot concentrated mineral acids such as HCl, HNO_3, H_2SO_4, $HClO_4$ and HF that is weak, mono-oxidizing acid but vital for silicates decompositions. The robustness of these acids has been utilised in closed vessel microwave techniques (Ehi-Eromosele *et al*., 2012; Dimitrakakis *et al*., 2009; Mello *et al*., 2015; Oguchi *et al*., 2012; Gutiérrez-Gutiérrez et al., 2015) to achieve better reproducible results. The supremacy of microwave digestion hinges on high temperatures achieved through compressed vessels with uniform heating of samples (Yang *et al*., 2013).

One way to eliminate challenges in wet acid dissolution is to employ alkali fusion digestion as a technique because of its total dissolution capabilities. Fusions are generally more aggressive to sample dissolution than acid digestion methods which make it more suitable for many refractory, difficult-to-dissolve minerals such as chromite, ilmenite, spinel, cassiterite, and minerals of the tantalum-tungsten solid solution series. Fusion analyses are presumed to provide complete chemical analysis and are referred to as a “total” analysis (Uchida *et al*., 2005). This protocol is not a straightforward technique as it requires a proper balance of sample, choice of flux and apparatus. To date, the use of this technique has been utilised in geological analyses (Panteeva *et a*l., 2003; Pinto *et al*., 2012), soils and sediments (Makombe *et al*., 2016; Huang *et al*., 2007), raw and finished products (Ramos *et al*., 2016).

The focus of our study is to expand the capability of this technique to rare earth elements in e-waste and environmental samples derived from e-waste sites. Though a lot of digestion methods have been published for trace metal analysis in e-waste samples (Aguirre *et al*., 2013; Holgersson *et al*., 2018; Knoop *et al*., 2014; Maragkos *et al*., 2013; Terena *et al*., 2017; Yamane *et al*., 2011), very few have attempted the determination of rare earth elements despite their presence in most electronic waste materials. Moreover, no one method has been tried for REEs determination in electronic waste utilising the alkali fusion technique. The advantages of using the proposed procedure with ICP-OES finish include the complete dissolution of refractory elements, stable solution after fusion, dilution capabilities for highly concentrated samples and better homogeneity (Malherbe *et al*., 2013). The optimisation of various parameters such as sample to flux ratio, choice of flux, realising agent, oxidising agent, temperature, and time will be carefully studied.

4.3. Materials and Methods

4.3.1. Electronic waste sampling

The electronic waste components (EWC) utilised in this study emanated from mobile phones and printed circuit boards (PCBs) from computers, obtained from some electronics repair shops in Cape Town, South Africa as detailed in Chapter 3 section 3.2.1. A composite mobile phone sample consisting of different smartphone models was chosen as representative of e-waste for optimising the alkali fusion procedure.

4.3.2. Chemicals and reagents

All chemicals were of analytical grade. Water was purified using an ion-exchange deionisation process and its conductivity was tested for purity before use. The water was used for dilution and preparation of all standards and solutions. Nitric acid (65%), hydrochloric acid (32%), perchloric acid (60%) and hydrofluoric acid are all supplied by Merck (South Africa). Multi-element rare earth and 'Geo' elements standard solution SM60A, 100 µg g^{-1}, were supplied by VHG Labs (Manchester, USA), and used for the preparation of analytical standards (0.001 to 5 µg g^{-1} for ICP-OES in 10% v/v of 65% HNO_3). A control analytical standard of 2 µg g^{-1} was prepared from pure reference solutions of 1000 µg g^{-1} individual REE standards (De Bruyne Standards, South Africa). Standard reference material - a rare earth ore NCS DC86312 from China National Analysis Centre (CNAC), the ideal available reference material in terms of composition and quality was used. High purity lithium metaborate flux ($LiBO_3$, lithium tetraborate ($Li_2B_4O_7$), lithium Iodide (LiI) and Lithium Bromide (LiBr) were all provided by Claisse (Claisse, Québec, QC G1P 4P3, Canada). High purity $NaCO_3$, $NaNO_3$, and KNO_3 all crystals were all supplied by Merck (South Africa). Food grade citric acid (Buffalo Chemicals) was used for cleaning platinum ware.

4.3.3. Electronic waste sample preparation and procedure

The sampling and size reduction of e-waste materials are described fully in Chapter 3 section 3.2.1 and section 3.2.2. The metallic and aluminosilicate components in circuit boards, speakers, mouthpieces, and liquid crystal displays (LCD) were crushed and milled as per the procedures described in the sections above. The crushed sample was then put in a porcelain or nickel crucible for a slow thermal decomposition to 550 ^{o}C in a muffle furnace, after the weight was recorded as detailed in Chapter 3 section 3.2.3. This process burns all remaining non-metallic fractions which include organics and plastics. After this stage all the intact components became loose, organic material burnt off, weight recorded, metallic frames and plates removed. The millable electronic waste components were pulverised to a 90% passing pore size of 53 µm sieve in a 100 cm^2 tungsten pot size on a swing mill.

4.3.4. Pre borate fusion preparation

To perform sample fusion, the sample under test, fusion flux and an oxidiser were weighed on an analytical scale (0.0001 g) weights recorded and mixed to an exact ratio with the fusion flux. The mixture was placed in a Pt/Au (95%/5%) crucible and mixed before a fusion machine (M4 fluxer supplied by claisse, Inc, Canada) is used.

4.3.5. Borate fusion and homogenisation

The fluxer is fully automated to heat the mixture until it melts together to form a single homogenous hot liquid. A minute realising agent volume to improve fluidity was added during fusion before complete melt. The equipment as detailed in Chapter 3 section 3.7.4 is driven by M4 PC LINK program (Claisse, Canada) and equipped with a magnetic stirrer to aid the dissolution of the molten solution. The crucibles were cleaned by dipping them in 25% (w/v) citric acid ($C_6H_8O_7$) in an ultrasonic bath to remove any impurities and avoid cross-contamination. The melt was poured into a Teflon beaker with diluted acid (10% HNO_3 v/v) and stirred to dissolve the glass. The mixture was transferred and made to mark in a volumetric flask.

4.3.6. Instrument procedure for electronic waste determination

Sample preparation with further analyte determination by spectrometric techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES) and ICP-MS, allows high sample throughput and suitable limits of quantification (LOQ). The Spectro Arcos ICP-OES is equipped with charge-coupled device (CCD) detectors and a side-on plasma interface (SPI) or commonly known as radial that provides high precision and stability for less sensitive requirements. The instrumental principle and methodology are laid out in Chapter 3 section 3.9.1 and the verification by ICP-MS in section 3.9.2. The instrument optimised conditions for spectroscopic determination of REEs in EWC were adapted from optimised REE sediment analysis (Makombe *et al.*, 2017).

4.3.7. Calibration

Matrix matched standards and blanks with a composition of 1.5% w/v flux in 10% v/v HNO_3 (65%) was prepared for external calibration. The matrix matching is vital to control sample transport differences to curb problems associated with the external calibration procedure. Calibration plots with a range of concentrations for all the REEs measured gave linear graphs of a minimum 0.9997 correlation coefficient. The calibration plots were used in the quantitative analysis of REEs with satisfactory accuracy. A multi-element standard of 44 elements matrix-matched to the composition of samples digested by the microwave and open acid digestions was used in a 7-point calibration curve construction. To control stability, such as instrument drift, a control matrix-matched standard measured at the beginning of the run and after every ten-sample interval was inserted. A first-order linear fit plot of concentration vs intensity over a wide range of concentrations (seven orders of magnitude) was used to determine the concentration.

4.3.8. Methodological approach

The scheme in Figure 4.1 shows optimised conditions for the improved fusion procedure for e-waste determination. The finely powdered e-waste is digested with multi acid on both microwave assisted and open vessel digestions.

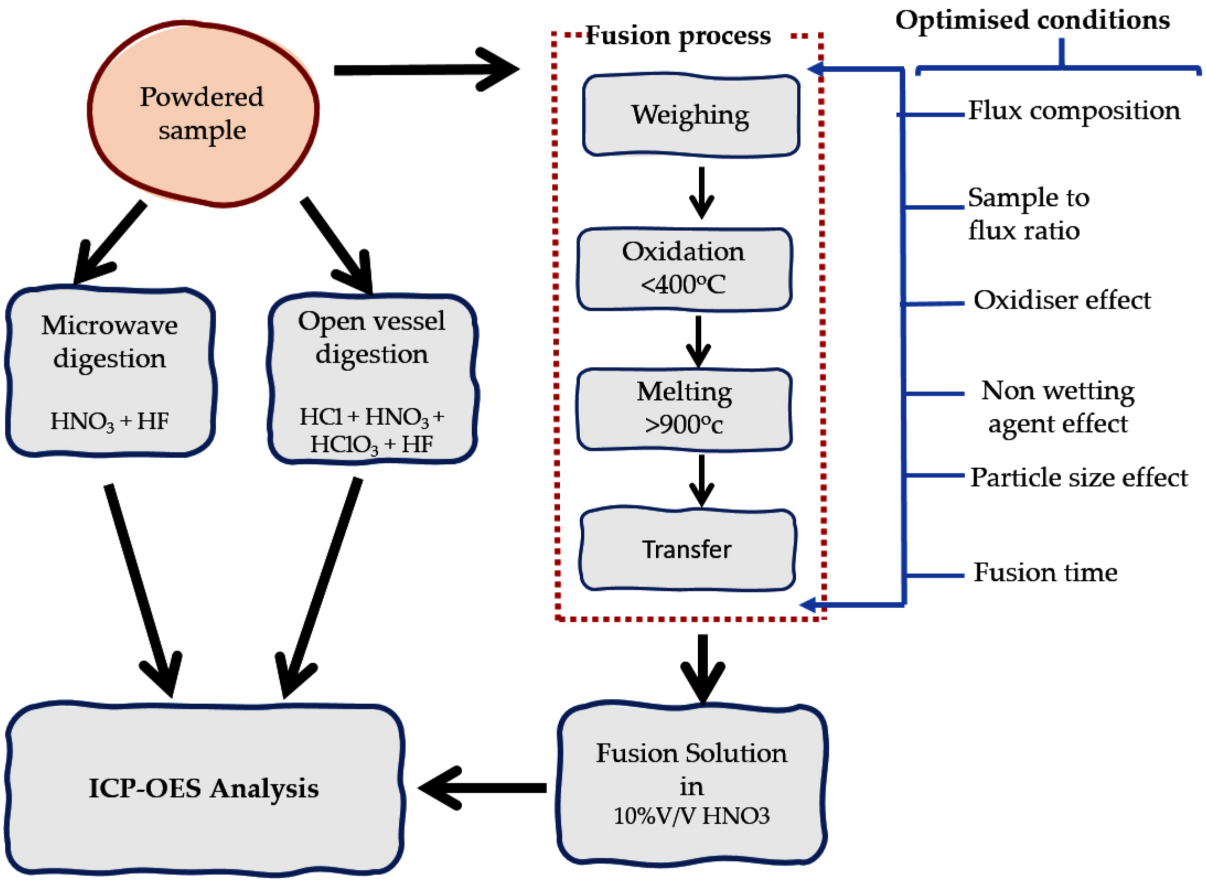


Figure 4. 1: Scheme of borate fusion and optimisation parameters applied and optimised in this chapter.

4.4. Results and discussion

4.4.1. Characterisation of electronic waste components

The particle size distribution was determined by dry sieving the sample after it has been crushed. The shredding of the e-waste released particles that led to fractions of between (20 mm to 90 µm) that were investigated for the presence of metals. The main aim of this characterisation was to determine what other constituencies and quantities are in the e-waste being investigated and in what particle size fraction the prevalent REEs can be found.

Figure 4.2 reveal the results of La and Nd measured as representative of other REEs, Cu included because of its abundance in PCBs and easy acid dissolution capabilities. Microwave digestion with ICP-OES analysis and fused glass bead XRF analysis was employed, also from a comparative point of analysis. It was observed that the REEs were less in gross fractions than in fine fractions, while copper results showed the opposite trend. Figure 4.2 shows that La and Nd have the largest percentage distribution in less than 0.09 mm fraction, whilst Cu is dominant in gross fractions from 0.06 mm to 2 mm. The copper is mainly in large connectors and wires in PCBs, whilst REEs are in small devices like the mouth and earpieces of mobile phones, which also break up easily to fine particle size fragments.

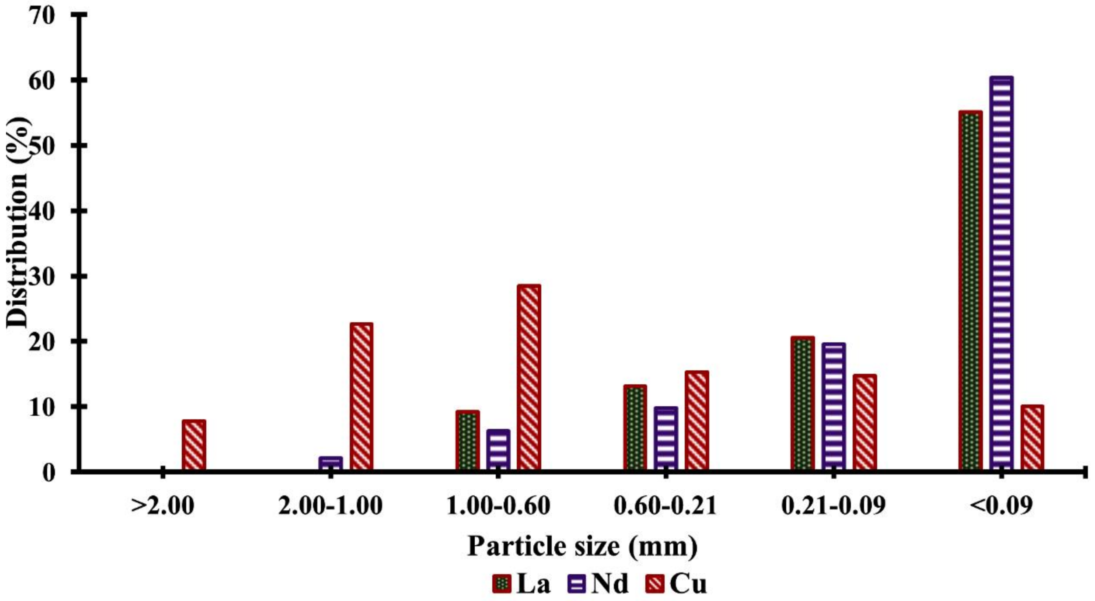


Figure 4. 2: **Metal distribution at different particle sizes on e-waste material.**

4.4.2. Flux components optimisation

The two main lithium salts of boric acid optimised are lithium metaborate (LiM, $LiBO_3$) a “basic” flux and lithium tetraborate (LiT, $Li_2B_4O_7$) an “acidic” flux. A eutectic composition of combined fluxes has the power to dissolve both basic and acidic oxide compositions and this robustness has been utilised for the first time in e-waste alkali fusion dissolution in this study. The pure fluxes of 100 LiM and 100 LiT were used to make subsequent compositions such as 90/10 LiM/LiT, 80/20 LiM/LiT, 65/35 LiM/LiT, 50/50 LiM/LiT and 35/65 LiM/LiT, respectively.

Figure 4.3 shows the concentration of La, Nd, and Dy obtained by ICP-OES analysis and after fusion with different flux components, whilst all other parameters remain constant. The composite EWC sample was fused with different flux compositions, for which three replicates were analysed. The pure lithium tetraborate (100 LiT) did not produce desired results as plenty of the flux got stuck to the crucible walls and only a fraction poured out. The flux also took a long time to dissolve as compared to the LiM matrices. The ideal condition and output of REEs . A slight diminish is noted on 100% LiM for all the REE elements, though this flux has been reported to be ideal for making fusion solutions (Watanabe, 2015). This showed that the dissolution of e-waste needs both acidic and basic flux. The flux 90/10 LiM/LiT was chosen because of its high output of results and good dissolution in acidic solution. It combines the superior melt characteristics of $LiBO_2$ and $Li_2B_4O_7$ to dissolve the heterogeneous EWC mixture. It is noted that from 65/35 LiM/LiT to 100LiM the percentage recovery was high with the 90/10 ratio having a quicker melt. The LiM has lower viscosity and lower melting point than the LiT thereby producing better melt that resulted in higher results.

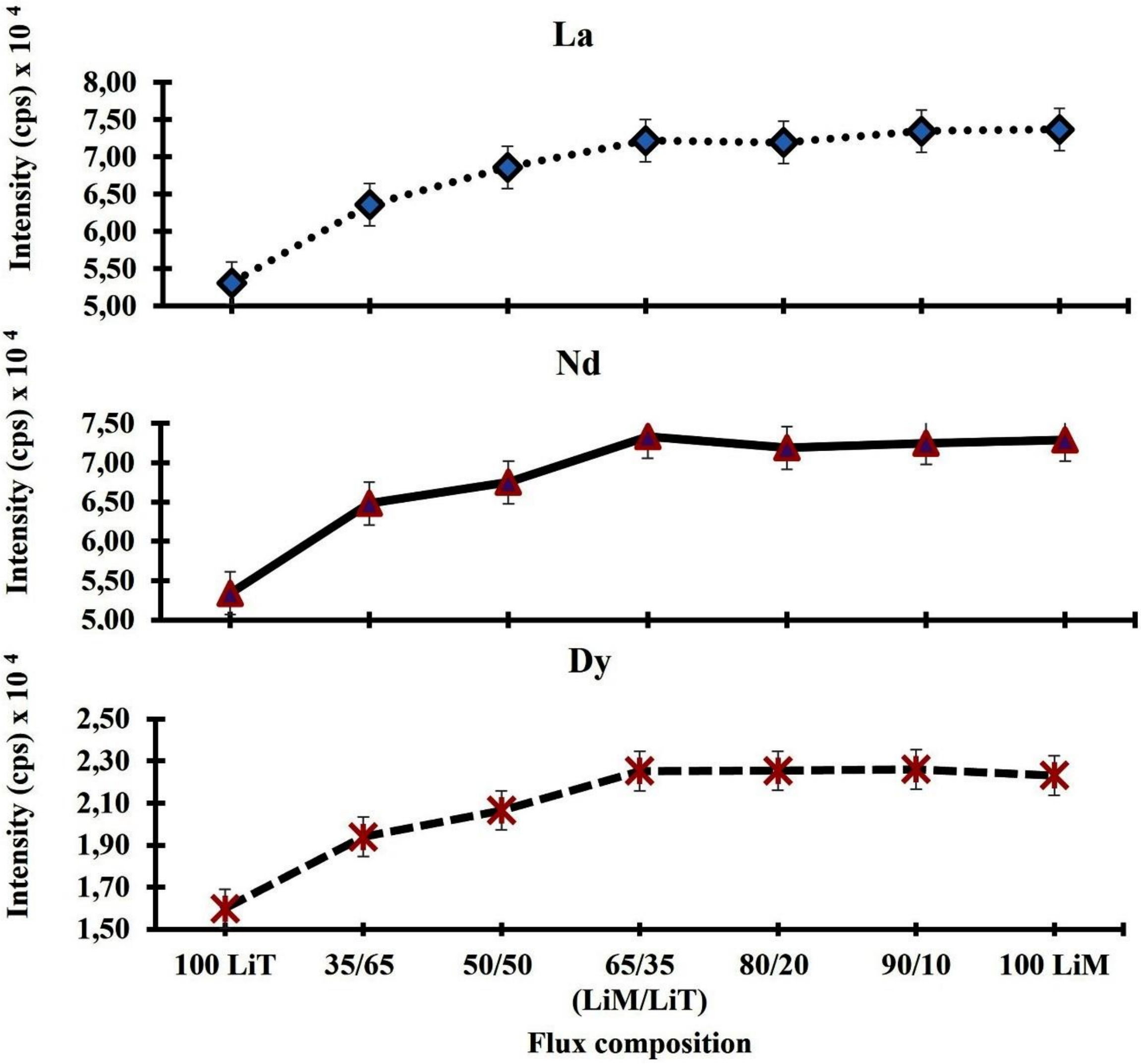


Figure 4. 3: **Intensities of La, Nd and Dy were obtained after fusion of the EWC sample with different compositions of borate flux. Weight of sample and flux mixture was at 0.2 g and 1.8 g respectively. oxidant (Na2CO3: NaNO3) 100 mg, non wetting agent 250 µl of 25% LiBr and 12 minutes fusion time.**

4.4.3. Sample to flux ratio

The flux to sample ratio is an important factor to take into consideration during the borate fusion procedure. The influence of the sample to flux ratio determines how the sample dissolves in the given flux and the consequences of high solids in the solution. The sample weight was varied from 0.05 to 0.20 g, while flux was varied from 1.00 to 2.00 g. This protocol is comparable to the investigation done in an earlier study by Makombe et al. (2016), where flux to sample ratio was investigated in sediment samples. The major aim of experimenting the ratios was to obtain optimum conditions for the dissolution and was observed physically similar to protocol in Table 4.1. This was important to safeguard the platinum corrosion due to insufficient flux. Too much flux is perfect for dissolution but not for the ICP-OES where too much solids in the sample will affect aspiration and cause quartz torch to melt. The digestion solution of 2 g flux to 0.2g sample was the maximum solid content with complete digestion but was not perfect for ICP-OES readings. In this section, the physical checking and monitoring fusion was considered critical than elemental intensities from the instrument.

The e-waste studied proved more difficult to dissolve than sediments, and a low sample to flux ratio was considered to allow more flux to act on a small sample size. This ratio also helps to avoid much contact of the sample with the crucible. The optimum sample/flux ratio considered for the metallic EWC of < -53 µm size fraction was 0.1 g sample to 1.5 g Flux, which is a 1: 15 ratio.

4.4.4. Effects of oxidisers and pre-oxidation

The bulk of the EWS is rich in metallic, carbon and sulphide compounds that are all reducing species and a danger to Pt-Au crucibles, as reported by Ling et al. (2014) on sulphide ores fusion. The oxidant is an additive to the flux that helps ensure the sample is in an oxidised state to avoid potential reduced species in the sample to damage Pt – Au crucibles. The oxidation process that was utilised in this study was roasting the sample at 550 ^{o}C to eliminate the organics and the addition of chemical oxidants to the flux before the fusion stage. The oxidants that were investigated were Na_2CO_3, $NaNO_3$, $NaNO_3$-Na_2CO_3, and KNO_3, respectively. The mass of each oxidant was varied from 10 mg to 80 mg on a sample mass of 0.1 g, 1.5 g flux, constant non wetting agent and time. All the fusion was done on the same e-waste sample and the intensities of lanthanum recorded on ICP-OES as shown on Figure 4.4 (a). The other possible oxidants such as $Sr(NO_3)$, Li_2CO_3, $LiNO_3$ and NH_4NO_3 were not evaluated, but the choice of the alkali metal on the oxidant did not matter much since only REEs were of interest in the study. Most of these chemicals are very deliquescent and problematic to handle, great care on weighing and avoiding wet conditions was considered key to avoid erroneous results. In addition, low relative humidity storage conditions of these chemicals are essential. The use of coated pellets of the oxidants may be considered to avoid the high moisture affinity.

The EWC from mobile phones was investigated for intensities of REEs. Figure 4.4 (a) displays the Lanthanum (La) results as representative of all REE elements obtained under the conditions stated earlier. Low- temperature fusion was preferred below 1000 ^{o}C to avoid the oxidant's vaporisation before the fusion reached completion. The mass of oxidants was varied from 10 mg to 80 mg for a total fusion mixture of 1.5 g. The increase of Na_2CO_3 oxidant show a minimal effect on REEs intensities but a substantial increase of intensities was observed when $NaNO_3$, $NaNO_3/Na_2CO_3$ and KNO_3 oxidants were applied. However, the combination of $NaNO_3/Na_2CO_3$ reveals the increase in intensities for all elements from 10 mg to 50 mg and decreased on 80 mg weight. The excessive use of the oxidant may alter the sample composition and reduce its concentration hence the minimum amount of oxidant producing good intensities that can save chemicals was chosen. The mixture of $NaNO_3/Na_2CO_3$ presents the best oxidant, followed by the Na_2CO_3, $NaNO_3$, and KNO_3 on the intensities of all elements under study. The combination of $NaNO_3/Na_2CO_3$ at 50 mg was chosen for further studies. The combination of both will provide enough oxidation of samples from low temperatures to high temperatures giving desired Pt-Au crucible protection. Secondly, the mixture aids the flux solvent power by converting the sample's cationic constituents to acid-soluble oxides or carbonates and enabling increasing dissolution power of the REEs.

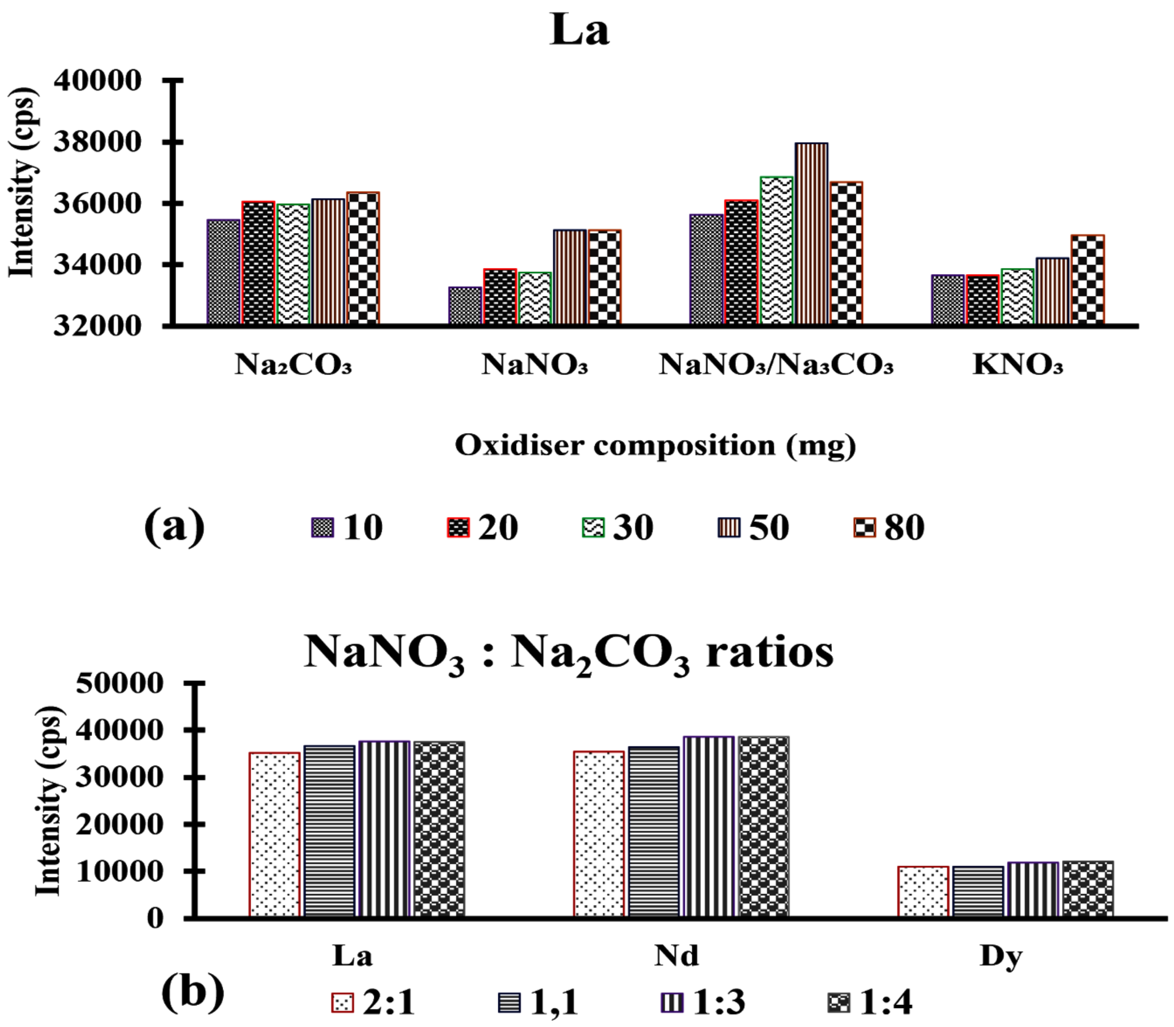


Figure 4. 4: **The effect of various oxidants of Na_2CO_3, $NaNO_3$, $NaNO_3/Na_2CO_3$ and KNO_3 in increasing amount to the intensity of La. (a) Ratio optimisation of oxidising agent on the intensities of La, Nd and DY (b).**

The optimum ratio of $NaNO_3/Na_2CO_3$ oxidant was further investigated and results elaborated in Figure 4.4(b). The oxidant was mixed in different proportions to ascetain its effectiveness on the fusion of e-waste sample. All other factors such as sample and flux mass, volume of non wetting agent, oxidant mass and time were kept constant. The ratios 1:3 and 1:4 of $NaNO_3$: Na_2CO_3 produced the slightly better intensities for all the REEs, of which 1: 3 was chosen as the combination of choice in this study. This implies that a mass of 12.5 mg $NaNO_3$ mixed with 37.5 mg Na_2CO_3 to make 50 mg was used in each sample for analysis.

4.4.5. Effect of non-wetting agent

Non-wetting agents (NWAs) volatility increases with increasing atomic weight. The heavier halides bromine and iodine bonded to the cation, commonly lithium, sodium and potassium make an ideal non-wetting agent (NWA). However, according to Loubser et al. (2004), 50% of LiBr and 90% of LiI is lost during 10 minutes of fusion time, respectively. In this study, we investigated the effects and ideal quantities of LiBr and LiI as NWAs for EWC determination. Fig. 5 displays the results for the weight increment of LiBr and LiI with all other experimental conditions unchanged as in section 4.4.4. The EWC intensities of REEs La, Nd, and Dy behaved similarly as expected, despite the non-wetting agent mass variation.

The mass of the LiBr was varied from 10 mg to 120 mg, with the best intensities obtained between 40 mg and 120 mg. This showed the optimum transfer of the melt requires at least 50 mg of LiBr. The LiI was likewise varied from 10 mg to 100 mg with no significant variations of REEs intensities. The optimal intensities were obtained between the mass of 50 mg to 100 mg but with 10% less intensity than in corresponding masses of LiBr. This is elucidated by the volatility of the halides, where Br is less volatile than iodine (Claisse, 2003). The extreme hygroscopic nature of the LiI compounded by its high volatility make the weighing wearisome; hence LiBr was chosen as the NWA in this study. The application of a liquid non-wetting agent was deemed necessary for accurate and repeatable results.

Additionally, preliminary studies were conducted on weighing the solid NWA and mixing it with the sample prior to fusion, but inconsistent results were recorded. To overcome this problem a 50% w/v solution of NWA was prepared and added to the sample by a micropipette corresponding to the solid weights. The optimum volume considered for the complete transfer of melt was 100 µl, representing 50 mg of NWA. Within the mixture, the halide atom stays at the surface of the melt while the cation penetrates inside, thereby unsettling the strong boron-oxygen bonds. However, this will create a distinct physical separation between the oxygen atoms in molten glass and oxygen atoms bedded on the platinum crucible protective layer.

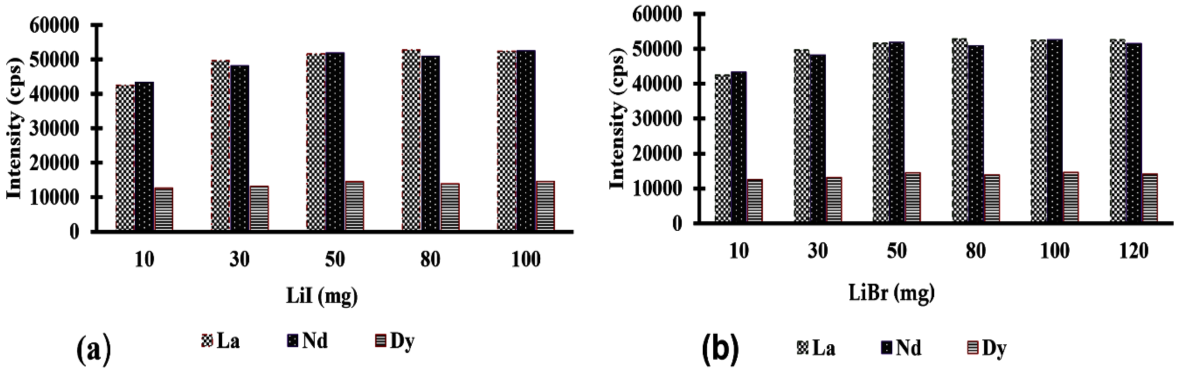


Figure 4. 5: **The effect of quantity of NWA LiI (a) and LiBr (b) on intensities of La, Nd and Dy. Weight of sample and flux mixture at 0.1 g and 1.5 g respectively. oxidant (Na2CO3: NaNO3) 50 mg and 12 minutes fusion time.**

4.4.6. Particle size effects

The particle size of the EWC sample has relevance on its solubility into the flux. By keeping all the other factors constant, like the flux composition mass (1.5 g), the fusion temperature (> 900˚C), sample mass (0.1 g), oxidant ratio $NaNO_3/Na_2CO_3$ (1:3), amount of non-wetting agent (NWA) (50 mg) and oxidant mass (50 mg) , the dissolution increased by reducing the particle size. A crushed, milled and sieved smartphone sample was used to investigate this section of the study. A series of sieves with aperture sizes varying from 90 µm to 53 µm were investigated, with the results shown in Figure 4.6.

The dissolution test was observed physically and by the intensities of REEs on ICP-OES analysis. At the particle size of >75 µm, the dissolution was problematic and finer metallic particles were observed. These particles agglomerated to make bigger metallic pieces, which were like a copper sheet and became hazardous to the platinum ware. Figure 4.6 displays a graph of intensities obtained for La at different particle size fractions, starting with a coarse fraction of less than 90 µm to less than 53 µm. The intensities increased with a reduction in particle size. This showed that the best dissolution was achieved by small particle size where the flux had more surface area to act upon the sample. It was observed that for the same sample, by only decreasing the particle phase it was able to obtain a homogenous solution without undissolved particles.

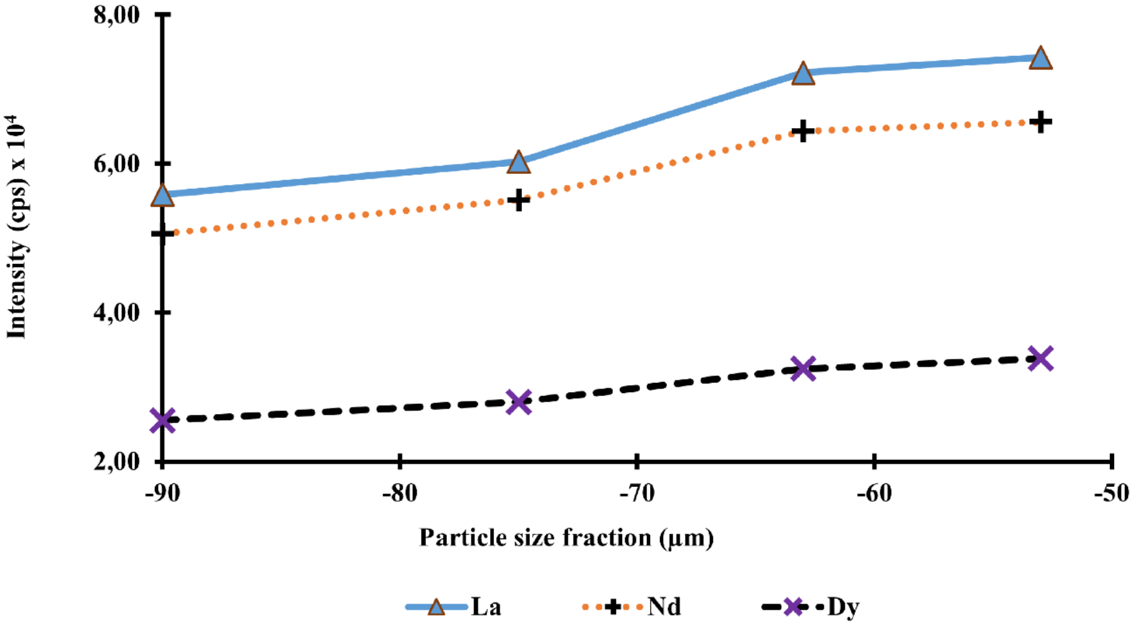


Figure 4. 6: **The graph of results for La, Nd and Dy intensity at different particle size fractions obtained after sieving.**

4.4.7. Effect of fusion time

The crucible containing the sample was heated from a low to a high temperature by controlling the gas. Table 4.1 elaborate on the trial conditions necessary for the entire dissolution of the sample. The sample mixture was heated to initiate and speed up the oxidation reaction that quickly followed. Complete digestion of the sample is the primary objective to get accurate analytical results. The heating time was adjusted on three heating stages of the fluxer machine to achieve this total melt. Stages 1, 2 and 3 use 20%, 50% and 60% of the gas, respectively. The temperature was ramped gradually by increasing the gas to allow the oxidiser to melt before sample dissolution. In some trials shown in Table 1 clearly shows that the sample may still be undissolved after the fusion steps but may dissolve after extended stirring. In trials number 1 and 2, the solution was not dissolved even with extended stirring. The trials with complete sample dissolution after fusion were considered, and trial number 7 was chosen as the optimum time conditions for EWC dissolution in borate fluxes. The step was performed to allow the oxidiser to melt first whilst avoiding its volatilisation before the sample melt.

Table 4. 1: Time conditions for the optimisation of the dissolution procedure.

Trial	**Heat stage 1 (Gas=20) Time (min)**	**Heat stage 2 (Gas=50) Time (min)**	**Heat stage 3 (Gas=60) Time (min)**	**Condition of solution post-fusion**	**Condition after extended stirring**	**Total Fusion time (min)**
1	5.0	1.5	0.5	Incomplete dissolution	Not clear/undissolved	10.0
2	4.0	1.0	1.0	Incomplete dissolution	Not clear/undissolved	9.0
3	3.0	1.0	2.0	Partly dissolved	Clear solution/dissolved	8.5
4	2.0	4.0	1.0	Completely dissolved	----	9.0
5	3.0	3.0	1.0	Completely dissolved	----	10.0
6	2.0	2.0	1.0	Partly dissolved	Clear solution/dissolved	8.0
7	3.0	4.0	1.0	Completely dissolved	----	10.0
8	3.0	5.0	1.0	Completely dissolved	----	11.0

This study aimed to determine optimum preparation conditions of alkaline fusion procedure as elaborated in Table 4.2. The design of the optimisation process prioritised essential parameters for a safe and fast fusion protocol. In the series of experiments for optimisation it is crucial to start with flux composition, then sample to flux ratio and end with time variation as displayed in Figure 1. Modification of the order of variables may cause problems such as damage to platinum ware and incomplete fusion. For the safe fusion of electronic waste components, the optimum conditions are summarised in Table 4.2.

Table 4. 2: Summary of the optimal conditions for improved sample preparation and alkaline fusion procedure to determine REEs on electronic waste components.

Parameter	**Condition**
Size Fraction (µm)	53
Loss on Carbon (LOC) Temperature (ºC)	550
Flux composition	90%$LiBO_2$ + 10% $Li_2B_4O_7$
Mass of Flux (g)	1.500
Oxidant (mg)	50
Oxidant ratio	$NaNO_3$: Na_2CO_3 (1:3)
Non wetting agent (NWA)	200 µl of 25% LiBr
Mass of sample (mg)	100
Sample to flux ratio	1:15
Fusion time (total) mins	10

4.4.8. Composition of other metals in electronic waste components

Line selection was performed for 15 rare earth trace elements using a solution e-waste material digested by the fusion analysis and rare earth ore reference material. The ICP OES spectroscopy has been widely embraced for REE determination, but at the same time, it suffers from interferences. Careful line selection studies have been adopted in this study to meet precision, sensitivity, accuracy, and spectral interferences. The Spectro Arcos is equipped with a plethora of emission lines for each element. However, many of them interfere with matrix effects and inter-element from sample composition. Table 4.3 has shown that EWCs are also rich in more elements other than REEs, such as Cu, Ti, Ba, which pose a threat to interfere with

REEs lines. The elements shown in Table 4.3 were more predominant in EWCs samples analysed from a list of other 55 elements scanned. The elements Cu, Ba, Fe, Ni, Ti, and Zn, appear in all samples tested. The FP-02 feature phone (non-smartphone) is Cu reach with 44.64% and PC-B1 with 9.36%. Fe is also predominant in smartphone sample (SM-01) with 22.90% and computer printed circuit board (PC-B1) with 15.68%. The composition of other elements recorded in Table 4.3 were all less than 0.45% but became valuable in studying interferences and selecting the ideal REEs analytical lines. The results obtained were expected since e-waste is rich in metallic waste however, it was noted that different smartphones models and brands contain variable range of elements.

Table 4. 3: **Composition of selected major elements in EWC samples (a) Smartphone (SM-01), (b) Feature phone (FP-02 and Computer PC board) PC-B1).**

Sample type	**Elements (%)**													
	Cu	**Fe**	**Ni**	**Ba**	**Ti**	**Zn**	**Ag**	**P**	**Mg**	**Na**	**K**	**Pb**	**Sb**	**Sr**
SM-01	17.77	22.9	7.17	6.83	1.6	0.6	0.4	0.34	0.33	0.21	0.12	0.06	0.03	0.29
FP-02	44.64	3.23	3.5	1.01	0.43	2.06	0.18	0.47	0.16	0.04	0.09	0.17	0.01	0.08
PC-B1	9.36	15.68	0.39	0.76	0.36	0.22	0.05	0.16	0.32	0.22	0.07	0.28	0.1	0.07

4.4.9. Line selection and interferences

The spectral interferences are encountered in diverse ways such as direct spectral overlap, wing overlap and close emission lines that may alter the background (Gaines, 2011). This was monitored during this study and alternate lines that do not require spectral and complex background corrections were chosen. The copper levels in EWC interfered with some lines such as the Cu301.084 line on the Gd301.013 line, the Cu417.951 line on the Pr417.939 line, but the small intensity of this line did not cause harm to the Pr417.939 line. The Na314.928

line impacted the Nd314.929 line, the Fe379.500 line on the La379.478 line, the Ag338.289 line on the Dy338.502 line, the Ti337.280 line on the Er337.271 line and the Te212.600 line, the Ti337.280 line on the Er337.271 line, the Cu212.604 line on the Tb212.600 line. Results from Tb emission lines should also be selected with care as Tb suffers greatly from spectral interferences. The behaviour and chemistry of REEs are so similar that spectral interferences cannot be avoided completely. The following line interferences have been observed for the Sm422.533 line on the Pr422.582 line, the Gd448.900 line on the Ce448.691 line, the Nd359.259 line on the Sm359.260 line, and the Sm337.280 line on the Er337.271 line. Based on the present results, the best lines used for EWC are shown in Table 4.4

4.4.10. Limit of detection

The relative standard deviation (RSD) was determined under the optimised conditions from 10 measurements of the blank solution for each analytical line. The limits of detection (LOD) given in Table 4.4 is defined as the concentration required to give a signal three-fold greater than the standard deviation of the background fluctuation (3σ) and the calibration curve slope (s) according to the formula:

$$LOD = \frac{3\sigma}{s} \qquad Eqn\ 4.1$$

The relative standard deviation was measured from 5 replicates of the sample on each analytical line as given in Table 4.4. The results indicate that the LODs for the REEs determined by the proposed method correspond to those obtained by other techniques used in this study as elaboraated on Table 4.6 despite high solid content in the solution. Good linearity (regression coefficients > 0.998) was observed for all elements analysed by ICP-OES.

Table 4. 4: **ICP-OES analytical spectral lines and detection limits for REEs determined by 10 consecutive 10 % HNO_3/1.5 % borate flux blank solution measurements.**

Element	**Wavelength (nm)**	**Detection limit*** ($\mu g\ g^{-1}$)	**RSD** # **(%)**
La	408.672	0.20	4.61
Ce	418.660	2.77	5.01
Pr	333.749	3.14	5.02
Nd	401.225	0.49	7.80
Sm	442.434	2.68	1.27
Eu	381.967	0.15	5.21
Gd	335.047	0.83	9.42
Tb	350.920	1.73	1.65
Dy	353.170	2.93	3.55
Ho	345.600	0.86	4.60
Er	349.910	0.30	4.27
Tm	313.126	1.58	3.21
Yb	369.419	0.31	2.56
Lu	261.542	1.46	2.52

*Ten blank replicates; #Five sample replicates

4.4.11. Accuracy and precision

The proposed methodology's accuracy and precision were assessed by performing recovery studies on feature phone (non-smartphone) sample FP – 02. The REEs (La, Pr, Nd, and Dy) with known concentrations were added to determine the alkaline fusion method's (AFM) recovery and accuracy, as presented in Table 4.5. The addition of the spike volume was done on the e-waste pulverise sample dried before the fusion process. The good recoveries of the results showed that not much volatilisation of the analyte occurred during the fusion process. The least recovery was 90.1% for Nd, followed by 91.4% for Dy, with values of 94.5% for Pr and La at 101.6%, respectively.

Table 4. 5: Results for the recovery studies obtained for the determination of REEs in electronic waste samples.

	Sample FP – 02			
	La	**Pr**	**Nd**	**Dy**
Base value (µg g^{-1})	557.7 ±9.1	60.9 ±3.2	1749.9 ±32.3	125.5 ±4.7
Added value (µg g^{-1})	100.0 ±4.2	10.0 ±0.8	200.0 ±11.6	20.3 ±1.5
Recovered value (µg g^{-1})	660.3 ±11.2	70.4 ±3.7	1930.1 ±40.7	143.8 ±5.4
Recovery (%)	101.6 ±4.3	94.5 ±5.1	90.1 ±4.9	91.4 ±3.6

4.4.12. Influence of digestion procedures on electronic waste determination.

The proposed method's applicability was evaluated for e-waste samples, mainly PCBs of mobile phones and computers. Three samples (i) SM-01 represented a composite material from smartphone models, (ii) FP-02 from feature phones and (iii) PC-B1 originated from computer PCBs. The currently developed technique of alkaline fusion digestion (AFD) was validated against established methods for four acid digestion (4AD) and microwave digestion (MWD). The digestate from the three procedures was all determined on ICP-OES using different matrix-matched standards. The results displayed in Table 4.6 explicitly reveal that the composite sample from smartphone models have the highest concentration of REEs with Pr and Nd in per cent levels, Yb with the least concentration and Lu not detected in all samples. The feature phone models show a considerable amount of REEs but far less than the smartphone models. The computer PCB showed the least REEs values with six elements below detectable levels. A rare earth ore reference material DC86312 was used to determine the method recoveries and optimise instrumental conditions. No matrix-matched reference material from e-waste was found. Good recoveries were obtained for the reference material with the best recoveries from the alkaline fusion procedure. The complex nature metallic components of samples were more resistant to the microwave digestion technique. Some particles agglomerate and were found after digestion meaning the dissolution was not complete. The four-acid digestion produced a clear digestate solution and the results were close to the alkaline borate fusion protocol. However notable differences of at least 15% less on few elements such as La, Gd, Sm and Tb were recognised. The REE ore DC86312 compared well for most elements on all digestion protocols with microwave-assisted digestion producing the least recoveries. The developed alkaline fusion method showed superiority in repeatability, as evidenced by the results' lower deviation as elaborated in Table 4.6.

From a set of replicate results for each digestion method the mean, standard deviation and confidence interval was calculated for La, Nd and Dy. The 95% confidence interval (CI) was given with the equation 4.2 as follows

$$CI = \overline{x} \pm Z \left(S_{/\sqrt{n}}\right) \qquad Eqn\ 4.2$$

Where $\overline{x}$ = mean, Z = 1.960, S = standard deviation and $\sqrt{n}$ = square root for the number of measurements

Example 1: La for sample SM-01 on alkaline fusion method (AFD)

CI = 369 ± 1.960 (5.0/$\sqrt{3}$) = 369 ± 5.66 µg g^{-1}

Range = 363.34 - 374.66 µg g^{-1}

Example 2: Nd for sample SM-01 on alkaline fusion method (AFD)

CI = 62302 ± 1.960 (840/$\sqrt{3}$) = 62302 ± 950.58

Range = 61351.42 – 63252.58 µg g^{-1}

Table 4. 6: **Results obtained for the concentration of REEs from three digestion techniques (confidence interval 95%, n = 3) Alkaline fusion digestion (AFD), 4-acid digestion (4AD) and Microwave-assisted digestion (MWD).**

Element	**SM-01 (µg g^{-1})**			**FP-02 (µg g^{-1})**			**PC-B1 (µg g^{-1})**			**DC 86312 (µg g^{-1})**			
	AFD	4AD	MWD	AFD	4AD	MWD	AFD	4AD	MWD	AFD	4AD	MWD	**Ref** [a]
La	369 ± 5	316 ± 7	272 ± 7	558 ± 14	493 ± 11	512 ± 16	23.0 ± 1.1	17 ± 1.2	16.8 ± 1.5	2353 ± 22	2329 ± 29	2295 ± 31	2362 ±170
Ce	3.7 ± 0.4	3.7 ± 0.6	3.3 ± 0.6	ND	ND	ND	ND	ND	ND	180 ± 9	179 ± 9	166 ± 10	187 ± 10
Pr	14576 ± 142	12693 ± 124	8894 ±107	59.8 ± 3.2	60.9 ± 3.7	42.7 ± 2.5	3.0 ± 0.4	3.6 ± 0.4	2.7 ± 0.3	461 ± 19	456 ± 25	404 ± 28	447 ± 30.
Nd	62302 ± 840	52698 ± 726	31117 ± 598	1768 ± 26	1635 ± 29	1771 ± 23	15.0 ± 0.8	13.8 ± 0.9	13.1 ± 1.0	1584 ± 32	1556 ± 27	1368 ± 39	1595 ±100
Sm	1932 ± 17	1637 ± 15	1410 ± 19	19.4 ± 0.5	20.2 ± 1.0	22.3 ± 1.2	23.3 ± 0.6	23.7 ± 0.9	21.6 ± 1.0	293 ± 11	274 ± 14	252 ± 15	285 ± 30
Eu	5.0 ± 0.4	5.8 ± 0.4	4.2 ± 0.5	2.0 ± 0.2	2.1 ± 0.1	1.7 ± 0.2	ND	ND	ND	67.9 ± 4.3	67.4 ± 5.2	60.4 ± 6.1	65.4 ±4.0
Gd	508 ± 17	385 ± 19	248 ± 18	50.4 ± 3.2	39.9 ± 2.3	47.0 ± 2.7	0.5 ± 0.1	ND	ND	222 ± 13	218 ± 11	198 ± 25	226 ± 30
Tb	1706 ± 21	1474 ± 24	886 ± 17	56.5 ± 3.1	61.4 ± 3.8	44.1 ± 1.8	5.1 ± 0.4	4.4 ± 0.4	5.6 ± 0.5	38.6 ± 2.1	42.9 ± 2.5	25.3 ± 3.7	34.6 ± 2.6
Dy	2318 ± 17	1949 ± 19	1426 ± 15	196 ± 3	181 ± 3	169 ± 4	177 ± 3	153 ± 3	163 ± 4	183 ± 2	182 ± 3	179 ± 3	183 ± 20
Ho	83.8 ± 1.2	75.7 ± 1.0	40.7 ± 0.7	13.8 ± 0.1	13.5 ± 0.2	12.6 ± 0.2	ND	ND	ND	35.1 ± 0.8	34.7 ± 1.0	35.0 ± 0.9	35.5 ± 4.6
Er	227 ± 11	233 ± 13	157 ± 9	0.6 ± 0.1	0.7 ± 0.1	0.4 ± 0.1	ND	ND	ND	101 ± 6	98.5 ± 5.5	97.6 ±4.9	96.0 ± 10.0
Tm	8.8 ± 0.4	6.0 ± 0.5	6.9 ± 0.5	8.0 ± 0.4	6.9 ± 0.4	8.0 ± 0.5	0.7 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	14.0 ± 1.0	13.2 ± 0.8	12.4 ± 1.1	13.2 ± 1.3
Yb	2.4 ± 0.2	1.6 ± 0.1	3.0 ± 0.4	1.3 ± 0.1	0.9 ± 0.1	1.3 ± 0.1	28.7 ± 1.4	24.1 ± 1.5	20.8 ± 1.6	89.0 ± 3.4	89.0 ± 3.3	85.6 ± 5.2	88.0 ± 12.0
Lu	ND	ND	ND	ND	ND	ND	ND	ND	ND	13.3 ± 1.2	13.0 ± 1.2	11.6 ± 1.1	12.0 ± 1.0

4.4.13. Comparison of spectroscopic techniques: ICP-OES versus XRF

The digestion process for the two techniques involved borate fusion which, as expected, produced a more homogeneous solution for ICP-OES and fused glass bead for XRF. The primary difference between the two preparatory procedures is the weight of the sample used and the flux combination. For the XRF a 1:10 sample to lithium borates flux (66.67% $Li_2B_4O_7$ – 32.83% $LiBO_2$ – 0.5% LiI) ratio was utilised. To validate the developed protocol, three e-waste samples, SM-01, FP-02 and PC-B1, were evaluated by comparing results for La, Pr and Nd obtained from the two spectroscopic instruments as shown Figure 4.7. The values of Pr and Nd in sample PC-B1 were below the detection limit of the XRF technique. The XRF technique did not detect the Dysprosium (Dy) due to low intensity. The results compared well between the two spectroscopic techniques for the elements measured with a bias of slightly higher values in ICP-OES.

The mean comparison of each element after replicate results is very similar on both spectroscopic techiques. However, the comparison of the standard deviations showed lower deviations on XRF than ICP. The ICP Standard deviations for La, Pr and Nd were 6.11, 3.00 and 12.12 respectively for sample SM-01. For XRF for the same sample it was 7.02, 1.00, and 5.03 for La, Pr and Nd. Comparing with other samples it was noted that for lower values ICP gave lower standard deviations than XRF but at higher values like Nd results XRF gave more precise values. These results show that the ICP-OES is a more sensitive and good choice than the XRF technique for the samples digested based on the present conditions.

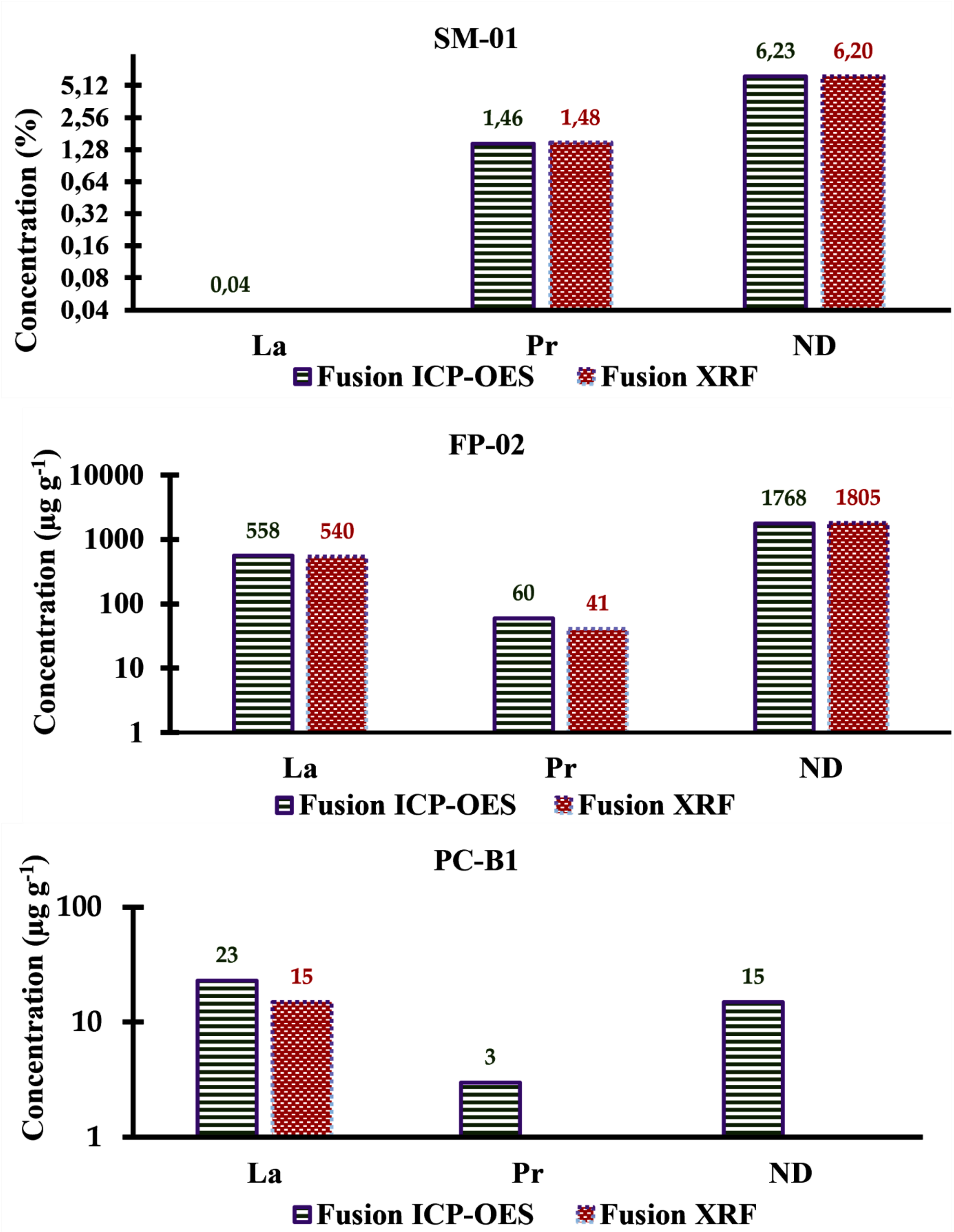


Figure 4. 7: Comparison of results of La, Pr and Nd from fusion ICP-OES vs fusion XRF in EWC samples (a) Smartphone (SM-01), (b) Feature phone (FP-02 and Computer PC board) PC-B1).

4.5. Summary

Some of the problems addressed using this approach were metallic content in samples. The pre-oxidation step of sample decomposition at 550 ^{o}C drove off volatile organics in the sample. Fine grinding increased surface area by reducing particle size to less than 53 µm. The pre-oxidation steps were further complemented by the addition of oxidising chemicals before the fusion steps. The experimental parameters were optimised to achieve the ideal dissolution conditions and safeguarding the corrosion of the platinum ware. To attain an ideal solution for ICP-OES introduction, the sample to flux ratio and final dilution of the acidic solution was investigated. Experimental results showed that this method applied to e-waste is precise less than 5% RSD on most REEs, robust and fast because of instrument automation. The alkaline fusion method showed that it is superior to the traditional mineral acid digestion procedures, such as microwave and multi-acid open digestions. The Fusion ICP-OES results compared well with fusion XRF results on investigated REEs for specific electronic waste component samples. The breakthrough of the method was the ability to carefully fuse samples with a plethora of metallic components in platinum crucibles, which is normally problematic due to the metal reaction with crucibles. The homogeneous mix and complete dissolution of the refractory nature of e-waste with rare earth oxides within a limited time frame were executed impeccably. The fusion technique has been successfully applied to electronic waste components for the first time.

CHAPTER 5

THE LEACHING BEHAVIOUR OF RARE EARTH ELEMENTS FROM ELECTRONIC WASTE SOURCES: A MICROCOSM

5.1. Introduction

In this chapter, we report the results of several microcosm studies using conditioned soil and crushed e-waste material to investigate the leaching of REEs in lab-scale experiments. The characterisation of the soil and e-waste materials used has been evaluated. Static column leaching studies have been done to better understand the leaching of REEs in natural soils. In order to comprehend the leaching of REEs from e-waste components, the batch leaching tests using various lixiviants have been optimized. Additionally, the effects of major variables on REE batch leaching were analysed, including lixiviant concentration, time, stirring speed, pH, and solid-to-liquid ratio. This chapter concludes with leaching comparisons of rare earth elements with other studies elsewhere.

5.2. Overview

Recovery of rare earth elements from electronic waste, rich in medium and heavy rare earth elements has been targeted in recent years to supplement global shortfalls of rare earth ores (Oh *et al*., 2003; Mishra and Rhee, 2014; Brewer *et al*., 2022). Acids such as H_2SO_4, HNO_3, H_3PO_4, and HCl are some of the acids used as leaching agents in hydrometallurgical recovery studies of rare earths from phosphate rock (Amine *et al*., 2019). Most inorganic and organic chemicals enhance metal leachability (Yang *et al*., 2021). Taggat *et al*., (2018) discovered that NaOH or Na_2O_2 increased the leachable rare earth elements on roasted coal fly ash to 80–90% of the total. Chu and Ko (2018) investigated acid leaching techniques for removing heavy metals from contaminated farmland. Leaching is the process of a solute becoming detached from or extracted from its carrier substance (solvent) by way of a liquid solvent. The solvent partially dissolves the solid material so that the desired solute can be carried away. It usually operates at an elevated temperature to increase the solubility of the solute in the solvent (Ashiq *et al*., 2019).

Shin et a*l*. (2015) and Brisson et al. (2016) report that bioleaching techniques have become more effective in recent years at recovering valuable minerals from ores while avoiding hazardous emissions to the environment. Ilyas et al. (2013) and Mishra and Rhee (2014) reported metal bioleaching from electronic waste. Qu et al. (2013) utilised citric acid and oxalic acid to successfully bioleach rare earth and radioactive elements from red mud using *penicillium tricolor*. The removal of substances from porous solids is accomplished through two major actions: (1) the physical movement of water as it interacts with material surfaces, and (2) chemical interactions with surfaces. Many metallurgical and extraction processes have relied on the chemical interactions of leaching (Um and Hirato, 2013; Jha *et al*., 2016; Zhang and Honaker, 2020). Leaching has also been linked to environmental pollution, such as acid rain and metal leaching from contaminated soils (Wen *et al*., 2013; Dijkstra *et al*., 2004).

REEs have been leached from primary and secondary resources for hydrometallurgical and extraction purposes. However, little is known about the behaviour of REEs derived from secondary resources in the environment. A soil and e-waste-based microcosm were created in this study to investigate the leaching behaviour, characteristics, and chemical interactions of the REEs associated with e-waste and in soils. Column leaching tests are used to evaluate the leaching potential of common soil in Cape Town by simulating e-waste or site-specific leaching conditions. As a result, this chapter focuses primarily on the specifics of REEs leaching from simulated natural habitats involving e-waste disposal.

5.3. Materials and Methods

5.3.1. Soil preparation

The soil utilised for macrocosm studies was sampled, prepared and treated as described in Chapter 3 section 3.2.3. A portion of the sieved soil was subjected to a particle size distribution (PSD) of 2 mm to 0.045 mm as detailed in Chapter 3 sections 3.3.1 and 3.3.2. A portion of the sieved soil with a particle size of less than 625 mm was labeled untreated soil (TS-01). A sub-sample of the untreated soil was thoroughly mixed with the ground e-waste material at a 9-soil part to 1 e-waste part ratio, yielding a 10 percent e-waste in the soil and labelled treated soil (TS-02).

5.3.2. Electronic waste preparation

The electronic waste preparation used in this microcosm study was prepared in the same manner as reported by Makombe et al. (2021) and in chapter 3 section 3.2 of this thesis. However, because e-waste from various components is difficult to homogenize, a particle size of less than 0.425 mm was employed in this work for column and batch leaching to increase homogeneity. For total elemental analysis, pulverized e-waste material with a particle size of less than 0.053 mm was used. To determine the magnetic and nonmagnetic fractions, the crushed intermediary particle size (> 0.250 to 0.5 mm) was subjected to magnetic separation using a Capro magnetic separator and the procedure is detailed in Chapter 3 section 3.3.3. The

XRD characterisation of the e-waste material and leached residue were prepared for analysis using a back-loading method (Guinier. 1994) and as described in Chapter 3 section 3.9.5.

5.3.3. Column leaching

The column leaching setup is described in Chapter 3 section 3.8.1.1**.** The purpose of this column experiment was to simulate the potential leaching of REEs from electronic waste disposal in landfill sites through accelerated study. The liquid passes through the stationary solid with no agitation. Column leaching tests estimate the types and quantities of pollutants that are likely to mobilize and migrate into the environment from a wetted solid sample.

5.3.4. Batch leaching

Several batch leaching studies (static extraction) on simulated e-waste material were conducted using various solutions and based on some of the current methods (Townsend *et al*., 2003; Kim, 2005; Almeida *et al*., 2016). The Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPL) are 2 distinct kinds of leaching procedures (SPLP) commonly used. The contents of this procedure are outlined in Chapter 3 Section 3.8.1.2.

5.3.5. Chemical analyses

To fully understand the leaching behaviour of REEs from e-waste, the evaluation of the following parameters was investigated on a sample of crushed and milled e-waste material: lixiviant type, lixiviant concentration, pH, stirring speed, and solid to liquid ratio. All experiments were conducted at room temperature at 25 ± 1 °C. These parameters can be described by the shrinking core model (Batarseh *et al.*, 1989). The leaching kinetics were studied on leaching with HNO_3 acid by the collection of leachates at a time interval from the onset of the test. The leachate collected was filtered and analysed for REEs on ICP-OES as described in Chapter 3 section 3.9.1. REEs leaching efficiency was calculated according to equation 5.1.

$$Leaching\ Recovery\ of\ REEs, \% = \frac{Leached\ REE\ ion\ Conc}{Original\ REE\ ion\ Conc}\ X\ 100\% \qquad Eqn\ 5.1$$

5.3.6. Chemicals and Materials

The leaching and digestion chemicals used were sulphuric acid (H_2SO_4) 98%, nitric acid (HNO_3) 70%, hydrochloric acid (HCl) 32%, hydrofluoric acid (HF), acetic acid (CH_3COOH) 99.7%, citric acid ($H_6H_8O_7$) 99.5% all analytical grades (AR) were purchased from Ace Chemicals (South Africa). The calibration standard solutions were of high purity grade and supplied by VHG Labs (Manchester, USA). The water used for all the experimental work, including standards preparation, was purified using an ion-exchange deionisation process.

5.3.7. Quality control

To ensure accuracy and reproducibility, the chemical and leaching tests were performed in triplicate. For each batch of leaching experiments, a blank of deionised water was run, and the untreated soil was used as a control. Where necessary, a geological REE reference material was used to check the accuracy and recoveries of spectroscopic determinations but its use was limited due to matrix differences. All glass and other consumables were thoroughly rinsed with deionized water after being cleaned with 5% v/v nitric acid (HNO_3)/ 0.1% hydrofluoric acid (HF).

5.4. Results and discussions

5.4.1. Characterisation of soil and e-waste used in macrocosm experiments

The results for the untreated soil (TS01) and treated soil (TS02) are displayed in Table 5.1. The Table displays the soil characterisation results for pH, electrical conductivity (EC), alkalinity (HCO_3), total dissolved solids (TDS), bulky density (ρb**),** total organic content (TOC), loss on ignition (LOI), REE and major elements content. The soil used was basically sand, with a SiO_2 content of more than 95% and the total REEs of the background soil at 30.7 mg/kg, while the treated soil had 303 mg/kg. The mixing of the sand and e-waste to make the treated soil raised the values of other elements and physiochemical parameters, as shown in Table 5.1.

Table 5. 1: Characterisation results of untreated and treated soils.

Soil type	pH	EC	HCO_3	TDS	La	Pr	Nd	Dy	∑REEs
		μs/cm	mg/L	mg/L	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Untreated (TS01)	7.4 ± 0,2	102 ± 5	125 ± 8	51 ± 4	<1.0	14.2 ± 1,3	3.1 ± 0,6	<1.0	30.7
Treated (TS02)	8.4 ± 0,2	1481 ± 57	200 ± 8	735 ± 41	<1.0	64.6 ± 4,2	203 ± 9	7.2 ± 0,6	303.4

continued

Soil type	ρb	Cu	Al_2O_3	CaO	Fe_2O_3	TiO_2	SiO_2	TOC	LOI
	g/cm^3	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Untreated (TS01)	1.53 ± 0,2	<0.01	0.47 ± 0,01	0.17 ± 0,01	0.61 ± 0,02	0.12 ± 0,01	96.8 ± 0,81	1.67 ± 0,04	1.73 ± 0,03
Treated (TS02)	1.55 ± 0,2	1.05 ± 0,01	0.48 ± 0,02	0.18 ± 0,01	0.63 ± 0,02	0.13 ± 0,01	95.6 ± 0,78	1.74 ± 0,05	1.84 ± 0,03

Table 5.2 displays the cell phone electronic waste (PEW1) characterisation results. From the table it showed that the e-waste sample is rich in REEs, Cu content and the majority being magnetic fraction. The material was used for the leaching behaviour in batch experiments and the treatment (conditioning) of the soil used (TS-02).

Table 5. 2: Characterisation of electronic waste material used in microcosm study.

E-waste	La	Ce	Pr	Nd	Dy	ΣREEs	Magnetic	Non-magnetic
	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}	(%)	(%)
PEW1	27 ± 2	298 ± 6	1729 ± 40	8757 ± 125	273 ± 7	11874	96.04 ± 0.27	3.96 ± 0.02

Continued

E-waste	Al	Ba	Ca	Cu	Mg	S	Ti	Pb
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
PEW1	3.49 ± 0.02	3.15 ± 0.02	2.26 ± 0.01	25.99 ± 0.98	4.52 ± 0.02	0.21± 0.01	0.32± 0.01	0.53 ± 0.02

5.4.2. Column leaching experiments

The column leaching experiments were conducted to assess the leaching and transport of REEs from e-waste components mixed with soil. The column unlike batch leaching closely simulates the conditions in natural environments and similar natural conditions. The leachates were collected after every 24 hours for 7 days after the elution with 150 mL of the lixiviant. Two inorganic acid lixiviants 0.1 M H_2SO_4 and 0.1 M H_3PO_4, organic acid 0.1 M $C_6H_8O_7$ (CiA) and rainwater adjusted to pH 4 as control were investigated as shown in Figures 5.1 to 5.4 respectively. The leachates were collected after every 24 hours for 7 days after the elution with 150 mL of the lixiviant. The concentration of REEs in the leachates is shown in Figures 5.1 to 5.4. The highest concentrations were obtained from the first leaching eluent and declined steadily to day 4 for lixiviant H_2SO_4, $H_6H_8O_7$ and rainwater and day 6 for H_3PO_4. This is shown from the cumulative graph that the increase steadied as we approached day 7. The amounts of REEs released on the first day of extraction were the highest for H_2SO_4, with 64.36% Pr, 71.36% Nd and 55.26% Dy on H_2SO_4. This showed that the REEs exposed to soils are easily leached out with dilute acids even at a minimum volume. The other lixiviants produced less than 40% Pr and Nd and less than 50% Dy for the column extractable elements. The total extractable REEs after 7 days were 73.91%, 45.79%, 16.85% and 10.55% for lixiviants H_2SO_4, H_3PO_4, $C_6H_8O_7$ and rainwater, respectively.

The leaching of REE $^{3+}$ ions under similar conditions to natural environments, such as low acid concentration, slow flow rate, temperature, pH, and soil texture, proved that the REEs are leachable depending on the lixiviant solution. It was also noted that some REE ions would not be easily leachable even after an extended contact time under the same experimental conditions. However, changing the concentration of the lixiviant as was observed in batch leaching experiments (in discussions to follow), will impact on the solubility and transport of REEs from the solid sample.

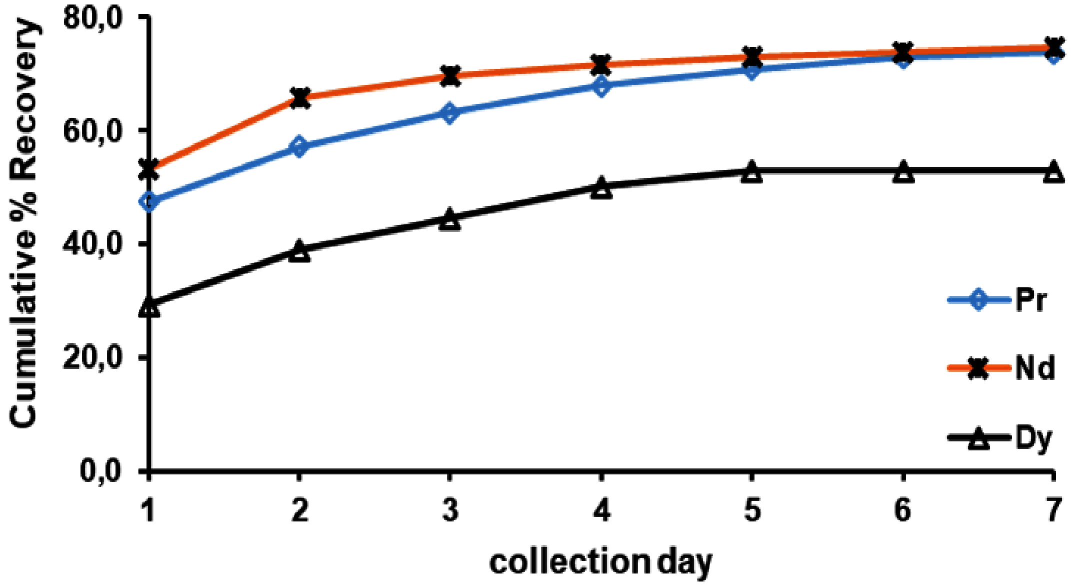


Figure 5. 1: **Column leaching of rare earth elements (Pr, Nd and Dy) from e-waste treated soil into effluent with 0.1M H_2SO_4 lixiviant.**

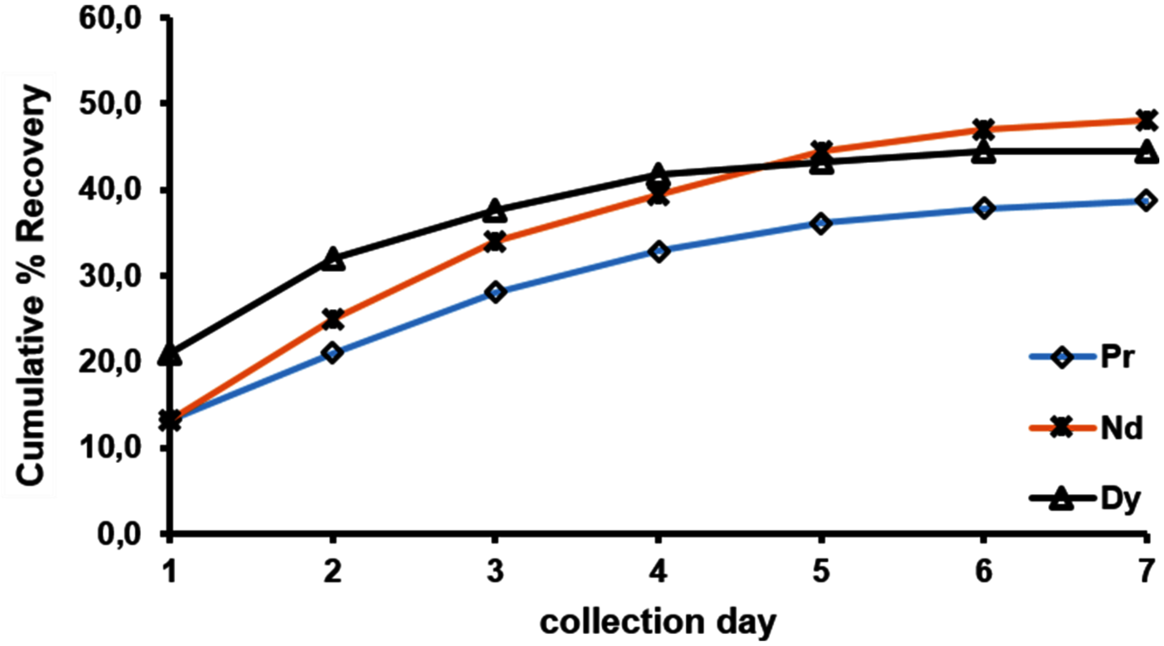


Figure 5. 2: Column leaching of rare earth elements (Pr, Nd and Dy) from e-waste treated soil into effluent with 0.1 M H_3PO_4.

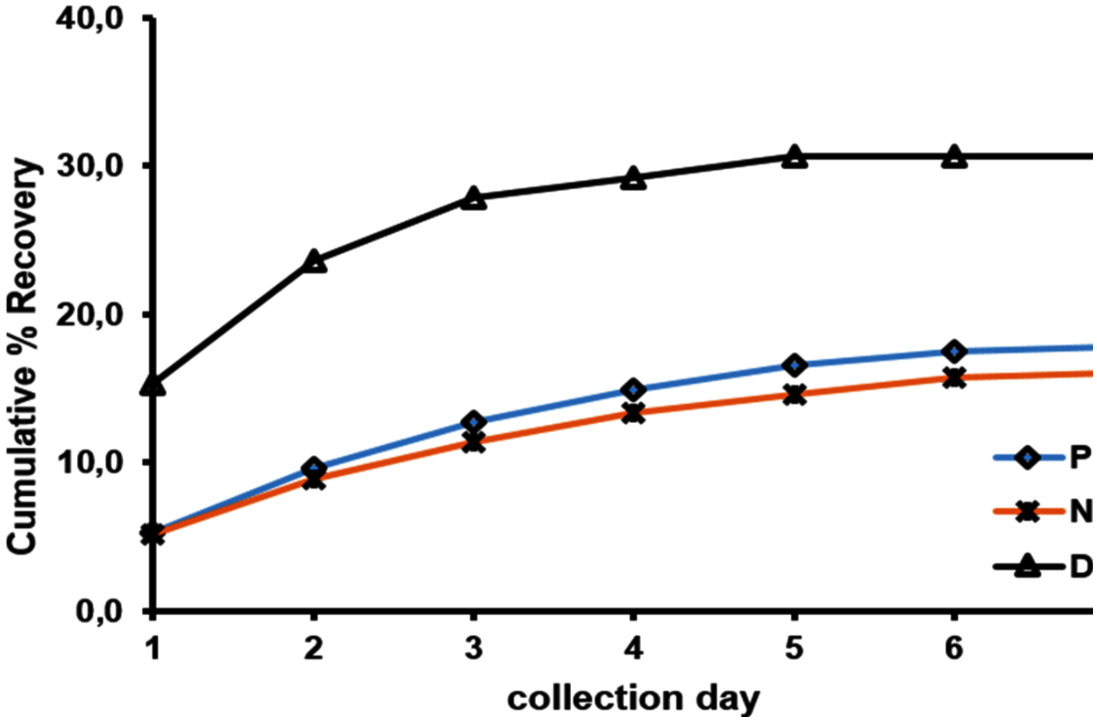


Figure 5. 3: Column leaching of rare earth elements (Pr, Nd and Dy) from e-waste treated soil into effluent with 0.1 M CiA.

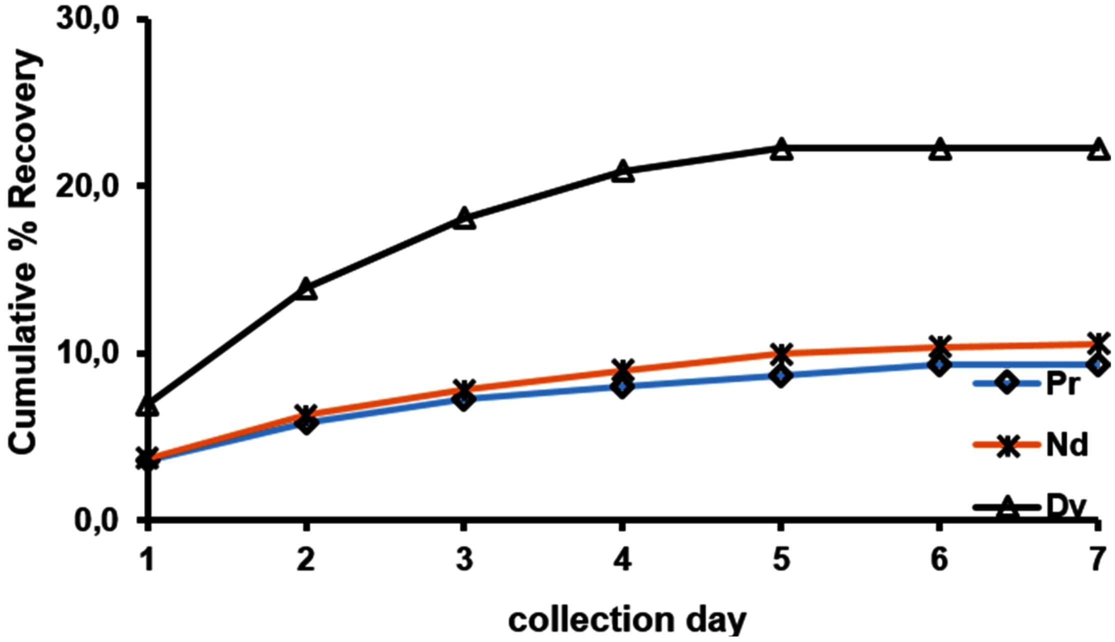


Figure 5. 4: **Column leaching of rare earth elements (Pr, Nd and Dy) from e-waste treated soil into effluent with rainwater adjusted to (pH=4.0).**

5.4.3. Batch leaching tests

This section provides the results of batch tests conducted under different experimental conditions. All batch leach tests utilised the crushed and partially milled e-waste (PEW1) material and treated soil (TS02). The milling improved the sample's homogeneity. The total elemental results of the sample PEW1 was obtained after complete digestion with the developed borate fusion method presented in Chapter 4. The effectiveness of leaching in this section was evaluated by calculating the recoveries based on the full results of PEW1 in Table 5.2.

5.4.3.1. The effect of lixiviant type

The lixiviant's strength and stability influence how quickly REEs dissolve were investigated (Liu *et al*., 2020). A series of experiments in Figure 5.5 were carried out to evaluate the solubility of REEs from semi-milled cell phone waste using various lixiviants.

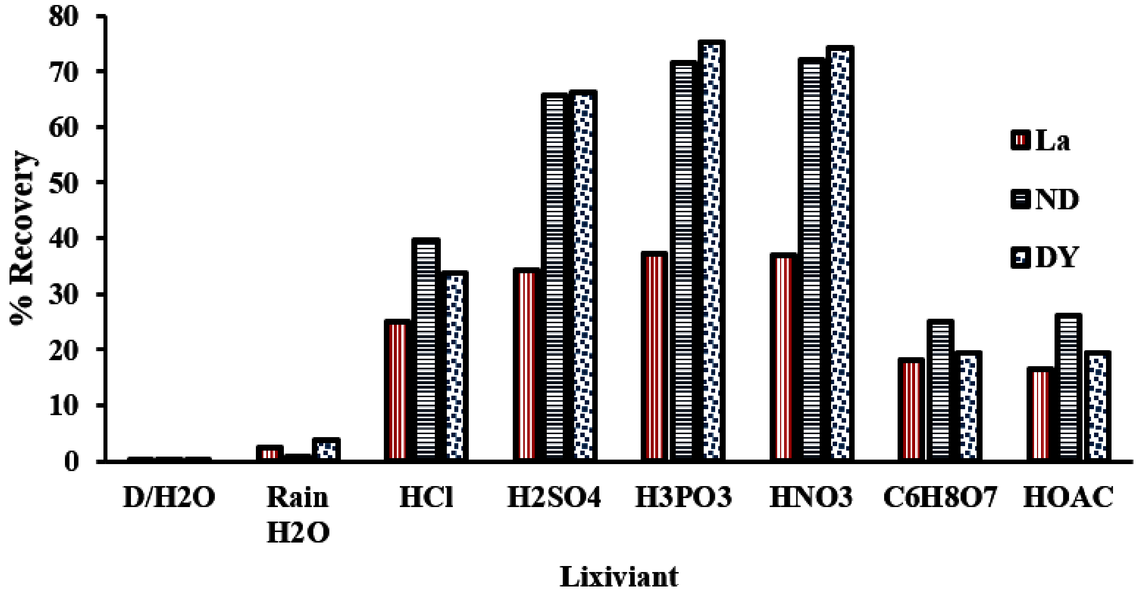


Figure 5. 5: **The effect of lixiviant type on the leaching efficiency of rare earth elements (La, Nd and Dy) contained in crushed cell phone waste (leaching time 10 min, 450 rpm stirring speed, S/L ratio at 50 g/L and all acids concentration at 1 mol. L^{-1}.**

The following inorganic acids: HCl, H_2SO_4, HNO_3, and H_3PO_4 and organic acids: $C_6H_8O_7$ (CiA) and CH_3COOH (HOAC), all at 1.0 mol L^{-1} concentration were evaluated for the leaching recovery. The deionised water and rainwater adjusted at pH 4.0 were used as control. The dominant % recovery was obtained from HNO_3 acid on neodymium at 72% and H_3PO_4 acid on lanthanum at 34.34% and dysprosium on 75.18%. The HCl was the weakest inorganic acid with all elements and less than 40% recovery was obtained. The organic acids citric and acetic gave poor recoveries with all elements less than 30% as compared to inorganic acids. These recoveries are similar to the results of Soukeur et al. (2021) obtained from REEs from waste products of phosphate. In earlier studies of REEs from fire clay seam coal, Yang and Honaker (2020) found that HCl rather than H_2SO_4 produced the highest recovery rates.

HNO_3 is a strong oxidizing agent with a low pKa value, indicating that it is a strong acid that dissociates easily. REE ions are very soluble in HNO_3, resulting in higher recoveries (Equation 5.3), whereas H_3PO_4 is a strong conjugate base with easy dissociation.

The REEs in the form of oxides in e-waste components are dissolved quickly by addition of acids to trivalent state as shown in equation 5.2.

$$REE_2O_3 \ + 6H^+ \ \rightarrow 2REE^{3+} + 3H_2O \qquad Eqn\ 5.2$$

The reactions with HCl, H_2SO_4 and H_3PO_4 are expressed in Equations 5.4 to 5.6. The high concentration of SO_4^{2-} anion in the leaching solution of H_2SO_4 may limit solubility. When in contact with inorganic lixiviants, the dissolved oxides converted to metallic form are oxidized into trivalent ions as follows (Um, 2017). The REEs are quite electropositive and reacts quickly with dilute acids or hot water.

$$REE\ (s) + HNO3 = REE^{+3} \ + NO_2^- + \ H_2O \qquad Eqn\ 5.3$$

$$REE\ (s) + 3HCl = \ REE^{+3} + \ 3Cl\_ \ + \ 3/2\, H_{2\,(g)} \qquad Eqn\ 5.4$$

$$REE\ (s) + \ 3H_2SO_4 + \ 3/2\, O_{2\,(g)} \ = REE^{+3} \ + 3SO_4^{-2} + 3H_2O \qquad Eqn\ 5.5$$

$$REE\ (s) + \ H_3PO_4 \ + \ 3H^+ = \ REE^{+3} + \ PO_4^{3-} + \ 3H_{2\,(g)} \qquad Eqn\ 5.6$$

The rare earth oxides (REE_2O_3) or (Ln_2O_3) are precipitated into sulphate in sulphuric acid solution as shown by the chemical reaction in Equations 5.2 and 5.7 (Um and Hirato, 2013). In an aqueous solution, the sulphate ions may form complexation reactions with REE cations (Equation 5.7), but it is still very effective and a cheap acid to use.

$$2REE^{3+} + 3SO_4^{2-} + 5H_2O \ \rightarrow \ REE_2(SO_4)_3\,.5H_2O \qquad Eqn\ 5.7$$

5.4.3.2. Effect of Lixiviant Concentration

A series of leaching experiments was carried out using different HNO_3, H_2SO_4 concentrations (0.1 M to 2.0 M). The other variable leaching conditions were kept constant. From the results in (Figure 5.6), the recovery of La, Nd and Dy increased with increase of concentration from

0.1 M to 1.0 M and decreased steadily up to 2.0 M. The low recovery at lower concentration is due to insufficient acid to completely dissolve the REE oxides. The solubility also decreases with increasing acid concentration above 1.0 mol L^{-1} for HNO_3 and H_2SO_4 as shown in (Figure 5.6a and 5.6b). The common ion effect of increasing NO_3^- and SO_4^{2-} ions concentration would decrease the solubility (Senanayake *et al*., 2016).

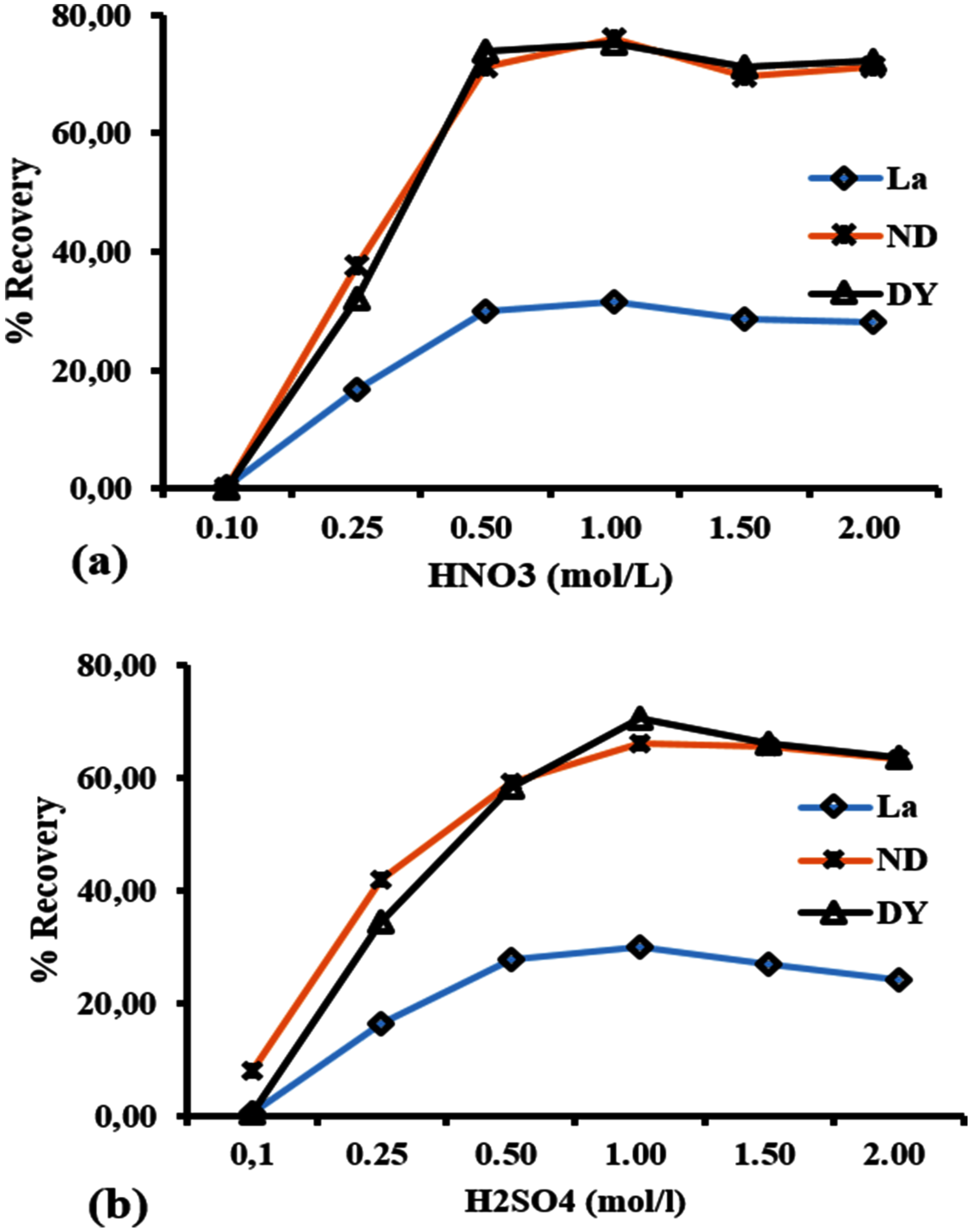


Figure 5. 6: The effect of HNO_3 acid (a) and H_2SO_4 (b) at concentration (0.1, 0.25, 0.5, 1.00, 1.50, and 2.00 mol/L) on the leaching efficiency of rare earth elements (La, Nd and Dy) contained in crushed cell phone waste. The temperature kept constant at 25 ± 1ºC, time at 10 minutes, stirring speed at 450 rpm and S/L ratio of 50 g/L.

5.4.3.3. Effect of Contact Time

Using selected extractants 1 mol/L HNO_3 acid on crushed e-waste (Figure 5.7a) and on e-waste treated soil (Figure 5.7b), the leaching trend of REEs was tracked during leaching time intervals of 1, 5, 10, 15, 30, and 60 minutes. The extraction of REEs is time-dependent, as seen in both plots in (Figure 5). The best recoveries in crushed e-waste were 37.0 %, 74.7 %, and 76.2 % after 10 minutes for La, Nd, and Dy, respectively. After 15 minutes of leaching e-waste treated soil with 1 mol/L HNO_3, the best recoveries for La, Nd, and Dy were obtained at 53.5%, 84.3%, and 81.9%, respectively. The decline in recoveries over time may be attributed to the complexation of REEs and inorganic anions, which promotes the formation of an insoluble complex as shown by the hydrolysis of REE in equation 5.8 and the dissolution in acidic media (Equation 5.9). The longer the duration of leaching contact the more adverse reactions appear in the solution. Other metallic components in e-waste, as shown in Table 5.1, tend to react and interfere with the elements under observation.

$$REE^{-3} + 3OH^{-} \Leftrightarrow REE(OH)_{3\,(s)} \qquad Eqn\ 5.8$$

$$REE(OH)_{3(s)} + 3HCl_{(aq)} = REECl_{3(s)} + 3H_2O \qquad Eqn\ 5.9$$

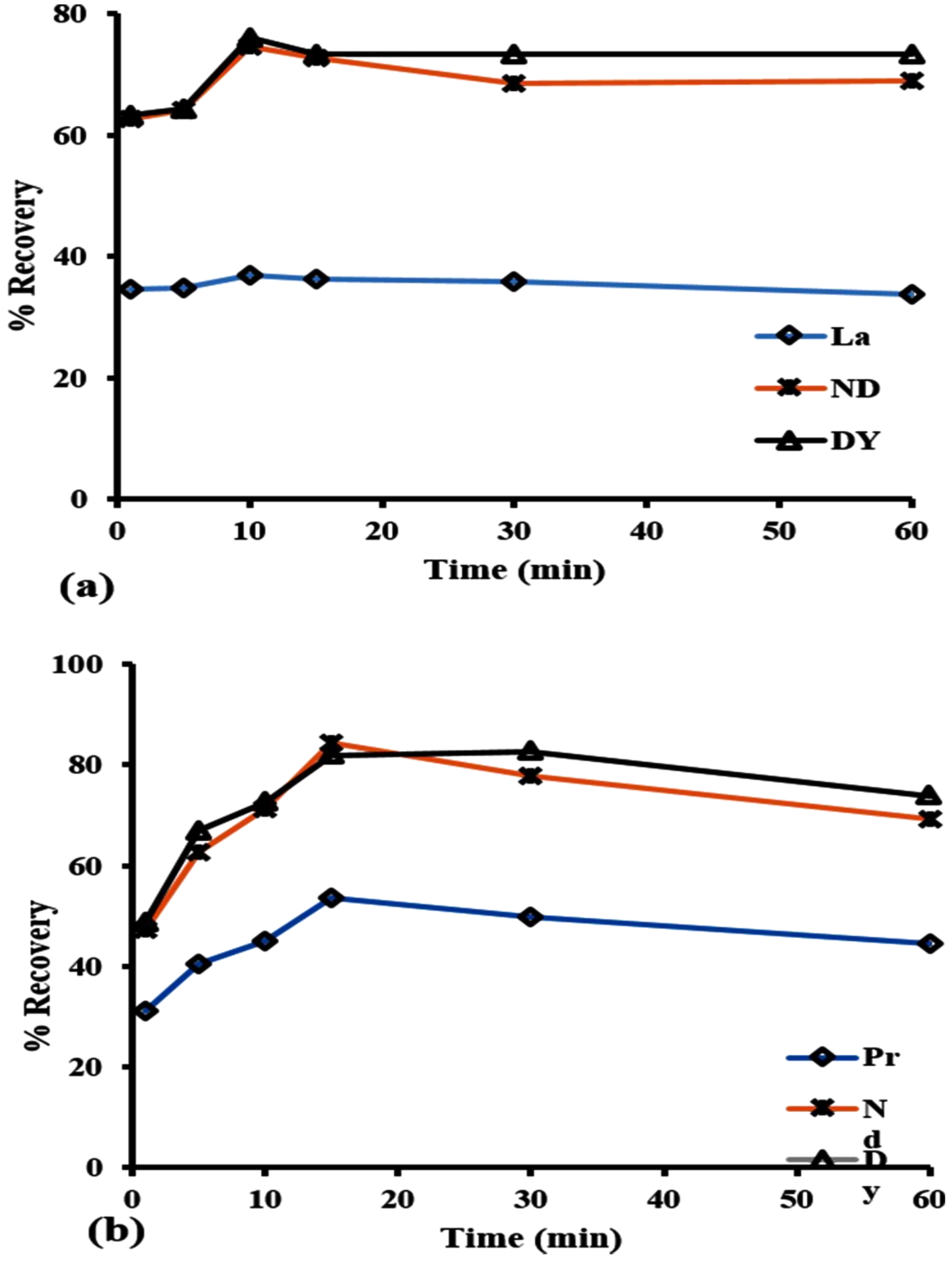


Figure 5. 7: Effect of contact time on the leaching recovery of REEs (La, Pr, Nd and Dy) contained in crushed e-waste (a) and e-waste treated soil (b) (1 mol/L HNO_3, 450 rpm stirring speed, S/L ratio at 50 g/L, temperature kept constant at 25 ± 1°C.

5.4.3.4. Effect of Liquid-to-Solid (L/S) Ratio

The effect of solid to liquid ratio on the leaching recovery of REEs was evaluated in the range from 20 g/L to 100 g/L while other variable parameters were kept constant, as shown in Figure 5.8. The lixiviant volume was kept at 20 mL, while the mass of the sample was varied from 0.4 g to 2 g. This range of solid-to-liquid ratios did not show a significant difference in the recovery of REEs, meaning the volume used was enough to dissolve the e-waste measured. La had the least variability, as measured by the standard deviation of 1.06, followed by Nd with 2.54 and Dy with 2.63. A lower volume of 10 mL was tried, but not enough volume was recovered after the filtration process. At a solid−liquid ratio of 50 g/L, the highest leaching rate of 30.6 ± 2.3%, 68.9 ± 4.01% and 71.2 ± 4.22% was attained for La, Nd and Dy respectively. The increase of solid to liquid ratio promote the agglomeration of the solid particles which would reduce the full contact of the material with the leaching solution. In addition, the mobility of the material is hindered that will reduce the REE ions in the leaching solution, thereby reducing the leaching efficiency. At low solid-liquid ratios the energy for particle interaction is reduced, which slows the solubility reaction of the solids in solution, though it is not clearly visible within the range investigated.

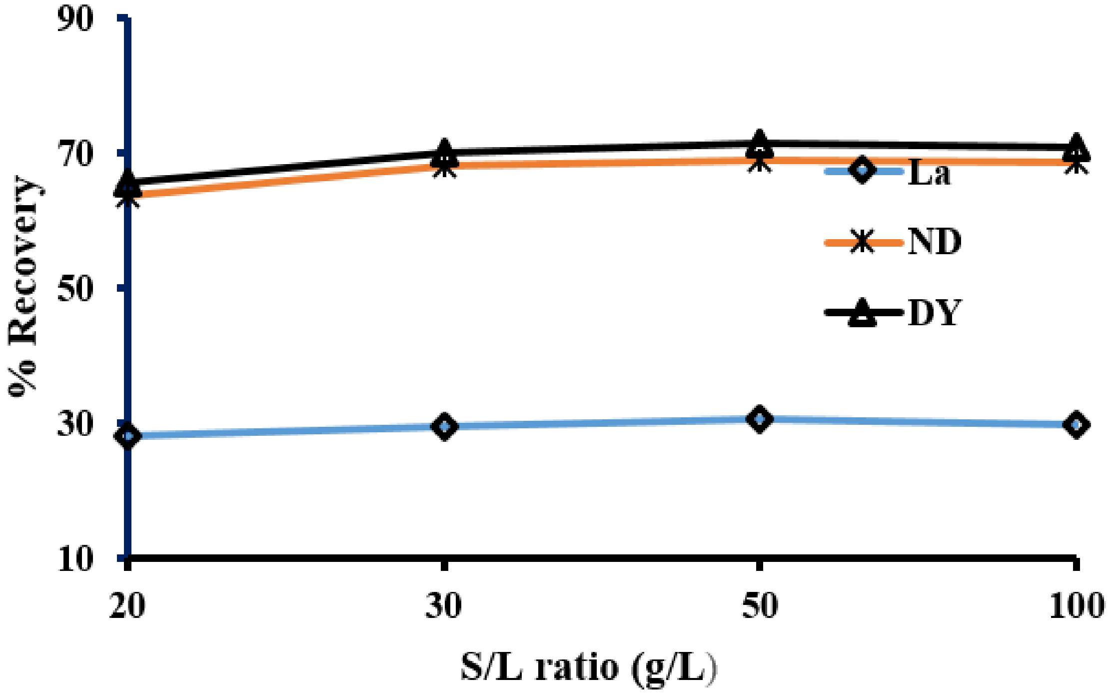


Figure 5. 8: **Effect of solid to liquid ratio on the leaching recovery of REEs (La, Nd and Dy) contained in crushed e-waste (1 mol/L HNO_3, 450 rpm stirring speed, leaching contact time 15 min, temperature kept constant at 25 ± 1°C) and lixiviant volume 20 mL.**

5.4.3.5. Effect of pH on REEs under controlled conditions

The effect of pH on REE leaching was investigated using 1 M citric acid (CiA) and 1 M acetic acid (AcOH) with a leaching time of 10 minutes, a stirring speed of 450 rpm, and a S/L ratio of 50 g/L. At pH values ranging from 1 to 11, we investigated how the pH of the leaching solution affects the release of REEs from pulverized soil treated with electronic waste. Figure 5.9 depicts the results for the Pr, Nd, and Dy recoveries obtained at various leaching solution pH levels. The elements studied show that recoveries decrease with increasing pH, from acidity to basicity level. At pH=7, the REEs recoveries dropped sharply to less than 22% on all elements, and at pH=9 and pH=11, the recoveries were negligible, with Dy in citric acid recovering the most at 2.5% at pH=9. Montross et al. (2020) investigated REE recoveries from citrate pH=3 to pH=6 solutions on leaching of REEs from coal seam underclays. Kim et al. (2012) revealed on Eh-pH diagrams that $Ce^{3+,}$ Nd^{3+} and La^{3+} have higher solubilities under slightly alkaline conditions, while Th^{4+} only exists in strongly acidic conditions. The complexation of REE-citrate and REE-acetate in e-waste is influenced by pH changes. Increasing the acidity of citric and acetate acids leads to higher pKa values and, as a result, an increase in the number of deprotonated anions for greater REEs solubility. Most REE ions exist in their REE^{3+} or REE^{4+} forms in acidic or neutral pH solutions and are stable in aqueous solutions. As the pH rises to alkaline levels (pH > 7), the formation of insoluble REE hydroxides ($Pr(OH)_3$, $Nd(OH)_3$, and $Dy(OH)_3$) commences. The REEs citrate and acetate are represented by the Equations 5.10 to 5.12 (Zanonato *et al.*, 2001).

$$REECit_{(s)} \Leftrightarrow REE^{3+} + 3OH^- \qquad Eqn\ 5.10$$

$$REECit \Leftrightarrow REE^{3+} + Cit^{3-} \qquad Eqn\ 5.11$$

$$REE^{3+} + 3HOAC \Leftrightarrow REE(HOAC_3)3 \qquad Eqn\ 5.12$$

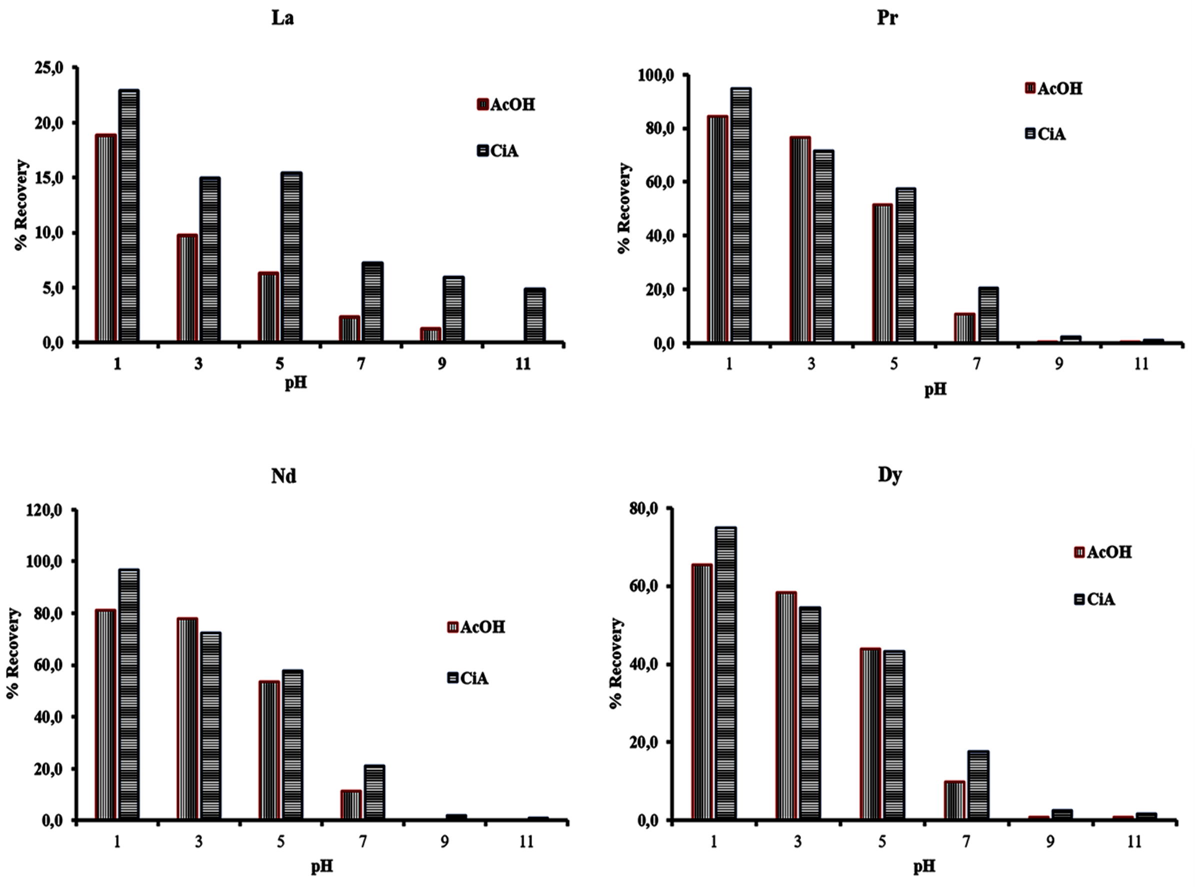


Figure 5. 9: **Effect of acetic (AcOH) and citric (CiA) acids pH on the leaching recovery of REEs (La, Pr, Nd and Dy) contained in e-waste treated soil (450 rpm stirring speed, S/L ratio at 50 g/L, leaching contact time 10 min, temperature kept constant at 25 ± 1ºC).**

5.4.4. XRD e-waste characterisation

Figure 5.10 shows the XRD spectrum of the e-waste PCBs (P01), leached e-waste residue (P06), and washed soil as blank. The most intense peaks were identified for phases of SiO_2 at 2Ɵ values of 26.06, 31.05, 36.95 and 58.93. Cu peaks were dominant in e-waste at 50.81 and 59.46. The phases of Nd_2CuO_4 at 36.97, 58.81 and 59.59. Nd_2O_3 at 35.92 and 66.30 and appeared on both P01 and P06. Magnesite ($MgCO_3$) phases appeared on 33.25, 35.89 and 43.20. Another phase of neodymium aluminium carbide (Nd_3AlC) was visible on multiple 2Ɵ of 37.30, 43.20, 52.77 and 74.17. Two less intense peaks of PrO_2 were observed on P01 at 2Ɵ values of 37.10 and 44.78. From the XRD patterns, it is clear the P01 sample has more phases than P06 since other phases were leached out. The data also reveals the strong magnetism of the e-waste from smartphones by multiple phases of Nd and Pr. The XRD data corresponds to the data obtained from ICP though other phases could not be interpreted on XRD due to element concentration and crystallite size orientation. Similar observations were made by Lie and Liu (2021) on spent NiMH batteries.

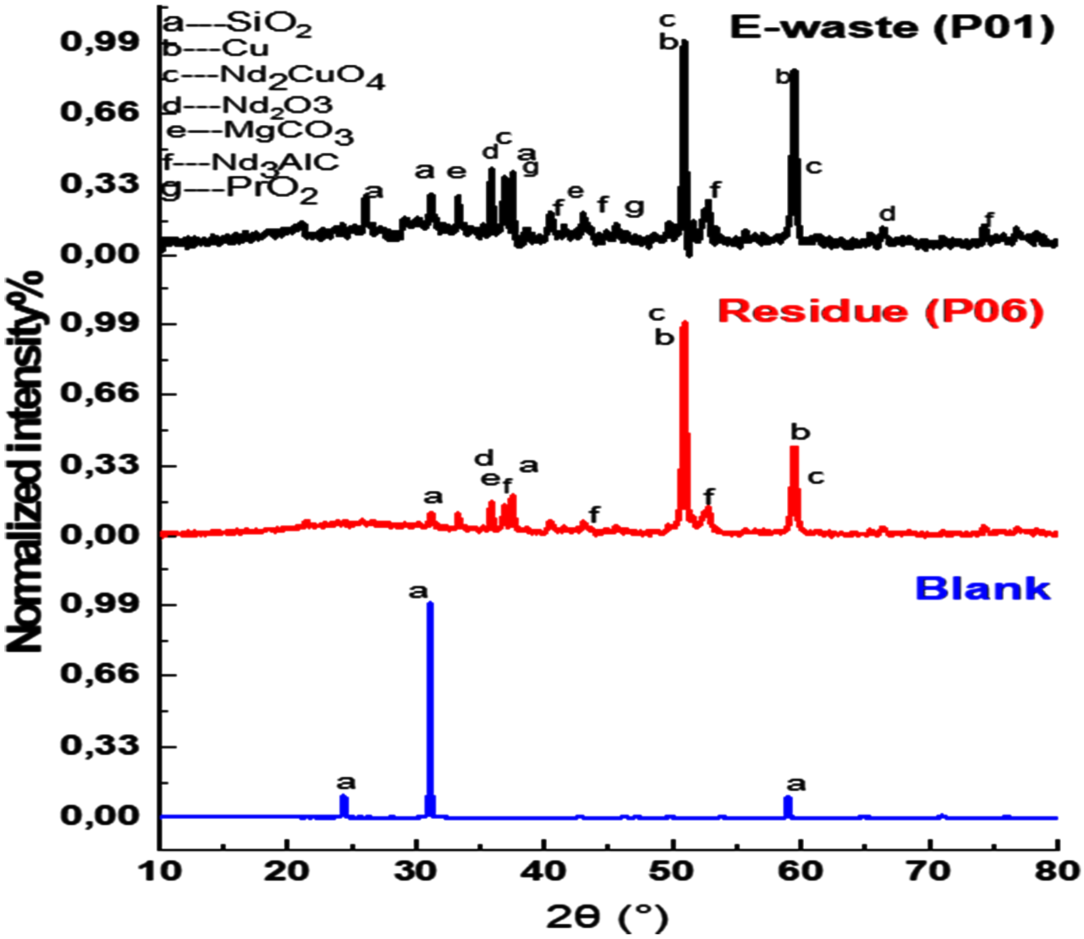


Figure 5. 10: **XRD pattern of original smartphone e -waste (P01), residue of acid leaching using 0.1 M HNO_3, S/L of 50g/L for 10 minutes (P06) and untreated soil as blank.**

5.4.5. Comparison of leaching with other published data

In Table 5.3, previous studies of the leaching behaviour of REEs from e-waste materials employing different protocols are compared to the present study. The leaching behaviour and kinetics of rare earth metals from secondary resources such as waste printed circuit boards (WPCBs) and waste electrical and electronic equipment (WEEE) differ depending on the material. The leaching reagents and other parameters not shown in the table, such as, temperature, particle size, pH, and solid to liquid ratio, clearly differ. This complicates the comparison of leaching recoveries due to the heterogeneous nature of the material. The optimal leaching time in most of these studies ranges between hours and days, except for the studies by Peelman et al. (2018) and the present study. Except for Peelman et al. (2018), who used a fine fraction of less than 75 µm, which accelerated their leaching, all previous research employed a similar particle size fraction of between 0.4 mm and 0.2 mm. Our recoveries are comparable to those of Diaz et al. (2016), but they used a longer leaching time of 72 hours with 1 mol/L H_2SO_4 than we did with 1 mol/L HNO_3 over 10 minutes. We assimilated for normal environmental temperature in our current research, so we used cold leaching rather than heating, which was used by most researchers at temperatures ranging from 70^oC to 90^oC. The REEs are highly soluble in H_2SO_4, HCl, and HNO_3 acids, but in this study, we preferred HNO_3 due to the superior solubility of REE salts in it. But because H_2SO_4 is cheaper, it may still be the acid of choice for commercial recovery processes. The waste magnets utilised by researchers in Table 5.3 are more susceptible to attack by inorganic acids than PCB components and other accessories. In this study, the percentage of recoveries could have been higher if the same conditions had been used, but the goal was to understand how cold leaching works so that it could be used to simulate natural conditions. Based on the results in Table 5.3 the use of HNO_3 can still be a good leaching reagent for REEs commercially especially when the HNO_3 acid is readily available and at lower cost.

Table 5. 3: Summary of REEs leaching recoveries from secondary sources.

Material	**Leaching reagents**	**Elements**	**Time**	**Recovery (%)**	**Reference**
Roasted magnets waste	3 mol/L H_2SO_4; 1mol/L HCl	REEs	3 Hrs	99.4	Liu et al. 2020
Nd magnet waste	Organic acids (citric and acetic acids)	REES	24 Hrs	> 99.0	Gergoric et al. 2018
WPCBs	Multiple inorganic acids	REEs	45 mins	> 60.0	Baez et al. 2022
NdFeB cell phone magnets	1 mol/L H_2SO_4	Pr Nd Dy	72 Hrs	91.7 66.7 54.9	Diaz et al. 2016
Spent batteries	10% w/v 2 mol/L H_2SO_4	REEs	1 hr	80.0	Pietrelli et al. 2002
Roasted NdFeB magnets	0.02 mol/ L HCl	Nd, Dy	1 hr	>80.0	Koyama et al. 2009
Scrap shredded WEEE	3% H_2SO_4	ND	5 Mins	>90.0	Peelman et al. 2018
WPCBs (Cell phones and computers)	1 mol/L HNO_3	La Pr Nd Dy	10 mins	31.4 74.2 75.9 75.2	Current study

5.5. Summary

According to the findings of current microcosm leaching studies, REEs (La, Pr, Nd, and Dy) are leached out of e-waste material depending on various parameters. The results of an accelerated 7-day static column leaching of e-waste treated soil revealed that the REEs were slowly leached out, with the highest leachates on the first day Pr (47.5%), Nd (53.3%) and Dy (29.2%) with H_2SO_4 as the lixiviant and gradually decreasing 0.9%, 0.8% and 0% respectively on day 7. However, after a few days, even when the majority of the REEs remain unleached, the cumulative recovery becomes constant. It was also demonstrated that REEs are not easily leached by natural or rainwater (pH=4.0) after just a few days. The H_2SO_4 lixiviant had the highest accumulative recovery efficiencies for Pr, Nd, and Dy, with 73.8%, 74.7%, and 52.9%, respectively. At the same time, rainwater (pH=4) recovered the least, with 9.3%, 10.5%, and

22.3% for Pr, Nd, and Dy, respectively. The total extractable REEs after 7 days were 73.91%, 45.79%, 16.85% and 10.55% for lixiviants H_2SO_4, H_3PO_4, $C_6H_8O_7$ and rainwater, respectively.

The batch leaching tests revealed that the REEs were best leached out strongly on lixiviant HNO_3 at concentrations of 1.0 mol L^{-1}, a contact time of 10 minutes, a solid-to-liquid ratio of 50 g/L, and an acidic pH range at room temperature with a 450 rpm agitation speed. The best batch leaching efficiency achieved was 31.4%, 74.2%, 75.9%, and 75.2 for La, Pr, Nd and Dy respectively. These findings were consistent with those of previously reported studies, even though the leaching time was reduced from several hours or days to just 10 minutes. In contrast to other studies, leaching was performed without heating.

When REEs in e-waste interact with lixiviants, chemical reactions occur, which can result in complexes and the formation of insoluble hydroxides. The major elements, high copper and sulphur content in e-waste, also interfere with the efficiency of REE leaching in acidic media. When the solubility conditions are met, the likelihood of REEs being leached out of secondary resources such as e-waste is high. Finally, because these findings are important for the recovery of REEs from secondary resources, precautions should be taken to limit the release of these metals into the environment. In this way, the present study contributes to the consolidation and advancement of methods used to evaluate the environmental impact of recycled materials.

CHAPTER 6

EVALUATION OF POTENTIAL RISK OF RARE EARTH ELEMENT CONTAMINATION FROM LEACHATE ORIGINATING FROM ELECTRONIC WASTE DISPOSAL

6.1. Introduction

In this chapter, the physical and chemical characterisation of the assimilated e-waste dump is presented. The soil and resulting leachate were quantified using standard methods and optimised instrumental techniques such as ICP-OES, ICP-MS, XRF and XRD. Specifically, the investigations of the dump activities were studied for a period of 4 years. The effect of leaching variables on rare earth elements was evaluated. The chapter also presents the results of physiochemical parameters that impact REE leaching from the dump components. The data obtained will help with a novel predictive modeling approach of REE leaching based on several leaching parameters and to be used on a large scale and in different natural environments. The novel approach is based on REEs' reactions to their disintegration, solubility, complexation/precipitation, and permeation in the natural environment. This chapter will end with a summary of the major findings from the leaching of REE from e-waste dumps over a period of time under natural conditions.

6.2. Overview

Electronic trash is hazardous, non-biodegradable, and accumulates in the environment, affecting soil, air, water, and living things. Toxic pollutants are released into the environment when open-air burning and acid baths are employed to recover precious elements from electronic components (Rao, 2014; Saha *et al*., 2021). Nowadays electronic is made to be replaced (planned obsolescence} large amounts of e waste in landfills releasing toxicity. Electronics have always produced waste, but the quantity and speed of discard has increased in recent years. E-waste has been speeded by the idea of pushing consumers to buy new gadgets quickly thereby rendering old ones obsolete. As a result, increased REE release into the environment may have ecotoxicological effects on humans and other organisms.

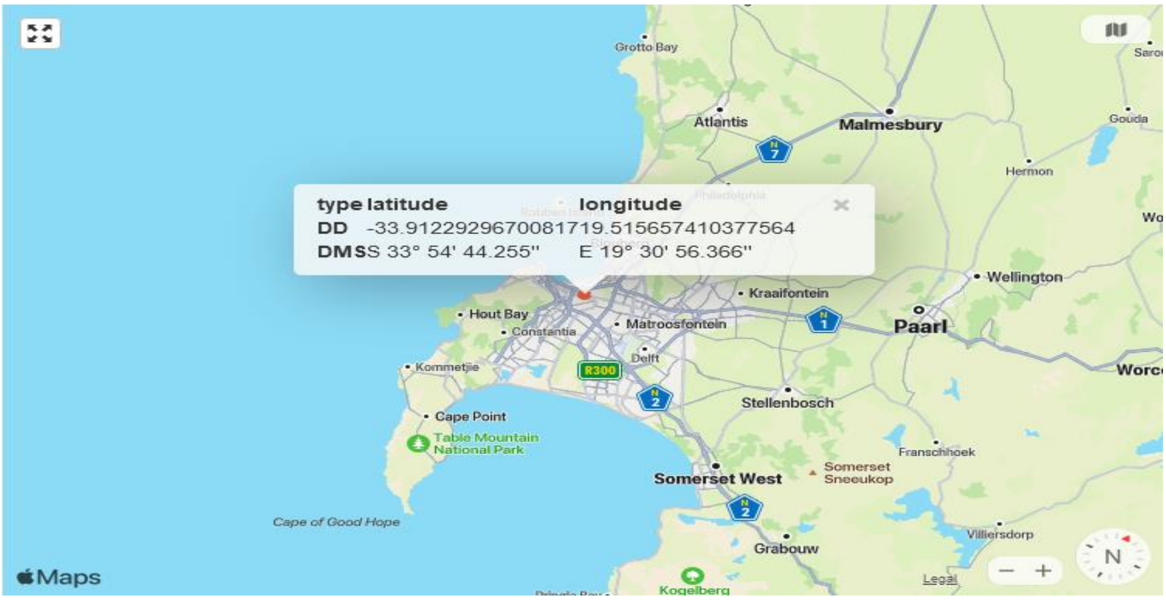
Metals tend to sink into sediment beds in aquatic habitats, but under different redox conditions, they may be released into the water column. Waste electrical electronic equipment (WEEE) waste dumps serve as a major depository of REEs and represent a potential secondary source for REEs. Environmental factors such as redox potential, pH, temperature, organic matter (OM), Fe, Mn, and Al content all influence REE mobility (Edahbi *et al*., 2018; Mihajlovic *et al*., 2019).

Since most of the e-waste contains amounts of REEs, it is vital to study the behaviour of these elements in exposed environmental conditions. Besides, the impact, release, and transport of REEs from e-waste in dumpsite has not been fully evaluated. Thus, this study aims to elucidate the potential leaching of REEs from solid e waste within the investigated disposal sites exposed to natural conditions over a period.

6.3. Materials and methods

6.3.1. Study area

The study was conducted at the Ndabeni industrial area of Cape Town University to examine the effects of various natural conditions on rare earth elements transport and leaching from electronic waste. The experiments were under a well-controlled simulated electronic waste dump (EWD) exposed to natural conditions to mimic other natural waste dumps. The city has a Mediterranean climate, with rainy winters and dry summers. The winter months are from May to August with daily temperatures ranging from 11°C – 22°C and an average of 10 rainy days monthly. In summer the average temperatures range 17°C – 29°C mostly sunny days and an average of 3 rainy days monthly (World Weather Online, https://www.worldweatheronline.com/).



type	latitude	longitude
DD	-33.91229296700817	19.515657410377564
DMS	S 33° 54' 44.255"	E 19° 30' 56.366"

Figure 6. 1: Geographical location of the experimental site (© Google Maps).

6.3.2. Sample collection and simulated e-waste dump preparation

Three categories of e-waste are computer components including printed wire boards (PC-PCBs), smartphone and feature phone were collected dismantled and cut into smaller pieces. The last category served as a control which was the same as other categories but without e-waste. Three equally wooden square cubicle dumpsites of surface dimension 30 cm x 30 cm and depth of 50 cm were constructed and exposed to different e-waste categories. At each cubicle dumpsite, an amount of 2 kg of shredded and only dismantled e-waste was exposed at the surface for the duration of the study. At each location, samples were collected at depths of 10-15 cm from the surface with e-waste materials. The detailed procedure for the e-waste dumpsite is outlined in Chapter 3 section 3.4.

6.3.3. Materials

All glassware used was thoroughly washed with liquid detergent and subsequently soaked overnight in 10% v/v nitric acid, rinsed 3 times with de-ionised water and dried in an oven at ± 95°C. Ultra-pure deionised water was prepared in the laboratory using an ion exchange deionisation process. All reagents used during the experiments were supplied by Ace Chemicals (South Africa). Throughout the experiments, acids such as hydrochloric acid 32%, hydrofluoric acid nitric acid 70%, and sulphuric acid 98%, hydrogen peroxide 50%, were used for the sample digestion process. The following sequential analysis reagents supplied by Merck South Africa were used to prepare the leaching solutions, ammonium acetate (AR), sodium acetate (AR) and Hydroxylamine hydrochloride (AR). The calibration standard solutions were of high purity grade and supplied by VHG Labs (Manchester, USA).

6.3.4. Methods

The physicochemical parameters procedures are outlined in Chapter 3 section 3.5, rainwater sampling section 3.6 and the detailed digestion procedures in section 3.7. For REE speciation the sequential extraction procedure as outlined in section 3.8.2 of Chapter 3 was utilised in this study. The total REE determination was done by a novel borate fusion procedure in Chapter 4 (Makombe *et al*., 2021). The major metals in pulverised soil were extracted by 10 mL of HNO_3 and 1 mL of HF in a microwave digester. Digestion lasted for 45 minutes at a maximum temperature of 200 °C followed by the boric acid neutralisation step. After digestion, topped to volume with deionised water, a clear aliquot was decanted for ICP-OES measurement. Other spectroscopic REE determination methods such as XRF, XRD, ICP-OES and ICP-MS are mentioned in Chapter 3, section 3.9.

Sampling of liquid leachates from the assimilated e-waste dumpsites was performed whenever there was a leachate flow. The liquid leachates collected were filtered and measured for physiochemical tests and acid addition to match the matrix for ICP-OES elemental analysis. During the rainy winter season, more leachate was collected and each point of leachate was put in one container for the half-yearly sample. For the determination of REEs, the collected leachate samples were acidified with 10% v/v nitric acid 70%. The samples were stored in a refrigerator at 3 ± 1°C before laboratory analysis. The summer season of Cape Town is usually dry with minimum rainfall, thereby limiting the leachate production.

6.4. Results and discussions

6.4.1. Dumpsite soil characterisation

The characterisation of the dumpsite was important to determine the physical and chemical properties before the exposure of the e-waste. Table 6.1 shows the psysiochemical, rare earth elements, bulky, major elements, the total organic content (TOC) and the loss on ignition (LOI). The results revealed trace amounts of REEs and major elements. The bulky content of the soil is silica, which is above 96%. The total REE concerntration in untreated soil is very low at 3.7 mg/kg. The total organic content at 1.51± 0.2 % and LOI at 1.62 signify very low organic mass in the soil. The soil density of 1.52 ± 1.4 is normal for sand soils with little organic mass.

Table 6. 1: Results of characterisation of the dump soil.

Soil type	**pH**	**EC**	**HCO_3**	**TDS**	**ρb**	**La**	**Pr**	**Nd**	**Dy**	**ΣREEs**
		µs/cm	**mg/L**	**mg/L**	**g/cm^3**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Untreated dump soil	7.1 ± 0.2	82 ± 3	75 ± 3	28 ± 1	1.52 ± 0.40	<1.0	1.0 ± 0.1	1.1 ± 0.2	<1.0	3.7

Continued

Soil type	**Cu**	**Al_2O_3**	**CaO**	**Fe_2O_3**	**TiO_2**	**SiO_2**	**TOC**	**LOI**
	(%)	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**
Untreated dump soil	<0.01	0.43 ± 0.10	0.17 ± 0.04	0.63 ± 0.08	0.11 ± 0.02	96.1 ± 0.80	1.51 ± 0.05	1.62 ± 0.02

6.4.2. Soil particle size distribution

The particle size distribution (PSD) is considered to be one of the most basic physical characteristics of the soil because it determines many other, more difficult to measure quantities such as air-water relation, pore size distribution and water movement in the profile (Huang *et al*., 2020). Knowing the texture of the soil is important in research.

The determination of PSD was done by sieve-sedimentation and instrumental particle size analyser methods. Soil is composed of, silt and clay particles. Sand particles range in size from 0.05–2.0 mm, silt ranges from 0.002–0.05 mm, and the clay fraction is made up of particles less than 0.002 mm in diameter. Gravel or rocks greater than 2 mm in diameter are not considered when determining texture. From Table 6.2 the sand fraction accounts for about 43%, silt 53% silt and 0.1% clay. Gravel and rocks >2 mm amounted to 2.53%. Soil texture determines the rate at which water drains through a saturated soil with water moving freely in coarse soils than in very fine soils.

The percentage of material retained on any sieve is given by Equation 6.1.

$$Pn = \frac{M_n}{M} \; x \; 100 \qquad Eqn\ 6.1$$

Mn = mass of soil retained on sieve 'n' M = total mass of the sample. The cumulative percentage of the material retained is expressed in Equation 6.2.

$$C_{n} = P1 + P2 + P3 + \ldots\ldots\ldots\ldots\ldots + P_n \qquad Eqn\ 6.2$$

Where P_1, P_2 etc are the percentages retained on sieve 1, 2 etc., which are coarser than sieve 'n'. The percentage finer than the sieve 'n' is given by:

100- Pn (percentage retained)

Table 6. 2: Particle Size Distribution of Soil by Sieving.

Sieve size	Weight on sieve	Cumulative weight	Weight	Cumulative weight	Passing through a sieve
mm	**(g)**	**(g)**	**%**	**%**	**%**
3.550	6.82	0.0	0	0	98.7
2.000	6.4	13.22	2.53	2.53	97.47
1.000	125.43	138.65	23.98	26.51	73.49
0.600	74.36	213.01	14.22	40.73	59.27
0.425	25.78	238.79	4.93	45.66	54.34
0.315	66.1	304.89	12.64	58.3	41.7
0.200	96.32	401.21	18.42	76.72	23.28
0.106	99.05	500.26	18.94	95.66	4.34
0.063	18.32	518.58	3.5	99.16	0.84
0.053	3.61	522.19	0.69	99.85	0.15
Total	**522.4**	**522.2**	**99.85**	**99.85**	

6.4.3. Rare earth element dumpsite soil analyses

For 36 months, half-yearly samples were collected from simulated e-waste dumpsites and analysed for specific rare earth elements. Liquid leachate samples were collected during the rainy months when leachate could be diluted by seepage of rainwater for a period of 42 months. The dumpsites were classified based on the type of e-waste components. Three categories were used: smartphone e-waste (VON), mobile feature phones (DEO), and computer boards (ADI) as shown in Figure 6.2. The control was a dumpsite free of e-waste. The pictures in Figure 6.2 were taken from different dumpsites (a, b and c) after 24 months. The pictured smartphones (d) and feature phones (e) PCBs from these dumpsites are visibly seen in their disintergration due to exposure to natural atmospheric conditions and very different to the original shiny appearance.

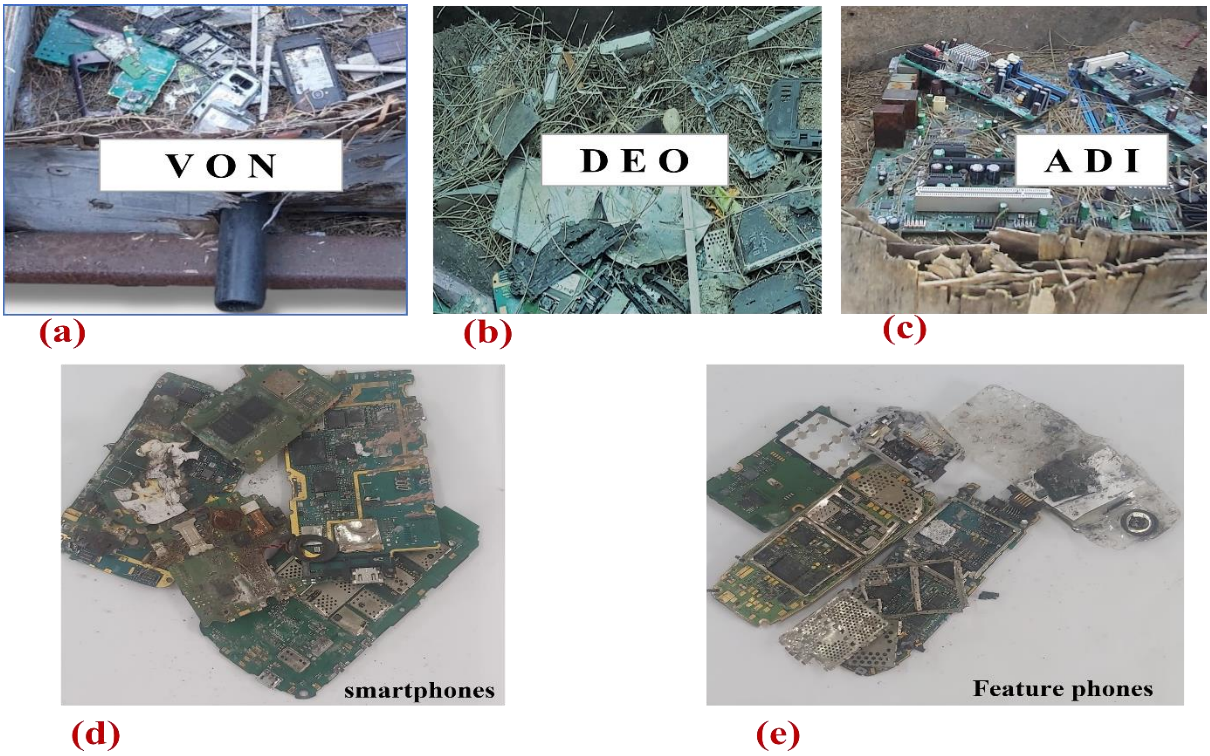


Figure 6. 2: **The exposure of different e-waste in simulated dumps (a) Smartphone (VON), (b) feature phones (DEO) and (c) Computer PCBs (ADI). After 24 months pictures of e-waste (d) Smartphones and (e) Feature phones were taken.**

The distribution of REEs (La, Pr, Nd, and Dy) was studied by sampling in the subsoil region of the simulated e-waste dump. From six to 36 months, the rare earth elements in sampled soil of all categories exhibited an upward trend as shown in Figures 6.3 to Figure 6.6. The background concentration of soil in the form of the control sample did not reflect an increasing concentration trend over time. Figure 6.3 to Figure 6.6 shows that metal leaching concentrations was minimal in the first six months but steadily increased thereafter. The relative abundance of the REEs analysed in sediments was determined as follows: Dy < La < Pr < ND. From 18 to 36 months, the concentration of REEs changed significantly for all elements studied.

All e-waste materials exhibited an increasing trend in REE leachate concentrations over time. However, fluctuations in mobile feature phone (VON) e-waste were observed, as evidenced by a slight decrease in 30 months (Figure 6.3). The 6, 12, 18, 24, and 36-month samples were collected during the dry season when rainfall is scarce, so the concentration of elements in the soil may be high. The order of leachate concentration in the soil from the highest is smartphones (VON), feature mobile phones (DEO), and computer boards (ADI). This arrangement is comparable to the abundance of REE concentration in actual e-waste material. In comparison to feature phones that do not have many features, the majority of smartphones are manufactured with a wealth of precious and REE elements, particularly their strong magnetism (Singh *et al*., 2018). The e-waste from smartphones and feature phones is also very light and has smaller components, so the disintegration of its constituents occurs more rapidly than that of computer waste. This phenomenon is also supported by Holgersson et al. (2017) studies, which found that smartphone leach results of Ag, Bi, Cu, and Ni were the highest, followed by mobile phones and internet routers. The majority of major elements, such as Al, Fe, and Si, were most commonly found in internet routers.

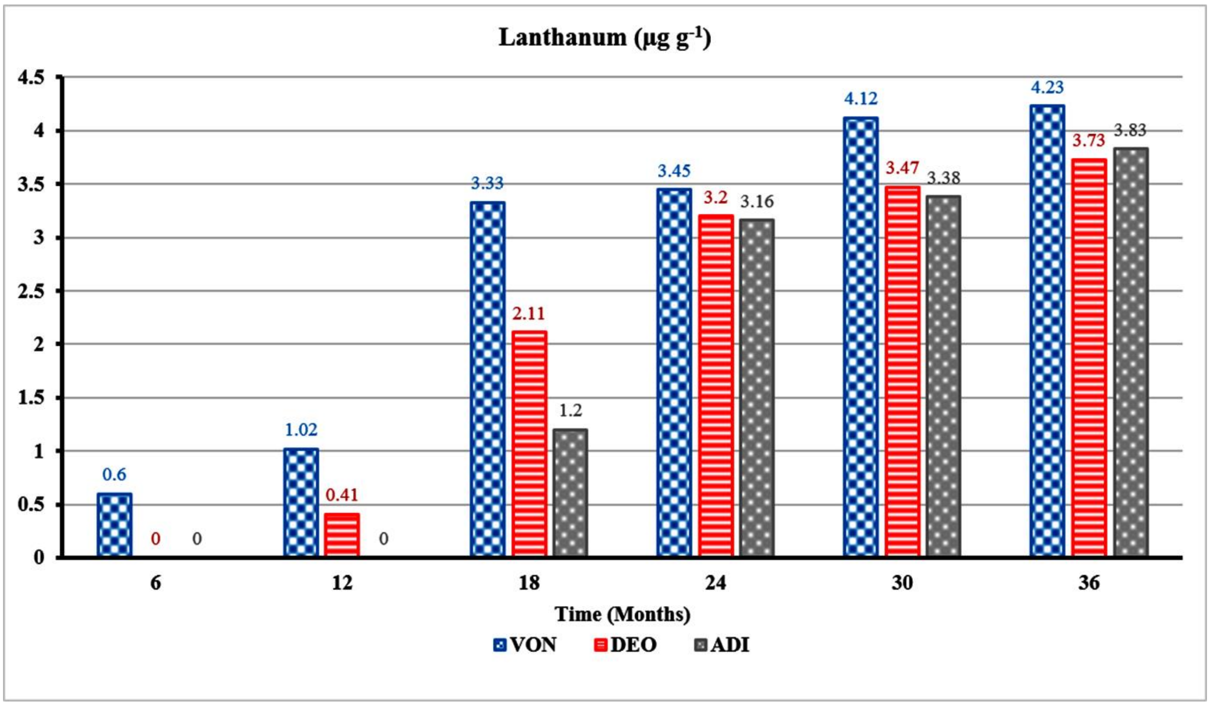


Figure 6. 3: **Concentrations of lanthanum in soil derived from e-waste dumps; smartphone (VON), mobile feature phone (DEO), and Computer (ADI) sampled after every 6 months for a period of 36 months.**

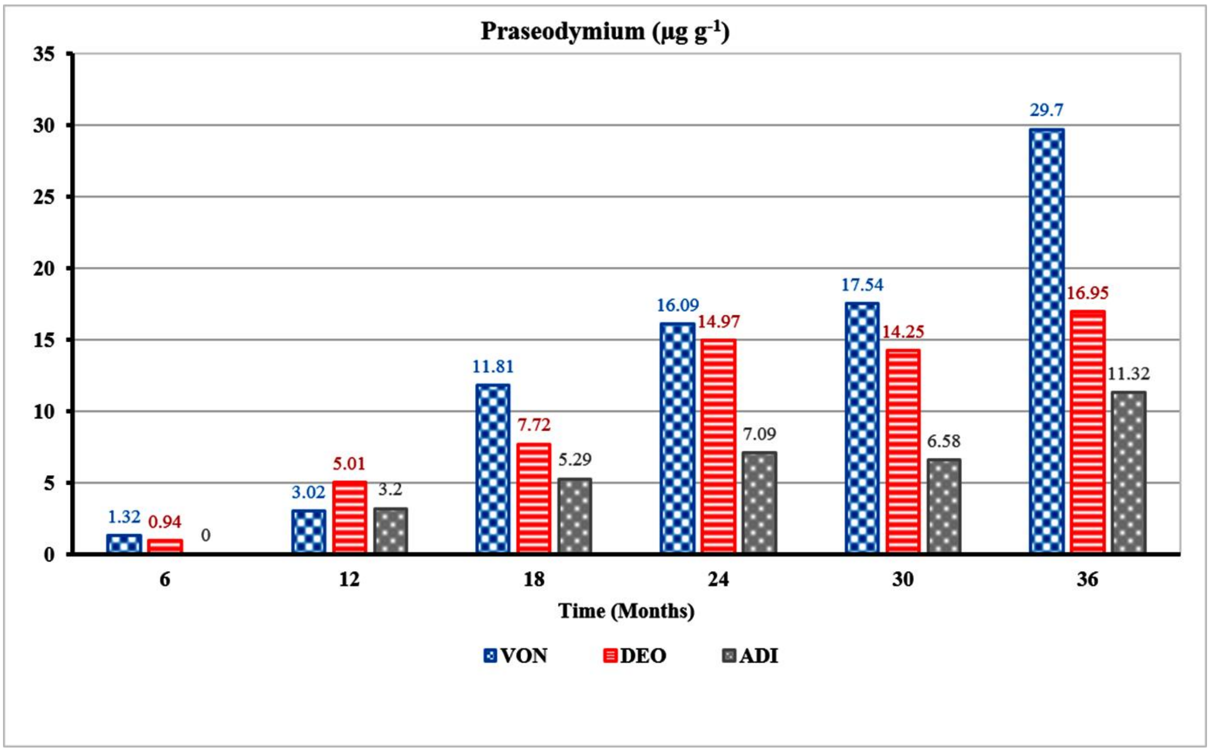


Figure 6. 4: **Concentrations of praseodymium in soil derived from e-waste dumps; smartphone (VON), mobile feature phone (DEO), and Computer (ADI) sampled after every 6 months for a period of 36 months.**

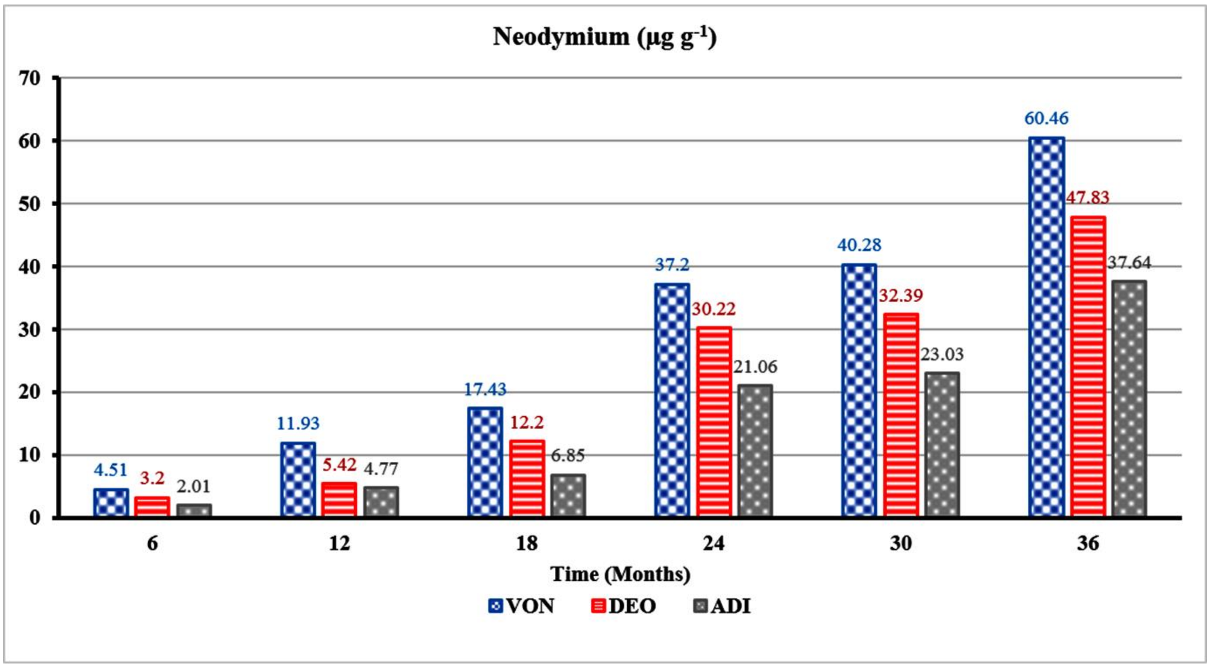


Figure 6. 5: **Concentrations of neodymium in soils derived from e-waste dumps; smartphone (VON), mobile feature phone (DEO), and Computer (ADI) sampled after every 6 months for a period of 36 months.**

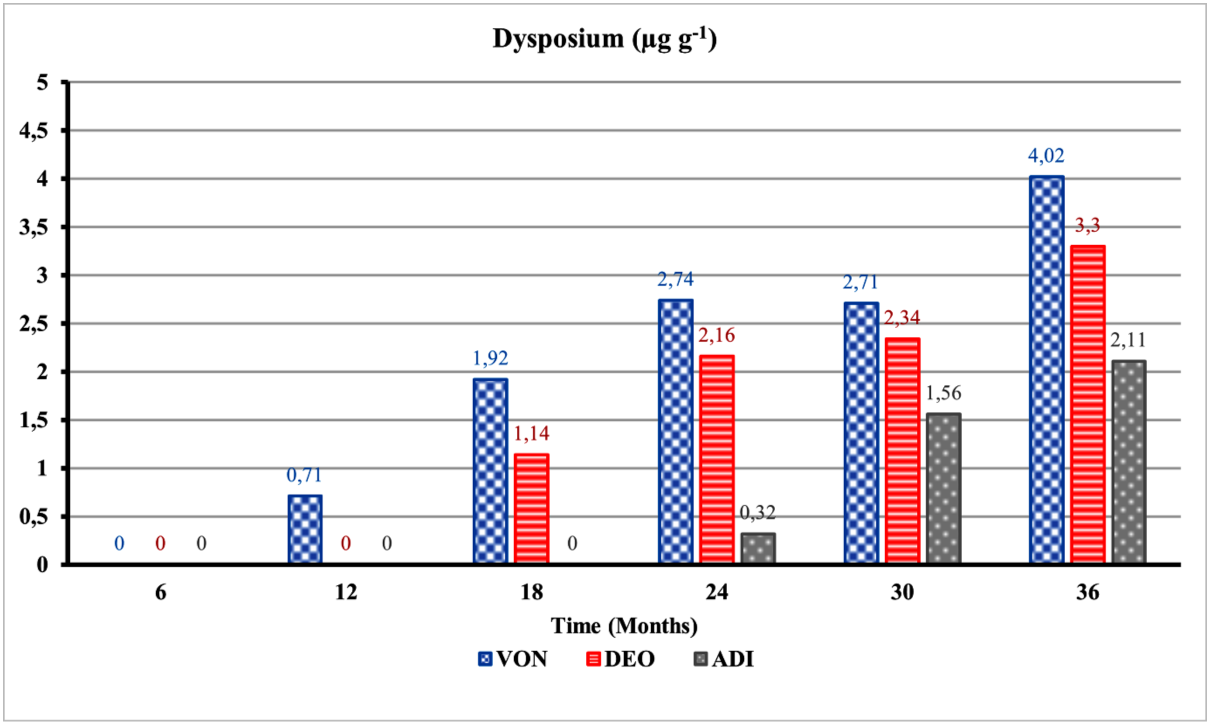


Figure 6. 6: **Concentrations of dysprosium in soil derived from e-waste dumps; smartphone (VON), mobile feature phone (DEO), and Computer (ADI) sampled after every 6 months for a period of 36 months.**

Several studies have reported metals leached from e-waste dumpsites but no analytical trend to determine the age of the dumpsite, monitoring of the waste type, quantity and enviromental conditions have been done (Adaramodu *et al*., 2015; Amankwa *et al.*, 2017; Chi *et al*., 2011; Guo *et al*., 2009; Olubanjo *et al*., 2015; Ofudje., 2015; Deval *et al*., 2015; Jang, 2010; Nnorom and Osibanjo, 2009). This study focused on monitoring the controlled leaching of REEs for a specific period for the first time. It can be concluded from the above results that leaching of REEs from e-waste will commence after several months of exposure.

6.4.4. Rare earth elements dump leachate analysis

Figure 6.7 to Figure 6.10 displays the changes in rare earth element concentrations in leachate over a period of three and a half years (42 months) for the simulated waste dumpsite. The conditions were maintained naturally throughout the study period. This prompted sampling of the leachate during the rainy season when the flow of leachate was observed. A minimum of six leachate samples were collected during the peak rainy months of June and July each year and analysed for rare earth element concentrations and physicochemical parameters. For each rainy season, the results of the two months (June and July) were averaged to make one result for the months 6, 18, 30, and 42. Generally, the amount of the REEs in leachate increased with time from the first 6 months to 42 months.

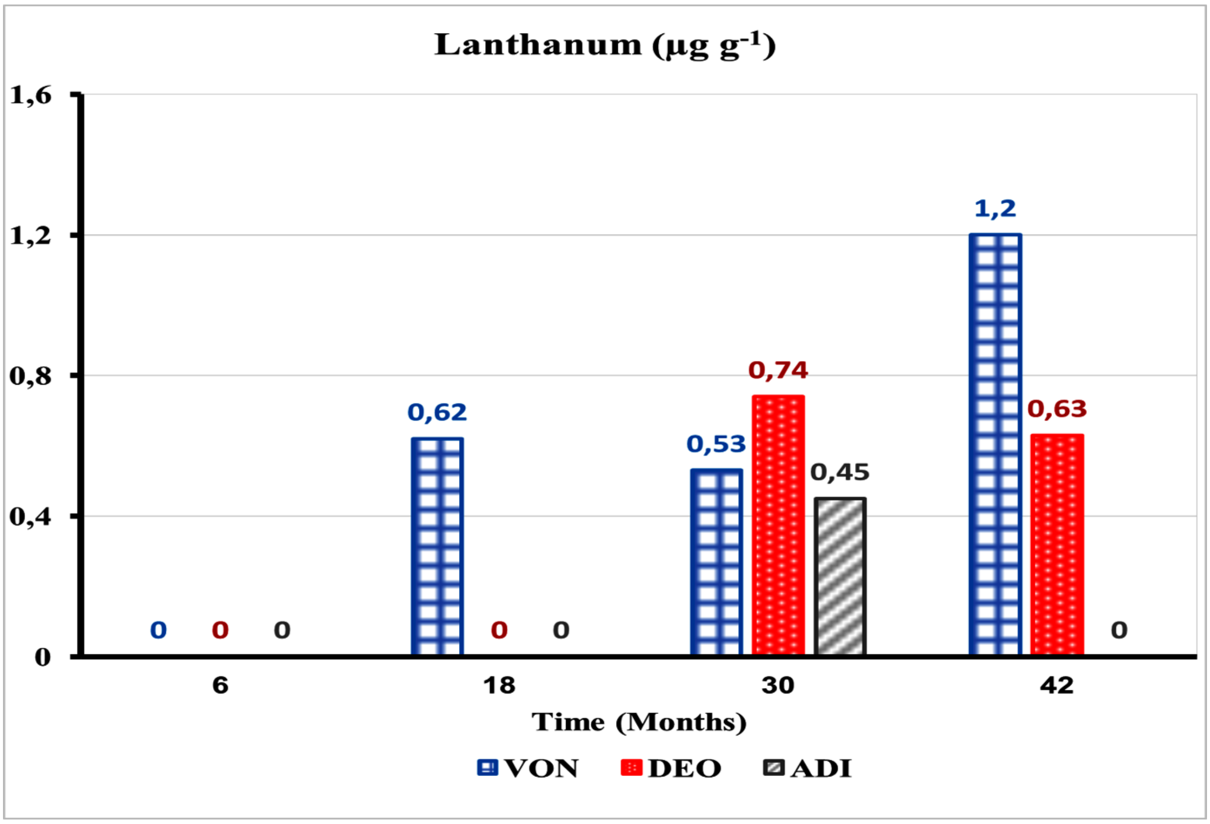


Figure 6. 7: **Concentrations of lanthanum in leachate derived from e-waste dumps; smartphone (VON), mobile feature phone (DEO), and Computer (ADI) sampled after every 12 months for a period of 42 months.**

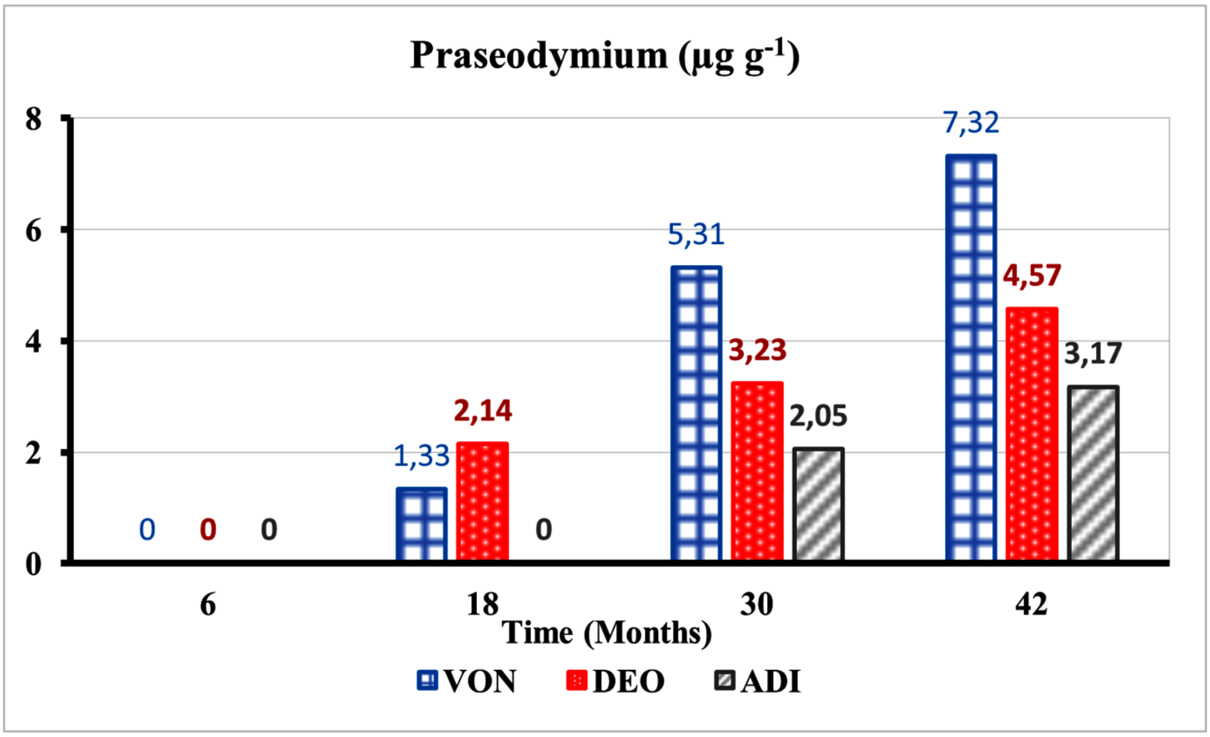


Figure 6. 8: Concentrations of praseodymium in leachate derived from e-waste dumps; smartphone (VON), mobile feature phone (DEO), and Computer (ADI) sampled after every 12 months for a period of 42 months.

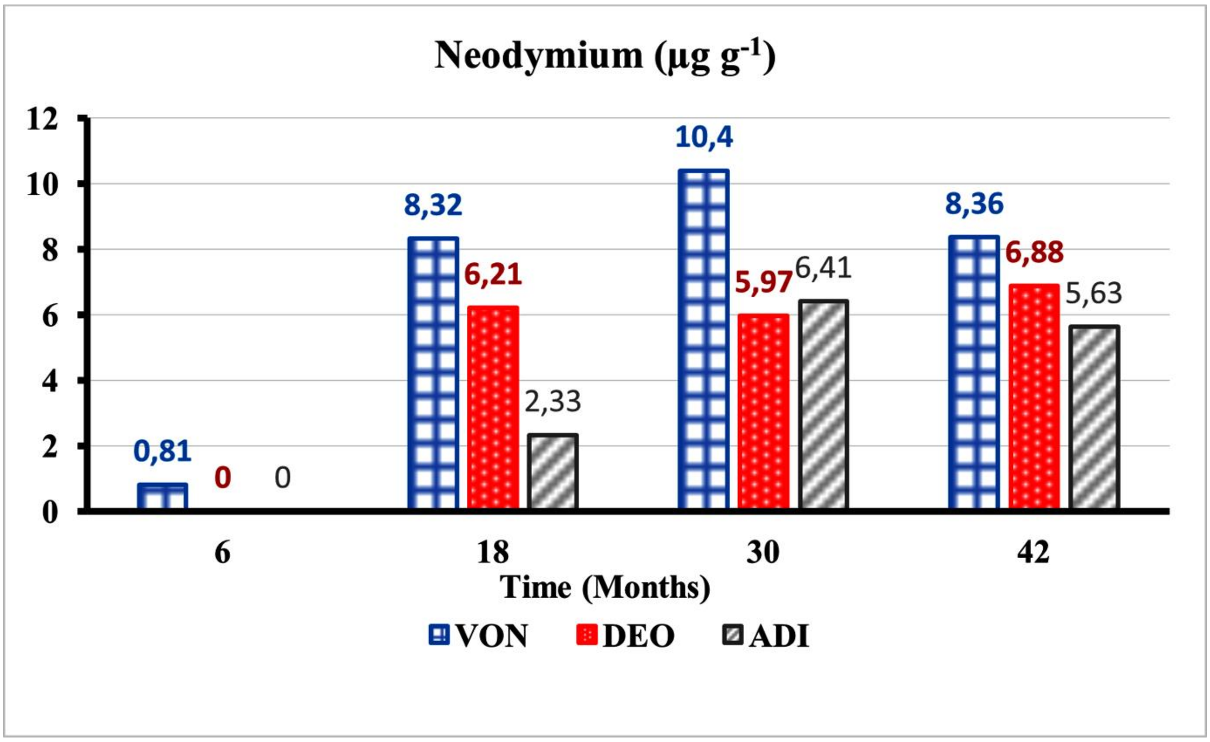


Figure 6. 9: Concentrations of neodymium in leachate derived from e-waste dumps; smartphone (VON), mobile feature phone (DEO), and Computer (ADI) sampled after every 12 months for a period of 42 months.

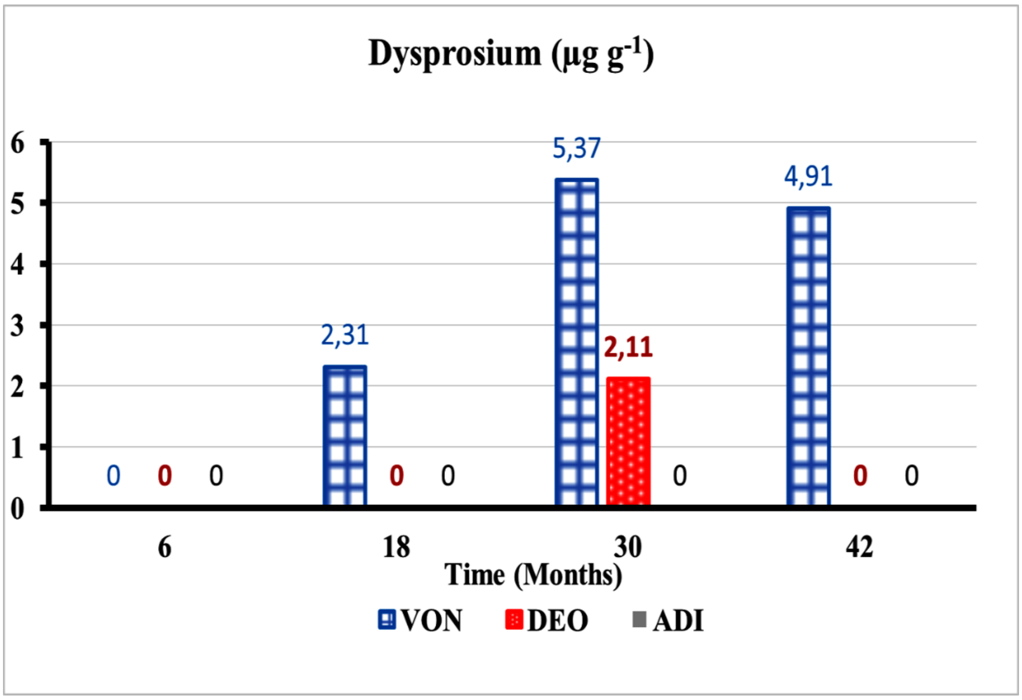


Figure 6. 10: **Concentrations of dysprosium in leachate derived from e-waste dumps; smartphone (VON), mobile feature phone (DEO), and Computer (ADI) sampled after every 12 months for a period of 42 months.**

The first 6 months almost recorded no leached metals, which clearly shows that the dissolution of e-waste and mobility had not commenced. This also showed zero background of REEs in the soil except for smartphone e-waste (VON) which recorded 0.8 µg g^{-1} Nd. The highest leached content of La was 1.2 µg g^{-1} on VON, 0.7 2 µg g^{-1} on feature phone (DEO), and 0.45 µg g^{-1} on computer (ADI) all after a 30-month period. The La present in e-waste was very minimum hence very low levels got leached. Pr 7.36 µg g^{-1} on VON, 4.37 µg g^{-1} on DEO and 3.17 µg g^{-1} on ADI all on the 42-month sampling recorded the highest leached content. Nd leached out the most due to its abundance in e-waste materials (its presence in the use of magnets). The highest Nd leach content on 30-month sampling was 10.44 µg g^{-1}, 6.88 µg g^{-1} and 6.41 µg g^{-1} for smartphone, feature phone and computer e-waste, respectively (Figure 6.9). A similar scenario was recorded for praseodymium on all samples where an increasing trend is recorded from 18 to 42 months. The dysprosium leached content was only significant on smartphone e-waste with the majority recorded on month 30.

These results emphasize the importance that the solubility of e-waste can be slow but will eventually be leached and transported into any evironmental compartments. Again, the larger the components the more difficult they can be leached as this was observed from computer waste in comparison with cell phone waste. As a result, smaller components have a tendency to degrade faster than larger components when exposed to same conditions. Metal mobility of heavy metals (Cd, Co, Cd, Cr, Ni, Pb, Zn) is determined by the type and quantity of soil surfaces present, the concentration of metal of interest, the concentration and type of competing ions, and complexing ligands (De Mantos *et al*., 2001; Domergue and Vedy,1992). Likewise, the concentration of anthropogenic REEs have a tendency to be more soluble and reactive (Kotelnikova *et al.*, 2021). Excessive amounts of heat, especially observed during summer temperatures will help in the decomposition of components, which will further open up and break when rains come and present further enviromental parameters to be assessed.

6.4.5. Chemical behaviour of e-waste dumps

Although the REEs in e-waste are soluble and leach out in water and acidic environments, the results indicate that the rate is very slow. It took several months for significant concentrations to be detected in soil or leachate from semi-crushed e-waste exposed to dumps. Other natural conditions such as climatic (rainfall index) and physical (particle size), pH of soil and composition of other metals have a significant impact on the rate of solubility (Saha *et al*., 2021). The effect of pH on the solubility of metals can also be described in terms of its influence on the precipitation–dissolution reaction (Rieuwerts *et al*.,1998).

According to Gramaccioli et al. (1999) and Hummel et al. (2002) the hydrolysis of REE^{+} species is more stable with increasing lanthanide atomic number and contraction of ionic radii and greater polarity of these cations. Therefore, the REEs in e-waste exposed to natural climatic conditions such as rain are sensitive towards water and the aqueous ions M^{3+} are hydrolysed in water according to Equations 6.3 (Bentouhami *et al.*, 2004). The oxides of the REEs are hydrated and soluble in water according to Equation 6.4:

$$[M + (H_2O)n]^{3+} + H_2O \leftrightarrows [M\ (OH)(H_2O)n - 1]^{2+} + H_3O^+ \qquad Eqn\ 6.3$$

where M represents REE

$$REE_2O_{3(s)} + 6H^+ \leftrightarrows 2REE^{3+} + 3H_2O \qquad Eqn\ 6.4$$

Despite the low concentrations in dumpsites and landfills, REEs can be easily extracted from the with weak acids and end up in water streams as was discussed earlier in chapter 5 of this thesis (Motross *et al.*, 2020).

6.4.6. Trend analysis

Generally, all three e-waste dump samples at the sub-soil level showed an increasing trend for all REE elements measured. The leached elements relatively increased steadily from 0 to 12 months and sharply thereafter, with the exception of neodymium which decreased from month 24 to month 36 for smartphone and computer PCBs waste dumps. This drop could be the result of excessive leachate flow from the rains in month 30 or poorly represented sample. However, this observation does, also coincide with a period of decreased pH (Table 6.7) which could not be independently validated. In general, the increasing trend of metals in the subsoil region implies more solubility of the metals. The soil pH also alters the soil geochemistry of the waste dumpsites by aiding the solubility of many metals other than REEs (Leelarungroj *et al.*, 2018). The distribution pattern of the REEs in the three waste dumps appeared more similar with leached content from smartphones, followed by feature phones and computer PCBs with the least increase in REEs. For the smartphone dumpsite scenario, neodymium increased from 17.5 to 70.4 µg g^{-1}, praseodymium from 7.3 to 29.7 µg g^{-1}, and lanthanum and dysprosium due to their low leachate concentration trend that was complicated to ascertain. The feature phone dumpsite neodymium increased from 7.9 to 57.84 µg g^{-1} and praseodymium from 7.9 to 16.9. The computer PCBs dumpsite the neodymium increased from 15.8 to 47.6 µg g^{-1} and praseodymium from 4.4 to 15.3 µg g^{-1}. Brewer et al. (2022) 's column leaching investigations demonstrated minimal leaching of REEs under natural conditions but improved by the use of Si-nanoparticles after only 35 days.

According to the results from this study, it is hypothesised that if the research had been exposed for a longer period, more REEs would have been released with the same environmental conditions. The leachate results from Table 6.11 to Figure 6.13 is still showing an upward trend of REEs measured.

The REE distribution of the leachate from Figure 6.11 to Figure 6.13 closely parallels the REE content available in e-waste components, inferring that (i) the REE release onto the dumpsites is influenced by the REE abundance regardless of atomic number as defined by the Oddo-Harkins rule. and (ii) the size of the e-waste components meaning larger units such as computer PCBs take longer to degrade and leach out.

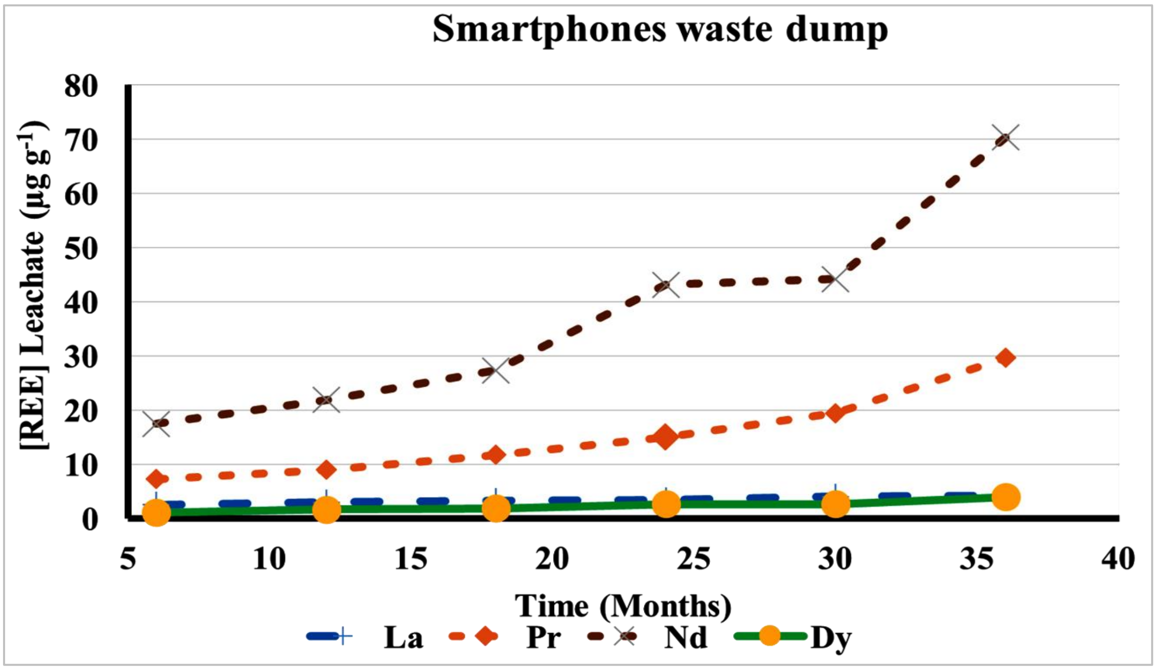


Figure 6. 11: Rare earth elements (La, Pr, Nd and Dy (leachate concentrations from smartphone dumpsite over a period of 36 months.

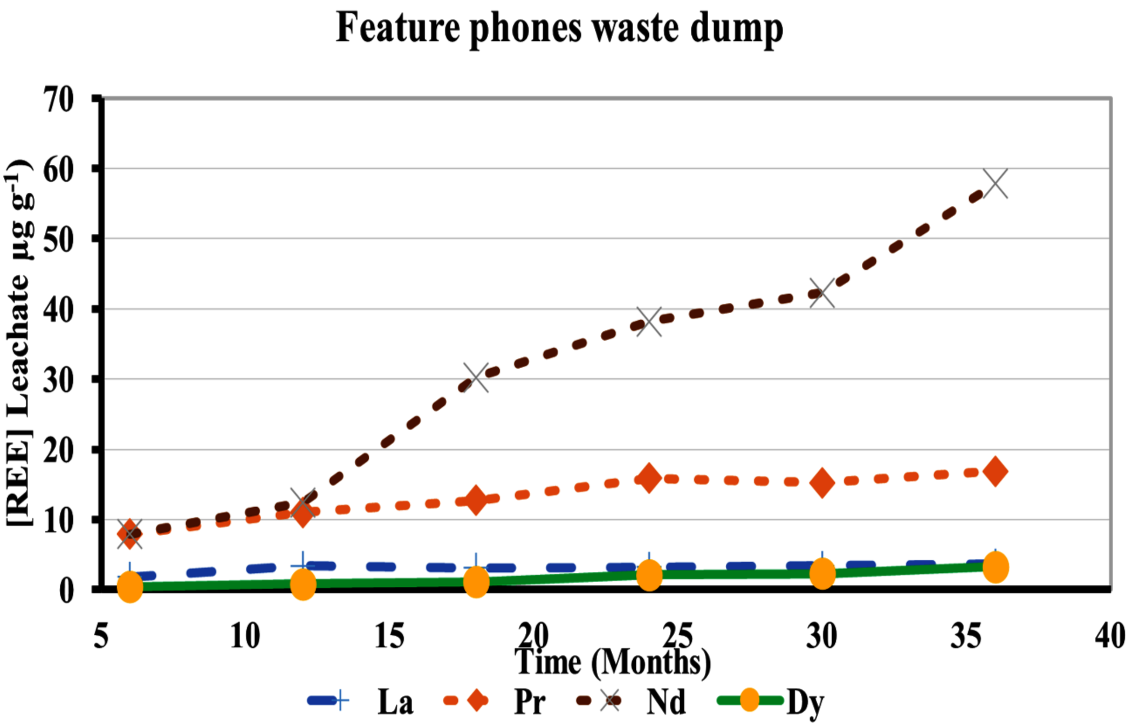


Figure 6. 12: Rare earth elements (La, Pr, Nd and Dy (leachate concentrations from feature phones dump over a period of 36 months.

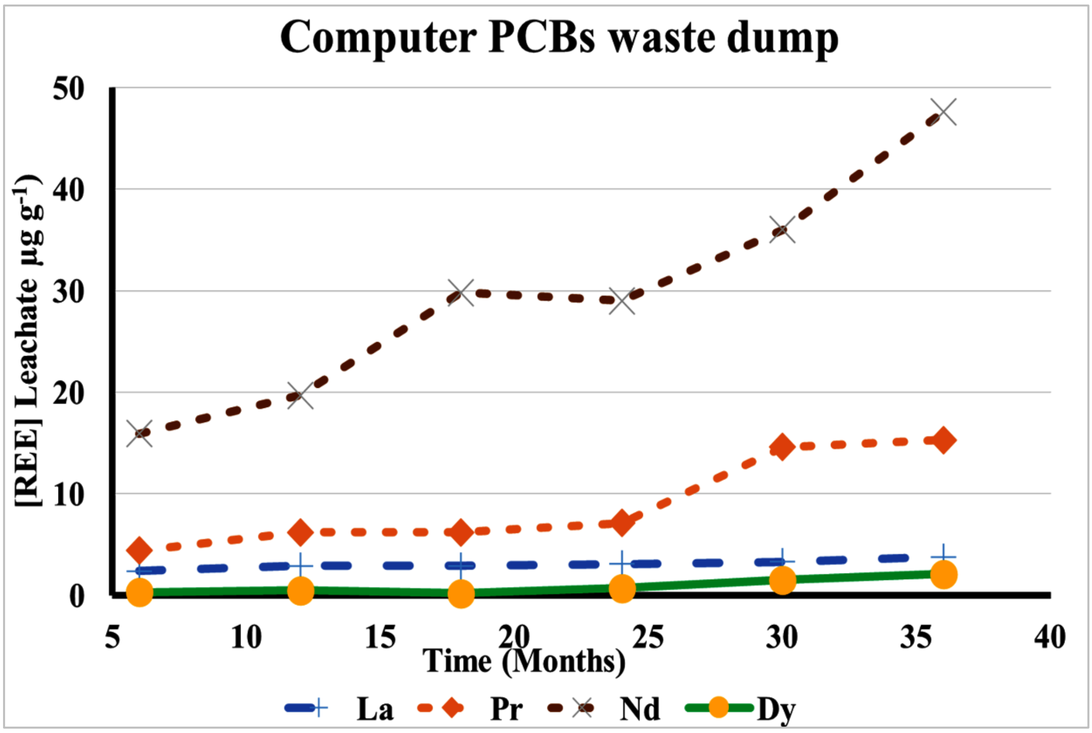


Figure 6. 13: **Rare earth elements (La, Pr, Nd and Dy) leachate concentrations from computer PCBs dump over a period of 36 months.**

6.4.7. Full rare earth elements determination

The full elemental contents of REEs in the leached soil were measured by ICP-OES and ICP-MS. An attempt of LIBS analyses did not yied results as all REEs were below the instrument detective limits. Samples were collected first at month 6 and then at 36 months to evaluate all REEs sinks in the soil and other metals contained in e-waste. Table 6.3 reveals the results of REEs from the e-waste dumpsites sampled at months 6 and 36. The light rare earth elements (LREE) La, Ce, Pr, Nd) and middle rare earth elements (MREE) Sm, Gd and Tb showed positive identification with more concentration obtained at month 36. The heavy rare earth elements (HREE) Dy, Ho, Er, Tm and Yb were very insignificant in concentration, though some values were obtained in a smartphone e-waste dump. The control dumpsite with e-waste material had no or very insiginificant REEs that did not vary for the period of 36 months as expected. All three e-waste categories smartphone, feature phone and computer PCBs showed an increase in REE concentration from month 6 to month 36. Most of the HREE were not recorded in all e-waste categories as they were below the detectable levels (bdl).

Table 6. 3: Full rare earth elements determination at month 6 and month 36.

Parameter (µg g^{-1})	**Control**		**Smartphone (VON)**		**Feature phone (DEO)**		**Computer PCBs (ADI)**	
	M 6	M36	M6	M36	M6	M36	M6	M36
La	ND	0.12 ± 0.01	0.6 ± 0.04	4.23 ± 0.64	ND	3.73 ± 0.14	ND	0.12 ± 0.01
Ce	0.12 ± 0.02	0.13 ±0.02	7,32 ± 0,42	13,71 ± 0,91	6,81 ± 0,48	11,42 ± 0,88	6,18 ± 0,41	9,34 ± 0,73
Pr	0.13 ± 0.02	ND	1.32 ± 0.06	29.70 ± 1.52	0.94 ± 0.05	16.95 ± 0.92	0.13 ± 0.02	ND
Nd	0.10 ± 0.01	0.21 ± 0.02	4.51 ± 0.22	60.46 ± 2.15	3.20 ± 0.20	47.83 ± 2.43	2.01 ± 0.11	37.64 ± 2.14
Sm	0,12 ± 0,02	0,13 ± 0,02	1,53 ± 0,06	11,36 ± 0,98	1,1 ± 0,04	4,36 ± 0,51	ND	3,21 ± 0,12
Eu	ND	ND	ND	0,41 ± 0,03	ND	0,12 ± 0,01	ND	ND
Gd	0,11 ± 0,01	0,10 ± 0,01	0,81 ± 0,05	7,21 ± 0,86	0,52 ± 0,65	3,31 ± 0,10	ND	0,28 ± 0,03
Tb	ND	ND	0,35 ± 0,04	0,83 ± 0,04	ND	ND	ND	ND
Dy	ND	ND	ND	4.02 ± 0.14	ND	3.30 ± 0.18	ND	ND
Ho	ND	ND	ND	0,21 ± 0,01	ND	ND	ND	ND
Er	ND	ND	ND	1,36 ± 0,11	ND	0,56 ± 0,07	ND	ND
Tm	ND	ND	ND	ND	ND	ND	ND	ND
Yb	ND	ND	ND	ND	ND	ND	ND	ND
Lu	ND	ND	ND	ND	ND	ND	ND	ND

M6 – Month 6; M36 – Month 36; ND – Not Detected

6.4.8. XRD characterisation of dump waste

The XRD spectra of smartphone dumpsite waste at 6 months (Figure 6.14) and 36 months (Figure 6.15) are shown below. Quartz is present in a substantial amount as silica at more than 98% for both spectra. Due to the low values of rare earth elements and other metals, it was difficult to identify those phases by XRD analysis. Fe at very low values was identified on both spectra and neodymium copper oxide at 36-month spectra. This showed that there was some leaching of both copper and neodymium into the soil.

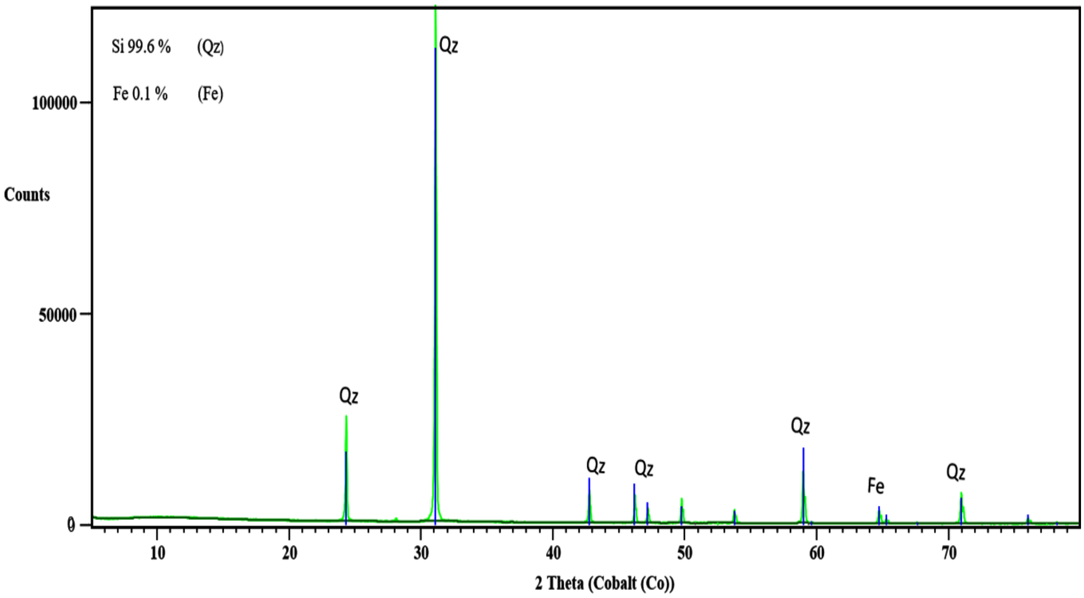


Figure 6. 14: XRD of a control sample (no e-waste) after 36 months.

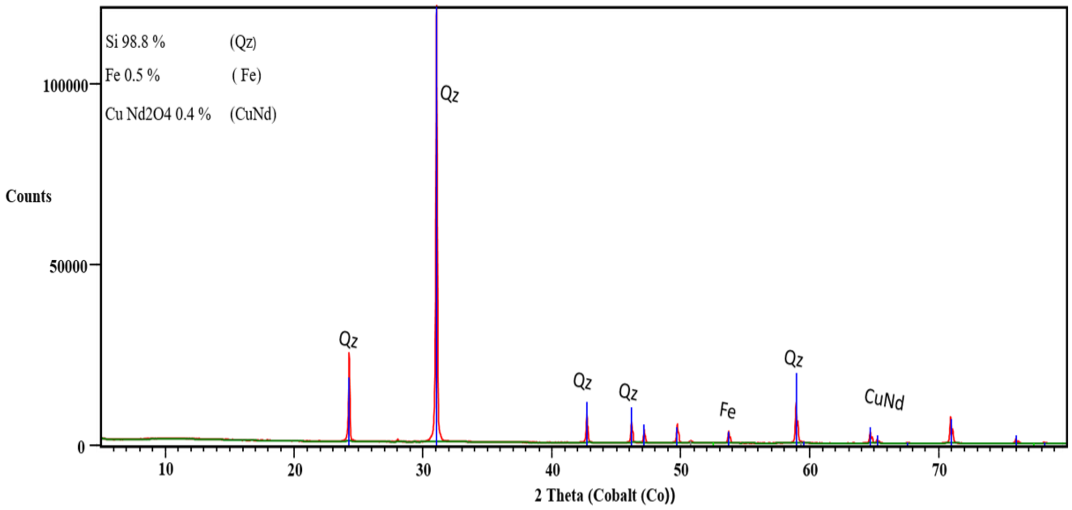


Figure 6. 15: XRD of a smartphone dump sample after 36 months.

6.4.9. Bioavailable rare earth elements

Table 6.4 reveals the results of REEs of e-waste sediment sampled from 6 to 36 months. The samples collected bi-annually were mixed in equal proportions to get a composite sample for each e-waste category. The samples were digested with two methods: the total dissolution of alkaline borate fusion and partial digestion of aqua regia acid (3:1, $HCl:HNO_3$). To reveal the bioavailability of REEs in soils, only the content that is loosely bound and that can be digested with partial aqua regia solution is necessary (Loell *et al.*, 2011). The adsorption abilities and bioavailability are significantly dependent on pH, cation exchange of the soil, precipitation, and complexation. The rare earth elements from the e-waste material studied showed that not all the content is bioavailable. The total REEs, including other REEs not shown in Table 6.4, gave 57.23 µg g^{-1} on LiM fusion method vs 22.03 µg g^{-1} on aqua regia method for smartphone (VON) e-waste, 40.92 µg g^{-1} vs 14.56 µg g^{-1} for feature phones (DEO), and 33.28 µg g^{-1} vs 12.50 µg g^{-1} for computer (ADI) e-waste. Basically, it showed that more than a third of e-waste REE content is bioavailable. This fraction seems to be more than bioavailable REEs from geological ores (Khan *et al.*, 2017).

Table 6. 4: Determination of the composite soil from e-waste dumps by LiM fusion and aqua regia methods.

	Smartphone (VON)		**Feature phones (DEO)**		**Computer (ADI)**	
Element (ug g^{-1})	LiM fusion	Aqua regia	LiM fusion	Aqua regia	LiM fusion	Aqua regia
La	3.63 ± 0.13	1.03± 0.14	2.30 ± 0.09	ND	3.01 ± 0.15	0.71 ± 0.06
Pr	14.81 ± 0.9	5.13± 0.21	10.23 ± 1.01	4.06 ± 0.32	6.42 ± 0.54	2.03 ± 0.08
ND	26.31 ± 1.93	9.78 ± 1.14	19.82 ± 1.63	7.32 ± 0.93	16.17 ± 1.78	6.12 ± 0.70
Dy	2.01 ± 0. 09	0.74± 0.05	1.21 ± 0.07	ND	0.62 ± 0.05	ND
ΣREE	57.23	22.03	40.92	14.56	33.28	12.5

5.4.10. Speciation of REEs in the electronic waste dumps

To reveal the underlying leaching mechanism, the sequential extraction process depicts the mobilisation behaviour of trace metals in contaminated soils and sediments. Speciation of REEs usually determines the solubility and bioavailability of a substance. The chemical fractions of rare earth metals (Pr and Nd) in e-waste polluted soils were investigated using the sequential extraction procedure (SEP) steps as elaborated in Table 6.5. The contribution of exchangeable and carbonate bound fraction amount to almost a third each for praseodymium followed by the Fe-Mn oxide bound fraction with 22.1% and 27.3% for smartphone (VON) and feature phone (DEO) e-waste. The residual (acid bound fraction) at less than 10% in both samples. The samples produced very little of the organic fraction. The Neodymium exhibited differently from praseodymium in that the largest fraction of content was in residual (step 5) > 45%, followed by carbonate (step 2) fraction with > 21%, Fe-Mn bound (step 3) > 15% and the least content in organic bound (Step 4) fraction in both e-waste samples.

Table 6. 5*:* **Sequential extraction procedure results for Pr and Nd in e-waste dumpsites soils.**

		Smartphone waste (VON)		Feature phone waste (DEO)	
Step	**Fraction**	**Pr (%)**	**Nd (%)**	**Pr (%)**	**Nd (%)**
1	Ion-exchangeable	31.3	8.3	26.1	9.8
2	Carbonate bound	34.7	25.1	33.4	21.7
3	Fe-Mn oxide bound	22.1	15.7	27.3	17.3
4	Oxidisable (Organic)	3.3	3.2	2.0	2.8
5	Residual	6.4	46.5	8.1	45.6

The other REEs studied in soils had a very low concentration to well understand their solubilisation through the SEP procedure. The mobilisation behaviour of REEs helps to assess the risk potential of contaminated media. Highly soluble elements pose a high risk of contamination than hardly immobile or inert elements. In sequential extraction methods, the samples in exchangeable and carbonate fractions are relatively very soluble and potentially classified as bioavailable elements. Pr showed more solubility than Nd and will leach, migrate and contaminate the surroundings faster. It reacts rapidly with water and will gradually accumulate in soils, sediments and water and this will eventually lead to increasing concentrations in humans, animals and soil particles. However, the solubilisation and mobility are dependable on other factors such as physicochemical parameters and organic matter of the sediment (Ohoro *et al*., 2022).

The quantity and combination of metallic elements in e-waste components make the leaching mechanism difficult to predict. These elements may inter-react when exposed to environmental conditions and this may alter the solubility conditions. Rare earth metals are not very soluble in water as ore deposits but their oxide from secondary sources differ as was observed in this current study.

Most ionic lanthanide and carbonate complex compounds are soluble in water. However, other compounds of lanthanides such as fluorides are insoluble (Gramaccioli *et al.*, 1999). The lanthanides have a tendency of decreasing solubility with increasing atomic number (La→ Lu) as the compouds become more covalent across the series. They react with water to liberate hydrogen gas and form Ln(H_2O) complexes as shown in Equations 6.5 and 6.6 media (Xu *et al.*, 2007). Praseodymium and neodymium react with water and oxygen when exposed to air. The light lanthanides oxidise much more rapidly than the heavy lanthanides. This solubility phenomenon is similar to what has been observed in this study from the exposed electronic waste, but the difference between LREEs and HREEs could not be verified due to low levels of some elements.

$$Ln(OH)_{3\,(s)} + 3H^{+}(aq) \leftrightarrows Ln^{3+}(aq) + 3H_2O(l) \qquad Eqn\ 6.5$$

$$Ln^{3+}(aq) + H_2O\,(l) \leftrightarrows Ln(OH)^{2+}(aq) + H^{+}(aq) \qquad Eqn\ 6.6$$

6.4.11. Physicochemical parameters

6.4.10.1. Physicochemical parameter measurements of the simulated electronic waste dumps

Table 6.6 shows the physiochemical characteristics of the leachate from the e-waste contaminated soil samples with noted differences in all the determined parameters over a period of 42 months. The pH of a dumpsite is controlled by many variables (Wdowczyk and Szymańska-Pulikowska, 2021), however, in this study, the variation from month 6 to 42 was not significant with pH decreasing from the neutral range to more acidic especially the VON sample with pH 5.1 on month 30. The electrical conductivity (EC), total dissolved substances (TDS), chloride, alkalinity, and sulphur all showed an increase in concentration from months

6 to 42 except for the control sample. The largest increase was noted on the VON sample and the least on ADI. As the degradation and solubility of e-waste occurred over time it caused the migration of soluble ions into the soil which enhanced the increase of these parameters with time. The metals analysed Ca, Mg, Na, Fe, and Cu exhibited a maximum increase of 300 % Ca on the DEO sample, 200 % Mg on VON, 210 % Na on DEO, 350 % Fe on VON and 350 % Cu on VON. The largest increase for the measured parameters is between month 6 and month 18. These results indicate the presence of ions in leachate from the decomposition of e-waste materials. The results from the control sample showed stability over the entire period which further proved the leaching of e-waste under natural conditions. The trend of these results correlates with the REEs results in the section to follow.

Table 6. 6*:* **Physicochemical characteristics of leachate originating from e-waste dumps.**

Simulated dump type	Time (Months)	PH	Ec (µs/cm)	TDS (µg g^{-1})	Chloride (µg g^{-1})	Alkalinity (µg g^{-1})	S (µg g^{-1})	Ca (µg g^{-1})	Mg (µg g^{-1})	K (µg g^{-1})	Fe (µg g^{-1})	Cu (µg g^{-1})
Smartphone (VON)	6	7,2	106	40	105	80	132	24	35	23	112	61
	18	7,8	135	57	220	103	352	41	37	26	252	127
	30	5,1	155	94	360	115	537	79	51	40	361	154
	42	5,4	171	90	332	119	523	76	72	38	413	161
Feature phone (DEO)	6	7,3	112	42	108	93	119	28	37	27	130	39
	18	7,9	128	63	208	99	298	37	41	45	291	89
	30	6,6	153	92	270	120	487	81	65	51	392	132
	42	6,3	165	99	303	115	517	89	69	59	388	149
Computer PCBs (ADI)	6	6,7	109	40	113	86	93	23	31	23	105	23
	18	6,6	143	51	187	95	156	27	36	25	191	62
	30	6,8	165	72	226	111	345	51	47	37	257	148
	42	5,8	179	81	249	113	361	63	44	41	268	183
Control (no e-waste)	6	6,7	89	33	82	77	52	17	27	22	8	3
	18	6,6	97	45	95	68	63	19	24	17	11	5
	30	6,1	90	37	88	75	51	19	31	19	10	2
	42	6,2	102	42	91	80	56	21	30	20	8	4

6.4.10.2. Physicochemical characteristics of rainwater

The rainfall characteristics impact landfill sites and waste dumps, as rainwater falls on organic and inorganic constituents. The nature of the rain will aid the dissolution, forming highly toxic chemicals leaching into groundwater (Linh *et al*., 2020). The parameters such as pH and alkalinity will measure the acidic nature of the rainwater. Table 6.7 show some of the physicochemical parameters that were measured during the rainy period of each study year. The average pH was slightly below 7, electrical conductivity 157 µS/cm, TDS 26 µg g^{-1}, alkalinity 38 µg g^{-1}, sulphur 3.9 µg g^{-1}, calcium 6.1 µg g^{-1}, magnesium 4.0 µg g^{-1} potassium 1.0 µg g^{-1} and other metals were below the limit of determination. The water that accumulates at the landfill's base after passing through these chemicals typically contains significant concentrations of harmful metals, toxic organic compounds, and microbes. The data acquired from four rainy seasons do not clearly differentiate the physicochemical results; hence, they have no bearing on the trend of REE results obtained in section 6.4.

Table 6. 7*:* **Physicochemical characteristics of rainwater collected at e-waste dump sites.**

# Time (months)	**pH**	**EC (µs/cm)**	**TDS (µg g^{-1})**	**Chloride (µg g^{-1})**	**Turbidity (NTU)**	**Alkalinity (µg g^{-1})**	**S (µg g^{-1})**	**Ca (µg g^{-1})**	**Mg (µg g^{-1})**	**K (µg g^{-1})**	**Fe (µg g^{-1})**	**Cu (µg g^{-1})**
6	6.9 ± 0.09	161 ± 1.14	63 ± 1.48	25 ± 1.48	2.7 ± 0.19	30 ± 2.74	2.9 ± 0.13	5.3 ±	3.2 ± 0.24	1.3 ± 1.00	<0.5	<0.5
18	6.6 ± 0.08	159 ± 1.22	73 ± 1.55	31 ± 1.53	3.3 ± 0.15	45 ± 3.31	4.2 ± 0.15	6.8 ±	5.1 ± 0.27	0.9 ± 1.00	<0.5	<0.5
30	6.6 ± 0.08	155 ± 1.30	66 ± 1.51	19 ± 1.46	2.1 ± 0.16	35 ± 2.93	3.7 ± 0.21	6.4 ±	3.4 ± 0.28	1.1 ± 1.08	<0.5	<0.5
42	6.5 ± 0.09	151 ± 1.20	71 ± 1.54	29 ± 1.61	2.5 ± 0.18	41 ± 3.33	4.8 ± 0.20	5.9 ±	4.1 ± 0.19	0.6 ± 0.06	<0.5	<0.5

- minimum number of collected samples and averaged = 5

6.4.12. Effect of rainfall on leachate generation

The amount of rainfall is significant in the production of dumpsite leachates. The leachate flow was only observed during the normal rainy months from May to August each year for four years as shown in Figure 6.15. It was also noted that during the first month of the rainy season in May very little or no leachate was obtained as compared to the other months. This has been attributed to the landfill still being very dry and requiring more rain to saturate and produce the leachate. Though there is a slightly positive correlation between rainfall and leachate produced from regression analysis as shown by the following Equations:

$$y = mx + b \qquad Eqn\ 6.7$$

$$y = 0.5939x + 11.08 \qquad Eqn\ 6.8$$

The correlation between the rainfall received and leachate produced was poor ($p < 0.05$, $r^2 = 0.511$, n=16). The value of $p > 0.05$ shows the model does not fully explain the variation as only rainfall accounts for 51% variance of leachate generation. According to Linh et al. (2020) excessive rains produce less leachate than normal rains due to changed flow conditions. This scenario was not verified in this study as we got very few leachate samples each year and the majority of rainy months except August 2019 received similar rainfall volume (Figure 6.16).

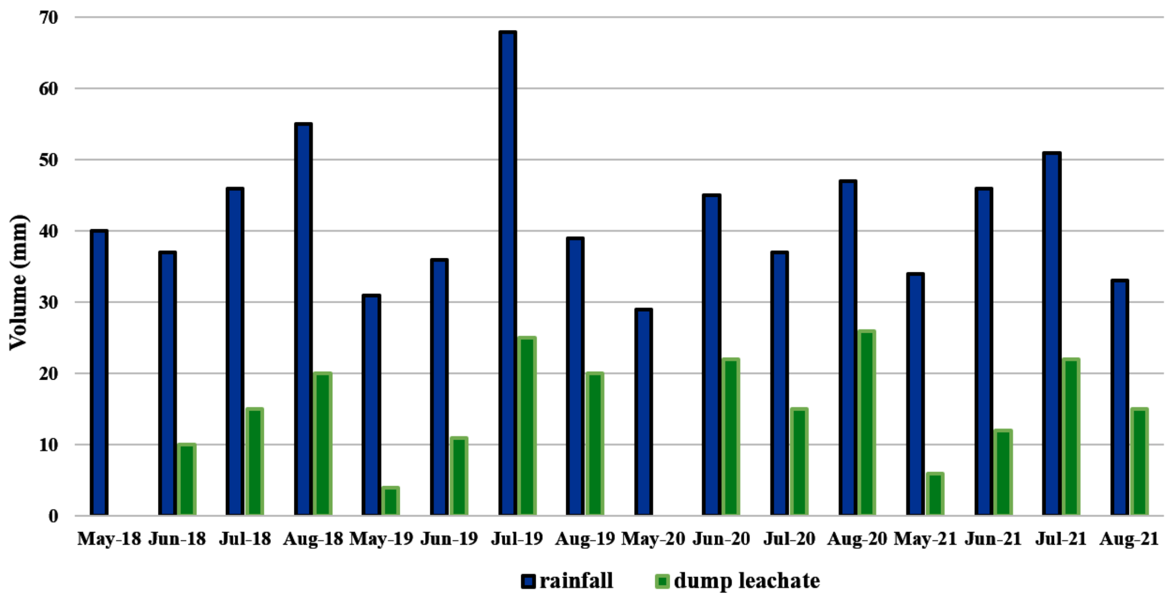


Figure 6. 16: **Comparison of rainfall and dump leachate volume during the study period's rainy months.**

6.4.13. Heavy and other metals content in e-waste dumpsites

The amount of heavy metals and sulphur content in e-waste dumps is represented in Table 6.8 The natural content of metals in particular soil is shown by the control dump where there was no e-waste material. It is clear that for the period from month 6 and month 36, no change was recorded from the control dumpsite. Some metals increased their concentration from month 6 to month 36 such as Al, Ba, Ca, Cu, Fe, K, Mg, Na, Pb and S in smartphone and feature phone dumpsites. Metals that did not significantly change were Cr, Mn, Ni, P, Ti, and Zn and this may be attributed to their low level in e-waste material under examination. However, metals like Cr and Ti are also refractory in that they could not be dissolved by natural conditions during the specified time.

The computer dumpsite showed some increases over time, but it was less than for the mobile phones. The components for computer waste are larger than mobile phones and the decomposition of those parts will take a long period of time as compared to minute parts in mobile phones. Cu which is widely used because of its good conductivity increased from 94 to

354 µg g^{-1}, 102 to 430 µg g^{-1} and 46 to 278 µg g^{-1} for smartphone, feature phone and computer PCBs waste dumpsite. Fe also changed significantly from 6697 to 8367 µg g^{-1}, 6105 to 7542 µg g^{-1} and 6204 to 6972 µg g^{-1} for smartphone, feature phone and computer PCBs, respectively. Quantities of Ca and Mg contribute to the hardness of the water when the leachate flows from the dumpsites. These heavy metal studies were carried out to help understand the behaviour, mobility and dissolution in relation to rare earth elements. The presence of other ions will impact on the leaching of REEs because of alteration of conditions in dump and its leachate.

Table 6. 8: **Other elements determination at month 6 and month 36.**

	Designated dump type							
Parameter	**Control**		**Smartphone (VON)**		**Feature phone (DEO)**		**Computer PCBs (ADI)**	
(µg g^{-1})	M6	M36	M6	M36	M6	M36	M6	M36
Al	2699	2586	3091	3340	2731	3021	3211	3219
Ba	40	38	82	185	61	113	49	56
Ca	878	887	1173	1336	987	1264	975	1032
Cr	9	10	23	32	23	24	15	13
Cu	9	8	94	354	102	430	46	278
Fe	6123	6159	6697	8367	6103	7542	6204	6972
K	74	70	137	333	95	154	81	111
Mg	52	56	107	198	121	163	97	137
Mn	14	12	40	37	35	37	35	37
Na	51	50	233	267	224	288	165	255
Ni	5	5	7	6	7	6	6	8
P	26	24	36	36	47	39	32	36
Pb	5	6	29	77	38	87	21	29
S	17	21	115	202	97	153	86	139
Ti	4	3	12	20	6	10	8	7
Zn	7	6	10	18	7	8	10	12

6.5. Summary

This chapter elucidated the rare earth element behaviour from dumped selected electronic waste exposed to natural conditions. The studies were done in simulated waste dumpsites exposed to e-waste materials in order to understand the environmental effects caused by such exposure. The study was investigated over three years, with a sampling of soil and leachate done periodically. The outcome suggests that the REEs hardly leached out in the first year of exposure but gradually increased in the second and third years. The order of leaching content was Nd > Pr > La > Dy, but this was largely due to the abundance of the elements in the original waste components. Also, the levels of the leached metals in the solid soil samples were significantly higher than in liquid leachate. The rainfall quantity determined the volume of liquid leachate, and the relationship was proportionate meaning more rainfall volume produced high leachate volume. Environmental conditions such as precipitation, temperature and physicochemical parameters affect the nature of the exposed e-waste components in disintegration and dissolution, and the rate will increase with time as the components get weaker, as evidenced by the findings in this chapter.

In sequential studies, Pr showed more solubility than Nd as it leached out more in four fractions than the residual fraction. The other metals were also measured to determine the content in soils derived from e-waste. They generally showed an increase with time, but refractory elements like Cr, Ni and Ti did not show an increase. Normally, lanthanide oxides are fairly soluble in aqueous media like water and this was confirmed in this study, but with extended time. Pr showed more solubility than Nd and will leach, migrate, and contaminate the surroundings faster. Another finding was not all REEs were bioavailable as only a fraction was digested, using the partial technique of dissolution. Total analysis of rare earth elements shows that small amounts of other elements like Sm, Gd, Tb, and Er were also present, especially after

36 months. Further and continuous studies are necessary especially in different soil environments to have a predictive REE leaching model from exposed e-waste.

CHAPTER 7

CONCLUSION, RECOMMENDATIONS AND FUTURE WORK

7.1. Introduction

This chapter gives a summary of the discussions, significant findings and conclusions of the results presented in the previous chapters. The novelty in the study and recommendations for further research on some aspects are outlined. This chapter presents all the obtained findings and their conclusions.

7.2. Overview

The aims and objectives of this study were firstly to determine quantitatively, the elemental composition of rare earth elements in electronic waste components with improved analytical technique. However, most of the methods that were in existence suffered some limitations in order to obtain accuracy due to solubility issues. The proposed alkaline borate fusion method aimed at closing the gaps of the shortfalls of other methods. Several parameters were optimised in order to deal with problematic metallic fractions in e-waste. The environment is polluted by toxic metals leached out or in small metallic fractions from solid e-waste substances. These metals include precious metals, heavy metals and rare earth elements contained in e-waste components.

Secondly, the macrocosm laboratory studies were investigated in order to ascertain the leaching conditions of REEs from e-waste. The conclusions obtained are essential to recycling technologies for urban mining in order to obtain secondary resources. Additionally, it will also help to gauge the conditions that enhance environmental leaching. The optimised leaching parameters will be helpful to recycling in hydrometallurgical processes.

Thirdly, the simulated dumpsites of different e-waste materials were set up and studied for four years with the aim to determine the leaching of REEs from e-waste under natural conditions. The trend and gravity of leaching was investigated. Physicochemical parameters for the contaminated soil and the leachate from the dumpsites were monitored. The sequential extraction scheme with a view of concentrating or leaching the REE in soil exposed to e-waste was investigated. The rainwater physicochemical parameters were also studied. In order to achieve the aims and objectives of this study, several analytical techniques such as ICP-OES, ICP-MS, XRD, XRF and LA were applied to characterize the e-waste and environments associated with e-waste components in the experimental design.

7.3. Conclusions

The determination of rare earth elements in e-waste and environmental samples was a daunting task but a success in this study. Chapter 1 presented the theme of the study, which included a brief introduction to e-waste challenges, rare earth elements, and quantification methods. The chapter also detailed the problem statement, the research hypothesis, research aims, objectives, the novelty of the study and the layout of the thesis.

In chapter 2, a review of the literature has summarised the physical and chemical properties of rare earth elements. The roles that REEs play in the production of technological equipment, highlighted the uses and properties that makes these elements critical in today’s electronic equipment production. The composition and impacts of e-waste on the environment have been discussed in detail as reviewed from the previous work done by other researchers. The present literature survey showed that the concentrations of pollutants from e-waste have increased significantly in the last decades in diverse environmental matrices both on terrestrial and aquatic environments. The chapter concludes with discussions on analytical procedures focusing on REEs in e-waste and associated environments. The major findings of this review chapter have been published as a book chapter.

In chapter 3, the experimental methods and analytical techniques were illustrated for the purpose of achieving the objectives set out in chapter 1. In this chapter, the main focus was experimental methods that include sampling, characterisation and determination of REEs by sensitive complete borate fusion dissolution technique applied to e-waste for the first time. The setup and methods to achieve column and batch leaching of REEs through laboratory microcosm and optimising leaching apparatus were successfully completed. Furthermore, the setup of e-waste dumpsites in order to study the leaching of REEs from e-waste was elaborated. The methods for all physiochemical parameters and rainwater determination are displayed and were applied. The chapter concludes with the spectroscopic techniques utilised in this study in order to achieve the planned objectives.

In chapter 4, the objective of having a fast, sensitive and accurate method for REEs determination in e-waste and environments associated with e-waste exposure has been successfully answered. The improved borate fusion method suitable for problematic e-waste determination has been achieved by a careful sampling and preparation of heterogenous e-waste components. The optimisation of pre-fusion stages that include: particle size distribution, particle size reduction, heat and chemical oxidation processes were critical. These processes were essential to safeguard the corrosion of platinum crucibles used in the fusion process due to the probable presence of metallic particles in the e-waste sample. These metallic particles will have an adverse reaction with platinum and cause damage. The fusion and instrumental parameters were optimised to obtain reproducible and accurate results. The comparison of the newly developed method was done with other classical dissolution techniques and different instrumental techniques used. The newly developed method presented in this chapter was superior to all in terms of reproducibility, selectivity, speed and accuracy. This enabled the quantification of REE in mobile phones and computer PCBs. The findings of this chapter have been published in a peer-reviewed journal.

Chapter 5 focused on the dissolution and solubility of e-waste investigated through column and batch leaching experiments. The leaching conditions were optimised in order to obtain the highest recoveries in a cold leaching set-up. The soil contaminated with e-waste was studied in a similar way to evaluate the leachability of REEs in natural environments. The batch leaching tests using different lixiviants produced better recoveries than column leaching, mainly due to the contact between the leaching solution and the solid matrix. Among the lixiviants investigated, HNO_3 at a concentration 1.0 mol L^{-1}, a contact time of 10 minutes, a solid-to-liquid ratio of 50 g/L, and an agitation speed of 450 rpm produced the highest leaching efficiency. The chapter revealed that when solubility conditions are met, the feasibility of REEs being leached out of secondary resources such as e-waste is high. The findings obtained in this chapter have been submitted for review in a peer-reviewed journal.

In chapter 6, leaching trend analysis was established from a smartphone, feature phones and computer e-waste exposed to simulated waste dumps. It took several months to obtain element content leached out from the solid e-waste matrice. After 18 months of e-waste exposure, significant content was obtained from soil exposed to the e-waste. The liquid leachate also revealed the content of metal residue, though at very low concentrations. The chapter explicates that the REEs can be soluble under natural conditions, migrate and have the potential to contaminate the surroundings. The gravity of contamination was not ascertained in this chapter as the sampling was done on the dumps and not any distance further. This chapter will also be prepared for publication.

7.4. Novelty

The significance of findings obtained in this research is of importance to recycling hydrometallurgy chemistry and environmentalists. The novel findings obtained by this research are as follows:

1. The development and optimisation of the alkaline borate fusion for the determination of e-waste components and soils derived from e-waste exposure. This method was applied for the first time on REEs determination in e-waste.

2. The leaching chemistry in view of REEs recycling technology has been evaluated in that; the dissolution and recovery was best with nitric acid rather than the traditional use of sulphuric acid used for other metals including REEs.

3. Though the REEs ores are refractory in nature and require aggressive dissolution methods, it was observed in this study that the REEs obtained from secondary resources like e-waste in oxide form or pure metal are easily leached out with even less concentrated mineral acids, acidic water and organic acids. For the first time, a study on REEs leaching lasting more than three years was conducted.

4. The exposure of e-waste components leads to the disintegration of small components thereby releasing metals that will be leached out with the help of atmospheric conditions. The novel approach is based on REEs' reactions from e-waste, their disintegration, solubility, complexation/precipitation, and permeation in the natural environment.

5. It has been proved under controlled conditions that REEs can be leached from solid e-waste materials into the environment. The dissolution and transport processes reactions may take a while but they will eventually commence.

6. The rainwater may aid the disintegration and dissolution of the metallic waste but the physiochemical parameters of Cape Town rainwater did not seem to affect dissolution rate during the studied period.

7.5. Recommendations

The data obtained from this study will help the community, recycling industry, and environmentalist to curb the unwanted pathway of these metals into the environment. Soil pollution is a significant environmental problem that involves both political powers and citizens to assist. Soil is not a renewable resource hence further investigations into the results outlined in this thesis could yield valuable additional information to curb environmental pollution. The findings here raise concern about metal contamination at different e-waste sites worldwide, and thus it is imperative for actions.

7.6. Future work

The replication and utilisation of the study outcome to different locations is a priority. This is one of the fundamentals of the research since e-waste monitoring will be done nationally or internationally. Studies based on different soil types and profiles, different e-waste components and weather conditions will be carried out to simulate other host places. Based on the results obtained in this study and more experimental studies, it is possible to have a model that can be used as a guideline.

To come up with a model prediction for contaminant leaching over a range of relevant conditions based on REEs' reactions from e-waste, their disintegration, solubility, complexation/precipitation, and permeation in the natural environment. Currently, the REEs contamination aspects seem not sufficiently considered in e-waste site risk assessments, like heavy metals, but with the increased usage in technological gadgets this need to change.

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