

CHALMERS



A study of the heavy metal extraction process using emulsion liquid membranes

Master's Thesis within the Innovative and Sustainable Chemical Engineering programme and Chemistry and Bioscience programme.

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Göteborg, Sweden 2011-2012

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ABSTRACT

The focus of this study is the extraction of heavy metals from wastewater using emulsion liquid membranes (ELM) in a way that contributes to green chemistry. A more robust ELM system may be used to reduce the toxic content in industrial effluents and to recover valuable metals. An ELM process consists of an external phase (feed phase, containing the metal to be extracted), an organic membrane phase and an internal phase (stripping or receiving phase). The internal phase and the membrane together compose a w/o emulsion, created through emulsification using homogenizer, and consists of an organic diluent, a mobile carrier, surfactants, eventual co-surfactants or stabilizers, and a dispersed aqueous phase containing a stripping agent that reacts with the extracted species. The w/o emulsion is dispersed into the external phase creating a multiple w/o/w emulsion in which the extraction process occur.

In this project we propose a novel ELM formulation consisting of the renewable material palm oil as the vegetable diluent. The mobile carrier TOMAC is included in the membrane to facilitate the metal transport and our system also incorporates the hydrophilic surfactant Tween 80 that facilitates the dispersion of the ELM phase in the external phase. Span 80 is used as surfactant and butanol as co-surfactant. The system achieved a removal efficiency of hexavalent chromium of over 99% when having an optimal concentration of 0.1 M NaOH as stripping agent and an external pH of 0.5. Important factors influencing the extraction were found to be the emulsion formulation, the agitation speed, and the maintenance of a pH gradient between the phases. The stability of the ELM is crucial and needs therefore further investigations. We also discovered that the type of water (deionized, distilled and tap water) does not have a significant influence on the extraction rate.

The possibility of extracting pentavalent arsenic with an emulsion ionic liquid membrane (EILM) system was also explored, when using kerosene as diluent, but without success. However, simple liquid-liquid experiments with TOMAC as carrier verified the compatibility between arsenic and TOMAC, with the optimal extraction efficiency at pH 9-10. Therefore a successful formulation may depend on the formulation of the ELM in terms of the components in the system such as the surfactant and stripping agent used.

Keywords: Emulsion liquid membrane, palm oil, hexavalent chromium, pentavalent arsenic, TOMAC, ionic liquid, green chemistry.

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List of abbreviations

ANOVA	Analysis of Variance
[BMIM] ⁺ [NTf ₂] ⁻	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
CSPO	Certified Sustainable Palm Oil
EILM	Emulsion ionic liquid membrane
ELM	Emulsion liquid membrane
HFSLM	Hollow fibre supported liquid membrane
HLB	Hydrophilic Lipophilic Balance
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
LOF	Lack of Fit
ppm	Parts per million
RSM	Response surface method
RSPO	Roundtable on Sustainable Palm Oil
RTIL	Room temperature ionic liquids
SLM	Supported liquid membranes
TOMAC	Tri-n-octylmethylammonium chloride
UN	United Nations
WHO	World Health Organization
w/o	water-in-oil
w/o/w	water-in-oil-in-water

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1 INTRODUCTION

The removal and recovery of heavy metals from wastewater and industrial effluents is environmentally and economically driven as much as it is a health issue. Efficient, economic and sustainable methods for this purpose are required and this project focuses on process intensification and investigation on extraction of hexavalent chromium and pentavalent arsenic from water. Both chromium and arsenic constitute a problem for the environment and a threat to human health, and in Malaysia and Southeast Asia the contamination of groundwater and water resources is a major concern.

The extraction capability of liquid membranes has been used successfully in many areas *i.e.* metal ion extraction, separation of inorganic species, and biochemical and biomedical applications [1] and the field is currently undergoing an expansion in research and in its application as an industrial separation processes. Emulsion liquid membrane (ELM) is a developed form of solvent extraction, with the difference that extraction and stripping occur simultaneously in the same stage. At, among other institutes, the University of Malaya this method is currently being optimized and substantially improved. One improvement of the ELM system has been the use of ionic liquid as stabilizer of the membrane, resulting in an emulsion ionic liquid membrane (EILM). The use of ELM for extraction of heavy metals is a method implemented only to some extent in industries and further investigations of this separation method are needed before industrial applications are possible on a larger scale. This includes stabilization studies of the emulsion membrane, improvements of the de-emulsification step and identification as well as intensification of various parameters influencing the efficiency. It also includes the development of a robust system that is affected as little as possible by the presence of other ions or impurities in the wastewater. The possibility to improve the sustainability of the ELM should also be explored, in order to minimize the use of non-renewable materials.

This work is divided into two subprojects, the first focusing on the development of a novel emulsion liquid membrane formulation based on a vegetable oil and the second focusing on the use of the already developed EILM formulation for extracting pentavalent arsenic. In addition, the effect of the purity of water is explored, by comparing the extraction rate when using water of different pre-treatments.

1.1 Subproject 1: using palm oil as diluent

From previous studies it is known that the carrier tri-n-octylmethylammonium chloride (TOMAC) is selective for extracting hexavalent chromium and an EILM formulation has been developed and optimized for this purpose [2]. In order to investigate the possibility of replacing the synthetic diluent kerosene based on fossil fuel for a renewable material, a system similar to that previously developed was chosen keeping the metal to be extracted unchanged. Palm oil was chosen as the alternative and renewable organic diluent, as it is readily available and may contain natural surface-active agents, which improve the stability of an emulsion [3]. In addition, palm oil has been found to work well for extraction of phenol using supported liquid membranes (SLM) [4]. Firstly, emulsion stabilization studies were preferred, as the ELM system demands a w/o emulsion stable for the time required for extraction to occur, and no optimized formulations were found in literature. Suitable surfactants and co-surfactants were explored for an optimal emulsion formulation. Secondly, extraction experiments were performed and investigations of various parameters affecting the removal efficiency were studied.

1.1.1 Purpose

The aim of subproject 1 is to explore the possibility of replacing the fossil-fuel based diluent kerosene in the ELM for a renewable vegetable oil. If the system works well using the ELM based on the vegetable oil, the subsequent aim is to optimize the removal efficiency of chromium from water using the novel

formulation. The parameters studied for removal efficiency are stabilization of the emulsion, surfactant and co-surfactant concentration, agitation speed, carrier concentration and stripping agent concentration.

1.1.2 Issues

Specifically, the following issues are investigated:

- Can the petro-chemically based diluent kerosene used in previous studies be exchanged for a vegetable oil?
- How can stability of the emulsion liquid membrane be achieved for a sufficient time, by using the materials at hand?
- Does the more viscous palm oil decrease the extraction rate?
- How is the extraction efficiency affected by the purity of the water?
- Which are the important factors influencing the efficiency of chromium extraction?

1.2 Subproject 2: arsenic extraction

In previous studies at University of Malaya an EILM formulation was developed using the ionic liquid $[\text{BMIM}]^+[\text{NTf}_2]^-$ as stabilizer in the membrane used for extraction of chromium with the help of the carrier TOMAC [2]. This EILM process has been optimized, and the results for the formulation are used in our study to investigate the suitability of extracting pentavalent arsenic using EILM. In previous studies arsenic has been successfully extracted using hollow fibre supported liquid membrane (HFSLM) with the mentioned carrier [5], but this technique requires a long extraction time (up to 24 h), compared to EILM (less than 15 min). In this subproject the compatibility between arsenic and TOMAC was first addressed through simple liquid-liquid extraction experiments in which suitable pH ranges of the external phase were also identified. Extraction experiments were performed using the optimized EILM formulation.

1.2.1 Purpose

The aim of subproject 2 is to examine the possibility of extracting pentavalent arsenic from water using an EILM system similar to that used for extracting hexavalent chromium, with kerosene as diluent.

1.2.2 Issues

The following specific issues are considered:

- Can the EILM formulation used in previous studies be applied for extraction of pentavalent arsenic? What ranges of pH are needed?
- Are there any improvements of the system needed?
- Which are the important factors influencing the efficiency of arsenic extraction?

1.3 Limitations

The whole research part took place at the University of Malaya, Kuala Lumpur. The time for the experimental part was limited wherefore investigations regarding de-emulsification and recovery of the metals were not performed. The material and apparatus to be used was limited to what was available within the time range and to what could be ordered and received during the start time of experimentations.

2 BACKGROUND

2.1 Environmental and sustainability aspects

Environmental aspects are often connected to the concept of a sustainable development, which today is a common goal and sometimes a demand in the industrial sector; a wish for a sustainable society is present in many countries. Green chemistry² is also an important concept and is what we strive for in this project. The sustainable development is described in the UN-Document “*Our Common Future*” from 1987³ [6] and implies an interaction of ecological, economical and social aspects closely linked together, since environmental issues are also issues of the society [7]. Human activities cause the environmental problems, and human activities should also solve them, which in industry and research means that it is beneficial to prioritize recycling, reuse and the use of environmentally friendly products that are biodegradable and produced from renewable raw material in a way that does not harm the environment. It also means that the environment should be kept free from toxic elements that can harm human health and destroy the ecosystem, and it is therefore important to minimize harmful emissions to the air, the soil and the waters.

This project focuses on the optimization of heavy metal extraction in order to reduce the toxic content in wastewater effluents and to reduce the overall environmental impact through using more sustainable components. The method used is emulsion liquid membranes (ELM), described in detail in Section 3. One benefit of using ELM from an environmental point of view is the low energy demand compared to pressure-driven membrane processes, another benefit is that the ELM can be prepared using relatively simple materials and equipment, [2] enabling versatility and opportunity to make the system as environmentally friendly as possible. The ELM process also allows the recovery of metals significant for recycling and reduces in that way the amount of metals being disposed. Other traditional methods for heavy metal removal are ion exchange, filtration and chemical precipitation that result in the disposal of the metals on landfills, which prevents the recovery of the metals and may cause leaching of toxic elements to the groundwater. These technologies also have issues of efficiency at low metal concentrations, low metal selectivity and high start-up or high operating costs [8]. Metals at high concentrations (>500 ppm) can be recovered with electrolysis, while at low concentrations (<5 ppm) the metals can be removed by biosorption or ion exchange. At concentrations between 5 and 500 ppm precipitation is possible, however it yields high volumes of sludge, with a low metal proportion [8]. ELM could be viewed as a development of the solvent extraction, or liquid ion exchange, which is well established in wastewater remediation. However, solvent extraction method alone still cannot meet the environmental standards for acceptable metal levels in discharged water and the method also requires high initial concentration of metal [8]. ELM on the other hand can handle low concentrations of metal and, if the process is optimized it may meet the environmental demands for the removal of the metals from wastewater.

2.2 Heavy metals in the context of environmental and health concerns

Heavy metals are known for their toxic effects on animals and humans, as well as their negative effect in the environment. In addition, anthropogenic activities such as industrial, agricultural and urbanisation lead to the contamination by these toxic elements. The contamination of heavy metals in Southeast Asia

² Green chemistry implies the design of chemicals and chemical processes that reduce or eliminate negative environmental impacts such as reduced waste products, non-toxic components, and improved efficiency.

³ The report is also called the Brundtland report, and describes the concept as a “*development that meets the needs of the present without compromising the ability of future generations to meet their own needs*”.

is a consequence of various industrial activities⁴ and the discharge of heavy metals in the environment leads to the pollution of rivers, which in turn contaminate the ground water and the sediment system [66].

2.2.1 Chromium

Chromium is quite abundant in the Earth's crust, and is naturally occurring in rocks, animals, plants, soil, volcano-dust and gases. Chromium occurs primarily in two valence states, trivalent chromium and hexavalent chromium, which both exist naturally in water as solved salts, although Cr(VI) is more soluble than Cr(III) compounds.



Figure 2.1: Cr(VI) dissolved in water has a yellow colour, the picture shows potassium dichromate in hydrochloric acid.

The metal does not exist naturally in its pure form but rather as chemical compounds, often with oxygen and in its' trivalent form [9]. The trivalent chromium is essential to humans⁵ and various other organisms in small amounts, but becomes poisonous for most organisms in high concentrations [9]. The hexavalent chromium on the other hand is highly poisonous, an oral dose of 2-5 g soluble of Cr(VI) can be fatal to an adult human [10]. The target organ for acute and chronic inhalation exposure of hexavalent chromium is the respiratory tract, several studies have shown that Cr(VI) increases the risk of lung cancer [11], and if ingested Cr(VI) causes liver and kidney damage [10]. The body has ways of detoxifying Cr(VI) by reducing it into Cr(III), although this will increase the level of Cr(III) in the body [11]. As the oxidation state of chromium decides the toxicity, and the oxidation state depends on the pH of the water and of the presence of reducing or oxidizing species, the water quality standards is based on the total concentration of chromium. World Health Organization (WHO) has a provisional guideline value of 0.05 ppm for the total chromium concentration in drinking water [12].

Important industrial sources of chromium waste include ferrochrome production, metal plating, steel fabrication, paint and pigment production, wood treatment, manufacture of dyes, leather production and tanning, and chromium milling and mining [10] [11]. Around 60% of the chromium produced is used in chromium-based alloys, around 20% in chemical processes such as electroplating and most of the rest is used in furnace bricks and other refractory products, and through leakage, poor storage or improper disposal practices the chromium is released into the environment and into water supplies [10].

⁴ Examples are dye industries, leather tanning, mining and electroplating, however, poor implementation of laws also poses a problem.

⁵ The major source of trivalent chromium is through food and a daily requirement of around 0.05 mg is recommended (the absorption of Cr(III) is about 3% when ingested).

2.2.2 Arsenic

Arsenic can be found all over the world and is known for and often associated with its' toxicity and usage as poison in homicides throughout history. As an example, the cause of death of the Swedish king Erik XIV in 1577 is believed to be arsenic poisoning. The mobilization of arsenic occurs by natural weathering conditions, biological activity and volcanic emissions, and most environmental problems related to arsenic are a consequence of natural mobilization [13].

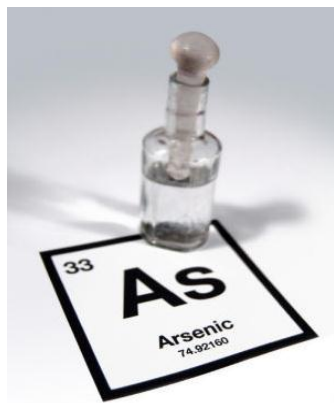


Figure 2.2: Arsenic is known for its use as poison.

A result of human activities such as mining, combustion of fossil fuels, the use of herbicides and pesticides containing arsenic and the use of arsenic additives to livestock is however a reason for additional arsenic contamination and environmental impacts. The presence of arsenic pollution affects the water resource qualities and the life of millions of people worldwide. The WHO guideline states that drinking water should not exceed the concentration of 0.01 ppm of arsenic, although some countries including India, Bangladesh and Argentina have adopted higher values as standard, and drinking water poses the largest threat to public health on behalf of arsenic [14]. Lethal doses in humans range from 0.1-3.5 g arsenic (1.5-500 mg/kg body weight), depending on the compound and oxidation state⁶ [15]. Long-term exposure to arsenic in drinking water causes pigmentation changes, skin thickening, nausea, muscular weakness and also various forms of cancer including skin, lung and kidney cancer, while acute arsenic poisoning typically causes vomiting, abdominal pain and diarrhea [13]. Arsenic is the most common cause of acute heavy metal poisoning among adults and one of the most toxic elements to be found, and it is therefore extremely important to control and minimize the exposure of arsenic to humans and to the environment. In Asia the arsenic problem is amplified by the pollution of rice paddles leading to the uptake of arsenic in rice grains, which in Asia is the primary food source [16].

2.3 Environmental and sustainability concerns regarding the chemicals involved

An ELM system is generally composed of internal reagent, organic diluent, surfactant, and carrier, and in order to obtain a sustainable system, all these components should be relatively cheap and as environmentally friendly as possible.

In previous studies **kerosene** has been commonly used as organic diluent, due to its' low viscosity, readily availability and non-polar character. Kerosene is a petroleum product, an organic liquid produced from the refining of crude oil [17] and is the major component of aviation fuel, but is also used as solvent, degreaser and domestic fuel. There are no natural sources of kerosene and release into the environment should be avoided. If kerosene is inhaled while being ingested toxicity occurs, and it is considered harmful and irritating to eyes and skin [18]. As kerosene is not considered environmentally friendly, it is highly desirable to replace it for a renewable material, like a vegetable oil.

We have proposed **palm oil** as an alternative organic diluent, since it is a vegetable oil and it is biodegradable. Palm oil is widely used in food and cosmetic industries, it is used as cooking oil in Southeast Asia and Africa and as food additive in processed food worldwide. Another use of palm oil is for the production of biofuels, such as biodiesel. The production of palm oil has grown rapidly the last decades and was in 2010 around 45 million tonnes of which the main part comes from Malaysia and

⁶ Trivalent arsenic is more poisonous than the pentavalent form, and arsine (AsH_3) is considered most toxic while DMA (dimethylarsinic acid) is the least toxic form.

Indonesia [19]. Nevertheless, palm oil is a controversial product; the large industry contributes to the destruction of the rainforests in these countries and considerations on how it has been produced and what consequences the production may have are of importance. The palm oil production is an important economical income source for Malaysia and Indonesia, but bad practice in parts of the industry brings high ecological and societal costs, such as fires to clear land for plantation and pressure on the species that need the rainforest. A significant debate over the environmental impacts of the palm oil production has occurred, regarding the diminishing of the rainforests as opposed to the efficient carbon assimilation and high productivity [20]. However, the industry is improving, concern is increasing and, according to the Roundtable on Sustainable Palm Oil (RSPO) in 2011, Malaysia is currently the world's largest producer of Certified Sustainable Palm Oil (CSPO) [21].



Figure 2.3: An oil palm tree cultivation plant in Malaysia.

The palm oil is produced from harvested fruits bunches of oil palm trees, and the trees are usually grown in large cultivation plants, see Figure 2.3. The fruits are separated from their bunches, digested and pressed to extract the palm oil [20] which is then fractionated into various portions with different properties. Despite the controversy of palm oil production, palm oil may still be regarded as harmless to health and environment compared to kerosene in terms of toxicity and biodegradability.

Span 80 is used as surfactant for the ELM formulation and Span is the commercial name for sorbitan fatty acid esters, which are non-ionic surfactants. Span 80 is a sorbitan monooleate and classified as environmentally friendly, as it is sugar based and produced from renewable sources and is also biodegradable [22]. **Tween 80** is the corresponding ethoxylated ester of Span, also classified as environmentally friendly, and is used as stabilizer for the *o/w* interface for the *w/o/w* multiple emulsions or as a co-surfactant for the palm oil based emulsion [22].

As a co-surfactant **1-butanol** is used, a biodegradable substance that is mildly toxic to humans [23]. Butanol is produced mainly from propylene and thereby not entirely environmentally friendly. On the other hand, ways of producing bio-butanol from fermentation of sewage sludge or sugar using bacteria, in a way similar to the production of bio-ethanol are now under development [24]. The **ionic liquids** used in the formulation, described in further detail in Section 3, are also considered environmentally friendly.

3 SURVEY OF THE FIELD

3.1 Liquid membrane

Liquid membranes consist of three distinct phases, the feed phase, the membrane phase and the stripping phase. The feed phase, also called the external phase, is the water containing the metal or the other species to be extracted and the stripping phase, also called the internal phase, is where the metal will be trapped. The different phases are defined for a simultaneous extraction and stripping to occur; the separation is achieved when permeation occurs from the aqueous feed phase to the receiving stripping phase.⁷ There are three different kinds of liquid membrane: bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM). Among these membranes, the double emulsion in ELM achieves the highest mass transfer area, which is a desired property in separation methods. Since the ELM system is the one used in this project, we will thoroughly and exclusively describe this one.

3.2 Emulsion liquid membrane (ELM)

ELM processes are gaining importance among other conventional separation methods and since its discovery by Norman Li for the separation of hydrocarbons [25] it has shown to be an easy way for the removal of chemicals from wastewater. Compared to ELM, permeable and semi-permeable membranes such as ultrafiltration, microfiltration and reversed osmosis have issues such as high capital cost, large equipment size, low selectivity and low mass transfer rate. ELM offers some intensity features such as larger interfacial area, high efficiency and simple operation methods. In terms of metal removal and metal recovery from wastewater, the ELM technique has higher separation efficiency than conventional methods [26]. Despite these advantages, ELM struggles with limitations in emulsion instability, breakage of the membrane due to swelling during high shear rate and stress rate throughout the separation process, which reduce the overall efficiency of the ELM processes. The ELM system consists of a double emulsion: a water-in-oil (w/o) emulsion dispersed in an external aqueous phase. In the water-in-oil-in-water (w/o/w) emulsion, the oil phase is the immiscible membrane phase, which separates the aqueous phases and allows a selective transport of several components. See Figure 3.1 for a schematic picture of a w/o/w multiple emulsion and representation of the phases.

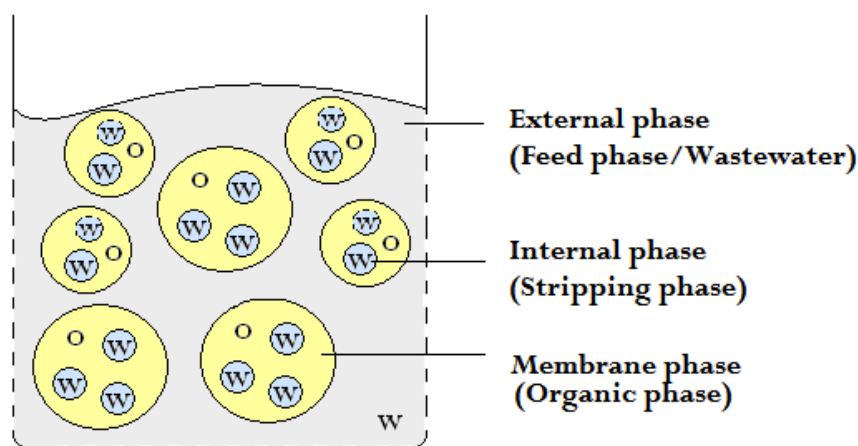


Figure 3.1: Schematic picture of a water-in-oil-in-water emulsion and the phases in a multiple (w/o/w) emulsion. O=Oil (Yellow) and W=Water (Gray for external phase and blue for internal phase)

⁷ In this report, the feed phase will further be referred to as the external phase and the stripping phase is referred to as the internal phase. The ELM phase include both the membrane (organic) phase and the internal phase.

A simple emulsion is a type of heterogeneous mixture of two or more immiscible liquids, where one liquid is dispersed in the other. An example of an emulsion is milk, which is fat dispersed in water [27]. The internal phase droplets are normally small, with a diameter in the order of 1-10 μm and the emulsion globules are generally larger, in the range of 0.1-0.2 mm in diameter [28].

3.2.1 Advantages of ELM

- The system has a *high interfacial area*, $3000 \text{ m}^2/\text{m}^3$ for ELM compared to $100\text{-}200 \text{ m}^2/\text{m}^3$ for SLM [29].
- The diffusivity through most liquids is much higher than through polymer membranes, where a very thin membrane must be developed to be able to compete with the *high flux* of ELM.
- ELM provides *high selectivity and high metal transfer flux* due to the possibilities to incorporate chemical components, which enhance the transport of the metal [26].
- *The extraction and the stripping coexist* in the same stage, which gives savings in the equipment volume.
- The overall mass transfer is not only dependent on equilibrium consideration, but also controlled by a combination of diffusion rate and the reaction rate of the extractant and the metal complex.
- The volume of the internal phase is much smaller than the volume of the external phase that enables metal concentration in the internal phase.

3.2.2 Disadvantages of ELM

- The ELM process struggles with *instability of the emulsion globules*, which is mainly influenced by osmotic swelling and globule breakage. The osmotic swelling occurs when the water in the external phase diffuses through the membrane phase and swells the internal droplet, causing dilution of the content in the internal phase. Breakage of the globules mainly occurs due to the interfacial shear between the external phase and the membrane phase.
- The process is often problematic in terms of the *de-emulsification*, which involves the recovery of the membrane phase and the metal. The most commonly used method is high voltage electrostatic fields, which is an energy demanding process.

3.3 Mechanism of ELM mass transport

The permeation of metals through the membrane in the ELM process occurs naturally by diffusion and various components can be used to enhance the separation such as additives, chemical reagents or specific carriers. Ways of improving the effectiveness of the separation are by maximizing the flux through the membrane and the capacity of the diffusion, where two related mechanisms are being known as *Type 1 facilitation* and *Type 2 facilitation*.

In the case of Type 1 facilitation a stripping agent is incorporated in the internal phase to increase the mass transfer. The stripping agent will react with the solute, resulting in a membrane insoluble product. The mechanism usually used for recovery of heavy metal and the mechanism considered in this project is Type 2 facilitation, or carrier-facilitated transport. In addition to the incorporated stripping agent in Type 1 facilitation, a carrier or a reactive component is also incorporated in the membrane phase to enhance the metal-transport. This mechanism is schematically described in Figure 3.2. The carrier forms a membrane-internal compound (for example $[\text{NR}_m^+\text{OH}]$ if NaOH is used as stripping agent) that is only soluble in the membrane phase, allowing diffusion through the membrane phase to the membrane-external interface. A reversible reaction with the metal complex ($[\text{MX}]^n$) to be transported occurs at the membrane-external interface [25]. The formed carrier-metal complex ($[\text{NR}_m\text{MX}]$) diffuses through the membrane to the membrane-internal interface and dissociates, thus releasing the metal in the internal phase. The carrier diffuses back to the membrane-external interface to repeatedly react with another metal complex from the external phase. This makes it possible for the carrier to be regenerated and

transport the metal many times, achieving a high degree of separation. When the metal is insoluble in the membrane phase and the only way the metal can be transported is by the formation of a carrier-metal complex, the concentration gradient is maximized by the reaction with a stripping agent at the membrane-internal interface.

Each step in Type 2 facilitation transport can be summarized as follows:

1. Reaction of the carrier and metal ion occurs at the interface of the external and the membrane phase.
2. The formed carrier-metal complex diffuses across the membrane phase to the internal-membrane interface.
3. The metal ion is released in the internal-membrane interface and the carrier is regenerated.
4. The metal ion diffuses from the internal-membrane interface to the bulk internal phase.
5. Carrier is returned across the membrane (mass transfer of extractant in the membrane phase from the internal-membrane interface to the external-membrane interface)

The ion flux through the membrane is created by a difference in chemical potential, which is due to the different pH between the two aqueous phases.

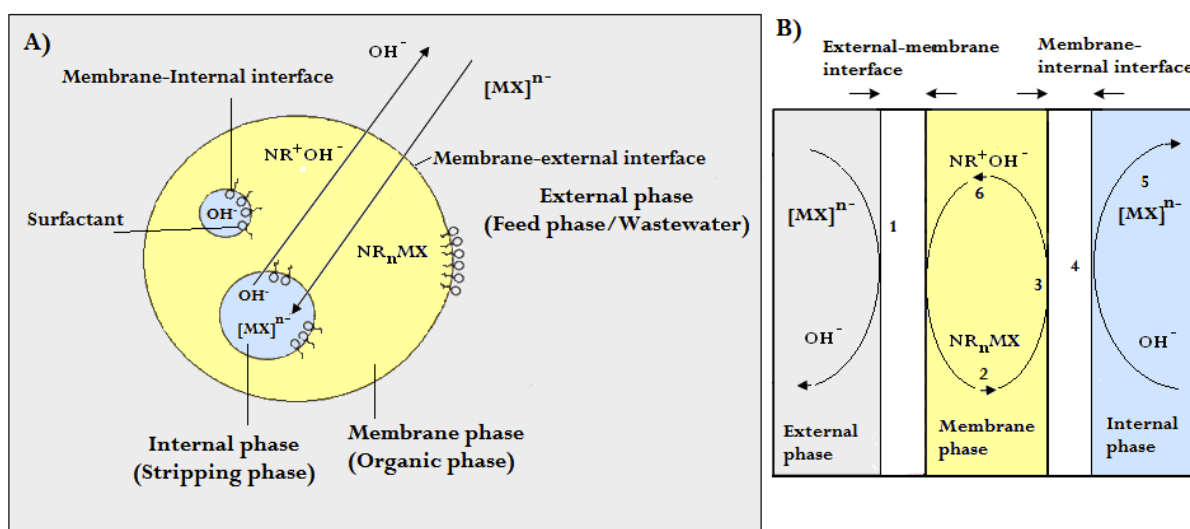


Figure 3.2: Transport mechanism in ELM process. A): a w/o emulsion droplet dispersed in the aqueous external phase, B): schematic picture of the reactions occurring at the interfaces.

3.4 Operational aspects of ELM

The different steps encountered in an ELM process are described as follows and also shown in Figure 3.3

1. Emulsification of the membrane and internal phase
2. Emulsion-external phase contacting
3. Separation of the emulsion and external phase after extraction
4. De-emulsification and recovery of the metal and the membrane phase

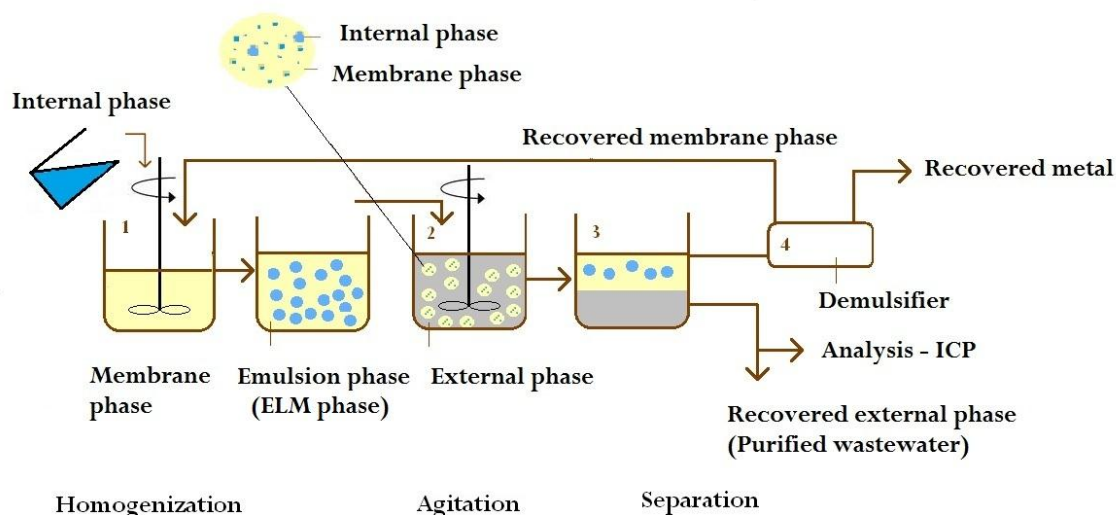


Figure 3.3: The operational steps in the ELM process.

Important aspects regarding the ELM process is its formulation in terms of the emulsification procedure, the choice of surfactants, carrier, stripping agent and diluent, which decide whether the process is successful or not. Some examples of different carriers, stripping agents and external solutions used in ELM processes depending on the metal ion to be extracted can be found in Appendix I (Table I-I), also specifying the kind of surfactant and diluent used. The different components have their own roles and requirements to enhance maximal extraction. The carrier should be selective to the target metal ion complex in the external and the internal aqueous phases while the stripping agent and the type of surfactant must be properly chosen to minimize the co-transport of water during the extraction process. The diluent should have a low solubility in water in order to create the membrane phase, it should also provide high extractant solubility, have a high-boiling point, be non-toxic and relatively cheap [30]. For the preparation of the emulsion phase either a high-speed mixer or a homogenizer is used, and when the emulsion phase is contacting the external phase it is common to use a baffled mixing vessel stirred by impellers.

3.4.1 Emulsification and surfactants

Surfactants are surface active agents, they are amphiphilic compounds, often organic, containing both hydrophobic groups (“tails”) and hydrophilic groups (“heads”) as shown in Figure 3.4. The amphiphilic character of the surfactant makes it soluble in both oils and water, however a good surfactant should have low solubility in the bulk phases and a strong tendency to migrate to the interfaces where it should pack densely. Surfactants are classified in four types according to the charge on their head, namely anionic, cationic, zwitterionic (dual charge) and nonionic [31]. In the case where water is mixed with oil, the surfactant molecule will adsorb at the interface between oil and water to lower the free energy of that phase boundary and facilitate the mixing. The surface tension between oil and water is reduced by the surfactant adsorbing at the liquid-liquid interface [31]. The addition of a co-surfactant can further reduce the interfacial tension, also through adsorbing in the w/o interface and thereby minimizing the repulsion of the hydrophilic head-groups of the surfactants, which contributes to a more efficient packing of the surfactants at the interface and reduces the water droplet size.

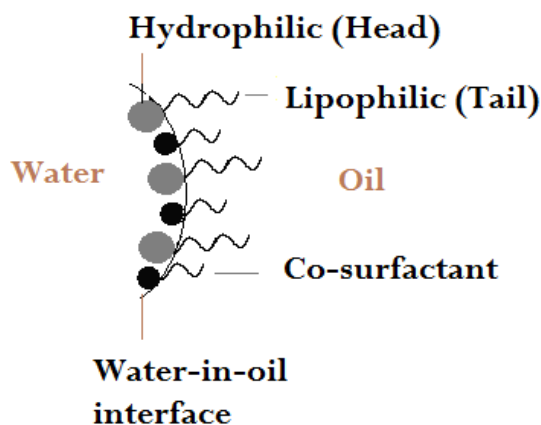


Figure 3.4: Schematic picture of the hydrophilic (“head”) and the lipophilic (“tail”) of a surfactant and a co-surfactant packed between the surfactants.

Bancroft’s rule states that water-soluble emulsifiers tend to give o/w emulsions and oil-soluble emulsifiers tend to give w/o emulsions. The concept of hydrophilic-lipophilic balance (HLB) may be used for a more quantitative approach when assigning the composition of a formulation, also utilized in this study to estimate the degree to which the surfactant is hydrophilic or lipophilic and to choose suitable surfactants for the multiple emulsion creation. A surfactant with HLB values in the range of 1-10 is more soluble in oil than in water, and those in the range 10-20 are more soluble in water than in oil. In Table 3.1 some common HLB values are given. It has also been found that the combination of two surfactants, one more hydrophobic and one more hydrophilic, is superior to the use of a single surfactant when making a stable emulsion and it contributes to a better packing of the surfactants in the oil-water interface, as the emulsifiers will have different critical packing parameters (CPP)⁸ [31].

Table 3.1: Common HLB value ranges and their applications [30].

HLB	Applications
1-1.3	Antifoams
3.5-8	Water-in-oil emulsifiers
7-9	Wetting and spreading agents
8-16	Oil-in-water emulsifiers
13-16	Detergents
15-40	Solubilizers

When creating a mixture, the total HLB will be calculated using x % of surfactant with HLB A and y % surfactant with HLB B by using Equation 3.1 [31].

$$\text{HLB}(A+B) = (\text{Ax}+\text{By})/(\text{x}+\text{y})$$

Equation 3.1

Multiple emulsion systems usually require at least two surfactants to create a stable emulsion: one lipophilic with a low HLB to stabilize the w/o interface and one hydrophilic with a high HLB for the o/w interface. The two emulsifiers are in interaction at the interfaces, therefore the chemical composition and compatibility of the emulsifiers is important. When creating a complex w/o/w emulsion the process is normally divided into two steps. In step one the aqueous internal phase is poured slowly into a beaker containing the oil phase, the lipophilic surfactant and other additives required and a

⁸ CPP is defined for a surfactant as the ratio $v/(l_{\text{max}}a)$ where v is the effective volume of the hydrophobic tail, l_{max} is the extended length of the alkyl chain (the tail) and a is the cross-sectional area of the head group.

high speed impeller, or a homogenizer, is used to disperse the aqueous internal droplets into the oil phase, and this results in a w/o emulsion. In the second step the created w/o emulsion is poured into the beaker containing aqueous external phase and a hydrophilic surfactant while agitated to disperse the w/o emulsion into the aqueous external phase. These steps and the procedure for creating a stable multiple emulsion is shown in Figure 3.5.

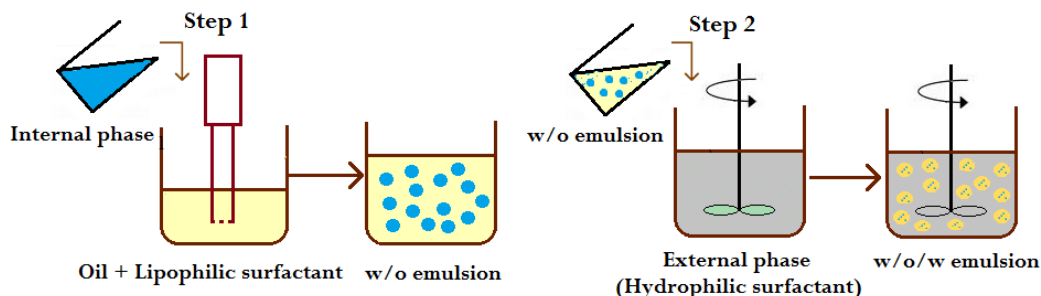


Figure 3.5: Creating water-in-oil (w/o) emulsion followed by a water-in-oil-water (w/o/w) emulsion.

However, in this project the methodology is modified in the case of creating the w/o/w emulsion. The created w/o/w emulsion should be stable enough to ensure a high contact surface area between the ELM phase and the external phase during the extraction. It should simultaneously be instable for a quick phase separation to occur when the extraction has been performed (when the agitation is turned off) where a quick recovery of the purified water is required before the breaking of the w/o emulsion. Because of this the hydrophilic surfactant is added in the first step together with the lipophilic surfactant intending that some of hydrophilic surfactant may migrate to the o/w interface of the multiple emulsion and facilitate the second emulsification. The chosen surfactants in this research are the commercially available Span 80 and Tween 80, both being viscous liquids at room temperature. The nonionic surfactant sorbitan fatty acid esters (commercial name Span) and the corresponding polysorbate, polyoxyethylene (POE) sorbitan fatty acid ester (commercial name Tween) are often used to stabilize multiple emulsions of w/o/w [32]. See Figure 3.6 for the structural formula of Span 80 and Tween 80 and the geometrical packing structure in an o/w emulsion.

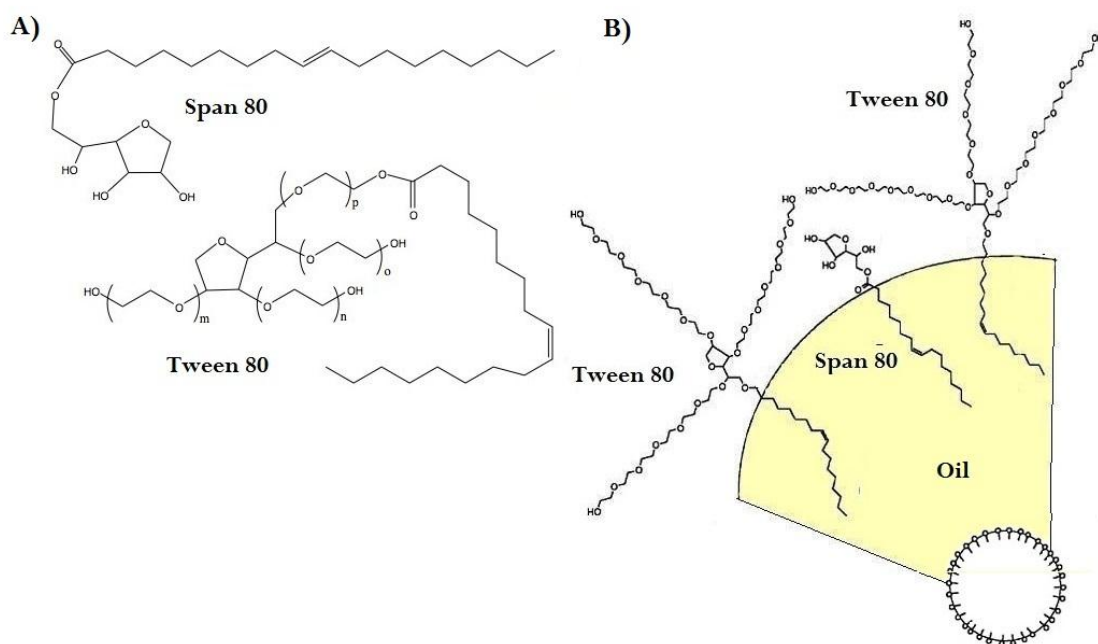


Figure 3.6: A) the structural formula of Span 80 (sorbitan monooleate, $HLB \approx 4.3$) and Tween 80 (ethoxylated sorbitan monooleate, $HLB \approx 15$). B) the geometrical packing of the surfactants at the oil-water interface in dispersed oil droplets.

The Spans are mixtures of partial esters of sorbitol and mono- and di-anhydrides with oleic acid, generally insoluble in water, corresponding to the lower HLB value. They are commonly used as water-in-oil emulsifiers and wetting agents [33]. The polysorbates (Tweens) are a complex mixture of sorbitol esters and mono- and di-anhydrides condensed with ethyleneoxides, resulting in a larger and more polar head group, hence a higher solubility in water. This is reflected in their higher HLB value, and they are commonly used as emulsifiers for oil-in-water emulsions [33]. The numbers in the commercial names denote the kind of hydrophobic groups present in the compound, and 80 represents oleate.

Multiple emulsions are limited by instability, with a consequent reduction of the overall removal efficiency in the ELM process. The instability is mainly due to the inherent thermodynamic instability and the complexities of their structure [34]. One limitation arises due to the immiscibility of the dispersed and continuous phase, where the dispersed phase breaks into droplets and the free energy of the surface increases. The increase of interfacial free energy causes thermodynamic instability of the dispersed phase, which leads to a droplet coalescence [31]. Another factor that affects stability is the osmotic pressure. If the external osmotic pressure is higher than in the internal aqueous phase, there will be water passing through the membrane phase leading to a swelling and eventually a rupture of the internal droplets, resulting in a leakage of the content into the external phase. Consequently, if the osmotic pressure is lower in the internal phase water will pass from the internal phase to the external phase resulting in shrinkage of the internal droplets. Ways of measuring the emulsion stability are limited because the stability of the internal droplets and external droplets must be determined. One direct way to examine the multiple droplets is by using microscopy [35]. In this project, due to the limited time, no such measurements were made.

3.4.2 Ionic liquid

Room temperature ionic liquids (RTILs) are by definition salts having a melting point lower than 100°C, thus in the liquid state at room temperature. The main properties of RTILs are that they have negligible vapor pressure, wide window of electrochemical stability, thermal stability at high temperature, excellent chemical stability and high ionic mobility [36]. These properties make them suitable replacers for volatile organic solvents in several chemical reactions [37]. However, the role of ionic liquid used as a stabilizer, carrier or surfactant in ELM is sparsely documented [26].

3.4.2.1 Stabilizer

Goyal et al showed that the stability of a w/o emulsion with kerosene as diluent was improved by incorporating the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[BMIM]^+[NTf_2]^-$) in the membrane phase as a stabilizer. Goyal et al showed that by the addition of 3 wt% $[BMIM]^+[NTf_2]^-$ the stability of the w/o emulsion could be enhanced from a few minutes up to 7 h [26]. $[BMIM]^+[NTf_2]^-$ will therefore be used in subproject 2 and has been chosen due to its low viscosity (52 mPas) compared to other ionic liquids, which facilitates the homogeneous dispersion in EILM. It is also hydrophobic, has a low toxicity and a low density. $[BMIM]^+[NTf_2]^-$ is a room temperature ionic liquid characterized by its melting point of 4°C and the molecular structure can be seen in Figure 3.7.

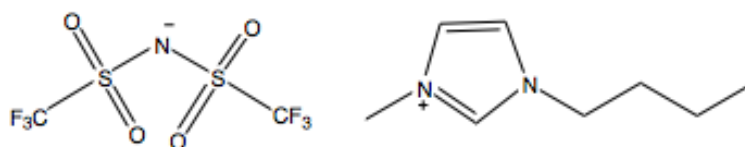


Figure 3.7: Molecular structure of the ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[BMIM]^+[NTf_2]^-$).

3.4.2.2 Carrier

The carrier, also known as extractant agent, is present in the membrane phase and is used to facilitate the metal-transport through the membrane. The chemical behaviour of the extractant is broadly classified into the three following categories [1]:

- Acidic: this category includes for example organophosphinic acids (*i.e.* Cyanex 272, DTPA) and organophosphonic acids (*i.e.* PCA 88A, Ionquest 801)
- Basic or anionic exchangers: quaternary ammonium salts (*i.e.* Aliquat 336) and tertiary amines (*i.e.* TOA, TNOA, Alamine 336) are included in this category and the extraction depends on the ability of the metal ion to form anionic species in the external phase. The metal is extracted as an ion pair by the amine salt.
- Solvating extractants: these carriers are used to compete with water as the first solvation shell around the metal ion. This facilitates the transfer of the metal ion complex into the membrane phase. Commercially used solvating extractants include phosphine oxides (*i.e.* TOPO, Cynaex 923) and phosphorous esters (*i.e.* TBP).

Important properties of the carrier that affect the overall removal efficiency are viscosity, density, solubility in the organic phase and insolubility in the aqueous phases. The carrier chosen for this research is a quaternary ammonium salt called tri-*n*-octylmethylammonium chloride (TOMAC or commercial name Aliquat 336) with a melting point of -20°C and viscosity of $500\text{ mPa}\cdot\text{s}$ at 30°C . As seen in Figure 3.8, TOMAC contains an electron deficient nitrogen group and a mobile chloride counter-ion, which contributes to a so-called anion displacement reaction between the carrier and the metal ion. This reaction is relatively fast in comparison to other complex formations *i.e.* ligand formation, this due to the presence of strong electrostatic interactions.

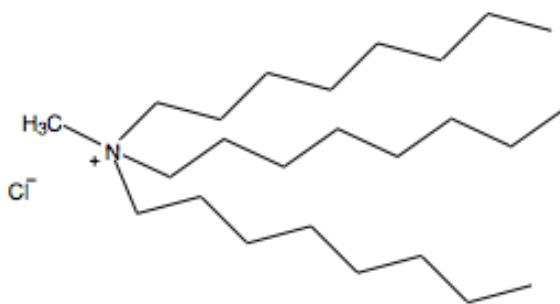


Figure 3.8: Molecular formula of tri-*n*-octylmethylammonium chloride (TOMAC)

3.4.3 Diluent

The diluent has an important function in the ELM process, since it is the major constituent of the membrane phase and the stability of the membrane is a vital factor for an effective metal-transport. A higher viscosity of the diluent can generally increase the emulsion stability (Shere and Cheung noted that emulsions with high viscosity oils are generally more stable) [38], but a high viscosity can also decrease the mass transport due to a higher resistance to diffusivity. Regarding solvent extraction a lower viscosity of the diluent benefits the overall capacity due to the decreased mass-transport resistance [39] and this is believed to be the case also for the ELM process. High enough density is necessary for an easier settling of the liquid phases, and for the phase separation between the external phase and the ELM phase, a high difference in density is beneficial. Low solubility in water is needed because the interaction with water breaks down the emulsion [40]. When it comes to the industrial use of the ELM process, the diluent stands for the largest amount wherefore other properties should also be considered such as

corrosivity (which increases the equipment cost or might require pre-treatments), easy recoverability, thermal and chemical stability and recyclability.

3.4.3.1 Palm oil as diluent

Venkateswaran et al studied several vegetable oils as diluents for the extraction of phenol in liquid membranes and palm oil was chosen when considering the removal efficiency, with a permeability of 8.5×10^{-6} m/s in acidic feed of pH 2.0 [4]. Very few previous studies were found using palm oil or any other vegetable oil as a diluent in the ELM process, which is the main purpose in subproject 1. As palm oil is easily available in Malaysia⁹ to a low cost it is a suitable replacer for the common petroleum based diluents such as kerosene, toluene, heptane and n-dodecane. This research uses cooking oil from the supermarket, which is a fraction of refined bleached deodorized palm oil called palm olein and consists mostly of unsaturated fatty acids [41]. Crude palm oil consists mainly of triglycerides, see Figure 3.9 for the molecular structure, but also of small amounts of monoglycerides and diglycerides. The fatty acid chain in palm oil triglycerides varies in the number of carbons and in structure, which also defines the chemical and physical properties [42]. The chain length of the fatty acids is between 12 to 20 carbons, half of the fatty acids are saturated (0,1% laurate, 1% myristate, 44% palmitate, 5% stearate) and the other half is unsaturated (39% monounsaturated oleate, 10% polyunsaturated linoleate, 0.3 % polyunsaturated alpha-linolenate). The degree of saturation determines the stability of the oil against oxidation. Palm oil has a density of 887.5 kg/m^3 [43] and a viscosity of $130 \text{ mPa}\cdot\text{s}$ at 20°C [4]. Random analyses of samples of palm olein have shown the presence of about 2% of 1,2-diglycerides, about 4% of 1,3-diglycerides and trace amounts of monoglycerides and other components [41]. The commercially used cooking oils are commonly enriched with vitamins, nutrients and flavours.

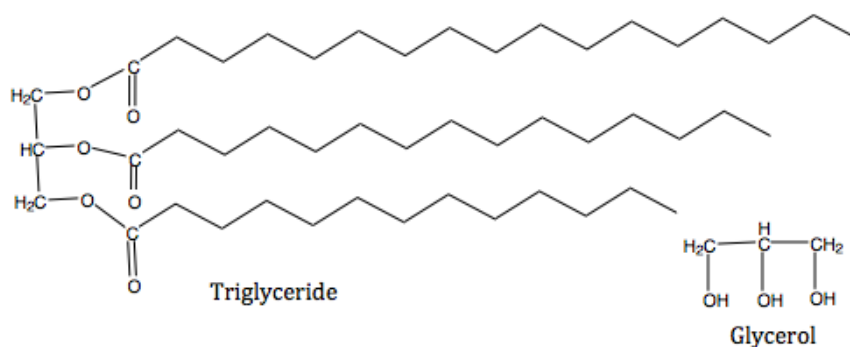


Figure 3.9 The molecular structure of saturated triglyceride and glycerol. [44]

3.4.3.2 Kerosene as diluent

One of the most commonly used diluents in ELM systems, and also the diluent used in subproject 2, is kerosene (also called paraffin), a thin clear liquid mixture of hydrocarbons with a viscosity of $1.64 \text{ mPa}\cdot\text{s}$ at 27°C [41] and a density of $0.78\text{-}0.81 \text{ g/cm}^3$. Kerosene is obtained through fractional distillation of petroleum between 150 and 275°C and its chemical composition depends on its source, but usually consists of 10 different hydrocarbons each containing 10-16 carbon atoms per molecule with the general formula $\text{C}_n\text{H}_{2n+2}$; see Figure 3.10 for the structure of a kerosene constituent with $n=12$. The main constituents of kerosene are straight chain and branched chain paraffins and also ring shaped cycloparaffins (naphtenes) [45]. Reasons for using kerosene is the easy availability in Malaysia for a low cost due to the subsidized price [46] and it has also been reported to form a more stable emulsion compared to toluene and n-dodecane [40].

⁹ Malaysia is, after Indonesia, the world's second largest producer of palm oil.

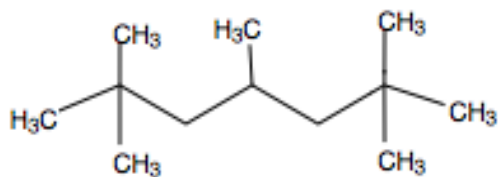


Figure 3.10: The molecular structure of branched chain kerosene.

3.4.4 Stripping agents

The purpose of the stripping agent is to react with the metal ion in the internal phase through a stripping reaction. This reaction converts the metal ion into a membrane insoluble compound hence trapping the metal in the internal phase droplets. It also enables transport against the metal concentration gradient. The stripping agent is incorporated in the internal phase and can be an acid or a base, depending on the specie to be extracted. As an example, NaOH can be used as stripping agent for the chromium removal from wastewater [26].

3.4.5 De-emulsification

The metal and the membrane phase is recovered during the de-emulsification step, where the breaking of the w/o emulsion occurs. There are two types of de-emulsification methods: physical and chemical ones [47]. Chemical methods include the addition of a de-emulsifier, which is the easiest way but limits the reuse of the component due to changes in the properties of the diluent, surfactant and carrier. Physical methods include heating, centrifugation, microwave radiation, high shear and solvent dissolution. The most commonly used de-emulsification technique is the use of electrostatic fields. However, this part is not included in the scope of this project, hence it will not be treated further.

3.5 Conditions affecting extraction rate and permeability

Various operating conditions affect the extraction rate and the permeability, including the membrane formulation, the stripping agent concentration, the stirring rate and the external phase conditions. Phenomena that are affected by these parameters are swelling and membrane breakage. As mentioned previously one of the disadvantages of ELM systems is the tendency of swelling of the emulsion globules. Two types of swelling exist: osmotic swelling and entrainment swelling. Osmotic swelling occurs as a result of a large difference in osmotic pressure between the internal and the external phase, causing a transfer of water from the external phase into the internal phase. Entrainment swelling is caused by the entrainment of the external phase into the internal phase through repeated coalescence and re-dispersion of emulsion globules during the dispersion procedure causing an increase in the volume of the internal phase. However, osmotic swelling cannot be differentiated from entrainment swelling and it is difficult to determine both the swelling and the breakage phenomena in the same experiment [1]. There are several proposed mechanisms to explain ELM globule swelling. The most probable mechanism is molecular diffusion of water from the external phase to the internal phase and water transfer via hydration of the surfactant molecules. Two other mechanisms proposed are micelle-assisted transport of water from the external phase to the internal phase and entrainment with a subsequent emulsification of the external phase caused by an excess of surfactant. Through general observations, several factors have been suggested to influence the rate of swelling such as the type and concentration of the surfactant, the stirring speed, the organic to internal phase ratio and the background electrolyte concentration [1].

3.5.1 Membrane formulation

The membrane phase consists of diluent, carrier, surfactant and co-surfactant, and requires an optimal formulation for the emulsion to be stable and for the extraction to take place. The surfactant concentration has an important role in the stability of the w/o emulsion where a higher surfactant concentration results in improved stability due to the lower surface tension, which in turn leads to a smaller droplets size and a larger mass transfer area. However, larger amounts of surfactant increase the viscosity of the membrane phase and decrease the removal efficiency due to lower diffusivity of the metal through the membrane phase [26] hence an optimum surfactant concentration is needed. Goyal et al showed that up to 3 wt% concentration (relative to the membrane phase) of Span 80 increases the removal efficiency in the chromium(VI) extraction [26]. A higher concentration of Span 80 increases the mass transfer resistance, leads to formation of micelles that result in membrane swelling but also makes the de-emulsification and metal recovery more difficult. Regarding the carrier concentration Goyal et al showed that a decrease in extraction rate occurred beyond a certain concentration (0.3 wt%) of the carrier [26]. These results motivates for the chosen surfactant and carrier concentrations in this project.

3.5.2 Stirring rate

The stirring rate has a large impact on the ELM extraction capacity, since it enhances the mixing during extraction and provides smaller emulsion droplets due to the shear force applied on the emulsion globules, providing a larger mass transfer area. However, a further increase in stirring speed may lead to a decrease in emulsion stability and leakage of the internal phase due to the breakage of emulsion droplets. When mixing the external phase and ELM phase the commonly used stirring rate is 100-800 rpm. The homogenization speed for the creation of the ELM phase is often performed at 3000-10 000 rpm [26].

3.5.3 Internal stripping agent concentration

The stripping agent concentration has an important role when it comes to the extraction rate. A higher concentration increases the metal extraction rate both due to the stronger pH gradient and the higher amount of stripping agent present. As mentioned earlier, the pH difference between the external phase and the internal phase is the main driving force for the transport of the carrier-metal complex through the membrane phase. Goyal et al showed that an optimal stripping agent concentration exists and a further increase has a negative influence on the removal efficiency [26]. Furthermore, an increase of the internal concentration gives a higher pH difference between the external phase and the internal phase, which may increase the osmotic pressure and cause membrane swelling.

3.5.4 Metal concentration of the external phase

The metal concentration in the external phase influences both the extraction rate and efficiency, which depend on the capacity of the internal phase to strip the metal. High initial metal concentration requires a high emulsion capacity and a low initial metal concentration means that the metal ions may have to compete with other ions present in the external phase.

3.5.5 pH of the external phase

In order to accomplish the extraction of diluted metals from water, the pH of the external phase has to be precisely controlled. Moreover, the chemistry of the different metal complexes in the external phase influence the carrier-metal transport, which can be controlled by choosing the proper pH of the external phase.

3.5.5.1 Chemistry of chromium

Hexavalent chromium ions exist in different forms in the aqueous phase depending on the pH (the chromate and the dichromate ions H_2CrO_4 , $\text{H}_2\text{Cr}_2\text{O}_7$, HCrO_4^- , HCr_2O_7^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$) [48]. For slightly acidic or basic pH the CrO_4^{2-} ion is the dominating form, an increase in the concentration of $[\text{H}^+]$ leads to a reaction with CrO_4^{2-} to form HCrO_4^- and upon further increase H_2CrO_4 is formed.

Figure 3.11 shows the abundance of the chromate ions depending on the pH of the external phase. Due to the basic properties of TOMAC, the target complex in this case requires an anionic chromium complex, and previous studies with successful chromium extraction have used pH low as 0.5 [26].

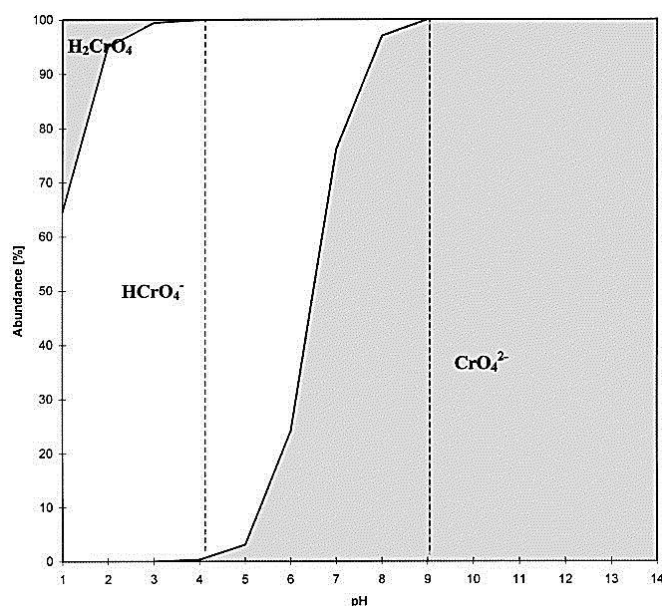


Figure 3.11: Abundance of chromium(VI) ions in water (reproduced from [49] with permission from the author's)

The reactions involved in the chromium extraction by ELM include the carrier reacting with the stripping agent and the metal complex.

The carrier diffuses through the membrane to the membrane-internal interface where it reacts with the stripping agent, as shown in Equation 3.2. This reaction yields chloride ions present in the internal phase, which also help to strip the metal complex [26].



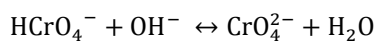
There are two types of carriers present in the membrane phase that react with the metal complex, TOMAC (NR_4^+Cl^-) and TOMAOH (NR_4^+OH^-). The following Equation 3.3 and Equation 3.4 shows the anionic displacement reaction with the two types of carriers and one of chromium anionic complex, HCrO_4^- .



The formed carrier-metal complex diffuses across the membrane phase to the membrane-internal interface, where the stripping reaction occurs and the metal is dissociated to the internal phase as shown in Equation 3.5. The created complex $\text{HCrO}_4^-\text{Na}^+$ is insoluble in the membrane phase and will therefore not diffuse back to the external phase, but will instead be trapped within the internal droplet [48].



The dissociated HCrO_4^- ion in the internal phase will remain in equilibrium after the reaction with the hydroxide ions as shown in Equation 3.6.



Equation 3.6

As the stripping reaction proceeds and hydroxide ions are released in the external phase, the pH increases due to exchange of the hydroxide ions with the metal complex. As the pH changes in the external phase, an increased amount of CrO_4^{2-} ions will be present which consequently react slowly with TOMAC and TOMAOH. Each CrO_4^{2-} species requires two extractant species for the reaction with the carrier to occur, resulting in a decreased reaction rate with time [26]. The pH of the external phase can be adjusted with different kinds of acids such as HNO_3 , HCl , H_2SO_4 . It is suggested in previous studies that the adjustment of the pH with HCl for the removal of chromium maintained longer membrane stability than with HNO_3 and H_2SO_4 [50].

3.5.5.2 Chemistry of arsenic

Arsenic exists in the oxidation states -3, 0, +3 and +5 [13]. The dominating species in ground water are arsenite (AsO_3^{3-} , arsenic(III) ion) and arsenate (AsO_4^{3-} , arsenic(V) ion). The presence dissociated or undissociated arsenic complexes depend on the pH of the water, as given in Figure 3.12. It can be seen that arsenic(V) is found as different neutral and ionic complexes in different pH ranges (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-}). The most common pH range in ground water is 6.7-8.8, where H_2AsO_4^- and HAsO_4^{2-} are dominant [51].

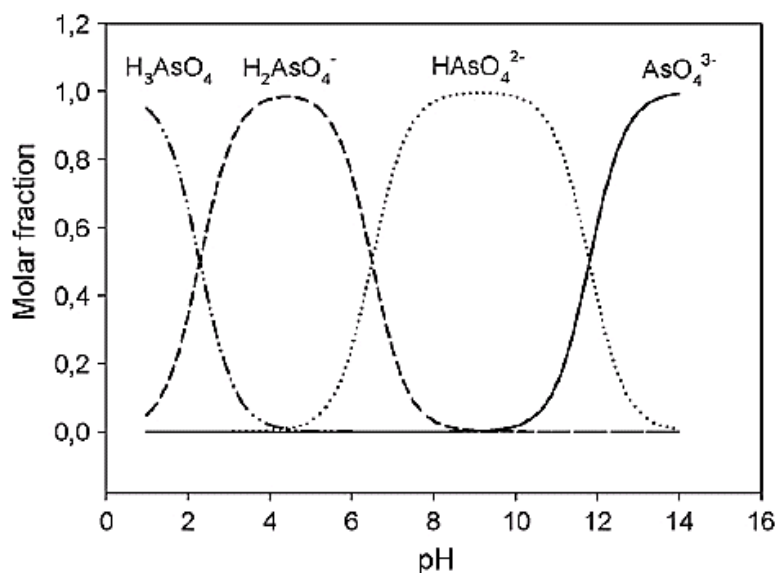
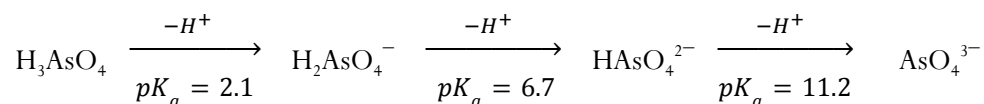


Figure 3.12: Molar fraction of arsenic(V) complex H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-} for different pH ranges (reprinted from [52] with permission from the author's)

The dissociation of arsenic(V) with the value of the logarithmic acid dissociation constant (pK_a) is described below



A suitable carrier can be chosen taking into consideration the form of the metal complex to be extracted. As mentioned previously the basic carrier TOMAC is used in this project and an anionic arsenic complex is necessary for the creation of the carrier-arsenic complex and the pH of the external phase chosen to facilitate the reaction. The pH of the external phase should be adjusted with a base to ensure a high pH where the anionic arsenic species are present.

3.5.6 Treat ratio

The treat ratio in this study is the volume ratio of the external phase to the ELM phase. It also measures the volume of ELM required per unit volume of the external phase, as shown in Equation 3.7.

$$\text{Treat ratio} = \frac{V(\text{external phase})}{V(\text{ELM phase})} = F/\text{ELM} \quad \text{Equation 3.7}$$

This ratio defines the effectiveness and the economy of the ELM process because a smaller volume of the membrane phase (a high F/ELM) reduces the overall cost. Goyal et al have discussed that an increase of the treat ratio increases the possibility of swelling and breakage of the emulsion but also that a reduction of internal phase volume results in decreased stripping [26]. A lower treat ratio increases the extraction rate due to the presence of a larger ratio of membrane and internal phase, and increases the capacity of extraction. The optimal treat ratio of 2 was found to be most efficient.

3.5.7 Organic to internal phase ratio (O/I)

The organic to internal phase ratio describes the weight ratio of the organic phase to the internal phase, as shown in Equation 3.8.

$$\text{Organic to internal phase ratio} = \frac{m(\text{oil phase})}{m(\text{internal phase})} = O/I \quad \text{Equation 3.8}$$

This ratio is important to control in order to achieve optimal emulsion stability where phase inversion (a change from w/o to o/w) depends on the relative volume of the different phases but also on the HLB values of the surfactants and on the temperature [26]. A decrease of the organic fraction relative to the internal phase causes an increase of the amount of stripping molecules and increases the stripping rate at the internal to organic interface.

4 METHODOLOGY AND EXPERIMENTAL TECHNIQUES

In this project confirmation and optimization of chromium and of arsenic extraction using an ELM system was investigated, and the discovery of the possibility of using a vegetable oil as organic diluent in the system was explored. A large number of experiments were required,¹⁰ and this section starts with a general description of the experiments performed followed by a more detailed description of the experiments carried out in the two subprojects.

4.1 Simple liquid-liquid extraction

As the ELM extraction process is of Type 2 facilitation, in which a mobile carrier is incorporated in the liquid membrane, the compatibility of the carrier and the current metal-complex must be confirmed. For this purpose a simple liquid-liquid extraction (or solvent extraction) is a fast and straightforward way to verify and ensure the compatibility. It can also be used to determine the pH range where the extraction is most efficient. The verification is performed as followed (see Figure 4.1 for a schematic picture):

1. The aqueous phase is prepared with a known metal concentration and pH is adjusted
2. The organic diluent (solvent) is mixed with the carrier in a beaker, using an agitator stirred by a straight blade impeller, with the carrier in molar proportion to the metal
3. The external phase is poured into the organic phase while stirring and the system is left for a certain time at a constant agitation speed
4. The agitation is turned off, the aqueous and organic phase are allowed to separate and samples are taken from the aqueous phase for concentration measurements with ICP-OES (See Section 4.2)

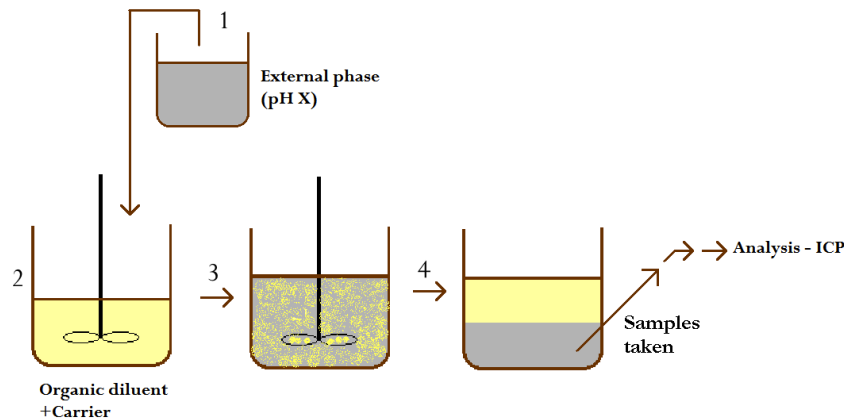


Figure 4.1: Schematic picture of the simple liquid-liquid extraction process.

4.2 Concentration measurements: analysis of removal efficiency

To measure the extraction efficiency, either from the simple liquid-liquid extraction or from the ELM extraction process, samples from the external phase are analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES). The initial concentration of the batch external phase is measured simultaneously to obtain the accurate amount of removal. The removal efficiency is calculated according to Equation 4.1, where c_i is the measured initial external phase concentration (mg/L) and c_e is the measured concentration (mg/L) of the metal in the sample taken as a function of time.

¹⁰ All of the experiments were performed at the University of Malaya, Faculty of Engineering: Department of Chemical Engineering

$$\text{efficiency}(\%) = \frac{c_i - c_e}{c_i} \times 100$$

Equation 4.1

4.2.1 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

Inductively coupled plasma (ICP-OES and ICP-MS) spectrometry and atomic absorption spectrophotometry (AA) are the most widely used analytical methods used for determining trace elements. However, Saravanan et al used a UV Jasco spectrophotometer for the detection of chromium [53]. The device used in this project was an Optima 7000 DV ICP-OES from PerkinElmer. The device has a dual-view design and a detection limit in the range of parts per billions. The basic principle ICP-OES consists of the excitation of elements, the detection of the characteristic wavelength of the emitted light (arsenic at 193.696 nm and chromium at 267.7 nm) and the measurement of its intensity to obtain the concentration of the element. More than one element can be analysed simultaneously and the analysis is relatively quick, one sample is analysed in 1-3 minutes, depending on the washing time and the number of measurements per sample. The device used can be seen in Figure 4.2.



Figure 4.2: The Optima 7000 DV ICP-OES used for concentration measurements.

Plasma that contains sufficient concentration of ions and electrons to make the gas electrically conductive is referred to as inductively coupled plasma. The plasma is created from a flow of argon gas through a torch that contains a Tesla unit, which creates a high voltage, low current, and high frequency alternating current electricity. The formation of plasma takes place through adequate electromagnetic field strength, introducing electrons into the gas stream and causing them to collide with argon atoms. Once the plasma is ignited, the Tesla unit is turned off. The inductively coupled plasma is used to excite atoms and ions and cause them to emit electromagnetic radiation at wavelengths characteristic for that particular element, and the intensity of the radiation is indicative to the concentration of the element. For this a calibration curve is established of the current element from samples of known concentration, 1, 5, 15, 30, 70 and 100 ppm of As(V) ions or Cr(VI) ions respectively. The calibration curves obtained of chromium and of arsenic can be seen in Figure 4.3.

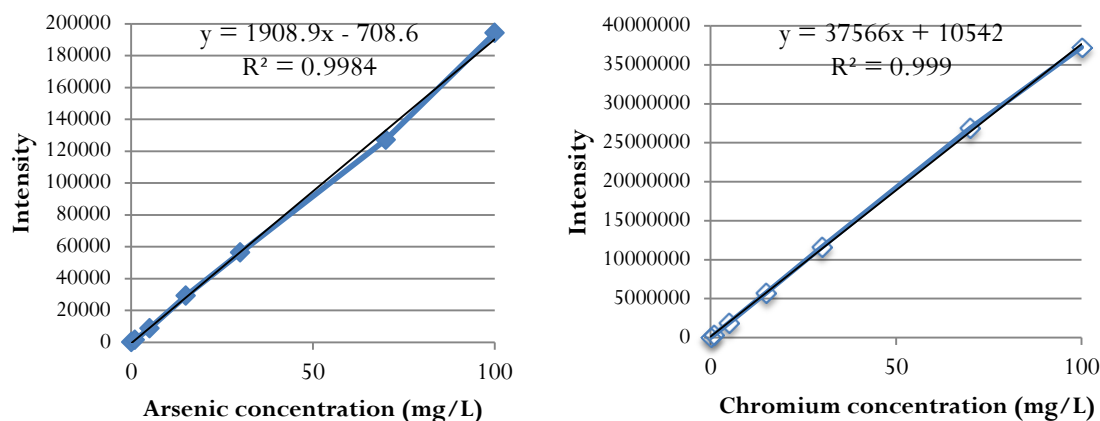


Figure 4.3: Calibration curves obtained from the ICP measurements for arsenic and chromium.

The measured intensity (y) of a sample with unknown concentration (x) is compared with the corresponding calibration curve, hence the metal concentration in the sample is obtained.

A sample size of at least 5 ml is required for reliable measurements and the device is controlled with WinLab32 software. Every sample was analysed three times whereby a corrected mean intensity was obtained and used for the determination of the sample concentration. The results obtained from the measurements contain both the intensities measured and the concentrations obtained.

4.3 Emulsification: creating the membrane and the internal phase

4.3.1 Preparation of a w/o emulsion

The emulsion type needed for the ELM system is a water-in-oil emulsion, in which the aqueous phase is dispersed in the organic oil phase. First the solubility of the different components in the oil is checked, and then the proper amounts of surfactant, eventual co-surfactants and/or stabilizer, carrier and oil composing the organic phase are weighed to the correct mass ratios and mixed using homogenizer. The aqueous solution (containing the stripping agent) is slowly added to the mixture using a pipette while still homogenizing. When all of the internal solution has been added, the homogenizer is kept on for the decided emulsification time and the final solution is checked to be macroscopically homogenous.

4.3.2 Exploring the stability of an emulsion

The stability and viscosity of a novel emulsion formulation was studied and the composition identified as the best possible could be determined for further investigation. If phase separation was observed or if the original state of the emulsion could not be regained upon slight application of shear stress the emulsion was considered destabilized.

Brief methodology:

1. Calculation of an approximate composition of the formulation using the HLB concept and comparison with earlier studies,
2. Preparation of a number of emulsion formulations while varying the composition, emulsification time and homogenization speed in a systematic manner,
3. Study of stability and viscosity,
4. Summary of results and choice of formulation for further studies.

The emulsion created in step 2 above is transferred to a marked separation funnel and in order to wait for phase separation to occur. The emulsion is left in ambient conditions and stability is checked within regular time intervals.

4.4 Metal extraction using ELM

In these experiments the whole extraction process of the metals using the ELM system is investigated. The chosen response variable is the removal efficiency, calculated as described in Section 4.2. The experiments are performed in the following steps (steps 2-5 are also shown in Figure 4.4):

1. Preparation of the external solution through dissolving the metal salt in water and adjusting the pH
2. Preparation of the ELM
 - a. Preparation of the internal phase solution with the desired stripping agent
 - b. Emulsification; preparation of a w/o emulsion as described in Section 4.3
3. Contacting external and ELM solutions in a 250 ml beaker using an agitator stirred by twisted impellers
4. Taking of samples within decided time intervals using syringes
5. Separation of external phase and ELM phase: the syringes are left undisturbed in order for phase separation to occur, and the aqueous (external) phase is taken out for analysis. If needed, the samples are diluted to obtain the desired volume of at least 5 ml
6. Analysis of samples from external phase, calculation of removal efficiency
7. Performance evaluation for chosen variables-only performed for the experimental design
8. Analysis of results and proposal of a model-only performed for the experimental design

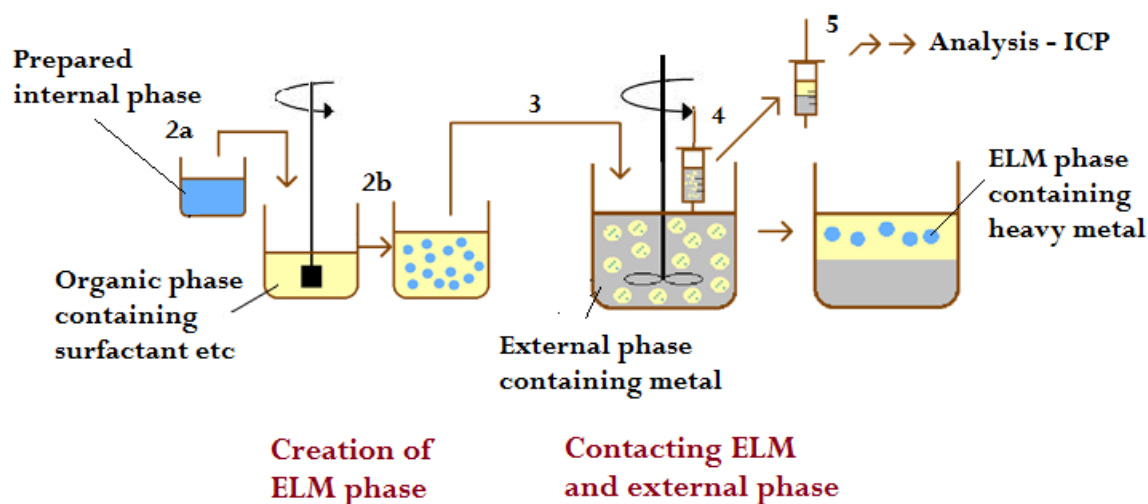


Figure 4.4: Schematic picture of the metal extraction experiments.

In step 1 of the process described above the external phase is created to imitate waste water. However, the external solution is prepared in the lab and no samples from industrial waste water were analysed. The pH of the solution was adjusted to the type of carrier used and the type of metal-complex desired.

The physical properties and basic information regarding the chemicals involved in the experiments, as well as the equipment used, are found in Appendix I. All chemicals were used as purchased without further purification. All equipment used, apart from the ICP and the pH meter, was cleaned using acetone or dish washed before each experiment.

4.5 Subproject 1: using palm oil as diluent

4.5.1 Emulsion stability studies

Before the metal extraction could be investigated, a novel emulsion formulation with palm oil as diluent suitable for the metal extraction needed to be developed. A relatively low viscosity and a stability time of at least one hour were desired. The parameters investigated can be seen in Table 4.1, and a number of different emulsions were prepared while varying these parameters.

Table 4.1: Parameters investigated in the emulsion stability studies.

Parameter	Range
O/I phase mass ratio	2 to 3
Emulsification time	6 to 15 min
Homogenization speed	3200 to 7000 rpm
Span 80	2 to 4 wt%
Tween 80	0 to 1.5 wt%
[BMIM] ⁺ [NTf ₂] ⁻	0 to 3 wt%
Butanol	0 to 3 wt%

The stability was studied by observing the phase separation in a separation funnel and the viscosity was only estimated by the naked eye inspection of the emulsion. From previous studies it is known that Span 80 works well as a surfactant in the ELM system [26]. To facilitate both the emulsification of the w/o emulsion and the creation of the double w/o/w emulsion for the extraction step, the use of the hydrophilic Tween 80 as a co-surfactant was investigated, while to improve the overall stability of the emulsion the use of butanol as co-surfactant was investigated. In addition to the palm oil based emulsions, some emulsions were prepared using kerosene as organic diluent with Tween 80 and butanol as co-surfactants in order to evaluate the effect of these.

4.5.2 Metal extraction experiments

In previous studies the compatibility of TOMAC and chromium has been ensured and the suitable pH range for extraction is known to be 0.5. Consequently, the metal extraction experiments conducted in this subproject directly assess the whole ELM process.

The external phase was prepared by solving 0.283 g of $K_2Cr_2O_7$ in 1 L water, obtaining a chromium ion concentration of approximately 100 ppm. The pH was adjusted using hydrochloric acid. The internal phase was prepared by solving the NaOH pellets in water to obtain a known molarity and the ELM was created through emulsification in a 100 ml beaker. The external phase and the ELM phase were contacted by pouring the ELM into the external phase solution, contained in a 250 ml beaker, while stirring and samples were taken using syringes at different time intervals (0.5, 1, 2, 4, 7, 11 and 15 min, however, not always for all times). As the Cr(VI) solution has a bright yellow colour it was possible to use the colour change as a rough indication of whether the extraction had been successful or not, before the concentration measurements were made by ICP-OES (see Figure 4.5). The external phase samples were diluted if needed while carefully noting the dilution factor, transferred into "ICP-tubes" and taken to the ICP-OES for concentration measurements. The concentrations of the samples obtained were multiplied with the dilution factor and finally the removal efficiency was calculated. The parameters investigated for the chromium extraction experiments can be seen in Table 4.2.

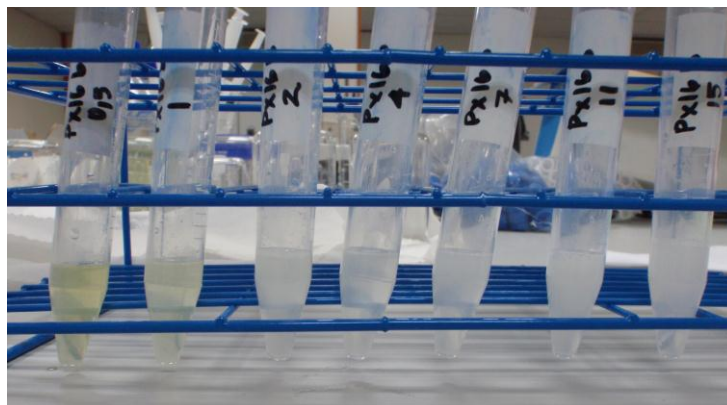


Figure 4.5: The change in colour during the extraction experiments can be seen as a function of time: The samples to the left are taken first and the yellow colour decreases as the extraction time increases, to the right.

Table 4.2: Parameters investigated in the metal extraction experiments.

Main area	Parameter	Range
ELM formulation	Surfactant (Span 80) conc.	2.5-3 wt%
	Butanol conc.	0-2 wt%
	Tween 80 conc.	0-2 wt%
	Stripping agent (NaOH) conc.	0-0.5 M
	Carrier (TOMAC)	0-0.4 wt%
	O/I phase mass ratio	2 to 3
External phase	Cr concentration	100 ppm and some experiments with 50 ppm and 10 ppm
	Water type	Distilled /de-ionized /tap water
Contacting external and ELM phases	Agitation speed	400 – 800 rpm
	Treat ratio	1:1 to 1:3

Since it was showed by Güell et al that the presence of various anions in high concentrations gave no significant difference in terms of permeability for extraction of arsenic using SLM [52], the influence of the type of water was investigated through preparing both the external phase and the internal phase of the ELM with either de-ionized, distilled or tap water respectively.

4.5.3 Experimental design and optimization studies

For the experimental design study the Response Surface Method (RSM) was chosen. RSM is a collection of mathematical and statistical techniques for modelling and analysis of problems in which the response is influenced by several factors and the objective is to optimize this response. An experimental design of orthogonal columns was used for fitting the response, shown in Table 4.3. As can be seen, the parameters investigated were the agitation speed when contacting the external phase with the ELM, and the amount of butanol and Span 80 respectively in the ELM.

Palm oil was used as diluent, the amounts of 1 wt% Tween 80 and 0.35 wt% TOMAC, and a stripping concentration of 0.1 M NaOH were held constant. The ELM was prepared with an emulsification time of 11 min and a homogenization speed of 3400 rpm. The initial chromium concentration was 100 ppm and the pH of the external phase was 0.5. Due to the high viscosity of the ELM, an agitation speed of more than 600 rpm was required when contacting of the external phase with the ELM, and therefore the agitation was increased to 800 rpm for the first 30 seconds.

Table 4.3: Experimental design performed.

Run	X ₁ (coded)	X ₂ (coded)	X ₃ (coded)	X ₁ (actual)	X ₂ (actual)	X ₃ (actual)
				Agitation (rpm)	Span 80 (wt%)	Butanol (wt%)
1	0	-1	0	600	2,5	0,5
2	0	1	0	600	3	0,5
3	1	-1	0	800	2,5	0,5
4	1	1	0	800	3	0,5
5	0	0	-1	600	2,75	0
6	0	0	1	600	2,75	1
7	1	0	-1	800	2,75	0
8	1	0	1	800	2,75	1
9	-1	-1	-1	400	2,5	0
10	-1	-1	1	400	2,5	1
11	-1	1	-1	400	3	0
12	-1	1	1	400	3	1
13	-1	0	0	400	2,75	0,5
14	-1	0	0	400	2,75	0,5
15	-1	0	0	400	2,75	0,5
16	-1	0	0	400	2,75	0,5
17	-1	0	0	400	2,75	0,5
18	-1	0	0	400	2,75	0,5
19	-1	0	0	400	2,75	0,5

The polynomial models used to describe the response are seen in Equation 4.2 (first order linear model including interaction terms) and Equation 4.3 (second order linear model including interaction and quadratic terms). The parameters (β_n) are obtained by regression analysis.

$$y = \beta_0 + \beta_{x_1}X_1 + \beta_{x_2}X_2 + \beta_{x_3}X_3 + \beta_{x_1x_2}X_1X_2 + \beta_{x_1x_3}X_1X_3 + \beta_{x_2x_3}X_2X_3 + \varepsilon \quad \text{Equation 4.2}$$

$$y = \beta_0 + \beta_{x_1}X_1 + \beta_{x_2}X_2 + \beta_{x_3}X_3 + \beta_{x_1x_2}X_1X_2 + \beta_{x_1x_3}X_1X_3 + \beta_{x_2x_3}X_2X_3 + \beta_{x_1x_1}X_1^2 + \beta_{x_2x_2}X_2^2 + \beta_{x_3x_3}X_3^2 + \varepsilon \quad \text{Equation 4.3}$$

The calculations and regression analysis were performed using a MATLAB programs designed by Jan Rodmar.

4.6 Subproject 2: Arsenic extraction

4.6.1 Compatibility and pH ranges

As no previous studies of using TOMAC as carrier in an ELM for arsenic extraction were found, it was necessary to verify the compatibility between the carrier TOMAC and the As(V) complex and to assess the suitable pH range of the external phase. A series of simple liquid-liquid extraction experiments were performed, varying the pH of the external phase from pH 2 to pH 12. The external phase batch was prepared by dissolving 0.416 g of $\text{HAsNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$ in 1 L distilled water, hence obtaining a concentration of approximately 100 ppm As(V)-ions. The solution was transferred into six separate bottles, each pH adjusted to obtain pH 2, 4, 6, 8, 10 and 12 respectively using $\text{HCl}(\text{aq})$ and $\text{NaOH}(\text{aq})$. A treat ratio of external phase to membrane phase 2 was desired to simulate ELM process conditions and

a molar excess of TOMAC was needed, as the metal extracted would bind to the carrier in the organic phase but due to the lack of internal phase, will not be released and therefore no regeneration of the carrier is possible. At low and intermediate pH H_2AsO_4^- and HAsO_4^{2-} are present, requiring a molar ratio of TOMAC to As(V) of at 2:1, and at higher pH the ion AsO_4^{3-} is dominating, requiring a molar ratio of 3:1. To facilitate the experiments, a molar ratio of at least 3:1 was kept for all solutions. The extracting solvent (the organic phase) was prepared by mixing 6.6 g kerosene with minimum 0.04 g TOMAC for 1 min at agitation speed 200 rpm. Some experiments were performed with 6.6 g palm oil and minimum 0.04 g TOMAC as well, and 26 ml of the external phase was used in each experiment. Then a new series of liquid-liquid extractions were performed, adjusting the pH of the external phase to pH 6, 9 and 12, and in these experiments the agitation speed was varied from 200-800 rpm and extraction time was varied from 3-11 min. The samples taken from the aqueous phase after the separation were taken to the ICP-OES for concentration measurements.

4.6.2 Arsenic extraction using EILM

The next step was to perform metal extraction experiments with the EILM system and from the results obtained in the liquid-liquid extraction a suitable pH of the external phase could be determined. The internal phase was kept acidic, with concentration of 0.01-0.1 M HCl and the external phase was kept basic, at $\text{pH} > 8$, adjusted using NaOH(aq). The membranes were prepared by emulsification and experiments were performed with both kerosene and palm oil as diluents, Span 80 as surfactant, $[\text{BMIM}]^+[\text{NTf}_2]^-$ as stabilizer and in some experiments Tween 80 and butanol as co-surfactants. The agitation speed was kept at 400 rpm.

5 RESULTS AND DISCUSSION

5.1 Subproject 1: using palm oil as diluent

5.1.1 Emulsion stability studies

5.1.1.1 Solubility tests – palm oil

The different components were mixed with the diluent in order to investigate the solubility, and the observations are seen in Table 5.1. As shown, the ionic liquid $[\text{BMIM}]^+[\text{NTf}_2]^-$ does not seem compatible with palm oil and consequently it is probably not a useful component in the palm oil based emulsion.

Table 5.1: Solubility tests.

Diluent	Component/s	Observation
Palm oil	Tween 80	No sign of separation after one week
Palm oil	$[\text{BMIM}]^+[\text{NTf}_2]^-$	Cloudy upon stirring. $[\text{BMIM}]^+[\text{NTf}_2]^-$ sinks to the bottom after 1.5 hrs
Palm oil	Span 80	No sign of separation after one week
Palm oil	$[\text{BMIM}]^+[\text{NTf}_2]^-$ and Tween 80	$[\text{BMIM}]^+[\text{NTf}_2]^-$ sinks to the bottom after 10 min

5.1.1.2 Stability studies – palm oil

The main purpose of the emulsion stability studies was to evaluate the possibility of using palm oil as an organic diluent for the metal extraction process. Important aspects of the emulsion used in the ELM are viscosity and stability. General observations regarding stability and apparent viscosity are summarized here

- The stability of palm oil-based emulsion is increased by:
 - Organic to aqueous phase weight ratio 3:1
 - Use of Span 80 as surfactant
 - Addition of butanol and/or Tween 80
- The viscosity of palm oil-based emulsion is decreased by:
 - Addition of Tween 80
 - Lower homogenization speed <3500 rpm



Figure 5.1: A homogeneous emulsion with palm oil as diluent.

Figure 5.1 shows an emulsion prepared with palm oil as organic diluent, and containing 1 wt% Tween 80, 0.35 wt% TOMAC and 3 wt% Span 80. The solution is homogeneous and phase separation of this emulsion was observed after approximately one hour.

It was found that a relatively high HLB (>7) was possible while maintaining a w/o emulsion with palm oil as diluent and the organic to internal phase ratio $O/I=3$, verified by dilution tests. It was also found that the use of $[\text{BMIM}]^+[\text{NTf}_2]^-$ as a stabilizer did not enhance the stability of the palm oil based emulsion. $[\text{BMIM}]^+[\text{NTf}_2]^-$ is not soluble in palm oil, probably because of its polarity but also due to its higher density compared to palm oil. The triglycerides and diglycerides present in palm oil are generally not amphiphilic enough to be soluble in water and may therefore not contribute to the reduction of the surface tension between the aqueous and oil phase in the emulsion, consequently the main inherent contribution to the stability is the high viscosity of the oil, or the presence of other

surface-active compounds.

From the results obtained in the emulsion stability studies, extraction experiments were made using emulsions containing palm oil, Span 80 (2.5-3 wt%), TOMAC (around 0.35 wt%), varying content of Tween 80 and of butanol and with an O/I=3. The surfactant concentration of around 3 wt% is consistent with previous studies [26], however, these studies use kerosene as diluent and due to the high viscosity of palm oil extraction experiments were performed with a lower surfactant concentration, in order to decrease the viscosity of the ELM.

As the addition of Tween 80 lowers the viscosity of the emulsion, it was desirable to develop a formulation containing the mentioned component. It is also known that Tween 80 and Span 80 are commonly used together to facilitate the formation of a multiple w/o/w emulsion, which will be developed in the extraction experiments. The CPP of the surfactants also has an influence on the stability of an emulsion and whether a w/o or an o/w emulsion is formed, as the CPP determines the curvature of the emulsion droplets. An efficient packing of the surfactants in the interfaces makes the emulsion droplets more stable and to achieve this butanol was used, which adsorbs in the w/o interface and minimize the repulsion of the hydrophilic head-groups of the surfactants. An increased stability time was observed for emulsions prepared with butanol as co-surfactant, and because of this extraction experiments containing butanol were carried out.

The homogenization speed in the emulsification step was kept at the lowest level for all extraction experiments, 3200-3400 rpm, because a higher speed resulted in a highly viscous, “mayonnaise-like” emulsion not sufficient for extraction. One reason for this may be due to a foaming mechanism, where air-bubbles are incorporated into the emulsion phase. The viscosity may also increase due to a higher dispersion of the internal phase and a larger number of smaller internal droplets, which may lead to a more rigid system. The emulsification time, including the time required for addition of the internal phase was kept at 11 min. Microscopic studies of the emulsion droplets size, how they are affected with respect to homogenization speed and also the change in size with respect to time remain to be explored. The more precise properties of palm oil and how these interact with the components of an ELM formulation also need more thorough investigations.

5.1.1.3 Stability studies – kerosene

Some stability studies were performed with kerosene as diluent, to verify suitability of the emulsion formulation known from previous studies and also to investigate the possibility of a further increase in emulsion stability through the addition of co-surfactants. The kerosene-based emulsions are used for the extraction of arsenic in subproject 2.

- The stability of kerosene-based emulsion is increased by:
 - Organic to Internal phase weight ratio 1
 - Addition of butanol and/or Tween 80
 - Homogenization speed > 7000 rpm

It was observed that the use of [BMIM]⁺[NTf₂]⁻ as stabilizer was necessary for the emulsion to be stable for longer than 30 min. As the viscosity of kerosene is low, the emulsion also has a very low viscosity. One reason for the increased stability of the emulsion containing [BMIM]⁺[NTf₂]⁻ is that it increases the viscosity, another is that it (like surfactants) decreases the surface tension of the o/w interface.

5.1.2 Chromium extraction experiments

To investigate the possibility of using palm oil as an alternative organic diluent in the ELM separation process, numerous chromium extraction experiments were performed. The results conclusively showed that the use of palm oil as an organic diluent seems to work well and also that the high viscosity of palm oil does not seem to cause problems in terms of extraction efficiency. However, it was observed that when contacting of the external phase with the ELM phase a higher agitation speed (>600 rpm)

compared to the kerosene-based ELM (<400 rpm) was needed in order for the solutions to mix well, and it was also observed that the use of Tween 80 as a co-surfactant in the membrane phase facilitated the mixing remarkably. Tween 80 is a highly hydrophilic surfactant and should therefore not be soluble in the oil phase of the system. As it is incorporated during the emulsification of the ELM phase, and therefore present at the membrane-internal interface, it is believed that some Tween 80 molecules are transported by microscopically small water droplets to the membrane-external interface, which lowers the interfacial tension and facilitates the second emulsification.

The treat ratio (F/ELM) was kept constant at 2, the initial metal concentration was 100 ppm and the pH of the external phase adjusted to 0.5 using HCl(aq) in all experiments, unless otherwise stated. Figure 5.2 shows how a sample is taken during the extraction experiments.

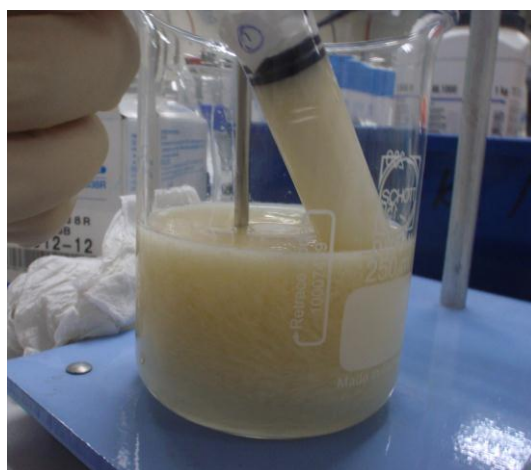


Figure 5.2: The taking of sample during contacting of ELM and external phase for extraction of chromium.

5.1.2.1 The use of palm oil as organic diluent

In Figure 5.3 the removal efficiency of chromium for three different ELM formulations is displayed as a function of extraction time with the internal stripping agent concentration of 0.1 M NaOH.

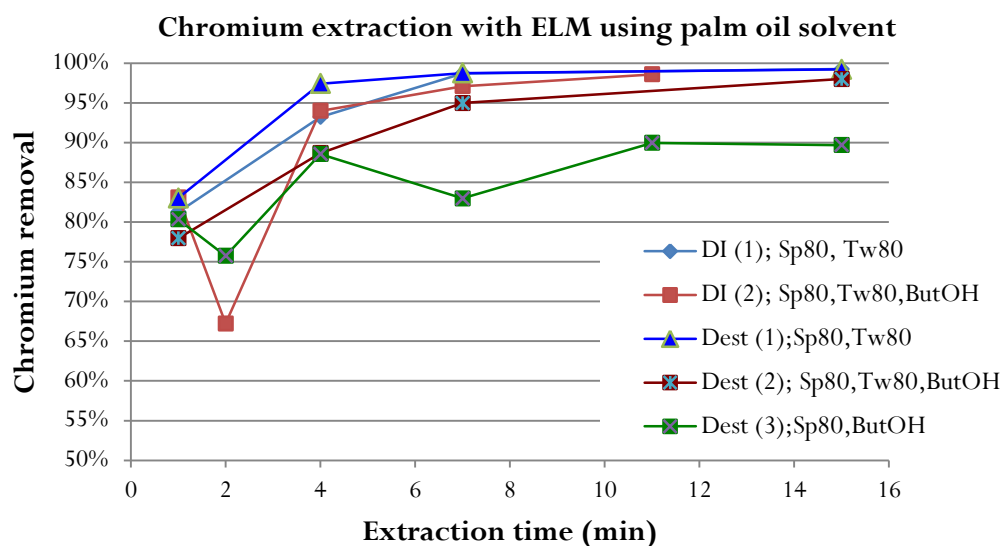


Figure 5.3: The graph shows removal of chromium as a function of time. Data are plotted for three ELM formulations as shown in the legend, all containing TOMAC. "DI" and "Dest" denote de-ionized and distilled water respectively. Sp80, Tw80 and ButOH denote Span 80, Tween 80 and butanol respectively. NB: the y-axis starts at 50%.

The systems denoted with “DI” in the figure above were prepared using doubly de-ionized water for both the external phase and for the internal phase, and the systems denoted “Dest” were prepared using distilled water in the mentioned phases. The numbers denote the different formulations of the membranes, of which all contains approximately 0.35 wt% TOMAC, 3 wt% Span 80 and have O/I=3. The first ELM formulation (DI (1) and Dest (1)) contains 1 wt% Tween 80 in addition to the already stated components, and this formulation shows the highest extraction rate. The second ELM formulation, DI (2) and Dest (2), also contains 1 wt% Tween 80 and in addition to this 1 wt% butanol. The Dest (3) formulation contains 1 wt% butanol besides the stated components and has the poorest performance in terms of removal efficiency. The concentration of TOMAC was chosen to obtain a molar ratio of more than 2 moles TOMAC for each mole of chromium ions, this to ensure that the extraction is not hindered by the lack of carriers available.

The expected appearance of the removal efficiency as a function of time is a steady increase towards a maximum extraction, however some of the results, in particular Dest (3), show fluctuations in the removal percentage. A reason for these fluctuations is probably that the mixing of the external phase and the ELM phase is not entirely homogeneous, reflected in the samples taken during the experiment. A poor mixing leads to a decrease of the surface area available for mass transfer and will lower the extraction efficiency. As previously mentioned, the presence of Tween 80 in the membrane phase decreases the fluctuations, due to the facilitation of creating the multiple w/o/w emulsion, and this can be seen in Figure 5.3 when comparing the removal of the Dest (3) experiment to the other results, as this is the only formulation not containing Tween 80. The presence of fluctuations is especially present for the first two minutes of the extraction, and this will be observed in various results throughout the project. The agitation speed when contacting the external phase with the ELM also has a significant influence of the extraction efficiency. In the experiments of DI (1) and Dest (1) the agitation speed was kept at 800 rpm for the first minute and then lowered to 400 rpm, while in the three other experiments the agitation was kept at a constant speed of 600 rpm. It was observed that an initial agitation speed below 600 rpm resulted in poor mixing, but the agitation could be lowered once the solution had achieved a somewhat homogeneous appearance.

5.1.2.2 *Effect of carrier concentration on chromium extraction*

To verify the function of the carrier TOMAC in the palm oil-based ELM, metal extraction experiments were carried out with a membrane phase prepared without the incorporation of TOMAC. The carrier has a significant influence on the extraction process, it is not needed in a large amount but its absence would lead to a large reduction of the removal efficiency, see Figure 5.4 below. As can be seen in the graph, only a small fraction of the metal is extracted in the absence of carrier, the removal is only facilitated by the mass transfer of the metal through the membrane to the internal phase, in which a reaction with the stripping agent NaOH occurs. As the pH of the external phase is kept at 0.5, chromium exists in an anionic form, quite reluctant to be soluble in the oil phase of the membrane.

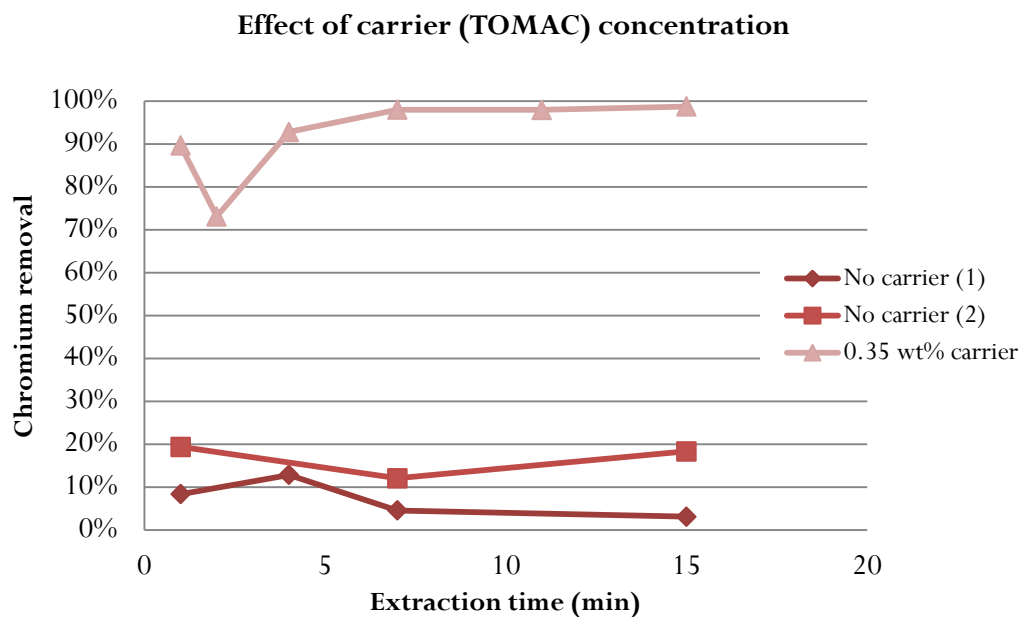


Figure 5.4: Efficiency of chromium removal for ELM formulations with carrier (pink) and without carrier (red)

The results from the experiments in Figure 5.4 confirm the need for an incorporated carrier in the ELM formulation and evidence the role and impact of TOMAC on the overall process.

5.1.2.3 Effect of water type on chromium extraction

Three types of waters were compared; double de-ionized water, distilled water and tap water. The results indicate no significant difference in removal efficiency when varying the water type, which can be seen in Figure 5.5. The graph shows duplicated experiments conducted with ELM formulations identical to DI (1) and Dest (1) stated above.

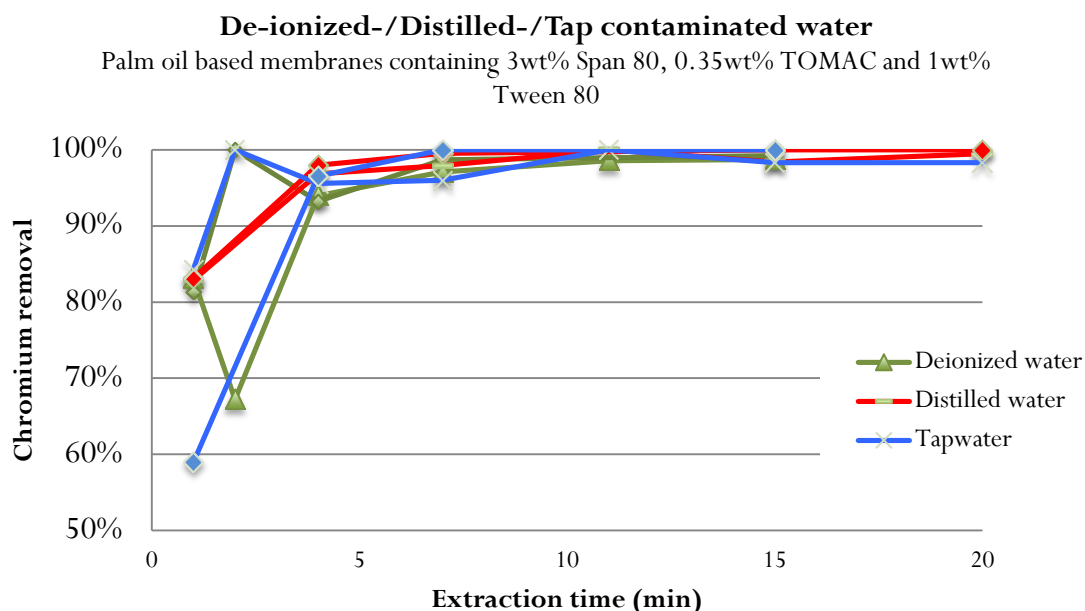


Figure 5.5: Extraction efficiency for different water types.

From the results in the graph above, the influence of the water type seems to be negligible in terms of final removal efficiency and the same results were obtained in other experiments carried out with varying ELM content. This means that the system is not disturbed by the presence of other ionic species

in the water, which is beneficial when considering the implementation of the ELM technique in industry. The tap water in Malaysia contains iron and other ionic species such as chlorides, sulphates and nitrates.

5.1.2.4 Effect of internal stripping agent concentration on chromium extraction

The stripping agent used for the extraction of chromium was NaOH, and the effect of its concentration on the removal efficiency can be seen in Figure 5.6. The experiments were performed to ensure that a similar optimal concentration of NaOH was obtained in the ELM with palm oil as diluent compared to previous studies of ELM with kerosene as diluent.

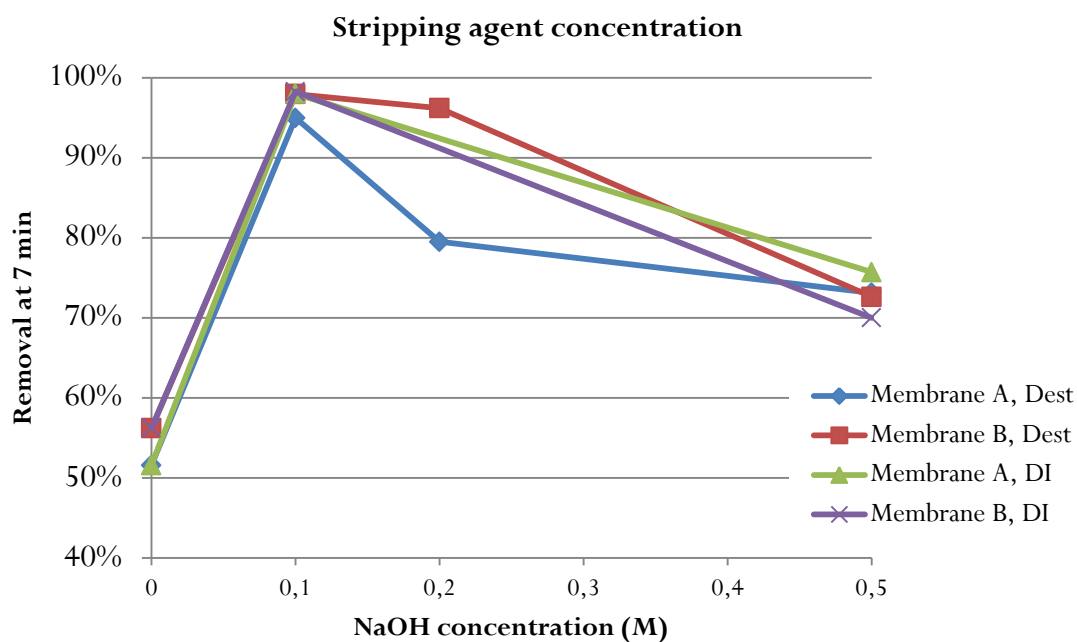


Figure 5.6: The effect of stripping agent concentration on the extraction of chromium. “Dest” denotes distilled water and “DI” denoted de-ionized water. Both membranes contains 3 wt% Span 80, 1 wt% Tween 80, 0.35 wt% TOMAC and membrane A contains 1 wt% butanol in addition.

The graph shows the removal percentage of a sample taken at an extraction time of 7 min as a function of stripping agent concentration. The same trend is observed regardless of water type: the efficiency is highest when the internal phase has a concentration of around 0.1 M NaOH, with a pH of around 11.4. This result is consistent with the results obtained by Goyal et al for an ELM with kerosene as diluent. A concentration of NaOH higher than 0.1 M leads to a strong pH gradient, increasing the difference in osmotic pressure and consequently the risk of swelling of the internal droplets, which eventually leads a rupture of the membrane. The consequence of the rupture is that the internal phase is released into the external phase, which reduces the amount of NaOH available for the stripping reaction of the metal complex. Another explanation can be that NaOH has a tendency to react with Span 80 [54], thereby modifying the properties of these components through forming other compounds that decrease the emulsion stability.

5.1.2.5 Effect of external phase concentration on chromium extraction

The graph in Figure 5.7 shows the removal efficiency when the initial concentration of chromium was 50 ppm. As can be seen in the graph, the extraction is very fast and almost all chromium is extracted.

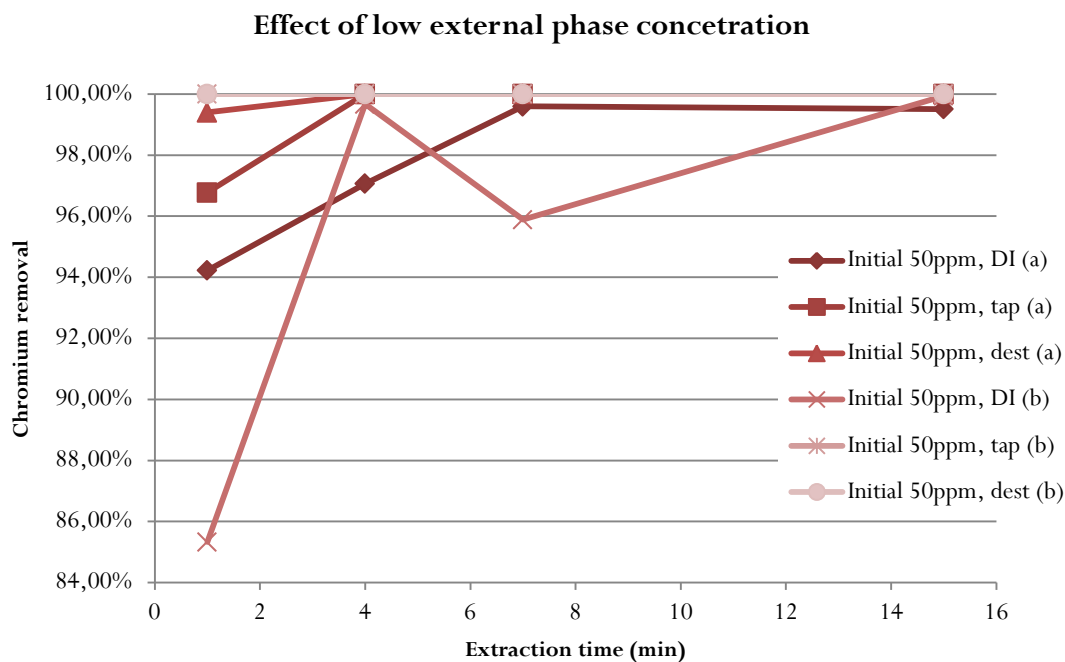


Figure 5.7: Extraction of chromium with the initial concentration of 50 ppm. "Dest" denotes distilled water, "DI" denotes de-ionized water and "tap" denotes tap water. The membranes are based on palm oil, have the organic to aqueous phase ratio 3:1 and membrane (a) contains 3 wt% Span 80, 1 wt% Tween 80, 0.35 wt% TOMAC and 1 wt% butanol while membrane (b) contains 3 wt% Span 80, 0.35 wt% TOMAC and 1 wt% Tween 80.

At a lower concentration of chromium, when the initial concentration was 10 ppm, the extraction rate is even faster. All chromium was extracted within 2 min in these experiments, hence the extraction rate increases with a decreasing initial concentration of the metal. A reason for the efficient removal of metal at low concentrations is that the emulsion droplets are not saturated by the metal and a higher amount of stripping agents are available, in addition to a molar excess of TOMAC, which facilitates the extraction.

5.1.3 Experimental optimization and parameter interaction studies on Chromium extraction using palm oil diluent

To optimize the ELM process developed using palm oil as diluent, an experimental design was performed. The parameters studied for interaction was the agitation speed when contacting the external phase with the membrane, and the concentration of butanol and of Span 80 in the membrane (see Table 4.3). These parameters were chosen by analysing previous results, and also verified by results from previous studies, where the optimum concentration of stripping agent is 0.1 M NaOH and a suitable pH of the external phase is 0.5. Butanol was included in the design to explore whether the concentration of Span 80 could be decreased, consequently decreasing the viscosity of the ELM, if butanol is incorporated as co-surfactant. The initial concentration of chromium of 100 ppm was chosen because a lower concentration leads to the removal of almost all of the metal, making it difficult to study the interactions. A concentration of 1 wt% Tween 80 was incorporated in the membrane, as it had been noted that the presence of Tween 80 enabled a more homogeneous mixing in addition to a lower viscosity of the ELM phase, hence a larger surface area available for mass transfer. The removal of chromium is shown in Figure 5.8 as a function of time and for the low extraction times a large variation in the results can be seen. This is mainly due to human factors and inhomogeneous mixing and as the extraction time proceeds, the results from the different experiments are consistent. The precise compositions of the components in the shown experiments (PX1-PX19) can be found in Appendix II.

Optimization and interaction: membrane based on palm oil

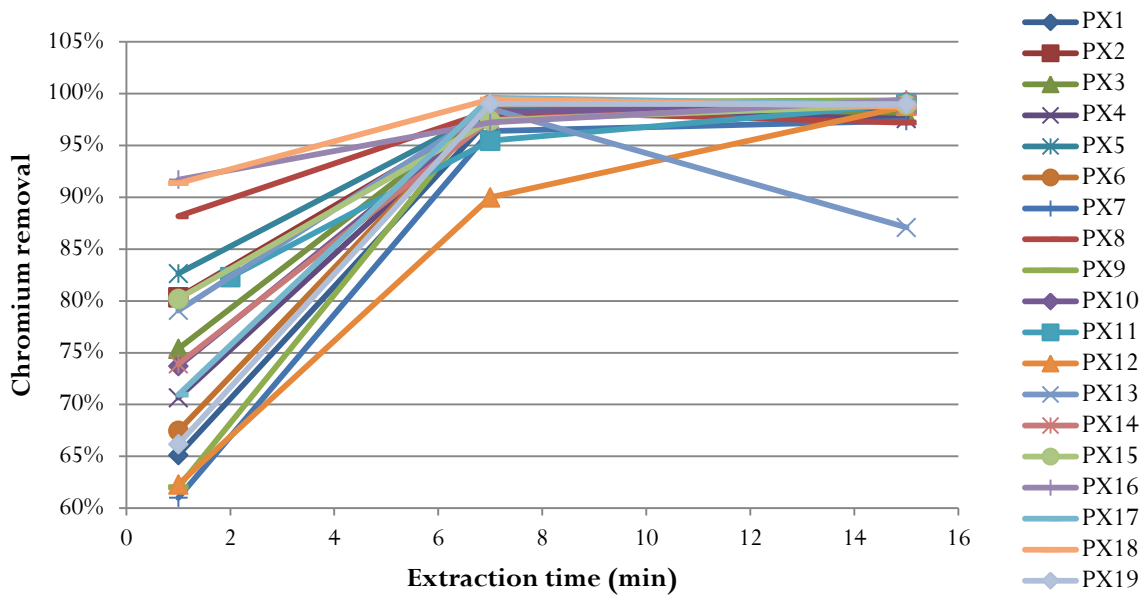


Figure 5.8: Removal of chromium (%) as a function of time from the experiments of the interaction and optimization studies. The y-axis starts at 60 %

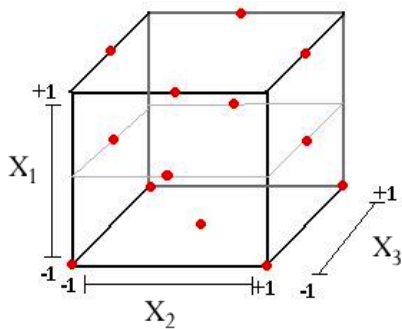


Figure 5.9: The experimental design performed.

Regarding the design of the experiments, a mistake was made when planning the trials. The experimental runs were based on a three variable Box Behnken design [55]. The low value for the agitation speed was accidentally assumed to be the centre point, obtaining the design shown in Figure 5.9, still maintaining orthogonal columns. The use of orthogonal experimental points provides accuracy of the model and makes it possible to study linear and interaction effects. MATLAB statistical tools were used for all calculations.

The empirical model used was fitted to the response through a regression analysis, and the best fit was obtained when including the linear, interaction and squared terms. However, the results from the experiments in the design have a low variance at high extraction time (15 min) and the results obtained at 1 min had a too high variance, consequently only the removal percentage after 7 min could be used in order to get a significant model. The parameter table obtained is seen in Table 5.2, and a p-value<0.05 signifies that the parameter in question is significant¹¹.

¹¹ If a parameter is not significant it means that it has a very small influence on the response. According to the hierarchy principle, which indicates that if a model contains a high-order term (i.e. X_1X_3), it should also contain all of the lower order terms that compose it (i.e. X_1 and X_3). Because of this, X_1 and X_3 with corresponding parameters are also included in the model [55].

Table 5.2: Parameter table showing the significance of the parameters in the model.

Parameter table					
Variable index	Param. val	StdErr	t _{obs}	p-value	
Model	99.596	0.70599	141.07	2.2966e-016	Significant
X ₁	0.43915	0.353	1.2441	0.2449	
X ₂	-1.0785	0.4418	-2.4411	0.037297	Significant
X ₃	-0.14823	0.4418	-0.3355	0.74492	
X ₁ X ₂	1.5813	0.51015	3.0996	0.01273	Significant
X ₁ X ₃	1.3534	0.51015	2.6529	0.026349	Significant
X ₂ X ₃	-1.1163	0.5982	-1.8661	0.09488	
X ₁ X ₁	-0.76844	0.69459	-1.1063	0.29728	
X ₂ X ₂	-1.2682	0.56525	-2.2436	0.051537	Significant
X ₃ X ₃	-1.4257	0.56525	-2.5222	0.032648	Significant

The ANOVA (Analysis of Variance) table for the regression analysis obtained from MATLAB can be seen in Table 5.3 and was used as a test for the significance and the fitness of the model as a whole. The observed F-value (F_{obs}) indicates that there is 1% chance that the β -parameters obtained in the model is only due to noise or obtained by random, thus not explaining the response. It can be seen also on the p-value that the model is significant. The adequacy of the model was checked through residual analysis, shown in Appendix II (Figure II-I) where the studentized residuals¹² are compared to the experimental number. The studentized residuals should be structure-less, which they are, however a larger spread was observed for the first experimental runs. This could be a consequence of the human factor (we got better at performing the experiments hence reducing the error). None of the residuals exceed the absolute value of three.

Table 5.3: ANOVA table of the regression analysis.

Regression ANOVA					
Source	Source	Degrees of freedom	MS	F _{obs}	p-value
Regression	Regression	9	7.6595	5.3511	0.0100
Residual	Residual	9	1.4314		
Total	Total	18			

Table 5.4: R² values and "Lack of Fit".

R-squared	R-squared, adj	F _{LOF}	F _{stat}
0.84255	0.68509	2.2027	4.7571

Table 5.4 shows the R-squared values obtained, which are a prediction of the response value estimated by the model. The R^2 and R^2_{adj} differ by 0.15756, because some of the parameters in the model are not significant, nevertheless the values can be considered acceptable. F_{LOF} in Table 5.4 is smaller than the F_{stat} value, indicating that the lack of fit (LOF)¹³ due to model error is insignificant in comparison to pure error by chance. The obtained parameters can be seen in Equation 5.1, in which \hat{y} represents the predicted removal efficiency (the response), X_1 is the coded variable for agitation speed, X_2 and X_3 for the concentrations of Span 80 and butanol respectively.

¹² The studentized residuals are scaled (the residual is divided by an estimate of its standard deviation) to give them the same variance. As a rule of thumb, if an experiment has a residual >3 or <-3 , the result may be considered an outlier.

¹³ To check the LOF is of great importance, a model with a LOF cannot be used.

$$\hat{y} = 99.596 + 0.439X_1 - 1.079X_2 - 0.148X_3 + 1.58X_1X_2 + 1.35X_1X_3 - 1.27X_2^2 - 1.43X_3^2 \quad \text{Equation 5.1}$$

The optimized values obtained from this model were an agitation speed of 522.6 ($X_1=-0.387$), a Span 80 concentration of 2.58 wt% ($X_2=-0.680$) and a butanol concentration of 0.515 wt% ($X_3=0.031$). The optimal response from this model is a removal of 99.88% chromium.

As can be seen, the interaction between the agitation speed and the concentration of Span 80 is significant. Figure 5.10 shows the response surface from the model, where the concentration of butanol is kept at its optimum and the interaction between Span 80 concentration and agitation speed can be seen. The interaction can be explained in terms of stability and viscosity of the membrane; an increase in Span 80 concentration contributes to an increase in the stability of the emulsion due to the decrease in interfacial energy of the oil and water interface. However, it also increases the viscosity of the membrane. If the viscosity is increased, a higher agitation speed is required for the external and membrane phase to mix well, but this also induces shear stress on the membrane, which could contribute to emulsion breakage. Therefore, at higher agitation speed, a higher concentration of Span 80 is required to compensate for this. The same reasoning can be applied for a lower agitation speed, allowing a lower concentration of Span 80, and the optimum response was found when both the agitation speed and the concentration of Span 80 are lowered below their centre-points in these experiments.

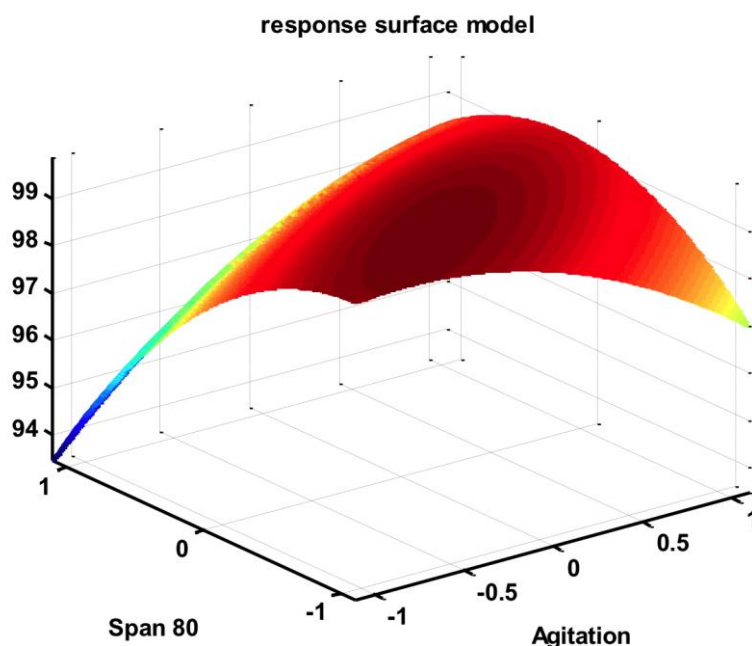


Figure 5.10: Response surface plot for the interaction of Span 80 concentration and agitation speed. Butanol concentration is held constant at 0.515 wt% ($X_3=0.031$).

Figure 5.11 shows the response surface plot of the interaction between the concentration of butanol and the agitation speed, which is also significant. The concentration of Span 80 is held constant at the optimum level, and the plot shows that a higher agitation speed and a lower concentration of butanol (close to 0 wt%) result in a lower response, which could be explained by a decreased stability of the membrane. Butanol is believed to enhance the stability of the membrane by acting as a co-surfactant in the emulsion, through adsorbing at the w/o interface and in that way minimize the repulsion of the

hydrophilic head groups of the surfactants. This reduces the interfacial tension of the w/o interface, gives a higher water solubilisation and decrease the water droplet size. However, an increased amount of butanol together with a decreased agitation speed also lowers the response, and the optimum was found at a concentration around 0.5 wt%. As the butanol is soluble in both the water phases and the oil phase it may, when present in higher concentrations, migrate from the interfaces to the external phase and react with HCl, producing a chlorobutane and water. This would increase the pH in the external phase and affect the extraction rate, since the pH gradient is critical for efficient extraction.

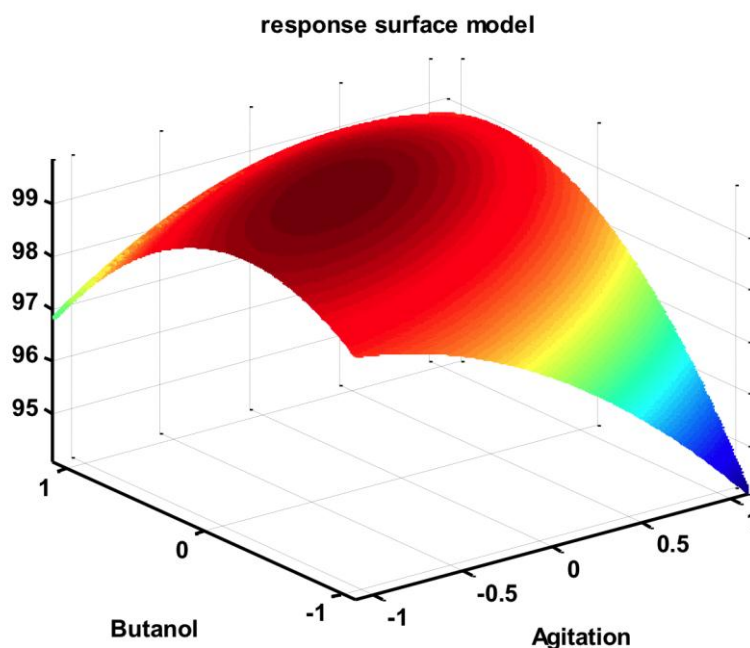


Figure 5.11: Response surface plot for the interaction of butanol concentration and agitation speed. Span 80 concentration is held constant at 2.58 wt% ($X_2 = -0.680$)

5.2 Subproject 2: arsenic extraction

5.2.1 Compatibility of arsenic and TOMAC

To verify the compatibility of arsenic(V) together with TOMAC, simple liquid-liquid extractions were performed to investigate at what pH range TOMAC creates a complex with the arsenic(V) ion compound. As mentioned in Section 3.4.2, the basic property of TOMAC favours reaction with anionic complexes. Arsenic(V) exists in the form of H_3AsO_4 , H_2AsO_4^- and HAsO_4^{2-} and AsO_4^{3-} in the different pH investigated. At higher pH, HAsO_4^{2-} is dominant, while H_3AsO_4 and AsO_4^{3-} may be present in strong acidic or strong basic conditions respectively, see Figure 5.12 or Figure 3.12 [13].

The results from the experiments using kerosene as diluent in the liquid-liquid extraction are shown in Figure 5.12 (blue line). The results are in agreement with literature, where TOMAC unlikely reacts with the neutral arsenic complex H_3AsO_4 under acidic conditions (pH 2-4) and prefers to react with the anionic H_2AsO_4^- and HAsO_4^{2-} when increasing the pH (pH > 4). The figure also shows that in the case where kerosene is used as diluent, for strong basic conditions (pH > 10), the removal of arsenic(V) decreases. Similar liquid-liquid extraction experiments were performed using palm oil as diluent, see Figure 5.12 (brown line), this to study the flexibility of the choice and role of the diluents in the ELM process. The few experiments that were performed showed that the extraction rate is considerably lower compared to the use of kerosene as diluent, and that the extraction increases with increasing pH. However, at pH 10, which was the optimal pH for extraction when using kerosene as diluent, the

extraction of arsenic when using palm oil as diluent is still very low. It was observed during the experiment that the viscosity of the mixed palm oil and external phase increased at this pH range, and this could be a reason for the lower extraction. In any case, the two experiments show different maximum values.

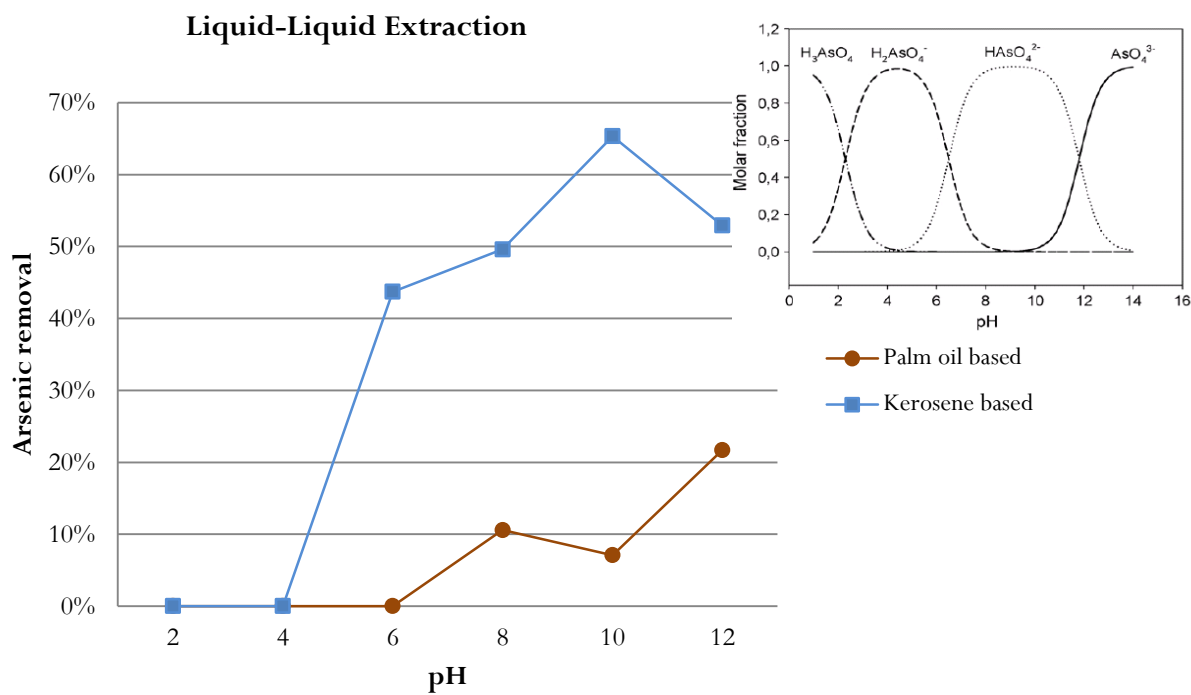


Figure 5.12: The removal efficiency of arsenic using kerosene (blue) and palm oil (brown) as diluent and the predominated species of arsenic(V) for various of pH.

Considering the results from the kerosene based extraction, an explanation to why the extraction decreases at pH 12 (where the concentration of HAsO_4^{2-} and AsO_4^{3-} is equal according to literature) is either because there is no extraction of AsO_4^{3-} and all of the HAsO_4^{2-} species are extracted, or that there is a lower extraction for both species. If TOMAC extracts HAsO_4^{2-} to a larger extent than AsO_4^{3-} the explanation could be that because there is only one electron deficient nitrogen present in TOMAC, and the latter reaction requires a higher amount of moles of TOMAC, the complex is unlikely to be created. It could be simply a charge effect, as TOMAC has a single positive charge it rather forms a complex with anionic specie with a charge of the same magnitude. However, if this would be the case, TOMAC should have extracted H_2AsO_4^- at the lower pH conditions. Li and Yan mentioned that arsenic(V) may create a large complex in the presence of strong acid ($[\text{AsCl}_4]^+[\text{AsCl}_6]^-$), which is unlikely to penetrate the membrane in the ELM process [48], and this could also hinder the extraction during the simple liquid-liquid extraction process. Similar impact could be the case in the presence of strong basic conditions, where the complex would be too large to penetrate the oil phase. In addition, the presence of a high amount of chloride ions at low pH could decrease the selectivity of TOMAC for the reaction with the arsenic(V) species and the same reasoning may be applied for strong basic conditions, where a high concentration of hydroxide ions exist in the external phase that could decrease the selectivity.

A series of simple liquid-liquid extraction was also performed using three different agitation speeds and extraction times, and showed that the same overall trend occurred regardless. Finally, the results show that TOMAC is compatible with the anionic complex of arsenic(V), preferably at the pH range of 9-10

and give a direction of the kind of optimal conditions preferred for the external phase or waste water when extracting arsenic(V) using TOMAC as a carrier in the ELM process.

5.2.2 Arsenic extraction using EILM

No results were obtained that showed a consistent extraction of arsenic using the EILM formulation containing kerosene, Span 80, [BMIM]⁺[NTf₂]⁻, TOMAC and/or Tween 80 and/or butanol, even though the liquid-liquid extraction showed that TOMAC is compatible with the arsenic complex and suitable external phase conditions were created (basic conditions, pH adjusted using NaOH) for the reaction to occur. The concentration of TOMAC was chosen to obtain a molar ratio of 3:1 (TOMAC:As(V)) to ensure that the transport is not hindered by the lack of extractant. The internal phase was kept acidic to create a pH gradient, by varying the concentration of HCl from 0.1 to 0.01 M. An expected stripping reaction would yield [AsCl₄]⁺[AsCl₆]⁻, a large complex unlikely to diffuse back to the external phase. The formation of H₃AsO₄ is also likely to occur in the internal phase, due to the high presence of H⁺ ions.

Instead the results showed an *increase* in arsenic concentration in the external phase and no sign of metal removal, see Figure 5.13. The only way in which the concentration of arsenic can increase in the external phase is if water from the external phase is somehow removed. The difference in osmotic pressure contributes to a transport of water molecules to the internal phase, where the internal phase droplets increase in size. An increased amount of acid in the internal phase would lead to an increased pH difference between the internal and external phase, this would increase water permeability in the membrane. Since chemical potential difference between the internal phase and the external phase is the driving force for osmotic swelling an increase in the chemical potential difference will contribute to an increase in the osmotic pressure.

Wan and Zhang have observed that the type of surfactant used affects the swelling phenomena,¹⁴ and the use of amide-based surfactants with higher molecular weight is superior compared to the use of Span 80. The low molecular weight and the large hydrophilic group in Span 80 comprised of oxygen with high electronegativity have a higher hydration capacity and larger diffusivity compared to surfactants with a higher molecular weight and hydrophilic groups mainly comprised of nitrogen with relatively low electronegativity [56].

The organic to internal phase ratio was in most cases kept at 1, which is higher than recommended but chosen due to the increased emulsion stability, and questions arise whether that would be the problem in terms of risk for a phase inversion of the ELM phase. Sabry et al [57] showed that the internal phase volume fraction (I/O) cannot be increased indefinitely, they found an optimum value of the O/I ratio at 1 for lead removal, and because of this the suspected phase inversion may be discarded. Besides, if the phase inversion occurs it dilutes the external phase with the released aqueous internal phase.

¹⁴ Swelling increased in the following order: Span 80>Lan113A>ENJ-3029>LMA.

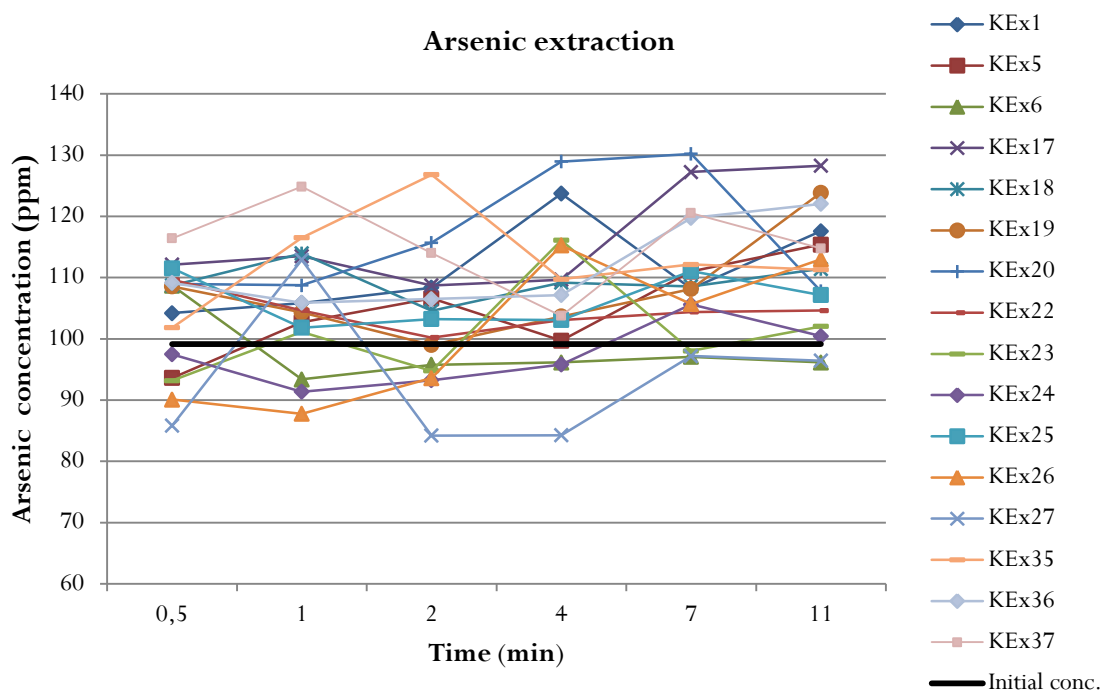


Figure 5.13: Results obtained from the arsenic extraction. The black line shows the initial concentration of arsenic in the external phase.

Samples taken from the external phase after the agitation had been stopped and the system had been left undisturbed for a couple of hours, hence obtaining a complete phase separation between the ELM phase and the external phase, also showed an increase in arsenic concentration (an average increase of 44% was observed). This is questionable because the w/o emulsion should have been broken, leading to a leakage of the internal phase out to the external phase, which would give the initial arsenic concentration or less due to dilution. However, emulsions can be very concentrated with above 90 % dispersed phase [31] and if the emulsion is still stable a further uptake of water is therefore possible. For spherical droplets it would require a broad distribution of droplet size, with smaller droplets filling the space between larger ones. This is doubtful due to the lack of supplied mechanical energy when the agitation has been stopped. Other packing structures such as hexagonal packing might be possible, depending on the structure and interactions of the surfactants and the ionic liquid $[\text{BMIM}]^+[\text{NTf}_2]^-$.

Furthermore, there are other reasons that could have hindered the extraction but these do not correlate truly to the results nor do they explain the increase in concentration. For example, the hydrochloric acid in the internal phase is quite likely to react with the esters of both Span 80 and Tween 80, which results in a partial loss of the surface-active properties and affect the ELM both in terms of viscosity and stability. Because the carrier has shown compatibility with the arsenic complex, it is not likely that the carrier is the issue. However, TOMAC could react with hydroxide ions in the external phase or the chloride ions in the internal phase, which decreases the selectivity towards arsenic.

6 CONCLUSIONS

We have found that the petro-chemically based diluent kerosene used in previous studies can be exchanged for the vegetable and more environmentally friendly palm oil. The use of palm oil as a diluent in the w/o emulsion was successful and the stability of the ELM was achieved for a time sufficient for the extraction to occur satisfactory. When concerning the creation of the w/o emulsion and the parameters effecting the emulsion stability a homogenization speed higher than 3500 rpm (for a solution contained in a 100 ml beaker) resulted in an emulsion highly viscous not suitable for extraction. The use of Tween 80 as a co-surfactant was beneficial as it decreased the viscosity of the emulsion and in addition a notable difference was observed when the external phase and the ELM phase were contacted for the extraction experiments: a more homogeneous solution was obtained when Tween 80 was present. The mixing is important, a high dispersion of the ELM phase increases the surface area available for mass transfer and a faster removal rate could be observed. The use of butanol as co-surfactant enhanced the stability of the emulsion, but might not be necessary for an ELM formulation used for extraction. Palm oil has a high viscosity, which is beneficial regarding the stability of emulsions but disadvantageous regarding the increased mass transfer resistance, but because the extraction of chromium was successful it can be concluded that the high viscosity of the palm oil does not decrease the extraction rate in our system.

The use of palm oil as organic diluent in emulsions and ELM formulations has many benefits. Palm oil is non-toxic, it is produced from renewable resources, and it is also cheap and readily available in Southeast Asia. Palm oil is an important economical income source for Malaysia and Indonesia, the main producers of the oil, and the productivity is high compared to many other vegetable oils. On the other hand, the production of palm oil is controversial and contributes to the devastation of rainforests in Malaysia and Indonesia in particular, and the ecosystem is destroyed when bio-diverse rainforest is replaced by the monoculture of oil palm trees plantations.

Experiments carried out with a low initial concentration of chromium in the external phase resulted in complete removal of the metal, and the lower the initial concentration was, the higher was the extraction rate. Whether the source of water and the presence of other ions in the external phase could effect the removal efficiency was studied by comparing external phases based on de-ionized water, distilled water and tap water. The results showed that extraction efficiency is not significantly affected by the difference in purity between the three investigated water types. This means that the system is robust and may be developed further for real industrial applications aimed at the removal of metals from waste water where various ions may be present.

The stripping agent concentration is important in regards to the emulsion stability, and a concentration higher than 0.1 M NaOH resulted in decreased removal efficiency presumably due to the high difference in osmotic pressure between the internal and external phase. The presence of carrier is crucial for an optimal chromium extraction. The absence of carrier, when the only transport mechanism is diffusion, resulted in 10-20% chromium extraction, meanwhile the presence of carrier results in >90% chromium extraction. An experimental design was performed and MATLAB software was used as modelling tool. The optimized parameters obtained gave a Span 80 concentration of 2.58 wt%, butanol concentration of 0.515 wt% and agitation speed of 522.6 rpm, and the optimal response from the modelling was a removal of 99.88% chromium. The interaction studies showed that, in general, for a higher agitation speed when contacting the external and ELM phases, a more stable emulsion is required, this achieved by a higher content of surfactant or co-surfactant in the ELM formulation. At a lower agitation speed, the content of surfactant need to be decreased, to decrease the viscosity and facilitate a homogeneous mixing. Our project has showed that the many factors that influence the efficiency of the extraction of

chromium also have their trade-offs and interactions, and optimization studies are required to obtain an optimal formulation.

In subproject 2 the extraction of pentavalent arsenic was studied and the simple liquid-liquid extraction experiments showed that the carrier TOMAC is compatible with the arsenic complex and that transport exists. The preferable pH condition in the external phase was in the range of 9-10, where the highest extraction was observed, which induced modification of the EILM system where the internal phase was kept acidic to maintain a pH gradient. With the compiled optimal ELIM composition, having kerosene as diluent, extraction experiments were performed without any significant removal of the metal, instead an increase in the arsenic concentration was observed. This could be due to membrane swelling, contributed by the osmotic pressure, causing an uptake of water to the internal phase of the ELIM, which would increase the arsenic concentration in external phase. The system needs to be improved and further studied in order to improve the system to achieve the extraction. This can be accomplished by choosing other components in the system, for example another carrier, surfactant or stripping agent.

7 FUTURE WORK

This project has explored the application of ELM for the extraction of heavy metals with a focus on using environmental friendly materials, and since ELM have shown to be an economical and efficient way of treating waste water it is important to continue improving the process.

An important parameter is *the stirring rate*, which must be adjusted to achieve a uniform dispersion of the ELM phase and to obtain a high surface area during the extraction. Two areas of future work is to use impellers of different blade size and to use beakers with baffles, which both are ways to improve the overall mixing performance and avoid dead zones in the beaker.

The emulsion stability has a large impact on the extraction efficiency; it should be stable for sufficient time and withstand high agitation speed when contacted with the external phase. Further investigation is needed regarding the emulsion used in subproject 2, where the internal to membrane ratio of 1 may not have been optimal for the extraction but necessary for keeping the emulsion stable. High priority should also be given to further explore the use of vegetable oil as diluent. Other stripping agents should be investigated to study whether a reaction of TOMAC and hydrochloric acid occurs that hinders the extraction. The use of other surfactants with a lower hydration capacity and a higher stability in acidic conditions could also be investigated.

The ELM used in subproject 1 contributed to almost 100% extraction, slightly depending on the initial concentration. However, the influence and *interactions* of all parameters affecting the process, in addition to the ones studied in this project, need to be studied in more detail to optimize the process. It is also possible to study whether the amount of the chemicals could be minimized, which would decrease the overall cost of the process. The de-emulsification step needs more attention, as this constitute the most difficult part of an ELM process. If all components in the system, including recovered metals, can be reused in an efficient way, the overall costs will be further reduced. The water recoverability is another important aspect is to further investigate. If all the water can be reused then the process could also be implemented in water scarce areas.

Regarding the extraction of chromium, the *choice of diluent* did not have a crucial impact and the question arises whether palm oil could be replaced for another vegetable oil, such as rapeseed oil, to make the process more flexible and easier to use in regards to the material availability.

Furthermore, no measurements of the *size of the droplets* in the emulsion were made and no quantitative emulsion stability studies were performed. Because of this, further investigations are needed regarding the development of an optimized emulsion formulation to be used for ELM metal extraction. A deeper understanding of the interaction that occurs between TOMAC, internal agent, diluent, Span 80, [BMIM]⁺[NTf₂]⁻, Tween 80 and butanol is necessary to be able to confirm and understand why the process works or not and for the creation of more reliable and efficient ELM process. This deeper knowledge would facilitate the incorporation of other components that could improve the ELM extraction or make the ELM process useful for the extraction of other metals without any larger change of the system.

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APPENDIX I

Table I-I: Type of carrier, surfactant, internal solution, external solution and diluents used in metals extraction using ELM processes [30].

Carrier	Metal ion	External solution	Surfactant	Internal solution	Diluent
Cyanex 272	Cu	CuSO ₄	ECA5025	6N H ₂ SO ₄	Tetradecane
LIX 63/LIX 64N		Cu salt	Span 80	HCl	Kerosene
Cyanex 272	Ni	NiNO ₃	ECA5025	6N H ₂ SO ₄	Tetradecane
D2EHPA		NiCl ₂		HNO ₃	Kerosene
PC-88A		NiSO ₄	Span 80	Dil H ₂ SO ₄	n-Heptane
Cyanex 272/DEHPA	Zn	ZnSO ₄	ECA5025	6N H ₂ SO ₄	Tetradecane
D2EHPA		ZnCl ₂	Span 80	HNO ₃	Kerosene
DEHMTPA		ZnSO ₄	ECA5025	Thiourea	n-Dodecane
D2EHPA	Ag	AgNO ₃	Span 80	HNO ₃	Toluene
D2EHPA	Pb	Pb(NO ₃) ₂	ECA5025	HCl	Toluene
PC-88A	Co	CoSO ₄	PX 100	H ₂ SO ₄	Paraffin oil
MSP-8	Pd	Simulated waste	ECA4360	H ₂ SO ₄	n-Heptane
TOA	Hg	HgCl ₂	Span 80	NaOH	Toluene
Adogen	Cd	Pure Cd	Span 80	NaOH	Dimethyl Benzene
Primene JMT	Ag	Ag salt	Not mentioned	H ₂ SO ₄	Tetradecane
Aliquat 336	MO	Na-Mo salt	Monesan	NaOH	Kerosene, Heptane
Aliquat 336	Cr	Cr(IV)	Span 80	NaOH	Kerosene

Table I-II: ELM Systems for the Separation of Chromium and Arsenic

Solute	External Feed phase	Extractant	Surfactant	Diluent	Internal phase	Efficiency recovery	Reference
Arsenic	5.5 mg=L As(III) (as As(OH) ₃) in 0.4 M H ₂ SO ₄	10 vol% 2-ethylhexanol	2 vol% ECA 4360 polyamine	88 vol% n-heptane	2 M NaOH >95%	>95%	[58]
Chromium	HCl	Aliquat 336	3 wt% SPAN 80	Kerosene	0.1 M NaOH		[26]
Chromium	Cr ₂ O ₃ 7 in 0.5 N H ₂ SO ₄	20% tri-n-butyl phosphate (TBP)	4%–5% SPAN 80	n-Hexane	0.1 N NaOH	>99%	[59]

Chromium	0.000962 N K ₂ Cr ₂ O ₇ pH 1.6	0.05 M alamine 336	-	89.8 wt% HYVIS 2, 10 wt% Shellsol 2046, 0.2 wt% polyisobutylene	0.25 M NaOH	80%	[60]
Chromium	75–100 mg=L K ₂ Cr ₂ O ₇ pH 5.1–5.4	0.5 vol% Aliquat 336	1.5 vol% Paranox 106	5 vol% decanol, kerosene	0.005– 0.01 M NaOH	-	[61]

Experimental data

Table I-III: Information regarding the chemicals involved in the experiments.

Component	Supplier	Viscosity (mPa s)	Boiling point (°C)	Density at 20°C (g/ml)	HLB	Molecular weight (g/mol)
Palm Oil	Buruh	130		0.89 (at 25°C)	-	
Kerosene	R&M Chemicals, Essex, UK	1.64	150-300	0.78	14	
Span 80 (C ₂₄ H ₄₄ O ₆)	MERCK, Germany	1000-2000	> 100	0.99	4.3	428
Tween 80	R&M Chemicals Essex, UK	375-480	> 100	1.08	15	
1-Butanol	MERCK, Germany	2.6	117	0.81	7	74.04
TOMAC (Aliquat 336)	MERCK Schuchardt OHG	500 mPa·s 30 °C	225	0.887- 0.890		403.45
[BMIM] ⁺ [NTf ₂] ⁻	MERCK, Germany			1.44		419.12
K ₂ Cr ₂ O ₇ (Potassium dichromate)	R&M Chemicals Essex, UK	Powder form	-	-	-	294.2
HAsNa ₂ O ₄ *7H ₂ O (Sodium arsenate dibasic heptahydrate)	SIGMA ALDRICH Co, India	Powder form	-	-	-	311.92
25% HCl (Hydrochloric acid)				1.12	-	36.45

Table I-V: Equipment used in the experiments.

Equipment	Brand/type	Use
pH meter	Mettler Toledo Delta 320 pH meter Probe: Eutech Instrument	For adjusting pH of the external phase
Agitation	IKA RW 11	For contacting the external phase and the ELM phase
High Speed Homogenizer	IKA T25 Digital ULTRA- TURRAX	For the emulsification
ICP	PerkinElmer, model: ICP Optima 7000DV with computer software: WinLab 32 ICP Continuous	For the concentration measurements
Viscometer	HAAKE VT550 Sensor: NV (8)	For viscosity measurements of the ELM phase
Beakers	50 ml, 100 ml, 250 ml	For emulsification and for contacting external phase with ELM phase
Syringes ICP test tubes		

APPENDIX II

Following table presents the ELM compositions for each run when performing the experimental design for the extraction of chromium.

Table II-I: The precise compositions of the ELM formulations used in the extraction experiments of the experimental design.

Run	Mass ratio		Agitation speed	ELM content			HLB	
	Removal (7min)	O/I	(rpm)	Span 80 (wt%)	Tween 80 (wt%)	TOMAC (wt%)	Butanol (wt%)	Surfactant mix
PX1	97,7%	3,0	600	2,5%	1,0%	0,34%	0,5%	7,6
PX2	98,0%	3,0	600	3,0%	1,0%	0,38%	0,5%	7,2
PX3	98,6%	3,0	800	2,5%	1,0%	0,39%	0,6%	7,6
PX4	98,3%	3,0	800	3,0%	1,0%	0,35%	0,5%	7,2
PX5	98,3%	3,0	600	2,7%	1,0%	0,36%	0,0%	7,5
PX6	98,9%	3,0	600	2,7%	1,0%	0,40%	1,0%	7,3
PX7	96,4%	3,0	800	2,8%	1,0%	0,38%	0,0%	7,5
PX8	98,3%	3,0	800	2,7%	1,0%	0,35%	1,0%	7,4
PX9	99,2%	3,0	800/400	2,5%	1,0%	0,38%	0,0%	7,7
PX10	98,2%	3,0	800/400	2,5%	1,1%	0,38%	1,0%	7,6
PX11	95,4%	3,0	800/400	3,0%	1,0%	0,43%	0,0%	7,3
PX12	90,0%	3,0	800/400	3,0%	1,0%	0,39%	1,0%	7,2
PX13	98,6%	3,0	800/400	2,8%	1,1%	0,39%	0,5%	7,5
PX14	97,5%	3,0	800/400	2,8%	1,0%	0,35%	0,7%	7,4
PX15	97,4%	3,0	800/400	2,8%	1,0%	0,35%	0,5%	7,4
PX16	97,2%	3,0	800/400	2,8%	1,0%	0,41%	0,5%	7,3
PX17	99,6%	3,0	800/400	2,7%	1,0%	0,37%	0,5%	7,5
PX18	99,4%	3,0	800/400	2,8%	1,0%	0,36%	0,5%	7,4
PX19	99,0%	3,0	800/400	2,7%	1,0%	0,37%	0,8%	7,3

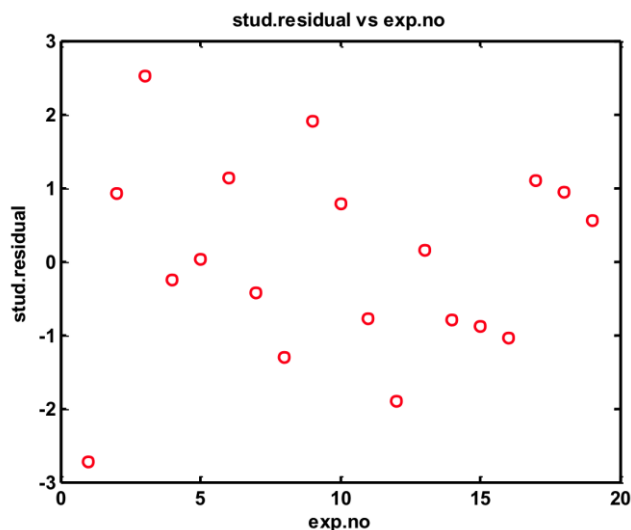


Figure II-I: The plot shows the studentized residuals vs. the experimental number (PX1-PX19)

APPENDIX III

Table III-I: Emulsion formulation of arsenic ELM extraction. The compositions of emulsion K13, K8 and K9 is shown below.

Run	External phase		ELM content		
	F/ELM (treat ratio)	pH	Emulsion	HCl (M)	TOMAC (wt%)
KEx1	2	6	K13	0,05	0,35
KEx5	1	6	K9	0,05	0,35
KEx6	3	6	K9	0,05	0,35
KEx17	1	9	K13	0,05	0,35
KEx18	3	9	K13	0,05	0,35
KEx19	1	9	K8	0,05	0,35
KEx20	3	9	K8	0,05	0,35
KEx22	2	9	K13	0,1	0,35
KEx23	2	9	K8	0,01	0,35
KEx24	2	9	K8	0,1	0,35
KEx26	2	9	K13	0,05	0,45
KEx27	2	9	K8	0,05	0,25
KEx35	3	9	K9	0,05	0,25
KEx36	3	9	K9	0,05	0,45
KEx37	3	9	K9	0,05	0,35

Table III-II: The formulation of emulsion K8, K9 and K13

Content:	Span 80	Tween 80	Butanol	[BMIM][NTf ₂]	I/O
Emulsion	(weight %)	(weight %)	(weight %)	(weight %)	(mass ratio)
K8	3	0	0	3	1
K9	3	1	1	3	1
K13	3	1	1	1	1