REMOVAL OF LEAD FROM WATER USING LIQUID-LIQUID EXTRACTION PROCESS

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering Chemical Engineering with Honours

Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"REMOVAL OF LEAD FROM WATER USING LIQUID-LIQUID EXTRACTION PROCESS"** was prepared by **CHUA SIEW HWEE** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Chemical Engineering with Honours at Universiti Tunku Abdul Rahman.

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Date : 19 MAY 2023

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ABSTRACT

Lead is considered as a hazardous heavy metal due to its toxicity and ability to bring a variety of harmful impacts on both humans and the environment. Liquid-liquid extraction is known as a powerful separation technology that is increasingly being employed in many chemical process industries to remove heavy metals from wastewater. However, the extensive usage of a large amount of hazardous conventional organic solvents in the liquid-liquid extraction process has significant drawbacks due to their relatively low volatility. Based on that, the greener ionic liquids have recently obtained essential attention as an alternative type of extractant to perform an effective extraction of lead from water through liquid-liquid extraction due to their excellent ionic characteristics. The study investigated the implementation of ionic liquids and organic extractants in the extraction of lead from water via a liquid-liquid extraction process. The study also examined various parameters that affect the removal of lead from water, in which including the effect of different types of extractants used, the impact of hydrochloric acid concentration in the aqueous phase, the initial lead concentration in water, and the volume-to-mass ratio between lead solution and extraction mixture. Based on the study findings, the highest removal efficiency of lead is achieved by Cyphos IL 101 (64.32%), which is followed by Trioctylamine (44.44%) and trihexyltetradecylphosphonium dicyanamide IL (37.97%). Additionally, the higher removal efficiency was achieved at higher HCl concentration for all extractants studied, as a result of the formation of quaternary ammonium cation, R_3NH^+ and lead tetrachloride, $PbCl_4^{2-}$ is required to promote a better extraction process for both complex formation and anionic exchange mechanism. Besides, the higher removal efficiency was attained at a higher initial lead concentration due to a higher concentration gradient between the aqueous phase and extractant phase were created. The performance of the extractants was also highly dependent on the volume-to-mass ratio between the lead solutions to extractant, where a lower removal efficiency was observed with the elevated volume-to-mass ratio as the extractants available within the extraction mixture is inadequate to accommodate the increased amount of lead ions in water.

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C_E	equilibrium concentration of solute in extract phase, ppm
C_{EM}	concentration of lead in extractant mixture, ppm
C_f	final lead concentration in the aqueous solution after extraction, ppm
C_o	initial lead concentration in the solution before extraction, ppm
C_R	equilibrium concentration of solute in raffinate phase, ppm
K	distribution coefficient
K_A	distribution coefficient of solute A
K_B	distribution coefficient of solute B
RE	removal efficiency
V_{aq}	volume of aqueous solution used in the experiment, mL
V_{EM}	volume of organic/extractant used in the experiment, mL
β	separation factor

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

The relationship between the natural environment and human activities is a major concern for environmental issues in which the rates and scales of alteration in the ecosphere are induced by both natural variability and human intervention. One of the most serious issues confronting the world presently is environmental pollution, which is causing severe and irreversible harm to the human society and natural world (Everything Connects, 2013). Human activities are wreaking havoc on the air, land, water, the ecosystem itself, and the numerous aspects of the environment. Consequently, approximately 40% of global mortality is attributed to the pollution of air, soil, and water (Everything Connects, 2013). Pollution can be exhibited in either visible or invisible form. Visible pollutants such as oil splits and plastic wastes are discovered in the water bodies and smog is potentially created by fog, smoke, chemical fumes, and suspended particles. These pollutants are able to be observed with our naked eyes. Most people are only aware of the seriousness and danger of pollution when they can sense it through smelling and seeing. In fact, the vast majority of pollution actually happens in amounts that are invisible and odourless but hazardous (Vital Strategies, 2019). Invisible pollution caused by human activities includes releasing excess concentrations of heavy metals, volatile organic compounds, and other toxic compounds into the environment. After certain time when they become cumulative, this pollution can cause the natural environmental system as a whole and the ensuing chain effects can deteriorate the environment to the point where it becomes lethal for humans (Appannagari, 2017).

Heavy metals are known as metallic elements with a relatively high density and are capable of causing toxicity at low concentration levels (Lenntech, 2019). Heavy metal pollution is becoming a great concern that poses grave dangers to the environment and humans due to its adverse impacts affecting all over the world, especially in developing countries (Cheng, 2003). Despite the fact that heavy metals are naturally occurring constituents of the crust of earth, they are also referred to as persistent environmental pollutants since it is hard to degrade or eliminate them completely once they have been contaminated.

Lead is classified as a heavy metal. As a result of the rapidly expanding metal industries and agriculture, inappropriate waste disposal, pesticides, and fertilizers, this inorganic pollutant is being released into our rivers, soils, and environment (Briffa, Sinagra and Blundell, 2020). Humans are being exposed to lead due to its potential to be discovered in the atmosphere, water sources, food chain, and consumer products.

In Malaysia, the quantity of hazardous heavy metals released into the environment has increased dramatically due to rapid industrialization and urbanization. According to Shazili, et al. (2006), numerous studies have been conducted on the levels of heavy metals in sediment from Peninsular Malaysia's coastal and offshore waterways since the west coast of Peninsular Malaysia is where the majority of the coastal resources, commercial activity, agricultural, and human population are situated. Lead, zinc, and copper have been detected in the sediments of rivers receiving considerable pollution from industry, sewage, and urban runoff. There is up to 117 µg/g of the dry weight of lead was found in the Juru River in Penang. Additionally, the western coast has been found to have the largest concentration of lead, with a reading of 128 ppm in the water at Port Klang, which is recognized as an industrial location (Yunus, Zuraidah and John, 2020). Besides, it has been reported that the concentration of lead ions in industrial wastewater can reach around 200-500 ppm (Arbabi, Hemati and Amiri, 2015). Almost all studies on the distribution of heavy metals that have been carried out in Peninsular Malaysia coastal have examined the concentration of lead since it is one of the most hazardous and significant sources of pollution to the ecosystem. Besides, the water quality will also be negatively affected by the heavy metal pollution. When the heavy metals are bio-accumulated, they pose a risk to both humans and animals who consume the water.

Presently, many conventional techniques are available to remove lead from wastewater (Fuerhacker, et al., 2012). Nevertheless, these methods may be costly, time-consuming, and non-environment friendly to apply. In contrast, liquid-liquid extraction which is ecologically acceptable, efficient, and yet has high selectivity of separation is increasingly attracting attention in the field of removing heavy metals from water. However, the conventional extractants are normally hazardous to the environment and public health. As a result, researchers gradually shifted their study to explore alternative extractants to replace those conventional.

1.2 Importance of the Study

According to Yao, et al. (2021), wastewater generation has dramatically increased as a result of the urbanisation and fast growth of the world population. The practice of discharging wastewater into the environment without suitable treatment is adopted by many countries, with the exception of the most developed nations. Untreated wastewater is directly exposed to the environment potentially causing negative impacts on public health as well as the quality of water resources and ecosystems. Despite wastewater is rich in nutrients and organic matter, which offers significant reuse possibilities as a fertilizer and a soil conditioner, this potential is generally not fulfilled since the wastewater contains hazardous heavy metals and viruses. Heavy metals, including lead are especially dangerous as they may eventually build up in the human body via the food chain because of their great solubility in aquatic environments. Additionally, the human body is absolutely poisonous to lead even at a low concentration owing to its carcinogenic properties. In accordance with the standards set by World Health Organization (WHO), the threshold concentration of lead that is allowed to be discharged as wastewater is 0.5 ppm while 0.05 ppm is the maximum limit concentration of lead in drinking water (Hubicki and Kotodyńska, 2012). Correspondingly, there is an alternative cost always associated with treating municipal and industrial wastewater. Therefore, the selection of suitable and effective wastewater treatment technologies is particularly important.

This study is of great importance in replacing ionic liquids as extractants from conventional volatile organic solvents in the liquid-liquid extraction method to remove lead from water. Liquid-liquid extraction is a powerful separation technology that is increasingly being employed in the chemical process industries to address challenging environmental issues, most notably the removal of trace organic contaminants from wastewater streams (Cusack, 1996). In the meantime, liquid-liquid extraction is ideally suited to be used to treat the non-volatility of lead as it operates on the principle of chemical structure rather than differences in volatility. However, the use of conventional volatile organic solvents in this technique currently has significant drawbacks as they are highly hazardous, flammable, environmentally harmful, and threaten public health due to their relatively low volatility. Therefore, the greener ionic liquids have recently obtained increasing essential attention as extractants to be utilized in the method of liquid-liquid extraction due to their excellent characteristics such as almost negligible vapour pressure and infinite range in their tunability, which are considered to be an appealing alternative to the conventional volatile organic solvents.

1.3 Problem Statement

The lead ion concentrations in industrial wastewater can reach around 200-500 ppm, where this range of concentration is considered very high as it exceeds many from the standards of water quality regulations (Arbabi, Hemati and Amiri, 2015). Lead is possible to contaminate the drinking water since plumbing materials that contain lead can have a chemical reaction known as corrosion with the water and release it into the water as ions (Centers for Disease Control and Prevention, 2020). Based on the WHO standards, the maximum allowable concentration of lead to be discharged as wastewater is set at 0.5 ppm while 0.05 ppm is the threshold allowable concentration of lead in drinking water (Hubicki and Kotodyńska, 2012). Thus, the high concentration of lead present in the wastewater must be reduced to a safe level before discharging it into the environment since lead can cause toxicity even at low concentration levels.

The current liquid-liquid extraction technique that is used to remove lead from water poses some limitations. The biggest limitation encountered in the liquid-liquid extraction process is that it always requires extensive usage of a large amount of hazardous and highly volatile conventional organic solvent that is applied to extract the targeted solutes. The high vapour pressure of these volatile organic solvents has encouraged them to escape from the liquid into the atmosphere and brought negative impacts on the environment, humans, and animals.

Based on the limitations encountered, an alternative type of extractant that can be performed with effective extraction of lead from water with a reduction or elimination of the hazardous impacts posed by the conventional solvents mentioned above is a necessity to be studied. Although excess lead in water can be removed by using conventional extractants through liquid-liquid extraction but this method will eventually create other undesired issues which make it not an environmentally friendly choice. Hence, ionic liquid, a greener alternative extractant to be used in the liquid-liquid extraction method to effectively remove lead from water, requires further study so that the conventional extractant can be replaced.

1.4 Aim and Objectives

The main goal of the study is to investigate the use of ionic liquids and organic extractants in removing lead from water using a liquid-liquid extraction process. The objectives of the project are as shown below:

- To evaluate the efficiency of different extractants in the removal of lead from water.
- To investigate the effects of different hydrochloric acid concentrations on the removal of lead from water.
- To investigate the effects of operating parameters including the initial concentration of lead and volume-to-mass ratio between the solutions to extractant on the removal of lead.

1.5 Scope and Limitation of the Study

This project studies the removal of lead from water using a liquid-liquid extraction process by different extractants. Various scopes of the study were presented in order to achieve the objectives of this study which include:

- Understand the characteristics of both lead contamination, ionic liquids, and the process of liquid-liquid extraction.
- Analyse the efficiency of different extractants which are Trioctylamine, Cyphos IL 101, and Trihexyltetradecylphosphonium dicyanamide in the removal of lead from water.

- Analyse the effects of different hydrochloric acid concentrations in the range of 0.1 M, 0.5 M, 1.0 M, and 1.5 M on the removal of lead from water.
- Analyse the effects of operating parameters which are the initial concentration of lead (50 ppm, 75 ppm, 100 ppm, 125 ppm, and 150 ppm) and volume-to-mass ratio between the lead solutions to extractant (5, 10, 20, 50, and 100) on the removal of lead.

CHAPTER 2

LITERATURE REVIEW

2.1 Lead

Lead (Pb) belongs to the group of heavy metals that are naturally present within the earth’s crust (National Institute of Environmental Health Sciences, 2018). Pb is known as a metallic element with a relatively high density and is capable of causing toxicity at low concentration levels (Lenntech, 2019). Pure Pb, also known as primary Pb, is extracted directly from lead ore, which includes galena, anglesite, and cerussite (Abadin, et al., 2007). Besides that, lead is also able to be obtained from recycled scrap lead through refined lead production by removing any unwanted impurities (Midland Lead, 2019). Hence, the lead recovered is referred to as the secondary lead.

2.1.1 Physical and Chemical Properties of Lead

Lead is bluish-white in appearance, and it is versatile due to its properties of being soft, dense, malleable, corrosion resistance, low melting point, low strength, simplicity of fabrication, chemical stability in the soil, water, and atmosphere, and the capacity to dampen mechanical vibration, waves of sound, and atomic radiation (United States Environmental Protection Agency, n.d.). The physical properties of lead involving its molecular weight, physical state at room temperature, odour, density at 20 °C, melting point, boiling point, and solubility are shown in Table 2.1.

Table 2.1: Physical properties of lead (Abadin, et al., 2007).

Property		**Lead**
Molecular weight		207.2 g/mol
Physical state		Solid
Odour		None
Density at 20 °C		11.34 g/cm^3
Melting point		327.4 °C
Boiling point		1 740 °C
Solubility	**Water at 25 °C**	Insoluble
	Organic solvents	Insoluble
	Nitric acid	Soluble
	Hot concentrated sulphuric acid	Soluble

According to Lyon (2010), the relatively high density of Pb has promoted its ability to attenuate electromagnetic waves and phonon vibrations. This led to a result of a high mass attenuation coefficient and a small neutron absorption cross-section of Pb, which causes it to be capable of radiation shielding from neutrons, X-rays, and gamma rays effectively. Furthermore, it is also effective at suppressing the propagation of sound waves due to its softness and comparatively high mass.

Moreover, Pb is used widely not only due to its physical properties but also its specific chemical properties. Pb is not flammable and combustible. However, finely-divided Pb is known as combustible dust, which has the potential to cause an explosion to happen when dispersed in the air (Canadian Centre for Occupational Health and Safety, 2020). Pb will undergo reactions with hydrogen peroxide, ammonium nitrate, sodium azide, chlorine trifluoride, zirconium, and sodium acetylide in a very aggressive conditions. Therefore, it is not compatible with oxidizing agents and strong acids (NJDOH, 2007). Based on the reactivity of Pb, it is resistant to corrosion from a wide variety of chemicals as it is attributed to the formation of a relatively insoluble, strong, and adherent surface film which is stable and impermeable in a normal atmospheric environment (Alhassan and Goodwin, 2005). The protective film is generated slowly when the Pb surface is oxidized into a thin, surface Pb oxide, which prevents further oxidation of the underlying metal. In addition, Pb also does not react with dilute sulphuric acids since an insoluble layer will be formed that protects the metal from corrosion (Abadin, et al., 2007).

2.1.2 Application of Lead

Pb is involved in agricultural, various industrial, and domestic applications (Tchounwou, et al., 2014). According to Lyon (2010), Pb was applied in the chemical industries as the lining of tanks, particularly in the manufacture of sulphuric acid, and in the electronics industry in the past. It is utilised as a main component of solder to link metals like heat exchangers and pipelines and to provide electrical contacts. Besides that, Pb is widely employed in the construction of cornices, bridges, roofs, railways, lighthouses, ships, and other steel structures despite the availability of alternative coatings (OSHA, 2004).

Apart from that, Pb is also involved in the production of lead-acid batteries, metal items, radiation shielding equipment, and ammunitions nowadays (Tchounwou, et al., 2014). The global Pb usage is distributed into several segments, which are batteries, pigment and other compounds, rolled or extruded products, miscellaneous, cable sheathing, and alloying elements as shown in Figure 2.1.

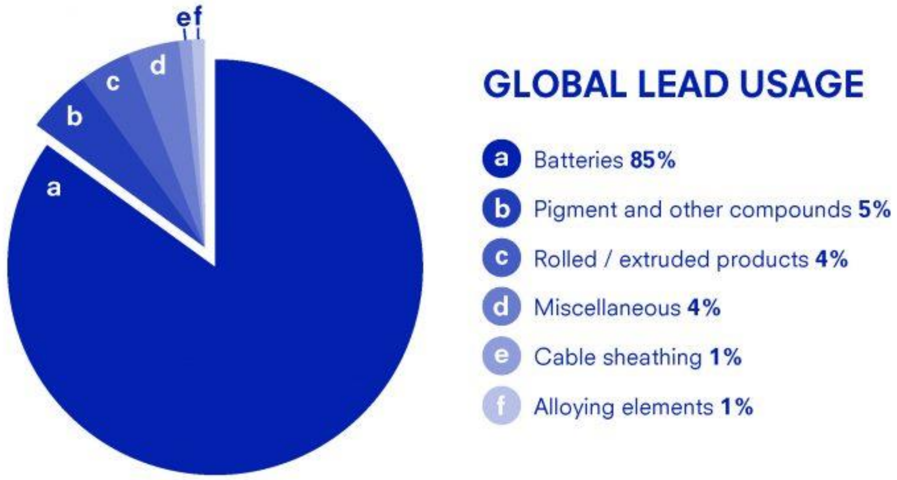

Figure 2.1: The distribution of global lead usage (Midland Lead, 2019).

Based on Figure 2.1, Pb is utilized mostly for the manufacture of Pb-acid batteries, which accounted for more than 50% of the distribution (Midland Lead, 2019). In sustainable markets including hybrid electric vehicles, grid storage for renewable energy generation, and start-stop automotive systems applications, the development and promotion of Pb-acid batteries have been triggered by modern technologies to create more advanced products such as the Advanced Pb-Acid Battery Consortium, ALABC (Prengaman and Mirza, 2017). In addition, the demand for lead-acid batteries is expected to grow due to the development of the market for electric vehicles since it is difficult to substitute Pb-acid batteries with other new batteries for a long time (JYC Battery Manufacturer Co., 2022).

Other than that, Pb is found in synthetic fabric dye that can be manufactured in huge amounts to dye fabrics (Cowley, 2019). Hence, Pb can be found in the fabric and yarn that are used to sew clothes and curtains (Department of Agriculture, Water and the Environment, n.d.). One of the earliest synthesised pigments is white Pb which contained Pb carbonate and Pb hydroxide, which were utilised for the purpose of the manufacture of paints (Kumar, et al., 2021).

2.1.3 Hazardous of Lead and Contamination

Pb is a hazardous metal with a hazard rating of level 4 under the health risk and level 0 for both flammability and reactivity rated by the New Jersey Department of Health (NJDOH, 2007). Level 4 of health risk indicates that Pb will impact health severely as it can affect health or cause serious injury during a very short exposure period, while level 0 of flammability and reactivity implies that Pb will not burn and be stable even after exposure to fire. Pb is classified as carcinogenicity, detrimental to reproduction, specific target organ toxicity-repeated exposure, and hazardous to the aquatic environment under the hazards identification (Vulcan, 2018). Thus, Pb is hazardous as it can bring a variety of negative short- and long-term health impacts (UW Environmental Health and Safety Department, n.d.). According to Jaishankar, et al. (2014), the reason that causes Pb toxicity in living cells is due to ionic mechanisms, which are related to oxidative stress. The biological metabolism of the cell will be disturbed ultimately as Pb metal ions are capable of substituting other monovalent and bivalent cations such as calcium ions, magnesium ions and sodium ions respectively. Hence, significant changes to numerous cellular processes, including protein folding, maturation, ionic transportation, enzyme control and others will be driven by the ionic mechanism of lead toxicity.

Some acute health effects may occur immediately following Pb exposure in a short period of time (NJDOH, 2007). The short-term health effects include irritating the eyes when in contact, causing irritability, declining memory ability, headache, changes in personality, disturbed sleep and mood, weakness and tiredness.

Long-term Pb exposure is likely to have a wide range of effects on a variety of body systems. Several pieces of evidence suggest that Pb could cause cancer in humans, since it can cause stomach, lung, kidney, brain, and kidney cancer in both humans and animals (NJDOH, 2007). Besides that, Pb intoxication frequently has negative impacts on the digestive system, involving loss of appetite coupled with weight loss, pain or discomfort in the abdomen, nausea, and vomiting (WHO, 2017). Other than that, neurological effects can also be brought by Pb poisoning, which leads to a more subtle alteration in neurological function in humans and a life-threatening encephalopathy caused by the disruption of brain function (WHO, 2017). In addition, the reproductive system and pregnancy are potentially being affected by overexposure to Pb (Centers for Disease Control and Prevention, 2021). The possible consequences are affecting the desire for sexuality and the quality of semen by decreasing the quantities of sperm, motility, integrity, and DNA integrity while increasing morphological defects (Kumar, 2018). The opportunities for miscarriages, preterm birth, and reduced fetal growth in a partner have been raised by reducing the potential for fertility. Besides, Pb can also induce the disruption of synthesis of haemoglobin, leading to anaemia and elevation in blood pressure (Lenntech, 2019).

In general, effects induced by Pb have a greater impact on children than on adults due to the higher absorption rate (Tchounwou, et al., 2014). Hence, children typically exhibit severe Pb toxicity symptoms at lower concentrations when compared with adults (Centers for Disease Control and Prevention, 2021).

Environmental contamination by Pb comes from different significant sources which are mining, smelting, production, and recycling operations and the usage of lead-based paint and aviation gasoline is still prevalent in some countries (WHO, 2021). Pb is emitted into the atmosphere directly as suspended particles and it can be inhaled or accidentally ingested where the airborne lead has been settled down onto dust or soil by humans (Texas Commision on Environmental Quality, n.d.).

Moreover, according to Agoro, et al. (2020), heavy metals including Pb have been found to enter aquatic resources through the discharge of municipal, industrial, and agricultural sewage and wastewater into rivers. The concentration of Pb ions in industrial wastewater can vary from 200 to 500 mg/L, which is an unacceptable amount compared to water quality standards (Arbabi, Hemati and Amiri, 2015). Once it is discharged into the water column, it potentially becomes a secondary pollution source, endangering aquatic and ecosystems since it can be adsorbed readily and become suspended in water then settling down in the riverbed. According to Orellana, et al. (2019), agricultural soils and pastures can also be polluted by Pb after being irrigated with contaminated water. It is highly harmful in the soil because of its persistence, toxic effects, and ability to accumulate in plants and animals like cattle and sheep. This element enters the human trophic chain through crops, vegetables, meat, milk, and their derivatives. Thus, it can build up over time in sediments, soils, plants, and animals, which can lead to negative impacts such as limiting plant growth and polluting drinking water and food supplies (SAMCO, 2021). There is also an alternative way that Pb can contaminate the drinking water where plumbing materials that contain Pb have a chemical reaction known as corrosion with the water, especially at high acidity or low mineral content (Centers for Disease Control and Prevention, 2020).

Based on the high demand for Pb in the production of Pb-acid batteries discussed Section 2.1.2, Pb recycling is needed to meet this demand and recycling of Pb-acid batteries acts as one of the main sources (WHO, 2017). However, a significant contributor to environmental contamination and human exposure is Pb recycling because of a considerable release of Pb particles and fumes into the air, water, other surfaces, as well as soil by inappropriate operations (UNEP, 2017). Besides, lead-contaminated dust has been discovered in buildings and lead-based paint was the key source of lead exposure to children in the United States before it was banned (US Environmental Protection

Agency, 2021). In addition, primary lead deposits are those where mining is boosted by lead as it is the primary or sole product (National Academies of Sciences, Engineering, and Medicine, 2017). However, lead emissions are largely caused by the mining and production of metals (Department of Agriculture, Water and the Environment, n.d.).

2.1.4 Threshold Concentration of Lead in Water and Wastewater

Different threshold concentrations for Pb have been set by the agency and department of the environment under government from various countries with the significant reason to safeguard the public from the threats to their health and the environment posed by Pb toxicity by enforcing the regulations, rules, and orders for the facilities to remove Pb from industrial effluents and water to an acceptable level that is considered safe (SAMCO, 2021).

According to the Environmental Quality (Industrial Effluent) Regulations 2009, there are two standards known as standards A and B, which are subjected to the permissible conditions for discharge of industrial wastewater or mixed effluent in Malaysia (Department of Environment, 2009). In the consideration of discharging the effluents that contain Pb, standards A and B are the acceptable concentration of Pb in the wastewater to be discharged into the water bodies that act as drinking water sources and for treated industrial effluent to be emitted into other water bodies except from drinking water sources, respectively. The threshold concentration of Pb in wastewater to be discharged into the sources of drinking water is set as 0.10 ppm (Standard A) while a 0.5 ppm (Standard B) of Pb is acceptable in the treated industrial effluent (Department of Environment, 2009). Apart from that, the Environmental Protection Agency, EPA in the United State has set a maximum level of 0.05 ppm for Pb concentration in industrial effluent (Shomar, et al., 2004, as cited in Agoro, et al., 2020).

Furthermore, according to the national standard for drinking water quality, the permissible limit of Pb in drinking water that is stated in Drinking Water Quality 1993 under the WHO Guidelines is only 0.01 ppm (Engineering Services Division Ministry of Health Malaysia, 2004). Other than that, the action level for Pb presence in public drinking water is set at 0.015 ppm by the

EPA Lead and Copper Rule (Agency for Toxic Substances and Disease Registry, 2017).

The Pb ion concentrations in industrial wastewater can reach around 200-500 mg/L, where this range of concentration is excessive compared to water quality regulations (Arbabi, Hemati and Amiri, 2015). Therefore, the high concentration of Pb must be reduced to a safe level before discharging the wastewater into the environment since lead can cause toxicity even at low concentration levels.

2.2 Conventional Methods

Several techniques are available to remove heavy metals from wastewater (Fuerhacker, et al., 2012). Adsorption, coagulation, chemical precipitation, membrane filtration, ion exchange, flotation, and electrochemical methods are considered as the treatment approaches (Fu and Wang, 2011). Nevertheless, depending on a variety of obstructions, development and control expenses, maintenance issues, and process constraints, the application of treatment techniques in many practical situations is restricted (Fuerhacker, et al., 2012). For example, chemical and biological extraction methods can be utilized to remove heavy metals from sewage sludge (Yao, et al. 2021). The metals can be oxidized into ions by using chemolithotropic bacteria under biological extraction, which is also known as bioleaching, but this process is normally very sluggish and needs at least one day to reach high levels of extraction. Although chemical extraction, which can be accomplished by interacting the wastewater with chelating agents or inorganic acids is typically more rapid and more efficient as some metals can be extracted up to 100% at low pH levels. However, based on their corrosiveness nature, the reactor involved must be constructed using acid-resistant materials and the pH of the end product must be neutralized with a huge amount or an equivalent of lime. Hence, the cost of treating the sewage sludge by chemical extraction using chelating agents or inorganic acids is relatively high. Besides, both of them are unable to be biodegraded, making the extraction process less environmentally friendly. Based on the associated limitations of those conventional techniques, a suitable heavy metal removal approach that meets both performance and cost criteria is increasingly in demand (Sujatha, et al., 2021).

2.3 Liquid-Liquid Extraction (LLE)

According to Hanson (1971), one of the issues encountered most commonly in chemical technology is the separation of the components of a homogeneous mixture. This issue can be resolved typically by introducing the LLE (also referred to as the solvent extraction) method, which is a separation process that allows homogeneous liquid solutions to separate their constituents as it entails the addition of a second liquid solvent that is immiscible or only partially miscible from the original and a component distribution of the mixture between the two phases.

Immiscible liquids are those liquids that are unable to mix together and separate into layers even when shaken together (Wadegaonkar, n.d.). The concentration dependence of the chemical potentials of various essential constituents must be different between the two phases for such distribution to promote a degree of separation (Hanson, 1971). This is because there will be the same chemical potential of a given component in each phase at equilibrium where the process conditions of temperature and pressure are assumed to be constant. In other words, extraction uses chemical differences instead of other driving forces like vapour pressure differences for separation. Based on the origins of this differential solubility, there are two main groups of extraction systems that can be distinguished (Hanson, 1971). In the first category, the differential solubility arises from purely physical differences, while in the second category, it is caused by the formation of a complex when one of the solutes interacts chemically with the solvent.

Furthermore, the two most significant industrial separation techniques are solvent extraction and distillation, both of which are old and well-established processes (Thornton, 2011). When Edeleanu’s process was used to extract aromatic hydrocarbons from kerosene, utilizing sulphur dioxide as the solvent for the petroleum industry in 1909, the first commercially successful operation of LLE was developed. Thus, the chemical, nuclear, petroleum, metallurgical, pharmaceutical, and food processing industries have begun to develop a wide range of additional processes after that.

However, LLE will be the preferred separation technique most of the time when distillation is ineffective or very difficult (Muller, et al., 2008). For example, the LLE method is employed for azeotropic mixtures, substances that are unable to withstand the temperature of distillation, or mixtures with close boiling points.

2.3.1 Process Description of Liquid-Liquid Extraction

A mass transfer process between the two phases is involved in LLE (Koncsag and Barbulescu, 2011). Based on the two immiscible solvents having different solubility or distribution coefficients, a constituent is transferred from one solvent to another through the process of extraction (Wadegaonkar, n.d.). The LLE process is shown in Figure 2.2.

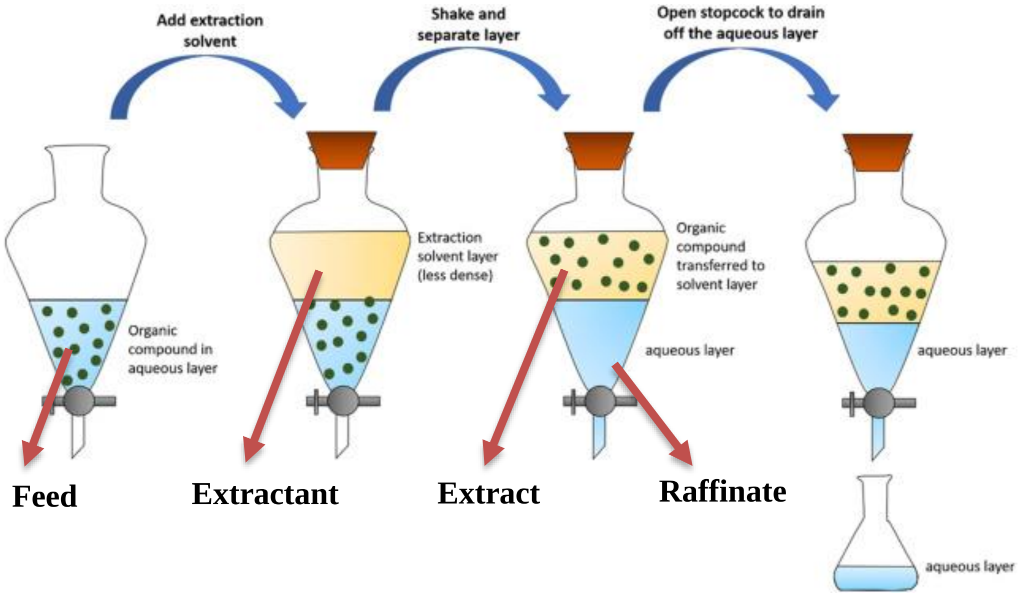

Figure 2.2: The LLE process conducted in a separation funnel (Nair, et al., 2022).

Based on Figure 2.2, there is one liquid phase of the feed that contains both solute and solvent while the other extracting solvent is present in the other phase (Koncsag and Barbulescu, 2011). During the extraction, the solute that is soluble in both phases is extracted and transferred from the feed to the solvent. The extracting solvent will be stirred with the feed during extraction to promote the transfer of solute and the extracting solvent will form a separate layer when stirring is stopped (Wadegaonkar, n.d.). After that, the feed becomes a raffinate due to the absence of a solute from the feed and the solvent transforms into an extract at the end of the extraction process. Some examples of LLE are employing ethanol as a solvent to extract oxygenated terpenoids from citrus essential oils, extracting penicillin from aqueous fermentation broth by butanol, and others.

LLE comprises a mixing stage followed by a phase separation step just like all extraction processes (Berk, 2018). Since liquid-liquid extraction involves the solute's transfer from one solvent to another where both solvents are immiscible or partially miscible with one another, thus, the two phases can be separated due to their immiscibility afterward (Ashall, 2007). However, the determination of solvents and modes of operation is significant and should be considered as both the mixing and separation steps strongly depend on them (Berk, 2018). This is because even though vigorous mixing promotes the extractable solutes to move from one solvent to the other, it may also be possible to make it more difficult to separate the phases by creating emulsions. Additionally, the solute which is being extracted is able to separate from the extract by a technique such as distillation. Then, the solvent is regenerated and it can be reused to carry out further extractions to remove more targeted solutes without any waste of it.

Besides that, the principles of extraction can be further described by the distribution coefficient, K and separation factor, β as they are crucial parameters that determine the number of extraction stages and usage of the solvent (GBH Enterprises, Ltd., n.d.). The definition of distribution coefficient (also referred to as partition coefficient), K is known as the ratio of the solute concentration in the extractive solvent over the solute concentration in the aqueous phase (Qureshi, 2014). The value of K can be represented as the ratio of the solute concentration in each layer that remains unchanged for each system once equilibrium has been attained (Wadegaonkar, n.d.). According to Berk (2018), K is defined as Equation 2.1:

$$K = \frac{C_E}{C_R} \tag{2.1}$$

where

C_E = the equilibrium concentrations of the solute in the extract phase

C_R = the equilibrium concentrations of the solute in the raffinate phase

The relative affinity of the solute for different solvents can be expressed by the distribution coefficient (Berk, 2018). The value of K is preferred to be high to promote an efficient extraction of the component as it identifies the amount of solvent needed to impact the recovery (GBH Enterprises, Ltd., n.d.). However, at a given temperature, the K is practically constant since it is independent of the concentration of the solute in ideal solutions where it is assumed that the chemical potential is proportionate to the concentration (Berk, 2018). Therefore, altering the K can significantly improve the efficiency of a liquid-liquid extraction process under some circumstances.

Based on the equilibrium coefficient, it is evident that a portion of a compound would remain unextracted in the aqueous phase (Wadegaonkar, n.d.). Then, a quantitative extraction of a constituent from the feed into the organic solvent phase is not possible to be done in single extraction instead several times of extraction are required. This can be illustrated in Figure 2.3.

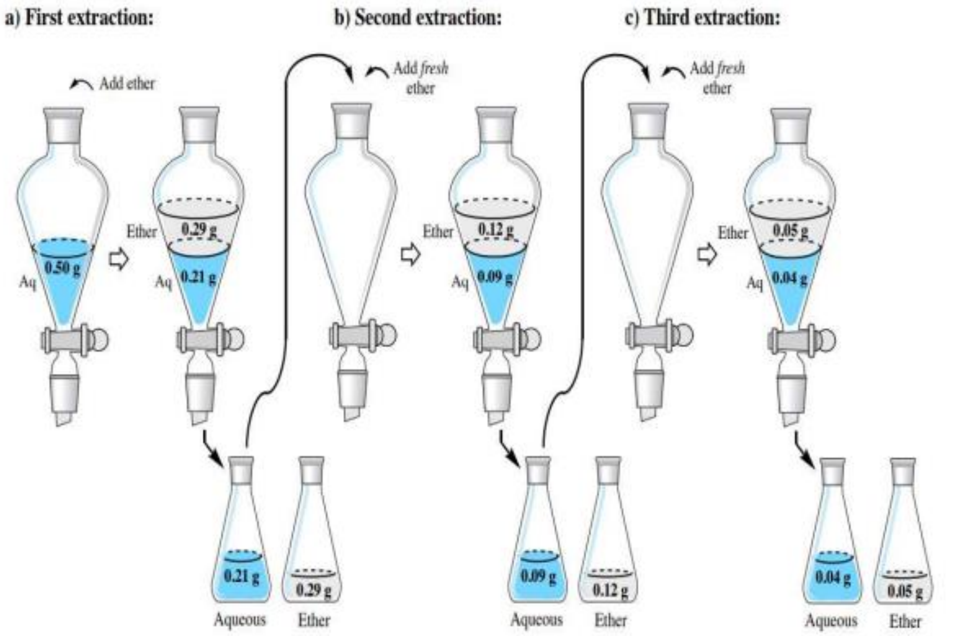

Figure 2.3: Multiple stages of liquid-liquid extraction (Wadegaonkar, n.d.).

Moreover, the definition of separation factor, β is shown as follows:

$$\beta = \frac{K_A}{K_B} \tag{2.2}$$

where

C_R = the distribution coefficient of solute A

C_E = the distribution coefficient of solute B

According to Wadegaonkar (n.d.), the separation factor is utilized to indicate the effectiveness of separation when there are two solutes (known as A and B in this case) from the feed which are to be extracted. If solute A is desired, then an extracting solvent that will dissolve a large amount of A and some B is preferred. Hence, a high value of β indicates that the two solutes are capable of being separated by liquid-liquid extraction otherwise clear separation will be highly challenging.

Apart from that, the mass transfer that happens in LLE is due to the two phases containing concentration variation (Doran, 2013). Mass moves from one region to another based on the effect of a concentration gradient in the system where the mass is transferred from locations of high concentration to locations of lower concentration. For example, when extracting penicillin from fermentation liquor utilizing butyl acetate as an organic solvent. By introducing the solvent broth, the broth consists of a relatively high concentration of penicillin while a low concentration of penicillin exists in the organic phase. Thus, the concentration gradient between the two phases has caused the mass transfer of penicillin to move into the solvent.

Moreover, the well-known double film theory can help to explain the mass transfer mechanism. The stationary double film theory of Whitman is the one that most accurately describes the LLE as it led to truly great results in identifying mass transfer coefficients (Koncsag and Barbulescu, 2011). This theory states that the two phases are isolated through an interface and one for each phase in a double film adheres to this interface. Based on the double stationary film, the mass transfer occurs exclusively by the molecular diffusion mechanism. In a closed system, the concentration at the interface in both raffinate and extract will approach the equilibrium as time passes by based on the double film theory (Koncsag and Barbulescu, 2011), which is explained in Figure 2.4.

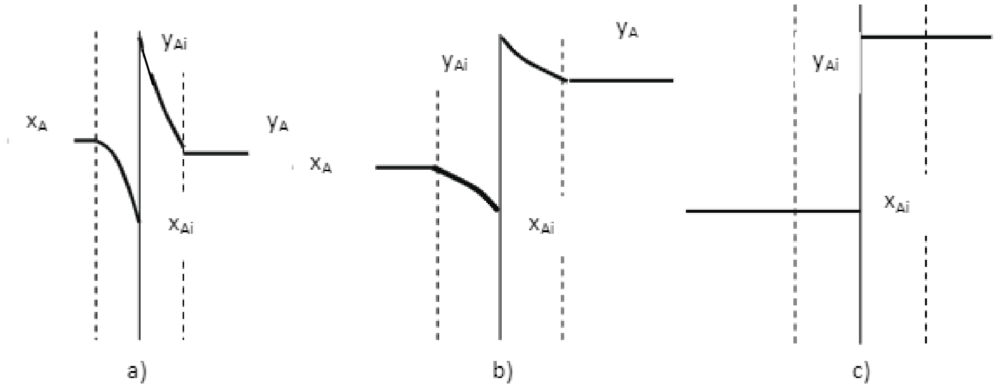

Figure 2.4: The changes in the concentration of solute in the vicinity of the interface within a closed system (Koncsag and Barbulescu, 2011).

Based on Figure 2.4 shown above, the notations of X_{Ai} and Y_{Ai} represent the solute A concentration at the interface respective to raffinate and extract, while X_A and Y_A are referred to as the solute A concentration in the bulk of raffinate and extract, respectively. The mass transfer is shown within a closed system originated from the initial state (state a) to the final equilibrium state (state c). There is a decrease in solute concentration in the bulk feed (or known as raffinate after extraction) with time while the solute concentration in the bulk solvent (or known as extract) increases with time until equilibrium concentrations are achieved. Hence, the interface concentrations are constant and connected with the equilibrium equation.

Furthermore, there are numerous factors to be considered when selecting a solvent to carry out its duty in the LLE process. The factors that will affect the choice of solvent and its description are listed in Table 2.2.

Table 2.2: Factors affect the choice of solvent (GBH Enterprises, Ltd., n.d.).

Factors	Description
Selectivity	Solvent is prefer to pose a great selectivity for the solute over the carrier so that the requirement to recover the carrier from the solvent is minimised.
Distribution Coefficient	The ratio of the solute's solubility in the solvent contrasted to the feed. A large values of distribution coefficient are desirable as less amount of solvent is needed for a given degree of extraction.
Density	A significant difference in density with respect to the carrier to attain a high capacity in the extractor for solute's dissolution.
Viscosity	The ideal viscosity of the solvent is low to prevent inhibition of mass transfer and separation of the phases.
Interfacial Tension	A smaller interfacial tension between the two phases is desirable as
Volatility	A sufficiently different volatility from the solute is needed to allow distillation to recover the solvent.
Stability	Solvent should be stable to maximise the solvent life and minimise the solvent make-up requirement.
Toxicity	A non-toxic solvent is preferred as it is self-evident in considering inherent process safety.
Cost	Availability at a relatively low cost.

2.3.2 Application of LLE

LLE is a complex separation process that involves several fields of application (Sulzer, 2018). Some examples where LLE is utilized are: i) it is applied to a variety of components with widely disparate boiling points to separate them from each other simultaneously; ii) single components to selectively separate from a multi-component mixture; iii) the separation of high boiling products or pollutants that exit in only low concentrations; iv) the separation of components with close boiling points or components that form an azeotrope; and v) the separation of components from electrolytic solutions.

In addition, LLE is one of the essential separation approaches in scientific study and chemical analysis (Berk, 2018). It is extensively employed as a commercial process in the chemical and mining industries and is used in the downstream recovery of valuable fermentation products such as amino acids, antibiotics, and steroids from the broth for protein separation and purification. It is commonly involved as part of the workup, especially an acidic workup after a chemical reaction as it is capable to neutralizing acids and bases in an organic stream by converting a solute into an ionic compound, which is then transferred from an organic phase to an aqueous phase as the ionic compound becomes more soluble in water instead of organic solvent (Schaller, 2022). Other applications of LLE in chemical industries include recovery of reaction products from a broth (PSC, n.d.). For example, the reaction products of caprolactam and adiponitrile can be recovered from nylon production through liquid-liquid extraction.

Apart from that, LLE is a significant separation technology for metal ion separation from water (Ola and Matsemoto, 2018). In this approach, an organic solvent containing an extractant is mixed with the aqueous metal salt solution. After the metal ions become a hydrophobic complex with the extractant, they are moved to the organic phase from the aqueous solution. The movement of complexes from the aqueous to the organic phase is triggered by the different affinities of the complexes for the two phases as well as the relative solubility of the complexes in each.

LLE is a powerful separation technology that is increasingly being employed in the chemical process industries to address challenging environmental issues, most notably the removal of trace organic contaminants from wastewater streams (Cusack, 1996). LLE is also used to treat wastewater in order to remove high boiling point organic materials like phenol, amine, and aromatics since they are not able to be treated by conventional and common process treatment (PSC, n.d.). According to Cusack (1996), phenol is normally removed from wastewater by LLE due to phenol having a higher boiling point than water. Since stripping is not feasible so that LLE is applied as it can typically reduce phenol levels in the wastewater to less than 10 ppm and has achieved values of less than 0.02 ppm in pilot operations. Additionally, acetic acid is commonly found in the wastewater effluent of many chemical processes, especially those involving an oxidation reaction. The main concern is that it is typically present in fairly low concentrations, ranging from 0.5–3.0 % only. Since it is non-toxic, it almost always seems to be enough to just treat it with a biological treatment plant. However, it has become economical for companies to extract and recover the acetic acid before discharging the wastewater for biological treatment due to the rules and requirements for reducing chemical oxygen demand in plant outflows getting stricter. Thus, LLE is a more cost-effective technique to remove the acids even from streams with very low concentrations. Furthermore, some of the hydrogen-bounded chemicals, like formaldehyde, are also a common byproduct of oxidation reactions that are frequently present in wastewater from chemical activities. Based on the hydrogen bonding phenomenon, the formaldehyde molecules are bonded very strongly to the water molecules by static charges. This made it difficult to recover it from the water after it had been dissolved using other conventional techniques. Nevertheless, LLE can easily remove it from wastewater to a relatively low concentration. Non-volatility heavy metals or metal compounds are typically the results of contamination from industrial catalysts. Consequently, they often appear in the discharges of chemical process plants. As LLE operates on the principle of chemical structure rather than differences in volatility, it is ideally suited to solve these challenging removal issues.

2.3.3 Removal of Heavy Metal using LLE

As aforementioned, LLE is an effective technique to remove heavy metal compounds from water depending on their relative solubilities in two different immiscible liquid phases (Patel, et al., 2019). According to Peters and Shem (1993), practically every metal ion may be recovered or removed using an ion exchange process. Heavy metals that are discovered in water always exhibit an ionic form, which is known as cations since they are positively charged (NIE online, 2016).

When allowing LLE process to happen between the heavy metals contained water with extractant which composed of certain cations and anions, the metal ions will tend to exchange with the cations that originated in the extractant through cation exchange mechanism. Hence, the heavy metal can be removed from the phase of water into the extractant. However, sometimes hydrochloric acid is used to ensure the pH of water is always below seven (Keller, 2005). This is because some heavy metals such as Pb can appear in a precipitated non-ionic colloidal form when the pH of water is exceeds seven which causing it become infeasible to remove by an ion exchange process (Keller, 2005). Thus, hydrochloric acid is utilised to create a low pH environment to make sure that Pb is in ionic form (Ooi and Ng, 2018). Then, an anionic exchange mechanism is performed to remove Pb rather than cation exchange mechanism as hydrochloric acid also will provide chloride ions, Cl^- for the conversion of Pb (II) cations, Pb^{2+} into the complex anion form of Pb tetrachloride, $PbCl_4^{2-}$.

$$Pb^{2+} + 4Cl^- \rightarrow PbCl_4^{2-} \tag{2.3}$$

As an outcome of the anion exchange mechanism when allowing the Pb solution to come into contact with the extractant composed of its cation and anion, the excessive anions of the extractant will compete with the $PbCl_4^{2-}$ to form a complex with the cations of the extractant (Ooi and Ng, 2018). The anion exchange mechanisms are shown in equation 2.4 as follows:

$$PbCl_4^{2-} + 2[Cation]^+[Anion]^- \rightarrow [Cation]_2PbCl_4 + 2[Anion]^- \tag{2.4}$$

Generally, extraction of Pb using the anionic exchange mechanism and equilibrium extraction can be attained with sufficient extraction time. Since chemical potential force has driven the transfer of heavy metals from one phase to another (Patel, et al., 2019). Therefore, the entire system of protons and electrons which form the solvents and solutes is in a more stable state after the completion of the transfer process.

2.3.4 Current Limitation of LLE

LLE has proven to be an effective process among other diluted waste solutions to remove hazardous substances (Kislik, 2012). Since there is increasing concern over the effects of chemical operations on the environment in the future, LLE might be a good choice to replace a lot of current polluting operations as it is an environmentally friendly process which does not cause air or water pollution when the plant flows are properly designed. Despite the application of conventional LLE being widespread, it is subjected to several of significant limitations (Watson, 2018).

According to Ola and Matsumoto (2018), the main limitation of the LLE process is that it requires extensive usage of a large amount of hazardous and/or flammable organic solvents such as toluene, dichloromethane, kerosene, diethyl ether, and others, which makes it harmful to the environment. The organic solvents not only cause harm based on their volatility and flammability but also pose a threat to public health if their vapors are released into the atmosphere. Based on United States Environmental Protection Agency (2019), most organic solvents are referred to as volatile organic compounds (VOCs), which can evaporate easily at room temperature due to their high vapor pressure. When the VOCs are emitted into the air, they will react with nitrogen oxide to create ozone molecules, leading to a contribution to the formation of ground-level ozone (Minnesota Pollution Control Agency, 2017). Besides, it also acts as the main pollutant that causes smog. According to the American Lung Association (2020), VOCs can have a negative impact on animals' and humans' health as most of them can irritate the eyes, throat, and nose, lead to breathing problems and nausea, harm the central nervous system and other organs like the liver and kidney. Some of them can even cause cancer.

2.4 Ionic Liquids (ILs)

Ionic liquids (ILs) are liquid at temperatures below 100 °C (Smith, Abbott and Ryder, 2014). According to Kianfar and Mafi (2020), ILs are also referred to as salts that are liquid at room temperature, in contrast to molten salts at high temperatures. This is made possible by the structure of ionic liquids since they are comprised of discrete anions and cations. The common factor groups of cations and anions are shown in Figure 2.5.

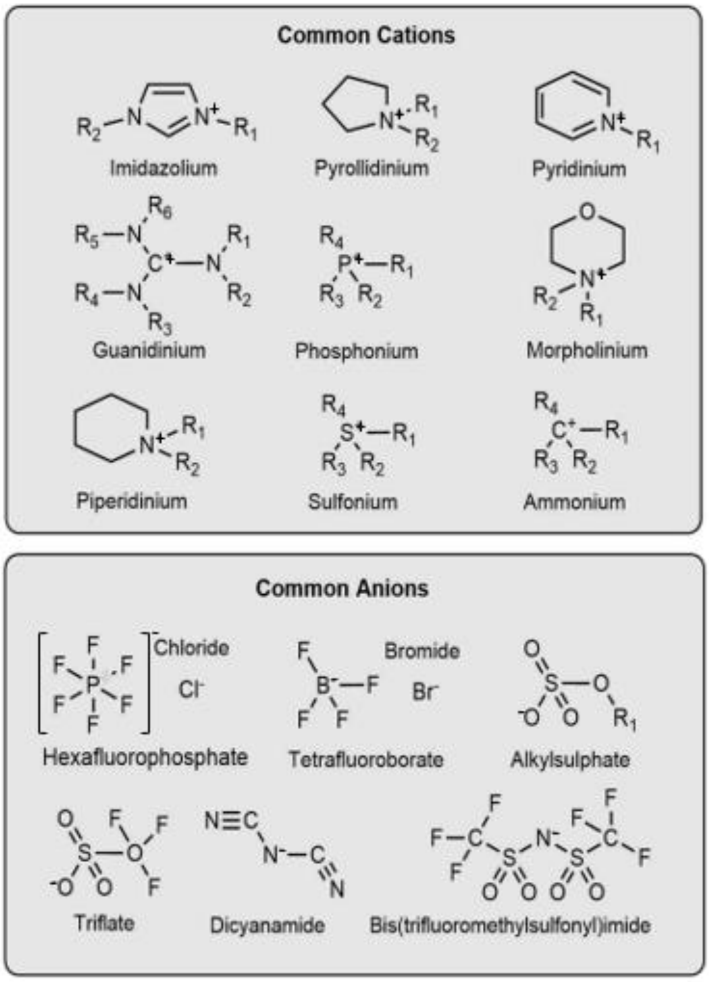

Figure 2.5: The common factor group of cations and anions (Kianfar and Mafi, 2020).

The anions involved are inorganic in structure and substantially smaller in volume when compared with the cations, which are often represented by big organic compounds (Kianfar and Mafi, 2020). The bond between the anions and cations of ionic liquid is weak because of their size gap. Despite ILs having a structure akin to salts, the strong crystalline structure of salts is contributed by the strong bond between cation and anion that have similar size, load, and nature, which makes them different compared to ILs. Thus, ILs have a considerably lower melting point than salts.

In 1914, the first IL of ethylammonium nitrate was discovered by Paul Walden (Lei, et al., 2017). He created the ethylammonium nitrate IL which has a melting point of 12 °C through neutralizing ethylamine with concentrated nitric acid (Shah, An and Muhammad, 2020). The scientific community did not pay much attention to ILs at that time but later in the 1980s, ILs began to show promise in a number of electrochemical applications. According to Lei, et al. (2017), ILs are experiencing faster growth rates when compared to other scientific fields, as evidenced by the remarkable expansion in the number of SCI articles published on ILs from just a few in 1996 to more than 5 000 in 2016. This shows a growing number of academics and researchers are engaged in researching and studying this field, which is giving abundant results.

Furthermore, there are various generations of ILs that are classified as first, second, and third generations (Kianfar and Mafi, 2020). The first generation indicates those ILs with unique tunable physical properties. Besides, ILs that not only satisfy the physical properties mentioned in the first generation but also have chemical efficiencies are known as the second generation of ILs. The second generation is referred to as ILs with specific chemical use because they contain one or more particular functional groups on the cation that can interact and perform a particular chemical function. The third generation introduced those ILs with the combination of targeted biological properties with selected physical and chemical properties, as some active pharmaceutical compounds have classical ionic units that are biologically active with typically low toxicity. The tunable physical, chemical, and biological property sets of ILs can be enhanced by altering the constituent cations or anions (Gilmore, 2011).

Nowadays, ILs are increasingly used in many different fields of science and technology (Kianfar and Mafi, 2020). It is also involved in a wide range of applications where the utilization of ILs as a green solvent instead of a volatile organic solvent is the most important application among others. ILs can be used in catalytic reactions as a two-phase catalyst or substrate to stabilize other catalysts. Besides, clumpy reaction environments where nanocatalysts are bound together and lead to a great deduction of their activity can be avoided by employing an IL medium. According to Kianfar and Mafi (2020), they are popularly used by electrochemists in power systems due to their great electrochemical stability, broad performance range of temperature, and high conductivity. ILs also play an important role in liquid-liquid extraction to separate the desired solute from the feed stream.

2.4.1 Advantages of ILs

Recently, traditional industrial solvents, which are mostly VOCs have increasingly been replaced by ecologically friendly ILs due to the VOCs emissions that have caused the disruption of ecological balance drastically (Stark and Seddon, 2007). The primary cause of environmental pollution in the pharmaceutical and chemical industries comes from organic volatile solvents (Kianfar and Mafi, 2020). As discussed in Section 2.2.4, conventional solvents are highly hazardous, flammable, environmentally harmful, and threaten public health due to their relatively low volatility. Although most of the ILs are known as green solvents but few of them are toxic (Kianfar and Mafi, 2020). However, based on the unique characteristics of ILs, they still have the potential to decrease the use of hazardous and polluting organic solvents. Thus, the greatest benefit of ILs is their characteristics and distinctive properties that enable them to substitute conventional organic volatile solvents.

One of the important advantages of ILs is that they have a near-zero vapour pressure and are non-volatile in conditions near ambient (Wasserscheid, 2006). Besides, most ILs do not really exhibit any distillation characteristics below the temperature at which they thermally decompose. The extremely high enthalpies of vaporisation and low vapour pressure in ILs (also known as Coulomb fluid) are reflections of the strong interaction between anions and cations (Fumino and Ludwig, 2014).

Apart from that, the ability of ILs to dissolve a wide range of organic, inorganic, vital molecules, metal-organic compounds, and metal ions also serves as one of the advantages of ILs (Kianfar and Mafi, 2020). According to Shukla and Mikkola (2020), ILs are capable of reacting with both non-polar and polar solutes depending on the charge density of the anion that decides whether ILs will behave as hydrophobic or hydrophilic. Since most organic solvents are non-polar and exhibit low polarity that is typically not combined with the aqueous phase, ILs that are highly polar based on their ionic structure are incompatible with those organic solvents (Kianfar and Mafi, 2020). Nevertheless, ionic liquids that are insoluble in water can be generated by lengthening the alkyl chain attached either to the cation or anion. Thus, these ILs can also be employed as organic phases.

In addition, ILs exhibit ionic conductivities (up to about 0.1 $\Omega^{-1}cm^{-1}$) that are relatively better than organic solvents or electrolyte systems (Endres and Abedin, 2006). The conductivities of ILs are expected to be high because they are made entirely of ions. However, the conductivity of every solution is not only based on the quantity of charge carriers but also their mobility. Additionally, the ionic packing is also affected by the high degree of asymmetry in the molecular structure of ILs that leads to a reduction in Coulombic attraction between the ions (Welton, 1999, cited in Shah, An and Muhammad, 2020). Therefore, constituent ions that are bigger in size will tend to decrease ion mobility and result in poorer conductivity performance (Endres and Abedin, 2006). The conductivity and viscosity of ILs are inversely related. Nonetheless, ILs commonly have viscosities of 10 mPa to 500 mPa at ambient temperature, making them more viscous than regular molecular solvents. This issue can be resolved by elevating the temperature since all ILs exert a substantial viscosity reduction at a higher temperature, which in turn, increases the conductivity.

Moreover, the other advantage of ILs is that they are generally stable and resistant to heat up to 450 °C (Endres and Abedin, 2006). The strength of the bonding between heteroatom-carbon and heteroatom-hydrogen in ILs is the factor that determines their thermal stability. Since there are various types of bond formation exhibited within the ILs like dipole-dipole interaction, van der Waals forces, hydrogen bonding, and others, more heat will be needed to break down those bonds. Based on ILs' characteristics of non-flammable and high thermal stability, they are considered the safest solvents in a variety of high temperature applications.

Furthermore, ILs applications could be said to be very flexible due to the distinct structural tunability of the cations and anions involved (Sowmiah, et al., 2009). As ILs have an unlimited range in their tunability, they are also known as "designer solvents". Since simply altering the combination of anions and cations can change the chemical and physical characteristics of ILs (such as viscosity, solubility, and thermal stability), they are able to provide a variety of new reaction media that may be more diverse in character and use in comparison to the conventional solvents they are intended to replace (Gilmore, 2011). For example, introducing the desired functional groups to the anion and/or cation can generate task-specific ILs (TSILs) that can interact with solutes in a specific manner (Zhao and Anderson, 2012).

In conclusion, previous discussions have shown that ILs have numerous benefits over volatile organic solvents, including non-volatility, great thermal and chemical stability, non-flammability, strong extraction ability, and tunable miscibility (Xu and Cheng, 2021).

2.4.2 Application of ILs in Heavy Metals Removal

According to recent research studies, the removal of heavy metals by extraction with ILs is being employed more frequently as a substitute for conventional industrial wastewater treatment (Fuerhacker, et al., 2012). The application of ILs to remove heavy metals promotes a more sustainable chemical extraction approach since a faster extraction that requires no neutralization of the end product can be achieved and provides fewer harmful impacts to the environment (Yao, et al. 2021). The comparison of three treatment methods for the Pb removal from wastewater is shown in Table 2.3 since this study will only focus on the removal of lead from water.

Table 2.3: Comparison of three treatment approaches for the removal of Pb from wastewater.

Treatment Methods	Operation Style	Initial concentration, C_o (ppm)	Removal efficiency (%)	References
Solid sorption	Type: Batch experiments; Adsorbent: Clinoptilolite; Dosing rate: 20 g/L	1 036	55	Inglezakis, et al. (2007)
Precipitation	Using calcium oxide (CaO)	100	99.37-99.67	Chen, et al. (2009)
ILs	Using [PR4][MTBA]	0.005 - 1	>85	Fuerhacker, et al. (2012)

Based on Table 2.3, although the removal efficiency of ILs is not the highest but it is also able to achieve a high removal efficiency of more than 85%, which is satisfactory to be used for industrial effluent treatment plants to remove

Pb (Fuerhacker, et al., 2012). Even though chemical precipitation holds the highest removal efficiency, but this method is associated with a massive quantity of treatment chemicals in order to reduce the amounts of heavy metals to meet the current regulations. Meanwhile, the precipitation-produced sludge must be dewatered first before it is disposed of in landfills. Then, it raises the expense of this treatment process. Besides, the solid sorption method with a relatively low removal efficiency is not desired. Hence, ILs seem to be more successful in the removal of PB from water than conventional methods in terms of several aspects.

According to Goutham, et al. (2022), the mechanism for extracting heavy metal cations by ILs is distinguished from that employed by conventional organic with aqueous mixtures owing to the ILs' charged nature. Only complexes that exhibit a neutral form can be separated from the aqueous phase into an organic phase in conventional systems. In turn, it is reported that amphiphile self-assembly has contributed to a microscopic scale of heterogeneous architecture toward ILs. As an outcome, the hydrophobic tails will cluster together to form a discrete non-polar domain while the charged anions with a head group of cation will create a continuous polar network that surrounds the non-polar domain. Due to the amphiphile self-assembly of ILs, anions and cations composed of ILs are free to be transferred into the aqueous phase. Hence, a remarkable ion-exchange mechanism for ILs is generated and makes it unique from the conventional extraction system.

A simple, rapid, and sustainable method for the removal of heavy metals can be achieved by using LLE with ILs (Leyma, et al., 2016). Hydrophobic ILs can be used to contact the contaminated water so that the metal ion separation can be induced by extracting the metal ions towards the ILs involved (Fuerhacker, et al, 2012). According to Leyma, et al. (2016), the hydrophobicity of these ILs enables the creation of biphasic liquid-liquid systems suited for aqueous solution extraction. ILs of phosphonium, imidazolium, ammonium, and pyridinium are the most prevalent options for metal extraction. Besides, the usage of Cyphos IL 101 and Aliquat 336 can be considered in this case since they are particularly water-repellent due to their long alkyl chains. Nevertheless, the leaching of these ILs into the aqueous phase during their application in LLE methods may pose additional environmental hazards. It has been proposed to integrate the features of quaternary phosphonium and ammonium cations with various functionalized anions that display strong affinity towards specific metals in order to generate task-specific ILs, TSILs. In addition, an alternative strategy to increase the metal affinity for IL phase can be done by introducing a strong coordinating anion into it (Regel-Rosocka and Wisniewski, 2011). For example, both phosphonioum- and ammonium-based ILs with aromatic anions as constituents also exhibited lower water solubility and water absorption (Leyma, et al., 2016). The higher the metals' affinity for the IL phase, the greater the extraction yield (Regel-Rosocka and Wisniewski, 2011).

Furthermore, numerous studies have been conducted on removing Pb from water and wastewater using various types of ILs. It has been proven that room-temperature ILs of 1-butyl-3-methylimidazolium hexafluorophosphate, which is also referred to as BMIM-PF_6 and commercially available ILs, including Cyphos 101 and Aliquat 336 can be used to extract Pb^{2+} ions successfully (Goutham, et al., 2022). The IL of BMIM-PF_6 is able to achieve an extraction efficiency of Pb up to 97.82% at pH 5.33 (Dungca, Hevey and Patenaude, 2008). Apart from that, trihexyltetradecylphosphonium chloride has also been studied as an extractant to remove Pb from water on a lab scale (Ooi and Ng, 2018). When it is used together with toluene as diluent, 80% of its removal efficiency can be reached in 5 minutes. If the efficiency is maintained over a longer period of time, the extraction equilibrium has been reached. Therefore, the application of ILs in the LLE technique seems to be a promising method for the removal of Pb in water.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Chemical Materials and Reagents

The organic extractant of Trioctylamine (TOA) and ILs of Cyphos IL 101 and trihexyltetradecylphosphonium dicyanamide were utilised as extractants to remove Pb from water. A non-toxic organic solvent of cooking oil was used as an extraction diluent in this study to ensure the extractants were well dispersed. The Pb solution was prepared from lead nitrate, $Pb(NO_3)_2$, which is the source of Pb ions. Hydrochloric acid, HCl was being used as a conditioning reagent in this study to convert Pb (II) cations, Pb^{2+} into the complex anion form of Pb tetrachloride, $PbCl_4^{2-}$ to allow an anion exchange mechanism to occur.

3.2 Equipment

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was the analytical technique used in this study to determine the remaining concentration of Pb in the Pb solution after each extraction test. Besides, a magnetic stirrer was used to allow mass transfer between the two phases and improve dispersion.

3.3 Flowchart of Work Plan

The primary objective of this study was to analyse the use of various types of extractants in removing Pb from water. There were four parts involved in this study which included performing a literature review, preparation of materials, conducting experimental tests, and analysis. The flowchart of the work plan is presented in Figure 3.1.

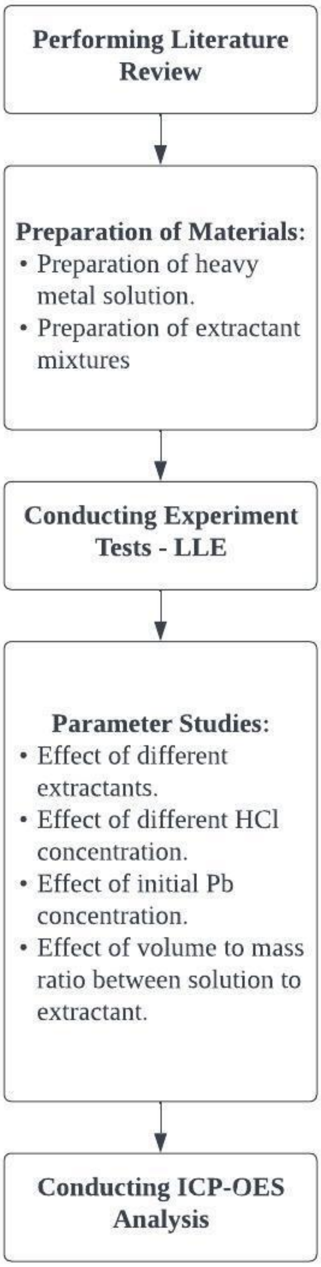

Figure 3.1: The Flowchart of Work Plan.

The Literature review was conducted in Chapter 2 to understand the characteristics of both Pb contamination and ILs, as well as the process of LLE. The preparation of heavy metal solutions and extractant mixtures was discussed in this chapter. Material preparation was the first step to be considered before experiment tests can be performed. After that, the experiment tests were carried out to study the effects of different HCl concentrations on three types of extractant mixtures. The most effective HCl concentration for each of the extractant mixtures was carried forward to continue with other experiment tests to study the effect of the initial concentration of Pb and the volume-to-mass ratio between the solutions to extractant. The samples collected after each extraction test were analysed using ICP-OES.

3.4 Experiment Procedures

3.4.1 Preparation of Lead Solution

A Pb stock solution was prepared from Pb (II) nitrate salts. The pre-calculated quantity of 0.1598 g of $Pb(NO_3)_2$ was dissolved in 100 ml of deionised water in a volumetric flask to produce a 1000 ppm of Pb solution.

During the experimental test, the concentration of the Pb solution was diluted to the desired concentration based on the needs of the experiment tests by using an HCl solution.

3.4.2 Preparation of Extractant Mixtures

The extraction mixture was prepared by adding the three extractants which were TOA, Cyphos IL 101, and trihexyltetradecylphosphonium dicyanamide into the cooking oil respectively. For each experiment cycle, a 12 g of 5 wt% of each extraction mixture was made by mixing 0.6 g of the respective extractant with 11.4 g of cooking oil.

3.4.3 Liquid-Liquid Extraction

The extraction of Pb was performed by mixing a volume of 10 ml of Pb solution with 2 g of the prepared extractant mixture in a scintillation vial. The mixture was stirred to homogenize for 15 minutes utilizing a magnetic stirrer. After 15 minutes of the extraction process, the mixture was left stagnant to allow the phase separation. A pipette was used to draw 3 ml of the samples out of the aqueous phase for analysis purposes using ICP-OES.

3.4.4 Experiment Planning

3.4.4.1 Effect of Extractants and HCl Concentrations on Pb Extraction

Each of the 5 wt% of extraction mixture was contacted with four different Pb solutions that were being dissolved with various HCl concentrations from 0.1 M, 0.5 M, 1.0 M, and 1.5 M in a scintillation vial. The initial concentration of the Pb solution was set as a constant parameter of 150 ppm. Each respective set of the mixture was mixed and LLE was performed based on the procedure as discussed in section 3.4.3.

The extraction efficiency and distribution coefficient can be determined after analysis using ICP-OES. According to the analysis, the best performance for each of the extractants from different HCl concentrations in Pb solutions was identified.

3.4.4.2 Effect of Different Operating Parameters on Pb Extraction

The HCl concentration that gives the best removal performance for each of the extraction mixtures from the study in Section 3.4.4.1 was applied to study the effect of the initial concentration of Pb and volume-to-mass ratio between the solutions to extractant.

The prepared Pb solution was diluted with HCl solution into the desired concentrations as 50 ppm, 75 ppm, 100 ppm, 125 ppm, and 150 ppm. After that, the extraction mixture was mixed with different concentrations of Pb solution to investigate the effect of the initial concentration of Pb on the removal process.

The effect of the volume-to-mass ratio between the Pb solutions to extractant was also examined. The volume-to-mass ratio involved in this study was set as 5, 10, 20, 50, and 100. Based on the volume-to-mass ratio, an amount of 150 ppm of Pb solutions with an appropriate HCl concentration identified from previous tests mentioned was mixed with a known quantity of 5 wt% of extraction mixtures to enable LLE to perform. The desired volume to mass ratio to be studied was conducted as follows:

- 10 ml of lead solution was mixed with 2 g of extraction mixture to obtain a volume-to-mass ratio of 5.
- 10 ml of lead solution was mixed with 1 g of extraction mixture to obtain a volume-to-mass ratio of 10.
- 10 ml of lead solution was mixed with 0.5 g of extraction mixture to obtain a volume-to-mass ratio of 20.
- 10 ml of lead solution was mixed with 0.2 g of extraction mixture to obtain a volume-to-mass ratio of 50.

- 10 ml of lead solution was mixed with 0.1 g of extraction mixture to obtain a volume-to-mass ratio of 100.

3.5 Analytical Method

The ICP-OES was employed in this study to analyse and determine the remaining concentration of Pb in the Pb solution after each extraction test. Before the analysis can be conducted, 50 ml of a blank solution and five known concentrations of Pb solutions (which are 4 ppm, 8 ppm, 12 ppm, 16 ppm, and 20 ppm) were made in individual centrifuge tubes to create the calibration curve for ICP-OES analysis. Based on the created calibration curve, the unknown Pb concentration can be quantified using linear regression. The prepared solutions were labeled and placed on the tray appropriately and the analysis was performed.

After the completion of each extraction process, 0.5 ml of the aqueous solution was sampled and it was diluted with 9.5 ml of deionised water in a centrifuge tube. The step involved dilution of the sample collected was necessary to be carried out to assure the samples which were interested to analyse had corresponding matrices with the calibration standards. A dilution factor of 20 was gained after the dilution step. The diluted samples were appropriately labeled and located on the tray before the analysis was performed.

From the results obtained from the ICP-OES analysis, Pb removal efficiency and distribution coefficient using each extractant under different parameters can be evaluated. The removal efficiency and distribution coefficient were calculated based on Equations (3.1) and (3.2), respectively.

$$RE(\%) = \frac{(C_o - C_f)}{C_o} \times 100\% \tag{3.1}$$

where

RE = the removal efficiency of Pb, %,

C_o = the initial concentration of Pb in the aqueous solution before LLE, ppm,

C_f = the final Pb concentration in the aqueous solution after LLE, ppm.

$$K = \frac{C_{EM}}{C_f} \tag{3.2}$$

where

K = the distribution coefficient,

C_{EM} = the concentrations of Pb in the extractant mixture, ppm.

The concentration of Pb in the extractant mixture can be computed through the Equation (3.3) shown as follow:

$$C_{EM} = \frac{(C_0 - C_f)V_{aq}}{V_{EM}} \tag{3.3}$$

where

V_{aq} = the volume of aqueous solution used in the experiment, mL,

V_{EM} = the volume of extraction mixture used in the experiment, mL.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Extractants

The effect of extractants on Pb extraction from the water was investigated based on two types of extractants which were organic extractants (represented by TOA) and ILs (represented by Cyphos IL 101 and Trihexyltetradecylphosphonium dicyanamide). Since Pb can appear in a precipitated non-ionic colloidal form when the pH of water is higher than seven which causing it become infeasible to remove by the LLE process (Keller, 2005). HCl was utilised to create a low pH environment to ensure that Pb is in the ionic form of $PbCl_4^{2-}$ instead of Pb^{2+} to promote LLE process. Besides, it is generally asserted that for the formation of $PbCl_4^{2-}$ from Pb^{2+}, a low pH and high concentration of HCl are necessary to gain a better anion exchange. Based on that, the effect of extractants was studied by allowing the different 5 wt% of extractant mixture to mix with the 150 ppm of Pb solution in 1.5 M of HCl. The stirring speed was fixed at the value of 700 rpm. Figure 4.1 illustrates the effect of different extractants on the removal efficiency (RE) of Pb.

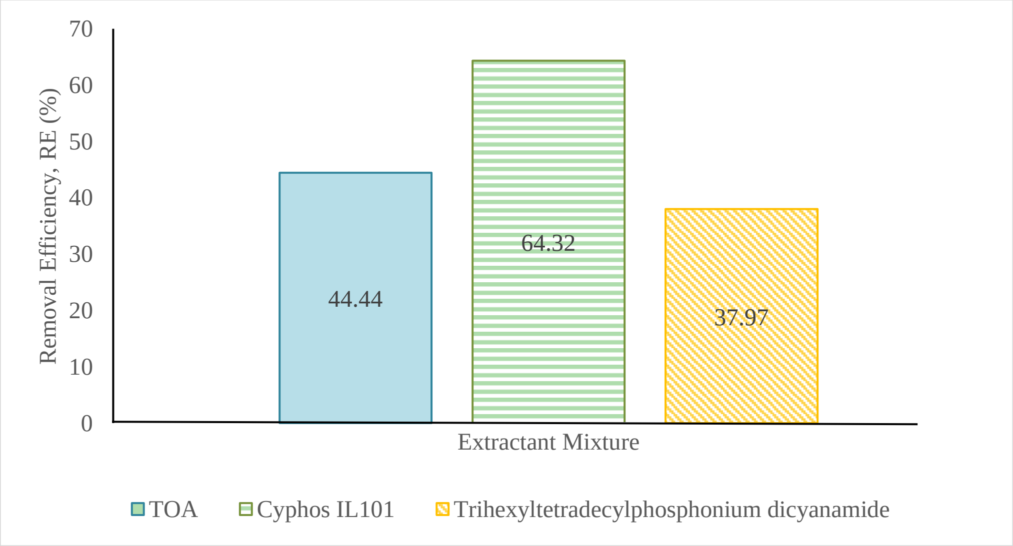

Figure 4.1: Effect of Extractants on the Extraction Efficiency of Pb.

According to Figure 4.1, Cyphos IL 101 possesses the highest Pb RE at 64.32% when compared to TOA and trihexyltetradecylphosphonium dicyanamide. On the other hand, trihexyltetradecylphosphonium dicyanamide was seem to have the poorest removal of Pb among the three extractants involved even though the RE between TOA and trihexyltetradecylphosphonium dicyanamide differed by only 6.47%.

The experiment was conducted to extract Pb from water in an acidic condition by using two types of extractants - organic extractants and ILs. As they possessed various properties, the extraction mechanism used for each can differ. The extraction process of Pb from water utilising TOA is believed to involve complex formation between TOA and Pb. TOA molecules in the organic phase tend to form stable coordination complexes with Pb ions in the aqueous phase, which can then be migrated into the organic phase. Since TOA is referred to as a long-chain aliphatic amine, hence the extraction process is driven by the ability of TOA to form covalent bonds with metal ions through its amine group. According to the work of Ghadiri, Ashrafizadeh, and Taghizadeh (2011), it stated that the existing amine groups which served as coordination sites for metal-binding will be protonated after being exposed to hydrogen ions, H^+ and become a chelating agents in the form of quaternary ammonium cation, R_3NH^+ as follows:

$$R_3N + H^+ \Leftrightarrow R_3NH^+ \qquad (4.1)$$

Moreover, for a divalent metal ion like Pb to appear in the form of $PbCl_4^{2-}$, two molecules of R_3NH^+ would typically binds with each metal ion to form a TOA-metal ion complex, as indicated by Equation 4.2:

$$PbCl_4^{2-} + 2R_3NH^+ \Leftrightarrow (R_3NH)_2PbCl_4 \qquad (4.2)$$

After that, the coordination of the metal ion with the TOA molecule leads to a change in the solubility of the complex form, making it more soluble in the organic phase than in the aqueous phase. Thus, the extraction process of

Pb from water by using TOA is believed to involve complex formation between TOA and Pb.

On the other hand, an anionic exchange extraction is considered for both ILs involved. During the anionic exchange extraction, the ILs will selectively remove the $PbCl_4^{2-}$ from the aqueous phase by exchanging them with the anion in the ILs. As referred to the work of Ooi and Ng (2018), an anionic exchange mechanism is performed to remove Pb as the presence of HCl will provide Cl^- for the conversion of Pb^{2+} into the complex anion form of $PbCl_4^{2-}$, as shown in Equation 4.3.

$$Pb^{2+} + 4Cl^{-} \rightarrow PbCl_4^{2-} \tag{4.3}$$

Therefore, the extraction mechanism involved for both Cyphos IL 101 and trihexyltetradecylphosphonium dicyanamide can be referred to as Equation 4.4.

$$PbCl_4^{2-} + [Cation]_{IL}^{+}[Anion]_{IL}^{-} \Leftrightarrow [Cation]_{IL}^{+} PbCl_4^{2-} + [Anion]_{IL}^{-} \tag{4.4}$$

Nonetheless, the findings of the experiment indicated that all three extraction mixtures were unable to achieve a 100% RE using the presence setup. The highest RE among the three extraction mixtures was 64.32% (obtained by Cyphos IL 101) while the lowest RE was 37.97% (gained by trihexyltetradecylphosphonium dicyanamide). Then, 44.44% of RE was able to achieve by TOA. In addition, the highest RE achievable by Cyphos IL 101 is due to the formation of a hydrophobic complex between its cation and the $PbCl_4^{2-}$. This complex has limited solubility in the extraction mixture, which causes a greater concentration of Pb ions to accumulate in the extractant phase (Imdad and Dohare, 2022). In other words, the complex formed between Cyphos IL 101 with $PbCl_4^{2-}$ is relatively stable in the extraction phase so that it will not disintegrate easily and release the Pb ions back into the aqueous phase (Nyamato, et al., 2022). As a result, the extraction efficiency of Pb is enhanced when Cyphos IL 101 is used as the extractant. Moreover, the capability of ILs to extract metal ions is strongly pertinent to the ability of its ions to create stable complexes with the metal ions and its affinity towards the metal ions (Diabate, et al., 2018). Based on that, trihexyltetradecylphosphonium dicyanamide has been considered to have the weakest affinity for Pb ions and is only able to form less stable complexes with Pb ions, which limits its effectiveness as an extractant.

4.2 Effect of HCl Concentration

The impact on the concentration of HCl in Pb solution was studied from 0.1 M to 1.5 M. The use of HCl played an essential role to contribute an acidic condition to make sure that the Pb is in ionic form so that it can be removed either by an ion exchange extraction or through complex formation. Figure 4.2 illustrates the effect of HCl concentration on the extraction efficiency of Pb in which the initial Pb concentration and the stirring speed were fixed at 150 ppm and 700 rpm respectively.

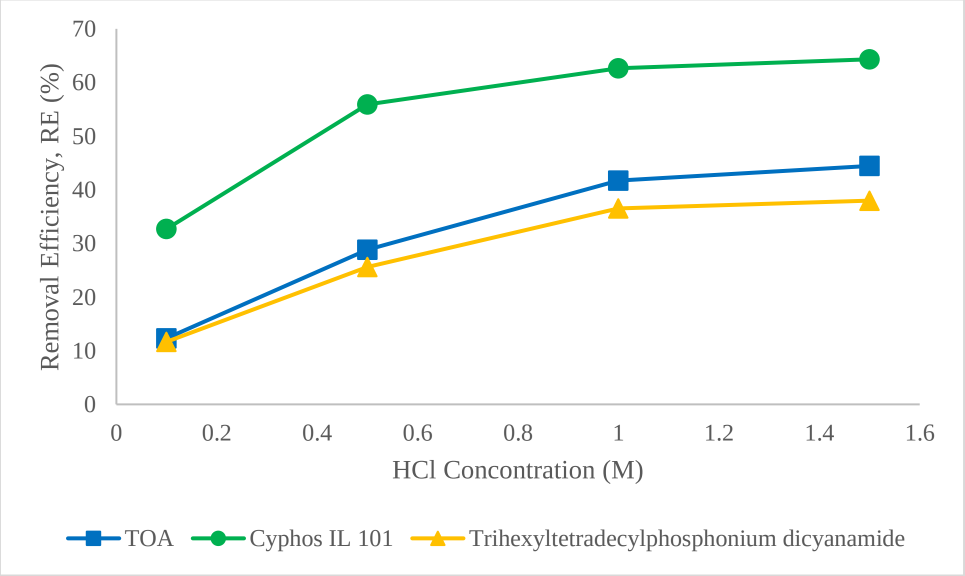

Figure 4.2: Effect on Concentration of HCl to the Removal Efficiency of Pb.

Figure 4.2 shows that the trends of RE for all three extraction mixtures are observed to increase with the increase of HCl concentration. The highest RE achieved by TOA, Cyphos IL 101, and trihexyltetradecylphosphonium dicyanamide were 44.44%, 64.32%, and 37.97% respectively, at 1.5 M of HCl. In contrast, only 12.32%, 32.71%, and 11.67% of RE were attained through TOA, Cyphos IL 101, and trihexyltetradecylphosphonium dicyanamide respectively, at 0.1 M of HCl. Therefore, it can be said that the HCl concentration has an essential effect on Pb extraction.

Furthermore, for the extraction mixture of TOA, the RE of Pb was able to improve by 32.12% when the HCl concentration was increased from 0.1 M to 1.5 M. Similar increasing trend of extraction efficiency was also possessed by the work of Ghadiri, Ashrafizadeh, and Taghizadeh (2014), in which the extraction of molybdenum from an aqueous phase was performed by using TOA. The behaviour of TOA in acidic media could be attributed to these outcomes. Since the amine group in the TOA must first form quaternary ammonium cation, R_3NH^+ by reacting with H^+ in order to allow the extraction of $PbCl_4^{2-}$ from the aqueous phase, which can be referred to Equations 4.1 and 4.2. Therefore, this can be achieved by reacting TOA with an acid that is responsible to provide the H^+. In other words, most TOA is only able to exist in its free form and cannot form a complex with the presence of Pb ions at low HCl concentration as the H^+ provided is limited.

In addition, the extraction mixture of Cyphos IL 101 and trihexyltetradecylphosphonium dicyanamide showed an improvement of 31.61% and 26.30% respectively in the RE of Pb when the HCl concentration was elevated from 0.1 M to 1.5 M. The anionic exchange mechanism represented by Equations 4.3 and 4.4 suggests that increasing the HCl concentration can lead to higher RE of Pb during the extraction process. This is because higher HCl concentration provides more Cl^- which can promote the formation of $PbCl_4^{2-}$ complexes. These complexes are more readily exchanged with the anions present in the IL phase. As a result, more Pb from the aqueous phase can be extracted into the IL phase, leading to a higher RE of Pb. The work of Xing and Lee (2018) also suggested that the predominant anionic species of metal are $MeCl^{2-}$ when the solution pH is low with the increased HCl concentration since the formation of the anionic complex of $MeCl^{2-}$ was depended on the concentration of chloride ions. Thus, higher HCl concentration is evidenced to promote a better anion exchange by the results obtained as more $PbCl_4^{2-}$ (which is exchangeable with the anion within the extraction mixture) was allowed to be formed in the aqueous phase.

From the results, it can be concluded that the RE of Pb could be enhanced by an increment of HCl concentration for all three extraction mixtures.

This relationship can be confirmed by the data presented in Figure 4.3, which shows the correlation between the HCl concentration and the distribution coefficients (K) of Pb. The increasing trend of K values indicates that the extraction efficiency of Pb ions from the aqueous phase into the extractant phase is improving. This suggests that increasing the HCl concentration in the aqueous phase leads to more favourable extraction conditions for Pb ions, resulting in higher RE. Although the greatest RE of Pb can be achieved at 1.5 M of HCl. However, an effective Pb RE for all three extraction mixtures was able to notice at 1.0 M of HCl concentration, as illustrated in Figure 4.2 and Figure 4.3. Although the RE of Pb at 1.5 M of HCl is the highest but the impact given was not strong anymore when compared with the Pb solution in 1.0 M of HCl. Therefore, it can be concluded that the HCl concentration that gives the best removal performance for the all extraction mixture was 1.0 M of HCl. In this case, Pb solution in 1.0 M of HCl will be maintained for all extraction mixtures to the continuation of other parameters in this study.

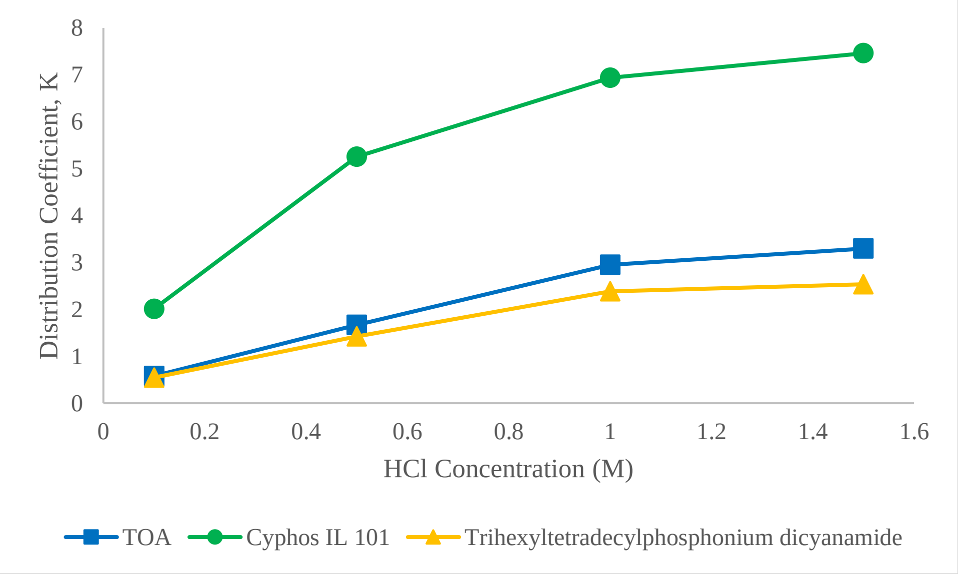

Figure 4.3: The Distribution Coefficient on the Effect of HCl Concentration.

4.3 Effect of Initial Pb Concentration

Figure 4.4 shows the effect of initial Pb concentration in the aqueous phase on the Pb extraction when all three extraction mixtures were allowed to contact with Pb solution in 1.0 M of HCl. The initial Pb concentration ranging from 50 ppm to 150 ppm was investigated in this study with a constant stirring speed of 700 rpm.

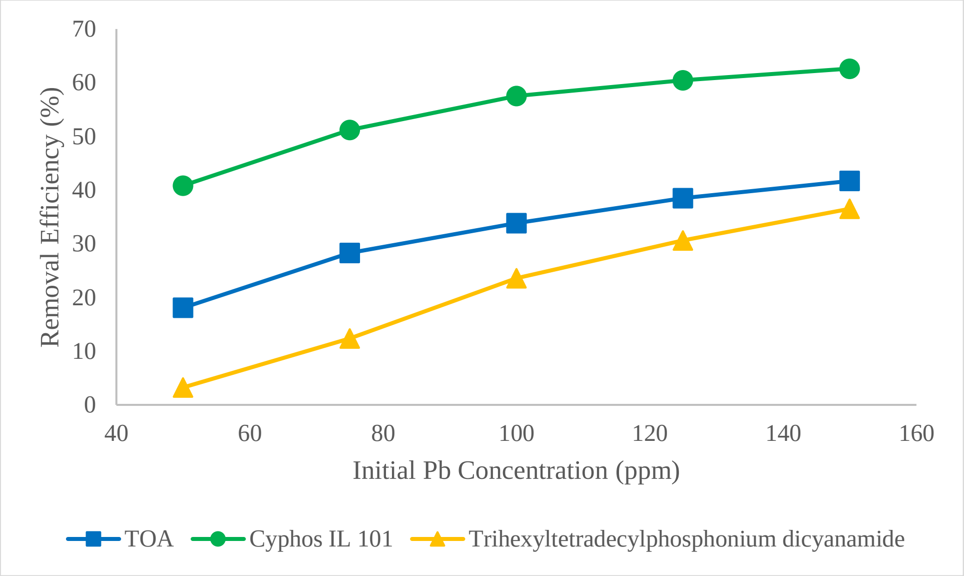

Figure 4.4: Effect on Initial Concentration of Pb to the Removal Efficiency of Pb.

Based on Figure 4.4, the outcomes demonstrated that the increment of the initial Pb concentrations in the aqueous phase leads to an enhancement in the RE of Pb for all three types of extraction mixtures. As the initial Pb concentration was elevated from 50 ppm to 150 ppm, the variation in the RE of Pb for TOA, Cyphos IL 101, and trihexyltetradecylphosphonium dicyanamide was in a range of 18.08% - 41.70%, 40.84% - 62.63%, and 3.24% - 36.52% respectively. The work of Ghadiri, Ashrafizadeh, and Taghizadeh (2014) to study the effect of initial concentration of molybdenum by using TOA as the extractant also showed a similar trend, in which the extraction efficiency was increased with the molybdenum initial concentration. Hence, the results obtained in Figure 4.4 suggested that a clear enhancement in the Pb RE was achievable by increasing the initial Pb concentration for all extraction mixtures involved. This outcome could be attributed to the concentration gradient between the aqueous phase and the extractant phase. When the initial concentration of Pb in the aqueous phase is increased, a greater difference in the Pb concentration between the two phases can be obtained, which then results in a higher driving force for the transfer of the Pb from the aqueous phase to the extractant phase. Therefore, the rate of mass transfer of the Pb across the phase boundary is also higher. This can result in a higher extraction efficiency, as a larger fraction of the Pb can be transferred to the extractant phase. However, it is noteworthy that the uptake of Pb from aqueous solutions increases considerably at greater initial Pb concentrations, as illustrated in the graph of Figure 4.4.

Moreover, the extraction mechanism of Pb was believed to be the complex formation as shown in Equation 4.2 for TOA while the anionic exchange mechanism as presented in Equation 4.4 for Cyphos IL 101 and trihexyltetradecylphosphonium dicyanamide, as discussed in section 4.1. Both equations suggested that the formation of the complex is a reversible reaction and equilibrium extraction will be attained. Figure 4.5 demonstrates that the K gradually increases with the elevating initial Pb concentration for all three extraction mixtures. The results suggest that an increment of the initial Pb concentration is able to benefit the extraction process significantly. Nevertheless, the trend of K was indicating the saturation uptake of Pb is not being reached yet by all three extraction mixtures, as shown in Figure 4.5.

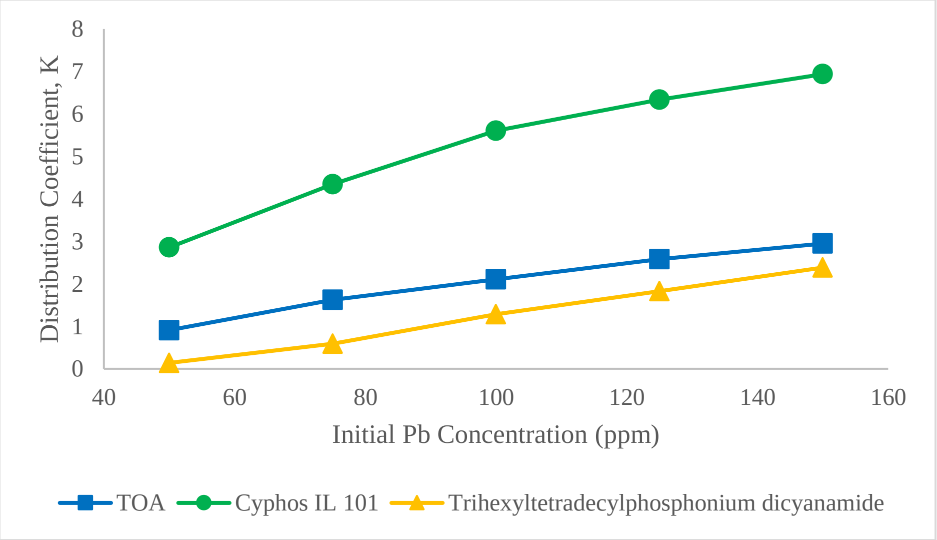

Figure 4.5: Distribution Coefficient on the Effect of Initial Pb Concentration.

4.4 Effect of Volume-to-Mass Ratio

The effect of the volume-to-mass ratio between the Pb solutions to the extractant was examined from 5 to 100. Figure 4.6 presented the results of the effect of volume-to-mass ratio on the Pb extraction.

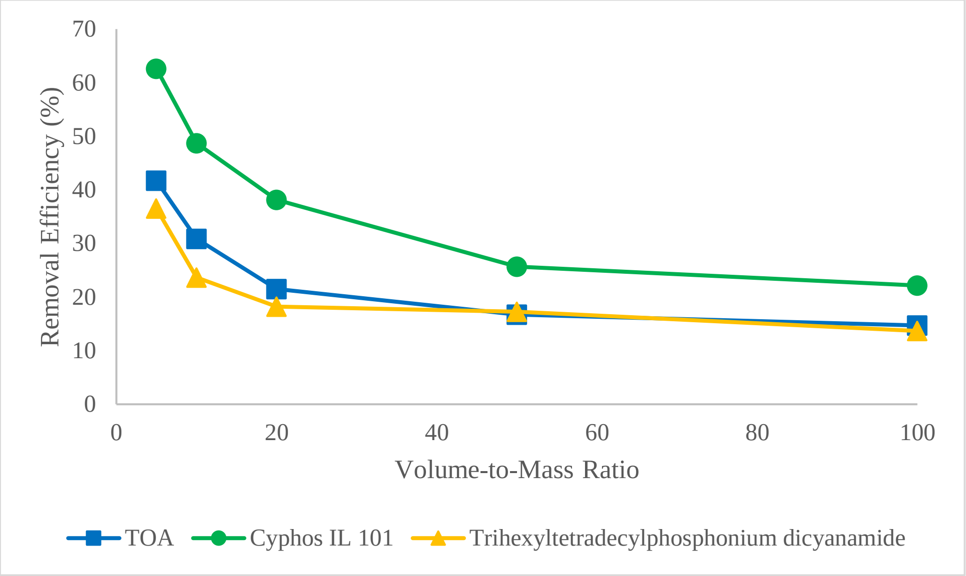

Figure 4.6: Effect of Volume-to-Mass Ratio on the Extraction Efficiency of Pb.

As illustrated in Figure 4.6, it is discovered that the RE curves for all three extraction mixtures declined as the volume-to-mass ratio increases from 5 to 100. The best RE was yielded at a volume-to-mass ratio of 5, for all types of extraction mixtures. The greatest RE of extraction mixtures of TOA, Cyphos IL 101, and trihexyltetradecylphosphonium dicyanamide were 41.70%, 62.63%, and 36.52%. In contrast, all three extraction mixtures obtained the lowest RE at a volume-to-mass ratio of 100 in which only 14.71%, 22.16%, and 13.68% were achieved by TOA, Cyphos IL 101, and trihexyltetradecylphosphonium dicyanamide respectively. The finding was consistent with the studies conducted by Guezzen and Didi (2016) and Buddin, et al. (2019). Buddin, et al. (2019) proposed that increasing the amount of extractant in the system can enhance the extraction efficiency, as a higher amount of extractant ensures its sufficient presence in the system. This is because when the volume of the Pb solution is increased, the ratio of Pb to be extracted also becomes higher. Hence, the extractant available within the extraction mixture will be insufficient to cater with the increased amount of Pb. Based on this fact, the number of extractants present was said to be inadequate to extract the existing Pb ions in the aqueous phase, limiting the extraction process. This limitation becomes more pronounced as the volume-to-mass ratio is elevated.

Furthermore, this phenomenon can be further explained by the relationship between the Pb uptakes by the extractant with the volume-to-mass ratio, as shown in Figure 4.7. According to outcomes shown in Figure 4.7, lower Pb uptakes by all three extractants were noticed at a higher volume-to-mass ratio. In more detail, it can be observed that the Pb uptake by the extractant gradually decreased and showed a tendency to reach constantly as the volume-to-mass ratio kept increasing. This is because the maximum extraction capacity would be reduced by the use of an inadequate extractant (Zhu, et al., 2018). In addition, the trend shown in Figure 4.7 is also suggesting that a lower contact area between the extractant and the Pb ions is obtained while the volume-to-mass ratio increases. Since contact area is one of the major factors that can affect the Pb uptake by the extractant. According to Zhu, et al. (2018), great extraction efficiency can be encouraged by elevating the contact area between the dispersive extractant and the aqueous solution. When the mass of the extractant is reduced, the extractant available is said to be not enough to completely surround the Pb ions (which are targeted to be extracted) that appear in the aqueous phase. In other words, the Pb ions might not be fully dispersed throughout the extractant. This situation can lead to an uneven extraction and lower the Pb uptakes as well as overall efficiency due to the interaction between the extractant and Pb ions being lowered.

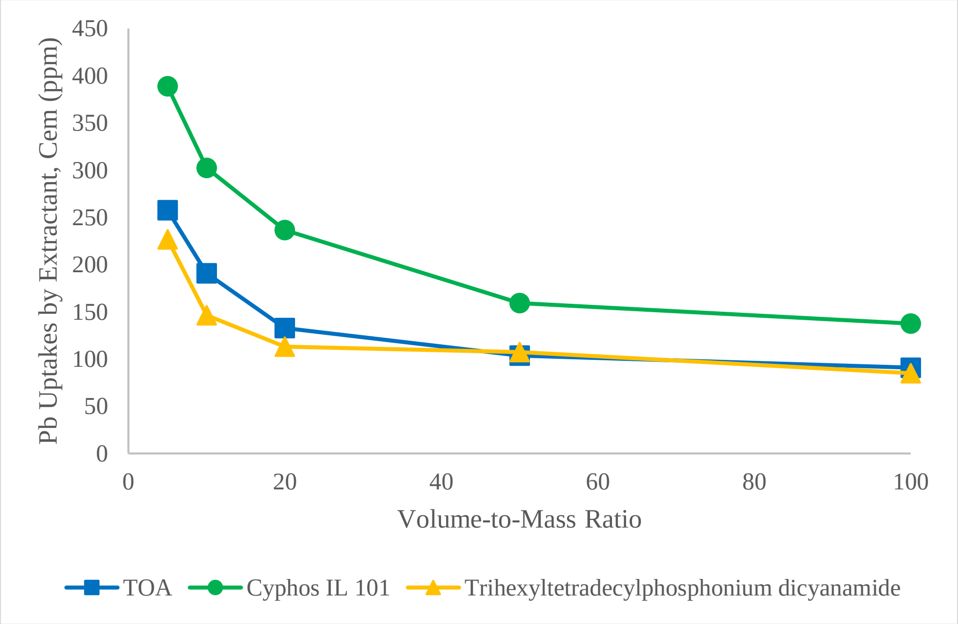

Figure 4.7: Pb Uptakes by Extractant over the Volume-to-Mass Ratio.

4.5 Comparison with Other Extractants

Table 4.1 summarised the extraction efficiency of removing Pb from water by different extractants adapted from the literature.

Table 4.1: The Extraction Efficiency of Pb for Different Extractants.

Extractants		**Condition**	**RE (%)**	**References**
ILs	**Cyphose IL 101**	• 1.5 M of HCl concentration • 150 ppm of initial Pb concentration • Volume-to-Mass Ratio of 5	64	This Study
	Trihexyltetradecylphosphonium dicyanamide	• 1.5 M of HCl concentration • 150 ppm of initial Pb concentration • Volume-to-Mass Ratio of 5	38	This Study
	Tetrapropylammonium tetrabutylammonium bis(trifluoromethylsulfonyl)amide [PR4][MTBA]	• pH: 6.5 • 0.005-1 ppm of initial Pb concentration	85	Fuerhacker, et al. (2012)
	N-octylpyridinium N,N-dioctyylsuccinamate $[C_8Py][N_{88}SA]$	• pH: 4 • 150 ppm of initial Pb concentration	95	Azra, et al. (2022)
	1-Methyl-3-octylimidazolium N,N-dioctylsuccinamate $[C_4mim][N_{88}SA]$	• pH: 6 • 150 ppm of initial Pb concentration	98	Azra, et al. (2022)

Table 4.1 (Continued)

Organic Extractants	**TOA**	• 1.5 M of HCl concentration • 150 ppm of initial Pb concentration • Volume-to-Mass Ratio of 5	44	This Study
	N-Salicylideneaniline in Chloroform	• pH: 4 • 3 ppm of initial Pb concentration • Volume Ratio of 3	43	Fetouhi, et al. (2016)
	2-Octylaminopyridine in Chloroform	• pH: 6 • 80 ppm of initial Pb concentration • Aqueous to Organic Ratio of 2.5	27	Mane and Anuse (2008)

Based on the outcomes shown in Table 4.1, most ILs achieved higher RE of Pb when compare with the organic extractants. The findings indicated that ILs exhibited superior RE for Pb compared to conventional organic extractants, with only one exception being trihexyltetradecylphosphonium dicyanamide IL which showed a lower RE than TOA and N-salicylideneaniline. Therefore, it is not always the case that ILs will provide a better extraction process than organic extractants. The effectiveness of heavy metal removal from water strongly depends on various factors such as the type and concentration of extractants, extractant properties, and operating conditions. Hence, understanding the extractants being applied and optimization of these factors for the specified extractant is essential for the efficient removal of Pb from water. Nevertheless, it is worth noting that each extractant possesses its unique set of properties, characteristics and extraction mechanism which make them more efficient in specific working environments. For example, even though the three extractants under this study is more preferable to extract Pb in a lower pH but the optimum pH for [PR4][MTBA] and [C_4mim][N_{88}SA] are known as 6.5 and

6 respectively. Nonetheless, both of them still exhibit a higher RE when compared with most of the extractants listed in Table 4.1. In spite of that, the ratio of an aqueous solution to extractant shows more similar results among all eight extractants. Based on the outcomes in Table 4.1, most extractants are found to work best at a lower aqueous solution to extractant ratio, in which a better RE of Pb could be attained.

ILs have been shown to be an appealing solvent option in both academic and industrial contexts to extract Pb from water due to their ionic properties, which provide them with more desirable qualities and characteristics than other typical organic solvents (Khan, et al., 2021). This is because ILs have possess distinctive characteristics such as low volatility, tunable solubility, and high thermal stability, which can make them more efficient and environmentally friendly, as discussed in section 2.4.1. In addition to their superior extraction efficiency, ILs may have an edge over traditional organic solvents as they can facilitate simpler product recovery and have the potential for repeated use in many cases (Freemantle, 2004). As ILs are more stable and non-volatile, they do not react and evaporate easily during the subsequent purification and recovery steps. In other words, simple approaches can be employed to separate the product from the ILs, and at the same time, the ILs can also be recovered and reused again. According to Zhou, et al. (2018), there are numerous techniques available for the recovery of ILs, which involve extraction, crystallization adsorption, distillation, membrane separation, external force field separation, and aqueous two-phase extraction. Among the different methods mentioned above, distillation and extraction are considered to be relatively simple and low-cost methods for the recovery of ILs. Then, the amount of waste generated and the cost of the overall process are potentially reduced through recovery and purification steps.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In a conclusion, this study evaluated the effectiveness of organic solvent TOA and ILs Cyphos IL 101 and trihexyltetradecylphosphonium dicyanamide as extractants for the removal of Pb from water in LLE under various operating parameters. The study findings indicated that Cyphos IL 101 can extract Pb from HCl solution effectively through an anionic exchange mechanism as it was able to achieve the highest removal efficiency of 64.32%. Although the same extraction mechanism is employed by trihexyltetradecylphosphonium dicyanamide IL but the lowest removal efficiency of 37.97% was obtained among the three extractants studied. Additionally, the organic extractant TOA attained a moderate removal efficiency of 44.44%, suggesting that chelation can also significantly extract the Pb ions that appeared in water in an acidic environment. From the view of the solution condition, it was discovered that higher removal efficiency was achieved at higher HCl concentration for all extractants studied, as a result of the formation of R_3NH^+ and $PbCl_4^{2-}$ is required to promote a better extraction process for both different mechanisms. However, the optimum HCl concentration in the Pb solution for the three extractants was 1.0 M as the impact given on removing Pb from the water was the strongest. Besides, the higher removal efficiency was noticed at higher initial Pb concentration as all three extractants involved were able to attain the greatest extraction efficiency at 150 ppm of Pb solution since a higher concentration gradient between the aqueous phase and extractant phase were potentially create a greater driving force for the extraction of Pb from aqueous to extractant phase. The performance of the extractants was also highly dependent on the volume-to-mass ratio, where the amount of extractants available to extract the existing Pb ions in the aqueous phase can be one of the main factors limiting the extraction process. Nevertheless, a lower removal efficiency was observed with the elevated volume-to-mass ratio as the extractant available within the extraction mixture was said to be insufficient to accommodate the increased amount of Pb ions in water.

5.2 Recommendations for future work

This study shows that Pb can potentially be removed from water by ILs and organic extractants via LLE. Nevertheless, there is still much that could be done to further studied and improve the removal efficiency. Thus, some recommendations are made in order to improve future work:

- More different extractants can be studied in the interest of determination of the best extractants to extract Pb from water as the highest RE of Pb obtained in this study was only 64.32% by Cyphos IL 101.
- More operating parameters such as extraction time, stirring speed, types of diluents, and temperature can be studied. This would allow us to have a better understanding of the effect of such parameters on the performance of the LLE process.
- Real industrial wastewater or polluted water can be used to carry out the experiments rather than only the Pb stock solution. It would be useful to investigate the effectiveness of the extractants if it is to be adopted in the industry. In the meantime, studies of the RE of Pb and the presence of other compounds are both possible.
- Further research can be done on using the method of LLE to study their effect on additional types of heavy metal or organic compounds.

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APPENDICES

Appendix A: Tables

Table A-1: Experiment Data of the Effect of HCl Concentration on Removal Efficiency for TOA.

HCl Concentration (M)	Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
0.1	150	131.52	12.32
0.5	150	106.72	28.85
1.0	150	87.45	41.70
1.5	150	83.34	44.44

Table A-2: Pb Concentration in Extraction Mixture and Distribution Coefficient for TOA under the Effect of HCl Concentration.

HCl Concentration (M)	Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
0.1	150	131.52	76.15	0.5790
0.5	150	106.72	178.33	1.6711
1.0	150	93.98	257.74	2.9472
1.5	150	83.34	274.67	3.2958

Table A-3: Experiment Data of the Effect of HCl Concentration on Removal Efficiency for Cyphos IL 101.

HCl Concentration (M)	Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
0.1	150	100.94	32.71
0.5	150	66.10	55.93
1.0	150	56.06	62.63
1.5	150	53.52	64.32

Table A-4: Pb Concentration in Extraction Mixture and Distribution Coefficient for Cyphos IL 101 under the Effect of HCl Concentration.

HCl Concentration (M)	Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
0.1	150	100.94	203.04	2.0115
0.5	150	66.10	347.23	5.2530
1.0	150	56.06	388.78	6.9350
1.5	150	53.52	399.29	7.4605

Table A-5: Experiment Data of the Effect of HCl Concentration on Removal Efficiency for Trihexyltetradecylphosphonium Dicyanamide.

HCl Concentration (M)	Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
0.1	150	132.50	11.67
0.5	150	111.60	25.60
1.0	150	95.22	36.52
1.5	150	93.04	37.97

Table A-6: Pb Concentration in Extraction Mixture and Distribution Coefficient for Trihexyltetradecylphosphonium Dicyanamide under the Effect of HCl Concentration.

HCl Concentration (M)	Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
0.1	150	132.5	72.48	0.5471
0.5	150	111.60	159.05	1.4252
1.0	150	95.22	226.90	2.3829
1.5	150	93.04	235.93	2.5358

Table A-7: Experiment Data of the Effect of Initial Pb Concentration on Removal Efficiency for TOA.

Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
50	40.96	18.08
75	53.78	28.29
100	66.16	33.84
125	76.90	38.48
150	87.45	41.70

Table A-8: Pb Concentration in Extraction Mixture and Distribution Coefficient for TOA under the Effect of Initial Pb Concentration.

Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
50	40.96	37.25	0.9094
75	53.78	87.44	1.6258
100	66.16	139.44	2.1076
125	76.90	198.20	2.5773
150	87.45	257.74	2.9472

Table A-9: Experiment Data of the Effect of Initial Pb Concentration on Removal Efficiency for Cyphos IL 101.

Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
50	29.58	40.84
75	36.60	51.20
100	42.48	57.52
125	49.40	60.48
150	56.06	62.63

Table A-10: Pb Concentration in Extraction Mixture and Distribution Coefficient for Cyphos IL 101 under the Effect of Initial Pb Concentration.

Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
50	29.58	84.51	2.8570
75	36.60	158.92	4.3421
100	42.48	238.05	5.6038
125	49.40	312.88	6.3335
150	56.06	388.78	6.9350

Table A-11: Experiment Data of the Effect of Initial Pb Concentration on Removal Efficiency for Trihexyltetradecylphosphonium Dicyanamide.

Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
50	43.38	3.24
75	65.7	12.4
100	76.39	23.61
125	86.75	30.60
150	95.22	36.52

Table A-12: Pb Concentration in Extraction Mixture and Distribution Coefficient for Trihexyltetradecylphosphonium Dicyanamide under the Effect of Initial Pb Concentration.

Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
50	43.38	6.71	0.1387
75	65.7	38.52	0.5863
100	76.39	97.79	1.2802
125	86.75	158.43	1.8263
150	95.22	226.90	2.3829

Table A-13: Experiment Data of the Effect of Volume-to-Mass Ratio on Removal Efficiency for TOA.

Volume to Mass Ratio	Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
5	150	87.45	41.70
10	150	103.68	30.88
20	150	117.74	21.51
50	150	124.86	16.76
100	150	127.94	14.71

Table A-14: Pb Concentration in Extraction Mixture and Distribution Coefficient for TOA under the Effect of Volume-to-Mass Ratio Concentration.

Volume to Mass Ratio	Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
5	150	87.45	257.74	2.9472
10	150	103.68	190.86	1.8409
20	150	117.74	132.93	1.1290
50	150	124.86	103.59	0.8296
100	150	127.94	90.90	0.7105

Table A-15: Experiment Data of the Effect of Volume-to-Mass Ratio on Removal Efficiency for Cyphos IL 101.

Volume to Mass Ratio	Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
5	150	56.06	62.63
10	150	76.98	48.68
20	150	92.82	38.12
50	150	111.52	25.65
100	150	116.76	22.16

Table A-16: Pb Concentration in Extraction Mixture and Distribution Coefficient for Cyphos IL 101 under the Effect of Volume-to-Mass Ratio Concentration.

Volume to Mass Ratio	Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
5	150	56.06	388.78	6.9350
10	150	76.98	302.20	3.9257
20	150	92.82	236.64	2.5495
50	150	111.52	159.25	1.4280
100	150	116.76	137.57	1.1782

Table A-17: Experiment Data of the Effect of Volume-to-Mass Ratio on Removal Efficiency for Trihexyltetradecylphosphonium Dicyanamide.

Volume to Mass Ratio	Initial Concentration, C_o (ppm)	Final Concentration, C_f (ppm)	Removal Efficiency (%)
5	150	95.22	36.52
10	150	114.65	23.65
20	150	122.70	18.20
50	150	124.10	17.27
100	150	129.48	13.68

Table A-18: Pb Concentration in Extraction Mixture and Distribution Coefficient for Trihexyltetradecylphosphonium Dicyanamide under the Effect of Volume-to-Mass Ratio Concentration.

Volume to Mass Ratio	Initial Pb Concentration, C_o (ppm)	Final Pb Concentration, C_f (ppm)	Pb Concentration in Extraction Mixture, C_{EM} (ppm)	Distribution Coefficient, K
5	150	95.22	226.90	2.3829
10	150	114.65	146.42	1.2771
20	150	122.70	113.08	0.9216
50	150	124.10	107.28	0.8644
100	150	129.48	84.99	0.6564