CRANFIELD UNIVERSITY

HYEYEON LEE

OCCURRENCE AND DISTRIBUTION OF ORGANIC COMPOUNDS IN LANDFILL LEACHATE AND THEIR INFLUENCE ON METAL MOBILITY AND RECOVERY

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Energy and Power

PhD Thesis
Academic Year: 2021 - 2022

Supervisor: Dr Stuart Thomas Wagland
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This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

ABSTRACT

Resource security has attracted increasing attention globally due to the growing demand for use in a wide range of products. Municipal solid waste landfills and leachate are significant untapped resources that can contribute to a sustainable and secure supply of raw materials. Recent studies reported heavy metals (HM) and rare earth elements within the waste mass buried in landfills that can theoretically be recovered and reintroduced within the material loop of the circular economy framework. However, metal recovery only cannot be visible economically due to its low concentration. Therefore, research is required to understand how metals can be effectively mobilised.

This research is carried out to develop a methodology to demonstrate the metals in landfill leachate as a potential secondary source. The batch and column percolation tests are performed to establish the relationship between metals recovery rate and other parameters. This PhD project investigates the influence of factors to increase metal mobility. Firstly, pH value and depth effect on metal release were analysed. The pH value plays a critical role to increase metal recovery rate; however, no significant correlation between depth and metal release was observed. As the analysis shows that metal release is highly increased in acidic conditions, column percolation was conducted at the optimise pH values with leachate recirculation. Leachate recirculation accelerates the degradation of organic waste, consequently enhancing the hydrolysis rate that may reduce the pH value. Lastly, different humic concentration on the metal(loid)s release from landfill leachate was investigated.

This thesis presents a high potential to help evaluate the environmental impact to control the pollution and recover metal(loid)s.

Keywords: Landfill, metal recovery, humic acid, leachate recirculation, pH, circular economy, sustainability

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My family is my everything.

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LIST OF ABBREVIATIONS

Al	Aluminium
As	Arsenic
ATR-FTIR	Attenuated total reflection-Four Transform-Infrared Spectroscopy
BOD	Biochemical oxygen demand
C	Carbon
Cd	Cadmium
Co	Cobalt
COD	Chemical oxygen demand
Cr	Chromium
Cu	Copper
DEFRA	Department of Environment, Food and Rural Affairs
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EC	Electrical conductivity
ELFM	Enhanced landfill mining
FA	Fulvic acid
Fe	Iron
H	Hydrogen
HA	Humic acid
Hg	Mercury
HM	Heavy metal
HPLC	High-performance liquid chromatography
HS	Humic substances
ICP-MS	Inductively coupled plasma mass spectrometry
IEA	International energy agency
LFM	Landfill mining
Li	Lithium
Mn	Manganese
MSW	Municipal solid waste
Ni	Nickel
OM	Organic matter
Pb	Lead
PGMs	Platinum group metals
REEs	Rare earth elements
SBR	Sequencing batch reactor
SOM	Soil organic matter
SRMs	Secondary raw materials

TOC	Total organic carbon
UV	Ultraviolet
VFA	Volatile fatty acids
WtE	Waste to energy
WtM	Waste to material
Zn	Zinc

1 INTRODUCTION

This chapter provides a brief background on the topics that lead to the beginning of the research project, the research aim and objectives.

1.1 Background

The use of critical raw materials, including rare earth elements, heavy metals from natural sources, are inherently unsustainable as mining depletes finite resources (National Research Council, 1996). However, the continued availability of minerals is vital to sustaining industrial growth and socio-economic welfare (Mitra, 2019). Currently, the global demand for metals continues to increase even though the available amount of metals on Earth is limited (DEFRA and BIS, 2012; Rötzer and Schmidt, 2018). Thus, securing a sustainable metals supply and ensuring their circular use in the economy is essential at the EU level and beyond (Coulomb et al., 2015; Vidal-Legaz et al., 2016; Blengini et al., 2017). Valuable secondary raw materials formerly discarded as waste exist within closed landfill sites. Landfills are indeed emerging as a potential source of such materials (Krook et al., 2018). In the past, the disposal of electronics waste was largely unregulated. It allowed society to discard a significant source of scarce and valuable metals in landfills before the hazardous waste treatment legislation and the Waste and Electronic Equipment (WEEE) Directive being established in 2002 (EC, 2003) (Stewart, 2010). Therefore, many waste products containing valuable metals were disposed of in landfills before the implementation of the EU Landfill Directive 1999/31/EC (European Parliament. Council of the European Union, 1999) and EU WEEE Directive (European Parliament. Council of the European Union, 2003), which have since been repealed into the 2006 EU Waste Framework Directive 2006/12/EC (European Parliament. Council of the European Union, 2006). There are around 20,000 closed landfill sites in the United Kingdom (UK) alone and over 150,000 within the European Union (EU) (EURELCO, 2017). There is, therefore, a significant opportunity across Europe and the UK to recover value from landfill sites, as they would have since evolved into localised long-term storage of secondary raw materials or metal mines. Recent studies and reviews on the role of enhanced landfill mining have highlighted the potential of a new supply for declining raw resources, including critical raw material and metals, which are found frequently in the electronic product (Somani et al., 2018; Esguerra et al., 2019; Parrodi et al., 2019; Wagland et al., 2019). Once metal-containing wastes are placed in the landfill, the mobility of metals will be limited by several attenuating mechanisms such as cation exchange, chelation with solid organic material, and precipitation (Jain et al., 2005). Therefore, to recover a large amount of much-needed metals economically within landfills, it is necessary to understand the mobility of metals.

In general, it is challenging to recover metals from landfills using leachate because of the neutral-alkaline pH values of leachate. Metals are more likely to mobilise in acidic conditions (Iskander et al., 2016). Recovering metals from landfill sites through *ex*-situ (excavation) processes is difficult to justify financially (Gutiérrez-Gutiérrez et al., 2015; He and Kappler, 2017). Nevertheless, recovering metals from landfills is a potentially effective solution that can alleviate the disparity between supply and demand in the depletion of metals.

Every change in environmental conditions and waste, such as pH value, waste composition, especially organic matter content etc., results in changes to the mobility of metals and, thereby, in their recovery rate. Thus, to recovery a large amount of much-needed metals economically within landfills, it is necessary to understand the mobility of metals.

To date, there is still limited scientific understanding of organometallic interactions and metal mobility in landfills. Therefore, in this study, the main research purpose is to investigate the factors affecting metal mobility and identify recirculation and organic matter influence metal mobility and recovery.

1.2 Research aim and objectives

The aim of this research was to provide a mechanistic understanding of the biochemical and organometallic processes contributing to metal mobility in landfill environments. In order to achieve this, the following objectives have been identified:

1. Critically review the literature on the mobility of metals and organic compounds in landfill environments and the factors affecting metal mobility.
2. Assess the influence of depth, percentage of organic and pH to find the optimise condition on the leachability of metals and metalloids using the batch test of statical condition.
3. Apply optimise conditions to recover metals in landfill leachate
4. Evaluate the recirculation effects on metal release and metal recovery rate
5. Perform and assess the effects of humic acid and recirculation cycle on recovered metals.

The following hypotheses formulated

“Metal content in leachate is indirectly proportional to the COD, VFA content and pH. Decrease of pH will increase COD and metals content in the leachate of aged landfill sites.”

2 Recovering metal(loids) and rare earth elements from closed landfill sites without excavation: leachate recirculation opportunities and challenges

This chapter critically reviews the literature on the factors affect metals mobility in landfill environments and the possibility of recovering metals in landfill leachate through leachate recirculation. It has been published in Chemosphere (see Appendix D)

2.1 Introduction

Metals, metalloids and REE, collectively termed ‘metals’, are finite natural resources with increasing demand. It is vital to find alternative sources to ensure supplies of these metals, especially for new technologies such as electric vehicles, renewable energy generation and battery storage (Jowitt et al., 2020). Several recent studies reported that a worthwhile amount of valuable secondary raw materials is available within closed landfill sites (Gutiérrez-Gutiérrez et al., 2015; Dino et al., 2017; Krook et al., 2018; Särkkä et al., 2018; Esguerra et al., 2019; Parrodi et al., 2019; Wagland et al., 2019). There are around 21,000 closed landfill sites across England and Wales (DEFRA, 2021; ENDS Report, 2021) and somewhere between 150,000 and 500,000 landfill sites within Europe, with an estimated 90% of them being non-sanitary (Jones et al., 2018). Closed landfills represent a significant opportunity across Europe and the UK to recover value from waste materials as they provide a previously unconsidered localised long-term storage deposit of secondary raw materials similar to traditional metal mineral resources. Enhanced Landfill Mining (ELFM) address the combined and integrated valorisation of distinct landfilled urban waste streams as both materials (Waste-to-Materials, WtM) and energy (Waste-to-Energy, WtE) while meeting the most stringent ecological and social criteria (Jones et al., 2013). ELFM provides an opportunity for combined resource recovery and reclamation of land while mitigating future environmental liabilities and remediation costs through excavation innovative transformation technologies (Jones et al., 2013; Esguerra et al., 2021; Vollprecht et al., 2021). However, existing technologies and good practices are unable to demonstrate the economic viability of such schemes. This is partly because mining processes for recovering material result in high capital costs. There are also important uncertainties about the actual abundance and concentration of suitable waste materials in landfill environments, which need to be known early on in the lifecycle of a metal's recovery project.

Two essential by-products of waste disposal by landfills are leachate and landfill gas. The former is formed when rainwater infiltrates and percolates through the degrading waste, the latter by microbial degradation of biodegradable waste materials under anaerobic conditions (Chu, 2008). Effective treatment methods are required as leachate contains trace chemicals, contaminating groundwater, surface water and soil, potentially polluting the environment and harming human health (Brennan et al., 2016). However, ambitions for the landfill management should go beyond protecting human health and the environment, with conservation of energy and recovery of natural resources high on the agenda. Landfill leachate comprises recoverable metals, organics, phosphorus, ammonia, and water (Iskander et al., 2017; Kurinawan et al., 2021). The presence of recoverable metals means that landfill leachate can be of great importance as an alternative to conventional mineral exploration as the sediment of the leachate showed presence of REEs content was more than twice the content in landfilled waste (Gutiérrez-Gutiérrez et al., 2015), but also it can negate the need for full-scale landfill mining.

There are four objectives of this review paper: i) to give an overview of the properties and metals content in landfill leachate to gain insight into the opportunities for metal recovery from leachate; ii) to explore the knowledge on various factors affecting metals solubility; iii) to evaluate the efficiency of recirculation for increasing metal recovery rates and; iv) to discuss the opportunities for metal recovery from leachate, analyse the challenges associated with the recovery, and present the perspectives for future research and technology development to maximise the benefits of metals recovery from closed landfill leachate.

2.2 Landfill leachate properties and metal content

Leachate can be formed as a result of chemical and biochemical processes within the landfill. There is nonuniform and intermittent percolation of moisture through the solid waste in the landfill due to leachate generation (Hughes et al., 2013; Edokpayi et al., 2018). Several factors influence leachate composition, such as the age of landfill, depth of the waste in the landfill, location of the site, and weather condition of the landfill site; another critical factor affecting leachate composition is the composition of the waste deposited in the landfill (Jang and Townsend, 2003; Kalčíková et al., 2011; Moody et al., 2017). Generally, the waste composition is categorised as organic (food and garden waste), paper, plastic, glass, metals, etc. Table 2.1 shows the composition of global waste. Waste comes in many different forms, and sources of waste can be broadly classified into four types: industrial, commercial, domestic and agricultural waste. According to waste types, there are four standard landfill types: municipal solid, industrial, residual and hazardous landfill (Hockstad and Hanel, 2018).

Table 2.1. Waste composition range

Component	Range (%)	References
Organic waste	15-58	Tapia, 2009; European Commission, 2016; Abdel-Shafy and Mansour, 2018; Kaza et al., 2018
Paper and cardboard	16-27	
Glass	2-4.5	
Plastic	9-20	
Wood	3-7	
Metal	3-9.2	
Textile	3-9	
Rest	3-18	

Metals play an essential part in modern societies and have been linked with industrial development and improved living standards. Surface engineering and related industrial sectors, such as automotive, printed circuit board and aerospace, produce waste streams that contain high concentration metals (Ebin et al., 2019). Therefore, there is an opportunity to recover metals from industrial waste. The waste can instead be perceived as a raw material for resource recovery. Agriculture wastes may have substantial quantities of organic carbon, which can be recovered for energy generation. A wide variety of metal contents is collected into the leachate as it drains through the pile of waste in the landfill (Eggen et al., 2010; Edokpayi et al., 2018). Leachate is also rich in ammonia and inorganic components such as iron, chlorine, sulphate, and metals (Ồman and Junestedt, 2008). Inorganic compounds may consist of potentially harmful elements such as Pb, Hg, and As in pure form or combined with other elements (Jan et al., 2015). As leachate contains a wide range of metals, it can be considered a great potential for metal recovery. However, there are also challenges associated with the method to meet the need for sustainable leachate management that maximises valuable metal recovery. The key challenge on metal recovery from leachate is the low concentration of metals which is often affected by landfill age and type (Table 2.2).

Table 2.2. The concentration range of chemical constituents of landfill leachate determined from available literature

References	Parameter	Concentration range (mg/l)	References	Parameter	Concentration range (mg/l)
Kjeldsen et al., 2002	Alkalinity (as CaCO3)	0-20,850	Kjeldsen et al., 2002	Nitrogen (Ammonia)	0-1,250
Kjeldsen et al., 2002	Aluminium	0-2	Kjeldsen et al., 2002	Nitrogen (Nitrate)	0-9.8
Christensen et al., 2001	Antimony	0-3.19	Christensen et al., 2001	Nitrogen (Nitrite)	0-1.46
Christensen et al., 2001	Arsenic	0-0.04	Christensen et al., 2001	Nitrogen (Organic)	0-1,000
Christensen et al., 2001	Barium	0-2	Christensen et al., 2001	Nitrogen (Total Kjeldahl)	1-100
Christensen et al., 2001	Beryllium	0-0.36	Christensen et al., 2001	Nickel	0-7.5
Akinbile et al., 2012	BOD5	0-4,000	Akinbile et al., 2012	Phenol	0.17-6.6
Kjeldsen et al., 2002	Boron	0.5-10	Kjeldsen et al., 2002	Phosphorus (Total)	0-234
Christensen et al., 2001	Cadmium	0-0.01	Christensen et al., 2001	Phosphate	1-10
Adamcová et al., 2016	Calcium	100-1,000	Adamcová et al., 2016	pH	4.5-9
Akinbile et al., 2012	Chloride	20-2,500	Akinbile et al., 2012	Potassium	0.16-3,370
Adamcová et al., 2016	Chromium	0-0.05	Adamcová et al., 2016	Selenium	0-1.85
Kjeldsen et al., 2002	Cobalt	0-7.58	Kjeldsen et al., 2002	Silicon	0-12
Christensen et al., 2001	COD	150-6,000	Christensen et al., 2001	Silver	0-1.96
Kjeldsen et al., 2002	Conductivity (µmho/cm)	480-72,500	Kjeldsen et al., 2002	Sodium	0-8,000
Adamcová et al., 2016	Copper	0-9.9	Adamcová et al., 2016	Thallium	0-0.32
Adamcová et al., 2016	Cyanide	0-6	Adamcová et al., 2016	Tin	0-0.16

Akinbile et al., 2012	Fluoride	0.1-1.3	Akinbile et al., 2012	TDS	0-42,300
Christensen et al., 2001	Hardness (as CaCO3)	400-2,000	Christensen et al., 2001	Titanium	0-1.5
Kjeldsen et al., 2002	Iron	0-5,500	Kjeldsen et al., 2002	TSS	140,900
Adamcová et al., 2016	Lead	0-5	Adamcová et al., 2016	TOC	335,000
Akinbile et al., 2012	Magnesium	16.5-15,600	Akinbile et al., 2012	TVA (as Acetic acid)	0-19,000
Adamcová et al., 2016	Manganese	0.05-1,400	Adamcová et al., 2016	Turbidity	40-500
Adamcová et al., 2016	Mercury	0-3	Adamcová et al., 2016	Sulphate	0-300
Christensen et al., 2001	Organic halides	0.32-3.5	Christensen et al., 2001	Zinc	0-1,000
Christensen et al., 2001	Benzene	0.1-0.6	Christensen et al., 2001	Phenols	0-4
Akinbile et al., 2012	Ethylbenzene	0-4.9	Akinbile et al., 2012	Toluene	0-3.2

Note: The grey shaded cell indicates metals and metalloids

The leachate produced in young landfills (< 5 years old) contains a substantial number of organic compounds derived from biodegradable organic water materials, which undergoes rapid anaerobic fermentation within confined landfills. As a result, volatile fatty acids (VFAs) are produced, e.g. acetic, propionic, iso-butyric, n-butyric, iso-valeric, and n-valeric acid. It is very well known that organic acids, such as VFAs, may play an essential role in the mobilisation of metals through either the formation of soluble ligand: metal complexes or a decrease of pH (Molaey et al., 2021). Thus, VFAs are considered valuable substrates for metal dissolution, increasing the release of metals in landfill environments. Young leachate is characteristic of its high content of biodegradable organic matter. BOD (Biochemical oxygen demand), COD (Chemical oxygen demand), and BOD/COD ratio act as indicators of microbial activities and organic pollution. BOD/COD describes the biodegradability level of materials by which organic matter containing leachate is readily broken down in the environment (Samudro and Mangkoedihardjo, 2010). Therefore, young leachate shows a high BOD/COD indicator.

As landfill age increases, the BOD/COD ratio in leachate decreases (Table 2.3). This is due to the decomposition of the majority of biodegradable compounds and small quantity changes of less degradable organic matter at the same time that acidic conditions begin neutralise (Talalaj, 2015). As a consequence, the higher pH condition results in decreasing metal release by complexation and precipitation (Zhang et al., 2018). Older leachate from the methanogenic phase is partially characterised by the lower concentration of VFAs. As the content of VFAs and other readily biodegradable organic compounds in the leachate decreases, the organic matter (OM) in the leachate becomes dominated by refractory compounds, such as humic acid (HA) and fulvic acid (FA), which are known to bind metals to their hydroxyl and carboxyl groups, and either mobilise metals or delay their release (Leung and Kimaro, 1997; Bozkurt et al., 2000; Kochany and Smith, 2001; Klavinsa et al., 2006; Gutiérrez-Gutiérrez et al., 2015). The humic substances (HS) give a dark colour with increasing pH due to the dissociation of protons (Stevenson, 1994). The decrease in VFAs increases pH; consequently, metals have a relatively low concentration in older landfill leachate as the solubility of metals is decreased with increasing pH.

Table 2.3. Selected characteristics of leachate according to landfill age

Parameter	Young	Intermediate	Old	References
Age (years)	<5	5-10	>10	Renou et al., 2008
pH	<6.5	6.5-7.5	>7.5	Bhalla et al., 2013
COD (mg/L)	>10,000	4,000-10,000	<4,000	Bhalla et al., 2013
TOC/COD	<0.3	0.3-0.5	>0.5	Abbas et al., 2009; Zhou et al., 2010
BOD_5/COD	>0.3	0.1-0.3	<0.1	Bhalla et al., 2013
Organic compounds	80% VFA	5-30% VFA + humic and fulvic acids	Humic and fulvic acids	Bhalla et al., 2013
Heavy metals (mg/l)	Low medium >2	Low <2	Very low <2	Renou et al., 2008
Molecular size distribution	Over a broad range-high fraction of low molecular weight organics	N/A	Over a narrow range-high fraction of high molecular weight organics	Abbas et al., 2009; Zhou et al., 2010
Biodegradability	Important	Medium	Low	Bhalla et al., 2013

2.3 Physico-chemical factors affecting metals solubility

Several factors affect metals solubility within solid waste deposits (Fig 2.1). Important processes include abiotic redox processes, dissolution/precipitation of minerals, sorption, ion exchange, organic matter biodegradation, and complexation. The resulting matrix redox changes strongly influence both the inorganic and organic biogeochemistry of the landfill and therefore influencing the behaviour and fate of metals within landfills (Christensen et al., 2001). Gaining insights into the geochemistry of landfill is therefore needed to better understand the solubility of metals and predict metals recovery.

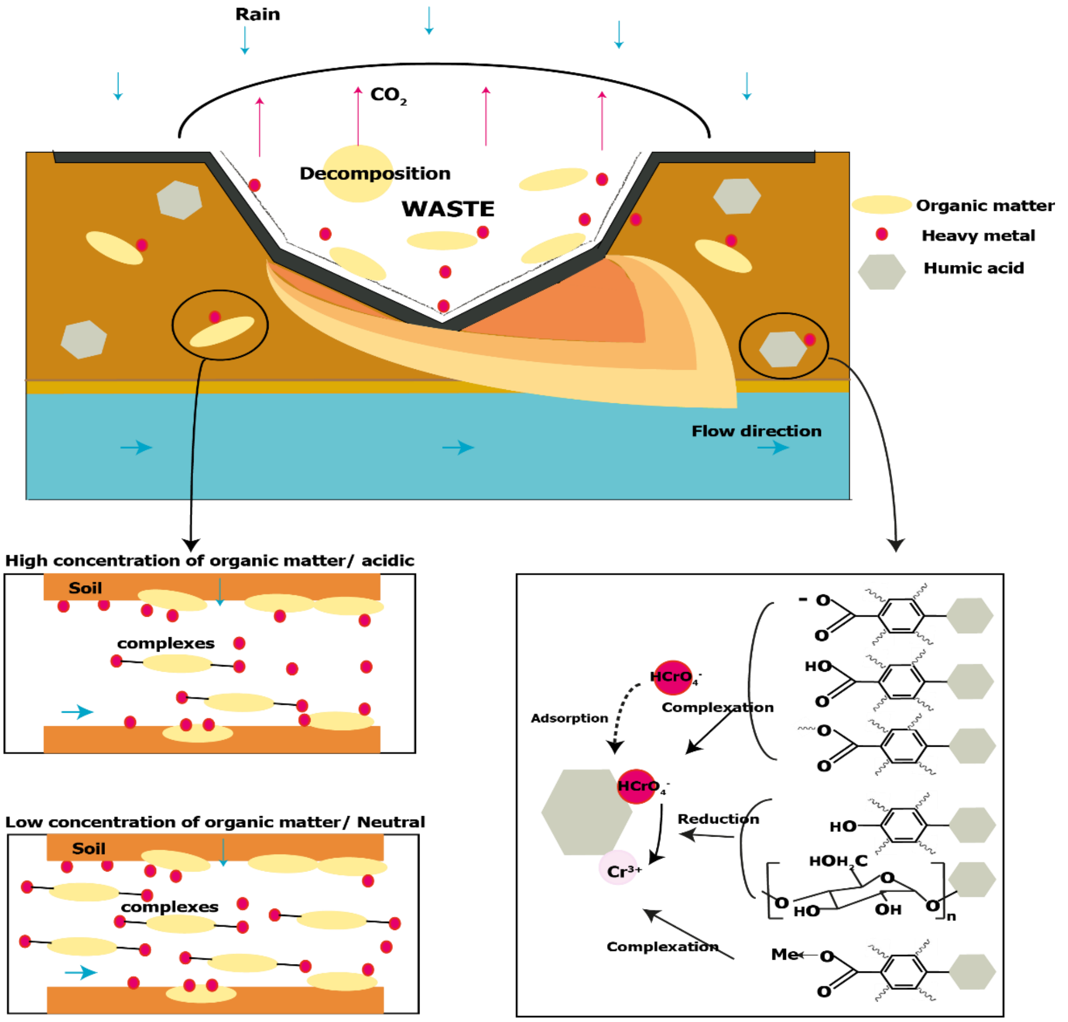


Figure 2.2.1. Processes occurring in landfills that affect metal solubility; natural attenuation, complexation of metals with organic matter and mechanism of humic acid for metals retention

2.3.1 Weathering and natural attenuation

The dissolution of metals can occur during natural events, such as weathering and natural attenuation. During weathering processes, a broad range of physical and chemical reactions such as hydrolysis, precipitation, pH neutralisation, oxidation/reduction of metals, sorption, and complexation will change the overall characteristics of metals (Chimenos et al., 2003; Polettini et al., 2004; Saffarzadeh et al., 2011; Takahashi and Shimaoka, 2012). Natural attenuation can be defined as a process by which the concentration of leachates is reduced to an acceptable level by natural processes. It can both mobilise and immobilise metals (Beaven et al., 2013). Based on the definition, *in-situ* natural attenuation mechanisms are identified as physical (diffusion, sorption, dispersion, dilution, and volatilisation), chemical (precipitation, adsorption, ion exchange, redox reaction) and biological (biodegradation) processes. For this reason, it is desirable to be able to predict how the metals in the landfill environment will behave over time when exposed to the weathering effects of infiltrating rainwater and the atmosphere. The effect of weathering on metals solubility is likely to be significant as pH is a dominant parameter in metals solubility and complexation (Stumm and Morgan, 1981). The redissolution of their respective hydroxide mainly causes the release of metals as pH is controlled by the solubility of $Ca(OH)_2$. Therefore, weathering reactions leads to a decrease in pH (Chimenos et al., 2003).

2.3.1.1 Oxidation

Several studies have been shown the formation of Fe/Al-(hydrate) oxides and calcite by weathering. It indicates that metals release may be controlled by sorption processes caused by weathering (Zevenbergen and Comans, 1994; Meima et al., 1997a; Meima and Comans, 1999; Saffarzadeh et al., 2011; Takahashi and Shimaoka, 2012). Saffarzadeh e*t al.* (2011) proposed the following order based on their direct metal uptake capacity: Fe-hydrate > Al-hydrate > calcite. Calcite is not adequate for direct metals sorption; however, they play a crucial role in buffering the system, pH neutralisation; consequently, it minimises metal leaching. Thus, weathering is expected to result in a reduced metal solubility in the long term (Meima and Comans, 1999).

2.3.1.2 Sorption and precipitation

Temporal studies of metal mobility in soils show that mobility decreases over time, suggesting that a high proportion of metals within Municipal solid waste

(MSW) which consists of everyday items we use and then throw away, are insoluble (Peters and Shem, 1993; Aucott, 2006). The reasons for the reduced mobility of metals in soil include sorption on soil particles and particularly to HS, precipitation under anaerobic conditions, adsorption, and chelation with inorganic and organic ligands in landfills (Bozkurt et al., 2000). Christensen *et al.* (2001) reported that metals in landfills do not constitute a significant pollution problem due to strong attenuation by sorption and precipitation (Fig 2.2).

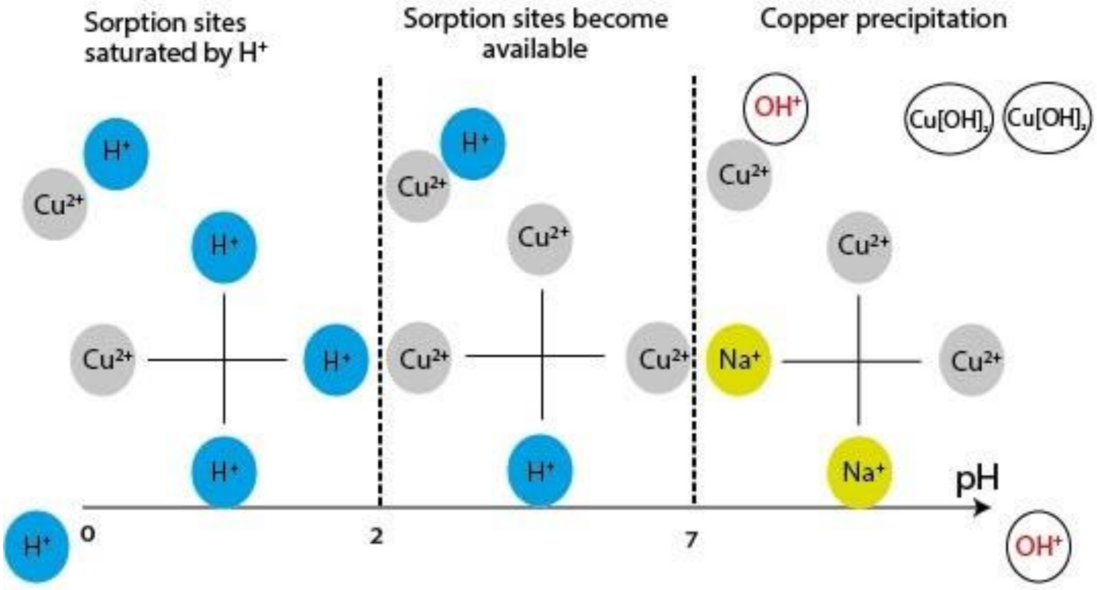


Figure 2.2.2. Effect of pH on the adsorption of copper: at lower pH, the adsorption sites are saturated by H^+, and the adsorption of copper is low; when the pH increases, the sorption sites become available, and the adsorption of copper increases. At higher pH, the copper precipitated (Adapted from Abbar et al., 2017)

In general, inorganic content of leachate ranges between 1 and 2000 mg/L. By raising the pH value, metallic hydroxide compounds become insoluble and precipitate from the solution. Alkaline conditions promote metal precipitation and adsorption, depending on the metal speciation (Lukman et al., 2013). Fig. 2.3 shows the solubility curves of selected metal ions and their respective solubility versus pH. Cu and Ni have a similar curve, albeit that the minimum solubility of Ni occurs at approximately pH 10.5 and the minimum solubility of Cu occurs at pH 9. Zn is amphoteric, being soluble in both acid and alkaline conditions. Cu and Zn readily form metallic complexes with ammonia. These metal complexes remain highly soluble at the higher pH values, prohibiting respective metal hydroxide precipitation. Cu sulphide is insoluble, and the presence of sulphide precipitates Cu as it dissociates from the ammoniacal complex. Precipitate in landfill environments strongly relates to organic decomposition and the formation of microorganisms during the process of methanogenesis (Li et al., 2015). According to Fig 2.3, precipitation is unlikely to occur in strongly acidic conditions except for Fe, Al, Pb and Zn.

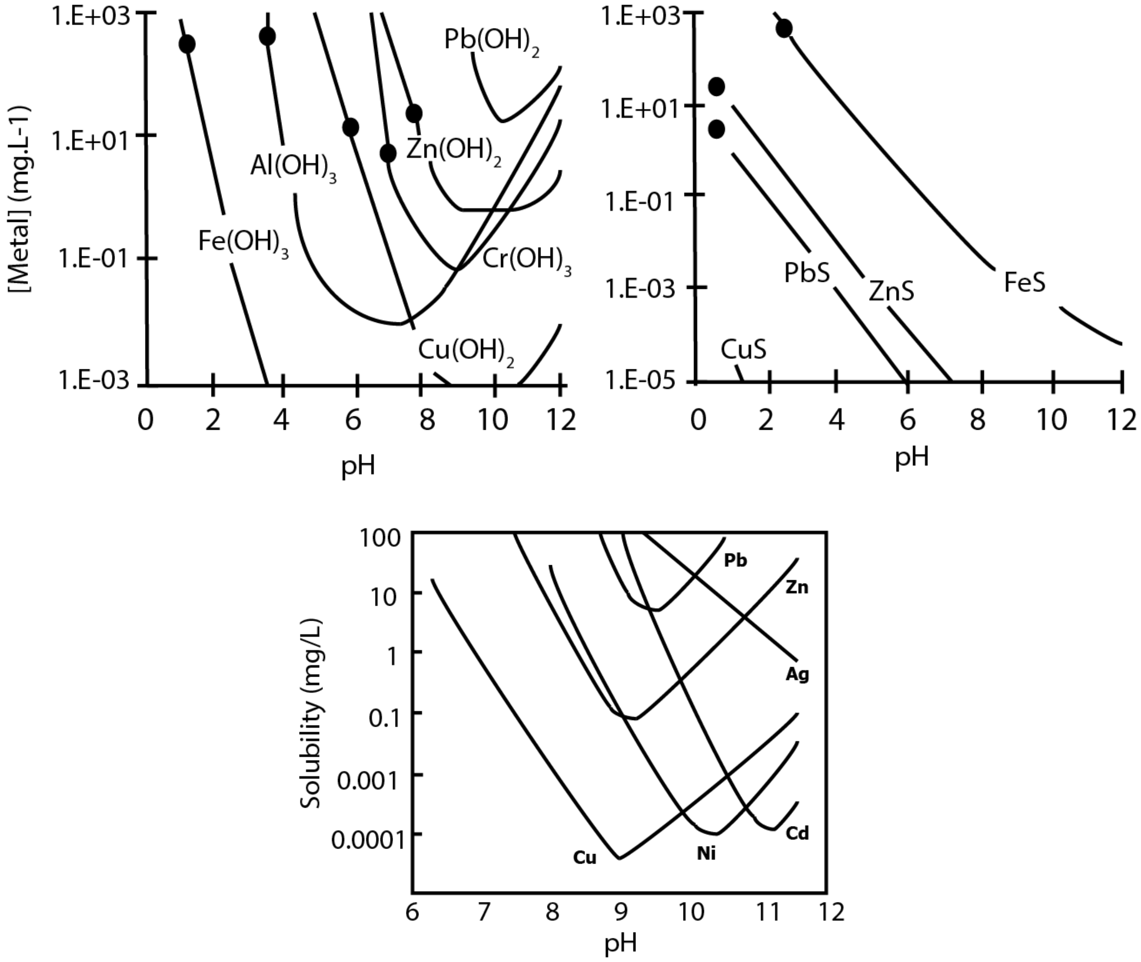


Figure 2.2.3. Solubility of metal hydroxides; solubility of metal sulphide; solubility of metal hydroxides as a function of pH (Marchioretto et al., 2005)

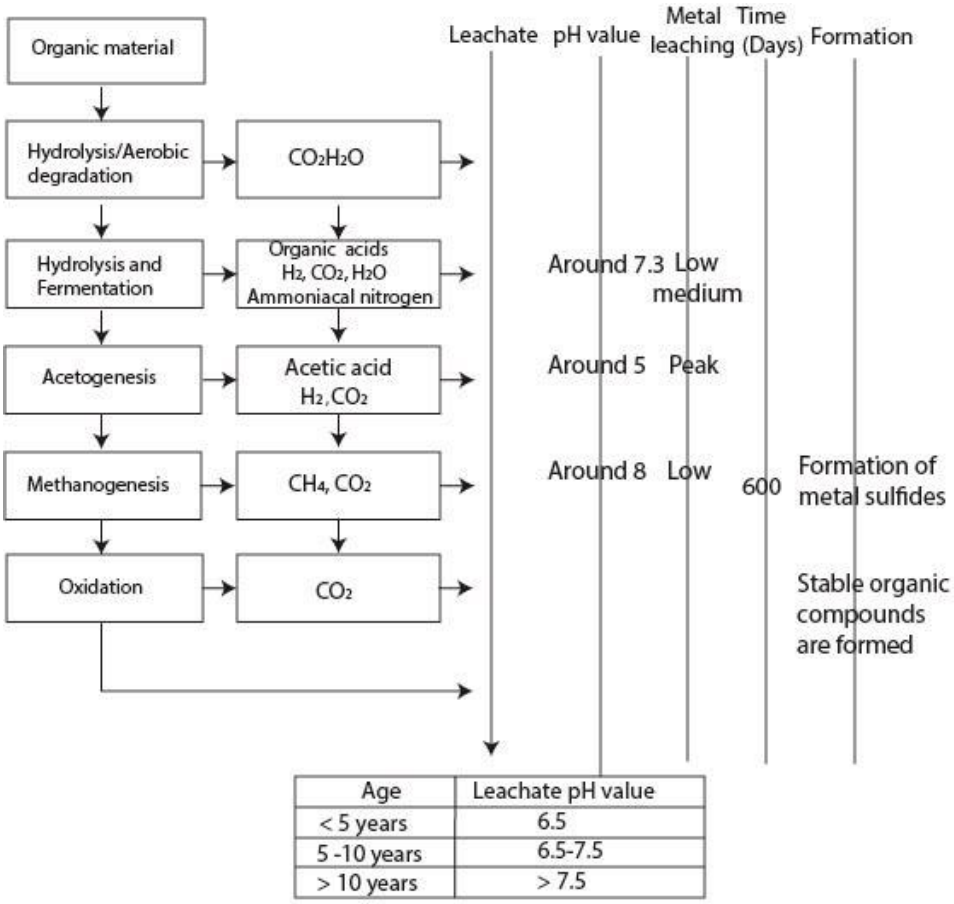
Marchioretto *et al.* (2005) reported that when Fe and Al are present in landfill leachate, adsorption and co-precipitation may occur between Cr, Pb, and Zn with $Fe(OH)_3$ and $Al(OH)_3$ as pH increases. The leachability of metals is also influenced by the chemical and physical affinity of metal ions and various waste materials under landfill conditions (Ward et al., 2005). Sulphates in waste are reduced to sulphide that forms insoluble precipitates with most metals or containing amino acids during anaerobic (Christensen et al., 2001). Dissimilatory microbial sulphate reduction is when certain bacteria use sulphate as the electron acceptor in the oxidation of organic matter. However, Cr does not form an insoluble sulphide; it is only precipitated out in the form of hydroxide. Sulphides of the metals are more difficult to dissolve, both in oxidising and reducing environments (Hammack and Edenborn, 1992).

2.3.1.3 Carbonation and redox

Carbonates are also capable of forming precipitates with metals and are abundant in landfill leachate. Nevertheless, the solubility of metal carbonates is generally high (Christensen et al., 2000). Metal precipites of carbonate will dissolve, where the carbonate release will buffer the pH value as the pH decreases, which is called the humic phase (Kjeldsen et al., 2010). As attenuation mechanisms affect metal concentration and stability, it should be considered the metal adsorption and precipitation-pH relationship for recovering metals with high concentration from an economic point of view. The redox potential influences precipitation and should be considered when considering metal solubility. Redox potential is a measure of the propensity of a chemical or biological species to either acquire or lose electrons through ionisation (Lu and Marshall, 2013). Various parameters in landfill leachate can reflect transformations in redox potential. For example, as sulphate is reduced, their concentrations decrease. An increase in redox potential effects on the oxidation of reduced sulphur compounds to SO_4^{2-}. Oxidation of metal sulphides takes place, leading to metals release. The redox conditions in landfill leachate affect metal-organic interactions through the organic ligands, as organics are sensitive to redox conditions (Merian and Clarkson, 1991). Abundant OM tends to have low redox potential values. The speciation of metals, which is related to their mobility, is dependent on pH, redox, and organic compounds (Baun and Christensen, 2004). Each of the oxidation states has different metal complexation constants, and organic compounds may mobilise it to an extent critically dependent upon the redox conditions (Herbert et al., 1993). For example, Tingzong *et al.* (1997) found that Pb was bound to iron and manganese hydroxide under oxidised conditions. As the landfilled waste shifted to reducing conditions, Pb was leached out. Chuan *et al.* (1996) also reported that the solubility of Pb, Cd and Zn in soils increased when redox potential decreased, and this was due to the dissolution of Fe-Mn ox-hydroxides under reducing conditions resulting in the release of metals. In contrast, Sims and Patrick (1978) found that soluble Zn decreased at low redox potential, which may be caused by different environmental conditions and soil types. Also, Kamon *et al.* (2002) found that low redox potential and alkaline conditions induced by anaerobic respiration in landfill sites tend to prompt immobilization of Zn but a mobilization of Iron. Overall, redox potential strongly affects the behaviour of metals in leachate even though there uncertainty remains regarding to what degree such as different environmental conditions.

2.3.2 Organic matter decomposition and metal leachability

As landfill age increases, the leachate passes through successive stages of organic substance decomposition, which influences metal leachability. Metal leachability is highest when hydrolysis, fermentation and acetogenesis dominate due to an accumulation of VFA and a pH decrease (Fig 2.4). The primary acids formed during fermentation are acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$) and ethanol (C_2H_5OH). Carboxylic acids act as chelating agents, and there may be an increase in carboxylic functional groups on humic compounds due to the waste being oxidised (Kjeldsen et al., 2010). Qu *et al.* (2008) demonstrated that metals in leachate are bound to organic substances such as fatty acids, FAs and HAs. The fatty acids, FAs, and HAs content in leachates decrease as landfill age increases (Fan et al., 2006; He et al., 2006; Qu et al., 2008). The fatty acids are accumulated during the acid phase of the waste stabilisation (Christensen and Kjeldsen, 1989). FA predominates in young unstable leachates, and its concentration decreases as landfill age increases. The HA-forming processes are dependent on microbial degradation of OM, and the HA increases with the age of leachate, eventually reducing due to the leachate becomes more stable and diluted (Artiola-Fortuny and Fuller, 1982). HA has more carboxylic groups than FA and contains bands of aromatic C=C (Gustafsson and Berggren, 2005; Shirshova et al., 2006). The binding capacities of HS to metals within leachate and solid waste may imply that the solubility of HS strongly influences the mobility of metals (Qu et al., 2008). To the best of our knowledge, no work has been reported on the effects of organic matter decomposition on metal release in landfill environments. It is expected that different metals have different impacts on the decomposition processes of organic matter. Further research is required on the role of organic matter degradation on the release of individual metals.



Age	Leachate pH value
< 5 years	6.5
5 -10 years	6.5-7.5
> 10 years	> 7.5

Figure 2.2.4 Biological decomposition process, metal leaching process in a landfill and leachate pH value (Adapted from Zainol et al., 2012, Adhikari et al., 2014)

2.3.2.1 Leaching test methods

Extensive testing procedures have been developed to simulate the leaching processes of metals in landfills or natural environments in order to estimate the release potential of metals/ materials over a range of possible waste management activities. Leaching methods can be divided into two categories by whether the leaching fluid is a single addition (statical tests) or is renewed (dynamic tests) (Tiwari et al., 2015). The purpose of the statical tests is that at the end of the entire period of the process, will be given a stable state of molecules. The substances resulting in leaching continuously flow through the sample in the dynamic test. Chemical aspects influencing the leaching relate to the fundamental processes controlling the solubility of solids. These include: (1) the influence of pH on controlling the solubility, (2) the influence of dissolved-phase complexing agents, which increase the dissolution and (3) the role of oxidation-reduction potential in increasing solubilisation (Tiwari et al., 2015). Recent characterisation of materials, such as soil, waste, sediments, and sludge employing more extended leaching tests and associated chemical speciation modelling has led to much more detailed insights into release controlling processes. Geochemical modelling such as Visual MINTEQ is potentially valuable source to identify and describe the dynamic leaching processes of metals from waste materials as well as their further rate of transport in the environments such as soil and groundwater. Therefore, the approach of geochemical modelling can be used to predict the simultaneous leaching of a wide range of major and trace elements such as Cd, Pb, Ni and Al and organic matter like fulvic and humic acid from MSW under widely different statical and dynamic conditions (Dijkstra et al., 2008).

Previous studies have used Visual MINTEQ to calculate equilibrium aqueous speciation, adsorption, solid-phase saturation states, precipitation and dissolution of metals (Zhang et al., 2008; Quina and Bordado, 2009; Yao et al., 2011; Taha t al., 2018; Mahedi et al., 2019). Also, Visual MINTEQ can prove to be able to provide valuable insights into the leaching characteristics of heavy metals. Therefore, the distribution and characteristics of aqueous metal(loid)s in the leachate may be investigated with this model.

2.3.2.2 A multivariate statistical analysis of metal leaching

Multivariate statistical analysis is considered a helpful tool for evaluating the significance of geochemical anomalies concerning any individual variable and the mutual influence of variables on each other (Albanese et al., 2018). Correlation analysis can be used to find the relationships between the physicochemical parameters of the landfill samples. Principal component analysis (PCA), factor analysis, and hierarchical cluster analysis (HCA) are some of the most widely used multivariate analysis techniques applied to geochemistry (Albanese et al., 2018). This method can represent the intensity of each metal for each factor. PCA is used to reduce data dimensions, thereby visualizing overall patterns and trends within the dataset and identifying which parameters are most important in separating classes while allowing for the evaluation of relationships between observed variables (McGregor et al., 2012). HCA is for sorting individuals with similar characteristics into groups (Li et al., 2015).

Previous research has used a multivariate analysis to compare environmental risk levels in relation to several factors such as age, particle size and depth and to identify of heavy metal sources (Facchinelli et al., 2001; Zhou et al., 2008; Zamani et al., 2012; Hou et al., 2017; Chandrasekaran et al., 2015; Jin et al., 2019). Therefore, to assess the factors influencing metal mobility in landfill leachate, a multivariate analysis would be required to identify the controlling processes in complex data and highlight the similarities and differences.

2.3.3 Chelation and complexation with organic substances

Most metal ions bind to neutral molecules in different oxidation states called a ligand, defined as an ion or molecule that binds to a central metal atom to form a complex (both organic; carboxylic acids, amino acids, HAs and inorganic) (Table 2.4). Ligands lead to the formation of metal complexes and metal chelates (Fig 2.5). Complexation with organic ligands is known to influence the mobility of metal by either increasing or decreasing its sorption on mineral surfaces. Many organic substances have been commonly identified in leachates worldwide (Details in appendix Table A.1) (Paxéus, 2000; Staley et al., 2006; Zhang and Zhang, 2009).

Table 2.4. Mechanisms of adsorption of organic compounds in soils (adapted from Sposito, 1984)

Mechanisms	Principal organic functional group
Cation exchange protonation	amines, ring NH, heterocyclic N amines, ring NH, Heterocyclic N, carbonyl, carboxylate
Anion exchange water bridging	carboxylate amino, carboxylate, carbonyl alcoholic OH
Cation bridging	carboxylate, amines, carbonyl, alcoholic OH
Ligand exchange hydrogen bonding	carboxylate amines, carbonyl, carboxyl, phenylhydroxyl
Van der waals bonding	uncharged, nonpolar organic functional groups

Among the organic ligands, HS are the main organic compounds present in landfill leachate (Zhou et al., 2015). HS are the main component of soil OM or humus, most of which combine with the inorganic constituents in the soil (Pettit, 2004). HS have several functional chemical groups (carbonyl, hydroxyl carboxylic acid, phenolic ring, and quinine), which may combine with ions such as Fe^{3+}, Mg^{2+}, and Ca^{2+} and form chelate complexes (Fig 2.6); thus change the solubility of metals (Tipping et al., 2002). Generally, the potential for complex formation between metals and organics increases with pH alkalisation (Hummel et al., 2000). Farrah and Pickering (1997a) showed that the proportions of metal bound as hydroxyl complexes increase at pH 5 and above although the capacity for complexation shows no dependence on pH (Antelo et al., 2000). Instead the metal-organic interaction depends on the stability of complex formation and metal concentration. Esakku *et al.* (2003) reported higher stability constants for Cu complexes with OM and that these lead to higher Cu content in the organic fraction. Phenolate, amino, and carboxylate groups enhance the formation of metal complexes at high pH, thus become increasingly stable at higher pH levels

(Rieuwerts et al., 1998). Carboxylic and hydroxyl functional groups show acid-base behaviour.

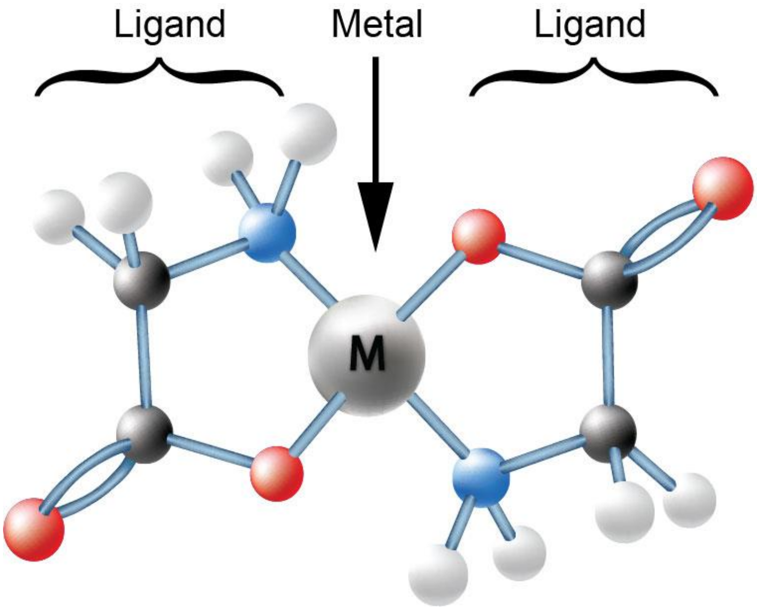


Figure 2.2.5. An amino acid chelates (Albion Technology, 2021)

At low pH, hydrogen ions compete with the metal ions for these sites, and as pH increases, less hydrogen ions are present and complex site availability for metal ions increases (Scott et al., 2005). There are challenges to understanding the complexation of different metal ions, e.g. i) organic compound functional groups influence the type of reaction it has with metals; and ii) the length of hydrocarbon chain length in carboxylic acid increases its metals adsorption capacity but decreases its stability as complex (Abollino et al., 2003).

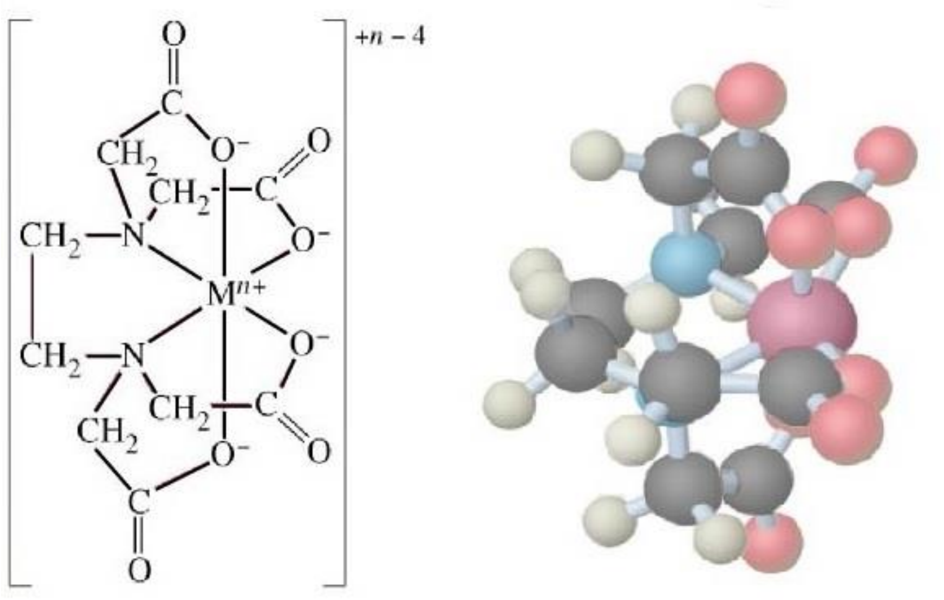


Figure 2.2.6. Metal ion complexation and chelate effect (Adapted from Tsezos et al., 2006)

Soil organic matter can influence the mobility and speciation of metal, where complexation reactions modify its accumulation potential (Kennou et al., 2015). For example, when organic materials, rich in soluble organic carbon and a large proportion of FAs are applied to soil, metal mobility increases due to the formation of soluble metal-organic complex (Pérez-Esteban et al., 2014). In contrast, when a chelating agent binds to a metal ion in more than one place simultaneously, chelated compounds become more stable (Pohlmeier, 2004). It has long been recognised that complexation may lead to increase metal solubility or decrease adsorption (Cavallaro and McBride, 1978; Bradl, 2004; Güngör and Bekbölet, 2010; Ahmed et al., 2019). Similar observations have been shown to occur within the landfilled waste. A variety of organic compounds can be expected in the leachates, which afford the potential for metal-organic interactions through the organic ligands. Previous studies established that dissolved organic matter (DOM) in MSW has a high affinity for metals, especially for Cu and Pb (Christensen et al., 1996; Christensen et al., 2000; Huo et al., 2008). Most insoluble metals are present in their refractory chemical form, i.e. PbSO4. Over time the oxidation/ reduction of these metals to a soluble form through complexation appears likely (Takahashi et al., 2010). If insoluble metal-DOM complexes are formed, the mobility of the metals in question and the DOM to which they are complex decreases. Metal mobility is less clear when soluble complexes are created with DOM (Jansen et al., 2003). On the one hand, it may increase because, i) the mobility of DOM is affected by its functional groups and adsorption to soil particles (Kaiser et al., 1997); ii) binding to DOM prevents immobilisation by precipitation of inorganic metal complexes. On the other hand, the mobility of soluble metal-DOM could decrease complexes when they bind to soil particles through cation bridging (Guggenberger and Zech, 1993).

The leachability of metals could be enhanced through ligand complexation where organic acids such as carboxylic acids and phenols, formed during the decomposition of organic compounds, decrease pH. The pH determines the number of acidic functional groups on deprotonated DOM, which increases the availability of sorption sites for binding metals (Stevenson, 1994).

Jensen *et al*. (1999b) determined organic complexes of heavy metals in landfill leachate polluted groundwater in the Vejen landfill. They found that organic complexes made up a significant part of the total content of heavy metals: Cd 85%, Ni 27-62%, Zn 16-36%, Cu 59-95%, and Pb 71-91%. Kalis *et al.* (2006) found that the metal-humic acid complexes become the dominant complexed species when humic acid is present. Yu *et al.* (2018) reported that most of the complexes between Cd and the HS would be insoluble, and the complexation could contribute significantly to the reduction in the concentration of Cd in soil solution. Van Ginneken *et al*. (2001) discovered that the stability of chelated metals and noncyclic metal complexes depends on several factors, including pH, metal oxidation state, and ionic strength. Organic-metal complexes are increasingly stable at higher pH levels due to the ionization of functional groups (Jones and Jarvis, 1981; Rieuwerts et al., 1998). Conversely, organic acids present in the dissolved organic carbon (DOC) may act as chelating agents, enhancing the mobilisation of metals (Christensen et al., 1996).

Complexing behaviour significantly influences metal attenuation as it affects their mobility and saturation indices (Qu et al., 2019). As metal-organic complexation plays a critical role in the mobility of metals in landfill environments, lab and field experiments would be required to establish the relationship between complexing characteristics and observed metals leaching, performed under varying environmental conditions to optimise metals recovery.

2.3.3.1 FTIR Analysis on metal-organic in landfill leachate

It is known that humic substances and particularly soluble HA may serve as a complexing agent for metal ions leached in the environment (Tseng, 2005). Metal complexing by humic substances has been widely studied, and while it is well known to bind strongly to organic molecules. Attenuated Total Reflection (ATR) Fourier Transform Infrared (FTIR) spectroscopy is a label-free, non-destructive analytical technique that can be used extensively to study a wide variety of different molecules in a range of different conditions (Chan and Kazarian, 2016). FTIR identifies the presence of organic and inorganic compounds in the samples, and provides information on molecular structures, chemical environments, orientations, and conformations of polymer chains. It is a technique used to obtain an infrared spectrum of absorption of samples (Sindhu et al., 2015).

Many researchers have investigated metal adsorption mechanisms on such as soil minerals and functional groups of metal-organic using FTIR (Alberts and Filip, 1998; Martyniuk and Wieckowska, 2003; Erdogan et al., 2007; Papageorgiou et al., 2010; Tsang and Hartley, 2014; Yang et al., 2019).

Therefore, the interaction of metal ions with humic acid can be studied using FTIR spectroscopy. This method would be able to prove helpful concerning to metal binding to understand better the potential sites of bonding within the humic acid.

2.4 Leachate recirculation strategy for metal recovery

Leachate recirculation within landfills has been widely used for a range of purposes since the 1970s, including leachate management, enhanced landfill gas generation or recovery, and improved landfill sustainability (EPA, 2009). Leachate recirculation is a process where leachate is re-introduced into the landfill through an artificial recharge system (White et al., 2011). This technique aims to encourage saturation to stimulate the degradation processes, leading to more rapid stabilisation of the landfill (Scott et al., 2005). However, leachate recirculation can also increase the chloride content. Chloride contents may also be an important controlling factor for metal release. Chloride affects the behaviour of metals by binding the metals on humic acids and the adsorption of metals, such as the adsorption of Cd on iron hydroxides or their desorption mobility (Guevara-Riba et al., 2005; Begeal, 2008; Damikouka and Katsiri, 2020). The ionic forms of Cu and Cd can form metal compounds with the anions such as $CuCl_2$, $CdCl_2$ or $CuSO_4$, leading to chloro-complexation and the formation of dissolved metal-chloride compounds increase the mobility of metals (Kirkelund et al., 2010; Damikouka and Katsiri, 2020). This implies that leachate recirculation affects metal recovery. Leachate recirculation can significantly influence metal behaviour and fate within waste matrices (Ledakowicz and Kaczorek, 2004). For example, Yao *et al.* (2014) found that leachate recirculation contributed to faster stabilisation of the landfill and reduced leachability of Cu and Zn from the landfill. He *et al.* 2007 have also shown that recirculating leachate, which is by the sequential reactors, in landfills in the early stage allowed methanogenesis to be reached much earlier and that this was accompanied by a reduction of total metals released from landfills. In contrast, Qu *et al.* (2008) demonstrated that the initial stage of leachate recirculation had low leachate pH (5-6) and highly VFA levels (acetate 4500-700 mg/L, propionate 1450-2950 mg/L and butyrate 4500-7200 mg/L) due to the acidification stage, in resulting the concentration of the metals was high at this stage. Bilgili *et al*. (2007) showed that the release of metals can significantly increase at the beginning of leachate recirculation as in the early stages of the waste degradation, pH of the leachate is low contributing to higher solubility of metals and dissolution into leachate (Fig 2.7).

As stated previously, due to the low concentrations of metals, the way to make it economically viable in recovering metals is to maximise metal concentrations. Recirculating leachates will accentuate the potential for increased metal mobility within and from the landfill when oxidised conditions are introduced. Leachates have been shown to have an increased capability to enhance metal mobility when oxidised (Mårtensson et al., 1999). It implies that leachate recirculation provides higher extractable metals in the initial leaching phase.

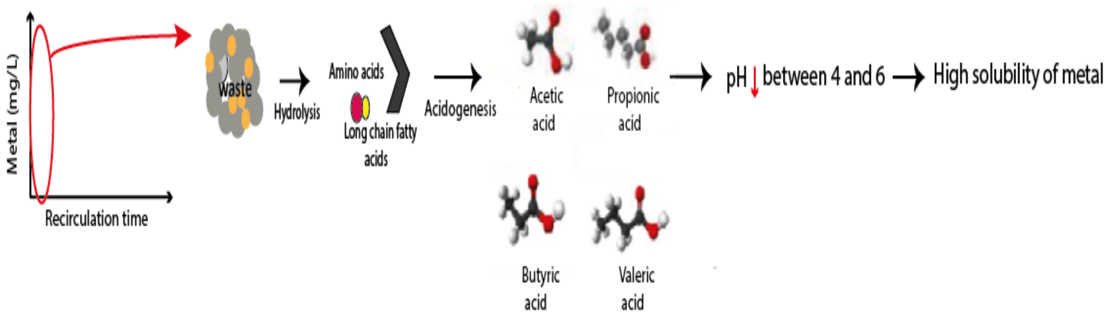


Figure 2.2.7. Leachate recirculation strategy for metal recovery

Therefore, regarding the critical challenges in metal recovery in leachate, this suggests that where leachate recirculation is applied with combining organic matter such as HA and pH could increase the economic feasibility.

2.5 Opportunities for metals recovery from landfill leachate

Leachate contains a wide range of metal such as Cu, Zn, Cr, Cd in addition to REEs (Kjeldsen et al., 2002). Therefore, leachate in landfill sites has a great potential for metal recovery. There are several ways for recovering metals from waste, such as recycling, physico-chemical, thermo-chemical, pyro-metallurgical, hydro-metallurgical, bio-metallurgical, landfill-mining methods (Wang et al., 2017). Due to the lack of economically and operationally feasible primary resources for the production of metals, many countries are forced to depend on recycling metals from secondary sources such as industrial residues and end-of-life products. Table 2.5 shows various methods to recover metals from waste streams and leachate, suggesting the possibility of recovery metals in landfill leachate. Despite published research works on recovering metals from leachate, studies are scanty in an application towards the recovery of metals from real landfill leachate in the site. The main problem to recover metals from leachate is further compounded for metals that exist at low concentrations (Table 2.2), which can be affected by many factors such as landfill age, type, and chemical and physical mechanism in landfill environments. The concentration mainly ranges from µg/L to mg/L, so to make the recovery of such commodities more meaningful, technologies should be developed to treat a large amount of leachate while efficiently concentrating the targeted metals. Also, the strong acidic condition can affect the environment; thus, it may later pose harmful risks to the environment if not managed well. The concentration of metals varies widely, and REEs has a very low concentration (1 or 2 µg/g waste), which is limiting the economic viability of the recovery. The minimum 1 mg/L of metal is needed to make metals recoverable from wastewater (Kjeldsen et al., 2002; Baun and Christensen, 2004; Wu et al., 2015). Relatively, high concentrations of over 1% are needed to approach the cost-effective recovery metals (Umeda et al., 2011). Therefore, process optimisation is important to maximise the concentration of metals or co-extraction of other added-value materials such as nitrogen and phosphorus, improving the process's cost-effectiveness and efficiency. By understanding the processes, including organic-metal interaction in leachate, recovering metal can achieve higher average productivity.

Barriers remain in recovering valuable materials present due to the unknown concentrations and distributions of metals in landfills and not meet the reasonable financial level. Metal recovery from leachate has not been investigated before, but prior studies have demonstrated that metals can be recovered from wastewater and aqueous solutions. However, the methods remain limited; for example, physicochemical methods are energy and capital intensive due to the costs of chemicals, oxidants, and membranes; the biological treatment process is limited by treatment effectiveness and energy requirement (Ahn et al., 2002; Kargi and Pamukoglu, 2003).

Table 2.5. Metal recovery from wastewater and liquid solution

Source	Method	Characteristics	Effects	Reference
Leachate from landfill waste	Bioelectrochemical systems (BES)	·BES employs biological and electrochemical reactions to recovery resources from a wide range of substrates.	·The electrical conductivity of leachate makes it favorable for electricity generation, and it contains a high concentration of ammonium nitrogen, which may be recovered for agricultural application. ·Metal also may be recovered by the modified microbial electrolysis cells.	Iskander et al., 2016
Sulfate leachate of cathode scrap of Li-ion batteries	Liquid-liquid extraction	1) The cathode scraps undergo heat treatment to completely liberate the cathodic materials from aluminum foil. 2) Solubilise Co, Li, Fe, Mn, Ni, and Al by leaching the cathodic materials in sulphuric acid in the presence of H_2O_2. 3) Oxidative precipitation of Mn from liquor with $KMnO_4$ and extraction of Al and Fe using D2EHPA. 4) Treat to recover the metals.	·Focuses on selective recovery of Co, Ni, and Li from the sulphate leachate of cathode scarp generated during the manufacture of Li ion batteries. ·High-purity Co in a solution can be recovered by solvent extraction using the sodium salt of PC-88A. ·The metals extraction efficiency and separation factor depend upon the extractant concentration and the equilibrium pH of the aqueous phase.	Nguyen et al., 2014
Solution and leachate derived from electronic scrap	Biogas	·Precipitates metals from solution using the off-gas ·Recovery Au, Pd, and Ag from leachate derived from electronic scarp; safe microbiologically	·Au was recovered from electronic scrap leachate with selectivity against Cu using biogas as they could partially separate Au from Cu.	Macaskie et al., 2007

			·In acidic conditions, Au and Cu are removed rapidly and separated from the liquor. ·The solid Pd and Ag will not easily be separated in water via biogas. ·Amines must be avoided for recovering metals using biogas.	
End of life electronic wastes	Hydrometallurgical process	·Ferric sulphate concentration range (at 1:10 and 1:5 Cu to sulphide molar ratio 1) filled up by using N2 gas for anaerobic conditions 2) add of 10 ml of $Na_2S·9H_2O$ solution	·Effect of Fe^{3+} on leaching of Cu and selective recovery of Cu from the polymetallic leachate. ·Lixiviant concentration and pH were the important parameters in $CuSO_4$ precipitation. ·The precipitation mostly occurs in the acidic pH range (0.5 to 1.5). ·$CuSO_4$ can be further pyro/hydrometallurgical processed to produce Cu metal.	Sethurajan and Hullebusch, 2019
Aqueous solutions	Biosorption	·The phosphorylation yeast cells were used in Cu adsorption experiments with 0.1 M HCl, which is strongly influenced by the pH of the solution. ·Recovering metals from aqueous solutions. The biosorption of metals is a complex process affected by the adsorbent, the types, and the concentrations of metals in the solution.	98% of the Cu ions adsorbed to phosphor cells could be recovered by treating the cells with HCl.	Ojima et al., 2019

Sulfuric acid leaching liquor of spent Li-ion batteries	Hydrometallurgical process	·Needs to refine the residues into a purer form such as salts, hydroxides and metals. 1) selective precipitation method by adding dimethylglyoxime (DMG, $C_4H_8N_2O_2$) reagent 2) extraction using cobalt loaded phosphoric acid (D2EHPA) 3) 4Separation and recovery of metal (Ni, Mn, Co, and Li) from sulfuric acid leaching liquor	High purities of Co and Li were recovered as $CoC_2O_4 \cdot 2H_2O$ and Li_2CO_3.	Chen et al., 2015
Acid mine leachate	Sequential precipitation	1) Sequential precipitation; add a sodium hydroxide solution of 5 M 2) Selective dissolution; pre-concentrates of the valuable elements were re-dissolved into solution 3) Oxalic acid precipitation; dissolving 8 g oxalic acid dehydrate in 50 ml deionised water using an ultrasonic batch 4) Na_2S precipitation; 1 M Na_2S REEs, Cu, Zn Ni and Co recovery from an acid mining leachate. The sample was collected from a coal preparation plant.	·95% of the Cu and Zn were recovered from the residual liquid using Na_2S at pH 2 and 3. ·The optimise the oxalic precipitation for the REE recovery is using a solution pH of 1.2	Zhang and Honaker, 2020
Sludge	Precipitation	·Add 3 mol dm^{-3} NaOH, ·The recovery process of heavy metals from polluted sludge leachate with biosurfactant elution by batch and column experiments.	The recovery efficiency of heavy metals (Pb, Ni, and Cr) reached over 90% by the precipitation method with pH 10.9.	Gao et al., 2012
Wastewater	Cementation	·Add Fe, Al, and Zn metallic powders into 250 mL of wastewater	·Cu, Au, and Pd can be recovered by using Fe and Al powder.	Umeda et al., 2011

		·Stir continuously with a magnetic stirrer	·Precious metals can be effectively recovered by combining processes (cementation, neutralisation and reduction)	
Wastewater	Photoelectrochemical cell	·A stock solution was prepared by dissolving the metal salts into deionised water ·The photoanode and the Pt strip cathode were connected with a commercial Cu wire ·The photoanode was irradiated with a UV lamp	·Heavy metals were recovered by mechanical scratching of the cathode surface.	Wang et al., 2017
Wastewater	Electrochemical reactor	·Prepare solutions using deionised water ·Determining the quality characteristic to be optimised. ·Identification of the noise factors and test conditions. ·Identification of the control parameters.	·The highest efficiencies were obtained for Pb and Cu recovery from diluted solution: 75.8 % and 89.9 %	Kaminari et al., 2007

Bioelectrochemical systems (BES) is an environmental strategy that employs biological and electrochemical reactions to generate electricity and recovery resources from a wide range of substances. Organic compounds in BES tends to produce electricity and other value-added compounds by oxidising microorganisms. However, a high concentration of metals in landfill leachate can be recovered through BES, and the reduction in leachate volumes can be achieved using osmotic processes integrated with BES. Also, hydrometallurgical processes have gained considerable attention as they show effectiveness in the extraction of metals (Gunarathne et al., 2020). Hydrometallurgical metal recovery is typically performed in three main stages: metal dissolution, concentration and purification, and metal recovery (Gupta,2006). Thus, further research should be studied to take a circular approach, recovering metals from landfill leachate using BES after enhancing metal concentration through leachate recirculation or hydrometallurgical processes using less toxic chemical solvents to be used as leaching agents and assist of acids and pH value.

2.6 Conclusion

The literature review on landfills has shown a metals recovery opportunities in landfill leachate using factors influencing metal mobility in landfill environments. Landfill leachate is a significant potential resource in landfill as it contains a large variety of dissolved extractable metals. Metal’s recovery opportunities may increase by several factors, influencing metal mobility in landfill environments as an excellent challenge for metal recovery from leachate is the low concentration of metals. Younger landfill leachate (>5 years old) has higher organic matter content due to the generation of dissolved and solubilised organic matter, consequently increasing metal release. Therefore, it implies that metal recovery may be effective in younger landfill leachate. Physio-chemical processes affect soluble metal concentration, which is critical to predicting metal recovery as they can govern the mobility of metals. More knowledge is required concerning the complexes in leachate in general and specifically on the importance of the organic matter in leachate, which led to an increase in the metal release rate. This article has also identified the gaps and has indicated that further efforts are required concerning leachate recirculation. It may ensure that maximising the concentration of metals from landfill leachate will be the economic feasible. Although mature technological advances provide opportunities for recovering metals from landfill leachate, significant challenges await us ahead as they can hardly be regarded as economical. Therefore, the chemistry mechanism of landfill environments should be well understood and fundamental and practical barriers of the recovering process in landfill leachate, which will lead us one step closer to resource recovery paradigm for a circular economy in closed landfill.

3 Influence of pH, depth and humic acid on metal and metalloids recovery from municipal solid waste landfills

The findings in this chapter showed the pH and humic acid effect on metal recovery from the landfill at three different depths. It has been published in Science of the Total Environment (see Appendix C)

3.1 Introduction

The growing resource use has, for many people, strengthened social foundations, incomes and welfare. However, it has also produced negative effects; the world faces resource shortages. To provide the necessary resources to meet demand (European Commission, 2010), the transition towards resource-efficiency is required. The global demand for metals has accelerated to an extent where it is widely considered a threat to economical and societal functioning (Watari et al., 2021). Therefore, waste management recently moves towards a Circular Economy by recycling pre-consumer manufacturing scrap/residues and End-of-Life products (European Commission, 2018a). Reduction and re-use are the most effective ways to save natural resources, and as the UK's recycling rate has increased from 44.5% in 2015 to 45.5% in 2020 (DEFRA, 2020), there has been a gradual decrease in the amount of waste sent to landfills. Nevertheless, the total amount of waste has been showing consistent growth (DEFRA, 2020). Therefore, turning waste into a resource is a crucial key to a circular economy. Landfills are still a major route for waste disposal throughout the world. It has been estimated there are around 500,000 landfill sites across Europe (EURELCO, 2016) and approximately 22,000 historic landfill sites in the UK, of which 90% were closed before 1996 (Wagland et al., 2019). Landfills contain substantial amounts of materials, including metals, thus being a new potential resource base that can become part of the Circular Economy (Wagland et al., 2019). Metal(loid)s are an irreplaceable component, used in various technological applications such as mobile devices, computers, vehicles and medical technologies. Therefore, sustainable supply of metals is essential. Ensuring supply from secondary raw materials, reducing reliance on raw material supply, is undoubtedly part of a resilient and circular economy. Enhanced landfill mining

(ELFM) is a potential approach to meeting expected global demand of metals by mining disposal of metals. Krook *et al.,* (2012) define landfill mining as “a process for extracting materials or other solid natural resources from waste materials that previously have been disposed of by burying them in the ground.” However, it is mainly to remediate the site, and its success and practice in materials recovery have been limited by economic infeasibility and the performance of technology, i.e., what quality levels (Kook et al., 2012; Wagner and Raymond, 2015). The concept of ELFM, which started to develop in 2008 (Jones et al., 2013; Canopoli et al., 2018), focuses on maximising the valorisation of waste as materials (WtM) and energy (WtE), which supports sustainable materials management by recovering and recycling of waste generated through the creating of the consumer product (Jones et al., 2013). However, there is uncertainty regarding the economic feasibility and environmental consequences of ELFM (Pastre et al., 2018).

In-situ landfill mining could enable the recovery of metals without excavation through the recovery of metals from landfill leachate (Kurniawan et al., 2021). Challenges remain in recovering metals to high efficiency and yield. A primary challenge for metal(loid)s recovery from leachate is the low concentration of many metals influenced by several factors such as landfill age, type and pH. The critical factors that affect the leachability of heavy metals are pH and chemical mechanisms such as precipitation, adsorption and ion-exchange and biological processes such as microbiomes which can dissolve metals (Dijkstra et al., 2004; Saveyn et al., 2014; Gutiérrez-Gutiérrez et al., 2015; Gu et al., 2018; Roy et al., 2021). The sorption characteristics of metals in landfills are important with recovering metals from landfills, and the presence of organic matter influences this sorption process (Spark et al., 1997; Sapsford et al., 2017). Natural organic matter in landfills originates from food, wood, paper, yard trimmings. Natural organic matters in landfills are converted to humic substances (HS) via humification (Mallick, 2017). Organic matter is biodegradable in the leachate at the early stage of landfills and becomes non-biodegradable at the late stage of landfills such as HA. Thus, HS are the main organic compounds in landfill leachate, and HA represents the most active HS fraction (Zhou et al., 2015). It is widely recognised that humic acid [HA] affects metal speciation behaviour (Qu et al., 2019), solubilisation and adsorption of hydrophobic pollutants, mineral growth and dissolution, redox behaviour in soil (Scott et al., 1998; Liu et al., 2018; Qu et al., 2019). Therefore, knowledge about HA’s roles and interactions with pH is essential for recovering metals from landfill environments. Several studies have investigated the characterisation of HA in landfill leachate and distribution of heavy metals with HA (Bozkurt et al., 1999; Boru˚vka and Dra´bek, 2004; Klavinsa et al., 2006; Gutiérrez-Gutiérrez et al., 2015). However, the information about HA’s interaction, heavy metals, and pH in landfill environments are still insufficient. Thus, this study aims to investigate the leaching characteristics of major metals in landfill environments under the influence of pH changes using the batch leaching technique. The recovery should target valuable metal(loid)s that have relatively higher concentrations in landfill environments or be extensively used in our life or listed as critical raw materials. In this work, 12 metal(loid)s including Lithium and Cobalt, which are critical raw materials and strategically important for the European economy but have a high risk associated with their supply (Blengini et al., 2020), were selected to investigate the metal release performance and correlation of HA with metals from the MSW in different pH and depth. Visual MINTEQ software was used to explain pH-dependent leaching characteristics of metals and predict HA effects on metal mobility.

3.2 Materials and methods

3.2.1 Sample collection and preparation

A total of thirty drilled municipal solid waste (MSW) core samples were collected from four MSW landfills located in the UK at depths between 3 and 55 m. Different cores were drilled vertically across the landfill area, and samples were taken by a specialised private company hired by the landfill sites operator (Table 3.1). The samples were grouped according to the depth of the buried MSW as follow: 3-9 m (2 waste samples), 23-30.5 m (3 waste samples) and 48-55 m (3 waste samples). Each sample weight was measured, and Table 3.1 shows the average and standard deviation to show how to spread out the values are in the samples. pH analysis was made in duplicates. The samples were stored in a cold room at

4°C until analysis. The samples sorted manually into metal, paper, textile, wood, glass and other materials, and weighed.

Table 3.1. Waste composition of the samples collected from the studied landfill site (Canapoli et al., 2020)

	Total number of samples	**Depth (m)**	**Years**	**pH**	**Waste sample (g)**	**Paper/ cardboard (g)**	**Metals (g)**	**Glass/ ceramic (g)**	**Textile (g)**	**Wood (g)**	**Soil/fine fraction (g)**	**Other (g)**
	2	3-9	<10		11561	2493	356	69	1463	1776	3647	1757
Average				7.43	5781	1247	178	35	732	888	1824	879
SD				0.03	2148	1511	215	49	895	505	2013	241
	3	23-30.5	>10		12762	1405	768	21	569	1092	6490	2417
Average				7.58	4254	468	256	7	190	364	2163	806
SD				0.02	1338	366	373	8	329	283	1628	571
	3	48-55	>10		12892	1148	245	151	331	1321	5147	4549
Average				7.64	4297	383	82	50	110	440	1716	1516
SD				0.03	2264	491	93	35	98	294	1426	971

3.2.2 Leaching tests

The batch leaching tests were carried out following BS EN 12457:2002. Briefly, 50 g of raw material composite waste sample was mixed with 500 ml deionised waste to evaluate the level of metals released from the waste in a wide range of pH values in the controlled site. Before the leaching test, the samples were ground to a size of <1.5mm using a Retsch SM 2000 grinder. The analysis was carried out for six pH values; 2, 4, 6, 7, 8, 10. The pH was adjusted using 1.8 M nitric acid solution or 1 M sodium hydroxide solution. All leaching tests were made in duplicates. The tests were conducted in a 1500 mL cylindrical jars with ribbed cap. The experiments were performed with liquid-to-solid ratio 10:1, which represents typical field conditions (Bestgen et al., 2016) (L/S, where L is deionised water, and S is solid waste, mL g). The jars were manually agitated for 3 repetitions of 5 minutes with 10-minute intervals between repetitions. The mixture was then allowed to settle for 30 minutes and then was pressure filtered through clean 0.45-µm pore size filtration membranes and then collection of the leachate. The leachate was collected in polyethene bottles and stored in a cold room at 4°C until metal analysis and performed analysis within three weeks.

3.2.3 Humic acid analysis

A stock solution of HA was prepared by dissolving 1 g of HA in 1 L of deionised water for investigating the impact of the presence of HA in leachate on the leachability of metals. HA content was determined by ultraviolet light absorbance at 254 nm. The values were converted using a calibration curve. For that purpose, serial dilutions of the concentrated HA stock solution were prepared: 1, 2, 5, 7, 10, 15, 20, 50, 100 mg. Samples for UV_{254} were filtered through 0.45 µm membrane filter. UV_{254} was measured through a 1 cm quartz cell. The test was conducted in duplicate.

Table 3.2. Common properties of HA (Adapted from Chamoil, 2013, Sillanpää, 2015)

Elemental composition (% by weight)	HA	Functional group distribution (% of oxygen is indicated in functional groups)	HA
Carbon	50-60	Carboxyl (-COOH)	14-45
Hydrogen	4-6	Phenol (-Ph)	10-38
Oxygen	30-35	Alcohol (-R-OH)	13-15
Nitrogen	2-4	Carbonyl (-C=O_	4-23
Sulphur	1-2	Methoxyl (-O-CH_3)	1-5
Solubility in strong acid	Not soluble		

3.2.4 Metal analysis

The metals content was analysed by inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX) after microwave-assisted acid digestion following the extraction procedure used in previous studies (Gutiérrez-Gutiérrez et al., 2015; Cipullo et al., 2018; Wagland et al., 2019). Briefly, Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg were determined by pre-digesting 30 mL leachate with 1.5 mL concentrated trace metal grade nitric acid for leachate samples. For solid samples, 0.5 g of samples was mixed with 6 ml of HCl and 2 ml nitric acid in Teflon tubes and left overnight. The vessels for leachate samples were placed in the Mars Xpress microwave (CEM system, EPA 3015-8). Then, the vessels were cooled, and the solution was filtered through Whatman No. 2 paper and made up to 50 ml with deionised water. As for the solid samples, they were placed in a microwave digester (Multiwave 3000, Anton paar) for 45 minutes at 800 W, and then the solution was filtered through Whatman No. 2 paper, and the liquid diluted to 100 ml. A blank digest was carried out in the same way. The microwave is an efficient and fast digestion technique method. Calibration standards were spiked with several certified standard solutions. The concentration ranges were 0.05, 0.1, 0.15 and 0.2 mg/L/ for the elements.

3.2.5 Geochemical modelling

Visual MINTEQ ver. 3.1 software program was used to estimate the chemical species and the equilibrium mass distribution of dissolved metals in leachate according to different pH and HA value. Data inputs included pH, alkalinity, temperature, and dissolved organic carbon (DOC). A temperature of 25 °C was used for all the model calculations. A sensitivity analysis of the model was performed. The sensitivity analysis is based on the elementary effect method (Morris, 1991). The sensitivity analysis was undertaken to identify the organic matter important in controlling metal speciation. The sensitivity analysis was run individually on each data set by compiling the data form, responding to changes in the fraction of active SOM by independently varying SOM in the range 10-100%. The range was used in a sensitivity analysis for organic matter, while keeping other constituent constant. The Stockholm Humic Model was selected to evaluate metal(loid)s binding to humic acid due to its known success in describing metal and DOC complexation (Baker, 2012). Typically, fulvic acid (FA) is more abundant than humic acid (HA). However, to better understand the effects of humic acid has on metal(loid)s leaching, of the active the total solid organic matter (SOM), humic acid set as 90 % and fulvic acid formed as 10%. The input values used included total concentrations of metals Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg and ionic strength was also considered.

3.2.5.1 Modelling process

Modelling has been used in various leaching operations to understand the process and subsequently help in decision making (Ramasami et al., 2019). The first step on modelling is to answer the question: Why is modelling required for the model study? What are the resources available for the modelling? Then set up the model into a specific model that can be run in the selected model to be able to reach the aim. In order to determine whether the release of metal is solubility controlled or sorption controlled, modelling was carried out on all samples subjected to pH-dependent test (Gustafson, 2014). The equilibrium speciation model was based on precipitation/dissolution/complexation equilibrium reactions. The parameters needed for model inputting included the concentrations were obtained after the best test for the pH-dependence experiment. The major components and metal-binding ligands such as PO_4^{3-} and SO_4^{2-} were based on the determined values for the over 10 years old landfill leachate. The log K values of the aqueous species refer to the default values in Visual MINTEQ. This model was set to simulate and predict metal leaching behaviour from landfill leachate.

3.2.6 Statistical analyses

Multivariate analysis was performed using SPSS 26 software to identify statistically significant variance between the dependent variable tested and effect on the metal(loid)s leachability. A multivariable study was conducted considering the correlation matrixes. In these matrices, each individual square contains the ordinal coefficient of Spearman which varies between 1 and -1 and the significance level of estimated correlation for each pair of variables (Bisquerra. 1989). Significance level was set at 0.05.

3.3 Results and discussion

3.3.1 Influence of depth

The concentration of metal(loid)s in the waste samples (according to depth) are provided in Table 3.3. Among all metal(loid)s, Hg had the lowest concentration, and Al was the highest. Intense source reduction efforts have been implemented to reduce the Hg content in municipal waste landfills, resulting in Hg is not expected as a high concentration in MSW (Cheng and Hu, 2011). The concentrations of metal(loid)s tend to have a higher concentration at 3-9 m than other depths, indicating greater depth may reduce hydraulic permeability and increase waste densities. This is likely due to higher proportions of non-degraded organic materials distributed variably in the surface waste layers; higher organic carbon may increase soluble metals while organic matter bound to soil particles may enhance the retention of metals (Frank et al., 2017). The concentration of Mn and Cd at 3-9 m was remarkably higher than other metals; the composition and distribution of the sample may cause it.

Table 3.3. The concentration of metal(loid)s in the MSW according to depth

	Li (mg/kg)	Al (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Co (mg/kg)	Ni (mg/kg)
3-9 m	34	22,200	78	4,620	19.2	104
23-30.5 m	22	21,300	52	980	10.2	90
48-55 m	28	26,500	76	800	15	68
	Cu (mg/kg)	Zn (mg/kg)	As (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Hg (mg/kg)
3-9 m	1,062	2,950	40	5,410	5,036	8.8
23-30.5 m	1,256	750	8	1.56	3,534	4.2
48-55 m	320	594	20	1.66	506	3

Therefore, metal(loid)s in the surface layer from the old MSW landfill have a higher concentration because degradation occurs slower than at deeper depths. This finding is in agreement with the findings of Reinhart et al. (2002), suggesting lower layers undergo limited waste stabilisation. Previous studies also found the composition of organic fine materials to increase with depth (Mor et al., 2006; Quaghebeur et al., 2013; Lozano-García et al., 2016). It consequently increases the complexation of metal(loid)s in organic waste residuals, and therefore metals are firmly bound to the compost matrix and organic matter, limiting their solubility with increasing depth (Smith, 2009). The composition of waste each landfill received, distribution of the waste, and landfill area background can influence the accumulation of certain metals and its content. There were observed significant negative correlations between depth and Li, Pb, Hg ($p < 0.05$), As and Cd concentration ($p < 0.01$). This is likely influenced by the metal content of the waste dispose and the binding of these metals within the landfill depths. The mobility of metals within solid waste are influenced by metals' complexation and by adsorption onto molecules of the waste (Adelopo et al., 2018). The concentration of Zn, Pb and Cu at 48-55 m was relatively lower than at 3-9 m and 23-30.5 m, implying Zn, Pb and Cu released in the upper layers may be immobilised by holding the metals through enhancing the formation of metal complexes in MSW that is over 10 years. It may indicate that Zn, Pb and Cu form strong complexes within stabilised organics. The strong metal sorption properties of compost produced from MSW have less opportunity for recovering metal in deeper depth landfill environments. The results demonstrate that waste composition influenced the composition of metals that can be recovered within a different layer of waste and aged. The amount of metals recovered in the surface layer of the landfill may be potentially increased, as shown in Table 3.4.

Table 3.4. Percentage change of metals at different depths relative to 3-9 m

	Li	Al	Cr	Mn	Co	Ni
Change of 23-30.5 m	53.61	4.23	49.03	373.04	50.33	14.34
Change of 48-55 m	20.92	-16.23	2.67	472.73	1.78	51.71
Average	37.26	-6.00	25.85	422.88	26.06	33.02
Variance	267.17	104.57	537.44	2484.51	589.21	349.11
	Cu	Zn	As	Cd	Pb	Hg
Change of 23-30.5 m	-15.52	293.33	365.65	348178.97	42.56	106.30
Change of 48-55 m	232.81	397.19	111.07	325146.49	894.08	199.77
Average	108.65	345.26	238.36	336662.73	468.31	153.04
Variance	15416.71	2696.60	16202.26	132623748.9	18127.6	2184.25

However, depth was not found to influence significantly the concentration of metal(loid)s recovered. This finding is consistent with the previous study of Gutiérrez-Gutiérrez *et al*. (2015) who reported that there is no clear pattern between metal concentrations and the depth of the waste. As waste would undergo different stages of degradation over various landfill ages, and composition, it is not appropriate to compare heavy metal contents sampled at different depths. Through waste materials disposed of in the landfill are the primary sources of metals in the landfill environment and leachate. Thus, further research is required to identify the factors controlling metals distribution, oxygen, which affects the redox at the site and the effect of waste composition on metals content for increasing economic viability in recovering metal.

3.3.2 Influence of pH

It is well known that pH plays a key role on the behaviour and speciation of metal(loid)s (Riba et al., 2004). Extracting metals from landfills and their leachate can hardly be regarded as environmentally friendly and operational cost-effective; therefore, it is crucial to recovering certain high value and amount metals. Thus, we need to find a pH value or range that maximises recovery of a wide range of metal(loid)s, especially those of high added value or demand such as Li and Co. (Tang and Steenari, 2016). Therefore, the release of metal(loid)s was examined in a broader pH range between pH 2 and 10 (Fig. 3.1). It was noted that the release of metal(loid)s was found to be higher in the lower pH range, especially at pH 2 (Fig. 3.1). According to the values of Pearson correlation coefficient, Mn, Co, Ni and Zn show a strong negative correlation ($p< 0.01$) with pH. The leaching amounts of metals tended to decrease from roughly 99% to 32% with increasing alkalinity of the leaching solution, although some metal elements were increased at alkaline conditions. The decrease of metal leaching amount in alkaline conditions may be caused by precipitation or sorption processes (Dijkstra et al., 2006). The effect of pH on metal leachability also differs among different metal(loid) species. However, the maximum amounts are released at pH 2 for all metals. Table 3.5 shows the recovery rates for the metals from the concentration of the initial metals found in the waste solid.

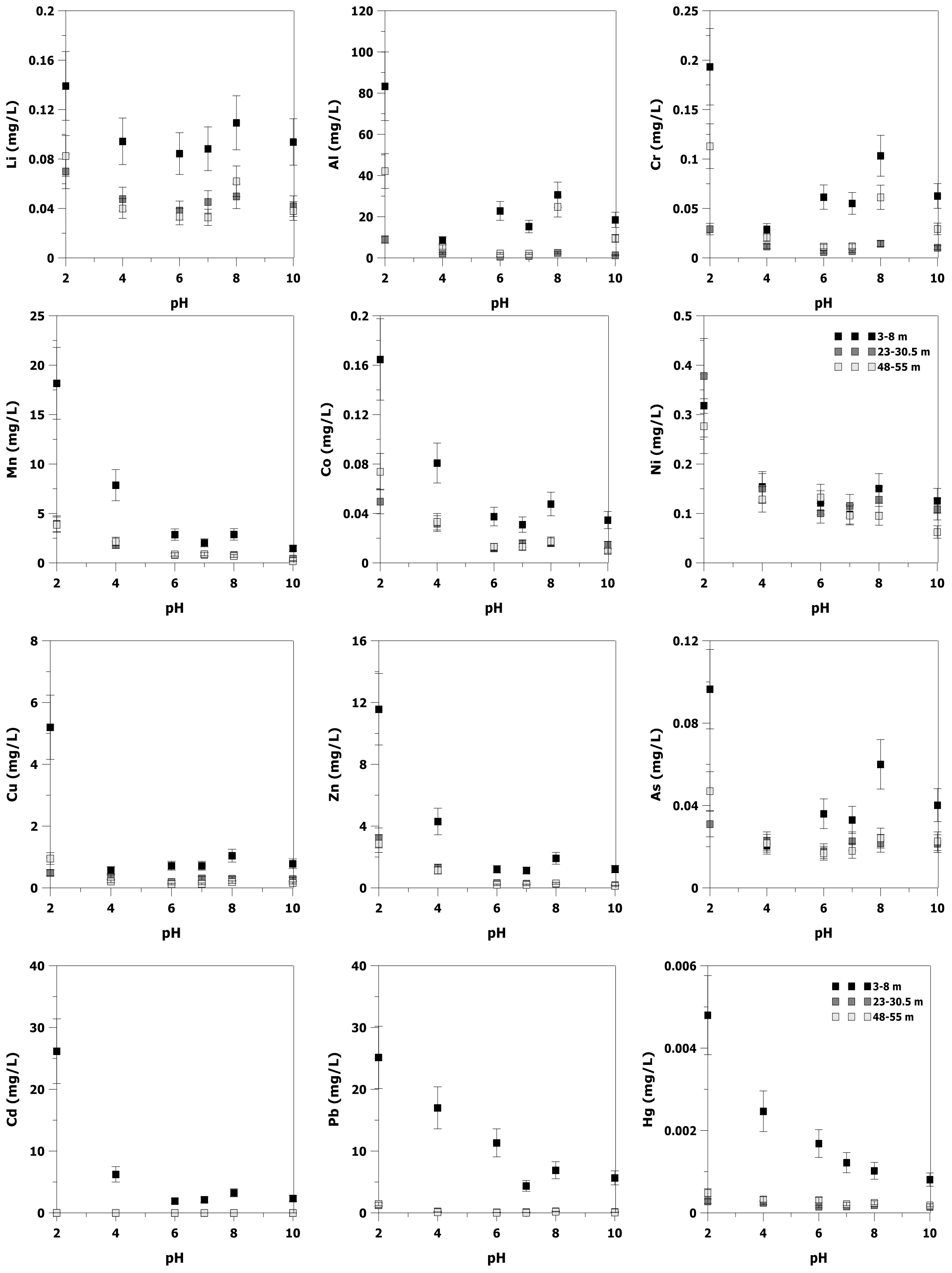


Figure 3.1. The leached concentration values of 12 metals in MSW landfills, following the depths (3-9, 23-30.5, 48-55 m) and pH values (2, 4, 6, 7, 8, 10)

The limited release was increased in at pH 8, except for Hg. At high pH of 8-10, solubility of metal(loid)s can increase to a certain extent since metals can form stable and soluble complexes with hydroxyl and dissolved organic carbon or are released from the dissolution of sulphide minerals (Ho et al., 2012). The concentration of heavy metal tends to increase again in alkaline condition, which is related to the formation of soluble metal hydroxides (Fig. 3.1) (van der Sloot et al., 2003; Cappuyns and Swennen, 2008; Krol et al., 2020).

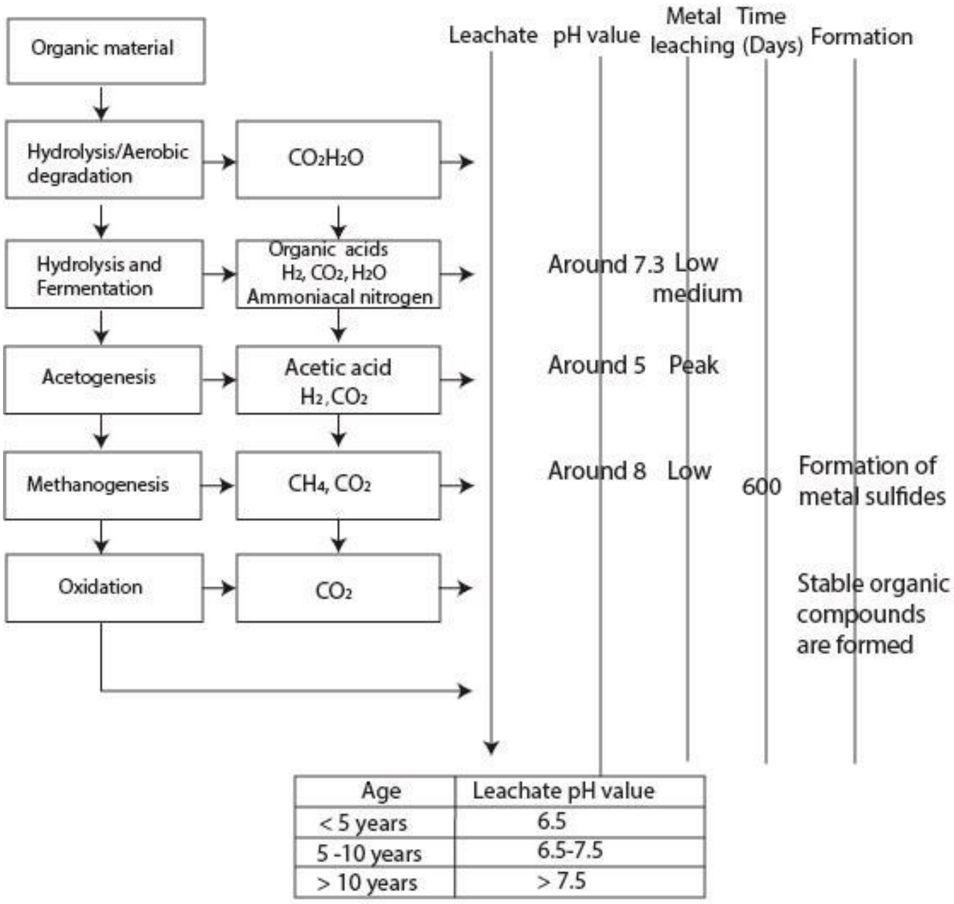
Table 3.5. Recovery rates of metals at pH 2 and at different depths (3-9,23-30.5, 48-55 m)

	Co (%)	Cd (%)	Zn (%)	Mn (%)	Ni (%)	Li (%)
3-9 m	89.91	96.74	78.42	78.64	61.41	83.5
23-30.5 m	98.03	91.42	86.22	81.23	83.46	64.52
48-55 m	98.66	89.98	96.63	95.87	80.98	59.86
Average	95.53	92.71	87.09	85.25	75.28	69.29
Variance	15.87	8.44	55.65	57.52	97.18	104.58
	As (%)	Cu (%)	Pb (%)	Al (%)	Cr (%)	Hg (%)
3-9 m	47.46	97.96	99.93	75.07	50.22	10.99
23-30.5 m	70.99	7.77	7.20	8.37	11.29	1.33
48-55 m	48.79	59.67	57.11	31.82	30.13	3.34
Average	55.75	55.13	54.75	38.42	30.55	5.22
Variance	116.51	1365.9	1436.1	763.32	252.63	17.33

The results are inconsistent with Krol *et al.* (2020), who reported a significant decrease in the concentration of Ni and Cr at pH 8 and Cu at pH 9. The results showed that As and Cr release was low at neutral or slightly acidic pH. However, they showed the highest leachability at pH 2; it caused by the dissolution of iron oxides that are the main components that bind to them in soils (Krysiak and Karczewska, 2007, Gersztyn et al., 2013). They notably showed the second-highest concentration at pH 8, which may be attributed to the mechanism of pH-related anion desorption, replacement of oxy-anion forming elements and their bound in the sorption complexes by hydroxide ions. The most important mechanism of As and Cr, which are oxyanion forming elements, is to be due to the dissolution of the organic components, including HA (Gersztyn et al., 2013). The characteristics of Cu solubility is in alignment with the findings of Cappuyns and Swennen (2008), who reported Cu is characterised by a lower solubility in the pH-range 2-6. The release of Al followed an amphoteric leaching pattern (Fig. 1), which is similar to results reported in previous studies (Zhang et al., 2016; Cui et al., 2019). The minimum leaching concentration occurred at pH 7. Cd release amounts decrease as the pH increases at acid condition, but the reduced amounts are not so much above pH 6. It may be due to the precipitation of the metal sulphide phase, resulting in Cd being pyritised (Morse and Luther, 1999). The release amount of Ni was lower at pH 7 for 3-9 m, pH 6 for 23-30.5 m and pH 10 for 48-55 m. The characteristics of Mn and Zn solubility follow the cationic pattern in which the concentration of metal element steadily decrease with pH. Chromium recovery trend was identical to that of As and Al (Fig. 1). Zn recovery was similar to that of Mn and Cd, which can be observed in Krol *et al.* (2020). Cu showed that similarity tendency with Pb. Pb are maximum 41 to 50 times more released at the pH 2 compared the leaching amount in the range of pH.

Overall, metal cations are most mobile in acidic conditions as shown in Figure 2. In contrast, anion release increase towards high pH. These results are consistent with the previous study of van der Sloot *et al.,* (2003). However, the release of metals does not always show a similar trend as the leachability of metals can change depending on the type and composition of the tested sample. In the case of Cu and Pb, the leachability curve typically makes V or U shaped (van der Sloot et al., 2003; Cappuyns and Swennen, 2008; Sloot et al., 2010). However, this study Pb does not show a clear upward trend between pH 8 to 10. But it still showed that Pb solubility increase at high pH of 8-10. Al, As and Cr presents a V-shape, similar to results reported in the previous studies (Rubions et al., 2011; Cui et al., 2019). The most pH-dependent metal was Mn in this study. Metals from landfill leachate are typically present in low concentrations; therefore, more effective and selective recovery methods under acidic conditions need to be determined for efficient recovering metal from landfill environments. In this study, the leaching of metal(loid)s from MSW at pH 2 and 4 gave the most efficient metal release and showed high concentration at pH 8.

Metal(loid)s leachability is highest when hydrolysis, fermentation and acetogenic bacteria dominate, due to an accumulation of VFA, and a pH decrease (Fig. 3.2). Previous studies showed that significant heavy metal leaching occurs during the initial stage of the landfill and pH values have a direct influence on metal mobility (Yao et al., 2014; Yao et al., 2017).



Age	Leachate pH value
< 5 years	6.5
5 -10 years	6.5-7.5
> 10 years	> 7.5

Figure 3.2. Metal leaching process in a landfill and leachate pH value (Adapted from Zainol et al., 2012, Adhikari et al., 2014)

However, depending on metal(loid)s, the characterisation of pH may differ, such as Cu having the amphoteric character, thus forming soluble anionic species, and strong acidic conditions can cause environmental problems due to most organisms cannot tolerate the conditions (Breeze, 2018; Król, et al., 2020). For this reason, a suitable pH value for each metal must be determined to fit the entire metal(loid)s recovery process by adjusting the pH value to the desired range and understand the character of metals with pH value. Further research should also develop alternative methods for recovering metals such as biodegradable extraction agents using organic acids (e.g. humic or acetic acid) to reduce reliance on strong acid.

3.3.3 Humic acid in the landfill

HA has a high sorption capacity, which makes them capable of holding metals. Therefore, metals may be retained and are not leached out easily. HA leaching tends to increase with the increase of depth (Fig 3.3). As depth is increased, the humification process increases. HA is weakly acidic with carboxylic-and phenolic-OH groups (Prado et al., 2011).

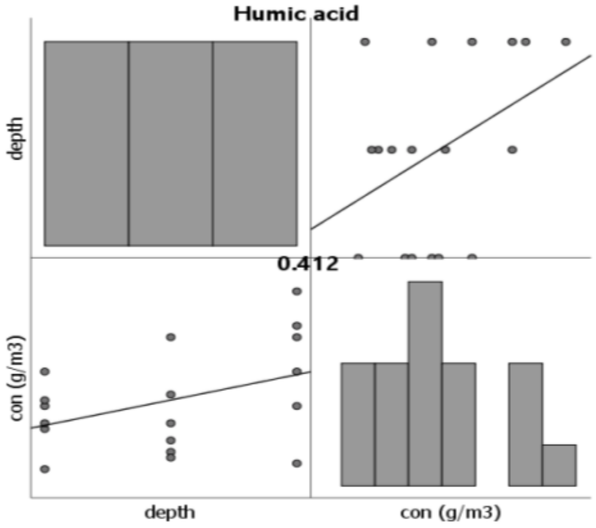


Figure 3.3. The leached concentration values of humic acid in MSW landfills, according to depths

The correlation between pH, metals, and HA is shown in Figure 3.4 (Details in appendix Figure B.1) Four metals among 12 metal(loid)s are illustrated in Figure 3.4. Li and Co are shown as they are critical raw materials and Al has been shown as there are concerns justifying focused recovery due to high content in the landfill. There was a strong positive relationship between pH and HA, i.e., HA leaching increases in higher pH value. Adsorption of organics on the surfaces would therefore be affected by pH. The amount of HA increased by 2% to 4% at pH 10 compared at pH 2 and increased by 0.4% to 4% as depth increased. The results may indicate that HA is not soluble at acidic conditions and become most soluble from pH 6. It may be due to carboxyl groups on HA be ionised in alkali condition. The ionisation would lead to a negative charge on HA molecules. Thus, HA is more leachable in alkali conditions due to lowered adsorption. This finding is in agreement with Sehaqui et al. (2015), who found that HA adsorption gradually increases with decreasing the pH. HA is known to bind metals to their hydroxyl and carboxyl groups, and either mobilise metals or delay their release (Leung and Kimaro, 1997; Bozkurt et al., 1999; Kochany and Smith, 2001; Klavinsa et al., 2006; Gutiérrez-Gutiérrez et al., 2015). Strong negative correlations were found between HA and Co, Ni, Zn ($p < 0.01$) and Mn ($p < 0.05$).

The Visual MINTEQ has been adopted to describe metals speciation in the leachate (Table 3.6). As significant numbers of closed landfills exist in the UK and across Europe, the model input used the batch test results at depth 48-55 m, which would be similar to the closed landfills parameters. The Stockholm Humic Model (SHM) was used to assess metal binding to HA. The results show that Li does not much affect by pH. However, all the metals show that high leachability at pH 2.

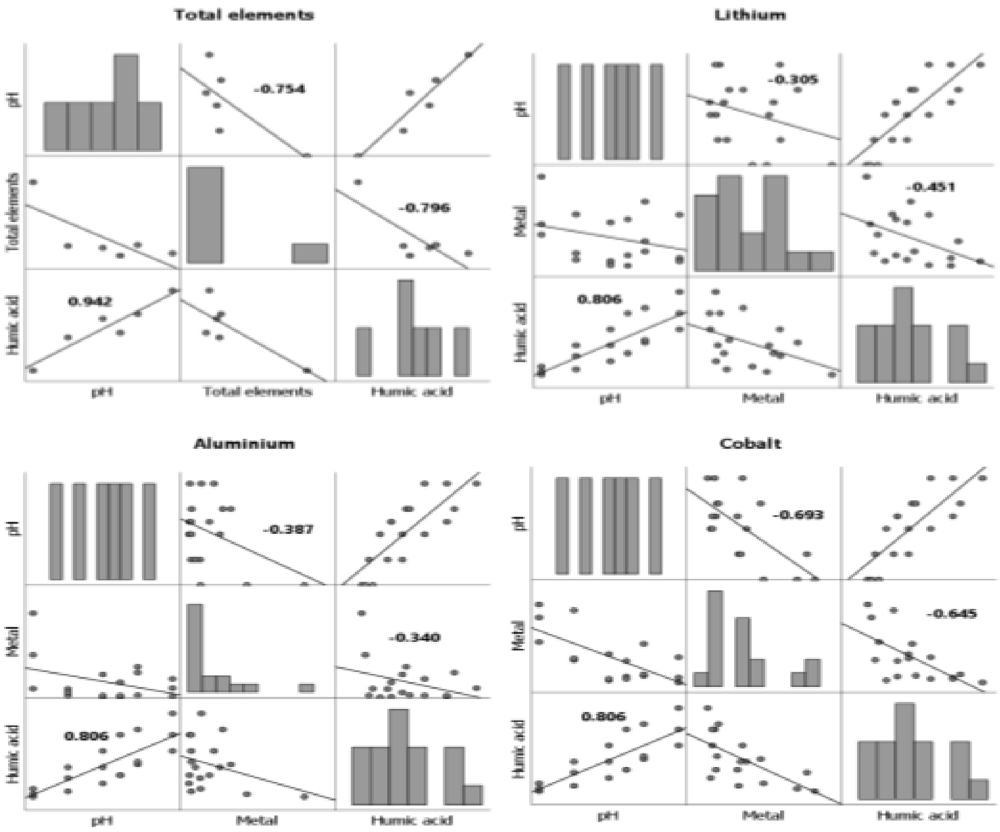


Figure 3.4. Draftsman’s plot resenting the relationship between waste depth (m), pH, metal (mg/L) and HA (mg/L)

The geochemical analyses also showed that HA accelerated metals leaching. This finding is in good agreement with the previous study of Usharani and Vasudevan (2016), where an increase in HA concentration increases the heavy metal leaching from sewage sludge. Cu, Pb, Ni, and Zn were all significantly affected by the presence of HA as their leachability increase roughly 6-17 %, especially at below pH 6 (Fig. 3.5).

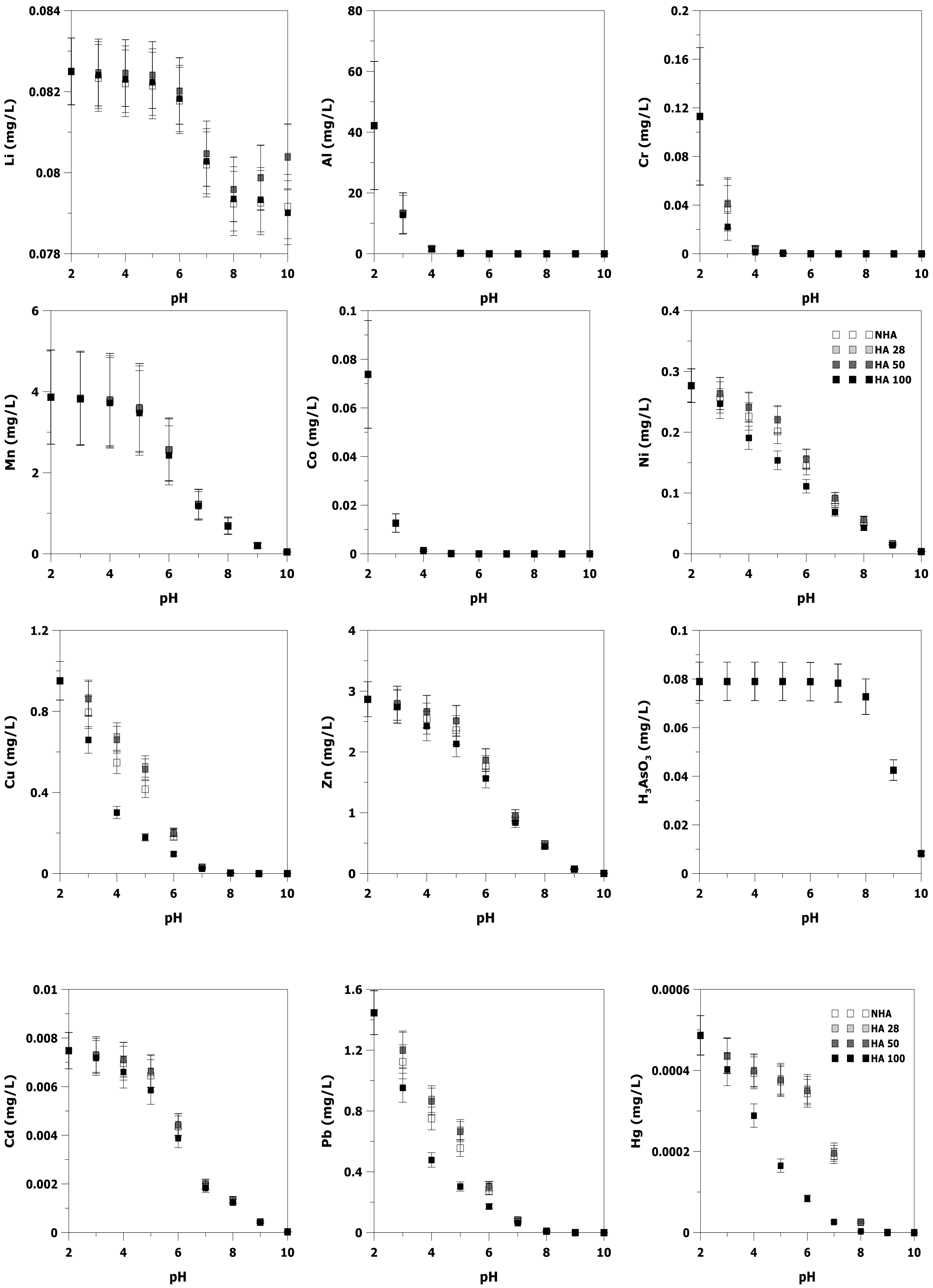


Figure 3.5. The leached concentration values of 12 metals at different humic acid concentration (0, 28, 50 and 100 mg/L)

Results expressed that a high concentration of HA can leach out metals but can be in lesser concentration depending on the metal, indicating that the visual MINTEQ model could predict free ion/labile species efficiently under different environments, such as the acidic environment. With an increase of HA concentration, the improvement of metal leaching rate is not apparent, which may be due to excessive HA can chelate with metal ions and reduce metals release (1).

$$(1)\ ROH + Cd^{2+} \longleftrightarrow ROCd^{+} + H^{+}$$

Metal ions can effectively chelate heavy metals, thus delay their release; in aerobic conditions, the HS lose their binding properties. In addition to chelating metals, HA is applied in the bioremediation of environmental contaminants as a redox mediator (Maurer et al., 2012; Liu et al., 2018). HA is redox-active for enhancing microbial reduction of nitrate, implying their great potential for acting as a redox mediator in enhancing multiple microbial reductions, resulting in affecting various biogeochemical processes (i.e., iron cycle, nitrogen cycle, etc.) as well as *in situ* remediations in an anaerobic environment (Zhang et al., 2018). The leaching efficiency of HA shows that be comparatively higher at pH 4 to 6. Most metals can be found at the beginning of the humic phase (Bozkurt et al., 1999; Gutiérrez-Gutiérrez et al., 2015). Therefore, Fig. 3.3 showed the sharp contrast which metal(loid)s release in acidic conditions and HA release in alkaline conditions. Chelate compounds “hold” metal and, in consequence, it can be immobilised metals in landfills. This is probably due to the distinctive ring structure of chelate compounds, in which metal ion is surrounded by a molecule like, for example, humic compounds (Zhou et al., 2015). Computer modelling revealed that the HA could strongly bind metals. Also, it showed that higher pH is more effective HA binding with metals and metals are more soluble at lower pH. These are caused by the fact that at lower pH values, less acidic functional groups on the DOM molecules were Deprotonated and available for metal binding (Stevenson, 1994). However, Li, Co, and As do not much affect by organic matter. Even the HA dominated DOC fractions in leachate, the leaching potentials for FA-metals complexes leaching out were relatively high. The solubility and complexation ability of HA is related to their interactions with metal(loid)s and other environmental conditions. This interaction leads to the formation of metal complexes and chelates, which influence leaching amounts of metal(loid)s, and the main factor influencing the interactions of HA with metals is pH value. According to the modelling results especially, Cu and Pb were bound very strongly in metal ion-humic complexes. In the acid to neutral pH range, HA is a vital biding constituent for metal(loid)s.

Table 3.6. Recovery of selected metal(loid)s species in the leachate sample at 48-55m depth by visual MINTEQ (content: %)

Li		Al		Cr		Mn	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content
Li^{+1}	96.05	$Al(OH)_2^+$	0.13	$Cr(OH)_2^{+1}$	3.12	Mn^{+2}	20.37
LiF (aq)	0.05	$Al(OH)_3$ (aq)	2.45	$CrOH^{+2}$	0.18	$MnOH^+$	0.02
LiCl (aq)	0.46	$Al(OH)_{4-}$	95.93	$Cr(OH)_3$ (aq)	68.22	MnF^+	0.11
$LiSO_{4-}$	0.062	AlF_{2+}	0.28	$Cr(OH)_4^-$	0.02	$MnCl^+$	0.09
$LiHPO_{4-}$	3.38	AlF_3 (aq)	0.83	$/HA_3Cr_2(OH)_2^+(s)$	4.92	$MnSO_4$ (aq)	0.22
		AlF_{4-}	0.17	$/FA_2Cr^+(aq)$	0.07	$MnNH_3^{+2}$	0.01
		$AlHPO_{4+}$	0.07	$/FA_3Cr_2(OH)_2^+(aq)$	23.46	$MnHPO_4$ (aq)	52.97
		$Al_2(OH)_2CO_3^{+2}$	0.08			$MnHCO_3^+$	3.75
		$/FA_2AlOH(aq)$	0.04			$MnCO_3$ (aq)	21.86
						$/HAMn^+(s)$	0.03
						$/FAMn^+(aq)$	0.58
Co		Ni		Cu		Zn	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content
$CoOH^{+2}$	87.89	Ni^{+2}	22.51	Cu^{+2}	0.50	Zn^{+2}	19.98
$Co(NH_3)5Cl^{+2}$	12.11	$NiOH^+$	0.09	$CuOH^+$	0.51	$ZnOH^+$	0.64
		NiF^+	0.07	$Cu(OH)_2$ (aq)	0.05	$Zn(OH)_2$ (aq)	0.40
		$NiCl^+$	0.04	$Cu(NH3)_2^{+2}$	0.08	ZnF^+	0.07
		$NiSO_4$ (aq)	0.27	$CuNH_3^{+2}$	0.41	$ZnCl^+$	0.26
		$NiNH_{3+}^2$	0.92	$CuHPO_4$ (aq)	6.57	$ZnSO_4$ (aq)	0.26
		$Ni(NH_3)_2^{+2}$	0.01	$CuCO_3$ (aq)	63.61	$ZnNH_3^{+2}$	0.25
		$NiH_2PO_4^+$	0.06	$CuHCO_3^+$	0.29	$ZnHPO_4$ (aq)	40.32
		$NiHPO_4$ (aq)	19.83	$Cu(CO_3)_2^{-2}$	23.20	$ZnCO_3$ (aq)	24.62
		$NiCO_3$ (aq)	17.91	$/HA_2Cu(s)$	0.02	$ZnHCO_3^+$	5.84
		$NiHCO_3^+$	25.63	$/HACu^+(s)$	0.09	$Zn(CO_3)_2^{-2}$	1.16
		/HANi+(s)	0.56	$/HA_2CuOH^-(s)$	0.03	$/HAZn^+(s)$	0.15
		/FANi+(aq)	12.10	$/FA_2Cu(aq)$	1.15	$/FAZn^+(aq)$	6.04
				$/FACu^+(aq)$	0.82	$/FA_2Zn(aq)$	0.03
				$/FA_2CuOH(aq)$	2.63		
As		Cd		Pb		Hg	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content

H_3AsO_3	94.84	Cd^{+2}	13.40	Pb^{+2}	0.88	$Hg(OH)_2$	2.83
$H2AsO_{3-}$	5.16	$CdOH^+$	0.03	$PbOH^+$	0.71	$HgCl_2$ (aq)	8.70
		CdF^+	0.04	PbF^+	0.02	$HgCl_3^{-1}$	0.98
		$CdCl^+$	5.71	$PbCl^+$	0.14	$HgCl_4^{-2}$	0.07
		$CdCl_2$ (aq)	0.16	PbSO4 (aq)	0.03	HgClOH (aq)	11.07
		$CdSO_4$ (aq)	0.19	$PbHPO_4$ (aq)	1.09	$Hg(NH_3)_2^{+2}$	9.85
		$CdNH_3^{+2}$	0.37	$Pb(CO_3)_2^{-2}$	22.33	$HgCO_3$ (aq)	0.08
		$CdHPO_4$ (aq)	66.38	$PbCO_3$ (aq)	64.11	$Hg(CO_3)_2^{-2}$	0.03
		$CdHCO_3^+$	3.92	$PbHCO_3^+$	6.50	$HgOHCO_3^-$	0.71
		$CdCO_3$ (aq)	6.73	$/HAPb^+(s)$	0.14	$/HA_2Hg(s)$	2.86
		$Cd(CO_3)_2^{-2}$	0.66	$/HA_2Pb(s)$	0.05	$/FA_2Hg(aq)$	62.83
		$/HACd^+(s)$	0.12	$/FAPb^+(aq)$	2.58		
		$/FACd^+(aq)$	2.28	$/FA_2Pb(aq)$	1.42		

3.4 Conclusion

The leaching performance of metal(loid)s and HA from MSW at various pH was investigated. Batching leaching tests showed that the optimum conditions were pH 2 and HA 28 mg/L for recovering a broad range of metal(loid). Al, Mn, Cu and Zn may suggest recovery opportunities as their contents in MSW are high. Analysis of the mobility of the metals through the MSW suggested that these metals are not being vertically transported completely, and no clear pattern was identified between the release of the metals and depths due to waste would undergo different stages of degradation over various landfill ages, and composition. However, the metals showed higher concentrations in the surface layer in MSW. The recovery rates at different depths are following: Pb > Cu > Cd > Co > Li > Mn > Zn > Al > Ni > Cr > As > Hg for 3-9 m, Co > Cd > Zn > Ni > Mn > As > Li > Cr > Al > Cu > Pb > Hg for 23-30.5 m, Co > Zn > Mn > Cd > Ni > Li > Cu > Pb > As > Al > Cr > Hg for 48-55 m. For most metals, their concentrations have decreased with increasing pH. Analysed metals increased at pH 8 except Hg. HA are sparingly soluble in acidic pH. HA promote metal mobilise, but an additional amount of humic acid may assist metals removal. High levels of HA can lead to extensive complexation and chelation of metals. Metal recovery in MSW landfill may have high efficiency in the surface layer, at pH 2 and 4, with an appropriate HA concentration. However, the relationship between HA and metals is still unclear. The capability of humic acid for interactions with metals is strongly dependent on pH. Therefore, further work is required to explore the mechanism of the organometallic process because it can govern the mobility of metals, resulting in enhanced sustainability and economic opportunity by recovering metals by understanding these effects on metal mobility.

4 Increasing recovery opportunities of metal(loid)s in MSW landfill leachate: role of recirculation

The finding in this chapter presented the opportunity to enhance the metals recovery rate from landfill leachate using leachate recirculation.

4.1 Introduction

Natural resource exploitation is accelerating in the face of resource decline, while at the same time, people are generating ever-growing fluxes of wastes (Velenturf et al., 2019). Metals are an essential part of modern living. Not only that but metals such as Li, Ni, Co, Mn and Al are also required to produce electric cars, solar panels, wind turbines and other clean energy technologies, which will help the climate crisis (IEA, 2021). Ensuring the future supply of metals is a critical issue in science, politics, and economics because the available amount of mineral resources is limited (Rotzer and Schmidt, 2018). Landfills are the most common method of waste disposal worldwide (Tongue et al., 2019) and are also regarded as secondary stocks and resource reservoirs for the future recovery of valuables (Bhatnagar et al., 2017). Therefore, the concept of Enhanced Landfill Mining (ELFM) has been proposed (Quaghebeur et al., 2013). One of the main reasons for ELFM is the valorisation of waste materials excavated, such as metals from landfills (Quaghebeur et al., 2013). However, it is not always economically viable and can cause unfavourable odour, escape of leachate and air pollution (Vaverková, 2019). The liquid that has percolated through and been generated by decomposition waste material is known as leachate. It is considered one of the types of wastewaters with the most significant environmental impact because of high concentrations of organic matter, ammonium and heavy metals which, can be an excellent opportunity to recover resources from a wide range of substrates (Iskander et al., 2016). Several studies investigated that landfill leachate comprise recoverable metals (Iskander et al., 2017; Kurinawan et al., 2021). However, there are also limitations associated with the method to meet the need for metals recovery in landfill leachate (Lee et al., 2022). The critical limitation on metal recovery from leachate is the low concentration of metals and yield; therefore, it is not economically viable overall. The key challenges to recovering metals from leachate are economics and in maximising the concentration of metals (Lee et al., 2022). Leachate recirculation may be a crucial key in overcoming the limitations. some studies have shown that the initial stage of leachate recirculation had low pH (5-6) due to the acidification stages, resulting in relatively high concentration of metals (Bilgili et al., 2007; Qu et al., 2008). Leachate recirculation can increase the chloride content, which is an important controlling factor for metal release. Chloride affects the release of metals through the binding the metals on humic acids and the adsorption of metals (Begeal, 2008; Damikouka and Katsiri, 2020). The transition to a more circular economy, where the value of end-of-life products and waste materials is extended, reduces potential remediation costs accrued when land used for waste disposal needs to be reclaimed for contemporary purposes (Hageluken et al., 2016; Savini, 2021). Leachate recirculation can be used as a relatively controlled anaerobic filter to treat leachate, provide accelerated waste stabilisation, reduce the volume of leachate by maximising evaporative losses during recirculation, and minimise leachate migration into the subsurface environment while recovering valuable metals (Bilgili et al., 2007). Therefore, leachate recirculation in municipal solid waste (MSW) landfills contributes towards achieves a more circular economy. However, limited research has been conducted to investigate the influence of recirculation on metal recovery. Therefore, the main purpose of this research is to determine the effect of leachate recirculation on metal recovery. Different ages of leachate samples were used for the experiment to investigate the influence of leachate age on metal recovery. A recirculation experiment of leachate was performed in the laboratory with 10 cycles to estimate the chemical consumption as well as the recovery of the metal(loids). The analysis includes the recovery of 12 metal(loids), including critical raw materials which are subject to supply risks and, for which there are limited natural alternatives.

4.2 Materials and methods

4.2.1 Sample collection and preparation

Different ages of municipal solid waste (MSW) and leachate samples were collected from two MSW landfills located in the UK. The old waste sample was collected in south Gloucestershire from a landfill in operational between 1841 to 1991 without engineered controls. The old landfill received 60,000 m^3 of inert, industrial, commercial and household waste. Older landfill leachate was collected in Elstow landfill, which is a closed site that was operated by Bedfordshire County Council. Leachate, used for the old waste from the site, was extracted and treated through an onsite Sequencing batch reactor (SBR) leachate treatment plant. The young waste sample was collected in Suffolk. The landfill receives minerals, mixed municipal waste and other waste from the mechanical treatment of waste. Leachate for the young waste was collected from the same site where the waste sample was collected. The samples were taken by a specialised private company hired by the landfill sites operator. The samples were stored in a cold room at 4°C until analysis. The waste samples were sorted manually into metal, paper, textile, wood, glass and other materials, and the composition of the samples in this experiment by wet weight are in Table 4.1.

Table 4.1. Composition of the MSW samples collected from the studied landfill sites

Samples no.	**Years**	**Waste sample (g)**	**Paper/ cardboard (g)**	**Plastic (g)**	**Metals (g)**	**Glass/ ceramic (g)**	**Textile (g)**	**Wood (g)**	**Soil/fine fraction (g)**	**Other (g)**
1	<10	62230	1410	4623	224	10	520	842	54437	164
2	>1	59470	4692	7094	2212	3663	3911	1112	35944	762

4.2.2 Experimental setup

Two sets of semi-pilot scale columns were set up without biogas production monitoring. Each opened Perspex column was 0.21 m in diameter and 1.02 m in height, with a working volume of 4 L. One of the columns was filled with young waste (> 1 year old), and another column was filled with old waste (<10 years old) and the same weight of waste (10 kg) was placed in each column. In order to make comparison possible among different compositions from the samples, the samples were mixed well together manually. The outlet port at the bottom was used for recycling leachate using a peristaltic pump. Gravel was filled at the bottom of the column to a height of 0.05 m to serve as a drainage layer and prevent clogging of the leachate outlets. Waste was filled into the column and compacted to a height of 0.25 m. Cover layers consisting of 0.1 m sand were placed on top of the waste samples to decrease the amounts of air penetrating the column. Leachate was collected and stored in the leachate collection tank. Less than 100 mL/d flow rate for peristaltic pumps with leachates are very few, and it is likely to get blocked. Although a high recirculation flow rate can accelerate the stabilisation of landfills, excessive recirculated leachate will impose a heave working load on the leachate collection system, which is not secure and cost-effective (Feng et al., 2018). Therefore, leachate was continuously recirculated using the peristaltic pump with adjusted flow rates (800 mL/day). The average landfill size is 600 acres, where the leachate recirculation flow rate can be adjusted as 815 ton/d.

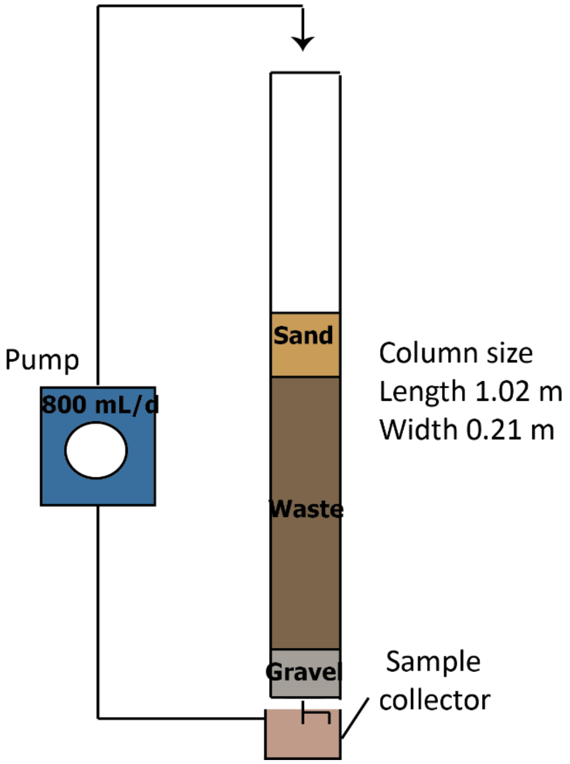


Figure 4.1. Schematic diagram of the column percolation test

4.2.3 Sampling and analytical methods

Leachate samples were collected from the leachate outlet port (250 mL). In order to keep the volume equilibrium of leachate before recirculation, the same volume of tap water (250 mL) was added to the leachate after sampling. The leachate was collected in polyethene bottles and stored in a cold room at 4°C until metal analysis and performed analysis within three weeks. The samples collected were analysed for pH, chemical oxygen demand

(COD), redox potential, total organic carbon (TOC), volatile fatty acid (VFA), and conductivity (Table 4.2).

Table 4.2. Physico-chemical parameters and methods of analysis

Parameters	Instrument used to identify the parameters
pH	Electronic pH meter
Conductivity	Conductivity meter
TOC	Shimadzu TOC-V
COD	Photometer
Redox potential	Redox potential meter using micro-electrodes
VFA	High-performance liquid chromatography

4.2.4 Metal analysis

The metals content was analysed by inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX) after microwave-assisted acid digestion following the extraction procedure used in previous studies (Gutiérrez-Gutiérrez et al., 2015; Cipullo et al., 2018; Wagland et al., 2019). Briefly, Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg were determined by pre-digesting 30 mL leachate with 1.5 mL concentrated trace metal grade nitric acid for leachate samples. For solid samples, 0.5 g of samples was mixed with 6 ml of HCl and 2 ml nitric acid in Teflon tubes and left overnight. The vessels for leachate samples were placed in the Mars Xpress microwave (CEM system, EPA 3015-8). Then, the vessels were cooled, and the solution was filtered through Whatman No. 2 paper and made up to 50 ml with deionised water. A blank digest was carried out in the same way. The microwave is an efficient and fast digestion technique method. Calibration standards were spiked with several certified standard solutions. The concentration ranges were 0.05, 0.1, 0.15 and 0.2 mg/L for the elements. In reporting recovery rates of metals from the leaching test, the following method of calculation is commonly used:

$$Recovery\ rate = \frac{Lc}{Ic} \times 100$$

Where Lc, leaching concentration of metal; Ic, initial metal concentration.

4.2.5 Statistical analyses

Multivariate analysis was performed using SPSS 26 software to identify statistically significant variance between the dependent variable tested and its effect on the metal(loid)s leachability. A multivariable study was conducted considering the correlation matrices. In these matrices, each individual square contains the ordinal coefficient of Spearman which varies between 1 and -1 and the significance level of estimated correlation for each pair of variables (Bisquerra. 1989). Significance level was set at 0.05.

4.3 Results and discussion

4.3.1 pH and conductivity

Variations of pH and conductivity values of the leachate samples collected during its recirculation are given in Fig. 4.2. Monitoring the pH during recirculation was one of the parameters which made it possible to differentiate the various phase of degradation (Christensen and Kjeldsen, 1989). Also, it is a great parameter to predict metal release, as pH is one of the main factors, and the effect of pH on the speciation of metals is of great significance to the migration of metals (Zhang et al., 2018). The pH was lower in young landfill leachate compared to old landfill leachate, which was 7.05 and 8.44. The pH value was decreased at the first recirculation cycle, which reflects the acidogenesis phase. Afterwards, the pH value increased until six cycles in young landfill leachate and four cycles in old landfill leachate, which might be due to the aerobic degradation of the organic acid by the residual oxygen in the landfills. Values of pH remained relatively steady at around 7.7 and 8.7 until the end of the experiment.

The conductivity of a solution reflects its total concentration of ionic solutes and measurers of the solution’s ability to convey an electric current (Sekman et al., 2011). During monitoring, the recorded electrical conductivity (EC) in the leachate varied between 11.65 and 13.52 mS/cm for young landfill leachate and 5.56 and 7.73 mS/cm for old landfill leachate. Strong negative correlations between the pH values and EC values were obtained in the study. This finding is consistent with the previous study of Rychla *et al.* (2011), who reported that the conductivity correlated negatively with pH. High values of EC indicate the presence of dissolved inorganic materials in samples. The conductivity values of leachate in both samples showed a decreasing trend by the recirculation cycle and showed young landfill leachate has a higher EC value. This finding is in agreement with the findings of Mousavi *et al.* (2021), suggesting the average EC showed that the electrical conductivity decreased with the landfill age.

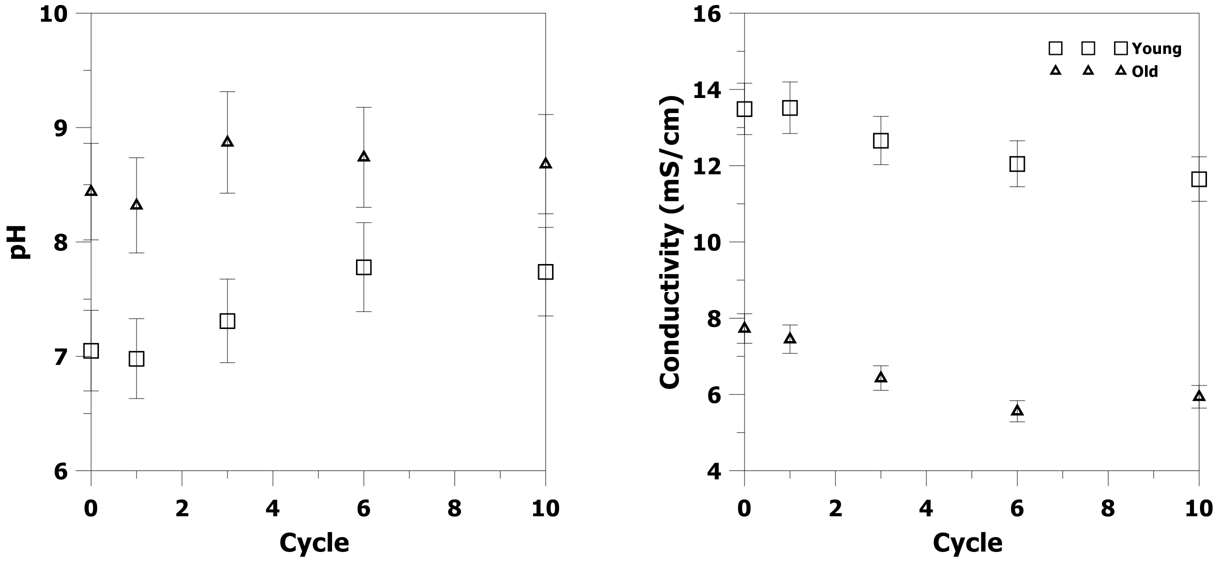


Figure 4.2. Variations of pH and conductivity in the leachate from young and old landfill leachate; 1 recirculation cycle is linked to 25 days in a typical landfill, and 10 recirculation cycles are linked to 150 days in a typical landfill with standard rainfall data

The decrease in conductivity in this experiment is assumed to bedue to the washout of some easily mobilised ions (metals, chloride and sulphate) and a combination of other factors, including the conversion of sulphate to sulphide under increasingly reducing conditions, and the subsequent precipitation of sulphide as heavy metal-sulphides which would tend to withdraw significant ionic strength from solution (Sekman et al. 2011).

4.3.2 Oxidation-reduction potential (ORP)

The ORP values of the leachate collected during the ten recirculation cycles are given in Fig. 4.3. The redox potential within a landfill determines the mechanism of waste degradation (Bilgili et al., 2007). The initial cycle of recirculation resulted in low ORP values. The ORP values decreased to 48.8 mV in young landfill leachate and 136.9 mV in old landfill leachate at the first cycle. After the first cycle, the ORP values increased to 55.6 mV in fresh waste and 222.4 mV in old landfill leachate, indicating the prevalence of anaerobic environmental conditions. ORP in old landfill leachate reached above 200 mV after ten cycles. The measurements are consistent with Top *et al.* (2019) results, which indicated a redox increase in leachate during aerobic degradation of MSW. However, the result is inconsistent with James *et al.* (2004) and Ntwampe *et al*. (2008), who reported that ORP decreased with increasing pH as old landfill leachate has a higher pH value.

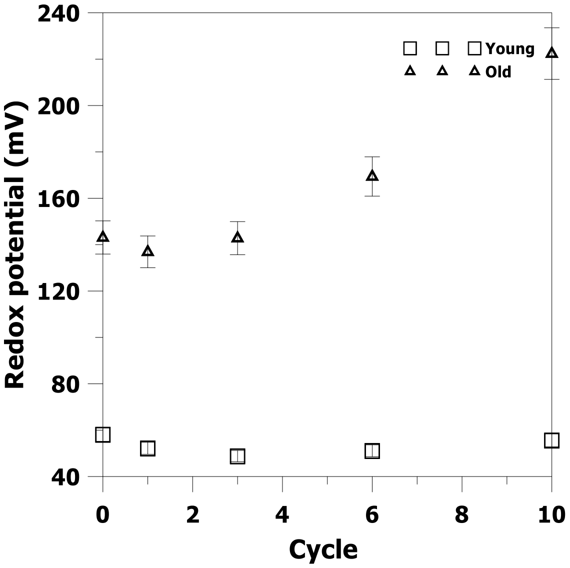


Figure 4.3. Variations of ORP in the leachate from young and old landfill leachate; 1 recirculation cycle is linked to 25 days in a typical landfill, and 10 recirculation cycles are linked to 150 days in a typical landfill with standard rainfall data

ORP has been considered as a crucial parameter in controlling the fate of pollutants in the environments, particularly affecting the pollutant's reactions on the soil-water interface. However, metals mobility is driven by various mechanisms that include precipitation, sorption, and ORP. Therefore, ORP may be a key indicator of metal solubility. The result showed that the ORP values tend to increase by the recirculation cycle, similar to results reported in the previous study (Bilgili et al., 2007). High redox potential (aerobic conditions) causes accelerated degradation of waste (Shearer, 2001).

4.3.3 COD and TOC

The chemical oxygen demand (COD) and total organic carbon (TOC) concentrations of the leachate collected during its recirculation are given in Fig. 4.4. Leachate consists of many different organic and inorganic compounds that may be either dissolved or suspended and biodegradable and non-biodegradable (Reinhart, 1996).

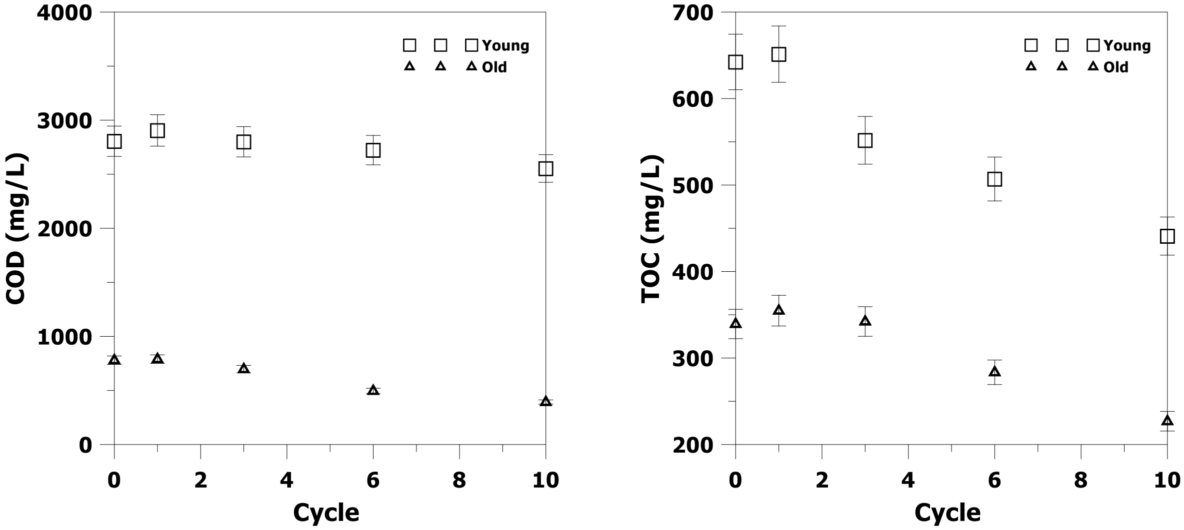


Figure 4.4. Variations of COD and TOC in the leachate from young and old landfill leachate; 1 recirculation cycle is linked to 25 days in a typical landfill, and 10 recirculation cycles are linked to 150 days in a typical landfill with standard rainfall data

The leachate COD concentration showed similar behaviour to TOC concentration. COD increased by 1.3% to 3.6%, and TOC increased by 1.4% to 4.5% at the first cycle compared to the start value. It may be due to the hydrolysis of organic from the solid waste into the leachate was rapidly released in the initial stage. Leachate recirculation may be significant in improving the rate of hydrolysis and acidogenesis and redistributing nutrients (Nag et al., 208). After increasing at the first cycle, the concentrations of both parameters then decreased and stabilised, which is similar to results reported in previous studies (Cossu et al., 2003; Nag et al., 2018; and Luo et al., 2019). The decrease in COD and

TOC concentration from leachate was the result of the dilution and washout mechanisms. The present study results showed that leachate recirculation has a positive effect on the rate of solid waste degradation in landfills (Bilgili et al., 2007). The concentration of COD and TOC in young landfill leachate was higher than in old landfill leachate. This indicated that the total amount of organic material in the landfill was decreasing with increasing age.

4.3.4 VFAs

The volatile fatty acids (VFAs) concentrations of the leachate collected during its recirculation over 10 cycles are given in Fig. 4.4. Organic matter in landfills is hydrolysed, and as a consequence of fermentation processes, VFAs will be generated (Li et al., 2016).

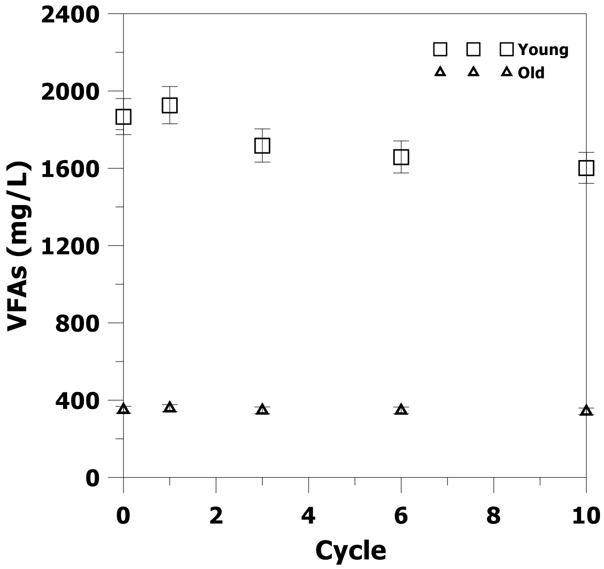


Figure 4.5. Variations of VFAs in the leachate from young and old landfill leachate; 1 recirculation cycle is linked to 25 days in a typical landfill, and 10 recirculation cycles are linked to 150 days in a typical landfill with standard rainfall data

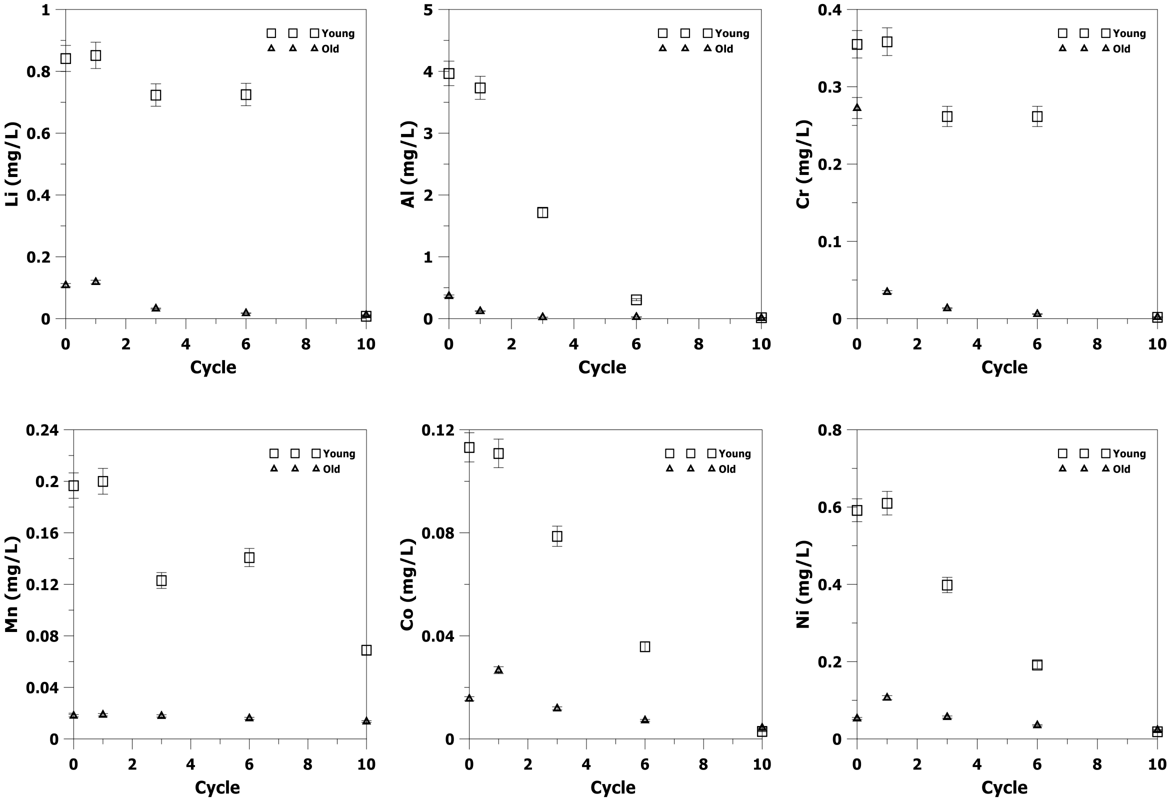
As shown in Fig. 4.4 and Fig. 4.5, the TOC, COD and VFAs concentration changes in the experimental were similar. VFAs increased by 2.3% to 3.2% at the first cycle compared to the start value. As a result of the high degradation rate in aerobic landfills, the concentrations of VFAs decreased since the first cycle (Bilgili et al., 2012). Young landfill leachate is well known to be characterised by high VFAs, COD and TOC (Renou et al., 2008; Bhalla et al., 2013). The results showed that VFAs of young landfill leachate was about 78% higher than old landfill leachate. Furthermore, VFAs of the leachate in both landfill leachate showed a variation corresponding to the variation of the pH. VFAs are short-chain organic acids; they contain a carboxyl group (-C(=O) OH) attached to the alkyl (R-) group (R-COOH). These organic acids may play an essential role in the mobilisation of metals through either the formation of soluble ligand: metal complexes or a decrease of pH (Molaey et al., 2021).

4.3.5 Metal(loid)s

Initial concentration of metal(loid)s is shown in Table 4.3 and metal(loid)s concentrations in the leachate collected during its recirculation over ten cycles are given in Fig. 4.6. These data demonstrated a decreasing trend for both landfills, which is consistent with previous studies (Benson et al., 2007; Long et al., 2010; Yao et al., 2013). Owing to leachate recirculation, metals in leachate were brought back to the landfill. The leachate migration in landfills may result in metals to be immobilised in landfills through of absorption, complexation and precipitation (Long et al., 2009). Leachate recirculation accelerates the decomposition of landfills, which can reduce VFAs in leachate and increase the early settlement in landfills. It could be expected to increase rates of degradation in landfills, while metals cannot be degraded and thus accumulate in the landfill. As a result, it decreases metal ion leaching. However, the metal(loid)s release in leachate was high at the first recirculation cycle. Also, it was noted that the concentration of metal(loid)s was higher in young landfill leachate. It is related to pH change; metal(loid)s release in the leachate increases as pH decrease at the first recirculation cycle as it is in the acidification phase of the waste degradation process when pH value is low.

Table 4.3. The initial concentration of metal(loid)s in less than 1 year old landfill leachate (young) and over 10 years old landfill leachate (old)

	< 1 years	> 10 years		< 1 years	> 10 years
Li (mg/L)	0.84	0.11	Cu (mg/L)	4.97	0.01
Al (mg/L)	3.97	0.37	Zn (mg/L)	1.62	0.38
Cr (mg/L)	0.36	0.27	As (mg/L)	0.31	0.00
Mn (mg/L)	0.20	0.02	Cd (mg/L)	0.00	0.00
Co (mg/L)	0.11	0.02	Pb (mg/L)	0.07	0.00
Ni (mg/L)	0.59	0.05	Hg (mg/L)	0.00	0.00



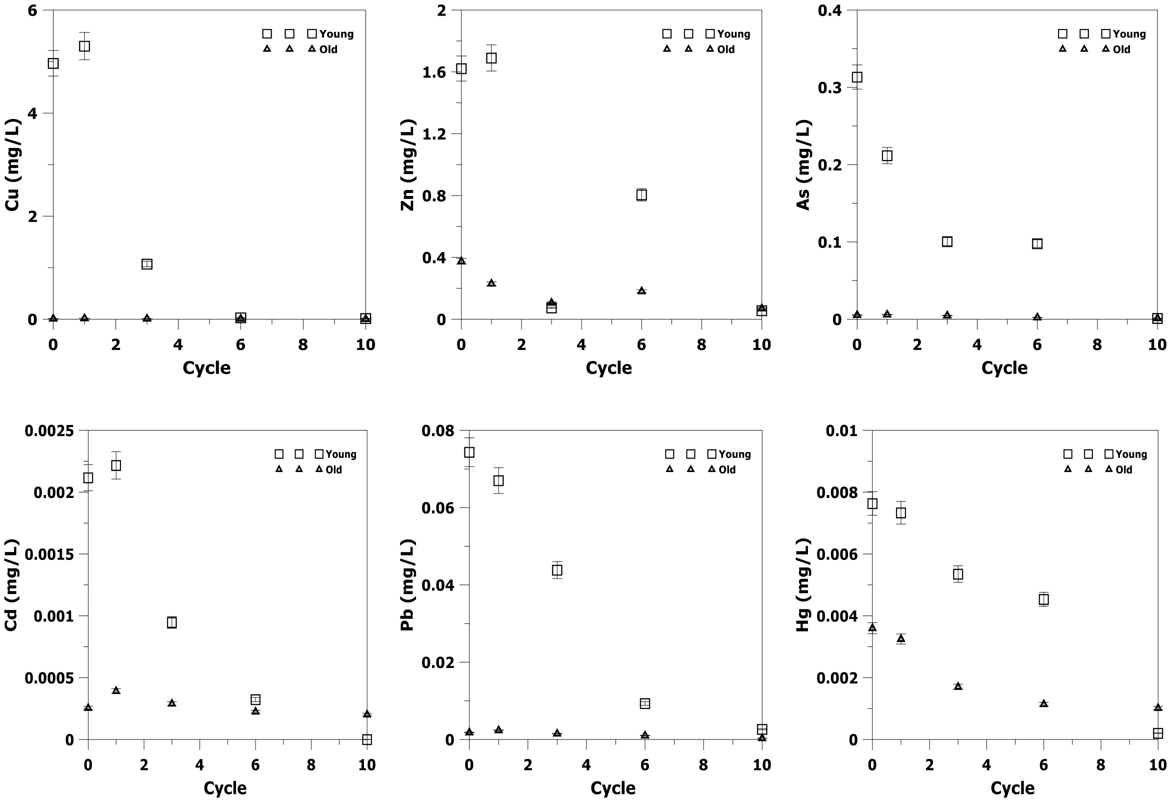


Figure 4.6. Variations of metal(loid)s in the leachate from young and old landfill leachate

Tables 4.4 and 4.5 show the recovery rates for the metal(loid)s from the initial leachate according to the recirculation cycle. Tables 4.4 and 4.5 showed that metal(loid)s recovery rate was over 100% at the first cycle except for Al, Co, As, Pb and Hg in young landfill leachate and Al, Cr, Zn, and Hg in old landfill leachate. At the initial recirculation cycles, the pH of leachate is low in the acidogenesis stage, so the metals had high solubility and dissolved into leachate. Also, there was metal dissolution into the liquid from the solid MSW sample due to the degradation of organic matter of the solid MSW sample and the leachate recirculation at the initial stage of the experiment. Therefore, high recovery rates were observed. After that period, pH was increased to neutral as it reached methanogenesis stage, and the metal could precipitate and be trapped in the samples. On average, the metal(loid)s recovery rate was 14.59% higher at the first recirculation cycle in old landfill leachate.

Table 4.4. Recovery rates of metal(loid)s from young landfill leachate according to recirculation cycle

Cycle time	Li (%)	Mn (%)	Cr (%)	Hg (%)	Ni (%)	Co (%)
1	101.19	101.70	100.94	96.07	103.10	97.94
3	85.940	62.54	73.71	70.09	67.32	69.51
6	86.14	71.61	73.71	59.39	32.39	31.66
10	0.97	35.06	0.45	2.65	3.19	2.61
Average	68.56	67.73	62.22	57.05	51.50	50.43
Variance	1561.16	565.80	1392.02	1164.22	1405.84	1315.05
Cycle time	Pb (%)	Cd (%)	Zn (%)	Al (%)	As (%)	Cu (%)
1	90.13	104.72	104.21	94.12	67.55	106.71
3	58.97	44.72	4.55	43.28	32.07	21.58
6	12.53	15.27	49.64	7.73	31.22	0.60
10	3.56	0	3.45	0.45	0.37	0.32
Average	41.30	41.18	40.46	36.39	32.80	32.30
Variance	1237.18	1604.37	1701.98	1373.32	565.66	1919.97

Zn showed that the similarity similar tendency to Mn and Li was similar with Cr in young landfill leachate. Co exhibited the same behaviour as Ni and Cd in old landfill leachate. Zn and Mn showed another increase at the third recirculation cycle in the old landfill leachate, and Zn increased again at the third recirculation cycle in the young landfill leachate. This may be caused by the metal's experienced various balances such as absorption-desorption, precipitation-dissolution and complexation-dissolution, which means the metals in leachate may be the express proportion after saturation of balances in waste (Long et al., 2009). Another possible reason is the degradation of waste, which release a part of the metals bound with the organic matter in the waste.

Al, Cu and Zn have relatively higher concentrations than other metals, which can be a great opportunity. Cu showed an excellent recovery rate at the first recirculation cycle. However, the recovery rate by recirculation of Al and Zn were not effective. Co, Ni, Cd and Pb in old landfill leachate showed a high recovery rate at the first recirculation cycle. The results demonstrate that the amount of metals recovered in the leachate may be potentially increased by recirculation.

Table 4.5. Recovery rates of metal(loid)s from old landfill leachate according to recirculation cycle

Cycle time	Cd (%)	Ni (%)	Cu (%)	Mn (%)	Co (%)	Pb (%)
1	153.59	201.26	166.18	104.17	170.94	130.04
3	113.69	106.78	97.90	99.14	75.97	82.78
6	88.24	66.62	86.99	88.89	46.27	55.88
10	79.27	43.34	39.99	75.03	27.84	18.01
Average	108.70	104.50	97.76	91.81	80.26	71.68
Variance	831.27	3635.55	2033.76	124.11	3036.11	1664.90
Cycle time	As (%)	Hg (%)	Li (%)	Zn (%)	Al (%)	Cr (%)
1	110.33	90.28	109.47	61.33	33.24	12.66
3	88.92	47.31	30.16	28.44	6.43	4.93
6	43.31	31.77	16.35	48.18	7.37	2.19
10	23.95	28.25	10.80	18.79	2.87	0.79
Average	66.63	49.40	41.70	39.19	12.48	5.15
Variance	1193.04	608.34	1580.70	275.67	146.52	21.05

There are several factors affecting the mobility of metal(loids), Table 4.6 shows the correlations between metals and other variables.

Table 4.6. Correlations coefficients for metals and physico-chemical parameters for [young/ old] landfill leachate recirculation samples

	Li (%)	Al (%)	Cr (%)	Mn (%)	Co (%)	Ni (%)
COD	0.83**	0.67*	0.68*	0.91**	0.73*	0.74*
pH	-0.88**	-0.84**	-0.77**	-0.94**	-0.88**	-0.88**
Conductivity	0.86**	0.74*	0.75*	0.93**	0.79**	0.80**
Redox	-0.75*	-0.57	-0.64*	-0.82**	-0.65*	-0.66*
TOC	0.90**	0.80**	0.75*	0.97**	0.84**	0.86**
VFAs	0.87**	0.78**	0.72*	0.96**	0.82**	0.83**
Age	-0.79**	-0.62	-0.61	-0.88**	-0.67*	-0.69*
	Cu (%)	Zn (%)	As (%)	Cd (%)	Pb (%)	Hg (%)
COD	0.61	0.59	0.72	0.61	0.72*	0.66*
pH	-0.78**	-0.72*	-0.84**	-0.79**	-0.87**	-0.80**
Conductivity	0.68*	0.66*	0.77*	0.68*	0.78**	0.73*
Redox	-0.51	-0.52	-0.62	-0.52	-0.63	-0.61
TOC	0.75*	0.72*	0.84**	0.75*	0.84**	0.77**

VFAs	0.74*	0.70*	0.82**	0.73*	0.82**	0.73*
Age	-0.56	-0.54	-0.68*	-0.55	-0.68*	-0.58

**. Correlation is significant at the 0.01 level
*. Correlation is significant at the 0.05 level

According to the Pearson correlation coefficient values, all metal(loid)s shows a strong negative correlation with pH. Also, negative correlations of Li, Al, Cr, Mn, Co, and Ni were observed with redox potential. All metal(loid)s shows a strong positive correlation with COD, VFAs and conductivity. TOC and VFAs showed a similarity tendency with COD. However, Cu, Zn, As, and Cd did not correlate with TOC unlike COD and VFAs. It indicates that metals release was strongly affected by pH, COD and VFAs.

4.4 Conclusion

A Semi-pilot scale of column percolation test was performed to investigate the recirculation effects on metal recovery in landfill leachate. Landfills of different age were studied and compared for metals recovery. Between young and old landfills, the young landfill sample presented a high concentration of metal(loid)s. Al, Mn, Cu and Zn may suggest recovery opportunities as their contents in leachate are high. Leachate recirculation promotes the release of the metal at the first cycle, resulting in an increased metal recovery rate. The recovery rates in the young and old landfill leachate at the first recirculation cycle are as follows: Cu > Cd > Zn > Ni > Li > Mn > Cr > Co > Hg > Al > Pb > As for young landfill leachate, Ni > Co > Cu > Cd > Pb > As > Li > Mn > Hg > Zn > Al > Cr for old landfill leachate. However, after the first recirculation cycle, recirculation immobilises the metals as observed from the low metals' concentration in leachate. This is due to the direct adsorption of metal-humic complexes on the soil mineral surface. Therefore, the operation of landfills with leachate recirculation can increase metals recovery rate at the initial stage and then attenuate metals. Therefore, leachate recirculation is an excellent opportunity for a combined resource-recovery and remediation strategy, which will drastically reduce future remediation costs, reclaim valuable land while at the same time unlocking billions of tons of valuable metals contained within the landfill environment. Leachate recirculation also increases organic matter at the first cycle; COD, TOC and VFAs concentrations are increased in the range of 1.28-3.56%, 1.40-4.54%, 2.33-3.16%, which indicated the landfills were in the acidification stage. The results show that metals concentration was significantly related to COD, TOC and VFAs. Organic matter plays a crucial role in the mobilisation of metals by metal complexes or a decrease in pH. Therefore, further work is required to explore the influence of organic matter on metal recovery with leachate recirculation to maximise metals recovery rate.

5 The influence of humic acid on metal(loid)s release for increasing recovery rate from MSW landfills

The finding in this chapter presents the influence of humic acid on the release of metals in landfills to increase the concentration of metals from landfill leachate.

5.1 Introduction

With the rapid economic development, more and more metals and metal-bearing solid waste are produced from household products, such as batteries and fluorescent light (Xiaoli et al., 2012). Our everyday life and technical progress are based on various metals (Friedrich., 2019). The secure supply of metals has become a global strategic issue. The metal supply is finite and using metals from a natural resource cannot be replaced entirely.

According to the European Commission (2017), 60% of the annually produced waste from 500 million EU inhabitants ends up in landfills. Therefore, landfills may be the door for the sustainability of metals. They contain enormous volumes of valuable materials such as metals and plastic that constitute an essential driving for resource recovery, indicating leachate constituents by inorganic ions such as heavy metals. Therefore, a new approach for leachate treatment to remove contaminants and recover valuable metals can be proposed as extraction metals in landfills have disadvantages such as operational problems, high energy requirements and cost (Lee et al., 2022).

However, the recovery is affected by metal concentrations and values in landfill leachate. Metal behaviour relies on various reactions, such as complexation, ion exchange, sorption and desorption, precipitation and dissolution reactions (Bang and Hesterberg, 2004). Organic matter content is considered as one of the main factors affecting metal release. This is mainly due to the presence of high molecular weight organic substances that display a high affinity for metals and form liquid-insoluble metal complexes. Complexation reactions with organic ligands are known to influence metal mobility by either increasing or decreasing its sorption of mineral surface (Gungor and Bekbolet, 2010). Among the organic ligands, humic substances are the principal constituent of organic matter in nature, the occurring mixture of organic compounds (Aiken et al., 1985). Humic substances can be divided into three main fractions: humic acids, fulvic acids and humin (Tobiasova et al., 2018). Humic substances (humic and fulvic acids) bind metals to their hydroxyl and carboxyl groups (Leung and Kimaro, 1997; Bozkurt et al., 2000; Kochany and Smith, 2001; Klavinsa et al., 2006; Gutiérrez-Gutiérrez et al., 2015). In soil, the humic acid concentration is generally significantly greater than that of fulvic acid (Spark et al., 1997). It is well known that humic acid has the advantage of complexing with heavy metal ions (Hankins et al., 2006).

The main functional groups of humic acid are carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulphate, amides, and sulphides, and all these groups are able to interact with metal species in solution (Senesi, 1992). Therefore, it is vital to understand the solubility characteristics of humic acid and how this solubility influences the metal release.

In chapter 3, the leaching of metal(loid)s from municipal solid waste at pH 2, and 4 with humic acid gave the most efficient metal release. In chapter 4, leachate recirculation increases the metal recovery rate at the first recirculation cycle. Therefore, the objective of the present chapter was to investigate the impact of changing the humic acid on metal recovery from landfill leachate by adding humic acid and recirculation operation.

5.2 Materials and methods

5.2.1 Sample collection and preparation

Different ages of municipal solid waste (MSW) and leachate samples were collected from two MSW landfills located in the UK. The old waste sample was collected in south Gloucestershire, and it was operational between 1841 to 1991 without engineered controls. The old landfill received 60,000 m3 of inert, industrial, commercial, and household waste. Older landfill leachate was collected in Elstow landfill, which is a closed site that was operated by Bedfordshire County Council. Leachate, used for the old waste from the site, is extracted and treated through an onsite Sequencing batch reactor (SBR) leachate treatment plant. The young waste sample was collected in Suffolk. It receives minerals, mixed municipal waste, other waste from mechanical treatment of waste. Leachate for the young waste was collected in the same site where the waste sample was collected. The samples were taken by a specialised private company hired by the landfill sites operator. The samples were stored in a cold room at 4°C until analysis. The waste samples were sorted manually into metal, paper, textile, wood, glass and other materials, and the composition of the samples in this experiment were by wet weight is in Table 5.1.

Table 5.1. Waste composition of the samples collected from the studied landfill sites

Samples no.	Years	Waste sample (g)	Paper/ cardboard (g)	Plastic (g)	Metals (g)	Glass/ ceramic (g)	Textile (g)	Wood (g)	Soil/fine fraction (g)	Other (g)
1	<10	62230	1410	4623	224	10	520	842	54437	164
2	>1	59470	4692	7094	2212	3663	3911	1112	35944	762

5.2.2 Experimental set-up

Twelves sets of semi-pilot scale columns were set up (Fig 5.1). Each opened Perspex column was 0.21 m in diameter and 1.02 m in height, with a working volume of 4 L. Six of the columns were filled with young waste (> 1 year old), and other six columns were filled with old waste (<10 years old) and the same weight of waste (10 kg) was placed in each column. In order to make comparison possible among different compositions from the samples, the samples were mixed well together manually. The outlet port at the bottom was used for recycling leachate using a peristaltic pump. Gravel was filled at the bottom of the column to a height of 0.05 m to serve as a drainage layer and prevent clogging of the leachate outlets. Waste was filled into the column and compacted to a height of 0.25 m. Cover layers consisting of 0.1 m sand were placed on top of the waste samples, which will decrease the amounts of air penetrating the column. Leachate was collected and stored in the leachate collection tank. Less than 100 mL/d flow rate for peristaltic pumps with leachates are very few, and it is likely to get blocked. Although a high recirculation flow rate can accelerate the stabilisation of landfills, excessive recirculated leachate will impose a heave working load on the leachate collection system, which is not secure and cost-effective (Feng et al., 2018). Therefore, leachate was continuously recirculated using the peristaltic pump with adjusted flow rates (800 mL/day).

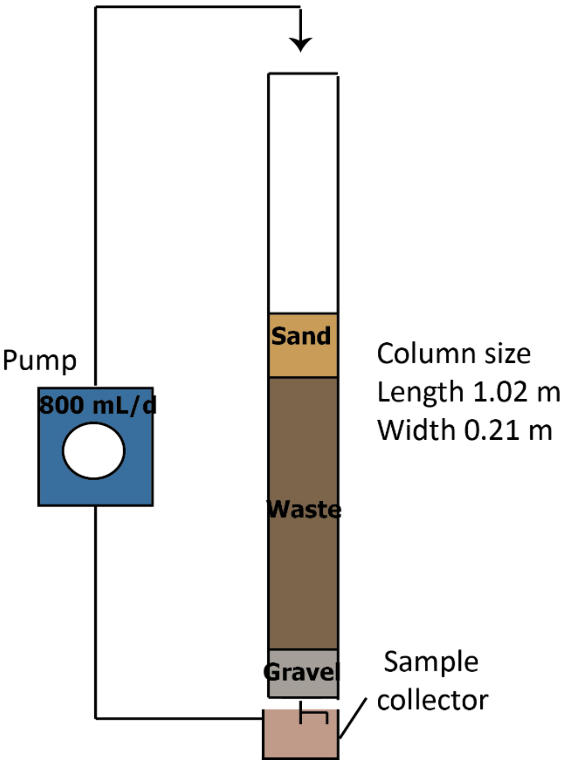


Figure 5.1. Schematic diagram of the column percolation test

The effect of different concentrations of humic acid (w/v) (0.1% and 0.5%) at pH 4 and 6 were studied. The pH was adjusted using 1.8 M nitric acid solution or 1 M sodium hydroxide solution. The same samples and columns with chapter 4 were used for this study. The experiment was conducted in the columns with a total of 5 times leachate recirculation. 0.1and 0.5 g of humic acid was added in every 100 mL of tap water; 4 g of humic acid was added in 0.1%, and 20 g of humic acid was added in 0.5% with 4 L of tap water.

5.2.3 Sampling and analytical methods

Leachate samples were collected from the leachate outlet port (250 mL). In order to keep the volume equilibrium of leachate before recirculation, the same volume of tap water (250 mL) was added to the leachate after sampling. The leachate was collected in polyethene bottles and stored in a cold room at 4°C until metal analysis and performed analysis within three weeks. The samples collected were analysed for pH, chemical oxygen demand

(COD), redox potential, total organic carbon (TOC), volatile fatty acid (VFA), and conductivity.

5.2.4 Metal analysis

The metals content was analysed by inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX) after microwave-assisted acid digestion following the extraction procedure used in previous studies (Gutiérrez-Gutiérrez et al., 2015; Cipullo et al., 2018; Wagland et al., 2019). Briefly, Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg were determined by pre-digesting 30 mL leachate with 1.5 mL concentrated trace metal grade nitric acid for leachate samples. For solid samples, 0.5 g of samples was mixed with 6 ml of HCl and 2 ml nitric acid in Teflon tubes and left overnight. The vessels for leachate samples were placed in the Mars Xpress microwave (CEM system, EPA 3015-8). Then, the vessels were cooled, and the solution was filtered through Whatman No. 2 paper and made up to 50 ml with deionised water. A blank digest was carried out in the same way. The microwave is an efficient and fast digestion technique method. Calibration standards were spiked with several certified standard solutions. The concentration ranges were 0.05, 0.1, 0.15 and 0.2 mg/L/ for the elements.

5.2.5 Humic acid analysis

A stock solution of HA was prepared by dissolving 1 g of HA in 1 L of deionised water for investigating the impact of the presence of HA in leachate on the leachability of metals. HA content was determined by ultraviolet light absorbance at 254 nm. The values were converted using a calibration curve (Fig 5.2). For that purpose, serial dilutions of the concentrated HA stock solution were prepared: 1, 2, 5, 7, 10, 15, 20, 50, 100 mg. Samples for UV_{254} were filtered through 0.45 µm membrane filter. UV_{254} was measured through a 1 cm quartz cell. The test was conducted in duplicate.

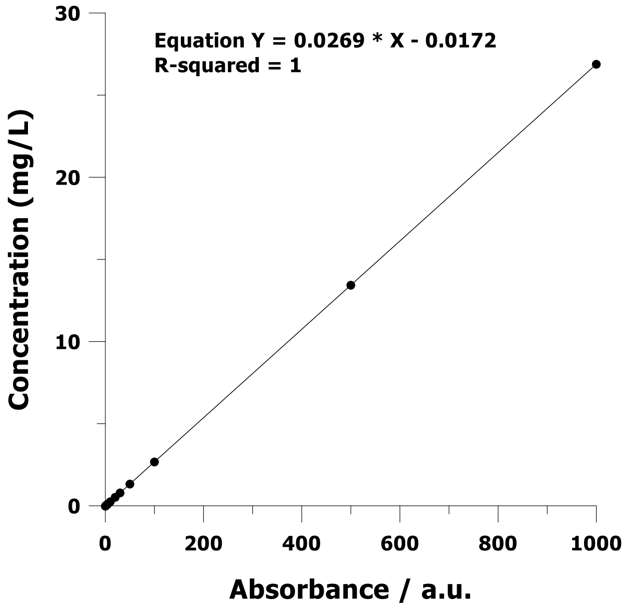


Figure 5.2. Humic acid standard calibration curve at 254 nm.

The E_4/E_6 ratio (ration of the absorbance at 465 nm and at 665 nm) has been widely used to study the humic acid fraction. The ratio is considered to be inversely proportional to molecular weight, acidity and to their degree of humification. The value of E_{280} is used as an indicator for the aromaticity of sample's structure, because $\pi - \pi$ electron transition occurs in this UV region for phenolic arenes, benzoic acids, aniline derivatives, polyenes, and polycyclic aromatic hydrocarbons with two or more rings (Uyguner and Bekbolet, 2005). Samples for E_4/E_6 ratio and E_{280} were filtered through 0.45 µm membrane filter. E_4/E_6 ratio and E_{280} was measured through a 1 cm quartz cell. The test was conducted in duplicate.

5.2.6 ATR-FTIR spectra

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) is performed at room temperature in the wavenumber range between 400-4000 cm^{-1} with 16 scans at a spectra resolution 4 cm^{-1} to detect any interaction between the metals and humic acid. FTIR spectroscopy shows the intensity of the peak absorbance of the function groups, which can identify the chemical bond in metals. The freeze-dried leachate samples were used for the device Bruker Platinum ATR. Table 5.2 shows the functional groups and its quantified frequencies.

Table 5.2. FTIR frequency range and functional groups (Ribeiro et al., 2001; Lingegowda et al., 2012)

Frequency range (cm^{-1})	Functional group
3854	O-H stretching vibration
3675	Amid
3550-3450	Hydroxyl compounds
3400-3200	Hydroxyl compounds
2854-2926	Methyl group
2855-2975	Cyclo alkane
2500-3300	Carboxyl acid
2353	C-O bond
2322-2138	C-N
2260-2100	C=C Stretching bond of alkynes
1725-1745	Carbonyl compounds
1458-1591	Phenol ring
1432-1621	Aromatic ring
1150-911	C-O-C group
858-733	C-H
600-700	C-S linkage
550-690	Halogen compounds (C-Br)
469	Alkyl halides

5.2.7 Statistical analyses

Multivariate analysis was performed using SPSS 26 software to identify statistically significant variance between the dependent variable tested and effect on the metal(loid)s leachability. A multivariable study was conducted considering the correlation matrixes. In these matrices, each individual square contains the ordinal coefficient of Spearman which varies between 1 and -1 and the significance level of estimated correlation for each pair of variables (Bisquerra. 1989). Significance level was set at 0.05.

5.3 Results and discussion

5.3.1 Solubility of humic acid

It is well known that the solubility of humic acid in leachate increases as pH and decrease landfill age and redox potential (Fan et al., 2006; He et al., 2006; Qu et al., 2008; Zhang et al., 2018; Lee et al., 2021). Figure 5.3 shows the correlations between humic and pH, landfill age and redox potential. There was a strong positive relationship between pH and HA ($p < 0.05$). This finding is consistent with the previous study of Lee *et al.* (2021). At neutral to high pH, humic acids are more negatively charged due to the ionisation of COOH and phenolic OH groups. Strong negative correlations were found between humic acid and redox potential ($p < 0.01$) and landfill age ($p < 0.01$).

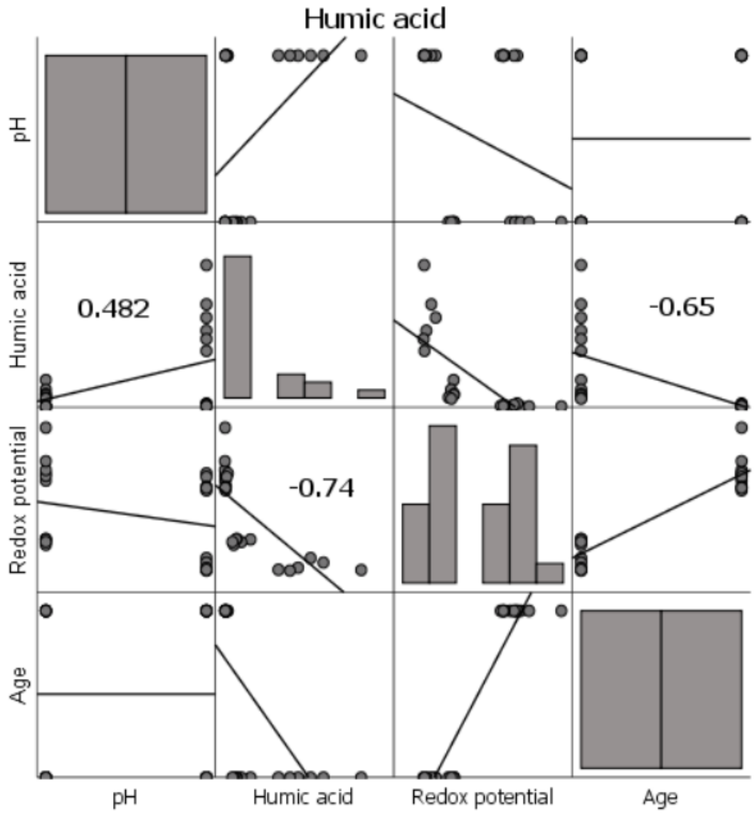


Figure 5.3. The leached concentration values of humic acid in landfills, according to pH, redox potential, and age

5.3.2 Effect of humic acid concentration on metal recovery

Chapter 3 showed that the leaching efficiency of HA is comparatively higher at pH 4 to 6, and the leachability of metalloids had a HA content of 28 mg/L. Previous studies showed that 0.1 to 2M of oxalic acid increased metal release, and 0.5% humic acid leached out Cd, Pb, Ni, Cu, and Zn twice that of 0% humic acid (Das et al., 2012; Usharani and Vasudevan). Therefore, the effect of humic acid concentration on the release of selected metal(loid)s was studied in 0.1% and 0.5% at pH 4 and 6 from young and old landfill leachate. Initial concentration of metal(loid)s at pH 4 in young landfill leachate is shown in Table 5.3 and initial concentration of metal(loid)s at pH 5 in old landfill leachate is shown in Table 5.4.

The control study results at pH 4 from different ages of landfills are present in Fig. 5.4 and 5.5. The results show that humic acid significantly accelerated Al, Zn and Pb in both landfill leachate. For 0.1% of humic acid content, Al release 0.48-4.38 mg/L, 0.34-3.18 mg/L, 0.06-4.52 mg/L and 0.24-4.53 mg/L for pH 4 in young landfill leachate, pH 6 in young landfill leachate, pH 4 in old landfill leachate and pH 6 in old landfill leachate, respectively. For 0.5% of humic acid content, Al release 1.87-21.33 mg/L, 0.12-20.33 mg/L, 1.80-15 mg/L and 1.92-20.83 mg/L for pH 4 in young landfill leachate, pH 6 in young landfill leachate, pH 4 in old landfill leachate and pH 6 in old landfill leachate, respectively. For 0.1% of humic acid content, Zn release 0.14-0.28 mg/L, 0.12-0.25 mg/L, 0.04-0.23 mg/L and 0.04-0.22 mg/L for pH 4 in young landfill leachate, pH 6 in young landfill leachate, pH 4 in old landfill leachate and pH 6 in old landfill leachate, respectively. For 0.5% of humic acid content, Zn release 0.20-0.28 mg/L, 0.14-0.34 mg/L, 0.05-0.38 mg/L and 0.04-0.15 mg/L for pH 4 in young landfill leachate, pH 6 in young landfill leachate, pH 4 in old landfill leachate and pH 6 in old landfill leachate, respectively.

For 0.1% of humic acid content, Pb release 0.003-0.02 mg/L, 0.006-0.019 mg/L, 0.0003-0.004 mg/L and 0.0006-0.005 mg/L for pH 4 in young landfill leachate, pH 6 in young landfill leachate, pH 4 in old landfill leachate and pH 6 in old landfill leachate, respectively. For 0.5% of humic acid content, Pb release 0.008-0.02 mg/L, 0.005-0.03 mg/L, 0.004-0.02 mg/L and 0.001-0.01mg/L for pH 4 in young landfill leachate, pH 6 in young landfill leachate, pH 4 in old landfill leachate and pH 6 in old landfill leachate, respectively. An overall increasing trend was attained in the release of metal(loid)s with respect to increasing humic acid concentration for both landfill leachate concentrations.This finding is in agreement with the findings of Usharani and Vasudevan (2016), suggesting humic acid can be used to leach out metals. The recovery rate of metal(loids) using humic acid 0.1% on average from young landfill leachate was 96.40% and 1208.24% at pH4 and 6. The recovery rate of metal(loids) using humic acid 0.5% on average from young landfill leachate was 144.03% and 267.16% at pH4 and 6. The recovery rate of metal(loids) using humic acid 0.1% on average from old landfill leachate was 1831.13% and 1603.18% at pH4 and 6. The recovery rate of metal(loids) using humic acid 0.5% on average from old landfill leachate was 387.74% and 216.10% at pH4 and 6. Therefore, metal recovery using humic acid from young landfill leachate may be more effective at pH 6 and from old landfill leachate may be more effective at pH 4. It may be related to humic acid solubility as they are insoluble in acidic conditions, in which young landfill has lower pH value.

Table 5.3. The initial concentration of metal(loid)s in young landfill leachate, following the humic acid concentration (0, 0.1, 0.5 %) and pH value (4)

	Humic acid concentration (%)				Humic acid concentration (%)		
(mg/L)	0	0.1	0.5	(mg/L)	0	0.1	0.5
Li	0.06	0.11	0.03	Cu	0.19	0.23	0.25
Al	0.62	4.38	21.33	Zn	0.12	0.28	0.28
Cr	0.01	0.01	0.06	As	0.01	0.00	0.07
Mn	0.10	0.09	0.08	Cd	0.00	0.00	0.00
Co	0.01	0.01	0.03	Pb	0.01	0.02	0.02
Ni	0.04	0.06	0.10	Hg	0.33	1.14	0.03

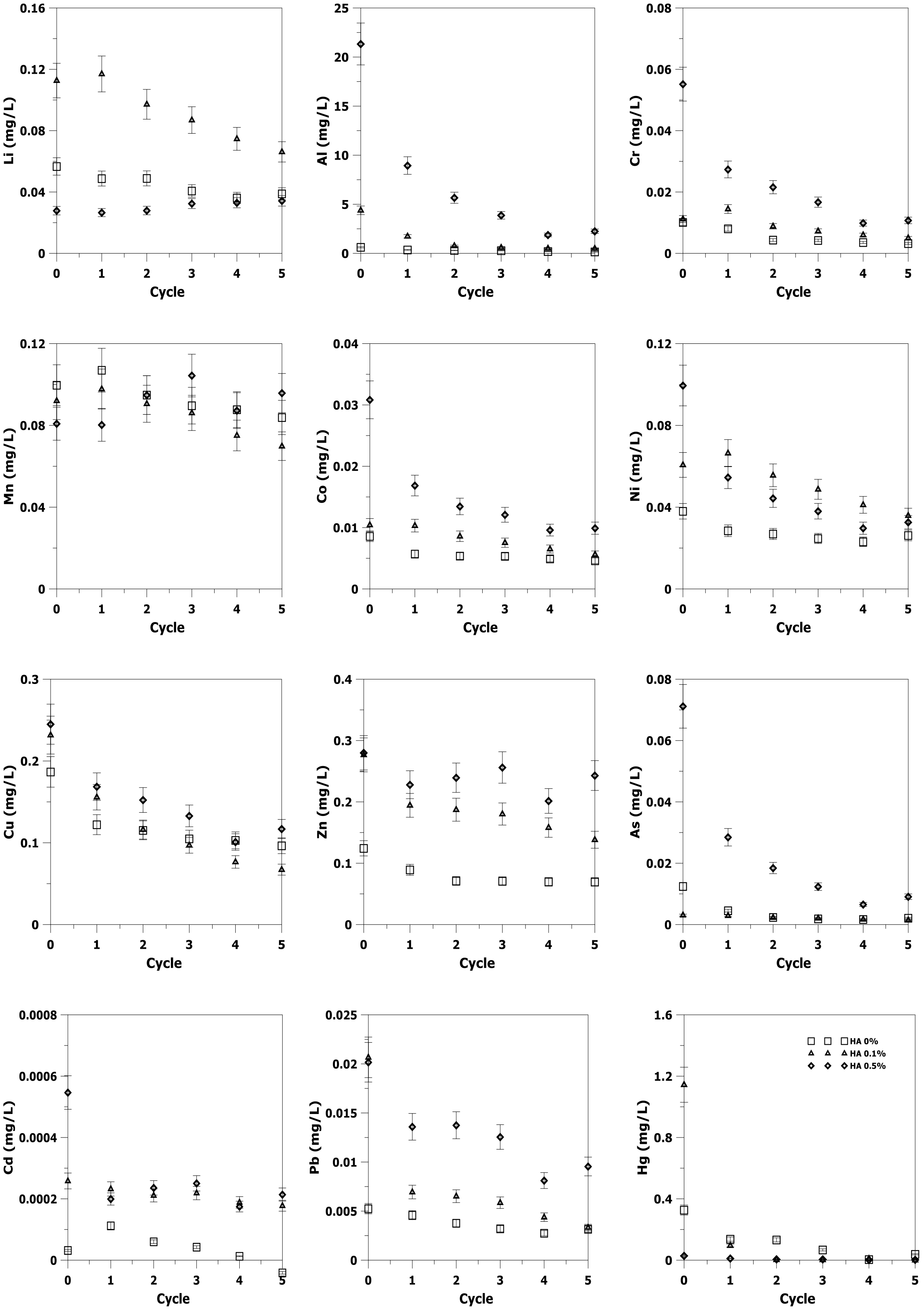

Li (mg/L)
0.16
0.12
0.08
0.04
0
Al (mg/L)
25
20
15
10
5
0
Cr (mg/L)
0.08
0.06
0.04
0.02
0
Mn (mg/L)
0.12
0.08
0.04
0
Co (mg/L)
0.04
0.03
0.02
0.01
0
Ni (mg/L)
0.12
0.08
0.04
0
Cu (mg/L)
0.3
0.2
0.1
0
Zn (mg/L)
0.4
0.3
0.2
0.1
0
As (mg/L)
0.08
0.06
0.04
0.02
0
Cd (mg/L)
0.0008
0.0006
0.0004
0.0002
0
Pb (mg/L)
0.025
0.02
0.015
0.01
0.005
0
Hg (mg/L)
1.6
1.2
0.8
0.4
0
0
1
2
3
4
5
Cycle
HA 0%
HA 0.1%
HA 0.5%

Figure 5.4. Concentrations of 12 metals extracted using 0%, 0.1% and 0.5% of humic concentration from young landfill leachate at pH 4

However, the improvement of Cu and Hg leaching rate is not apparent with increasing humic acid content. This finding is consistent with the previous study of Zhao *et al*. (2019) and Chou *et al.* (2018), who reported that there is no clear improvement in Cu with increasing humic acid content. It may be due to excessive humic acid can chelate with metal ions and reduce the concentration of Cu and Hg in leaching solution (Zhang et al., 2018). Several processes such as proton-induced dissolution, oxidative dissolution caused by oxygen attack, ligand-induced dissolution caused by humic acid adsorption or surface complexation, and protection of the mineral surfaces from proton and oxygen attacks by adsorbed humic acid may enhance or inhibit the dissolution of metals in the presence of humic acid (Chou et al., 2018). The recovery rate of metals at 0.1% of humic acid on average is 96.41% at pH 4, 1208.24% at pH 6 from young landfill leachate and 1831.13% at pH 4 1603.18% at pH 6 from old landfill leachate. On average, the recovery rate of metals at 0.5% of humic acid is 144.03% at pH 4, 267.16% at pH 6 from young landfill leachate and 387.74% at pH 4 316.10% at pH 6 from old landfill leachate. When humic acid concentration is the same, the release efficiency of metals is higher at pH 6 than at pH 4.

Table 5.4. The initial concentration of metal(loid)s in old landfill leachate, following the humic acid concentration (0, 0.1, 0.5 %) and pH value (4)

	Humic acid concentration (%)				Humic acid concentration (%)		
(mg/L)	0	0.1	0.5	(mg/L)	0	0.1	0.5
Li	0.00	0.00	0.02	Cu	0.05	0.11	0.13
Al	0.02	4.52	15.00	Zn	0.06	0.23	0.38
Cr	0.00	0.02	0.22	As	0.00	0.02	0.07
Mn	0.10	0.04	0.45	Cd	0.00	0.00	0.00
Co	0.00	0.01	0.02	Pb	0.00	0.00	0.02
Ni	0.00	0.07	0.19	Hg	0.01	0.01	0.00

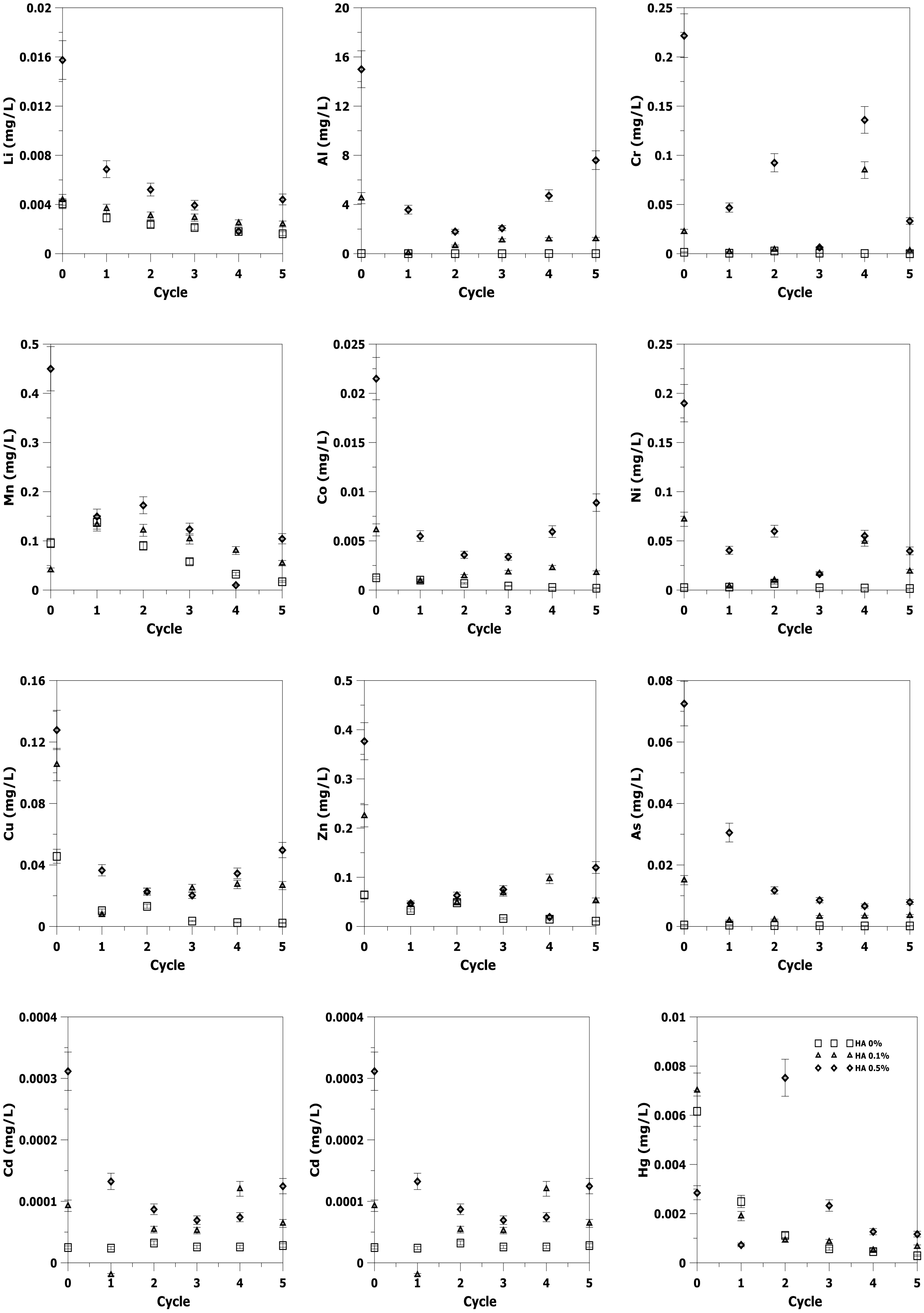

Li (mg/L)
Al (mg/L)
Cr (mg/L)
Mn (mg/L)
Co (mg/L)
Ni (mg/L)
Cu (mg/L)
Zn (mg/L)
As (mg/L)
Cd (mg/L)
Cd (mg/L)
Hg (mg/L)
Cycle
0
1
2
3
4
5
HA 0%
HA 0.1%
HA 0.5%

Figure 5.5. Concentrations of 12 metals extracted using 0%, 0.1% and 0.5% of humic concentration from old landfill leachate at pH 4

The correlation between HA, metals, recirculation cycle, and pH is shown in Table 5.5. There was a strong positive relationship between humic acid and Al, Cr, Zn, As, Cd, Pb ($p < 0.01$) and Cu ($p < 0.05$). However, Li shows a strong negative relationship with humic acid ($p < 0.05$). There was a strong positive relationship between Li and Mn, Cu, Zn, Cd, Pb, Hg ($p < 0.01$) and Co, Ni ($p < 0.05$). Metal(loid)s leaching tends to decrease with increasing recirculation, pH value and landfill age. The results of this study showed that humic acid at pH 4 increased the release of metals, thus raising its availability and recovery rate in landfill leachate.

Table 5.5. Correlations coefficients for metals and recirculation cycle, pH and humic acid for [young/ old] landfill leachate recirculation samples

	Li (%)	Al (%)	Cr (%)	Mn (%)	Co (%)	Ni (%)
Recirculation	-0.18	-0.40^{*}	-0.29^{*}	-0.19	-0.40^{**}	-0.45^{**}
Humic acid	-0.28^{*}	0.55^{**}	0.45^{**}	-0.12	0.52^{**}	0.46^{**}
pH	-0.11	-0.51^{**}	-0.37^{**}	-0.11	-0.52^{**}	-0.56^{**}
Age	-0.56^{**}	-0.18	-0.28	-0.23	-0.49^{**}	-0.64^{**}
	Cu (%)	Zn (%)	As (%)	Cd (%)	Pb (%)	Hg (%)
Recirculation	-0.48^{**}	-0.36^{**}	-0.41^{**}	-0.37^{**}	-0.39^{**}	-0.29^{*}
Humic acid	0.24^{*}	0.38^{**}	0.58^{**}	0.49^{**}	0.51^{**}	-0.12
pH	-0.56^{**}	-0.49^{**}	-0.53^{**}	-0.38^{**}	-0.51^{**}	-0.30^{**}
Age	-0.64^{**}	-0.62^{**}	-0.21	-0.49^{**}	-0.40^{**}	-0.14

**. Correlation is significant at the 0.01 level
*. Correlation is significant at the 0.05 level

5.3.3 Chemical characteristics and FTIR Spectra of humic acid

Adsorption coefficient at 280 nm (E280) and the ratio of absorption coefficients at 465 and 665 nm (E4/E6) were measured in this study (Fig. 5.7). There was a strong relationship between humic acid and E280 and E4/E6 ($p < 0.01$). It indicates that as humic acid increases, E280 decreases and E4/E6 increases but showed no clear trend with landfilling age. It implies that with increasing humic acid, the aromaticity of the samples becomes higher (Kang et al., 2002).

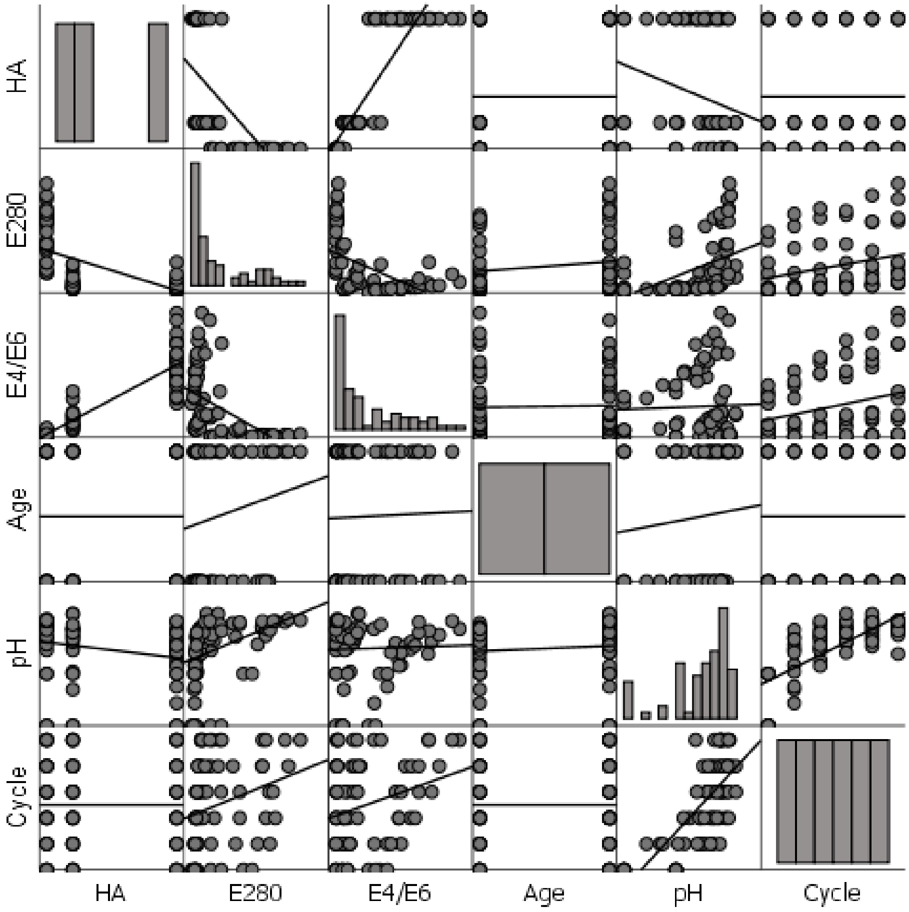


Figure 5.6. Draftsman's plot resenting the relationship between HA (mg/L), E280, E4/E6, age, pH and recirculation cycle

Fig. 5.8 is the FTIR spectra of leachate samples that give information about specific molecular structures and various functional groups, as well as for studies of interactions between humic acid and metals (Schnitzer and Khan, 1972). Different functional groups can be identified from characteristic peaks by FTIR peaks. The leachate's spectral features indicated that the leachate's aromatic character was in the order of HA 0.5% > HA 0.1% > HA 0%. This result is in agreement with humic acid characteristics.

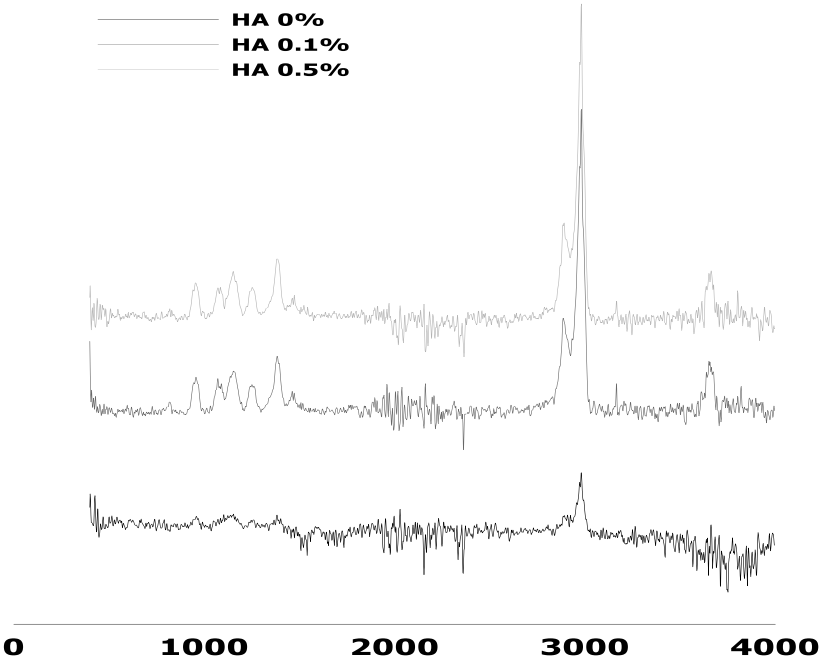


Figure 5.7. FTIR spectra peak in landfill leachate which was assigned to a stretching frequency of H_2O molecule coordinated metal ions and methyl group (CH stretching), following the humic acid concentration (0, 0.1, 0.5 %)

All spectra in different concentration of HA were similar. Adsorption bands observed at the wavelengths of 3751 cm^{-1} (H_2O stretching), 3533 cm^{-1} (N-H stretching), 3355 cm^{-1} (O-H stretching), 2981 cm^{-1} (C-H stretching), 2359 cm^{-1} (C-O stretching), 2029 cm^{-1} (Aromatics), 1682 cm^{-1} (C=O stretching), 1623 cm^{-1} (C-O stretching), 1107 cm^{-1} (C-O stretching) and 668 cm^{-1} (C-S stretching). The observed intense peaks indicate the existence of carboxylic. The presence of groups near the COOH group of a carboxylic acid affects the acidity, which increases metal mobility.

Leachate with humic acid has stronger aliphatic bands, carboxylic groups and aromatics. However, the strengths of the bands, which give differences in the relative distribution of each functional group, have some differences. The main metals binding sites of humic substances include the carboxylic acid site (Sawalha et al., 2007; Qu et al., 2008). Therefore, the high content of humic acid increases metal recovery as the acidity of the carboxylic acid is strong.

5.4 Conclusion

The effect of humic acid on metal recovery in landfill leachate was investigated in this chapter. It showed certain influence increasing metal recovery in landfill leachate. The recovery rates using humic acid 0.1% from young landfill leachate are following: Cd > Al > Zn > Li > Pb > Ni > Cr > Co > Hg > Cu > Mn > As for pH 4, Hg > Pb > Al > As > Cr > Cd > Ni > Li > Zn > Cu > Co > Mn for pH 6. The recovery rates using humic acid 0.5% from young landfill leachate are following: As > Al > Cr > Pb > Co > Hg > Zn > Cu > Cd > Mn > Ni > Li for pH 4, Hg > As > Al > Co > Cd > Zn > Cu > Pb > Ni > Cr > Mn > Li for pH 6. The recovery rates using humic acid 0.1% from old landfill leachate are following: Al > Pb > As > Ni > Cr > Cu > Co > Zn > Cd > Mn > Li > Hg for pH 4, Al > Cr > As > Cd > Co > Pb > Mn > Ni > Cu > Zn > Li > Hg for pH 6. The recovery rates using humic acid 0.5% from old landfill leachate are following: Al > Cr > Pb > As > Ni > Co > Mn > Hg > Li > Cu > Zn > Cd for pH 4, Al > As > Cr > Cd > Co > Pb > Ni > Cu > Zn > Li > Hg > Mn for pH 6. Recovering metals using humic acid is a sustainable method, which can help on saving costs and reduce adverse effects on the environment. This will provide a better understanding of organometallic chemistry contribution to enhanced landfill mining for recovering metals in landfills.

6 Conclusion and recommendation for future works

This chapter aims to summarise all the findings from the project and highlight the opportunity to effectively recover metals.

6.1 Overview

The overall aim of this research project was to provide a mechanistic understanding of the biochemical and organometallic chemical processes influencing metal(loid)s mobility and recovery from municipal solid waste landfill sites. Specifically, this PhD research investigated the effect of pH, leachate recirculation and humic acid on the metal(loid)s mobility and their recovery rate from landfill environments. The practical and economically viable processing strategy was required to recover metals.

The aim and objectives of this thesis are stated in Chapter 1. These thesis findings are presented according to the objectives in order to answer the hypothesis.

The literature review in Chapter 2 provided a systematic review of the critical factors and environmental conditions that influence the behaviour of metals within the landfilled waste and synthesis of how these may affect leachate recirculation efficiency for recovery in the context of a range of opportunities and challenges facing circular economy practitioners. The numerous factors influence metal release, which will help overcome the limitation of metal recovery from landfill leachate, which is the low concentration of metals. There have been numerous studies in the literature that pH, organic matter, landfill age, and leachate recirculation significantly increase or delay the metal release.

Therefore, Chapter 3 (batch test) describes the leaching of metal(loid)s under various pH value and identifies the relationship between pH and humic acid at three different depths of closed MSW landfill site. The results showed that the release amount of Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg are in the range of 0.03-0.14 mg/L, 0.65-83.33 mg/L, 0.01-0.19 mg/L, 0.18-18.17 mg/L, 0.01-0.09 mg/L, 0.06-0.38 mg/L, 0.12-5.2 mg/L, 0.14-11.57 mg/L, 0.02-0.10

mg/L, 0.00-26.17 mg/L, 0.03-25.17 mg/L, and 0.00-0.01 mg/L with deionised water as leachant at different pH. The release amount of HA was relatively increased from 0 to 2% in 48-55m compared to 3-9 m in the MSW landfill. HA can promote the leaching rate of metals with an appropriate amount. Based on the study results, the optimal condition of leaching metals was pH 2, and HA 28 mg/L at less than 10 m depth. The high concentration of metals in landfill leachate may be enhanced to effectively recover metals as the critical challenge of recovering metals from leachate is the low concentration of metals. Thus, the information can be useful for economically feasible in the recovery of metals.

Previous studies described that the operation with leachate recirculation could enhance the decomposition of the MSW and speed up the stabilisation, which indicates leachate recirculation directly affect COD, TOC, VFAs. As organic matter is highly related to metal release, the leachate recirculation impact on COD, TOC, VFAs, metals, redox potential was conducted under pH values 4 and 6 according to Chapter 3 results (A column percolation test). The results showed that the metal(loid)s recovery rate of Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb and Hg increased in the range of 101.19-109.47%, 33.24-94.12%, 12.66-100.94%, 101.70-104.17%, 97.94-170.94%, 103.10-201.26%, 106.71-166.18%, 61.33-104.21%, 67.55-110.33%, 104.72-153.59%, 90.13-130.04% and 90.28-96.07% at the first recirculation cycle. The mobilisation of metal(loid)s in landfill leachate was affected by high organic content, low redox potential, and pH. The fluctuation of Zn concentration was similar to that of Mn. These results help understand metal mobility in landfills, which could provide insights for economically feasible metals recovery. The initial rates of metal(loid)s may be enhanced by recycling the leachate back to the column; therefore, the first leachate recirculation could effectively recover metals as they release metals in landfills.

As the landfill passes the humic phase, it is possible that the mobility of metals will alter due to changes in the biological, chemical and physical conditions in the landfill. The optimum conditions and recirculation cycle determined from Chapter 5 were applied to a range of humic acid (0%, 0.1% and 0.5%) concentration and pH value (4 and 6) with leachate recirculation. Positive correlation between pH and humic acid was observed, and strong negative correlation between humic acid and redox and landfill age. The recovery rate of metals increased with increasing humic acid, decreasing landfill age, redox potential at the first cycle of leachate recirculation. The aromaticity of leachate become higher as landfill age increased. The recovery rates using humic acid 0.1% from young landfill leachate are following: Cd > Al > Zn > Li > Pb > Ni > Cr > Co > Hg > Cu > Mn > As for pH 4, Hg > Pb > Al > As > Cr > Cd > Ni > Li > Zn > Cu > Co > Mn for pH 6. The recovery rates using humic acid 0.5% from young landfill leachate are following: As > Al > Cr > Pb > Co > Hg > Zn > Cu > Cd > Mn > Ni > Li for pH 4, Hg > As > Al > Co > Cd > Zn > Cu > Pb > Ni > Cr > Mn > Li for pH 6. The recovery rates using humic acid 0.1% from old landfill leachate are following: Al > Pb > As > Ni > Cr > Cu > Co > Zn > Cd > Mn > Li > Hg for pH 4, Al > Cr > As > Cd > Co > Pb > Mn > Ni > Cu > Zn > Li > Hg for pH 6. The recovery rates using humic acid 0.5% from old landfill leachate are following: Al > Cr > Pb > As > Ni > Co > Mn > Hg > Li > Cu > Zn > Cd for pH 4, Al > As > Cr > Cd > Co > Pb > Ni > Cu > Zn > Li > Hg > Mn for pH 6.

Different types of waste contain different REE, critical and valuable metals in significant concentrations. Leaching and selective recovery of the metal(loid)s the best solution to meet the growing critical raw materials demands and also to reduce the environmental impacts caused by metals in the environment. The metal recovery is challenging to make it economically feasible to reuse as secondary raw materials because the metal concentration is relatively low. This study addressed the recovery of metals in the landfill leachates and investigated the influences of depths, pH, age and humid acid concentrations with leachate recirculation on the final recovery. Based on the investigation, the leached metal(loid)s concentration by 0.5% humic acid in weak acid and near-neutral pH tend to increase at the initial recirculation cycle. Eco-friendly leaching using humic acid results in metals in treated leachate and hence is safe from the ecological point of view for landfills. However, only looking at the metal recovering is insufficient as it requires some processing before it can be utilised. Hence, an effort needs to make to incorporate the application of the technologies in the field of waste-to-energy, metal recovering and circular economy. Also, as the landfill progresses, the pH rises to nearly 10, it is considered that the retained leachate in the site reaches its buffering capacity limit. In order to control of pH at full scale, it is crucial to consider number of factors, including moisture, temperature, and bacteria. However, these factors can be unpredictable, the ability of acid to lower a soil's pH can take several months. Therefore, it should be noted that primary laboratory data was used in the scale-up calculation and to the greatest extent possible.

The recovery of a smaller concentration of metal in leachate is a major concern for the industry as well as for the environment. Hence, increasing concentration to over 1 mg/L is critical to overcoming the processing challenges and costs. This thesis introduces to determine possible contamination migration pathways from closed landfill sites by understanding the processes that occur in landfill environments in the lab and semi-scale. Therefore, it will enhance the concentrations of metals to the minimum level to make metals recoverable from leachate and provide a base in the scale-up calculation

6.2 Limitations of the research

There are several limitations to the research project presented within this thesis.

- The waste composition was not consistent for the samples. For this reason, it was not possible to precisely compare the recovering rate of metals between different age landfills. Samples from different ages of the same waste composition could be analysed, emphasising ageing effects on metal recovery. However, Landfills are heterogeneous, which present different characteristics of samples (Chapter 3, 4, and 5).
- The toxicity of compounds may increase in acidic pH conditions and decrease growth in biological (Chapter 3).
- The analysis for humic-metal complexation was not extended for each metal type identified and has not been thoroughly investigated. Whilst a humic concentration effect on metal release and chemical characteristics of humic acid was investigated (Chapter 5).

- Replicate that the experiment and analysis could be more accurate. Due to the small amount of samples and time limitation, the column percolation test could not replicate and perform longer. However, Chapters 4 and 5 show that metals retain in the landfills after 4 leachate recirculation cycles, thus not much leached out.
- The odour problems in landfill environments are linked to the low pH conditions.
- Many uncertainties exist which are not incorporated at full-scale, such as macro-economic factors, metal price volatility, and costs associated with the operation of the recovery process.

6.3 Further works

The leachate recirculation with adding humic acid can be employed in modern landfills by taking the valuable metals and delaying the pollution. Regarding the green approach for metal recovery, further works is required to perform in a full-scale to implement the methodology at industrial.

- An investigation into the rare earth elements in the long-term test method would find out the real cost of recovering metals and economically viable.
- A pre-treatment of leachate before the leaching process should be studied to evaluate
- A comparison and analysis of the complexations with metals o fulvic and humic acids from landfill leachate at alkaline conditions as fulvic-metals complexes is relatively high.
- The method of measuring complexation using Amberlite XAD-7 resin or DAX-8 and extracting humic acid in leachate should be investigated to characterise humic substances extracted from various landfill environments.
- Perform pilot bioreactor to convert industrial waste carbon to VFAs, increasing metal release and reduce carbon dioxide.

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APPENDICES

Appendices A present the appendices date of chapter 3.

Appendices B present the appendices date of chapter 5.

Journal papers

Appendices C – Influence of pH, depth and humic acid on metal and metalloids recovery from municipal solid waste landfills, Science of The Total Environment, https://doi.org/10.1016/j.scitotenv.2021.150332

Appendix A Chapter 2

Table A.1 Organic compounds which influence on elements behaviour often found in landfill leachate (adapted from Fischer et al. (1997), Paxéus (2000), Staley et al. (2006), and Zhang and Zhang (2009))

Chemical group	Compound name
Carboxylic acids	2-hydroxyethanoic acid, 2,2-dihydroxypropanedioic acid, 3-methylacrylic acid, Prop-1-ene-1,2,3-tricarboxylic acid, Benzenecarboxylic acid, Benzene-1,2-dicarboxylic acid, Benzene-1,3,5-tricarboxylic acid, Tridecanoic acid (tridecylic acid), Hexadecanoic acid (palmitic acid), Hexacosanoic acid, methanoic acid, ethanoic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, Nonanoic acid, decanoic acid, Undecanoic acid, Dodecanoic acid, Tridecylic acid, 1-tetradecanoic acid (myristic acid), Pentadecylic acid, Palmitic acid, Heptadecanoic acid (margaric acid), Octadecanoic acid (stearic acid), Nonadecylic acid, Arachidic acid
Alcohols	Methanol, Ethanol, Propan-2-ol, Butan-1-ol, Pentan-1-ol2, Hexadecan-1-ol, Ethane-1,2-diol, Propane-1,2-diol, Propane-1,2,3-triol, Butane-1,2,3,4-tetraol, Pentane-1,2,3,4,5-pentol, hexane-1,2,3,4,5,6-hexol, Heptane-1,2,3,4,5,6,7-heptol, Prop-2-ene-1-ol, 3,7-Dimethylocta-2,6-dien-1-ol, Prop-2-yn-1-ol, Cyclohexane-1,2,3,4,5,6-hexol, Cyclohexane-1,2,3,4,5,6-hexol, 5-Methyl-2-(propan-2-yl)cyclohexan-1-ol, Phenols, trimethyl, Phenols, butyl, Phenols, bis, Phenol, 4, Phenols, tri-chloro, Phenol, penta-chloro

Amines	Aspartic acid, Threonine, Serine, Glutamic acid, Glycine, Alanine, Valine, Methionine, Isoleucine, Leucine, Tyrosine, Phenylalanine, Lysine, Histidine, Arginine, methylamine , 4-methoxyaniline, dimethylamine, trimethylamine, 4-Nitroaniline, N-Dimethylaniline
Heterocycles	Benzothiazole, 1,3-Benzodioxole, Benzene, Polychlorinated dioxins, Polychlorinated furans, Pyridine, Pentazole, Indole, Quinoline, Isoquinoline, 2-Methyl quinolone, 2,4(1H,3H)-Pyrimidinedione, Thiazole, Oxazole, Diazine

Table A.2 Leachate recirculation impact on landfill environments

Characteristics of sample	Scale	Recirculation method	Effects	Limitations	Reference
Synthetic solid waste shredded and compacted	Lab	·PVC pipe columns ·Periodically added 1 L of tap water ·Recirculated one to four times per week	·Frequent recirculation with pH control provided the highest degree of waste stabilization. ·The leachate recirculation increased methane gas concentrations	·Practical problems in the sites to operate with frequent recirculation; clogging, flooding, and precipitation.	San and Onay, 2001
Loose fresh waste mixed with and 8 years old compacted waste	Lab	·PVC columns ·Flow rate set to obtain a final waste moisture content of 42% ·The columns were saturated with tap water mixed with sewage sludge	·1.8 times more oxidizable matter released through recirculation in the leachate. ·Leachate recirculation reduced the time necessary to reach the methanogenesis phase, but only for fresh waste.	·Leachate recirculation can lead to the inhibition of methanogenesis due to volatile fatty acids or ammonia nitrogen accumulation. · Recirculation may maintain inevitable residual contamination within the waste.	Francois et al., 2007
MSW co-disposed and MSW incinerators bottom ash from the	Lab	·Reactor (W: 287 mm H: 1000 mm) ·Two inlet/outlet ports at the top of the lid ·The moisture content of the	·The pH increased from days 1 to 22. Once the pH value increased to 7.5, remained relatively steady afterwards. ·The concentration of Cu in the leachate with recirculation	·Metals leaching is controlled by the organic matter and pH value, but the pH value and organic matter were not handled in this study. ·The vague explanation for the	Yao et al., 2014

transport station (China)		samples was adjusted to 75% ·After samplin100 ml tap water added	tends to decrease, which is generally consistent with previous reports (Lo et al., 2009; Long et al., 2010). ·The concentration of Zn in leachate was generally lower due to the leachate recirculation.	mechanism between metals and organic matter.	
Raw MSW from the transport station	Lab	·Polypropylene ·The moisture content of the samples was adjusted to 75%	·The cumulative amount of leached Zn decreased and then maintained a stable level with leachate recirculation. ·Leachate recirculation can immobilize Zn release in landfills.	·It is difficult to evaluate the effects of leachate recirculation on the release of metals, as it investigated the specific release of Zn.	Hu and Long, 2019
Mixture of domestic waste (75-95% of organic waste)	Lab	·Cylindrical (W: 30 cm H: 100 cm) ·Temperature 35°C ·The recirculation rate set 30% of the reactor volume	·The high recirculation rate affected the COD concentrations negatively. ·High recirculation rate may deplete the buffering capacity. ·High recirculation rate may occur acidic conditions. ·Leachate recirculation reduces in organic matter, waste quantity and waste volume.	·The composition of the sample is biased on organic waste. ·The composition of samples does not present general waste composition. ·The acidic condition effects on metal release in landfill leachate.	Sponza and Agdag, 2004

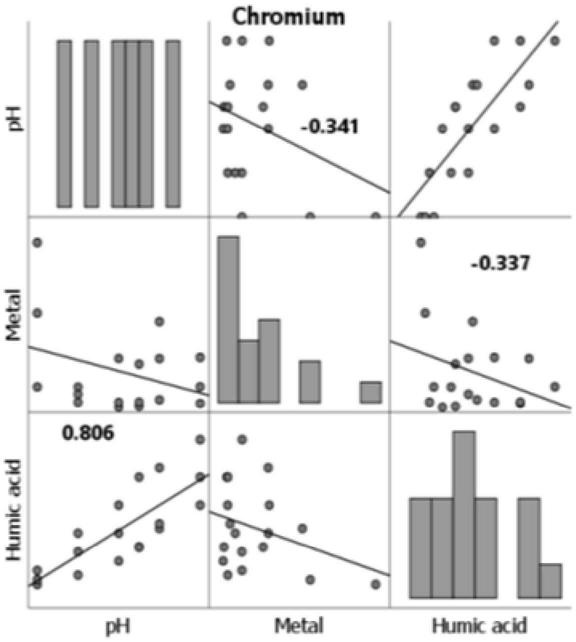
Daily municipal waste which is regarded as representative of typical waste in the landfill	Lab	·343 L cubic cell ·Temperature 22°C. ·12 L deionized water ·Flow rate: 8 L/d ·Added deionized water to maintain 5 L of leachate in leachate tank	·The initial pH value was 8.35, but after 65 days it had dropped, then increased to 8.1 and remained almost constant until the end of the experiment. ·Heavy metal was dissolution into the water phase at the beginning of the experiment due to the leachate recirculation. ·During the above period, heavy metals solubility increases.	·The lab-scale experiment does not represent the conditions that occur in old landfills. ·It was rapidly produced microbial activity by the heat. ·The temperature should be a representative dynamic of landfills.	Giannis et al., 2008
The MSW which is configured to simulate the composition of MSW in Singapore	Pilot	·A FRP tank (W: 2 m H: 4 m) ·Temperature 40°C. · Cycle time : 12 h	·The stabilization of the landfill cell was very fast with the low leachate recirculation rate. ·Leachate recirculation improved the microbial activity and the solubilization of organics in the landfill cell.	·The sample is not reflected in the typical waste in the landfill. ·Limited leachate recirculation conditions to the waste matrix ·Exploitation and fire risks according to high temperatures	Huang et al., 2016
Daily municipal waste	Pilot	·Concrete structure ·10 kg sewage sludge added to the influent leachate	·Ammonia nitrogen, phosphorus can be accumulated in the effluent leachate.	·A higher leachate recirculation rate may wash out large amounts of organic matter before the methanogenic phase of the	Jiang et al., 2007

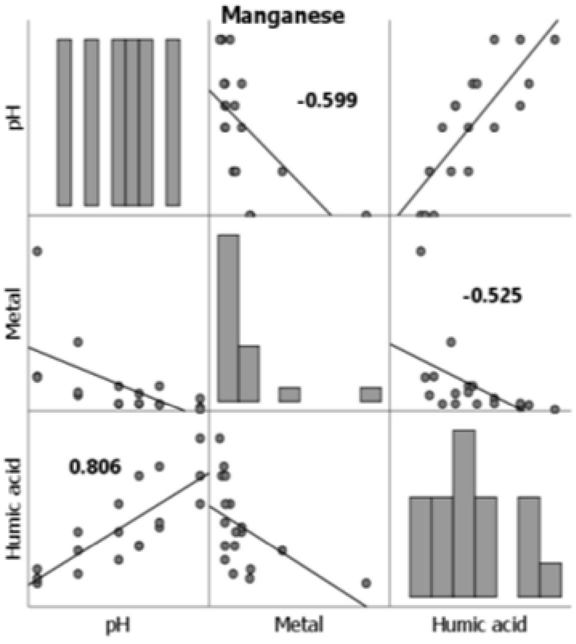
			·A higher rate of leachate recirculation can accelerate solid waste degradation, landfill stabilization and landfill gas generation.	waste, thereby, reducing the biological methane potential.	
Typical MSW	Pilot	·Hexagonal Lucite tanks (W: 0.71 m H: 0.55 m) ·Flow rate: 20 mL/min ·Replaced water to maintain 3 L	·Increased the rates of settling and stabilization ·Produce more environmentally benign leachate.	·Complex operation and management ·Energy consumption for forced aeration	Borglin et al., 2004
Sanitary landfill waste in Istanbul city	Lab	·Polypropylene (W : 50 cm H: 200 cm) ·Total 29.4 to 35 L of leachate recirculated within the landfill reactor	·Leachate recirculation increases the degradation rates and the pH reaches to neutral values earlier with leachate recirculation.	·It has not conducted to investigate the interaction between biodegradation of organic and migration of metals, and did not consider other pathways for metal migration in landfills exist	Bilgili et al., 2007
Household wastes	Field	·Recirculated using the sequencing batch reactor leachate ·0.25 m^3 per cycle	·Ammonium was converted into nitrate. ·Although biodegradable COD was rare, the bioreactor had high and stable denitrification rates.	·pH and temperature were held by force. ·Require a long accumulation time. ·Methanogenesis is inhibited by nitrogen-oxides.	Chung et al., 2015
Industrial waste from a	Lab	·Investigated the metal recovering	·The concentrations of leaching metals increased	·The solution for recirculation pH value was 0.5, which is not	Rivas et al., 2019

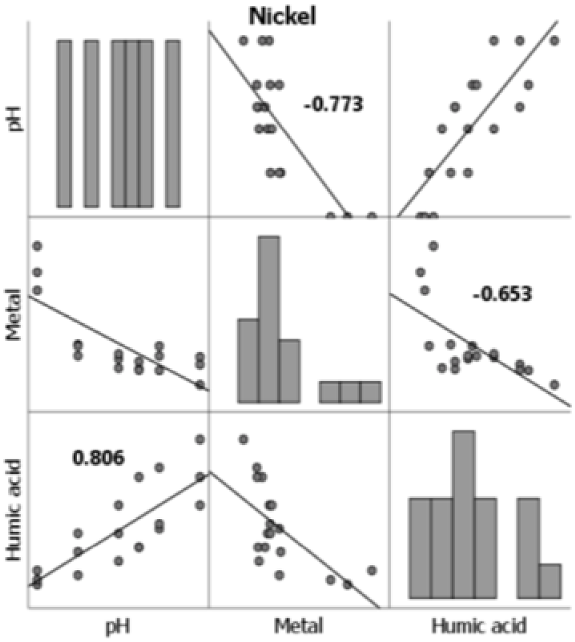
coal-fired power plant		from solid waste derived from decommissioning coal-fired power plant with the acid leaching solution.	with acidification due to the decomposition of sample structure at strongly low pH is produced. ·The leaching process with recirculation was fast.	reflected in the practical procedure.	

Appendix B Chapter 3

Figure B.2 Draftsman's plot resenting the relationship between waste depth (m), pH, metal (mg/L) and HA (mg/L)



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Metal
Humic acid
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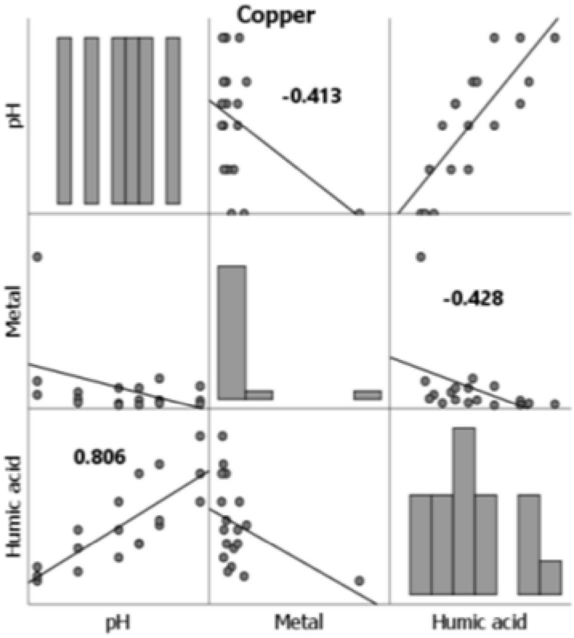
pH
Metal
Humic acid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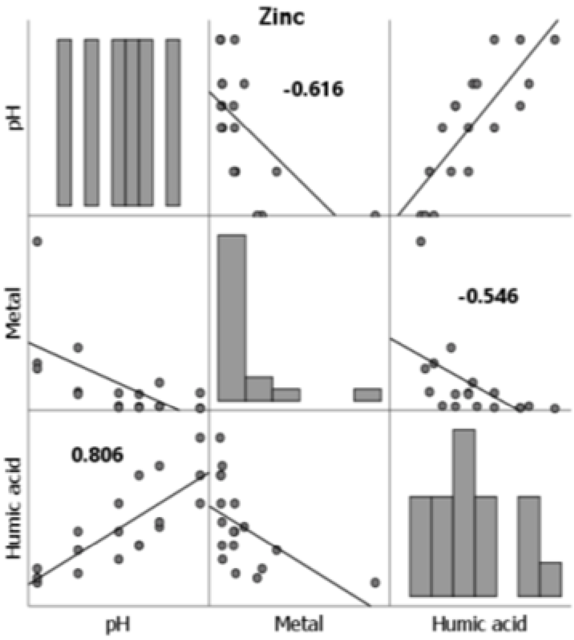
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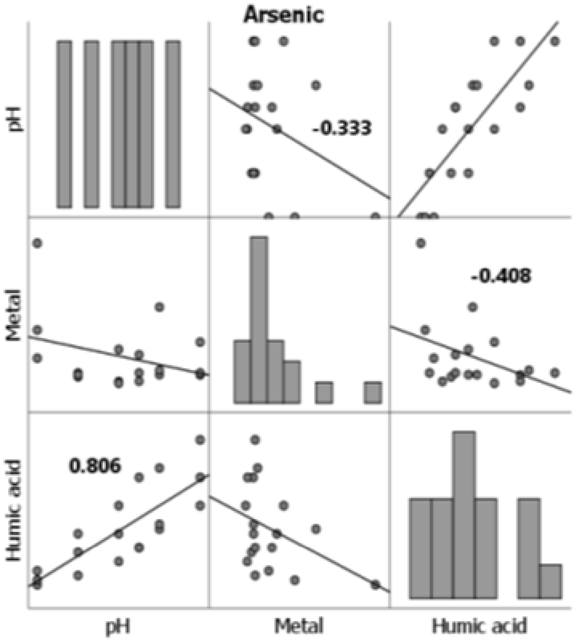
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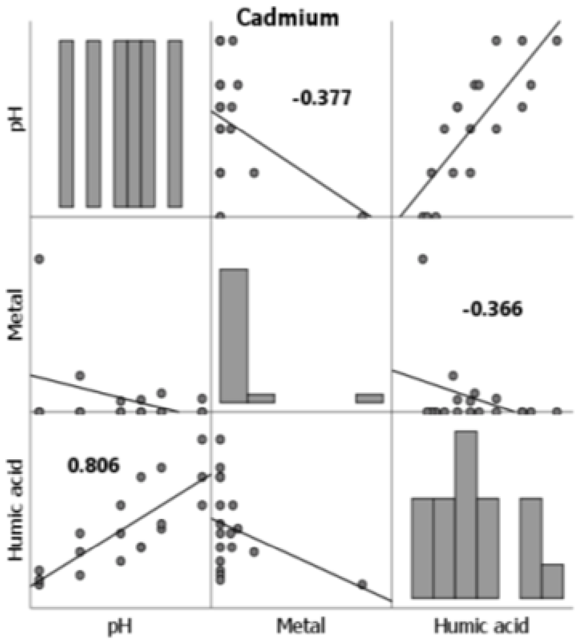
Humic acid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Metal
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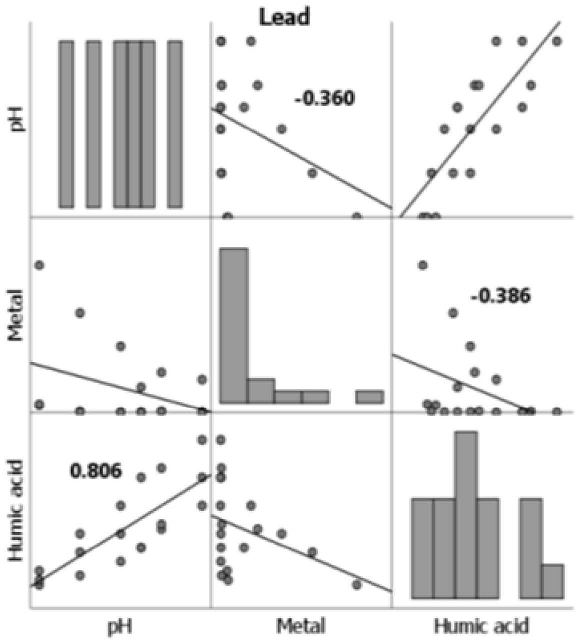
pH
Metal
Humic acid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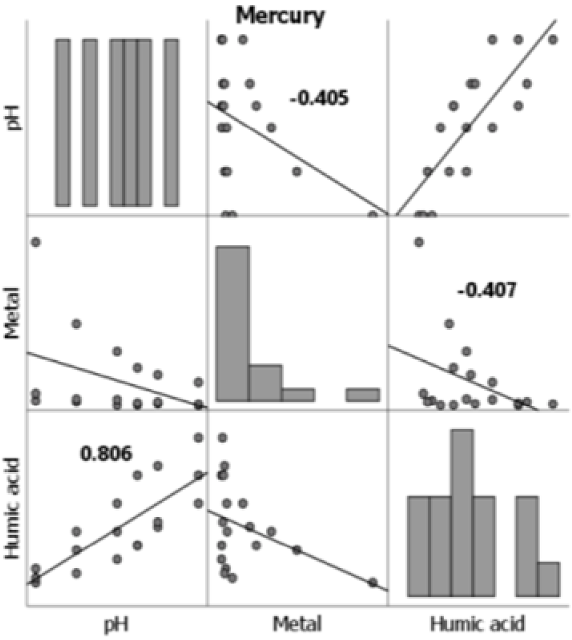
Humic acid
pH
Metal
Humic acid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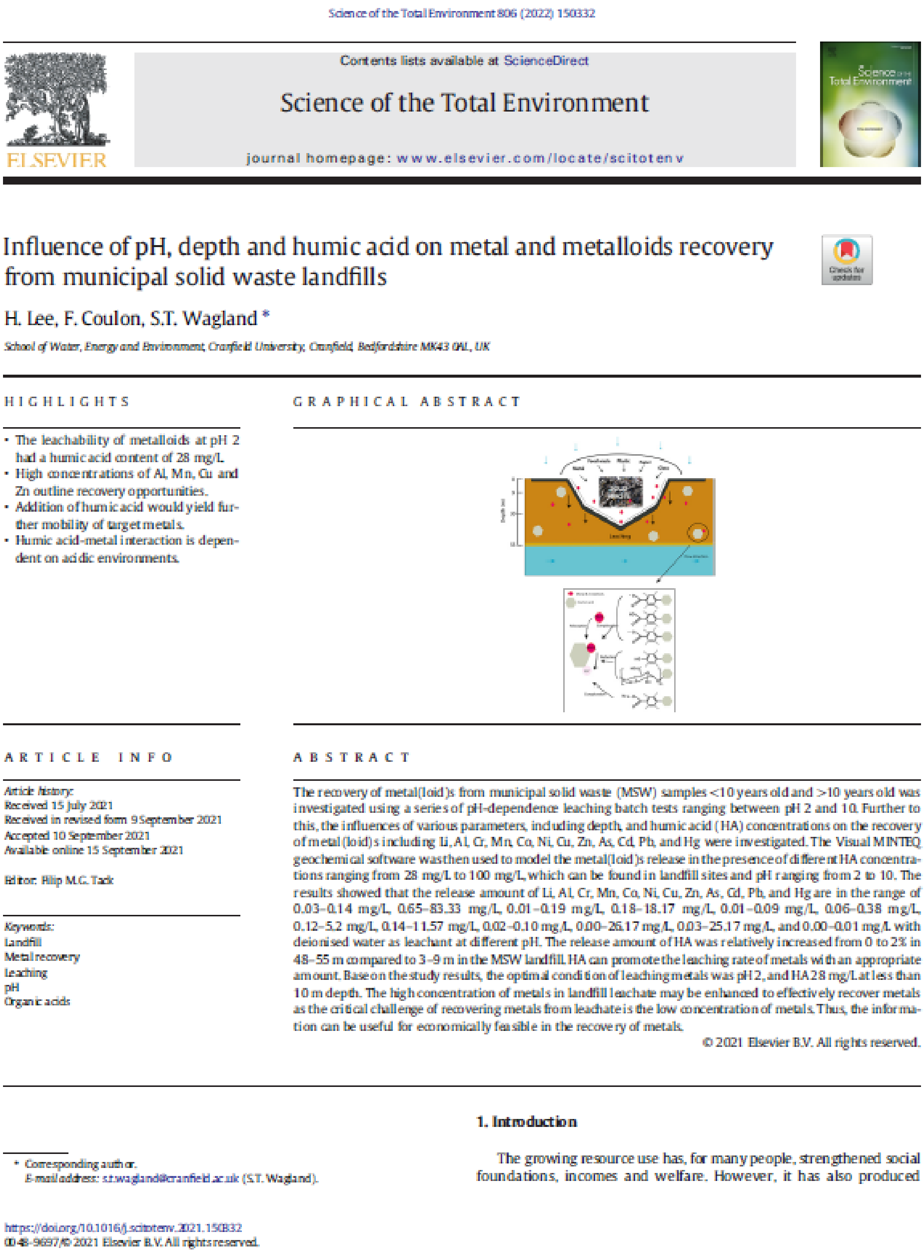
Metal
Humic acid

Appendix C (2022) Influence of pH, depth and humic acid on metal and metalloids recovery from municipal solid waste landfills. Science of The Total Environment, 806.



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Influence of pH, depth and humic acid on metal and metalloids recovery from municipal solid waste landfills

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HIGHLIGHTS

- The leachability of metalloids at pH 2 had a humic acid content of 28 mg/L.
- High concentrations of Al, Mn, Cu and Zn outline recovery opportunities.
- Addition of humic acid would yield further mobility of target metals.
- Humic acid-metal interaction is dependent on acidic environments.

GRAPHICAL ABSTRACT

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ABSTRACT

The recovery of metal(loid)s from municipal solid waste (MSW) samples <10 years old and >10 years old was investigated using a series of pH-dependence leaching batch tests ranging between pH 2 and 10. Further to this, the influences of various parameters, including depth, and humic acid (HA) concentrations on the recovery of metal(loid)s including Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg were investigated. The Visual MINTEQ geochemical software was then used to model the metal(loid)s release in the presence of different HA concentrations ranging from 28 mg/L to 100 mg/L, which can be found in landfill sites and pH ranging from 2 to 10. The results showed that the release amount of Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg are in the range of 0.03–0.14 mg/L, 0.65–83.33 mg/L, 0.01–0.19 mg/L, 0.18–18.17 mg/L, 0.01–0.09 mg/L, 0.06–0.38 mg/L, 0.12–5.2 mg/L, 0.14–11.57 mg/L, 0.02–0.10 mg/L, 0.00–26.17 mg/L, 0.03–25.17 mg/L, and 0.00–0.01 mg/L with deionised water as leachant at different pH. The release amount of HA was relatively increased from 0 to 2% in 48–55 m compared to 3–9 m in the MSW landfill. HA can promote the leaching rate of metals with an appropriate amount. Base on the study results, the optimal condition of leaching metals was pH 2, and HA 28 mg/L at less than 10 m depth. The high concentration of metals in landfill leachate may be enhanced to effectively recover metals as the critical challenge of recovering metals from leachate is the low concentration of metals. Thus, the information can be useful for economically feasible in the recovery of metals.

1. Introduction

The growing resource use has, for many people, strengthened social foundations, incomes and welfare. However, it has also produced

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negative effects; the world faces resource shortages. To provide the necessary resources to meet demand (European Commission, 2010), the transition towards resource-efficiency is required. The global demand for metals has accelerated to an extent where it is widely considered a threat to economical and societal functioning (Watari et al., 2021). Therefore, waste management recently moves towards a Circular Economy by recycling pre-consumer manufacturing scrap/residues and End-of-Life products (European Commission, 2018). Reduction and re-use are the most effective ways to save natural resources, and as the UK's recycling rate has increased from 44.5% in 2015 to 45.5% in 2020 (DEFRA, 2020), there has been a gradual decrease in the amount of waste sent to landfills. Nevertheless, the total amount of waste has been showing consistent growth (DEFRA, 2020). Therefore, turning waste into a resource is a crucial key to a circular economy.

Landfills are still a major route for waste disposal throughout the world. It has been estimated there are around 500,000 landfill sites across Europe (EURELCO, 2016) and approximately 22,000 historic landfill sites in the UK, of which 90% were closed before 1996 (Wagland et al., 2019). Landfills contain substantial amounts of materials, including metals, thus being a new potential resource base that can become part of the Circular Economy (Wagland et al., 2019). Metal(loid)s are an irreplaceable component, used in various technological applications such as mobile devices, computers, vehicles and medical technologies. Therefore, sustainable supply of metals is essential. Ensuring supply from secondary raw materials, reducing reliance on raw material supply, is undoubtedly part of a resilient and circular economy. Enhanced landfill mining (ELFM) is a potential approach to meeting expected global demand of metals by mining disposal of metals. Krook et al. (2012) define landfill mining as "a process for extracting materials or other solid natural resources from waste materials that previously have been disposed of by burying them in the ground." However, it is mainly to remediate the site, and its success and practice in materials recovery have been limited by economic infeasibility and the performance of technology, i.e., what quality levels (Krook et al., 2012; Wagner and Raymond, 2015). The concept of ELFM, which started to develop in 2008 (Jones et al., 2013; Canopoli et al., 2018), focuses on maximising the valorisation of waste as materials (WDM) and energy (WtE), which supports sustainable materials management by recovering and recycling of waste generated through the creating of the consumer product (Jones et al., 2013). However, there is uncertainty regarding the economic feasibility and environmental consequences of ELFM (Pastre et al., 2018).

In-situ landfill mining could enable the recovery of metals without excavation through the recovery of metals from landfill leachate (Kurniawan et al., 2021). Challenges remain in recovering metals to high efficiency and yield. A primary challenge for metal(loid)s recovery from leachate is the low concentration of many metals influenced by several factors such as landfill age, type and pH. The critical factors that affect the leachability of heavy metals are pH and chemical mechanisms such as precipitation, adsorption and ion-exchange and biological processes such as microbiomes which can dissolve metals (Dijkstra et al., 2004; Saveyn et al., 2014; Gutiérrez-Gutiérrez et al., 2015; Gu et al., 2018; Roy et al., 2021). The sorption characteristics of metals in landfills are important with recovering metals from landfills, and the presence of organic matter influences this sorption process (Spark et al., 1997; Sapsford et al., 2017). Natural organic matter in landfills originates from food, wood, paper, yard trimmings. Natural organic matters in landfills are converted to humic substances (HS) via humification (Mallick, 2017). Organic matter is biodegradable in the leachate at the early stage of landfills and becomes non-biodegradable at the late stage of landfills such as HA. Thus, HS are the main organic compounds in landfill leachate, and HA represents the most active HS fraction (Zhou et al., 2015). It is widely recognised that humic acid [HA] affects metal speciation behaviour (Qu et al., 2019), solubilisation and adsorption of hydrophobic pollutants, mineral growth and dissolution, redox behaviour in soil (Scott et al., 1998; Liu et al., 2018; Qu et al., 2019). Therefore, knowledge about HA's roles and interactions with pH is essential for recovering metals from landfill environments. Several studies have investigated the characterisation of HA in landfill leachate and distribution of heavy metals with HA (Bozkurt et al., 1999; Boruvka and Drábek, 2004; Klavins et al., 2006; Gutiérrez-Gutiérrez et al., 2015). However, information about HA's interaction, heavy metals, and pH in landfill environments is still insufficient. Thus, this study aims to investigate the leaching characteristics of major metals in landfill environments under the influence of pH changes using the batch leaching technique. The recovery should target valuable metal(loid)s that have relatively higher concentrations in landfill environments or be extensively used in our life or listed as critical raw materials. In this work, 12 metal(loid)s including Lithium and Cobalt, which are critical raw materials and strategically important for the European economy but have a high risk associated with their supply (Blengini et al., 2020), were selected to investigate the metal release performance and correlation of HA with metals from the MSW in different pH and depth. Visual MINTEQ software was used to explain pH-dependent leaching characteristics of metals and predict HA effects on metal mobility.

2. Materials and methods

2.1. Sample collection and preparation

A total of thirty drilled municipal solid waste (MSW) core samples were collected from four MSW landfills located in the UK at depths between 3 and 55 m. Different cores were drilled vertically across the landfill area, and samples were taken by a specialised private company hired by the landfill sites operator (Table 1). The samples were stored in a cold room at 4 °C until analysis. The samples sorted manually into metal, paper, textile, wood, glass and other materials, and weighed.

2.2. Leaching tests

The batch leaching tests were carried out following BS EN 12457:2002. Briefly, 50 g of composite waste sample was mixed with 500 mL deionised waste to evaluate the level of metals release from the waste in a wide range of pH values in the controlled site. Before

Table 1
Waste composition of the samples collected from the studied landfill site (Canopoli et al., 2020).

	Samples no.	Depth (m)	Years	pH	Waste sample (g)	Paper/cardboard (g)	Metals (g)	Glass/ceramic (g)	Textile (g)	Wood (g)	Soil/fine fraction (g)	Other (g)
	2	3–9	<10		11,561	2493	356	69	1463	1776	3647	1757
Average				7.43	5781	1247	178	35	732	888	1824	879
SD				0.03	2148	1511	215	49	895	505	2013	241
	3	23–30.5	>10		12,762	1405	768	21	569	1092	6490	2417
Average				7.58	4254	468	256	7	190	364	2163	806
SD				0.02	1338	366	373	8	329	283	1628	571
	3	48–55	>10		12,892	1148	245	151	331	1321	5147	4549
Average				7.64	4297	383	82	50	110	440	1716	1516
SD				0.03	2264	491	93	35	98	294	1426	971

the leaching test, the samples were ground to a size of <1.5 mm using a Retsch SM 2000 grinder. The analysis was carried out for six pH values; 2, 4, 6, 7, 8, 10. The pH was adjusted using 1.8 M nitric acid solution or 1 M sodium hydroxide solution. All leaching tests were made in duplicates. The tests were conducted in 1500 mL cylindrical jars with ribbed cap. The experiments were performed with liquid-to-solid ratio 10:1, which represents typical field conditions (Bestgen et al., 2016) (L/S, where L is deionised water, and S is solid waste, mL g). The jars were manually agitated for 3 repetitions of 5 min with 10-minute intervals between repetitions. The mixture was then allowed to settle for 30 min and then was pressure filtered through clean 0.45-μm pore size filtration membranes and then collection of the leachate. The leachate was collected in polyethene bottles and stored in a cold room at 4 °C until metal analysis and performed analysis within three weeks.

2.3. Humic acid analysis

A stock solution of HA was prepared by dissolving 1 g of HA in 1 L of deionised water for investigating the impact of the presence of HA in leachate on the leachability of metals. HA content was determined by ultraviolet light absorbance at 254 nm. The values were converted using a calibration curve. For that purpose, serial dilutions of the concentrated HA stock solution were prepared: 1, 2, 5, 7, 10, 15, 20, 50, 100 mg. Samples for UV_{254} were filtered through 0.45 μm membrane filter. UV_{254} was measured through a 1 cm quartz cell. The test was conducted in duplicate (Table 2).

2.4. Metal analysis

The metals content was analysed by inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX) after microwave-assisted acid digestion following the extraction procedure used in previous studies (Gutiérrez-Gutiérrez et al., 2015; Cipullo et al., 2018; Wagland et al., 2019). Briefly, Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg were determined by pre-digesting 30 mL leachate with 1.5 mL concentrated trace metal grade nitric acid for leachate samples. For solid samples, 0.5 g of samples was mixed with 6 mL of HCl and 2 mL nitric acid in Teflon tubes and left overnight. The vessels for leachate samples were placed in the Mars Xpress microwave (CEM system, EPA 3015-8). Then, the vessels were cooled, and the solution was filtered through Whatman No. 2 paper and made up to 50 mL with deionised water. As for the solid samples, they were placed in a microwave digester (Multiwave 3000, Anton paar) for 45 min at 800 W, and then the solution was filtered through Whatman No. 2 paper, and the liquid diluted to 100 mL. A blank digest was carried out in the same way. The microwave is an efficient and fast digestion technique method. Calibration standards were spiked with several certified standard solutions. The concentration ranges were 0.05, 0.1, 0.15 and 0.2 mg/L/ for the elements.

2.5. Geochemical modelling

Visual MINTEQ ver. 3.1 software program was used to estimate the chemical species and the equilibrium mass distribution of dissolved metals in leachate according to different pH and HA value. Data inputs included pH, alkalinity, temperature, and dissolved organic carbon (DOC). A temperature of 25 °C was used for all the model calculations. A sensitivity analysis of the model was performed, which responses to changes in the fraction of active SOM by independently varying SOM in the range 10–100%. The Stockholm Humic Model was selected to evaluate metal (loid)s binding to humic acid due to its known success in describing metal and DOC complexation (Baker, 2012). Typically, fulvic acid (FA) is more abundant than humic acid (HA). However, to better understand the effects of humic acid has on metal(loid)s leaching, of the active the total solid organic matter (SOM), humic acid set as 90% and fulvic acid formed as 10%. The input values used included total concentrations of metals Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg and ionic strength was also considered.

Table 2
Common properties of HA (Adapted from Chamoli, 2013, Sillanpää et al., 2015).

Elemental composition (% by weight)	HA	Functional group distribution (% of oxygen is indicated in functional groups)	HA
Carbon	50–60	Carboxyl (—COOH)	14–45
Hydrogen	4–6	Phenol (—Ph)	10–38
Oxygen	30–35	Alcohol (—R—OH)	13–15
Nitrogen	2–4	Carbonyl (—C=O)	4–23
Sulphur	1–2	Methoxyl (—O—CH_3)	1–5
Solubility in strong acid	Not soluble		

Table 3
The concentration of metal(loid)s in the MSW according to depth.

	Li (mg/L)	Al (mg/L)	Cr (mg/L)	Mn (mg/L)	Co (mg/L)	Ni (mg/L)
3–9 m	0.17	111	0.39	23.1	0.096	0.52
23–30.5 m	0.11	106.5	0.26	4.9	0.051	0.45
48–55 m	0.14	132.5	0.38	4.0	0.075	0.34

	Cu (mg/L)	Zn (mg/L)	As (mg/L)	Cd (mg/L)	Pb (mg/L)	Hg (mg/L)
3–9 m	5.31	14.75	0.20	27.05	25.18	0.044
23–30.5 m	6.28	3.75	0.04	0.0078	17.67	0.021
48–55 m	1.60	2.97	0.10	0.0083	2.53	0.015

2.6. Statistical analyses

Multivariate analysis was performed using SPSS 26 software to identify statistically significant variance between the dependent variable tested and effect on the metal(loid)s leachability. A multivariable study was conducted considering the correlation matrixes. In these matrices, each individual square contains the ordinal coefficient of Spearman which varies between 1 and −1 and the significance level of estimated correlation for each pair of variables (Bisquerra, 1989). Significance level was set at 0.05.

3. Results and discussion

3.1. Influence of depth

The concentration of metal(loid)s in the waste samples (according to depth) are provided in Table 3. Among all metal(loid)s, Hg had the lowest concentration, and Al was the highest. Significant efforts have been made to reduce Hg content at source, thus reducing the content of Hg in waste deposited in landfill. Therefore Hg is not expected to be

Table 4
Percentage change of metals at different depths relative to 3–9 m.

	Li	Al	Cr	Mn	Co	Ni
Change of 23–30.5 m	53.61	4.23	49.03	373.04	50.33	14.34
Change of 48–55 m	20.92	−16.23	2.67	472.73	1.78	51.71
Average	37.26	−6.00	25.85	422.88	26.06	33.02
Variance	267.17	104.57	537.44	2484.51	589.21	349.11

	Cu	Zn	As	Cd	Pb	Hg
Change of 23–30.5 m	−15.52	293.33	365.65	348,178.97	42.56	106.30
Change of 48–55 m	232.81	397.19	111.07	325,146.49	894.08	199.77
Average	108.65	345.26	238.36	336,662.73	468.31	153.04
Variance	15,416.71	2696.60	16,202.26	132,623,748.9	18,127.6	2184.25

present in high concentrations in MSW (Cheng and Hu, 2012). The concentrations of metal(loid)s tend to have a higher concentration at 3–9 m than other depths, indicating greater depth may reduce hydraulic permeability and increase waste densities. This is likely due to higher proportions of non-degraded organic materials distributed variably in the surface waste layers; higher organic carbon may increase soluble metals while organic matter bound to soil particles may enhance the retention of metals (Frank et al., 2017). The concentration of Mn and Cd at 3–9 m was remarkably higher than other metals; the composition and distribution of the sample may cause it.

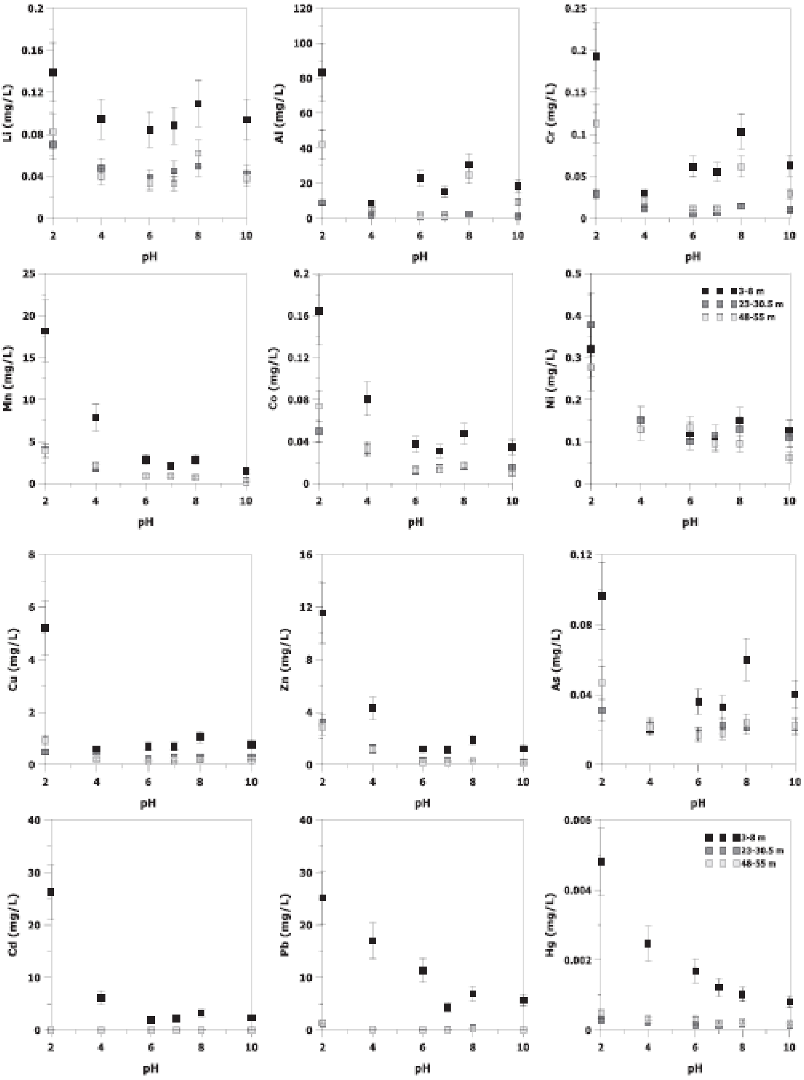


Fig. 1. The leached concentration values of 12 metals in MSW landfills, following the depths (3–9, 23–30.5, 48–55 m) and pH values (2, 4, 6, 7, 8, 10).

Table 5
Recovery rates of metals at pH 2 and at different depths (3–9, 23–30.5, 48–55 m).

	Li (%)	Al (%)	Cr (%)	Mn (%)	Co (%)	Ni (%)
3–9 m	83.5	75.07	50.22	78.64	89.91	61.41
23–30.5 m	64.52	8.37	11.29	81.23	98.03	83.46
48–55 m	59.86	31.82	30.13	95.87	98.66	80.98
Average	69.29	38.42	30.55	85.25	95.53	75.28
Variance	104.58	763.32	252.63	57.52	15.87	97.18

	Cu (%)	Zn (%)	As (%)	Cd (%)	Pb (%)	Hg (%)
3–9 m	97.96	78.42	47.46	96.74	99.93	10.99
23–30.5 m	7.77	86.22	70.99	91.42	7.20	1.33
48–55 m	59.67	96.63	48.79	89.98	57.11	3.34
Average	55.13	87.09	55.75	92.71	54.75	5.22
Variance	1365.9	55.65	116.51	8.44	1436.1	17.33

Therefore, metal(loid)s in the surface layer from the old MSW landfill have a higher concentration because degradation occurs slower than at deeper depths. This finding is in agreement with the findings of Reinhart et al. (2002), suggesting lower layers undergo limited waste stabilisation. Previous studies also found the composition of organic fine materials to increase with depth (Mor et al., 2006; Quaghebeur et al., 2013; Lozano-García et al., 2016). It consequently increases the complexation of metal(loid)s in organic waste residuals, and therefore metals are firmly bound to the compost matrix and organic matter, limiting their solubility with increasing depth (Smith, 2009). The composition of waste each landfill received, distribution of the waste, and landfill area background can influence the accumulation of certain metals and its content. There were observed significant negative correlations between depth and Li, Pb, Hg ($p < 0.05$), As and Cd concentration ($p < 0.01$). This is likely influenced by the metal content of the waste dispose and the binding of these metals within the landfill depths. The mobility of metals within solid waste is influenced by metals' complexation and by adsorption onto molecules of the waste (Adelopo et al., 2018). The concentration of Zn, Pb and Cu at 48–55 m was relatively lower than at 3–9 m and 23–30.5 m, implying Zn, Pb and Cu released in the upper layers may be immobilised by holding the metals through enhancing the formation of metal complexes in MSW that is over 10 years. It may indicate that Zn, Pb and Cu form strong complexes within stabilised organics. The strong metal sorption properties of compost produced from MSW have less opportunity for recovering metal in deeper depth landfill environments. The results demonstrate that waste composition influenced the composition of metals that can be recovered within a different layer of waste and aged. The amount of metals recovered in the surface layer of the landfill may be potentially increased, as shown in Table 4.

However, depth was not found to influence significantly the concentration of metal(loid)s recovered. This finding is consistent with the previous study of Gutiérrez-Gutiérrez et al. (2015) who reported that there is no clear pattern between metal concentrations and the depth of the waste. As waste would undergo different stages of degradation over various landfill ages, and composition, it is not appropriate to compare heavy metal contents sampled at different depths. Through waste materials disposed of in the landfill are the primary sources of metals in the landfill environment and leachate. Thus, further research is required to identify the factors controlling metals distribution, oxygen, which affects the redox at the site and the effect of waste composition on metals content for increasing economic viability in recovering metal.

3.2. *Influence of pH*

It is well known that pH plays a key role on the behaviour and speciation of metal(loid)s (Riba et al., 2004). Extracting metals from landfills and their leachate cannot be regarded as environmentally friendly

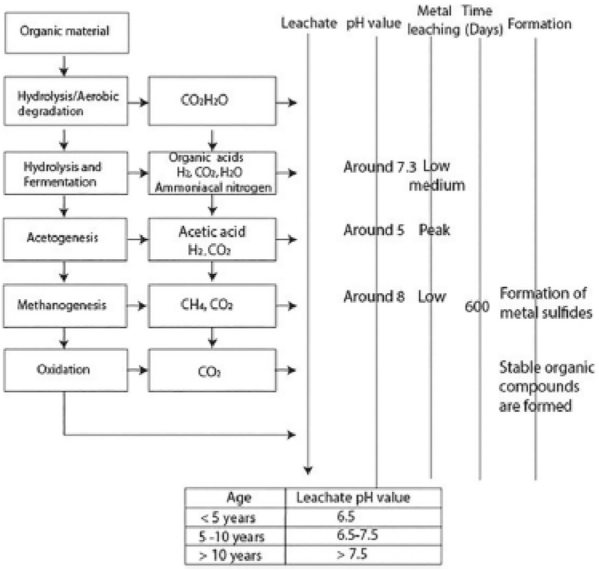


Fig. 2. Metal leaching Process in a landfill and leachate pH value (Adapted from Zainol et al., 2012, Adhikari et al., 2008).

and operational cost-effective; therefore, it is crucial to recovering certain high value and amount metals. Thus, we need to find a pH value or range that maximises recovery of a wide range of metal(loid)s, especially those of high added value or demand such as Li and Co. (Tang and Steenari, 2016). Therefore, the release of metal(loid)s was examined in a broader pH range between pH 2 and 10 (Fig. 1). It was noted that the release of metal(loid)s was found to be higher in the lower pH range, especially at pH 2 (Fig. 1). According to the values of Pearson correlation coefficient, Mn, Co, Ni and Zn show a strong negative correlation ($p < 0.01$) with pH. The leaching amounts of metals tended to decrease from roughly 99% to 32% with increasing alkalinity of the leaching solution, although some metal elements were increased at alkaline conditions. The decrease of metal leaching amount in alkaline conditions may be caused by precipitation or sorption processes (Dijkstra et al., 2006). The effect of pH on metal leachability also differs among different metal(loid) species. However, the maximum amounts are released at pH 2 for all metals. Table 5 shows the recovery rates for the metals from the concentration of the initial metals found in the waste solid.

The limited release was increased in at pH 8, except for Hg. At high pH of 8–10, solubility of metal(loid)s can increase to a certain extent since metals can form stable and soluble complexes with hydroxyl and dissolved organic carbon or are released from the dissolution of sulphide minerals (Ho et al., 2012). The concentration of heavy metal tends to increase again in alkaline condition, which is related to the formation of soluble metal hydroxides (Fig. 1) (van der Sloot et al., 2003; Cappuyns and Swennen, 2008; Król et al., 2020).

The results are inconsistent with Król et al. (2020), who reported a significant decrease in the concentration of Ni and Cr at pH 8 and Cu at pH 9. The results showed that As and Cr release was low at neutral or slightly acidic pH. However, they showed the highest leachability at pH 2; it caused by the dissolution of iron oxides that are the main components that bind to them in soils (Krysiak and Karczewska, 2007; Gersztyn et al., 2013). They notably showed the second-highest concentration at pH 8, which may be attributed to the mechanism of pH-related anion desorption, replacement of oxy-anion forming elements and their bound in the sorption complexes by hydroxide ions. The most important mechanism of As and Cr, which are oxyanion forming elements, is to be due to the dissolution of the organic components, including HA (Gersztyn et al., 2013). The characteristics of Cu solubility is in alignment with the findings of Cappuyns and Swennen (2008), who reported Cu is characterised by a lower solubility in the pH-range 2–6. The release of Al followed an amphoteric leaching pattern (Fig. 1), which is similar to results reported in previous studies (Zhang et al., 2016; Cui et al., 2019). The minimum leaching concentration occurred at pH 7. Cd release amounts decrease as the pH increases at acid condition, but the reduced amounts are not so much above pH 6. It may be due to the precipitation of the metal sulphide phase, resulting in Cd being pyritised (Morse and Luther, 1999). The release amount of Ni was lower at pH 7 for 3–9 m, pH 6 for 23–30.5 m and pH 10 for 48–55 m. The characteristics of Mn and Zn solubility follow the cationic pattern in which the concentration of metal element steadily decreases with pH.

Chromium recovery trend was identical to that of As and Al (Fig. 1). Zn recovery was similar to that of Mn and Cd, which can be observed in Król et al. (2020). Cu showed that similarity tendency with Pb. Pb are maximum 41 to 50 times more released at the pH 2 compared the leaching amount in the range of pH.

Overall, metal cations are most mobile in acidic conditions as shown in Fig. 2. In contrast, anion release increase towards high pH. These results are consistent with the previous study of van der Sloot et al. (2003). However, the release of metals does not always show a similar trend as the leachability of metals can change depending on the type and composition of the tested sample. In the case of Cu and Pb, the leachability curve typically makes V or U shaped (van der Sloot et al., 2003; Cappuyns and Swennen, 2008; Sloot and Kosson, 2010). However, this study Pb does not show a clear upward trend between pH 8 to 10. But it still showed that Pb solubility increase at high pH of 8–10. Al, As and Cr presents a V-shape, similar to results reported in the previous studies (Rubinos et al., 2011; Cui et al., 2019). The most pH-dependent metal was Mn in this study. Metals from landfill leachate

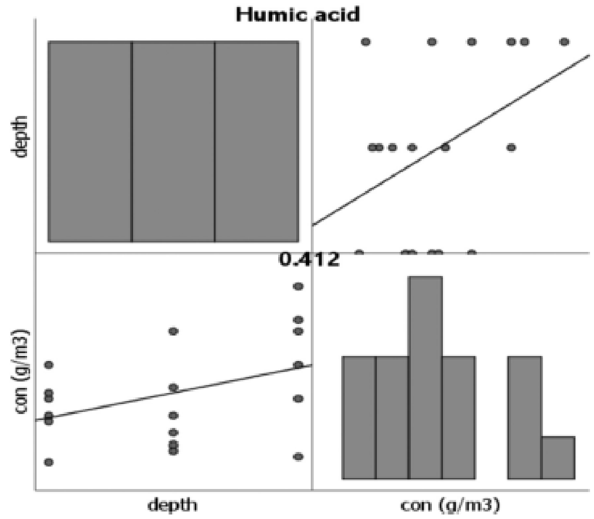
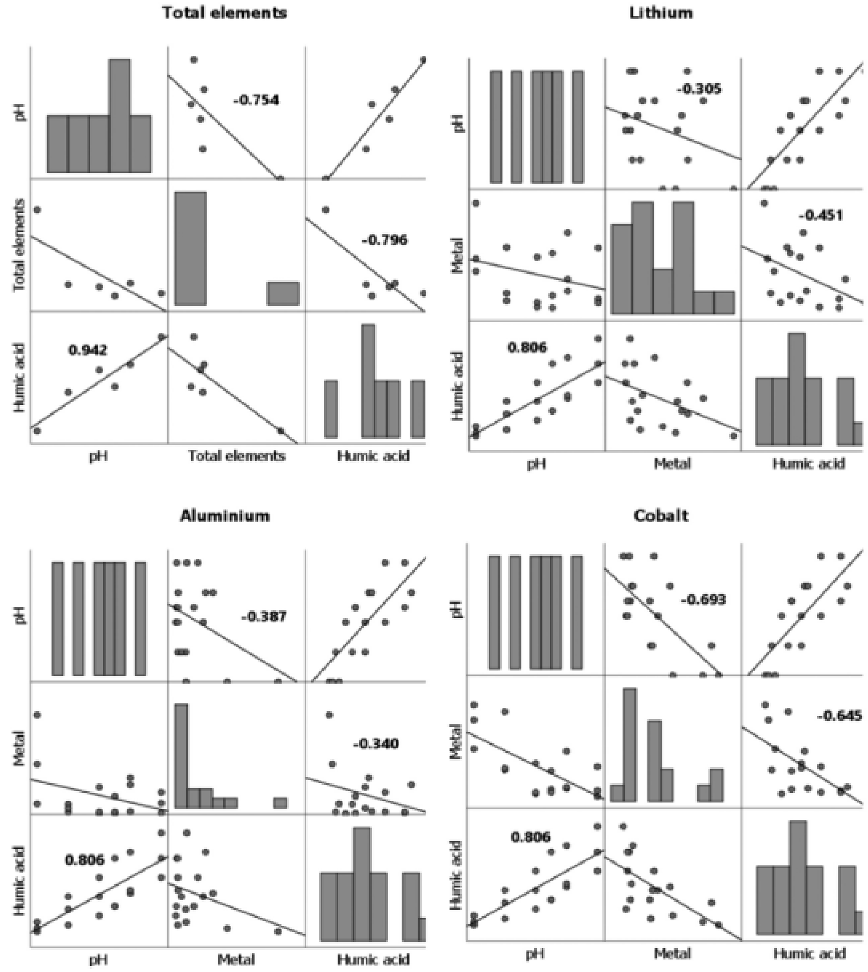


Fig. 3. The leached concentration values of humic acid in MSW landfills, according to depths.

are typically present in low concentrations; therefore, more effective and selective recovery methods under acidic conditions need to be determined for efficient recovering metal from landfill environments. In this study, the leaching of metal(loid)s from MSW at pH 2 and 4 gave the most efficient metal release and showed high concentration at pH 8.

Metal(loid)s leachability is highest when hydrolysis, fermentation and acetogenic bacteria dominate, due to an accumulation of VFA, and a pH decrease (Fig. 2). Previous studies showed that significant heavy metal leaching occurs during the initial stage of the landfill and pH values have a direct influence on metal mobility (Yao et al., 2014; Yao et al., 2017).

However, depending on metal(loid)s, the characterisation of pH may differ, such as Cu having the amphoteric character, thus forming soluble anionic species, and strong acidic conditions can cause environmental problems due to most organisms cannot tolerate the conditions (Breeze, 2018; Król et al., 2020). For this reason, a suitable pH value for each metal must be determined to fit the entire metal(loid)s recovery process by adjusting the pH value to the desired range and understand the character of metals with pH value. Further research should also



Total elements

Lithium

Aluminium

Cobalt

Fig. 4. Draftsman's plot resenting the relationship between waste depth (m), pH, metal (mg/L) and HA (mg/L).

develop alternative methods for recovering metals such as biodegradable extraction agents using organic acids (e.g. humic or acetic acid) to reduce reliance on strong acid.

3.3. *Humic acid in the landfill*

HA has a high sorption capacity, which makes them capable of holding metals. Therefore, metals may be retained and are not leached out easily. HA leaching tends to increase with the increase of depth (Fig. 3). As depth is increased, the humification process increases. HA is weakly acidic with carboxylic-and phenolic-OH groups (Prado et al., 2011).

The correlation between pH, metals, and HA is shown in Fig. 4 (details in Supplementary data Fig. 1). Four metals among 12 metal(loid)s are illustrated in Fig. 4. Li and Co are shown as they are critical raw materials and Al has been shown as there are concerns justifying focused recovery due to high content in the landfill. There was a strong positive relationship between pH and HA, i.e., HA leaching increases in higher pH value. Adsorption of organics on the surfaces would therefore be affected by pH. The amount of HA increased by 2% to 4% at pH 10 compared at pH 2 and increased by 0.4% to 4% as depth increased. The results may indicate that HA is not soluble at acidic conditions and become most soluble from pH 6. It may be due to carboxyl groups on HA be ionised in alkali condition. The ionisation would lead to a negative charge on HA molecules. Thus, HA is more leachable in alkali conditions due to lowered adsorption. This finding is in agreement with Sehaqui et al. (2015), who found that HA adsorption gradually increases with decreasing the pH. HA is known to bind metals to their hydroxyl and carboxyl groups, and either mobilise metals or delay their release (Leung and Kimaro, 1997; Bozkurt et al., 1999; Kochany and Smith, 2001; Klavins et al., 2006; Gutiérrez-Gutiérrez et al., 2015). Strong negative correlations were found between HA and Co, Ni, Zn ($p < 0.01$) and Mn ($p < 0.05$).

The Visual MINTEQ has been adopted to describe metals speciation in the leachate (Table 6). As significant numbers of closed landfills exist in the UK and across Europe, the model input used the batch test results at depth 48–55 m, which would be similar to the closed landfills parameters. The Stockholm Humic Model (SHM) was used to assess metal binding to HA. The results show that Li does not much affect by pH. However, all the metals show that high leachability at pH 2.

Table 6
Recovery of selected metal(loid) species in the leachate sample at 48–55 m depth by visual MINTEQ (content: %).

Li		Al		Cr		Mn	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content
Li^{+1}	96.05	$Al(OH)_2^+$	0.13	$Cr(OH)_2^{+1}$	3.12	Mn^{+2}	20.37
LiF (aq)	0.05	$Al(OH)_3$ (aq)	2.45	$CrOH^{+2}$	0.18	$MnOH^+$	0.02
LiCl (aq)	0.46	$Al(OH)_4^-$	95.93	$Cr(OH)_3$ (aq)	68.22	MnF^+	0.11
$LiSO_4^-$	0.062	AlF_2^+	0.28	$Cr(OH)_4^-$	0.02	$MnCl^+$	0.09
$LiHPO_4^-$	3.38	AlF_3 (aq)	0.83	$/HA_2Cr_2(OH)_2^+(s)$	4.92	$MnSO_4$ (aq)	0.22
		AlF_4^-	0.17	$/FA_2Cr^+(aq)$	0.07	$MnNH_3^{+2}$	0.01
		$AlHPO_4^+$	0.07	$/FA_2Cr_2(OH)_2^+(aq)$	23.46	$MnHPO_4$ (aq)	52.97
		$Al_2(OH)_2CO_3^{+2}$	0.08			$MnHCO_3^+$	3.75
		$/FA_2AlOH$ (aq)	0.04			$MnCO_3$ (aq)	21.86
						$/HAMn^+(s)$	0.03
						$/FAMn^+(aq)$	0.58

Co		Ni		Cu		Zn	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content
$CoOH^{+2}$	87.89	Ni^{+2}	22.51	Cu^{+2}	0.50	Zn^{+2}	19.98
$Co(NH_3)_5Cl^{+2}$	12.11	$NiOH^+$	0.09	$CuOH^+$	0.51	$ZnOH^+$	0.64
		NiF^+	0.07	$Cu(OH)_2$ (aq)	0.05	$Zn(OH)_2$ (aq)	0.40
		$NiCl^+$	0.04	$Cu(NH_3)_2^{+2}$	0.08	ZnF^+	0.07
		$NiSO_4$ (aq)	0.27	$CuNH_3^{+2}$	0.41	$ZnCl^+$	0.26
		$NiNH_3^{+2}$	0.92	$CuHPO_4$ (aq)	6.57	$ZnSO_4$ (aq)	0.26
		$Ni(NH_3)_2^{+2}$	0.01	$CuCO_3$ (aq)	63.61	$ZnNH_3^{+2}$	0.25
		$NiH_2PO_4^+$	0.06	$CuHCO_3^+$	0.29	$ZnHPO_4$ (aq)	40.32
		$NiHPO_4$ (aq)	19.83	$Cu(CO_3)_2^{-2}$	23.20	$ZnCO_3$ (aq)	24.62
		$NiCO_3$ (aq)	17.91	$/HA_2Cu(s)$	0.02	$ZnHCO_3^+$	5.84
		$NiHCO_3^+$	25.63	$/HACu^+(s)$	0.09	$Zn(CO_3)_2^{-2}$	1.16
		$/HANi^+(s)$	0.56	$/HA_2CuOH^-(s)$	0.03	$/HAZn^+(s)$	0.15
		$/FANi^+(aq)$	12.10	$/FA_2Cu(aq)$	1.15	$/FAZn^+(aq)$	6.04
				$/FACu^+(aq)$	0.82	$/FA_2Zn(aq)$	0.03
				$/FA_2CuOH(aq)$	2.63		

As		Cd		Pb		Hg	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content
H_3AsO_3	94.84	Cd^{+2}	13.40	Pb^{+2}	0.88	$Hg(OH)_2$	2.83
$H_2AsO_3^-$	5.16	$CdOH^+$	0.03	$PbOH^+$	0.71	$HgCl_2$ (aq)	8.70
		CdF^+	0.04	PbF^+	0.02	$HgCl_3^{-1}$	0.98
		$CdCl^+$	5.71	$PbCl^+$	0.14	$HgCl_4^{-2}$	0.07
		$CdCl_2$ (aq)	0.16	$PbSO_4$ (aq)	0.03	HgClOH (aq)	11.07
		$CdSO_4$ (aq)	0.19	$PbHPO_4$ (aq)	1.09	$Hg(NH_3)_2^{+2}$	9.85
		$CdNH_3^{+2}$	0.37	$Pb(CO_3)_2^{-2}$	22.33	$HgCO_3$ (aq)	0.08
		$CdHPO_4$ (aq)	66.38	$PbCO_3$ (aq)	64.11	$Hg(CO_3)_2^{-2}$	0.03
		$CdHCO_3^+$	3.92	$PbHCO_3^+$	6.50	$HgOHCO_3^-$	0.71
		$CdCO_3$ (aq)	6.73	$/HAPb^+(s)$	0.14	$/HA_2Hg(s)$	2.86
		$Cd(CO_3)_2^{-2}$	0.66	$/HA_2Pb(s)$	0.05	$/FA_2Hg(aq)$	62.83
		$/HACd^+(s)$	0.12	$/FAPb^+(aq)$	2.58		
		$/FACd^+(aq)$	2.28	$/FA_2Pb(aq)$	1.42		

The geochemical analyses also showed that HA accelerated metals leaching. This finding is in good agreement with the previous study of Usharani and Vasudevan (2016), where an increase in HA concentration increases the heavy metal leaching from sewage sludge. Cu, Pb, Ni, and Zn were all significantly affected by the presence of HA as their leachability increase roughly 6–17%, especially at below pH 6 (Fig. 5).

Results expressed that a high concentration of HA can leach out metals but can be in lesser concentration depending on the metal, indicating that the visual MINTEQ model could predict free ion/labile

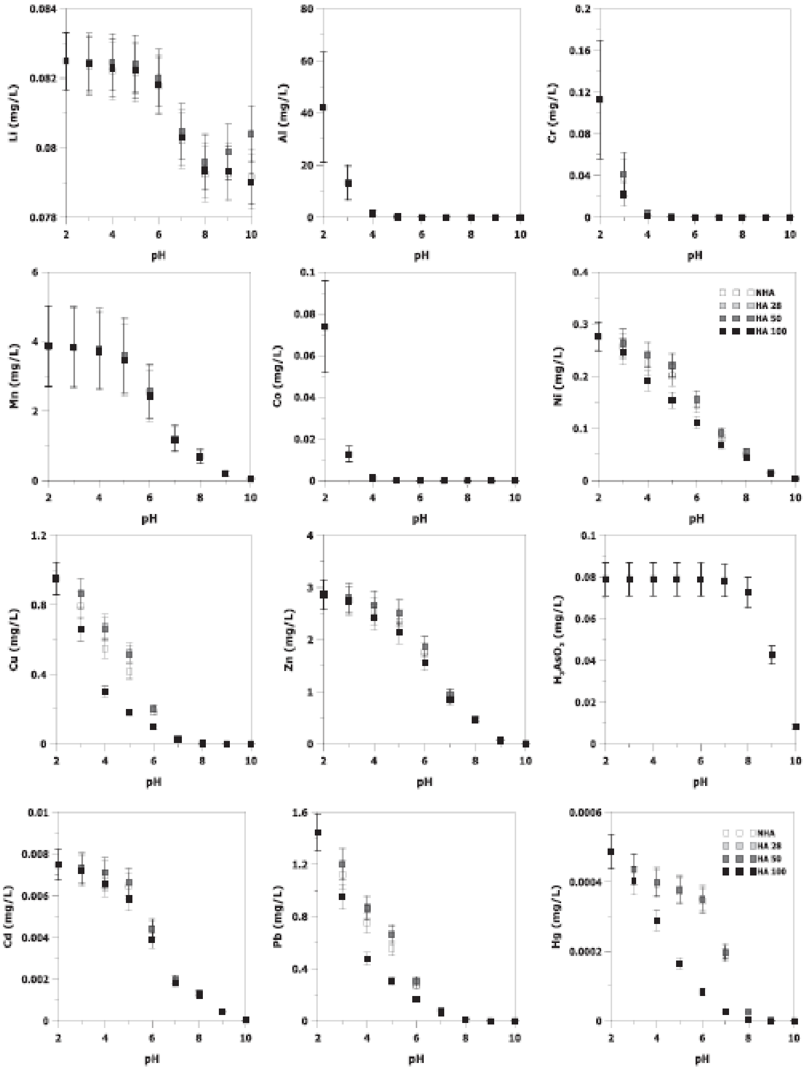


Fig. 5. The leached concentration values of 12 metals at different humic acid concentration (0, 28, 50 and 100 mg/L).

species efficiently under different environments, such as the acidic environment. With an increase of HA concentration, the improvement of metal leaching rate is not apparent, which may be due to excessive HA can chelate with metal ions and reduce metals release (1).

$$\mathrm{ROH} + \mathrm{Cd}^{2+} \leftrightarrow \mathrm{ROCd}^{+} + \mathrm{H}^{+} \tag{1}$$

Metal ions can effectively chelate heavy metals, thus delay their release; in aerobic conditions, the HS lose their binding properties. In addition to chelating metals, HA is applied in the bioremediation of environmental contaminants as a redox mediator (Maurer et al., 2012; Liu et al., 2018). HA is redox-active for enhancing microbial reduction of nitrate, implying their great potential for acting as a redox mediator in enhancing multiple microbial reductions, resulting in affecting various biogeochemical processes (i.e., iron cycle, nitrogen cycle, etc.) as well as in situ remediations in an anaerobic environment (Zhang et al., 2018). The leaching efficiency of HA shows that be comparatively higher at pH 4 to 6. Most metals can be found at the beginning of the humic phase (Bozkurt et al., 1999; Gutiérrez-Gutiérrez et al., 2015). Therefore, Fig. 3 showed the sharp contrast which metal(loid)s release in acidic conditions and HA release in alkaline conditions. Chelate compounds "hold" metal and, in consequence, it can be immobilised metals in landfills. This is probably due to the distinctive ring structure of chelate compounds, in which metal ion is surrounded by a molecule like, for example, humic compounds (Zhou et al., 2015). Computer modelling revealed that the HA could strongly bind metals. Also, it showed that higher pH is more effective HA binding with metals and metals are more soluble at lower pH. These are caused by the fact that at lower pH values, less acidic functional groups on the DOM molecules were deprotonated and available for metal binding (Stevenson, 1994). However, Li, Co, and As do not much affect by organic matter. Even the HA dominated DOC fractions in leachate, the leaching potentials for FA-metals complexes leaching out were relatively high. The solubility and complexation ability of HA is related to their interactions with metal (loid)s and other environmental conditions. This interaction leads to the formation of metal complexes and chelates, which influence leaching amounts of metal(loid)s, and the main factor influencing the interactions of HA with metals is pH value. According to the modelling results especially, Cu and Pb were bound very strongly in metal ion-humic complexes. In the acid to neutral pH range, HA is a vital biding constituent for metal(loid)s.

4. Conclusion

The leaching performance of metal(loid)s and HA from MSW at various pH was investigated. Batching leaching tests showed that the optimum conditions were pH 2 and HA 28 mg/L for recovering a broad range of metal(loid). Al, Mn, Cu and Zn may suggest recovery opportunities as their contents in MSW are high. Analysis of the mobility of the metals through the MSW suggested that these metals are not being vertically transported completely, and no clear pattern was identified between the release of the metals and depths due to waste would undergo different stages of degradation over various landfill ages, and composition. However, the metals showed higher concentrations in the surface layer in MSW. The recovery rates at different depths are following: Pb > Cu > Cd > Co > Li > Mn > Zn > Al > Ni > Cr > As > Hg for 3–9 m, Co > Cd > Zn > Ni > Mn > As > Li > Cr > Al > Cu > Pb > Hg for 23–30.5 m, Co > Zn > Mn > Cd > Ni > Li > Cu > Pb > As > Al > Cr > Hg for 48–55 m. For most metals, their concentrations have decreased with increasing pH. Analysed metals increased at pH 8 except Hg. HA are sparingly soluble in acidic pH. HA promote metal mobilise, but an additional amount of humic acid may assist metals removal. High levels of HA can lead to extensive complexation and chelation of metals. Metal recovery in MSW landfill may have high efficiency in the surface layer, at pH 2 and 4, with an appropriate HA concentration. However, the relationship between HA and metals is still unclear. The capability of humic acid for interactions with metals is strongly dependent on pH. Therefore, further work is required to explore the mechanism of the organometallic process because it can govern the mobility of metals, resulting in enhanced sustainability and economic opportunity by recovering metals by understanding these effects on metal mobility.

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CRediT authorship contribution statement

H. Lee: Conceptualization, Investigation, Writing – original draft. **F. Coulon:** Supervision, Conceptualization, Writing – review & editing. **S.T. Wagland:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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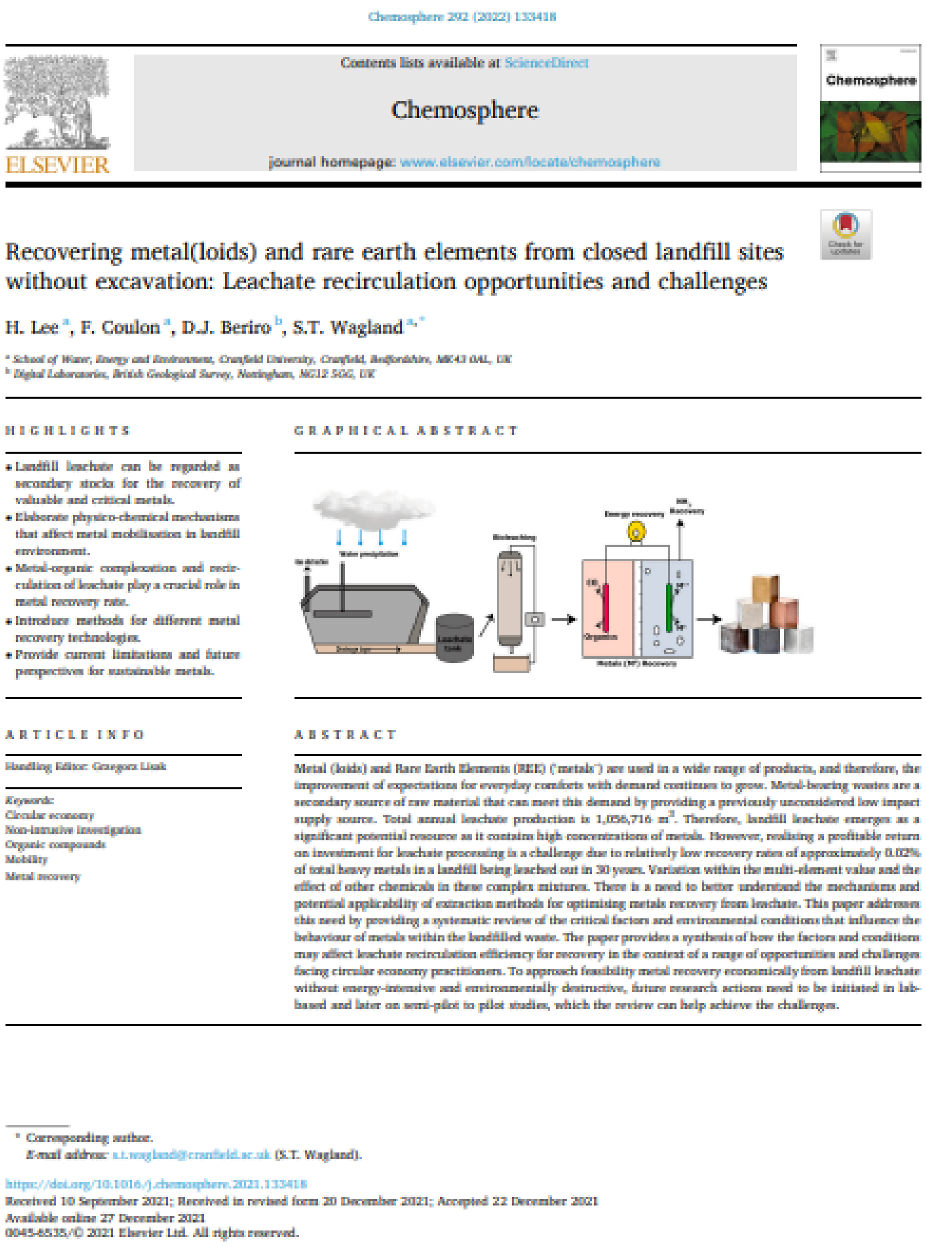
Appendix D (2022) Recovering metal(loids) and rare earth elements from closed landfill sites without excavation: Leachate recirculation opportunities and challenges. Chemosphere.



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Recovering metal(loids) and rare earth elements from closed landfill sites without excavation: Leachate recirculation opportunities and challenges

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HIGHLIGHTS

- Landfill leachate can be regarded as secondary stocks for the recovery of valuable and critical metals.
- Elaborate physico-chemical mechanisms that affect metal mobilisation in landfill environment.
- Metal-organic complexation and recirculation of leachate play a crucial role in metal recovery rate.
- Introduce methods for different metal recovery technologies.
- Provide current limitations and future perspectives for sustainable metals.

GRAPHICAL ABSTRACT

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ABSTRACT

Metal (loids) and Rare Earth Elements (REE) ('metals') are used in a wide range of products, and therefore, the improvement of expectations for everyday comforts with demand continues to grow. Metal-bearing wastes are a secondary source of raw material that can meet this demand by providing a previously unconsidered low impact supply source. Total annual leachate production is 1,056,716 m^3. Therefore, landfill leachate emerges as a significant potential resource as it contains high concentrations of metals. However, realising a profitable return on investment for leachate processing is a challenge due to relatively low recovery rates of approximately 0.02% of total heavy metals in a landfill being leached out in 30 years. Variation within the multi-element value and the effect of other chemicals in these complex mixtures. There is a need to better understand the mechanisms and potential applicability of extraction methods for optimising metals recovery from leachate. This paper addresses this need by providing a systematic review of the critical factors and environmental conditions that influence the behaviour of metals within the landfilled waste. The paper provides a synthesis of how the factors and conditions may affect leachate recirculation efficiency for recovery in the context of a range of opportunities and challenges facing circular economy practitioners. To approach feasibility metal recovery economically from landfill leachate without energy-intensive and environmentally destructive, future research actions need to be initiated in lab-based and later on semi-pilot to pilot studies, which the review can help achieve the challenges.

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1. Introduction

Metals, metalloids and Rare Earth Elements (REE), collectively termed 'metals', are finite natural resources with increasing demand. It is vital to find alternative sources to ensure supplies of these metals, especially for new technologies such as electric vehicles, renewable energy generation and battery storage (Jowitt et al., 2020; Krishnan et al., 2021). Several recent studies reported that a worthwhile amount of valuable secondary raw materials is available within closed landfill sites (Gutiérrez-Gutiérrez et al., 2015; Dino et al., 2017; Krook et al., 2018; Särkkä et al., 2018; Esguerra et al., 2019; Parrodi et al., 2019; Wagland et al., 2019; Lee et al., 2022). There are around 21,000 closed landfill sites across England and Wales (DEFRA, 2021; ENDS Report, 2021) and somewhere between 150,000 and 500,000 landfill sites within Europe, with an estimated 90% of them being non-sanitary (Jones et al., 2018).

Landfill technology is very different according to country. In many developing countries, open dumps still are in operation. In many developing countries, uncontrolled open dumpsites are more widely employed than controlled and engineered landfills as it requires minimum land and is an easy way of disposing of refuse. This means that no emission control occurs, and the waste is not compacted (Stegmann, 2005; Ayisi et al., 2021) thus posing a risk to human health and the environment. The risks posed by the leachate can be amplified by the lack of leachate containment systems, leading to high concentrations of organic and inorganic pollutants in the environment (Maiti et al., 2016; Vaccari et al., 2019). On the other hand, landfills are highly engineered facilities designed to minimise the adverse impact of waste on the surrounding environment. Even though are well-engineered many landfills still release methane and carbon dioxide from decomposing organic waste, affecting climate change. If leachate breaches the landfill lining, water contamination can occur.

Nevertheless, landfills are still the most common waste disposal method (Krook et al., 2018). A landfill site with good, engineered facilities should result in minimal negative environmental, social, and economic impact for waste compared to other waste management options. Also, waste from landfill sites can be used in several ways for energy generation and recycling resource. Closed landfills represent a significant opportunity across Europe and the UK to recover value from waste materials as they provide a previously unconsidered localised long-term storage deposit of secondary raw materials similar to traditional metal mineral resources. Enhanced Landfill Mining (ELFM) address the combined and integrated valorisation of distinct landfilled urban waste streams as both materials (Waste-to-Materials, WtM) and energy (Waste-to-Energy, WtE) while meeting the most stringent ecological and social criteria (Jones et al., 2013). ELFM provides an opportunity for combined resource recovery and reclamation of land while mitigating future environmental liabilities and remediation costs through excavation innovative transformation technologies (Jones et al., 2013; Esguerra et al., 2021; Vollprecht et al., 2021). However, existing technologies and good practices are unable to demonstrate the economic viability of such schemes. This is partly because mining processes for recovering material result in high capital costs (Frändegård et al., 2015). There are also important uncertainties about the actual abundance and concentration of suitable waste materials in landfill environments, which need to be known early on in the lifecycle of a metal's recovery project.

Two essential by-products of waste disposal by landfills are leachate and landfill gas. The former is formed when rainwater infiltrates and percolates through the degrading waste, the latter by microbial degradation of biodegradable waste materials under anaerobic conditions (Chu, 2008). Some are resistant to environmental degradation and have existed for a long time, referred to a persistent organic pollutants (POPs) (Alharbi et al., 2018). It is estimated that over 100,000 types of chemicals and their transformation products may present in the landfilled waste and are leached out by rainwater, forming landfill leachate (Öman and Junestedt, 2008). A wide range of POPs are present in landfill leachate (Paxeus, 2000; Sharma and Kumar, 2021). POPs associated with high production volume industrial chemicals directly or indirectly affect the environment and health even at low concentrations (Wojciechowska, 2013). Polluted environments increase the risk of exposure to contaminants, disease vectors, and other agents that may induce illnesses for humans (Adeola, 2004). Effective treatment methods are required as leachate contains trace chemicals, contaminating groundwater, surface water and soil, potentially polluting the environment and harming human health (Brennan et al., 2016). There are methods to remove organic pollutants from wastewater and water. For example, peroxymonosulphate can generate hydroxyl radicals and sulphate and the Z-scheme photocatalysts such as TiO_2 with high potential for degradation of organic pollutants (Ghanbari et al., 2020; Hassani et al., 2021). The electro-activated oxidant system also effectively removed organic pollutants (Ghanbari et al., 2021). However, ambitions for the landfill management should go beyond protecting human health and the environment, with conservation of energy and recovery of natural resources high on the agenda. Landfill leachate comprises recoverable metals, organics, phosphorus, ammonia, and water (Iskander et al., 2017; Kurniawan et al., 2021). The presence of recoverable metals means that landfill leachate can be of great importance as an alternative to conventional mineral exploration as the sediment of the leachate showed presence of REEs content was more than twice the content in landfilled waste (Gutiérrez-Gutiérrez et al., 2015), but also the presence of recoverable metals in landfill leachate can negate the need for full-scale landfill mining.

There are four objectives of this review paper: i) to give an overview of the properties and metals content in landfill leachate to gain insight into the opportunities for metal recovery from leachate; ii) to explore the knowledge on various factors affecting metals solubility; iii) to evaluate the efficiency of recirculation for increasing metal recovery rates and; iv) to discuss the opportunities for metal recovery from leachate, analyse the challenges associated with the recovery, and present the perspectives for future research and technology development to maximise the benefits of metals recovery from closed landfill leachate.

This review develops a critical evaluation of the factors that influence metal mobility. This will provoke and influence impactful research on novel in-situ projects to recover metals whilst reducing remediation costs for the land developers and associated beneficiaries in the future.

Table 1
Waste composition range.

Component	Range (%)	References
Organic waste	15–58	Tapia (2009); European Commission (2016); Abdel-Shafy and Mansour (2018); Kaza et al. (2018)
Paper and cardboard	16–27	
Glass	2–4.5	
Plastic	9–20	
Wood	3–7	
Metal	3–9.2	
Textile	3–9	
Rest	3–18	

2. Landfill leachate properties and metals content

Leachate can be formed as a result of chemical and biochemical processes within the landfill. There is non-uniform and intermittent percolation of moisture through the solid waste in the landfill due to leachate generation (Hughes et al., 2013; Edokpayi et al., 2018). Several factors influence leachate composition, such as the age of landfill, depth of the waste in the landfill, location of the site, and weather condition of the landfill site; another critical factor affecting leachate composition is the composition of the waste deposited in the landfill (Jang and Townsend, 2003; Kalčíková et al., 2011; Moody et al., 2017). Generally,

Table 2

The concentration range of chemical constituents of landfill leachate determined from available literature.

Parameter	Concentration range (mg/L)	Parameter	Concentration range (mg/L)	References
Alkalinity (as $CaCO_3$)	0-20,850	Nitrogen (Ammonia)	0-1250	Kjeldsen et al. (2002)
Aluminium	0–2	Nitrogen (Nitrate)	0–9.8	Kjeldsen et al. (2002)
Antimony	0–3.19	Nitrogen (Nitrite)	0–1.46	Christensen et al. (2001)
Arsenic	0–0.04	Nitrogen (Organic)	0-1000	Christensen et al. (2001)
Barium	0–2	Nitrogen (Total Kjeldahl)	1–100	Christensen et al. (2001)
Beryllium	0–0.36	Nickel	0–7.5	Christensen et al. (2001)
BOD_5	0-4000	Phenol	0.17–6.6	Akinbile et al. (2012)
Boron	0.5–10	Phosphorus (Total)	0–234	Kjeldsen et al. (2002)
Cadmium	0–0.01	Phosphate	1–10	Christensen et al. (2001)
Calcium	100-1000	pH	4.5–9	Adamcová et al. (2016)
Chloride	20-2500	Potassium	0.16–3370	Akinbile et al. (2012)
Chromium	0–0.05	Selenium	0–1.85	Adamcová et al. (2016)
Cobalt	0–7.58	Silicon	0–12	Kjeldsen et al. (2002)
COD	150-6000	Silver	0–1.96	Christensen et al. (2001)
Conductivity (μmho/cm)	480-72,500	Sodium	0-8000	Kjeldsen et al. (2002)
Copper	0–9.9	Thallium	0–0.32	Adamcová et al. (2016)
Cyanide	0–6	Tin	0–0.16	Adamcová et al. (2016)
Fluoride	0.1–1.3	TDS	0-42,300	Akinbile et al. (2012)
Hardness (as $CaCO_3$)	400-2000	Titanium	0–1.5	Christensen et al. (2001)
Iron	0-5500	TSS	140,900	Kjeldsen et al. (2002)
Lead	0–5	TOC	335,000	Adamcová et al. (2016)
Magnesium	16.5–15,600	TVA (as Acetic acid)	0-19,000	Akinbile et al. (2012)
Manganese	0.05–1400	Turbidity	40–500	Adamcová et al. (2016)
Mercury	0–3	Sulphate	0–300	Adamcová et al. (2016)
Organic halides	0.32–3.5	Zinc	0-1000	Christensen et al. (2001)
Benzene	0.1–0.6	Phenols	0–4	Christensen et al. (2001)
Ethylbenzene	0–4.9	Toluene	0–3.2	Akinbile et al. (2012)

Note: The grey shaded cell indicates metals and metalloids.

Table 3

Selected characteristics of leachate according to landfill age.

Parameter	Young	Intermediate	Old	References
Age (years)	<5	5–10	>10	Renou et al. (2008)
pH	<6.5	6.5–7.5	>7.5	Bhalla et al. (2013)
COD (mg/L)	>10,000	4000–10,000	<4000	Bhalla et al. (2013)
TOC/COD	<0.3	0.3–0.5	<0.5	Abbas et al. (2009); Zhou et al. (2010)
BOD_5/COD	>0.3	0.1–0.3	<0.1	Bhalla et al. (2013)
Organic compounds	80% VFA	5–30% VFA + humic and fulvic acids	Humic and fulvic acids	Bhalla et al. (2013)
Heavy metals (mg/l)	Low medium >2	Low <2	Very low <2	Renou et al. (2008)
Molecular size distribution	Over a broad range-high fraction of low molecular weight organics	N/A	Over a narrow range-high fraction of high molecular weight organics	Abbas et al. (2009); Zhou et al. (2010)
Biodegradability	Important	Medium	Low	Bhalla et al. (2013)

the waste composition is categorised as organic (food and garden waste), paper, plastic, glass, metals, etc. Table 1 shows the composition of global waste.

A wide variety of metal contents is collected into the leachate as it drains through the pile of waste in the landfill (Eggen et al., 2010; Edokpayi et al., 2018). Leachate is also rich in ammonia, which ranges from 50 to 11,000 mg/L and inorganic components such as iron, chlorine, sulphate, and metals (Ō; man and Junestedt, 2008; Luo et al., 2020; Zico et al., 2021). Previous studies concluded that ammonia is the principal pollutant in leachate, excluding organics (Kulikowska and Klimiuk, 2008). Ammonia nitrogen in the leachate accumulates due to there is no degradation pathway for ammonia. Therefore, a high concentration of ammonia-nitrogen in leachate occurs throughout the lifetime of a landfill (Berge et al., 2006; Couto et al., 2017), which means early leachate has a relatively low concentration of ammonia-nitrogen content. As landfill leachate ages, the concentration of ammonia increases, whilst the biodegradable fraction declines due to the stabilisation process (Abood et al., 2013). Ammonia nitrogen is rich in older landfill leachate due to hydrolysis and fermentation of the nitrogenous fractions of biodegradable substrates (Carley and Mavinic, 1991). The ammonia nitrogen concentration remains for at least 50 years in the range of between 500 and 1500 mg/L (Kulikowska and Klimiuk, 2008). Nitrogen compounds are common in leachate. The total nitrogen content of leachate is in the range of 2.6–945 mg/L (Mukherjee et al., 2015). It affects environmental such as eutrophication, acidification of water, toxicity to aquatic animals, and increased algal blooms (Camargo and Alonso, 2006). Aside from ammonia-nitrogen, total phosphorus is considered for water quality as it is a major limiting nutrient in water ecosystems for algal growth, which are harmful to most aquatic organisms (Said et al., 2004). Total nitrogen and total phosphorus measures indicated that total nitrogen levels in the waste decreased over time, whereas phosphorus levels remained steady throughout (Zhao et al., 2007). Inorganic compounds may consist of potentially harmful elements such as Pb, Hg, and As in pure form or combined with other elements (Jan et al., 2015). As leachate contains a wide range of metals and nutrients, it can be considered a great potential for metal and nutrients recovery. However, there are also challenges associated with the method to meet the need for sustainable leachate management that maximises valuable metal recovery. The key challenge on metal recovery from leachate is the low concentration of metals which is often affected by landfill age and type (Table 2).

The leachate produced in young landfills (<5 years old) contains a substantial number of organic compounds derived from biodegradable organic water materials, which undergoes rapid anaerobic fermentation within confined landfills. As a result, volatile fatty acids (VFAs) are produced, e.g. acetic, propionic, iso-butyric, n-butyric, iso-valeric, and n-valeric acid. It is very well known that organic acids, such as VFAs, may play an essential role in the mobilisation of metals through either the formation of soluble ligand: metal complexes or a decrease of pH (Molaey et al., 2021). Thus, VFAs are considered valuable substrates for metal dissolution, increasing the release of metals in landfill

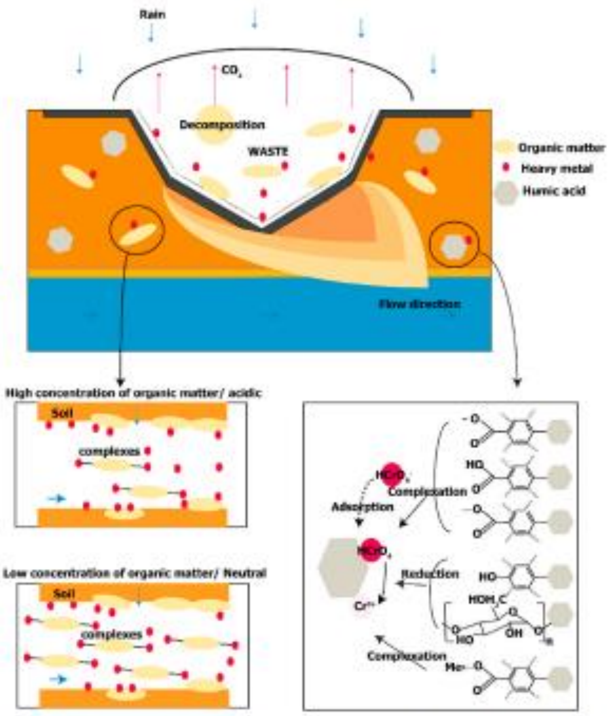


Fig. 1. Processes occurring in landfills that affect metal solubility; natural attenuation, complexation of metals with organic matter and mechanism of humic acid for metals retention.

environments. Young leachate is characteristic of its high content of biodegradable organic matter. BOD (Biochemical oxygen demand), COD (Chemical oxygen demand), and BOD/COD ratio act as indicators of microbial activities and organic pollution. BOD/COD describes the biodegradability level of materials by which organic matter containing leachate is readily broken down in the environment (Samudro and Mangkoedihardjo, 2010). Therefore, young leachate shows a high BOD/COD indicator.

As landfill age increases, the BOD/COD ratio in leachate decreases (Table 3). This is due to the decomposition of the majority of biodegradable compounds and small quantity changes of less degradable organic matter at the same time that acidic conditions begin neutralising (Talalaj, 2015). As a consequence, the higher pH condition results in decreasing metal release by complexation and precipitation (Zhang et al., 2018). Older leachate from the methanogenic phase is partially characterised by the lower concentration of VFAs. As the content of VFAs and other readily biodegradable organic compounds in the leachate decreases, the organic matter (OM) in the leachate becomes dominated by refractory compounds, such as humic acid (HA) and fulvic acid (FA), which are known to bind metals to their hydroxyl and carboxyl groups, and either mobilise metals or delay their release (Leung and Kimaro, 1997; Bozkurt et al., 2000; Kochany and Smith, 2001; Klavinsa et al., 2006; Gutiérrez-Gutiérrez et al., 2015). The humic substances (HS) give a dark colour with increasing pH due to the dissociation of protons (Stevenson, 1994). The decrease in VFAs increases pH; consequently, metals have a relatively low concentration in older landfill leachate as the solubility of metals is decreased with increasing pH.

3. Physico-chemical factors affecting metals solubility

Several factors affect metals solubility within solid waste deposits (Fig. 1). Important processes include abiotic redox processes, dissolution/precipitation of minerals, sorption, ion exchange, organic matter biodegradation, and complexation. The resulting matrix redox changes strongly influence both the inorganic and organic biogeochemistry of the landfill and therefore influencing the behaviour and fate of metals within landfills (Christensen et al., 2001). Gaining insights into the geochemistry of landfill is therefore needed to better understand the solubility of metals and predict metals recovery.

3.1. Weathering and natural attenuation

The dissolution of metals can occur during natural events, such as weathering and natural attenuation. During weathering processes, a broad range of physical and chemical reactions such as hydrolysis, precipitation, pH neutralisation, oxidation/reduction of metals, sorption, and complexation will change the overall characteristics of metals

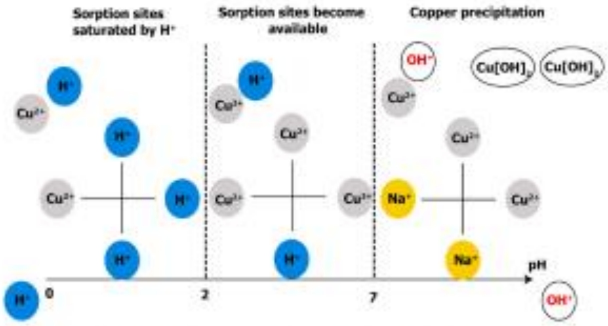


Fig. 2. Effect of pH on the adsorption of copper: at lower pH, the adsorption sites are saturated by H+, and the adsorption of copper is low; when the pH increases, the sorption sites become available, and the adsorption of copper increases. At higher pH, the copper precipitated (Adapted from Abbar et al., 2017).

(Chimenos et al., 2003; Polettini et al., 2004; Saffarzadeh et al., 2011; Takahashi and Shimaoka, 2012). Natural attenuation can be defined as a process by which the concentration of leachates is reduced to an acceptable level by natural processes. It can both mobilise and immobilise metals (Beaven et al., 2013). Based on the definition, *in-situ* natural attenuation mechanisms are identified as physical (diffusion, sorption, dispersion, dilution, and volatilisation), chemical (precipitation, adsorption, ion exchange, redox reaction) and biological (biodegradation) processes. For this reason, it is desirable to be able to predict how the metals in the landfill environment will behave over time when exposed to the weathering effects of infiltrating rainwater and the atmosphere. The effect of weathering on metals solubility is likely to be significant as pH is a dominant parameter in metals solubility and complexation (Stumm and Morgan, 1981). The redissolution of their respective hydroxide mainly causes the release of metals as pH is controlled by the solubility of $Ca(OH)_2$. Therefore, weathering reactions leads to a decrease in pH (Chimenos et al., 2003).

3.1.1. *Oxidation*

Several studies have been shown the formation of Fe/Al-(hydrate) oxides and calcite by weathering. It indicates that metals release may be controlled by sorption processes caused by weathering (Zevenbergen and Comans, 1994; Meima et al., 1997a; Meima and Comans, 1999; Saffarzadeh et al., 2011; Takahashi and Shimaoka, 2012). Saffarzadeh et al. (2011) proposed the following order based on their direct metal uptake capacity: Fe-hydrate > Al-hydrate > calcite. Calcite is not adequate for direct metals sorption; however, they play a crucial role in buffering the system, pH neutralisation; consequently, it minimises

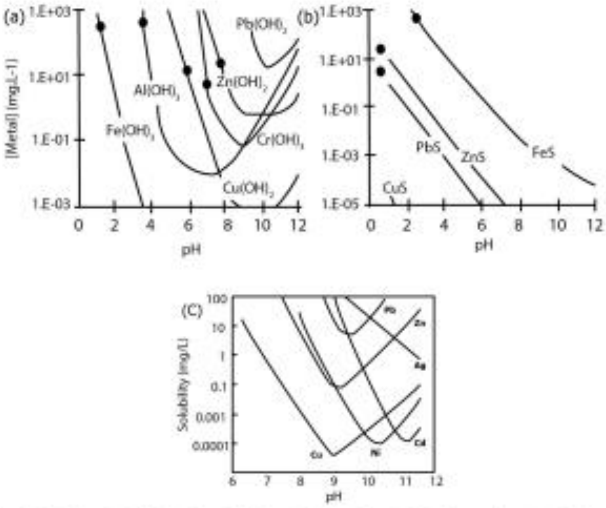
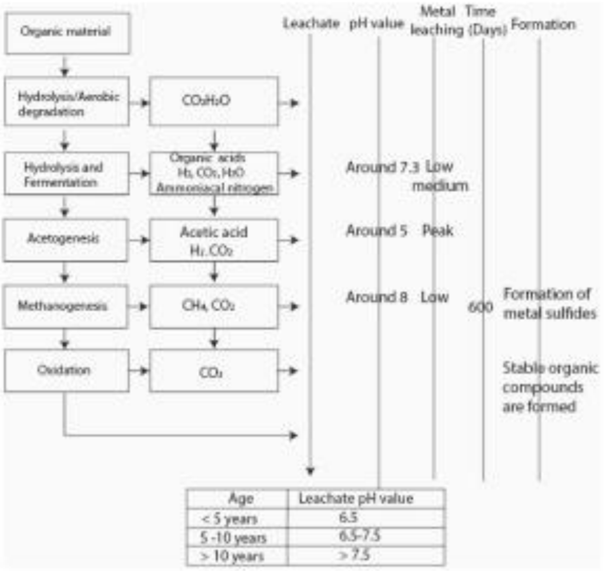


Fig. 3. a) Solubility of metal hydroxides, b) Solubility of metal sulphide, c) Solubility of metal hydroxides as a function of pH (Marchioretto et al., 2005).



Age	Leachate pH value
< 5 years	6.5
5 -10 years	6.5-7.5
> 10 years	> 7.5

Fig. 4. Biological decomposition process, metal leaching process in a landfill and leachate pH value (Adapted from Zainol et al., 2012; Adhikari et al., 2014).

metal leaching. Thus, weathering is expected to result in a reduced metal solubility in the long term (Meima and Comans, 1999).

3.1.2. *Sorption and precipitation*

Temporal studies of metal mobility in soils show that mobility decreases over time, suggesting that a high proportion of metals within Municipal solid waste (MSW) which consists of everyday items we use and then throw away, are insoluble (Peters and Shem, 1993; Aucott, 2006). The reasons for the reduced mobility of metals in soil include sorption on soil particles and particularly to HS, precipitation under anaerobic conditions, adsorption, and chelation with inorganic and organic ligands in landfills (Bozkurt et al., 2000). Christensen et al. (2001) reported that metals in landfills do not constitute a significant pollution problem due to strong attenuation by sorption and precipitation (Fig. 2).

In general, inorganic content of leachate ranges between 1 and 2000 mg/L. By raising the pH value, metallic hydroxide compounds become insoluble and precipitate from the solution. Alkaline conditions promote metal precipitation and adsorption, depending on the metal speciation (Lukman et al., 2013). Fig. 3 shows the solubility curves of selected metal ions and their respective solubility versus pH. Cu and Ni have a similar curve, albeit that the minimum solubility of Ni occurs at approximately pH 10.5 and the minimum solubility of Cu occurs at pH 9. Zn is amphoteric, being soluble in both acid and alkaline conditions. Cu and Zn readily form metallic complexes with ammonia. These metal complexes remain highly soluble at the higher pH values, prohibiting respective metal hydroxide precipitation. Cu sulphide is insoluble, and the presence of sulphide precipitates Cu as it dissociates from the ammoniacal complex. Precipitate in landfill environments strongly relates to organic decomposition and the formation of microorganisms during the process of methanogenesis (Li et al., 2015). According to Fig. 3, precipitation is unlikely to occur in strongly acidic conditions except for Fe, Al, Pb and Zn.

Marchioretto et al. (2005) reported that when Fe and Al are present in landfill leachate, adsorption and co-percipitation may occur between Cr, Pb, and Zn with $Fe(OH)_3$ and $Al(OH)_3$ as pH increases. The leachability of metals is also influenced by the chemical and physical affinity of metal ions and various waste materials under landfill conditions (Ward et al., 2005). Sulphates in waste are reduced to sulphide that forms insoluble precipitates with most metals or containing amino acids during anaerobic (Christensen et al., 2001). Dissimilatory microbial sulphate reduction is when certain bacteria use sulphate as the electron acceptor in the oxidation of organic matter. However, Cr does not form an insoluble sulphide; it is only precipitated out in the form of hydroxide. Sulphides of the metals are more difficult to dissolve, both in oxidising and reducing environments (Hammack and Edenborn, 1992).

3.1.3. *Carbonation and redox*

Carbonates are also capable of forming precipitates with metals and are abundant in landfill leachate. Nevertheless, the solubility of metal carbonates is generally high (Christensen et al., 2000). Metal precipitates of carbonate will dissolve, where the carbonate release will buffer the pH value as the pH decreases, which is called the humic phase (Kjeldsen et al., 2010). As attenuation mechanisms affect metal concentration and stability, it should be considered the metal adsorption and precipitation-pH relationship for recovering metals with high concentration from an economic point of view. The redox potential influences precipitation and should be considered when considering metal solubility. Redox potential is a measure of the propensity of a chemical or biological species to either acquire or lose electrons through ionization (Lu and Marshall, 2013). Various parameters in landfill leachate can reflect transformations in redox potential. For example, as sulphate is reduced, their concentrations decrease. An increase in redox potential effects on the oxidation of reduced sulphur compounds to SO_4^{2-}.

Table 4
Mechanisms of adsorption for organic compounds in soils (adapted from Sposito, 1984).

Mechanisms	Principal organic functional group
Cation exchange protonation	amines, ring NH, heterocyclic N, carbonyl, carboxylate
Anion exchange water bridging	carboxylate amino, carboxylate, carbonyl alcoholic OH
Cation bridging	carboxylate, amines, carbonyl, alcoholic OH
Ligand exchange hydrogen bonding	carboxylate amines, carbonyl, carboxyl, phenylhydroxyl
Van der waals bonding	uncharged, nonpolar organic functional groups

Oxidation of metal sulphides takes place, leading to metals release. The redox conditions in landfill leachate affect metal-organic interactions through the organic ligands, as organics are sensitive to redox conditions (Merian and Clarkson, 1991). Abundant OM tends to have low redox potential values. The speciation of metals, which is related to their mobility, is dependent on pH, redox, and organic compounds (Baun and Christensen, 2004). Each of the oxidation states has different metal complexation constants, and organic compounds may mobilise it to an extent critically dependent upon the redox conditions (Herbert et al., 1993). For example, Tingzong et al. (1997) found that Pb was bound to iron and manganese hydroxide under oxidised conditions. As the landfilled waste shifted to reducing conditions, Pb was leached out. Chuan et al. (1996) also reported that the solubility of Pb, Cd and Zn in soils increased when redox potential decreased, and this was due to the dissolution of Fe–Mn ox-hydroxides under reducing conditions resulting in the release of metals. In contrast, Sims and Patrick (1978) found that soluble Zn decreased at low redox potential, which may be caused by different environmental conditions and soil types. Also, Kamon et al. (2002) found that low redox potential and alkaline conditions induced by anaerobic respiration in landfill sites tend to prompt immobilization of Zn but a mobilisation of Iron. Overall, redox potential strongly affects the behaviour of metals in leachate even though there uncertainty remains regarding to what degree such as different environmental conditions.

3.2. *Organic matter decomposition and metal leachability*

As landfill age increases, the leachate passes through successive stages of organic substance decomposition, which influences metal leachability. Metal leachability is highest when hydrolysis, fermentation and acetogenesis dominate due to an accumulation of VFA and a pH decrease (Fig. 4). The primary acids formed during fermentation are acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$) and ethanol (C_2H_5OH). Carboxylic acids act as chelating agents, and there may be an increase in carboxylic functional groups on humic compounds due to the waste being oxidised (Kjeldsen et al., 2010). Qu et al. (2008) demonstrated that metals in leachate are bound to organic substances such as fatty acids, FAs and HAs. The fatty acids, FAs, and HAs content in leachates decrease as landfill age increases (Fan et al., 2006; He et al., 2006; Qu et al., 2008). The fatty acids are accumulated during the acid phase of the waste stabilisation (Christensen and Kjeldsen, 1989). FA predominates in young unstable leachates, and its concentration decreases as landfill age increases. The HA-forming processes are dependent on microbial degradation of OM, and the HA increases with the age of leachate, eventually reducing due to the leachate becomes more stable and diluted (Artiola-Fortuny and Fuller, 1982). HA has more carboxylic groups than FA and contains bands of aromatic C=C (Gustafsson and Berggren, 2005; Shirshova et al., 2006). The binding capacities of HS to metals within leachate and solid waste may imply that the solubility of HS strongly influences the mobility of metals (Qu et al., 2008). To the best of our knowledge, no work has been reported on the effects of organic matter decomposition on metal release in landfill environments. It is expected that different metals have different impacts on the decomposition processes of organic matter. Further research is required on the role of organic matter degradation on the release of individual metals.

3.3. *Chelation and complexation with organic substances*

Most metal ions bind to neutral molecules in different oxidation states called a ligand, defined as an ion or molecule that binds to a central metal atom to form a complex (both organic; carboxylic acids, amino acids, HAs and inorganic) (Table 4). Ligands lead to the formation of metal complexes and metal chelates. Complexation with organic ligands is known to influence the mobility of metal by either increasing or decreasing its sorption on mineral surfaces. Many organic substances have been commonly identified in leachates worldwide (Details in supplementary data Table 1) (Calace et al., 2001; Paxéus, 2000; Staley et al., 2006; Zhang and Zhang, 2009).

Among the organic ligands, HS are the main organic compounds present in landfill leachate (Zhou et al., 2015). HS are the main component of soil OM or humus, most of which combine with the inorganic constituents in the soil (Pettit, 2004). HS have several functional chemical groups (carbonyl, hydroxyl carboxylic acid, phenolic ring, and quinine), which may combine with ions such as Fe^{3+}, Mg^{2+}, and Ca^{2+} and form chelate complexes; thus change the solubility of metals (Tipping et al., 2002). Generally, the potential for complex formation between metals and organics increases with pH alkalisation (Hummel et al., 2000). Farrah and Pickering (1997a) showed that the proportions of metal bound as hydroxyl complexes increase at pH 5 and above although the capacity for complexation shows no dependence on pH (Antelo et al., 2000). Instead the metal-organic interaction depends on the stability of complex formation and metal concentration. Esakku et al. (2003) reported higher stability constants for Cu complexes with OM and that these lead to higher Cu content in the organic fraction.

Phenolate, amino, and carboxylate groups enhance the formation of metal complexes at high pH, thus become increasingly stable at higher pH levels (Rieuwerts et al., 1998). Carboxylic and hydroxyl functional groups show acid-base behaviour.

At low pH, hydrogen ions compete with the metal ions for these sites, and as pH increases, less hydrogen ions are present and complex site availability for metal ions increases (Scott et al., 2005). There are challenges to understanding the complexation of different metal ions, e.g. i) organic compound functional groups influence the type of reaction it has with metals; and ii) the length of hydrocarbon chain length in carboxylic acid increases its metals adsorption capacity but decreases its stability as complex (Abollino et al., 2003).

Soil organic matter can influence the mobility and speciation of metal, where complexation reactions modify its accumulation potential (Kennou et al., 2015). For example, when organic materials, rich in soluble organic carbon and a large proportion of FAs are applied to soil, metal mobility increases due to the formation of soluble metal-organic complex (Pérez-Esteban et al., 2014). In contrast, when a chelating agent binds to a metal ion in more than one place simultaneously, chelated compounds become more stable (Pohlmeier, 2004). It has long been recognised that complexation may lead to increase metal solubility or decrease adsorption (Cavallaro and McBride, 1978; Bradl, 2004; Güngör and Bekbölet, 2010; Ahmed et al., 2019). Similar observations have been shown to occur within the landfilled waste. A variety of organic compounds can be expected in the leachates, which afford the potential for metal-organic interactions through the organic ligands. Previous studies established that dissolved organic matter (DOM) in MSW has a high affinity for metals, especially for Cu and Pb (Christensen et al., 1996, 2000; HUO et al., 2008). Most insoluble metals are present in their refractory chemical form, i.e. $PbSO_4$. Over time the oxidation/reduction of these metals to a soluble form through complexation

Fig. 5. Leachate recirculation strategy for metal recovery.

appears likely (Takahashi et al., 2010). If insoluble metal-DOM complexes are formed, the mobility of the metals in question and the DOM to which they are complex decreases. Metal mobility is less clear when soluble complexes are created with DOM (Jansen et al., 2003). On the one hand, it may increase because, i) the mobility of DOM is affected by its functional groups and adsorption to soil particles (Kaiser et al., 1997); ii) binding to DOM prevents immobilization by precipitation of inorganic metal complexes. On the other hand, the mobility of soluble metal-DOM could decrease complexes when they bind to soil particles through cation bridging (Guggenberger and Zech, 1993).

The leachability of metals could be enhanced through ligand complexation where organic acids such as carboxylic acids and phenols, formed during the decomposition of organic compounds, decrease pH. The pH determines the number of acidic functional groups on deprotonated DOM, which increases the availability of sorption sites for binding metals (Stevenson, 1994).

Jensen et al. (1999b) determined organic complexes of heavy metals in landfill leachate polluted groundwater in the Vejen landfill. They found that organic complexes made up a significant part of the total content of heavy metals: Cd 85%, Ni 27–62%, Zn 16–36%, Cu 59–95%, and Pb 71–91%. Kalis et al. (2006) found that the metal-humic acid complexes become the dominant complexed species when humic acid is present. Yu et al. (2018) reported that most of the complexes between Cd and the HS would be insoluble, and the complexation could contribute significantly to the reduction in the concentration of Cd in soil solution. Van Ginneken et al. (2001) discovered that the stability of chelated metals and noncyclic metal complexes depends on several factors, including pH, metal oxidation state, and ionic strength. Organic-metal complexes are increasingly stable at higher pH levels due to the ionization of functional groups (Jones and Jarvis, 1981; Rieuwerts et al., 1998). Conversely, organic acids present in the dissolved organic carbon (DOC) may act as chelating agents, enhancing the mobilisation of metals (Christensen et al., 1996).

Complexing behaviour significantly influences metal attenuation as it affects their mobility and saturation indices (Qu et al., 2019). As metal-organic complexation plays a critical role in the mobility of metals in landfill environments, lab and field experiments would be required to establish the relationship between complexing characteristics and observed metals leaching, performed under varying environmental conditions to optimise metals recovery.

4. Leachate recirculation strategy for metal recovery

Leachate recirculation within landfills has been widely used for a range of purposes since the 1970s, including leachate management, enhanced landfill gas generation or recovery, and improved landfill sustainability (EPA, 2009). Leachate recirculation is a process where leachate is re-introduced into the landfill through an artificial recharge system (White et al., 2011). This technique aims to encourage saturation to stimulate the degradation processes, leading to more rapid stabilisation of the landfill (Chung et al., 2015; Francois et al., 2007; Hernández-Berriel et al., 2014; Scott et al., 2005). However, leachate recirculation can also increase the chloride content. Chloride contents may also be an important controlling factor for metal release. Chloride affects the behaviour of metals by binding the metals on humic acids and the adsorption of metals, such as the adsorption of Cd on iron hydroxides or their desorption mobility (Guevara-Riba et al., 2005; Begeal, 2008; Damikouka and Katsiri, 2020). The ionic forms of Cu and Cd can form metal compounds with the anions such as $CuCl_2$, $CdCl_2$ or $CuSO_4$, leading to chloro-complexation and the formation of dissolved metal-chloride compounds increase the mobility of metals (Kirkelund et al., 2010; Damikouka and Katsiri, 2020). This implies that leachate recirculation affects metal recovery. Leachate recirculation can significantly influence metal behaviour and fate within waste matrices (Ledakowicz and Kaczorek, 2004). For example, Yao et al. (2014) found that leachate recirculation contributed to faster stabilisation of the landfill and reduced leachability of Cu and Zn from the landfill. He et al., (2007) have also shown that recirculating leachate, which is by the sequential reactors, in landfills in the early stage allowed methanogenesis to be reached much earlier and that this was accompanied by a reduction of total metals released from landfills. In contrast, Qu et al. (2008) demonstrated that the initial stage of leachate recirculation had low leachate pH (5–6) and highly VFA levels (acetate 4500-700 mg/L, propionate 1450–2950 mg/L and butyrate 4500–7200 mg/L) due to the acidification stage, in resulting the concentration of the metals was high at this stage. Bilgili et al. (2007) showed that the release of metals can significantly increase at the beginning of leachate recirculation as in the early stages of the waste degradation, pH of the leachate is low contributing to higher solubility of metals and dissolution into leachate (Fig. 5).

As stated previously, due to the low concentrations of metals, the way to make it economically viable in recovering metals is to maximise metal concentrations. Recirculating leachates will accentuate the potential for increased metal mobility within and from the landfill when oxidised conditions are introduced. Leachates have been shown to have an increased capability to enhance metal mobility when oxidised (Mårtensson et al., 1999). It implies that leachate recirculation provides higher extractable metals in the initial leaching phase.

Therefore, regarding the critical challenges in metal recovery in leachate, this suggests that where leachate recirculation is applied with combining organic matter such as HA and pH could increase the economic feasibility.

5. Opportunities for metals recovery from landfill leachate

Technologies to extract metals are highly required to enhance and promote recovering metals as secondary raw materials. One of the modern economy models is a circular economy in which wastes should be considered a resource and used efficiently and sustainably (Wieczorek and Kwasniewska, 2018). Extracting metals from landfill leachate may solve the biggest challenges in landfill mining which is regarding the economy. Leachate contains a wide range of metal such as Cu, Zn, Cr, Cd in addition to REEs (Kjeldsen et al., 2002). Leachate in landfill sites has great potential for in-situ metal recovery processes. Consequently, in situ metals recovery can help mitigate climate change and preserve biodiversity by reducing environmental exposure of landfilled wastes. There are several ways for recovering metals from waste, such as recycling, physico-chemical, thermo-chemical, pyro-metallurgical, hydro-metallurgical, bio-metallurgical, landfill-mining methods (Wang et al., 2017a,b). Due to the lack of economically and operationally feasible primary resources for the production of metals, many countries are forced to depend on recycling metals from secondary sources such as

Table 5
Metals recovery from wastewater and liquid solution.

Source	Method	Characteristics	Effects	Reference
Leachate from landfill waste	Bioelectrochemical systems (BES)	- BES employs biological and electrochemical reactions to recovery resources from a wide range of substrates.	- The electrical conductivity of leachate makes it favorable for electricity generation, and it contains a high concentration of ammonium nitrogen, which may be recovered for agricultural application. - Metal also may be recovered by the modified microbial electrolysis cells.	Iskander et al. (2016)
Sulphate leachate of cathode scrap of Li-ion batteries	Liquid-liquid extraction	1) The cathode scraps undergo heat treatment to completely liberate the cathodic materials from aluminum foil. 2) Solubilize Co, Li, Fe, Mn, Ni, and Al by leaching the cathodic materials in sulfuric acid in the presence of H_2O_2. 3) Oxidative precipitation of Mn from liquor with $KMnO_4$ and extraction of Al and Fe using D2EHPA. 4) Treat to recover the metals.	- Focuses on selective recovery of Co, Ni, and Li from the sulphate leachate of cathode scarp generated during the manufacture of Li ion batteries. - High-purity Co in a solution can be recovered by solvent extraction using the sodium salt of PC-88A. - The metals extraction efficiency and separation factor depend upon the extractant concentration and the equilibrium pH of the aqueous phase.	Nguyen et al. (2014)
Solution and leachate derived from electronic scrap	Biogas	- Precipitates metals from solution using the off-gas - Recovery Au, Pd, and Ag from leachate derived from electronic scarp; safe microbiologically	- Au was recovered from electronic scrap leachate with selectivity against Cu using biogas as they could partially separate Au from Cu. - In acidic conditions, Au and Cu are removed rapidly and separated from the liquor. - The solid Pd and Ag will not easily be separated in water via biogas. - Amines must be avoided for recovering metals using biogas.	Macaskie et al. (2007)
End of life electronic wastes	Hydrometallurgical process	- Ferric sulphate concentration range (at 1:10 and 1:5 Cu to sulphide molar ratio 1) filled up by using N_2 gas for anaerobic conditions 2) add of 10 ml of $Na_2S \cdot 9H_2O$ solution	- Effect of Fe^{3+} on leaching of Cu and selective recovery of Cu from the polymetallic leachate. - Lixiviant concentration and pH were the important parameters in $CuSO_4$ precipitation. - The precipitation mostly occurs in the acidic pH range (0.5–1.5). - $CuSO_4$ can be further pyro/hydrometallurgical processed to produce Cu metal.	Sethurajan and Hullebusch, 2019
Aqueous solutions	Biosorption	- The phosphorylation yeast cells were used in Cu adsorption experiments with 0.1 M HCl, which is strongly influenced by the pH of the solution. - Recovering metals from aqueous solutions. The biosorption of metals is a complex process affected by the adsorbent, the types, and the concentrations of metals in the solution.	98% of the Cu ions adsorbed to phosphor cells could be recovered by treating the cells with HCl.	Ojima et al., 2019
Sulfuric acid leaching liquor of spent Li-ion batteries	Hydrometallurgical process	- Needs to refine the residues into a purer form such as salts, hydroxides and metals. 1) selective precipitation method by adding dimethylglyoxime (DMG, $C_4H_8N_2O_2$) reagent 2) extraction using cobalt loaded phosphoric acid (D2EHPA) 3) 4 Separation and recovery of metal (Ni, Mn, Co, and Li) from sulfuric acid leaching liquor	High purities of Co and Li were recovered as $CoC_2O_4 \cdot 2H_2O$ and Li_2CO_3	Chen et al. (2015)
Acid mine leachate	Sequential precipitation	1) Sequential precipitation; add a sodium hydroxide solution of 5 M 2) Selective dissolution; pre-concentrates of the valuable elements were re-dissolved into solution 3) Oxalic acid precipitation; dissolving 8 g oxalic acid dehydrate in 50 mL deionized water using an ultrasonic batch 4) Na_2S precipitation; 1 M Na_2S REEs, Cu, Zn Ni and Co recovery from an acid mining leachate. The sample was collected from a coal preparation plant.	- 95% of the Cu and Zn were recovered from the residual liquid using Na_2S at pH 2 and 3. - The optimize the oxalic precipitation for the REE recovery is using a solution pH of 1.2	Zhang and Honaker (2020)
Sludge	Precipitation	- Add 3 mol/dm^3 NaOH, - The recovery process of heavy metals from polluted sludge leachate with biosurfactant elution by batch and column experiments.	The recovery efficiency of heavy metals (Pb, Ni, and Cr) reached over 90% by the precipitation method with pH 10.9.	Gao et al. (2012)
Wastewater	Cementation	- Add Fe, Al, and Zn metallic powders into 250 mL of wastewater - Stir continuously with a magnetic stirrer	- Cu, Au, and Pd can be recovered by using Fe and Al powder. - Precious metals can be effectively recovered by combining processes (cementation, neutralization and reduction)	Umeda et al. (2011)
Wastewater	Photoelectrochemical cell	- A stock solution was prepared by dissolving the metal salts into deionized water - The photoanode and the Pt strip cathode were connected with a commercial Cu wire - The photoanode was irradiated with a UV lamp	- Heavy metals were recovered by mechanical scratching of the cathode surface.	Wang et al. (2017)
Wastewater	Electrochemical reactor	- Prepare solutions using deionized water - Determining the quality characteristic to be optimized.	- The highest efficiencies were obtained for Pb and Cu recovery from diluted solution: 75.8% and 89.9%	Kaminari et al. (2007)

(continued on next page)

Table 5 (*continued*)

Source	Method	Characteristics	Effects	Reference
		• Identification of the noise factors and test conditions. • Identification of the control parameters.		

industrial residues and end-of-life products. Table 5 shows various methods to recover metals from waste streams and leachate, suggesting the possibility of recovery metals in landfill leachate. Despite published research works on recovering metals from leachate, studies are scanty in an application towards the recovery of metals from real landfill leachate in the site. The main problem to recover metals from leachate is further compounded for metals that exist at low concentrations (Table 2), which can be affected by many factors such as landfill age, type, and chemical and physical mechanism in landfill environments. Also, the strong acidic condition can affect the environment; thus, it may later pose harmful risks to the environment if not managed well. The concentration of metals varies widely, and REEs has a very low concentration (1 or 2 μg/g waste), which limits the economic viability of recovery. Relatively, high concentrations of over 1% are required to ensure cost-effective recovery of metals (Umeda et al., 2011). There are many factors to be considered for the operational cost; leachate collection ($9.56 per m^3 for leachate treatment(), labour cost for operating the plant ($30), electricity cost per hour ($0.1042) and recovery by chemical leaching ($1060 per m^3) (Priya and Hait, 2017; Leflay et al., 2020). Therefore, process optimisation is important to maximise the concentration of metals or co-extraction of other added-value materials such as nitrogen and phosphorus, improving the process's cost-effectiveness and efficiency. By understanding the processes, including organic-metal interaction in leachate, recovering metal can achieve higher average productivity.

Barriers remain in recovering valuable materials present due to the unknown concentrations and distributions of metals in landfills and not meet the reasonable financial level. Metal recovery from leachate has not been investigated before, but prior studies have demonstrated that metals can be recovered from wastewater and aqueous solutions. However, the methods remain limited; for example, physicochemical methods are energy and capital intensive due to the costs of chemicals, oxidants, and membranes; the biological treatment process is limited by treatment effectiveness and energy requirement (Ahn et al., 2002; Kargi and Pamukoglu, 2003).

Bioelectrochemical systems (BES) is an environmental strategy that employs biological and electrochemical reactions to generate electricity and recovery resources from a wide range of substances. Organic compounds in BES tends to produce electricity and other value-added compounds by oxidising microorganisms. However, a high concentration of metals in landfill leachate can be recovered through BES, and the reduction in leachate volumes can be achieved using osmotic processes integrated with BES. Also, hydrometallurgical processes have gained considerable attention as they show effectiveness in the extraction of metals (Gunarathne et al., 2020). Hydrometallurgical metal recovery is typically performed in three main stages: metal dissolution, concentration and purification, and metal recovery (Gupta, 2004). Thus, further research should be studied to take a circular approach, recovering metals from landfill leachate using BES after enhancing metal concentration through leachate recirculation or hydrometallurgical processes using less toxic chemical solvents to be used as leaching agents and assist of acids and pH value.

6. Conclusion

Metal recovery from landfill leachate would contribute to sustainable resource use and will reduce environmental impacts for processes that involves critical and precious metals from raw materials. *In situ* metal recovery process may minimise noise, dust, and greenhouse gas impact and provide a safer place for workers and surrounding communities. This critical review has appraised metal recovery opportunities in landfill leachate using factors influencing metal mobility in landfill environments. From the study, it is obvious that metal's recovery opportunities may increase by several factors, influencing metal mobility in landfill environments as an excellent challenge for metal recovery from leachate is the low concentration of metals. In this regard, many past studies of various factors that influence metal recovery from landfill leachate are systematically summarised in this review. Based on the published research reviewed, using processes adopting technology-considered physicochemical properties would serve as an enhanced method for recovering of valuable metals from landfill leachate. This article has also identified the gaps and has indicated that further efforts are required concerning leachate recirculation. Therefore, this review is paving a way forward that can inform lab-based and later on semi-pilot to pilot studies to be effective for the recovery of metals. However, this review observes that limited data is available concerning the recovery of metals from landfill leachate, thus emphasises that further research is required to develop the scientific principles and suitable technologies to enable in-situ metal recovery. Although mature technological advances provide opportunities for recovering metals from landfill leachate, significant challenges exist as these processes are current not economically viable. It is clear that in situ recovery of metals from landfills is a novel technology area that links new sustainable remediation approaches for contaminated materials and land and is a great help to the development of a circular economy. Therefore, the chemistry mechanism of landfill environments should be well understood and fundamental and practical barriers of the recovering process in landfill leachate, which will lead us one step closer to resource recovery paradigm for a circular economy in closed landfill.

Author contribution

Hyeyeon Lee: Conceptualization, Investigation, Writing – original draft. Frederic Coulon: Supervision, Conceptualization, Writing – review & editing. Darren Beriro: Writing – review & editing. Stuart Wagland: Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.133418.

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