Mineral beneficiation from seawater: development and optimization of selective extraction techniques for essential minerals from seawater

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DECLARATION

I declare that this thesis is my own, unaided work. work. It is being submitted for the Degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

Candidate signature: **Date**: 05 September 2024

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ABSTRACT

The growing demand for essential minerals such as lithium and magnesium has underscored the need for sustainable extraction methods. Lithium plays a significant role in various industries since it is a promising metal for energy storage in electric vehicles as well as in electric devices. Magnesium is commercially used in the automotive industry. The governments of developed countries such as those in Europe, have imposed strict laws when it comes to vehicle emissions and have made the use of electric vehicles an alternative for more environmentally sustainable transportation. Traditional mining such as minerals in rock ore demands large amounts of water and energy, which is known to pose substantial environmental and health risks to the miners. Therefore, seawater mining has been reported as one of the strategies to mitigate the depletion of high-grade ores while offering reduced waste generation. This research contributes to finding technologies that align with the blue economy and addresses the environmental challenges of traditional mining.

This study focuses on the synthesis and optimization of polymer inclusion membranes (PIMs) to selectively extract essential minerals from seawater. However, the challenge is that lithium is present in extremely low levels approximately 0,17 mg/L in seawater. The approach was to synthesize PIM that will selectively extract the targeted analytes, leaving the non-targets behind when applied to real seawater samples.

The research was conducted in three phases. The first phase involved synthesizing PIMs and optimizing parameters such as membrane composition, stripping solution concentration, the effect of the pH and extraction time. The selectivity of the synthesized PIMs was tested in ultrapure water spiked with 15 mg/L of mineral salts such as magnesium carbonate, calcium carbonate, sodium carbonate and potassium carbonate, yielding a selectivity order of $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+} > Li^{+}$. In real seawater samples, the selectivity was $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$ and lithium was not detected. The density functional theory (DFT) studies were also conducted to investigate the binding ability of the carriers towards the targeted metal ions. The obtained selectivity was $Mg^{2+} > Ca^{2+} > Li^{+} \approx Na^{+} > K^{+}$. The selectivity of the metal ions obtained from the experiments slightly differs from DFT. However, the computational study contributes to finding suitable technologies that will take advantage of the blue economy. The method was optimised successfully and further applied to real seawater samples.

The second part of the study involved the synthesis of a PIM with different membrane compositions. The optimized PIMs demonstrated excellent selectivity for lithium which varied with the concentration of the HCl receiver solution. The selectivity obtained for the PIM that was in a 1:1 ratio utilising 0,05 M HCl of the receiver solution was $Li^+ > Na^+ > Ca^{2+} > Mg^{2+}$. As the receiver solution was increased to 0,1 M HCl and 1 M HCl, the selectivity shifted to $Li^+ > Ca^{2+} > Na^+ > K^+ > Mg^{2+}$ and $Li^+ > Ca^{2+} > Na^+ > K^+$, respectively. The selectivity obtained for the 2:1 ratio was $Li^+ > Ca^{2+} > Na^+ > Mg^{2+}$. When the concentration of the receiver solution was increased to 0,1 M HCl and 1 M HCl, the selectivity was $Li^+ > Ca^{2+} > Na^+ > K^+$ for both concentrations. Furthermore, the optimal parameters were further tested on the real seawater. The selectivity obtained was the same for the PIM at a 1:1 ratio for 0,05 M HCl, 0,1 M HCl and 1 M HCl receiver solution which was $Ca^{2+} > Na^+ > K^+$. When the second PIM in a 2:1 ratio was applied in seawater, the selectivity obtained for 0,05 M HCl of the receiver solution was $Ca^{2+} > Na^+ > K^+ > Mg^{2+}$ whereas for 0,1 M HCl the selectivity was $Ca^{2+} > Na^+ > K^+$ and for 1 M HCl the selectivity was $Na^+ > K^+$.

The third part of this study was a continuation of the first part. The optimised PIM was further employed for the extraction of minerals in seawater using a semi upscaled approach. A much bigger flat sheet membrane of approximately 270 mm (width) and 370 mm (length) was synthesized based on the optimised membrane composition. The other optimised parameters such as the concentration of the receiver solution and the effect of extraction time were tested in 0,05 M HCl and 0,1 M HCl receiver solutions for 39 days, respectively. The volume of the receiver solution was also investigated between 1 L and 2 L. The application was done in real seawater and the selectivity obtained for both volumes of the receiver solutions at 0,05 M HCl was found to be the same: $Na^+ > Mg^{2+} > Ca^{2+} > K^+$. However, when the concentration of the receiver solution was increased to 0,1 M HCl the selectivity changed to $Mg^{2+} > Ca^{2+} > K^+$ for both 1 L and 2 L respectively. The concentration of sodium at 0,1 M HCl in the receiver solution was not clear, thus it was eliminated from the results. Despite some deviations in selectivity compared to smaller-scale experiments, the study demonstrated the feasibility of using PIMs for mineral extraction from seawater on a larger scale.

Future work will focus on understanding the reasons for selectivity deviations in upscaled applications and further refining the PIM method to achieve consistent results. This research contributes to developing sustainable technologies for extracting valuable minerals from seawater aligning with the blue economy and addressing the environmental challenges of traditional mining.

DEDICATION

To the Almighty God,

I would like to humble myself before You. Thank you so much for your strength and for being with me throughout this challenging journey. I dedicate this work to you as a way of recognizing your infinite grace and blessings that have made me the person I am today. You have blessed me with such amazing mentors, colleagues, friends, and family who played a huge role in supporting me, which has greatly influenced the direction of my academic career.

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Izandla zedlula ikhanda!!!

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LIST OF ABBREVIATIONS

ADO	Adipate dioctyl
AAS	Atomic absorption spectroscopy
BLMs	Bulk liquid membranes
CTA	Cellulose triacetate
DBM	Dibenzylmethane
D2EHPA	Di(2-ethylhexyl) phosphoric acid
DFT	Density functional theory
DOPT	Dioctyl terephthalate
EDS	Energy dispersive spectroscopy
FTIR	Fourier transformed infrared spectrometry
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LIX 841	2-Hydroxy-5-nonylacetopnone oxime
LLE	Liquid liquid extraction
NF	Nanofiltration
NPPE	Nitrophenyl pentyl ether
NPOE	Nitrophenyl octyl ether
PIMs	Polymer inclusion membranes
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RO	Reverse osmosis
SA	South Africa
SE	Solvent extraction
SEM	Scanning electron microscopy

SILMs	Supported ionic liquid membranes
SPE	Solid phase extraction
TDS	Total dissolved solids
TODGA	N,N,N′,N′-Tetra-n-octyl diglycolamide
T2EHDGA	N,N,N′,N′-Tetra-2-ethylhexyl diglycolamide
TOPO	Trioctylphosphine oxide
TIOA	Triioctylamine
TTA	Thenoyltrifluoroacetone
XRD	X ray diffractometry
XRF	X-ray fluorescence

CHAPTER 1

This chapter gives a general background based on the importance of mineral extraction in seawater compared to the land based. It further highlights the essential major metal ions found in seawater as well as the techniques that have been employed for their extraction. In this chapter, the circular economy approach is also discussed.

1 INTRODUCTION

1.1 Background to the research

Mineral extraction has been considered as the most significant procedure for recovering minerals from the earth crust. These minerals occur naturally, and they are either liquid, solid or gaseous materials found on earth. The mineral extraction processes are driven by thermodynamic and kinetic processes which involve precipitation or separation based on the applied energy [1]. Mineral resources are natural minerals found on earth's surface such as hard rocks, clay minerals, underground brine reservoirs, groundwater, mineral spring water and the ocean [2–4]. The reason for their extraction is because of their chemical properties which are very useful for many applications thus contributing to the economy [5].

However, rock-ore mining requires large amounts of energy and water. This is because mining of minerals in rocks is often associated with drilling, crushing and heating which result in high carbon footprint production and acid-mine drainage. These activities are known to pose health risks to humans such as neurological disorders, kidney damage and cancer. The processes involved and the increase in waste generated are hazardous to the environment which is a critical societal challenge with profound implications. Subsequently, the production costs of water and energy increase [6]. Mining deep underground is difficult and dangerous because of the heat, lack of oxygen and rocks that can also collapse at any time due to pressure. Traditional land-based mining practices are environmentally harmful and contribute to resource depletion [6,7].

The extraction of minerals from seawater is becoming an attractive option because the minerals that are present in seawater are homogeneous and you will find that your target analyte is already dissolved in the solution. Moreover, there is no mineral grade difference compared to the land. It has been reported that there are more minerals in seawater as compared to those in land-based reserves. Nevertheless, ocean water contains about 33 to 37 g/L of dissolved salts. It has been estimated by earlier research that there are about 60 different metals dissolved in seawater. Some of these ions can be extracted using less energy consuming processes. Several major cations that are found in seawater including Na^+, Mg^{2+}, Ca^{2+} and K^+ that are commercially feasible due to their high concentrations among others. The extraction process in seawater is often beneficial because the element is present in the liquid ore and there is no need for drilling like in rock ore mining [2,7].

Seawater mining has been reported to be one of the better solutions to mitigate the depletion of high-grade ores and their beneficiation compared to land mining. Extraction of mineral salts in seawater using evaporation techniques is considered less energy intensive and it is environmentally friendly. Seawater extraction is associated with less disposal issues and other related problems. The extraction of minerals from seawater presents a sustainable alternative to traditional land-based mining. However, current extraction methods are facing challenges because minerals like lithium are normally found at very low concentrations in the ocean compared to land based [6,7].

1.2 Circular economy

Circular economy is a principle based on reusing and recycling products and materials, thereby generating less waste. The main objective of this model is to close industrial ecosystem loopholes. For example, the linear economy approach is to convert the raw materials into waste, whereas the circular economy motivates the use of the generated waste to make useful products for the next generation. Therefore, the circular economy strategy is good because it enables companies to create, recycle, repair and reuse [8]. One of the examples of a circular economy is the one that is employed in countries like the United Arab Emirates, whereby large amount of water that is used to manufacture concrete is generated from waste brine. Therefore, the reuse of rejected brine for concrete production can benefit the environment, thereby saving freshwater consumption and reducing the carbon footprint. This is due to the fact that the cement that is used for the production of concrete is not environmentally sustainable because it can generate approximately 5% of carbon dioxide [9]. Other countries that are in line with the circular economy include New Zealand, Canada, China, Hungary, Germany, Austria, and Ukraine [10].

Several methods have been employed to mine minerals directly from seawater. Such methods include the desalination process using electrolysis, solar evaporation and reverse osmosis [7,11–13]. Metal ions such as magnesium and potassium can be extracted using electrolytical methods that use ion exchange resins. Ion exchange resins have a relatively high selectivity for lithium recovery [7]. Solar evaporation is an old conventional technique that combines the use of solar energy with water evaporation. This method has been widely applied for the extraction of lithium [14]. Another technique is natural evaporation whereby the sun's energy is used to remove salt from the ocean. This process concentrates and crystallises the salt which is then further harvested using any mechanical means. For this technique, the evaporation ponds are very easy to operate, and they require low maintenance as well as less mechanical equipment. However, the limitations that come with this approach are mainly the fact that the evaporating ponds should be placed in a very large land area which then generates a large amount of carbon dioxide because the equipment used and extracted minerals may generate CO_2 depending on the distance and the mode of transportation used, however, the amount of carbon dioxide produced would be minimal due to natural evaporation taking place. Furthermore, the evaporation process is time consuming because it takes about 18 months [15]. This method is, however, environmentally friendly and economically feasible. This is due to the fact that this method uses the sun to evaporate and extract lithium and other metals without the addition of other toxic reagents. Salt-lake brines are complex systems that contain several numbers of dissolved ions. These ions include Li^{+}, K^{+}, Na^{+}, Rb^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, $SO4^{2-}$, $NO3^{2-}$, $CO3^{2-}$, HCO^{3-}. However, metal ions such as sodium, potassium and magnesium have high concentrations in natural brines, whereas lithium concentrations are relatively low. Therefore, pretreatment of brines via evaporation and crystallization methods to remove most of the sodium and potassium is normally used [16]. Reverse osmosis (RO) was also deployed in the previous study to extract mineral salts from brine. This method is also good because at the end of the process the waste generated comes in smaller volumes which is environmentally friendly [17].

Nowadays, polymer inclusion membranes (PIMs) have been reported to be a very suitable technique to extract several valuable metals from seawater overcoming stability issues [2]. However, the proposed membrane methods are not 100% selective, but it is possible to modify and improve them and further upscaled them for the extraction of valuable metals from seawater. The extraction of minerals from seawater brine is easier than extracting minerals straight from seawater. This is because brine is more concentrated than seawater. However, it becomes more challenging because the chances of the target analytes competing with each other increase, especially the ones that are present in high concentration. They tend to form complex compounds, thus making the separation difficult [2-7]. In addition, mineral extraction from seawater offers significant advantages such as reduced environmental impact, elimination of drilling and lower energy consumption compared to land-based mining. With increasing depletion of high-grade ores and the need for sustainable mining practices, developing efficient extraction techniques from seawater is crucial. However, scaling up of mineral extraction processes remains a challenge because large scale requires advanced technology to maintain efficiency and cost effectiveness. In addition, large scale extraction processes have the potential environmental impacts. Due to the above-mentioned reasons, this study aims to reduce the environmental impact of traditional mining, mitigate the depletion of high-grade ores and support the circular economy by utilizing seawater as a renewable resource. These will be carried out by developing, optimizing and upscale the polymer inclusion membrane (PIM) method for the efficient extraction of metal ions, specifically Mg^{2+}, Ca^{2+}, and Li^{+} from seawater The performance of the optimized PIM will be evaluated by extracting target metal ions from both simulated and real seawater samples. This will be followed by the investigation of the selectivity and efficiency of TTA and TOPO as carriers in the PIM method. Furthermore, the experimental findings will be implemented with density functional theory (DFT) simulations to understand the uptake mechanisms of TTA and TOPO.

Therefore, to the best of our knowledge this is the first study of its kind to investigate the uptake of a variety of minerals by PIM in seawater, with its results being further evaluated theoretically through the application of DFT to comprehensively understand the uptake mechanism. The findings will contribute to advancing sustainable and efficient mineral extraction processes offering a viable alternative to traditional land-based mining.

1.3 Thesis outline

The chapters that will follow are briefly described in the thesis outline that follows:

Chapter 2 offers a comprehensive literature review relevant to the current study. The review indicates that the different techniques have been developed by various researchers and have largely been applied for the extraction of essential minerals in seawater.

Chapter 3 presents the main aim and objectives of the study undertaken. It further describes the problem statement, justification of the study, research questions as well as the approach of how the study was carried out.

Chapter 4 is presented as papers and two of them have been submitted for publication.

This work was carried out by developing a PIM method and optimising of main parameters. First and foremost, different compositions of the membrane were synthesized to investigate which membrane works best in the extraction of targeted metal ions from seawater. The membrane was characterised before and after extraction using scanning electron microscopy (SEM), Fourier transformed infrared spectrometry (FTIR) and energy-dispersive spectroscopy (EDS) to study the morphology of the membrane, the chemical functional groups of the components and the metals that remained attached to the surface of the PIM after extraction respectively. The spiked ultrapure water was used for optimisation. The pH of the feed solution was varied as was the concentration of the acceptor solution. Furthermore, the time effect was also investigated to get an idea of how the PIM performs when deployed for a longer period of time. The developed PIM was further employed in real seawater samples.

The second study was carried out in a similar way as the first one. However, the components of the membrane were changed a little bit following a previous article as guide where the study of lithium extraction was done using a solvent extraction approach. Then, in this study the optimisation was done successfully extracting a high concentration of lithium compared to the other competing species. The developed method was further applied to real seawater.

The third part of this study is based on a semi-upscaled method using a bigger extraction device. The developed PIM from part 1 was then semi-upscaled for the extraction of targeted mineral salts from seawater samples. The investigation was carried out for a period of 39 days in the laboratory. Based on the results obtained, the developed PIM is promising.

Chapter 5 outlines the accomplishments of this work. Future recommendations for additional research are also outlined.

CHAPTER 2

This chapter provides an extensive literature review based on the origin of the targeted metal ions. Furthermore, it also highlights their uses, demand and consumption of essential metals. It also discusses the prevalent extraction techniques that have been employed for metal ion extraction in seawater and its brine.

2. LITERATURE REVIEW

2.1 The origin of minerals

Lithium (Li) has been reported to be a very good electrical conductor with a good specific heat capacity. This metal is used in many different industries including the battery industry, glass, ceramics, lubricating oils, polymer synthesis and pharmaceuticals [20,21]. In 1817, a Swedish chemist named Johan August Arfvedson was studying the mineral petalite ($LiAl (Si_2O_5)_2$) and he discovered lithium from this mineral. While doing his analysis, he classified lithium as an alkali metal. In 1855, another two scientists, August Matheiessen and Robert Bunsen, discovered lithium from the minerals known as silicate, spodumene and lepidolite. In 1869, these two scientists also discovered lithium in human tissues, seaweed, and spa waters. Thereafter, Dmitrie Mendeleev introduced lithium to the periodic table next to sodium. This led to the mining of lithium which began in South Dakota in 1898 [22].

Based on the analysis made by these scientists, they discovered that lithium had similar characteristics to magnesium and other alkaline earth metals [23]. In addition, magnesium can be found in minerals such as magnetite, brine water and seawater [24]. Magnesium is a widely distributed metal that was obtained mainly by ore smelting in the past decades [25]. Metal ions are found in higher concentrations in seawater and it's not difficult to recover those such as uranium. However, lithium is the primary focus because of its usage and abundance in the water [26]. Magnesium was also discovered as a magnesium alloy in the automotive industry. It was first used in 1921 and since then a demand of magnesium in car usage has increased steadily. This metal has been used by a German company for the production of trucks since 1927 [10]. Another crucial metal is calcium which was first discovered by Sir Humphry Davy in 1808. This mineral salt was discovered when the Romans used to burn lime and there were some remains of the solid residue from which they concluded that it must be calcium oxide (CaO) due to the decarbonation reaction that occurred during the process. Calcium comes in many different forms such as quick lime (CaO), slaked lime ($Ca (OH)_2$), limestone ($CaCO_3$), gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$) and hydroxyapatite ($Ca_5(PO_4)_3(OH)$. This might be an indication that humans have known about all these mineral salts since they have been using them for art. Moreover, these mixtures have been used as concrete for making buildings and bridges [27]. So, calcium was successfully isolated by the mentioned scientists, and they did a further study to determine its importance for the survival of all living things. The most abundant salt in the earth crust is sodium carbonate (Na_2CO_3). This salt is also known as soda which has been popular for decades. The Egyptians used to call 'natron' and the Romans tend to use a similar name which is ‘natrium’. In simple language this was referring to the chemical origin and its symbol (Na). Arabic people used to call it ‘suda’, meaning soda or to cure headache. In Latin, this word was further called ‘suda’ which later became ‘sodanum’. The word was evolving over time, and it was called sodium. Since then, sodium had a very positive impact on human lives. Human beings started to have their settlements made from salt springs. People started the business of trading with salt to get gold out of it. Most cultures have used salt in their art whereas some were making bread and giving away the salt to visitors as their way of welcoming them [28].

2.2 Metal ions and their uses

2.2.1 Lithium

Many recent studies have described lithium as one of the most critical metals due to its application in green technology [29]. Lithium is used in rechargeable batteries for mobile devices such as portable computers, electric cars, cell phones etc [30]. Lithium is also used in metallurgy to produce ceramics and glass. This metal acts as a lubricant by reducing friction on the surface of the steel and increasing corrosion resistance. The glass industry has observed that adding lithium to the glass batch during manufacturing saves a lot of energy due to its ability to lower the melting point, viscosity, and thermal expansion of the glass. The addition of lithium to ceramics increases mechanical strength [31]. This metal has been discovered as an effective treatment for humans suffering from gout. Furthermore, based on the previous studies lithium has been used to treat people with headaches, diabetes, epilepsy, hypertension, and joint inflammation. Lithium components such as lithium acetate, lithium aspartate, lithium citrate, lithium borate, lithium orotate and lithium sulphate have been used to manage manic depression [31,32]. Lithium has been observed to have a calming effect on patients with mental illnesses [31].

2.2.2 Magnesium

Magnesium (Mg) is considered a lightweight material that is beneficial to car production or the automotive industry. This metal is used in car parts such as gearboxes, steering columns, airbags, steering wheels, seat frames and fuel tank covers. Magnesium has been reported to save up to 70% of the weight of conventional parts. In the automotive industry, saving so much weight is very significant because that is what enhances a car’s performance by lowering rolling resistance and acceleration energy which will reduce fuel consumption and greenhouse gas emissions (CO_2). Then that means that the use of magnesium in vehicles has a positive environmental impact. Furthermore, magnesium also plays a crucial role in the formulation of high strength aluminium alloys used in the automotive industry [33]. Magnesium is also used to treat ulcers, gastrointestinal symptoms of dyspepsia, heartburn, gastroesophageal reflux disease and constipation because it acts as an antacid and laxative. This salt neutralises stomach acid. There are other salts that have similar characteristics to magnesium such as magnesium oxide and magnesium sulphate. All these salts are used for the treatment of constipation [34].

2.2.3 Potassium

Potassium is very important in the agricultural industry. This is because it provides plants with growth and metabolism. When the plant is going through potassium deficiency that results in inadequately formed roots, inactive development, poor disease resistance, delayed maturity, low seed production, and reduced yields. For the past few years, it has been well known as potash (K_2O. Therefore, a high amount of potassium is needed to ensure healthy plants because crop yield is highly affected by environmental conditions. The addition of potassium in a plant ensures that the plant does not suffer from diseases, pests, drought, salinity, cold, frost or waterlogging [35]. The addition of potassium in plants promotes synthesis. Different kinds of potassium bearing minerals that are used as fertilisers include potassium chloride (KCl), potassium sulphate (K_2SO_4), potassium magnesium sulphate (K_2SO_4.Mg SO_4) and potassium nitrate (KNO_3). Potassium sulphate is mostly used for potatoes, tobacco, fruit, and vegetables. These crops are known to be chloride sensitive which is why potassium sulphate is being applied to them. Potassium carbonate and potassium nitrate are known to be very expensive for agricultural purposes. However, potassium sulphate has a lower price and excellent physical properties and making it is more appropriate for chloride-sensitive crops [15].

2.2.4 Calcium

Calcium carbonate occurs naturally as the principal constituent of limestone, marble, and chalk. In the pharmaceutical industry, calcium carbonate is used as an acid suppressant in the stomach, and it has been found to be an excellent supplement for promoting bone growth in both children and young adults especially pregnant women. The allowable daily dose of calcium intake should be about 500 mg. These calcium supplements come in different forms such as chewable tablets, liquids, wafers and powders. Calcium is also important for healthy muscles and the circulatory system [36].

2.2.5 Sodium

Sodium is one of the most common and important elements that is highly abundant by mass on earth. This salt comes in many forms such as sodium sulphate ($NaSO_4$), sodium carbonate (Na_2CO_3) and sodium chloride (NaCl). These sodium derivatives are normally used for the production of soap, toothpaste, food, detergent, textiles, pulp and paper industries as well as medical supplies [6]. In pharmaceutical companies, sodium is used for the manufacturing of liquid chemicals and capsules. Such liquids are for haemodialysis and peritoneal dialysis. It is also used for IV (intravenous) solutions, oral rehydration salts and the extraction of biological heparin. Since population growth is increasing, renal dialysis is very important to patients especially those who need kidney transplantation. This is due to the shortage of donor organs. The intravenous solutions have various applications mainly regulation of blood pressure, hydration, electrolyte balance, medication and nutrition delivery, flushing, cleaning out IV lines and feed tubes, wound cleaning, renal dialysis and plasma collection [37].

2.3 Dissolved metal ions found in seawater and land

Lithium is one of the several metal ions that are critical because of its great significance in both economy and technology [26,38]. Among all metals, lithium has shown the largest price growth in this context, even resisting the decrease that has been occurring since April 2022. This significantly affects the price of manufacturing lithium-ion battery cells required to increase electromobility [39]. The ocean could be used as an infinite resource for useful materials for a very long time. The major anions that are normally found at higher concentrations in seawater include chlorides, sulphate and bicarbonate [40]. **Table 1** and **Table 2** show the estimated total dissolved cations and anions, respectively found in seawater and land. Among the other metals, sodium has a higher concentration than others followed by magnesium, calcium, and potassium. Lithium is found at very low levels are the rest of the metals presented in **Table 1**. The concentrations of metals in seawater are normally considered higher as compared to those found in land-based reserves. It has been reported that the amount of minerals that are extracted from the ocean globally is expected to be approximately 100 billion tons per year. However, the concentration of these metals depends on their abundance as well as their solubility [26]. The composition of anions in seawater is shown in **Table 2**. Chlorides are estimated to be the highest even when compared with sodium followed by sulphates (SO_4) and bicarbonate (HCO_3).

Table 1

The valuable minerals that can be economically mined from seawater with reported estimated concentrations found in seawater and land [26,41].

Element	Concentration in seawater (ppm)	Total oceanic abundance (tons)	Mineral reserves on land (tons)
Na	10800	1.40×10^{16}	-
Mg	1290	1.68×10^{15}	2.20×10^{9}
Ca	411	5.34×10^{14}	-
K	392	5.10×10^{14}	8.30×10^{9}
Li	0.178000	2.31×10^{11}	4.10×10^{6}
Ba	0.021000	2.73×10^{10}	1.90×10^{8}
Mo	0.010000	1.30×10^{10}	8.60×10^{6}
Ni	0.006600	8.58×10^{9}	6.70×10^{7}
Zn	0.005000	6.50×10^{9}	1.80×10^{8}
Fe	0.034000	4.42×10^{9}	1.50×10^{11}

Table 2

The estimated amount and concentration of dissolved anions in seawater [40].

Anions	Seawater (mg/L)
Cl	19000
SO_4	2700
HCO_3	142

2.4 Percentage of world mineral demand and consumption

2.4.1 Lithium

In developed countries the government is encouraging people to use electric cars to reduce emissions which have a negative impact on the environment. Lithium is the popular metal ion that is used in car batteries. Therefore, there are major countries that are leading producers of lithium such as Australia, Chile, and China. Australia is known to produce over 2 million tons of lithium while Chile produces over 7.5 million tons. China is estimated to produce approximately 7 million tons of lithium. Other countries such as Congo, Russia and Serbia also produce about 1 million tons of lithium each of which is 3 million tons in total. In addition, Brazil and Zimbabwe are estimated to have more than 100,000 tons each [42]. The proportion of each lithium application in the global consumption structure has increased dramatically in recent years. **Figure 1** below illustrates the consumption of lithium worldwide. Lithium- ion batteries have shown a great increase of about 71%. The production of ceramics and glass was estimated to be at 14%. An estimate of lithium used as a lubricant was roughly 4% with 2% going towards the production of polymers and more than 2% to the steel industry. The remaining 7% contributes towards various applications such as 1% for air treatment and 1% for aluminium metallurgy [43]. The World Economic Forum predicted that due to the high demand of lithium, by 2030 lithium battery consumption will be around 2,600 GWh worldwide. **Figure 2** displays the forecasts for the years 2021 through 2040. Nonetheless, the values for the years 2021–2030 are based on market demand, while the estimates for the years 2030–2040 are for market share forecasting [44].

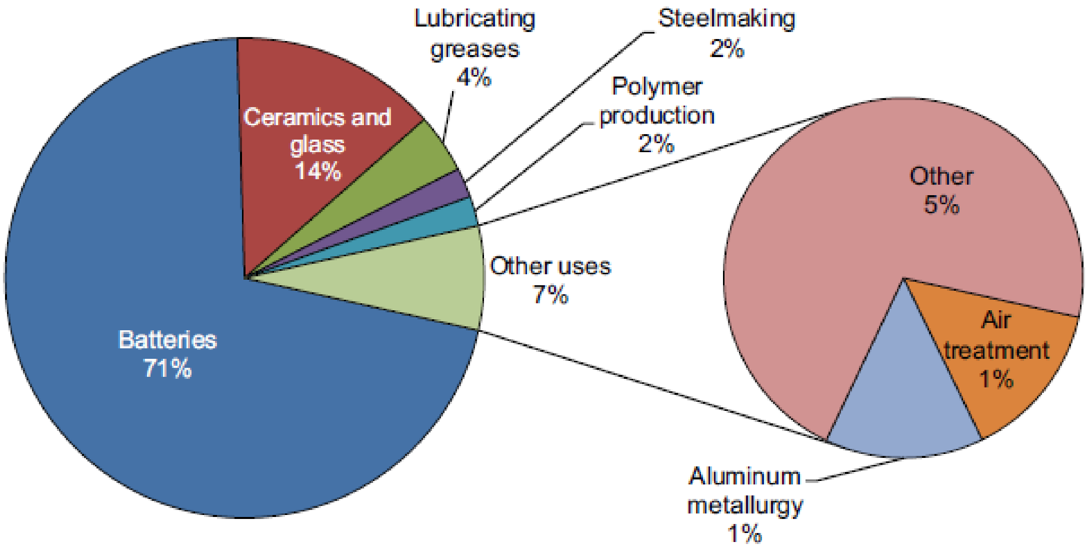

Figure 1. Pie chart showing the application of lithium as a percentage of global consumption in 2020 [43].

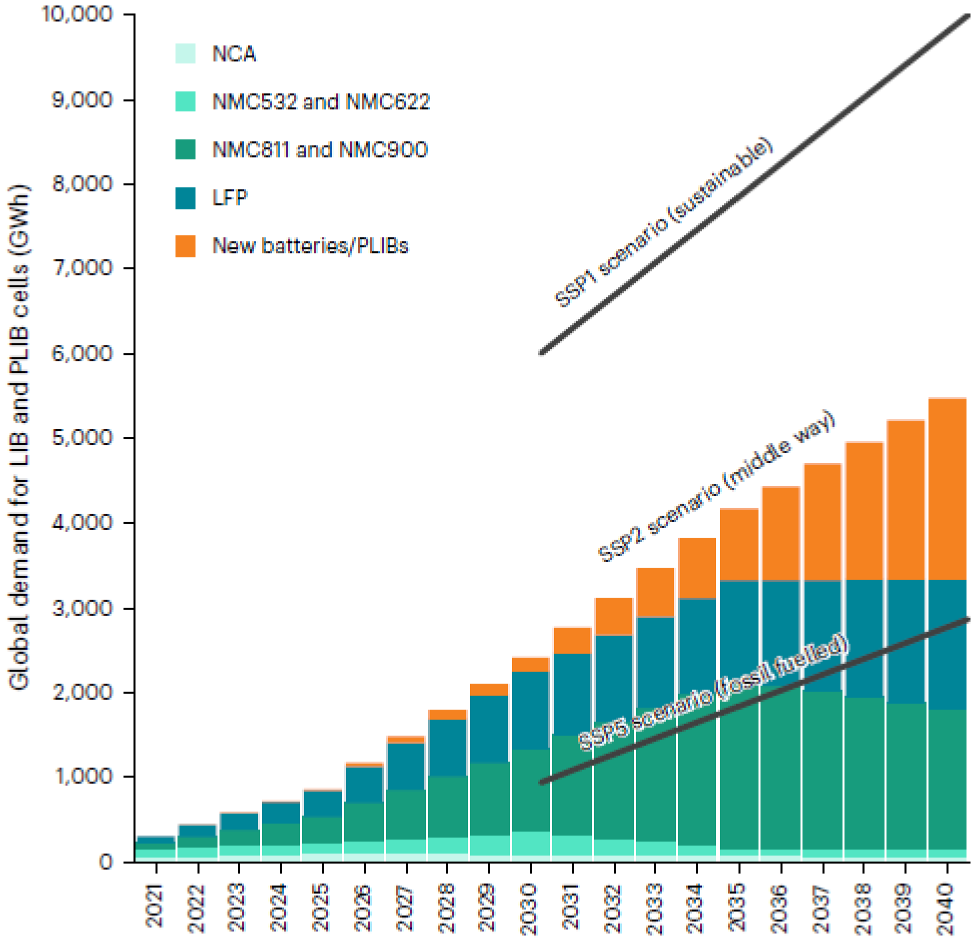

Figure 2. A bar graph showing the global demand for lithium batteries for the next 16 years [44].

2.4.2 Magnesium

Magnesium is considered the lightest material among all commonly used ones like aluminium in the automotive industry. Previous studies have reported that it is not easy to find this metal in its pure form since it can bond easily with other metals. This metal is recovered from natural minerals such as dolomite and magnesite. There are two approaches that are normally employed for the extraction of magnesium the Pidgeon process and the electrolysis process. These processes are popular in the United States. So, in the car industry they normally use alloys in which magnesium is always present such as aluminium alloys [10]. Magnesium is used for several applications as shown in **Figure 3**. Magnesium is highly used in dye casting, aluminium alloys, steel desulfurization, metal reduction etc. According to the European Commission's, magnesium is commonly used in the automotive industry, in packaging, construction, desulfurization, transportation including air transport, maritime and railway transport as well as other applications. Global demand for magnesium is rising rapidly and reports indicate that it accounts for roughly 6.8% and 4.1% of the increase in dye casting and aluminium alloys, respectively. Furthermore, it has been observed that magnesium has the potential to become a technology metal in various applications such as energy storage and biomedical products [45]. Shaanxi Province located in China is known to produce approximately 54% of the global magnesium supply. The increase in supply demand for magnesium in the automotive industry is expected to rise to 0,70 million tons (mt) by the year 2050 shown in **Figure 4**. According to the previous study it has been reported that the world's total energy and water consumption for the recycling of magnesium is expected to be approximately 40% which refers to non-functional casting. So, by 2050, functional and non-functional technologies seem to have negative impacts such as global warming with estimated emission of 5.62 and 29.66 mt of CO_2, respectively. The top producers of magnesium are China (970 kilotonnes (kt)), Russia (67 kt), Kazakhstan (25 kt) and Israel (21 kt). Production in China is very energy-intensive and generates too much emissions which may reduce the potential advantage of using magnesium in car parts [10]. Therefore, the car industry should try to enhance the fuel efficiency of vehicles by making these metals lighter for long term use.

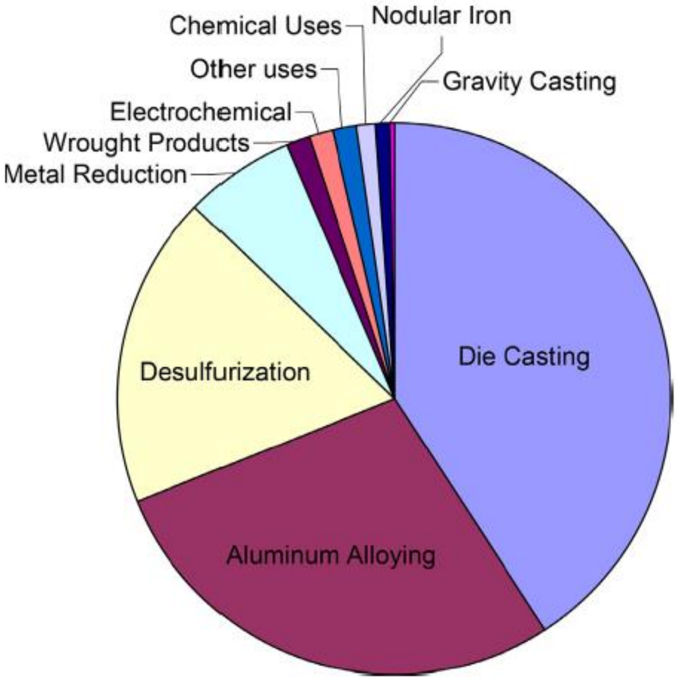

Figure 3. The industrial consumption of magnesium and magnesium alloys [45].

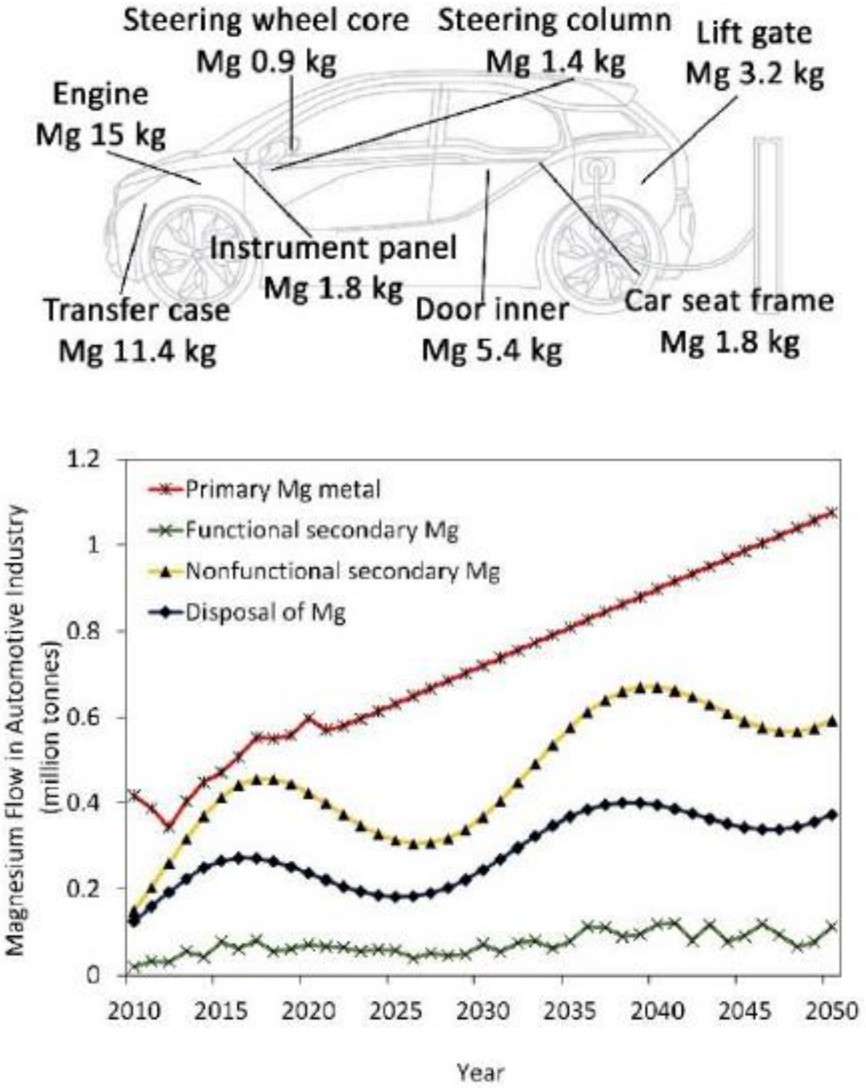

Figure 4. Magnesium produced primary and secondary for the automotive sector from 2010 to 2050. (a) shows magnesium usage in a vehicle while (b) represents the mass flow of magnesium in both primary and secondary [10].

2.5 Resources of essential metals

Lithium is widely distributed mainly in hard rocks, clay minerals and natural waters [26]. The resources of crucial metals are discussed below.

2.5.1 Brine

Brine refers to lakes, salars, oilfield and geothermal brines. For example, the procedure of lithium extraction from brine is obtained by drilling the brine from beneath to the surface and distributing it to evaporation artificial ponds which typical carry between 200 and 1400 mg/L of lithium. This process takes about a year depending on the climate change. During low rainfalls, low humidity and moderate winds the process tends to have the best evaporation rates

[12]. In brine lithium is recovered as lithium carbonate (Li_2CO_3) using lime soda evaporation to produce lithium as a metal [21]. After the evaporation process, the recovered salt is normally associated with chlorides, sulphates, potassium, calcium, magnesium, boron, and lithium. Another difficult and interfering salt is magnesium because it is not easy to remove it from the other metals. Therefore, it requires precipitation by the addition of calcium carbonate to remove magnesium carbonate from the solution: ($CaCO_3 + MgCl_2$ >>>> $CaCl_2 + MgCO_3$) [31]. Otherwise, without the precipitation process, the extraction of lithium is a challenge since the brine contains high levels of Mg^{2+} as compared to K^+ and Na^+ [21]. However, the procedure of removing lithium from brines needs a lot of fresh water which might negatively affect the environment. This is because the extraction of lithium is associated with harmful chemicals that might be a threat to the environment [31]. Lithium originates from the weathering of different kinds of rocks within a closed basin. Other elements in solution such as potassium and boron may be recovered as byproducts. Brines may also contain dangerous metals that need careful disposal. Typically lithium brine fields have geographical relationships with sodium chloride (NaCl) evaporite deposits [22]. **Figure 5** illustrates how lithium is obtained from hydrothermal fluids from different rock sources within a closed basin. As seen in the picture that volcanoes airfall tuffs are shown to be the primary source of lithium. In addition, lithium's solubility is high as compared to sodium and potassium. Lithium is mostly found in brine residues in the shallow sub-surfaces [22]. In salars the closed basins are typically linked to active faulting and occur in tectonically active basins. [22]. Another essential metal such as magnesium can be recovered from minerals which include seawater along coastlines, dolomite, serpentine and magnesium bearing evaporites. Magnesium bearing brine is known to contain billions of tons of such metal ions [46]. One of the salt lakes in Qinghai located in China, is very rich in potassium, magnesium, lithium and other essential salts that contribute to economic value [45].

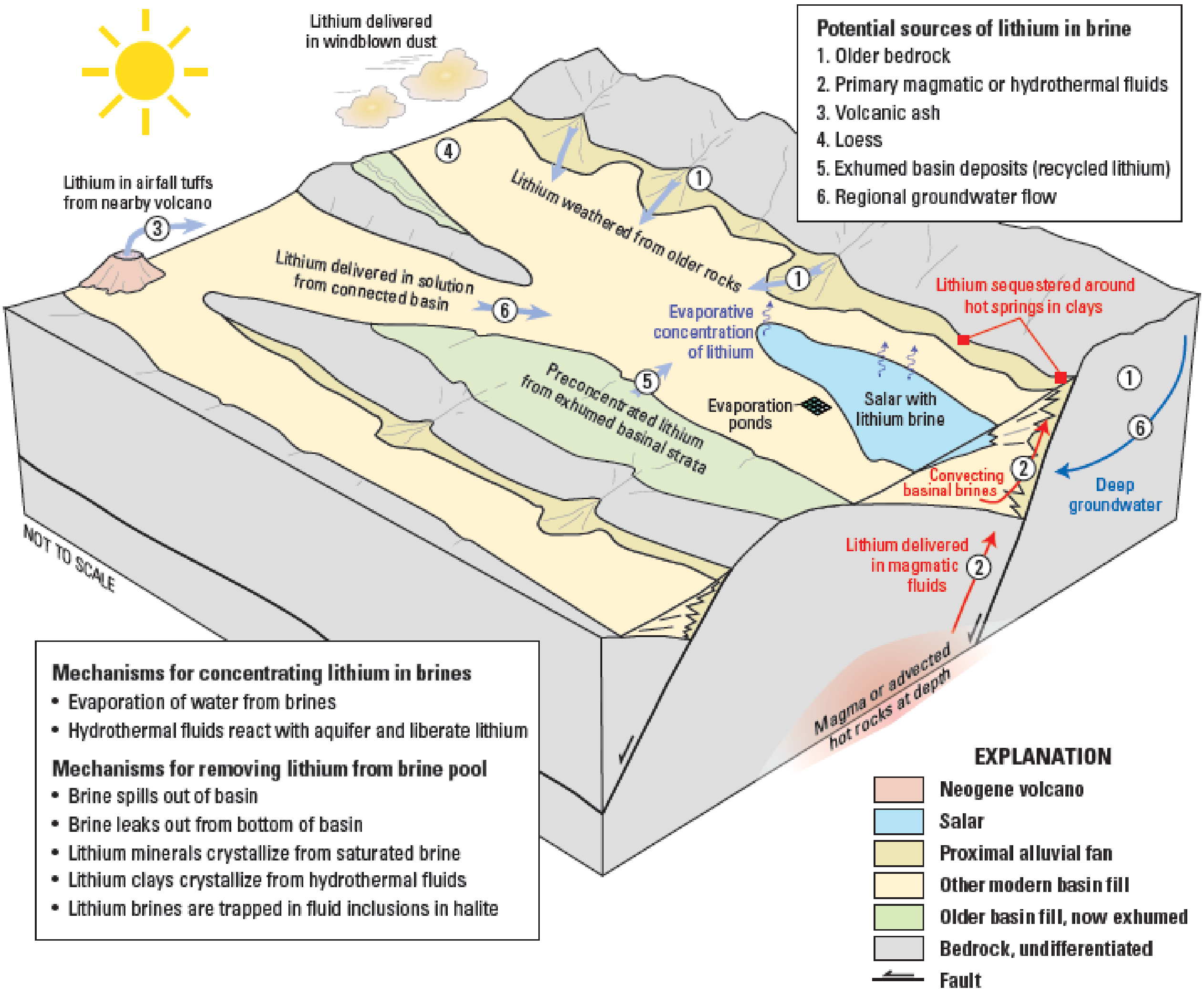

Figure 5. A model showing a lithium brine deposit in a closed basin system [23].

2.5.2 Minerals

The widely known mineral is found in a subset type of rock known as pegmatite. This mineral is complex because it is associated with spodumene ($Li_2O.Al_2O_3.4SiO_2$), lepidolite ($KLi_2Al\ (Al.\ Si)_3O10\ (F.\ OH)_2$) and petalite ($LiAlSi_4O_{10}$). Among these minerals, spodumene is the most popular one because it is used in the production of lithium carbonate and further processing to produce lithium as a metal. The production of lithium from spodumene occurs by the process of heating and cooling as well as the further addition of chemicals such as concentrated sulfuric acid (H_2SO_4). The hydrogen from sulfuric acid gets replaced by lithium metal in the solution forming lithium sulphate (Li_2SO_4) [12]. The pegmatite illustration is shown in **Figure. 6** which normally appears as a grained intrusive igneous rock formed from the crystallisation of magma at the depths of the earth's crust. Therefore, the pegmatite tends to become enriched with more diffuse metals such as lithium, boron, beryllium and other elements as a result of the late crystallisation stage [47]. A metal like lithium is common in spodumene minerals. Such pegmatite is linked with a high level of lithium and other incompatible metals. The model in **Figure. 6** shows a cross section of a concentric pattern of lithium in pegmatites and how they are aligned in pegmatite denoted in both small green and blue. Whereas the rest of the metals such as cesium (Cs), tantalum (Ta), beryllium (Be), rubidium (Rb) and tin (Sn) are shown in purple, green and blue colour [23].

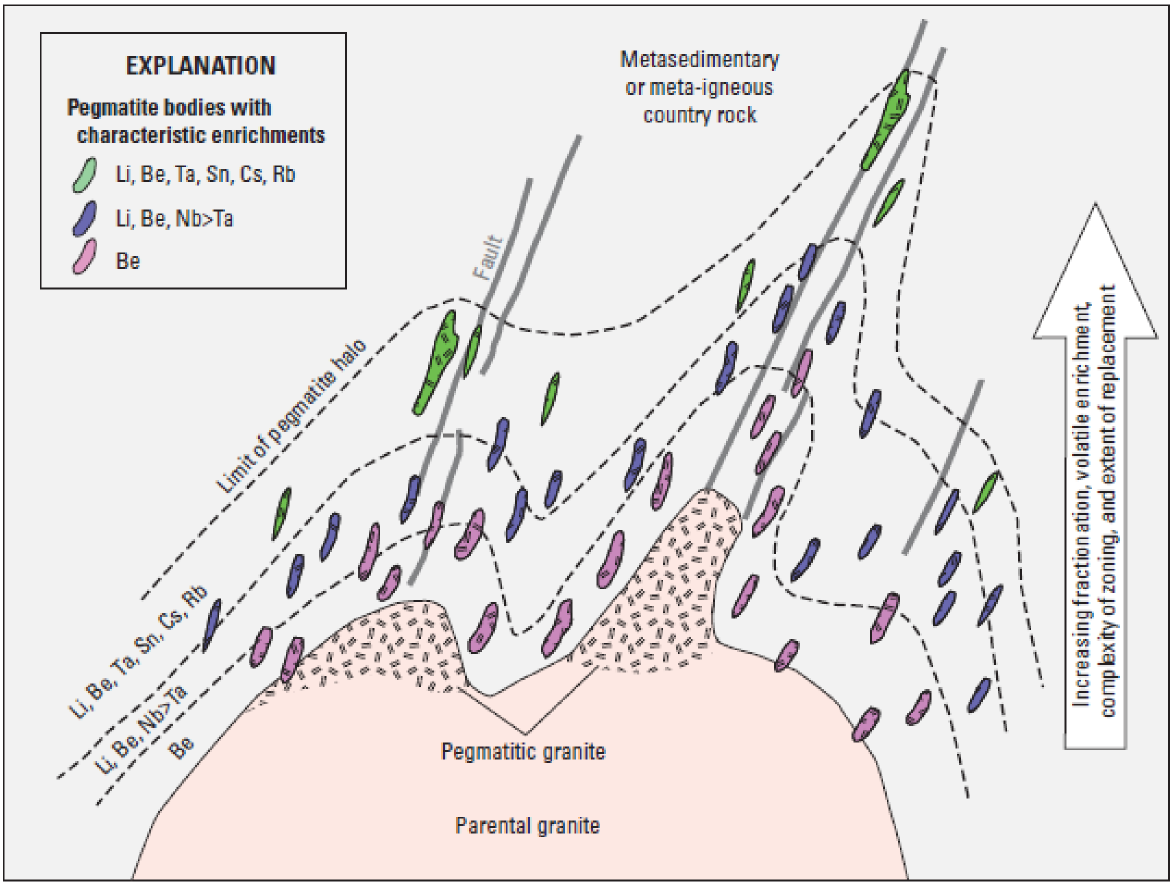

Figure 6. An illustration showing the arrangement of pegmatites enriched in rare minerals [23].

2.5.3 Bearing clays

Bearing clay deposits are known to contain about 7% of lithium resources globally. Lithium clays are normally formed in ash rich basins resulting from volcanic ash sediments. In that manner, the lithium becomes attached to the clay. The lithium bearing clays are normally found in the U.S in Arizona, California and Nevada. In the past years, these clays were not mined for lithium in particular, they were being used for water absorption [23].

2.6 Extraction techniques for essential metals

The most popular laboratory techniques for the extraction, purification and separation of the targeted analyte from a complicated mixture of constituents are listed below.

2.6.1. Polymer inclusion membrane (PIMs)

Polymer inclusion membranes (PIMs) are one of the approaches that have been demonstrated to be a good alternative compared to techniques such as liquid- liquid extraction for metal recovery as well as other emerging pollutants in aqueous solutions. This is a type of liquid membrane system in which the carrier or extractant is incorporated into the membrane interphase. The synthesis of polymer inclusion membrane is usually made from a solution containing a base which could be cellulose triacetate (CTA), a carrier such as thenoyltrifluoroacetone (TTA) or dibenzylmethane (DBM) and a plasticizer such as 2-Nitrophenyl alkyl ether [18,48]. **Figure 7** illustrates the representation of a polymer inclusion membrane (PIM) with its components and how it separates the two aqueous solutions [49]. CTA is capable of forming highly oriented hydrogen bonds with other components due to its polarity [50]. Furthermore, base polymer is very important as it provides membrane with good mechanical strength while plasticizer improves their flexibility and retention increases the distance between polymer chains and thus reduces intermolecular forces (Van der Waals forces) between the polymer chains [51,52]. Following are various types of extractants including basic, acidic, neutral, solvating, macrocyclic and macromolecular. It has been reported that extraction is not possible without extractants. The reason being, extractants are highly responsible for the binding and transportation of the analytes of interest across the PIM interphase [53]. Basic carriers mainly consist of amine compounds such as trioctylmethylammonium chloride known as aliquat 336 and triioctylamine (TIOA). Acidic and chelating carriers involve the exchange of metal ions with hydrogen ions in the carrier. These types of carriers include phosphorus, thiophosphorus acid ester, carboxylic acid and sulfonic acid compounds. Other popular carriers include Di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-Hydroxy-5-nonylacetopnone oxime (LIX 841) and β-Diketone (acetylacetone 3-propylacetylacetone and 3-benzyl-acetylacetone). Neutral and solvating carriers include trihexyl(tetradecyl)phosphonium chloride (cyphos IL 101), N,N,N′,N′-Tetra-n-octyl diglycolamide (TODGA) and N,N,N′ ,N′ -Tetra-2-ethylhexyl diglycolamide (T2EHDGA). Macrocyclic and macromolecular carriers include calixarenes 5,1 (7,Di-tert-butyl-11,23-bis[(1,4-dioxa-8-azaspiro[4,5]decanyl)methyl]25,26,27,28tetrahydroxy calix[4]arene). Additionally, there are several plasticizers such as nitrophenyl octyl ether

(NPOE), nitrophenyl pentyl ether (NPPE), dioctyl adipate (ADO), tri-(2-ethylhexyl) phosphate (T2EHP), tris(2-butoxyethyl) phosphate (TBEP) and dioctyl terephthalate (DOPT) [2,51].

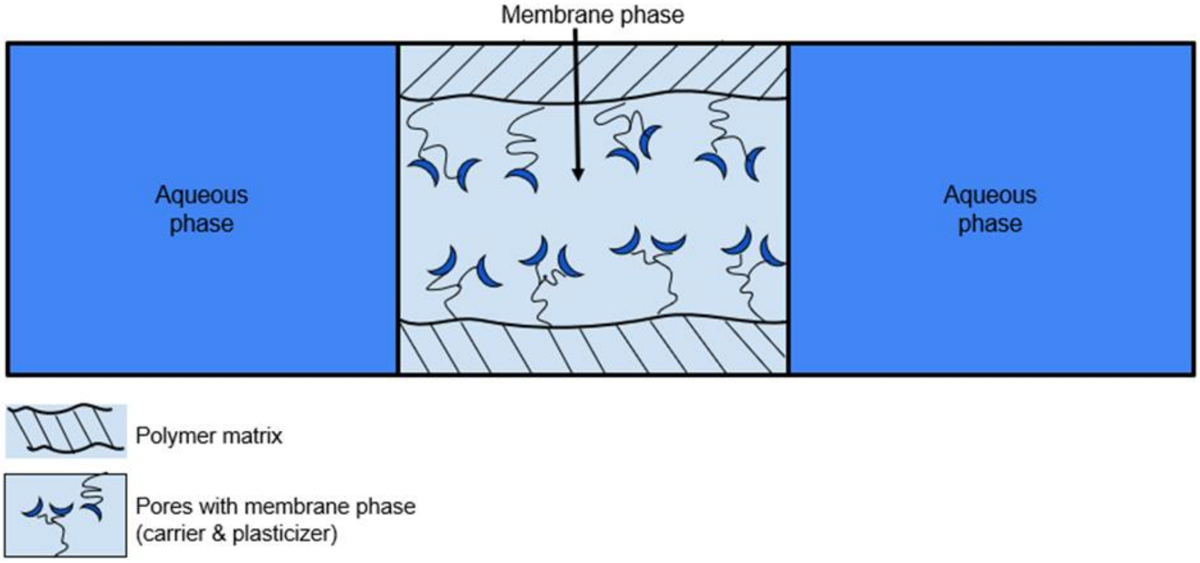

Figure 7. Schematic representation of a polymer inclusion membrane (PIM) [49].

PIMs are associated with many benefits which originate from their excellent stability, flexibility, and high permeability in comparison with other liquid membranes. Most importantly they have been reported to be environmentally sustainable [53]. Several studies have been conducted on the stability of the membrane whereby the same membrane was used for several cycles by renewing only the feed and the stripping solution [2]. It has been reported that PIMs do not suffer from loss of organic solvent due to their high stability and they have ease of operation at a very low cost compared to other liquid membranes [18]. This is due to the fact that extraction and back extraction occur concurrently which enhances the speed of the process and the use of a very small amount of solvent [51]. However, there are some limitations associated with the PIM technique which include a low mass transfer rate and small surface area which is small for large scale applications [54]. The transport mechanism depends on the type of carrier as one can be either a co-transport or a counter-transport [48]. The PIM may contain an acidic or basic type of carrier and the cations/anions will migrate from the feed solution where there is a high pH to the low pH region (receiver phase). In coupled counter-transport, the carrier reacts with the target analyte in the feed at the interphase, diffuses to the receiver side and at the interphase releases the analyte. The carrier then reacts with an anion like a proton (H^+) or chloride (Cl^-) in the acceptor phase and diffuses back to the donor phase interphase where the anion is released. The driving force in this case is the anion from the acceptor solution [2,48]. This mechanism is slightly different from other membrane technologies such as osmotic pressure. In osmotic pressure, a high pressure is being applied and water permeates through the PIM from the donor phase to the acceptor phase [2].

2.6.2 Supported Ionic Liquid Membranes (SILMs)

Supported Ionic Liquid Membranes (SILMs) are ionic liquid that act as extractants and are placed in the small pores of a polymer support. It uses a membrane support that absorbs in organic phase in order to divide two aqueous phases then the target analyte is transported from the feed region to the stripping region [55]. This technique was developed to overcome issues associated with other separation techniques such as chemical precipitation, reverse osmosis, adsorption, ion exchange and solvent extraction processes. SILMs became attractive to both researchers and practitioners because of their benefits. For the extraction and back extraction to occur in a single step it requires a relatively small amount of organic phase and an extractant which results in low capital and operating costs [56]. The usage of ionic liquids (ILs) as a liquid membrane phase has shown a huge improvement with regards to extraction [57]. However, SILMs have been reported to have very poor stability for long-term industrial use. This is because when ionic liquids are not employed in SILMs their stability suffers greatly from the presence of volatile solvents which raises the possibility of SILMs becoming more unstable [58].

2.6.3 Solid phase extraction (SPE)

Solid phase extraction (SPE) methods are used not only to extract traces of organic compounds from environmental samples, but also to eliminate the interfering species from complex matrices and provide cleaner extracts that contain the target analytes. For this technique to be successful there must be an interaction between the analytes of interest, solvent and sorbent [59]. SPE is associated with the emissions of extracts containing target analytes which are then run through columns filled with an appropriate sorbent conditioned by a suitable solvent. It is a multifunctional technique since the purification and concentration steps occur simultaneously [60]. The fundamental of SPE is similar to that of liquid-liquid extraction (LLE). However, LLE involves two immiscible liquids, whereas SPE is associated with solvent and analyte partitioning with a sorbent. On SPE, the column selection varies. For instance, if the analytes are polar, normal phase extraction is normally employed and if the analytes are less polar then reverse phase is applied [59]. The steps involved in SPE include conditioning whereby the solvent is passed through the SPE material to wet and activate the bonded functional groups of the sorbent to ensure effective interaction with targeted analytes. During the sample loading step, a solution of the analyte is transported via the conditioned column and the analyte is adsorbed onto the surface of a solid phase. A cleaning up step requires washing off the target analyte with a relatively small volume of an appropriate solvent. In this step, normally water is a better alternative to remove impurities. The solvent should be strong enough to remove all the impurities. However, one must ensure that it doesn't remove the targeted species out while leaving the analyte of interest behind. The eluting step involves the removal of the analytes of interest by fractions using a solvent that overcomes the primary and secondary retention interactions between the sorbent and the analytes of interest. The choice of an appropriate eluting solvent is dependent on the polarity of the analyte. For example, methanol is commonly used in SPE extraction due to its higher polarity which makes it more suitable for the extraction of moderately to strongly polar species. This is because methanol has a unique interaction with both polar and non-polar bonded chemical species. In recent studies, methylene chloride has been used to effectively elute non-polar analytes from nonpolar bonded phases [59].

During the development of the SPE methodology, the choice of the sorbent was very significant. There are different types of SPE sorbents namely free disks, disks in syringe and barrels cartridge which come in different sizes from micro-sized disks in 1 ml syringes to a 6 ml syringe The cartridge type remains the most used format with typically 40-60 µm of packing material [59]. SPE has been proven to work better than liquid-liquid extraction. This is because it is used for isolation and pre-concentration which then results in cleaner extracts with good recoveries of the analytes. Furthermore, it allows for the use of comparatively small volume of solvent while achieving high recoveries. This method is very easy to use and capable of extracting analytes in a wide polarity range in a very few steps [59,61,62]. However, there are drawbacks associated with it including the possibility of low recoveries because of interaction between the analyte of interest and the sorbent. In addition, if the sample loading volume reaches what is called a 'breakthrough' when the uptake has reached the equilibrium point then that can also result in low recoveries. Furthermore, the sample matrix may cause clogging by its suspended particles in the sorbent bed of the cartridges resulting in low recoveries. Moreover, during the extraction process, it might take longer than expected due the number of steps required [62]. In addition, working with non-filtered samples such as wastewater is time consuming.

2.6.4 Solvent extraction (SE)

The solvent extraction method (SE) is one of the significant methods mainly used for the removal, separation, and concentration of metal ions from the aqueous media. This extraction technique has been used for commercial purposes to remove metals from both primary and secondary resources. However, industrial solvent extraction of metal ions such as lithium is very rare [63]. A solvent extraction approach can be applied to selectively recover metals like lithium from brines using organic non-polar solvents. The commercial applications of SE approaches have been associated with the recovery of rare earth metals and base metals which include copper and nickel. When the target metal is in high concentration this technique becomes more efficient and cost-effective. However, the analysis of metal ions with the same behaviour is very difficult and that's when the crown ethers are included for such extraction [38]. This method is associated with an aqueous phase containing metal salt with an organic phase as an extractant. During the optimisation of this method, there are three most significant steps to follow such as extractants, diluents and pH. However, solvent extraction is not considered environmentally sustainable because it is linked with the use of toxic, harsh solvents in very large quantities such as kerosene, toluene and dichloromethane [56]. SE has its advantages as well, because the procedure is very simple and leads to quantitative results [64]. However, there are limitations because it often needs extraction using a large amount of solvent while generating secondary sludge and expensive disposal. This method is expensive and requires high operating costs because of its sensitive operating conditions. Solvent extraction is associated with low efficiencies [56].

2.6.5 Precipitation method

The precipitation technique is commonly used for the separation of metal ions with the aim of removing the interfering species while at the same time recovering analytes of interest in the sample matrix [65]. Precipitation refers to the formation of solid particles from a solution via a chemical reaction. It is normally used for the extraction of metal ions from aqueous solutions by an inclusion of counter-ions to reduce their solubility [66]. This process has been applied to industries on a large scale for the removal of metals such as lithium [67]. The precipitation process normally starts with evaporation step which involves heating seawater for a certain period of time. Once that is done it is followed by the addition of the precipitating agent to create the precipitant. After that the experiment is run either at room temperature or in heat depending on the optimisation process. When the experiment is done, the precipitant is separated from the filtrate. The filtrate is then dried using an oven in most cases and further prepared for characterization using instruments such as XRD, SEM and XRF to determine its phase formation, morphology, and chemical composition respectively. To determine chemical composition, the ICP-OES instrument is used. The precipitant obtained is then re-dissolved in order to have a sample in liquid form that is suitable for analysis [68]. The precipitation method is a very useful technique for the separation of metals since it has a high degree of selectivity. Furthermore, it is easy to use, low cost and very efficient for industrial applications. However, the drawbacks involved in the precipitation method include the high cost of operation and maintenance. Furthermore, after extraction a very large quantity of waste is generated [16,69].

2.7 Density functional theory (DFT) as a molecular modelling (MM) approach

Molecular modelling (MM) is a computational method that is very useful in predicting the behaviour and characteristics of molecules used in different fields of research especially in science. This technique involves the study of molecular structures, interactions and dynamics using computer simulations and algorithms [70]. Examples of molecular modelling include molecular mechanics (MM), molecular dynamics (MD), quantum mechanics (QM) which is known as density functional theory (DFT). However, DFT is now common in scientific research due to the evolution of computational chemistry [71,72]. The density functional theory (DFT) is a computational quantum mechanical method used for scientific purposes to investigate the structure of molecules, atoms and materials. The basic principles behind the interaction between the extractants and metal ions are crucial for solvent extraction in order to create selective reagents [71,72, 73]. Density functional theory (DFT) is one of the most successful methods for simulating molecules and materials, mostly due to its comparatively low processing cost and ability to give excellent calculations across many areas of interest [70]. However, it has limitations, such as a small simulation size and the inability to include the temperature effect since all simulations are run at 0^0C. This modelling approach is commonly employed in studies based on mineral surfaces either liquid, solid, or gas interfaces. In the past decades, computational chemistry in mineral processing has gained more popularity because it is widely used in understanding the basic properties of minerals [72]. DFT incorporates electronic structure computations and can handle several hundred atoms in a simulation. This approach relies on the exchange-correlation functional which combines the nuclear and effective potentials into a single external potential for each electron. The choice of exchange-correlation functional is critical to the accuracy of DFT computations. Population analysis is also conducted which is known as charge distribution. This is a postprocessing approach normally included in DFT studies. However, one must be aware of differences in the formulations used to predict atomic partial charges [70]. The link between the atomic surface structure and various physical and chemical properties of complex metals such as (metal oxides) is difficult because of the mixed ionic and covalent bonding that can exist in these materials [73]. This strategy is critical to combating the depletion of high-quality ores. This is because as minerals are depleted, we are left with more complex ores that are difficult to extract. Hence, the DFT approach assists in experimental studies while reducing time and providing knowledge and predicting the behaviour of electrons in complex systems [70, 72].

2.8 Detection techniques for metals

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

Inductively coupled plasma optic emission spectroscopy (ICP-OES) is a very powerful and popular analytical laboratory technique used for the determination of the concentration of certain elements with higher detection limits from the sample matrix. Sample introduction occurs via a peristatic pump and tubing which pump the liquid sample into the nebulizer. Then the nebulizer converts the solution into small and large droplets in the form of aerosols. The spray chamber removes the large droplets and sends them back as waste. This is because it is only the small droplets that are crucial for the plasma. So, these small droplets enter the base of the plasma via the injector tube they get dissolvated, vapourised, ionised and atomized. Plasma is the energy source that promotes or excites the electrons of the ions to move from the ground state to higher energy levels. The excited atoms and ions emit their characteristic radiation which is collected by the device and measures the element's emission energies at different wavelengths. The wavelengths are specific to certain elements thus only used to identify but quantification is through emission energy. Furthermore, the collected radiation is changed into electronic signals that are converted to concentration information to make things easier for the analyst after calibration [74]. This is a multi-element technique that allows fast and reliable simultaneous determination with a very simple sample preparation. Furthermore, it is less prone to matrix interferences because of the high temperatures in the plasma which allow full dissociation of a sample. It is capable of analysing elements over a very large dynamic range. A very small sample is needed. However, the instrument is expensive, has high detection limits and requires highly trained operators [75].

2.8.2 Principles of inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is widely used for the analysis of element concentrations at trace levels in the environment [75]. There are six principal components which include the sample introduction system, inductively coupled plasma (ICP), interface, ion optics, mass analyzer and detector. The sample is introduced into the nebulizer by a peristatic pump for the formation of aerosols. The nebulizer creates large and small droplets, and the spray chamber removes the larger droplets as waste. The small aerosols enter the argon plasma where they get ionised and atomized due to the high temperature involved thus resulting in ions. Moreover, ions are collected in the ionic optics and further directed into the quadrupole mass analyzer. This is where ions are measured by the detector according to their mass charge ratio (m/z) using mass analyser. ICP-MS can analyse a series of elements simultaneously. A relatively small amount of sample volume is needed. The sample preparation is very simple. It has a high level of interference control because most of the ICP-MS instruments have triple quadrupoles. This technique is able to detect elements at incredibly low detection limits in a very large analytical range. However, this technique comes with a lot of limitations as well because it is very expensive. To operate the instrument argon gas is required which is also expensive. ICP-MS must be operated with a high level of staff expertise. The ICP-MS room or environment must be clean and in a good state. The air conditioning must be switched on all the time which is expensive [75].

2.9 Application of analytical methods for the extraction of essential minerals in seawater

The demand for lithium in particular has been rising significantly because of its unique properties. However, extracting metal ions such as lithium from seawater using PIMs is not yet economically feasible on a large scale. However, more research is still going on in order to develop more environmentally sustainable methods for metal extraction. **Table 3** provide a summary of the studies that have been conducted in seawater for the extraction of metal ions using analytical techniques. In China they conducted a study where they have extracted lithium and magnesium using the precipitation method. Based on their results obtained, they reported about 99,2% of magnesium extracted while lithium was at 98,5% [76]. The method was never tested on a larger scale to identify potential challenges and deviations that might not be evident in lab-scale experiments. In this study, the experiments were conducted in three different stages and the detailed cost analysis for both stages including the costs of chemicals and energy for evaporation was not mentioned to evaluate economic feasibility. Furthermore, in this study the overall environmental impact such as waste generation was not mentioned as they are byproducts generated after the extraction given the fact that the brine was used. Another similar study was done in China for the extraction of lithium and magnesium. However, the precipitation approach was combined with the solvent extraction approach. The final recoveries obtained for lithium and magnesium were 99% and 67,4% respectively [14]. In this study, the effect of the impurities that might affect subsequent production of lithium were not mentioned.

In Spain they have conducted a study based on metal extraction from seawater using the SPE approach. These metals include Cr, Ni, Cd, Zn, Cu and Pb and their final recoveries obtained were between 92,2% - 110,6% [77]. Another study in Spain was done using PIMs for the extraction of Cr (VI). Their investigation was done using ultrapure water and the recoveries obtained were around 90% [78]. Although these methods seem to be working very well, most of the similar studies have been conducted in artificial seawater if not brine using PIMs in particular. Therefore, it is significant to conduct more studies in real seawater in order to have an idea of how the membranes perform in real-world applications beyond Cr (VI) extraction. Furthermore, based on their findings, it was never mentioned if their technique is scalable for industrial applications. Another study was conducted in China for the separation of lithium from sodium and potassium using polymer inclusion membrane (PIM). In their study, they have used a combination of two different carriers such as thenoyltrifluoroacetone (TTA) and trioctylphosphine oxide (TOPO) as the carrier molecules. Their reasoning of using a combination of two carriers instead of one was that their PIM was not selective for their targeted analytes. Their optimized results showed an initial flux (J_0) of Li(I) as high as 1.04×10^{-2} $molm^{-2}$ h^{-1} corresponding to permeability (P) of $3.62\times 10^{-3}mh^{-1}$ [48]. Their method was working well for the lithium uptake. However, their membrane was never tested in real seawater to investigate its behaviour in real-world scenarios. The trend is that most of these studies are not done in real seawater samples.

Table 3

The selected analytical methods for the extraction of essential metal ions from brine, seawater and ultrapure water.

Metal	Location	Matrix	Analytical technique	Extraction method	Recoveries (%)	References
Mg, Li	China	Brine	AAS	Precipitation	99,2%, 98,5%	[76]
Li, Mg	China	Brine	ICP-AES	Precipitation combined with (SE)	99%, 67,4%	[14]
Cr, Ni, Cd, Zn, Cu, Pb	Spain	Seawater	ICP-MS	SPE	92,2%- 110,6%	[77]
Cr (VI)	Spain	Ultrapure water	ICP-AES	PIM	90%	[78]
Li (I), Na(I), K(I)	China	Ultrapure water	ICP-OES	PIM	-	[48]

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CHAPTER 3

This chapter presents the aim and objectives of this study. It further highlights the problem statement and motivation.

3 AIMS AND OBJECTIVES

3.1 Aim of the study

The overall aim of this study was to develop techniques that have low costs, do not require high operation and maintenance costs and are also environmentally friendly which include polymer inclusion membranes (PIMs) for the extraction of valuable minerals from seawater.

3.2 Objectives

- To develop and optimise extracting methods based on polymer inclusion membrane (PIM). The targeted metals include calcium, magnesium and lithium. The membrane was prepared in the lab using commercial base polymer (CTA), carriers (TTA and TOPO) as well as the plasticizer (2-NPOE).
- To synthesize and optimise PIM parameters that governs the extraction process such as PIM composition, sample pH, time effect and concentration of the acceptor solution for the extraction of mineral salts.
- To compare the performance of the prepared membrane both in spiked ultrapure water and to optimised real seawater.
- To understand the carrier selectivity towards different minerals in seawater by performing density functional theory (DFT) studies where possible.

3.3 Hypothesis

The developed PIM-based approach will result in a highly selective and effective approach for the recovery of lithium, magnesium and calcium from seawater samples.

3.4 Problem statement

The demand for lithium is increasing significantly, driven primarily by its critical role in powering modern technological products including cell phones, energy storage systems and electric vehicles (EVs). Magnesium is also crucial in automotive industries. The essential minerals are mostly recovered from land-based ores. However, land mining is not environmentally sustainable and causes pollution because it involves drilling and high energy usage. Furthermore, mining lithium from seawater is difficult because of the low concentration of lithium regardless of the salinity. Current lithium extraction technologies are not suitable for this purpose due to their slow adsorption rate, low capacity and use of acid for desorption which may have a negative impact on the environment. Despite the vast potential of seawater as a source of valuable minerals, the current extraction methods are often expensive, energy-intensive and are not environmentally sustainable. Additionally, the existing extraction techniques are not sustainable in the long-term application. Developed countries like China and Europe are the leading producers of lithium followed by African countries such as Zimbabwe. South Africa (SA) is not as advanced as those leading countries. South Africa is still behind in terms of the status of minerals in seawater compared to leading countries in the field of seawater mineral extraction. Countries like China and various European nations have made significant advancements in lithium extraction technologies and have established robust infrastructure for processing seawater minerals. In contrast, South Africa has lagged due to limited infrastructure, resources and specialized analytical techniques necessary for efficient extraction from seawater. Based on the mentioned gaps above therefore, there is a need for improved, environmentally friendly and efficient extraction technologies for seawater extraction and the specific challenges faced by South Africa in terms of the infrastructure.

3.5 Motivation

Interestingly, seawater is considered a significant and promising resource for lithium and other essential metals since it is economically viable and environmentally sustainable. There is a need for innovative extraction techniques that are both cost-effective and environmentally friendly. This study aims to address these challenges by developing and optimizing polymer inclusion membranes (PIMs) for the time efficient, low-cost, selective, easy to process and environmentally friendly extraction of valuable minerals from seawater. By bridging the existing knowledge gaps in cost-efficiency, environmental impact, operational simplicity and selectivity. This study seeks to provide a sustainable extraction method. Subsequently, finding a suitable method on how to selectively extract lithium and other essential metals from seawater can boost our economy as well as play a huge role in reducing pollution and global warming. This is because lithium is highly used in electric vehicles. Therefore, this will help to fuel and shape future technology and industry as lithium demand is continually rising and that can reduce dependency on other countries and enhance our technological growth. The study aims to improve analytical techniques for better extraction of essential minerals. In this context, the present study considered the extraction of five major essential of mineral in both simulated and real seawater samples using PIMs.

CHAPTER 4

MANUSCRIPTS

This chapter presents the three manuscripts for consideration in the examination of this thesis. Tables and figures are also included in all the manuscripts as per the requirements of this thesis. The page numbers in all the manuscripts were also formatted to make these manuscripts suitable for submission for this thesis. However, the highlights as well as the graphical abstracts from all three manuscripts were not included here in this chapter.

4 Paper 1

The title of this paper says, 'Experimental and theoretical optimization of polymer inclusion membrane technique for calcium and magnesium extraction in seawater' This paper presents the optimisation of polymer inclusion membrane (PIM) in spiked ultrapure water and their application to real seawater samples for the extraction of magnesium and calcium. The density functional theory (DFT) studies were also carried out to study the interaction of carrier molecules with targeted metal ions. Due to the increase in economic importance of minerals particularly lithium and magnesium, this has led to an increase in demand for extraction methods. The rock ore mining is associated with a lot of pollution in the environment and health risks to the miners. The traditional methods for mineral extraction from seawater are challenging when it comes to cost, selectivity and efficiency. In most of the previous studies based on PIMs, the researchers were not testing their membranes in real seawater samples, and they were not using any computational modelling. This study develops and optimizes PIMs as a novel approach for the extraction of minerals in seawater to address these challenges. The density functional theory (DFT) analysis was also applied to understanding the mechanism of transport of the metals.

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Experimental and theoretical optimization of polymer inclusion membrane technique for calcium and magnesium extraction in seawater

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ABSTRACT

Mineral salts are in greater demand because of their economic importance. This work reports the usage of polymer inclusion membranes (PIMs) to extract minerals from seawater. The developed PIM was made of cellulose triacetate (CTA), plasticizer and carriers which are essential for the transport of calcium and magnesium across a membrane. This membrane was investigated to see if it could be used as a pilot study for possible commercial extraction of essential metals from seawater. The optimisation of various parameters was carried out in spiked ultrapure water using targeted analytes. The optimum membrane composition was found to be 60 wt % of the carriers, thenoyltrifluoroacetone and trioctylphosphine oxide (1: 1): 30 wt % (CTA): 10 wt % nitrophenyl octyl ether plasticizers with a sample pH of 8.5 and 0.05 M HCl as receiver solution. The optimised conditions were then applied to seawater. The selectivity for the extraction in seawater was nearly like spiked deionised water and was as follows; $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$. The selectivity was calculated based on the concentrations obtained from inductively coupled plasma optic emission spectroscopy. The order of selectivity was not the same as obtained from density functional theory analysis which followed the order of $Mg^{2+} > Ca^{2+} > Li^{+} \approx Na^{+} > K^{+}$. The study contributes to finding appropriate technologies that exploit the blue economy.

Keywords:

Polymer inclusion membrane; Trioctylphosphine oxide; Thenoyltrifluoroacetone; Density functional theory; Membrane transport

4.1. Introduction

The mining of mineral salts in oceans has been considered economically important. Seawater has a complex matrix due to the presence of a variety of metals in high concentrations such as Na^+, Mg^{2+}, Ca^{2+}, K^+ and Sr^{2-} and low concentrations of Li^+ [1]. There are also significant anions that are present in seawater, which include Cl^-, SO_4^{2-} and Br^- [2]. These metals are useful in several applications such as pharmaceuticals, agricultural industries. For example, calcium carbonate ($CaCO_3$) is used in the manufacturing of plastics, chalk, paper, thermostats, etc [3]. Magnesium carbonate ($MgCO_3$) is another crucial mineral salt that is widely used in pharmaceuticals to produce medicines for patients who have ulcers, gastrointestinal symptoms of dyspepsia, heartburn and constipation it acts as an antacid and laxatives as it neutralizes the stomach acid [4]. The estimated concentrations of major components in seawater include calcium and magnesium which are approximately 411 mg/L and 1290 mg/L, respectively. Furthermore, among other metal ions, sodium is known to have an extremely high concentration roughly 10800 mg/L. The estimated concentrations of potassium and lithium in seawater are 380 mg/L and 0.17 mg/L, respectively [5,6].

The extraction techniques that have been commonly used for the recovery of these mineral salts include solvent extraction, molecular sieve adsorption, precipitation, nanofiltration and solvent impregnated membrane separation [7]. Some of these separation technologies have disadvantages as they require excessive amounts of organic solvents. Membrane technology has been considered to be the most interesting extraction method among other processes because it is easy to use, environmentally friendly and there is less waste generated during its application, resulting in its classification as a non-toxic process in this regard [8]. Polymer inclusion membranes (PIMs) are frequently utilised in a wide range of separation processes which include the extraction of metals, anions, drugs and other environmental contaminants from aqueous media [9]. PIM is a highly promising extraction method for mineral extraction due to its higher stability, efficiency, permeability and selectivity in comparison to other techniques such as supported liquid membranes (SLMs) [8,10].

PIMs consist of base polymers such as polyvinyl chloride (PVC) or cellulose triacetate (CTA) [11]. These base polymers and carriers are ideal starting materials during the synthesis of the PIM [10]. They serve as the foundation of the PIM which gives it its mechanical strength. The carrier is in charge of binding and transportation of the targeted minerals by diffusing over the PIM from the feed to the receiver region forming a complex with the analytes. Some carriers have plasticizing qualities which increase the flexibility of the PIM. Consequently, other membranes are being synthesized without the use of plasticizers [11]. The plasticizer provides the membrane with flexibility and function as a solvent where the carrier molecule can disperse during the transportation of the analytes across the membrane. During membrane synthesis, a plasticizer helps to dissolve other components whereas during the transportation of metal ions across the membrane it enables the carrier molecules to be well-distributed and mobile within the polymer matrix. It provides softness and minimizes intermolecular interactions which then result in higher PIM permeability [12,13]. The plasticizers are known to be robust compounds that do not leach from the prepared PIMs throughout metal transportation [12]. The limitations of PIM applications include slow mass transfer which results in longer extraction times [7,9,11]. The carrier molecule selection is crucial because it affects the selectivity and kinetics of the transportation of the analytes across the feed to the receiver solution. The mechanism transport of the PIM depends on the type of the carrier as the PIM may contain an acidic or basic type of carrier. In this case the cations or anions will migrate from the feed solution where there is a high pH to the low pH region receiver phase [14,15]. Additionally, the use of PIMs on a laboratory scale is promising, but there is little literature on their applications at an industrial scale [8].

This work focused on the development and optimization of a PIM technique for the extraction of calcium and magnesium as well as other competing species, which include lithium, potassium and sodium from seawater. Previous work has investigated the extraction of lithium, sodium and potassium in spiked samples using similar carriers as in this study but no real seawater samples were tested [7]. Another study [17] used TTA and TOPO as carriers for solvent extraction of lithium ions from an aqueous solution and tested them in seawater. However, the transportation mechanism in solvent extraction is much different from the polymer inclusion membrane. In this context, the present study considered the extraction of a wide range of mineral salts in both simulated and real samples (seawater) using polymer inclusion membranes and with TTA and TOPO as carriers. Furthermore, the experimental work reported herein was complemented by a computational modelling approach through density functional theory (DFT) simulations that studied the selectivity of the two carrier compounds, thenoyltrifluoroacetone (TTA) and trioctylphosphine oxide (TOPO) (**Fig. 1**) towards the extraction of several ions such as Mg^{2+}, Ca^{2+}, Li^{+}, Na^{+}, and K^{+} in seawater.

This means the overall objective of the computational evaluation was to establish the binding ability of the carriers towards the selected metal cations to support experimental work. During the computational investigation, it was important to consider the number of water molecules that hydrate the individual ions, at least within the first solvation layer. For example,

Li^+ is understood to be hydrated by a maximum of four water molecules [18], whereas Mg^{2+}, Ca^{2+}, Na^+ and K^+ are all hydrated by about 6 water molecules in the first hydration shell [19,20]. On the other hand, Ca^{2+} is coordinated by 6 to 10 water molecules within the first solvation layer [21,22]. Therefore, the lower number of hydration water molecules was applied in this study to compare the results with other metal cations that are investigated in this work, and which have a maximum of 6 water molecules coordinated to them. Therefore, to the best of our knowledge this is the first study of its kind to investigate the uptake of a variety of minerals by PIM in seawater, with its results being further evaluated theoretically through the application of DFT to comprehensively understand the uptake mechanism. Furthermore, this work was further applied on a larger scale which is presented in **paper 3**. This was to investigate if the membrane can be utilised commercially for bulk extraction.

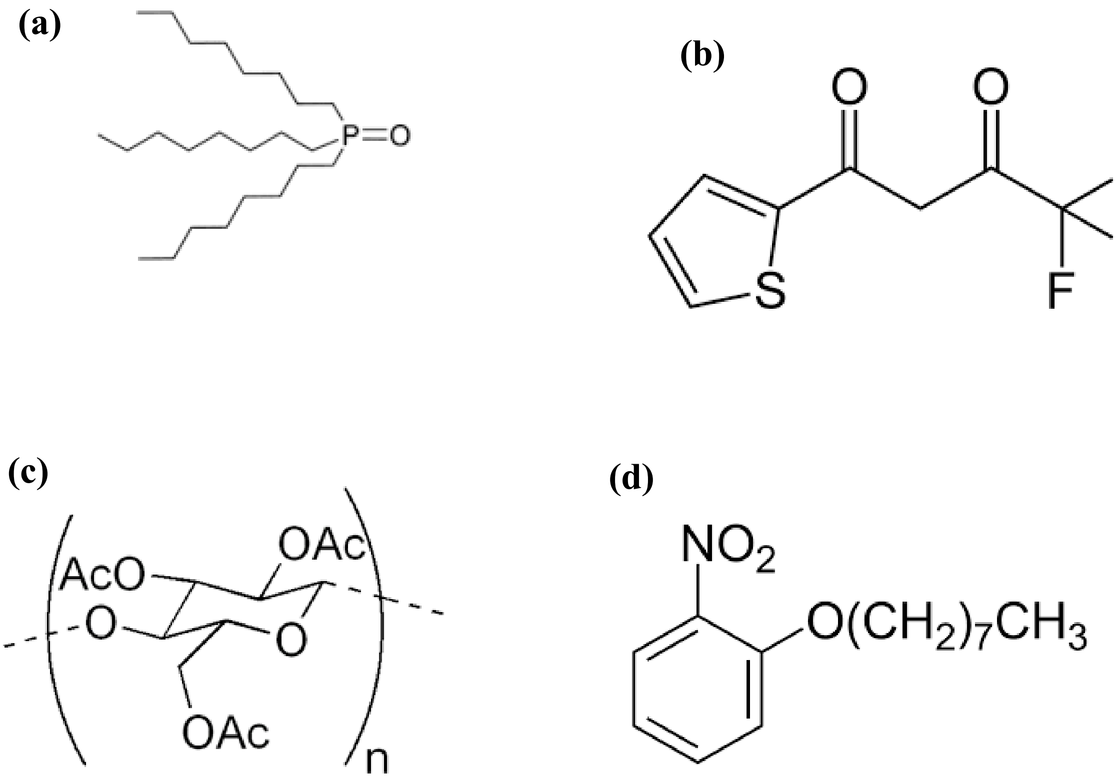


Fig. 1. Structures of the reagents used for PIM synthesis (a) trioctylphosphine oxide (TOPO), (b) thenoyltrifluoroacetone (TTA), (c) cellulose triacetate (CTA) and (d) 2-Nitrophenyl octyl ether (2-NPOE).

4.2 Materials and methods

4.2.1 Reagents and chemicals

All chemicals were supplied by Sigma Aldrich (Johannesburg, South Africa) as a pure analytical grade. These chemicals include CTA, TTA, TOPO, 2-Nitrophenyl octyl ether (2-NPOE), nitric acid (55%), dichloromethane (DCM) (99, 9%) HPLC grade, hydrochloric acid (HCl) (32%), mineral salts such as lithium carbonate (Li_2CO_3), magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$), sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3).

4.2.2 Instrumentation

In this study, various techniques were used for the analysis of targeted metals and characterization purposes. For example, the functional groups present in the synthesized PIMs were determined using Fourier transformed infrared spectrometry (FTIR) from Bruker (Johannesburg, South Africa) between the scale of 4000–400 cm^{-1}. The spectra were obtained using 32 scans at a resolution of 4 cm^{-1}. The morphology of the PIM was investigated using the scanning electron microscope (SEM) (Zeiss Evo 50, Oberkochen, Germany). All pH measurements were performed with a Five Easy FE20 pH meter from Mettler Toledo (Johannesburg, South Africa). An analytical top balance from Ohaus (Johannesburg, South Africa) was used to accurately weigh the mass of all the PIM components. The ultrapure water used in this study was collected from a Milli-Q-RO4 water system at Millipore (Bedford Massachusetts, USA). Metal analysis was performed with inductively coupled plasma-optical emission spectrometry (ICP-OES) from Spectro Genesis (Kleve, Germany).

4.2.3 Preparation of polymer inclusion membrane

Polymer inclusion membrane containing CTA as the base polymer and TTA: TOPO as carriers was prepared using the previously reported method [7] with modifications. Initially, different PIMs with different compositions of base and carriers were prepared shown in **Table 1**. The concentration of base polymer (CTA) ranged between 30 wt% - 60 wt%. The investigated ratios for carrier molecules; (TTA: TOPO) were 0:1, 1:1 and 2:1. One of the PIMs contained a plasticizer (2-NPOE) with a concentration of 10 wt%. The choice of the plasticizer was based on previous research [24] which found NPOE to be ideal compound with low viscosity and a high dielectric constant. Different carriers were used to enhance the selectivity because each carrier has varying affinities for different ions thereby leading to more efficient, selective and cost-effective extraction processes. All the prepared compositions with a total mass of 2 g were fully dissolved in 20 mL of DCM at room temperature. The resultant mixture was stirred for five hours to make a uniform solution. The resulting solution was transferred into a glass Petri dish (Sigma Aldrich, South Africa) covered with filter paper to avoid contamination from dust particles. The mixture was left to evaporate over 12h at room temperature until the evaporation of the solvent was complete. The synthesized membrane was transparent and homogeneous (**Fig. 2**).

Table 1

Different PIMs with different compositions containing carriers, base and plasticizer

Experiment number	**Carrier amount (g)**	**Ratio (TTA: TOPO)**	**Base amount (g)**	**Plasticizer amount (g)**	**Composition (wt.%) (Carrier: Base: Plasticizer)**
1	1,2	1:1	0,6	0,2	60:30:10
2	1,2	2:1	0,8	0	60:40:0
3	1,2	1:1	0,8	0	60:40:0
4	1,2	0:1	0,6	0,2	60:30:10
5	0,2	2:1	1,6	0	10:80:10

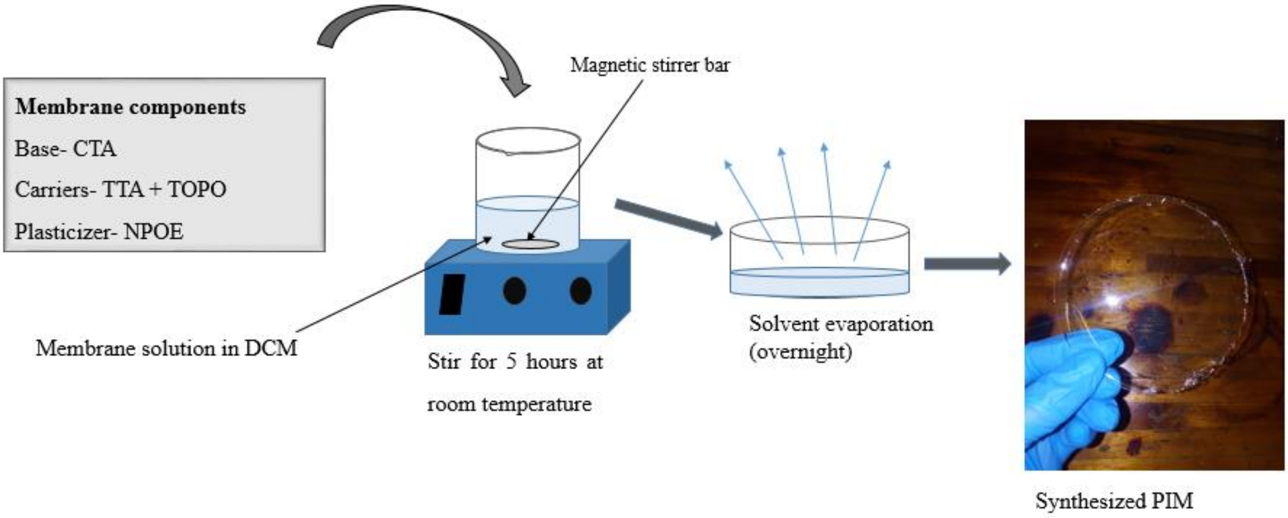


Fig. 2. Schematic representation showing the preparation of PIM with its components.

4.2.4 Statics experimental design

The prepared PIM was used in the extraction of both calcium and magnesium from simulated seawater. This was done using the extraction devices which are displayed in **Fig. 3**. The prepared membranes were sliced into small circles and inserted into a screw cap's window opening. The fabrication of the devices was performed in the physics department workshop of Witwatersrand University (Johannesburg, South Africa). To ensure sufficient extraction of both calcium and magnesium, various extraction conditions were optimized. These parameters include the composition of the PIM such as the base polymer, carriers and plasticizer, the pH of the feed solution, the concentration of the receiver solution and the extraction time.

Fig. 3. A representation of receiving chamber for a solution (a), screw cap showing a window opening where the membrane is placed (b) as well as closed passive sampler device (c).

4.2.5 Statics experiments using PIM

The optimized PIM composition was used for the analysis of calcium and magnesium in seawater samples. The extraction process was carried out by deploying the extraction devices into the seawater for 30 days while performing the extraction at room temperature. Statics experiments were carried out using extraction devices made of machined polytetrafluoroethylene (PTFE) based holders (**Fig. 4)**. The screw cap diameter was measured to be 21 mm and the receiver solution chamber was measured to be 24 mm in length. In these experiments, the main parameters were optimized using an extraction device and a glass beaker. The feed solution in the glass beaker contained ultrapure water which was spiked with 15 mg/L each of $MgCO_3$, $CaCO_3$, Li_2CO_3, K_2CO_3 and Na_2CO_3 salts. The synthesized PIM was used as a barrier between the feed phase from the receiving phase. The feed solution contained 2 L of the spiked ultrapure water which was stirred at 200 rpm at room temperature. The receiver solution chamber had 5 mL of the HCl solution. The pH of the feed solutions varied between 8.5 and 10. The real seawater samples were subjected to the optimized PIM conditions. Sample collection in the receiving phase was carried out in triplicates for the analysis of target analytes using the ICP-OES instrument.

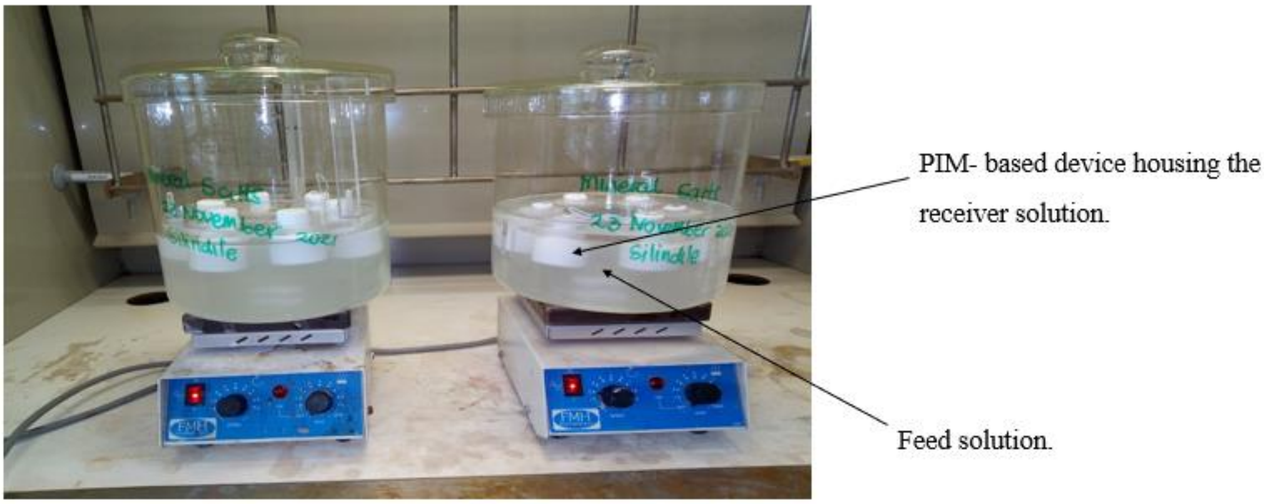


Fig. 4. Experimental setup for PIM based deployment.

4.2.6 Computational approach

The calculations for the isolated molecule and the interacting species were performed using the DFT approach by utilising the M06-2X meta-hybrid functional along with the 6-311++G (3df,2p) basis set. The M06-2X function is known to perform when optimising geometric structures, and relative energies and in the estimation of intermolecular interactions for systems that are scattered and ionic hydrogen bonding interactions [25,26]. The basis set selected includes both the polarisation and diffusion functions sufficient to account for the nature of the species included within the systems under study. The intermolecular interaction energy between a carrier molecule and the metal cations is estimated using the equation:

$$E_{inter} = E_{(PIM+xH_2O+M^{n+})} - E_{PIM} - E_{xH_2O} - E_{M^{n+}}$$

Where E_{PIM} stands for the energy of the carrier molecule, e.g., TOPO and TTA; $E_{M^{n+}}$ is the energy of the isolated metal cation, E_{xH_2O} is the energy of the water molecules (with x being the number of the water molecules for a given system) and $E_{(PIM+xH_2O+M^{n+})}$is the energy of the complex consisting of the carrier molecule, hydrating water molecule and the metal cation. The greater the interaction energy the stronger the interactions between the carrier molecule and the metal cation. The charge on the metal cation is estimated using the natural population analysis approach. The calculations were performed using the Gaussian 16 revision C [27]. However, the optimised structures were drawn using the Gauss View programme.

4.3 Results and discussion

4.3.1 Characterisation of the PIM

4.3.1.1 FTIR

Various PIMs were prepared with varying compositions. The first PIM with a composition of 60:30:10 (0:1) came out as powder and was never tested on the FTIR. The second and third membranes with a composition of (60:40:0) (1:1) and (60:30:10) (1:1) respectively were observed to be homogenous. However, PIM (60:40:0) (1:1) was not as clear as PIM (60:30:10) (1:1). All the membrane's functional groups were examined, and the results appeared to be similar to the reported spectra. Furthermore, it was discovered that the fourth PIM with a composition of (10:80:10) (2:1) was found to be non-uniform, appeared opaque and and had a very hard texture. As a result, the PIM with the composition (60:30:10) (1:1) was used throughout the study.

The FT-IR spectra of the synthesized PIM were obtained (**Fig. 5**). A comparison of the spectra was conducted between the spectrum attained for the membrane before the extraction and the same membrane after the extraction process was conducted over the course of 30 days. The stretching at 2923 cm^{-1} and 2856 cm^{-1} (**Fig. 5** (a-c)) corresponds to the asymmetric and symmetric stretching vibrations of CH_2 for TOPO respectively [7,8,10]. The vibrational modes at 2965 cm^{-1} (**Fig. 5** (a-c)) represent the CH_3 band for TOPO. The observed characteristic bands of the carbonyl groups 1641 cm^{-1} to 1745 cm^{-1} shown in **Fig. 5** (a-c) represent the base polymer (CTA) and carrier (TTA) which were used as carriers during the preparation of PIM. The main functional group of the plasticizer such as ($-NO_2$) is observed in all the spectra at 1526 cm^{-1}. The stretching observed in all the spectra at 1149 cm^{-1} corresponds to the P=O group for TOPO. Moreover, the C-H band appearing in **Fig. 5** (a-c) at 721 cm^{-1} corresponds to the long alkyl chain [7,8]. After observing the membrane bands before extraction, the results obtained are similar to those that have been reported by [7,10]. The results obtained are evidence that all the membrane components remained attached to the polymeric matrix without undergoing any chemical change. The band observed in **Fig 5** (a and b) for the ester group of the 2-NPOE appeared at approximately 1108 cm^{-1} seemed to have a slight shift combining a bit with the P=O peak for TOPO to produce one peak after the extraction in seawater shown in **Fig 5** (c). This may imply that the P=O group from the trioctylphosphine oxide carrier is one of the main functional groups that plays a huge role during the transport mechanism which might have resulted in its acetylation. This might be resulting from the observed spectral shifts are more likely due to complex formation and interactions [28]. In addition, the OH group with a vibration at around 3430 cm^{-1} corresponds to the asymmetric stretching in the TTA molecule [7].

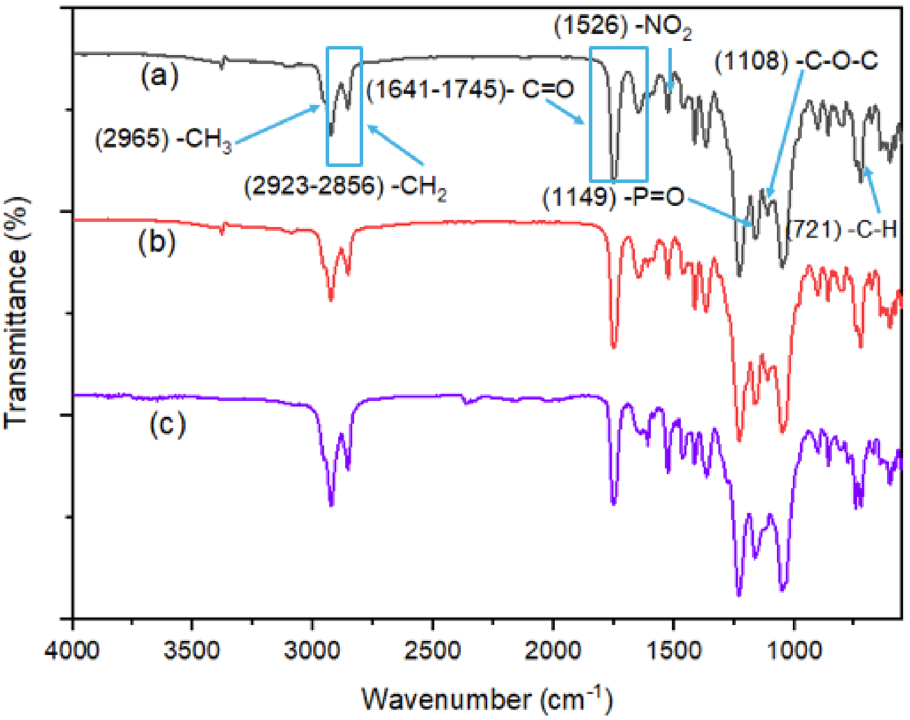


Fig. 5. FT-IR spectra of the (a) PIM before extraction of metal ions, (b) PIM after extraction of metal ions in spiked ultra-pure water and (c) PIM after the extraction of metal ions in seawater after 30 days using the synthesized PIM.

4.3.1.2 Scanning electron microscopy (SEM) analysis of the membrane morphology

The morphology of the PIM prepared with 60 wt % TTA and TOPO (1: 1): 30 wt % CTA: 10 wt % (2-NPOE) was investigated using SEM. This was done before the extraction of targeted analytes. In the present study, SEM images was ensured by performing the coating with gold-palladium as performed in another study [29]. The use of gold coating prevents charging of samples. The resulting SEM images of the prepared PIM are shown in **Fig. 6**. The membrane surface showed itself to be dense with the appearance of pores and a sponge-like appearance [28]. The membrane had pores because CTA is known to be hydrophilic, but the addition of other components such as plasticizers or carriers can alter its properties. Because the aqueous solution was present on both sides of the membranes, mainly in the feed and acceptor phases, whether the membrane developed pores on the surface or cross section, those were primarily for the distribution of the carriers and plasticizer [30]. The cross section appeared to have finger-like structures that are known to act as mechanical support for the membrane. These finger-like structures can grow only in the cast solution as the thickness of the fluid layer reduces during solvent evaporation prior to leaching increase. The assembly of such structures is generally associated with a high rate of precipitation [31]. In **Fig. 6 (b)** PIM appears to be dense with no visible porosity. This could be a result of the increased amount of carrier molecules intertwined in the pores of the base polymer [7].

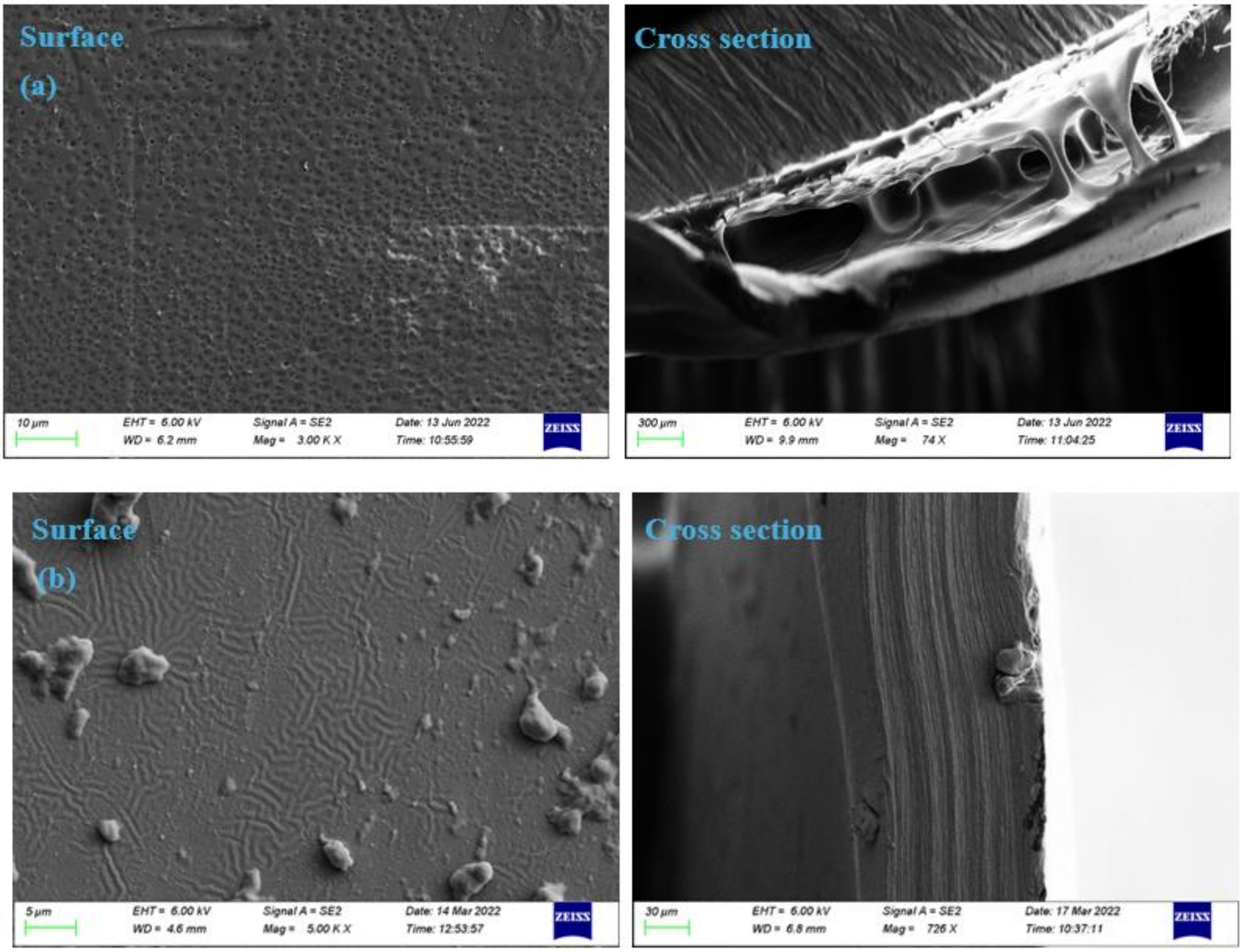


Fig. 6. SEM micrographs for a synthesized PIM with the components of (a) 60 wt % TTA and TOPO (1: 1): 30 wt % (CTA): 10 wt % (NPOE) plasticizer and (b) 60 wt % TTA and TOPO (2: 1): 40 wt % (CTA) before extraction.

4.4 Optimisation of the PIM method using spiked ultrapure water

4.4.1 PIM composition and pH effect

Different compositions of starting materials to produce PIMs as shown in **Fig. 7** were studied to determine the best PIM that can selectively extract mineral salts from seawater at high concentrations. The membrane was observed to be stiff and brittle when the carrier molecules concentration was less than 30 wt%. The optimum composition was found to be 60 wt % of the carriers, TTA and TOPO (1: 1): 30 wt % (CTA): 10 wt % (2-NPOE) plasticizer. This composition displayed high selectivity for magnesium followed by calcium. It was noticed that an increase in the carrier concentration resulted in higher metal uptake. The addition of the plasticizer also showed a great influence in the extraction which was evidence that the membrane was flexible, thus, resulting in good permeability. The affinity between the metal ions and the carrier may increase if the carrier concentration is high due to the proximity effect. This means that the metal uptake is enhanced by increasing the carrier composition thereby increasing the number of accessible binding sites. Moreover, increasing the plasticizer improves the flexibility and diffusion within the membrane [7]. On the basis of the obtained results, PIM containing 60 wt% carrier molecules (TTA and TOPO), and 30 wt% base polymer CTA and 10 wt% plasticizer (2-NPOE) was selected for the subsequent experiments.

The extractant TTA/TOPO is reported to have good interaction when combined for the removal of metal ions in alkaline conditions [7]. The extraction process appeared to be more selective for Mg^{2+} and Ca^{2+} at pH 8.5. To further optimize the extraction procedure, the pH of the feed solution was changed to 10. This means the pH value of the feed solution was then maintained between 8.5-10. The pH 8.5 appeared to be more conducive than pH 10. This would mean that high pH values resulted in metal ions forming a complex with OH^-, thus promoting precipitation, thereby causing a decrease in metal ion uptake in seawater [32]. Since seawater has a pH of approximately 8.5, a compromise pH of 8.5 was chosen for further experiments.

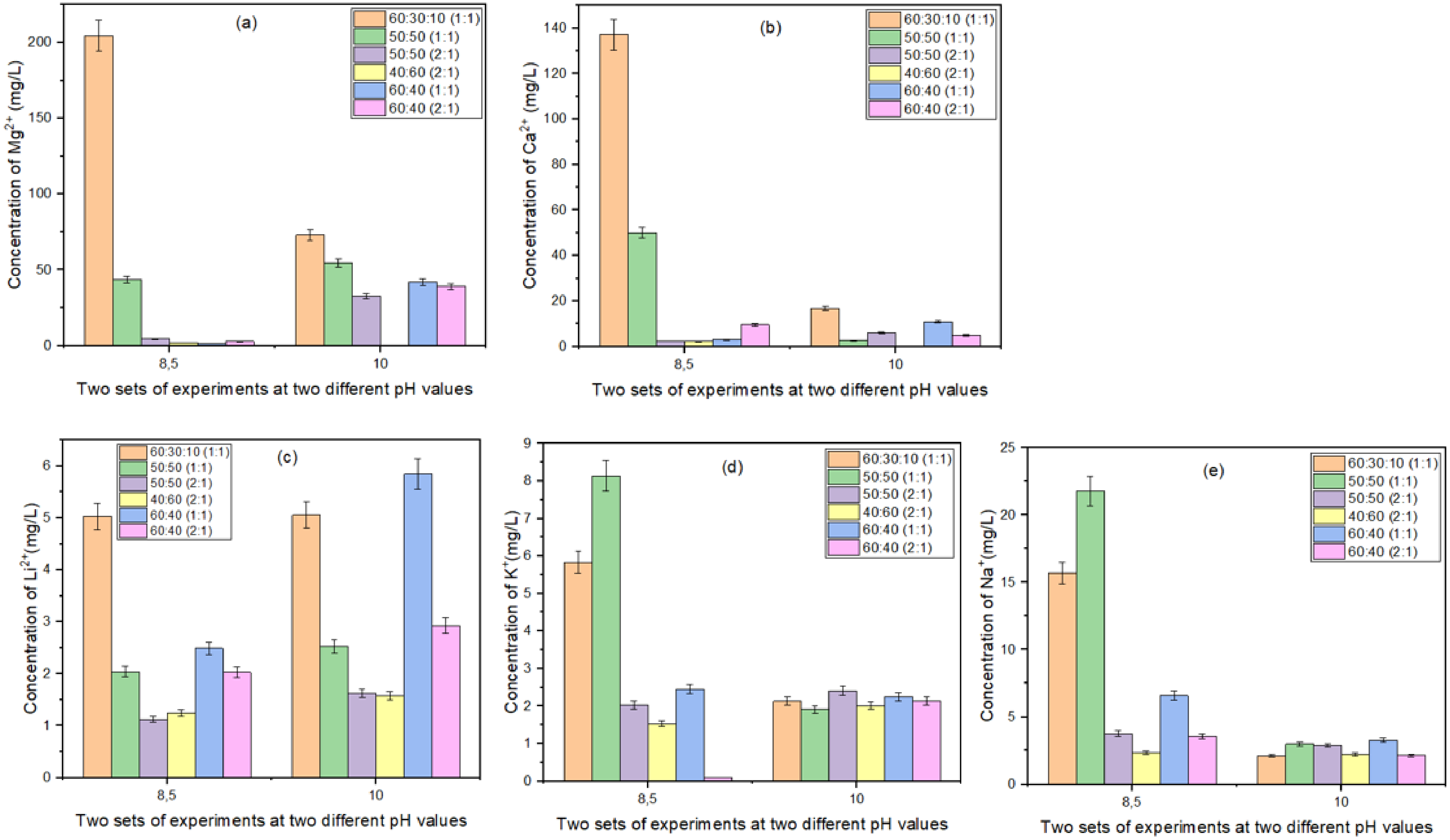


Fig. 7. PIMs with different compositions for the extraction of magnesium (a), calcium (b), lithium (c), potassium (d) and sodium (e) The numbers which makes the total of 100% represents wt% carriers: base: plasticizer in different ratios. The error bars are ±SD (standard deviation).

4.4.2 The effect of concentration of the receiver solution and extraction time

The concentration of the receiver acid has a substantial effect on the transport rate of metal ions is crucial to investigate its influence to ensure that the process is efficient. The effect of the concentration was investigated using 60 wt % TTA and TOPO (1: 1): 30 wt % CTA: 10 wt % NPOE. The aqueous phase of the receiver region was varied between 0.05 M HCl - 1 M HCl. In **Fig. 8**, it was observed that the PIM extracted Mg^{2+} and Ca^{2+} ions more effectively when the concentration of the receiver solution was 0,05 M HCl compared to 0,1 M HCl. The higher concentrations of the receiver solution resulted in low extraction for both magnesium, calcium, lithium, potassium and sodium. However, other minerals of interest were recovered at very low concentrations. A similar trend was observed elsewhere [7], with an increase in the concentration of the receiver solution resulting in a decrease in the extraction efficiency. The transport mechanism in this case is coupled counter transport where the carrier reacts with the target analyte in the feed at the interphase, diffuses to the receiver side and at the interphase releases the analyte. The carrier then reacts with a proton (H^+) in the acceptor phase and diffuses back to the donor phase interphase where the proton is released. The process is shown in **Fig. 9** when an acidic carrier is used. Thus, a more dilute acid that has a higher percentage of hydrogen ions in the solution is expected to give much better extraction as this is the driving force for the extraction. A different study also had similar findings whereby the low concentration of receiver solution resulted in a maximum transport rate [33]. This means an increase in the concentration of acid does not increase effectiveness of metal ion transport.

In this study, the optimum acid concentration adopted for the extraction of minerals was 0.05 M HCl. In this case, a lower concentration of the acid was deemed necessary for cost and safety reasons [7]. Furthermore, the application of HCl helps reduce the carrier's leakage risk from the membrane matrices and maintains the stability of the PIMs [34]. The effect of the extraction time on the extraction process was monitored between days 1 and 30. The extraction efficiencies for tested metals were increasing from day 1 to day 13, however, they seemed to be at equilibrium from day 13 to 25. This could be because the driving force which is the hydrogen ions in the acceptor solution or target analytes in the feed were depleted [35]. A similar study was observed by [36] whereby their membrane transport was shown to be at equilibrium because the uptake was constant for a certain period during the extraction of metals using PIM. Hence, day 13 was chosen as the optimum time for the extraction of minerals. This was necessary as the longer extraction times tend to promote fouling which is a major challenge for membrane-based extraction processes [37,38].

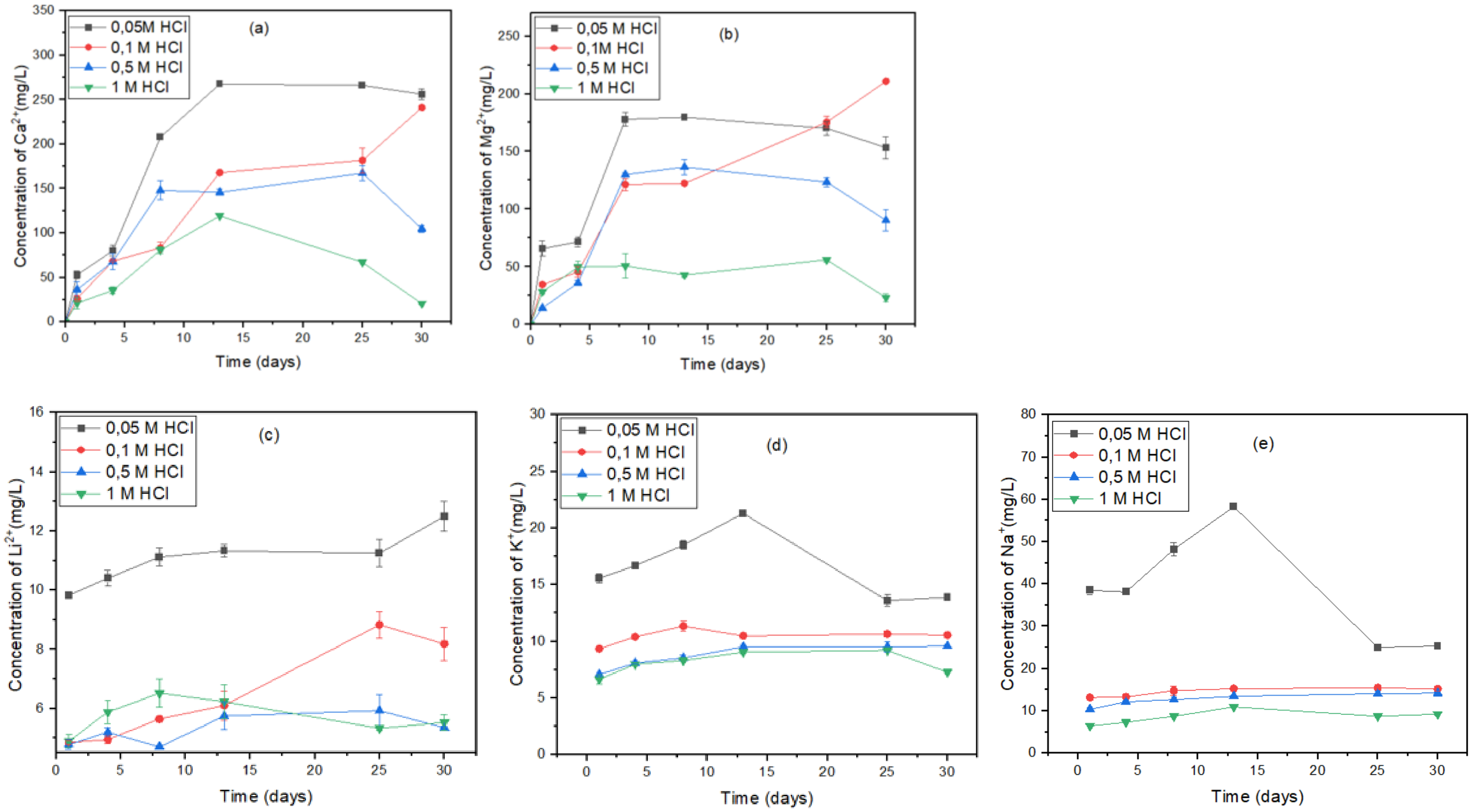


Fig. 8. Optimum PIM with composition of 60 wt.% (TTA+TOPO): 30 wt.% (CTA): 10 wt.% (2-NPOE) with concentrations varied for the extraction of magnesium (a), calcium (b), lithium (c), potassium (d) and sodium (e). The error bars are ±SD (standard deviation).

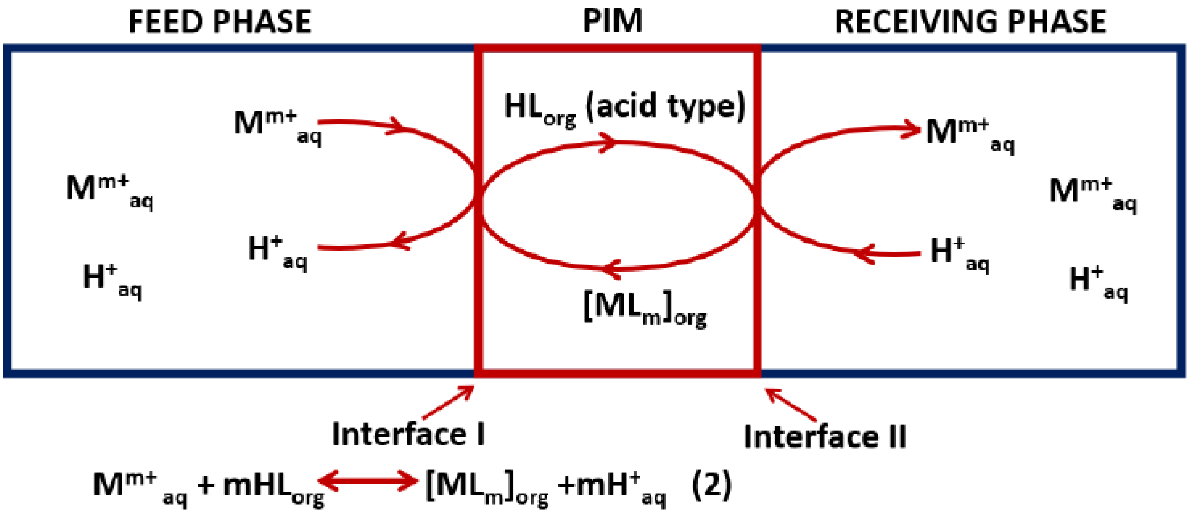
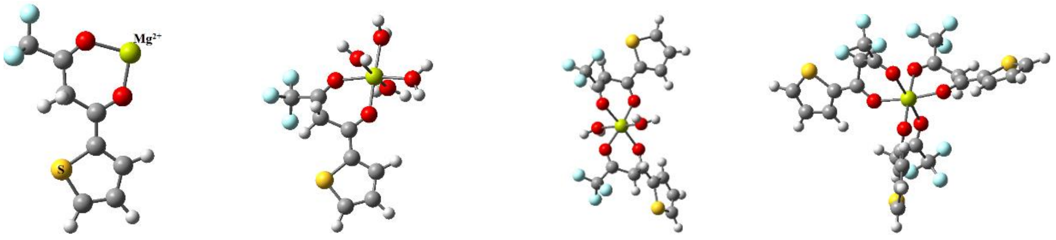


Fig. 9. An illustration showing a counter-coupled transport mechanism with acid type carrier [29].

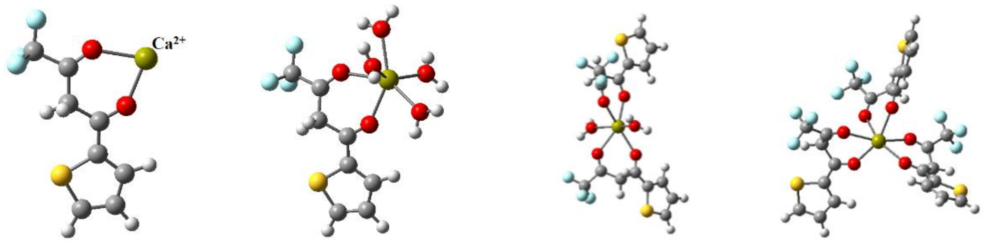
4.4.3 Computational simulation studies to investigate carrier M^{n+} interaction structures and binding energies toward Mg^{2+}, Ca^{2+}, Li^{+} Na^{+} and K^{+} metal ions

The optimised complexes for carriers with Mg^{2+}, Ca^{2+}, Na^{+}, Li^{+} and K^{+} cations species are shown in **Fig. 10** for TTA, **Fig. 11** for protonated carrier (HTTA) and **Fig. 12** for TOPO. The binding energies, M^{n+} ···TOPO and M^{n+} ···TTA bond distances are stated in **Table 2** for TOPO and **Table 3** for both TTA and HTTA. Both carriers show a stronger selective tendency towards chelation and eventual transport of M^{2+}cations than the M^{+}cation species. This factor is demonstrated by both the higher binding energy and greater M^{n+}charge dissipation when M^{2+} cation is used than when M^{+} is used. Among the M^{+}cation species, TOPO tends to prefer chelation of Li^{+} to that of K^{+} and Na^{+}. This result is consistent with previously reported experimental results [9]. The TTA species also tends to chelate Li^{+} much stronger than K^{+}. These findings show that the chelation ability of chosen carriers is determined by the atomic nuclear shielding of cation. The stronger the nuclear shielding the lesser the chelation ability of the carrier towards the cation. When an acidic environment is taken into consideration, analysis of the binding energy strength makes it possible to conclude that the HTTA species is a better chelator of the M^{n+} cation than TTA. This result is also consistent with previous experimental findings [39] as well as the experimental results reported herein on the system under investigation. Among the alkali earth metals, the interaction of PIM with Mg^{2+} results in stronger interactions than Ca^{2+} cations which is also consistent with previous experimental findings [34].

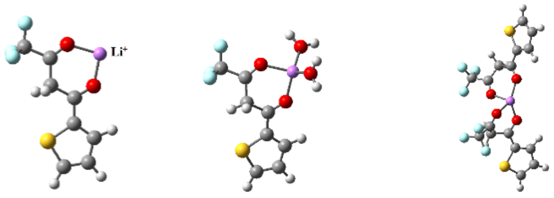
The binding energies for the 2:1 and 3:1 carrier: cation ratios are higher than in the 1:1 carrier: M^{n+} stoichiometric ratio while the charge on the M^{n+} is lower than in the 1:1 carrier: M^{n+} stoichiometric ratio, which suggests that high concentrations of the carrier favour stronger chelation of the metal cations, at least for the M^{2+} ions. A comparison of TOPO and TTA carriers in terms of their ability to bind the metal cations suggests that TOPO is a better metal cation chelator than TTA or protonated thenoyltrifluoroacetone (HTTA).



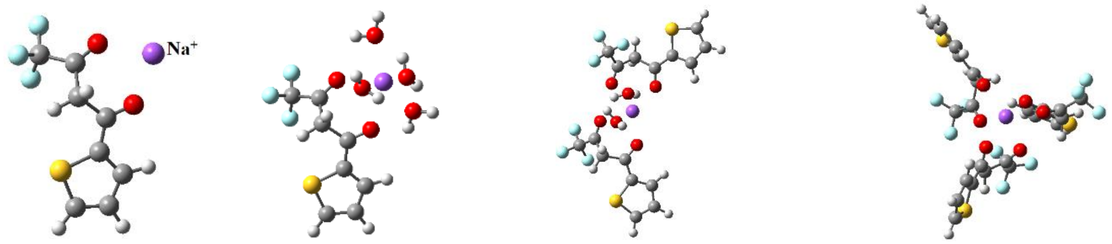
TTA: Mg^{2+} TTA: $Mg^{2+}(4H_2O)$ 2TTA: Mg^{2+} $(2H_2O)$ 3TTA: Mg^{2+}



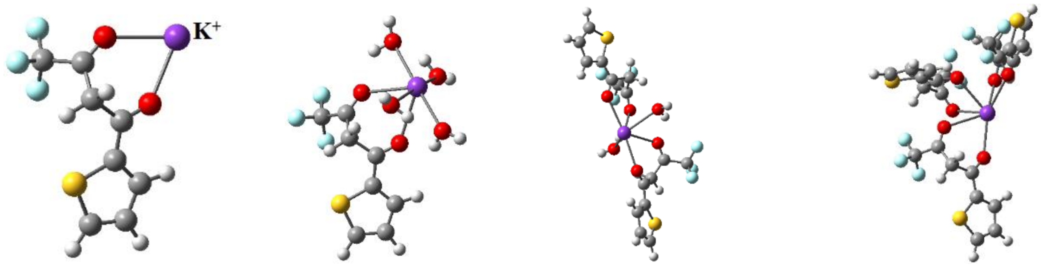
TTA: Ca^{2+} TTA: $Ca^{2+}(4H_2O)$ 2TTA: Ca^{2+} $(2H_2O)$ 3TTA: Ca^{2+}



TTA: Li^{+} TTA: $Li^{+}(2H_2O)$ 2TTA: Li^{+}

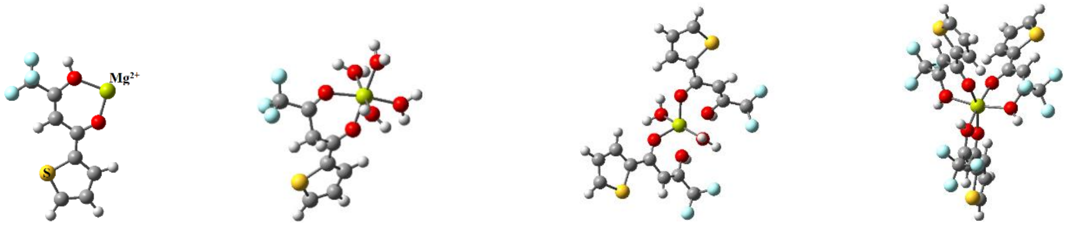


TTA: Na^{+} TTA: $Na^{+}(4H_2O)$ 2TTA: $Na^{+}(2H_2O)$ 3TTA: Na^{+}

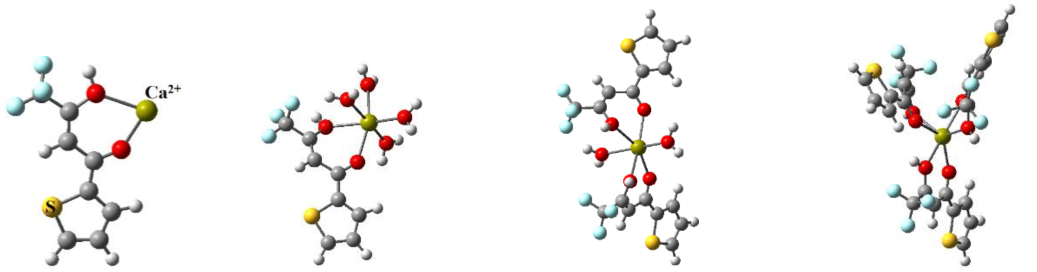


TTA: K^{+} TTA: $K^{+}(4H_2O)$ 2TTA: $K^{+}(2H_2O)$ 3TTA: K^{+}

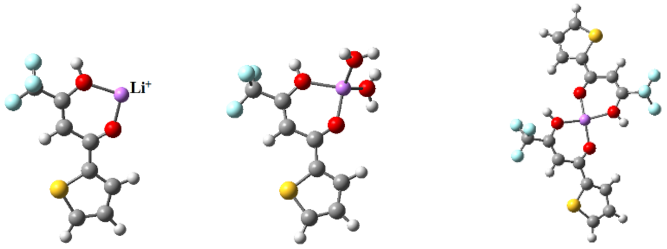
Fig. 10. Optimised 1:1, 2:1 and 3:1 carrier: cation ratio for the M^{n+} ···TTA complexes, where M^{n+} refer to the charged cation of interest.



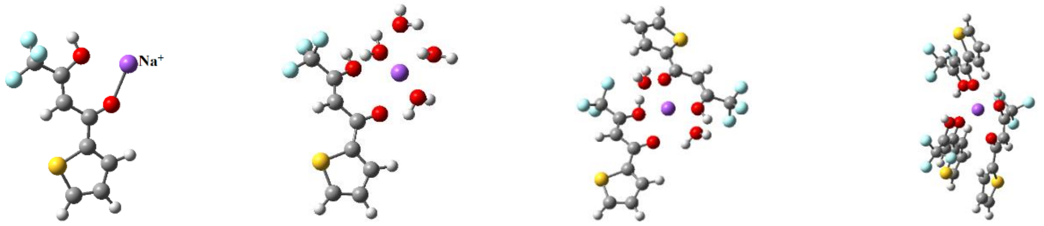
HTTA: Mg^{2+} HTTA: $Mg^{2+}(4H_2O)$ 2HTTA: Mg^{2+} $(2H_2O)$ 3HTTA: Mg^{2+}



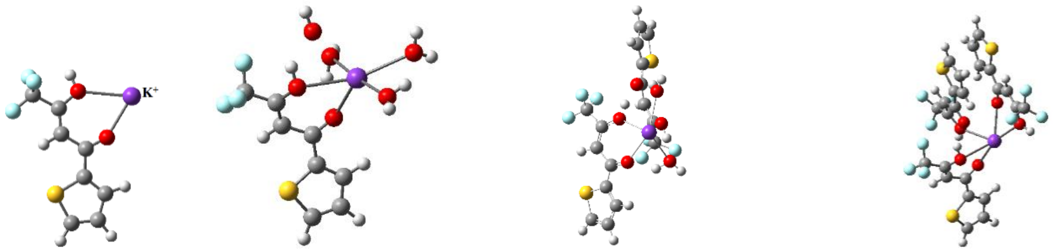
HTTA: Ca^{2+} HTTA: $Ca^{2+}(4H_2O)$ 2HTTA: Ca^{2+} $(2H_2O)$ 3HTTA: Ca^{2+}



HTTA: Li^+ HTTA: $Li^+(2H_2O)$ 2HTTA: Li^+

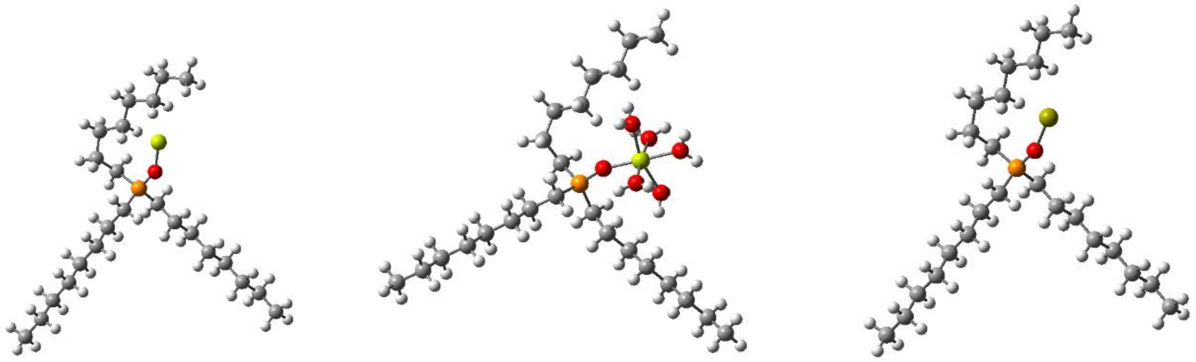


HTTA: Na^+ HTTA: $Na^+(4H_2O)$ 2HTTA: $Na^+(2H_2O)$ 3HTTA: Na^+

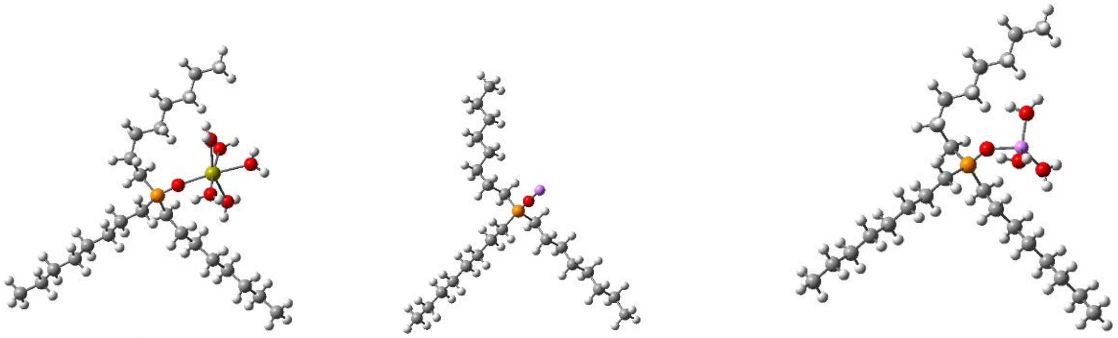


HTTA: K^+ HTTA: $K^+(4H_2O)$ 2HTTA: $K^+(2H_2O)$ 3TTA: K^+

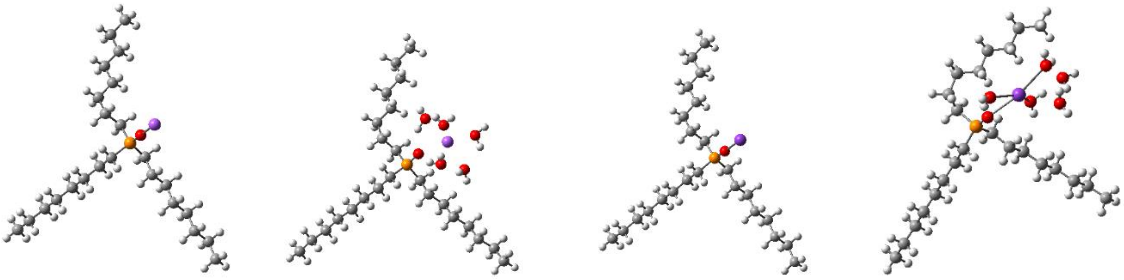
Fig. 11. Optimised 1:1, 2:1 and 3:1 carrier: cation ratio for the M^{n+} ···HTTA complexes, where M^{n+} refer to the charged cation of interest.



TOPO: Mg^{2+} TOPO: $Mg^{2+}(5H_2O)$ TOPO:Ca^{2+}



TOPO: $Ca^{2+}(5H_2O)$ TOPO: Li^{+} TOPO: $Li^{+}(2H_2O)$-



TOPO: Na^{+} TOPO: $Na^{+}(5H_2O)$ TOPO: K^{+} TOPO:$K^{+}(5H_2O)$

Fig. 12. Optimised 1:1 carrier: cation ratio for the TOPO···M^{n+} complexes, where M^{n+} refer to the charged cation of interest.

Table 2

Binding energy (kcal/mol), TOPO··· M^{n+} Bond distance (Å) and charge (*e*) on the complexed M^{n+} cation for the TOPO··· M^{n+} complexes.

Structure	**$\Delta E_{binding}$ (kcal/mol)**	**TOPO··· M^{n+} Bond distance (Å)**	**charge (*e*) on the complexed M^{n+}**
TOPO: Mg^{2+}	-222.130	1.813	1.863
TOPO: Ca^{2+}	-163.189	2.058	1.896
TOPO: Li^{+}	-71.181	1.681	0.987
TOPO: Na^{+}	-52.658	2.048	0.995
TOPO: K^{+}	-41.190	2.388	0.994
TOPO: $Mg^{2+}(5H_2O)$	-384.811	1.931	1.803
TOPO: $Ca^{2+}(5H_2O)$	-300.200	2.202	1.862
TOPO: Li^{+} $(3H_2O)$	-131.154	1.857	0.901
TOPO: Na^{+} $(5H_2O)$	-128.374	2.396	0.930
TOPO: K^{+} $(5H_2O)$	-107.172	2.611	0.947

Table 3

Binding energy ($\Delta E_{binding}$, kcal/mol), TTA··· M^{n+} Bond distance (Å) and charge on the complexed M^{n+} cation for the TTA··· M^{n+} complexes.

Structure	**$\Delta E_{binding}$ (kcal/mol)**	**TTA··· M^{n+} bond distance (Å)**		**Charge (*e*) on the complexed M^{n+}**
		O6'···M^{n+}	**O8'··· M^{n+}**	
TTA: Mg^{2+}	-172.851	1.842	1.926	1.917
TTA: Ca^{2+}	-122.849	2.114	2.239	1.925
TTA: Li^{+}	-58.398	1.804	1.879	0.968
TTA: Na^{+}	-39.030	2.187	2.263	0.980
TTA: K^{+}	-27.278	2.565	2.628	0.988
HTTA: Mg^{2+}	-183.677	1.8120	1.954	1.917
HTTA: Ca^{2+}	-134.057	2.063	2.327	1.920
HTTA: Li^{+}	-66.896	1.765	1.917	0.967
HTTA: Na^{+}	-48.514	2.118	2.327	0.981
HTTA: K^{+}	-37.371	2.461	2.756	0.988
TTA: $Mg^{2+}(4H_2O)$	-342.785	1.999	2.065	1.790
TTA: Ca^{2+} $(4H_2O)$	-260.841	2.290	2.386	1.863
TTA: Li^{+} $(3H_2O)$	-104.957	1.891	1.962	0.892
TTA: Na^{+} $(4H_2O)$	-105.466	2.383	2.395	0.921
TTA: K^{+} $(4H_2O)$	-85.894	2.767	2.757	0.963
HTTA: Mg^{2+} $(4H_2O)$	-343.620	1.96306	2.1309	1,792
HTTA: Ca^{2+} $(4H_2O)$	-261.495	2.255	2.431	1.861
HTTA: Li^{+} $(3H_2O)$	-107.453	1.843	2.002	0.890
HTTA: Na^{+} $(4H_2O)$	-107.416	2.288	2.414	0.924
HTTA: K^{+} $(4H_2O)$	-87.709	2.725	2.722	0.967
2HTTA: Mg^{2+} $(2H_2O)$	-347.252	1.979 1.979	2.152 2.152	1.783
2HTTA: Ca^{2+} $(2H_2O)$	-264.113	2.293 2.308	2.466 2.486	1.857
2HTTA: Li^{+}	-105.430	1.866 1.866	1.967 1.967	0.892
2HTTA: Na^{+} $(2H_2O)$	110.785	2.322 2.453	2.341 2.300	0.905
2HTTA: K^{+} $(2H_2O)$	92.626	2.647 4.012	2.668 2.947	0.974

Structure	$\Delta E_{binding}$ (kcal/mol)	TTA··· M^{n+} bond distance (Å) O6'···M^{n+}	 O8'··· M^{n+}	Charge (*e*) on the complexed M^{n+}
2TTA:Mg^{2+} ($2H_2O$)	-345.977	2.002 2.002	2.092 2.092	1.774
2TTA:Ca^{2+} ($2H_2O$)	-262.501	2.338 2.338	2.439 2.439	1.857
2TTA: Li^+	-98.966	1.872 1.887	1.992 1.969	0.889
2TTA: Na^+ ($2H_2O$)	96.350	2.295 2.295	2.428 2.428	0.893
2TTA: K^+ ($2H_2O$)	79.908	2.687 2.687	2.785 2.785	0.956
3TTA: Mg^{2+}	-350.055	2.039 2.000 2.008	2.063 2.100 2.120	1.762
3TTA: Ca^{2+}	-265.631	2.328 2.336 2.343	2.440 2.434 2.414	1.853
3TTA: Na^+	-97.069	2.263 2.278 2.379	2.501 2.412 2.316	0.898
3TTA: K^+	-77.603	2.645 2.674 2.773	2.713 2.855 2.733	0.946
3HTTA: Mg^{2+}	-355.429	1.969 2.006 1.984	2.135 2.117 2.120	1.774
3HTTA: Ca^{2+}	-269.494	2.284 2.305 2.347	2.427 2.468 2.472	1.857
3HTTA: Na^+	-106.535	2.242 2.448 2.243	2.346 2.329 2.329	0.895
3KTTA: K^+	-86.291	2.675 2.596 2.903	2.728 2.795 2.692	0.956

4.4.4 The effect of salt content

The seawater was spiked with pure sodium chloride (NaCl) to examine the impact of adding salt on the concentration of Mg^{2+} and Ca^{2+}. When varying salt concentrations, an amount of 50% (w/v) salt was added to seawater samples. The concentrations of the minerals of interest were observed to slightly increase compared to the concentrations in seawater without any additional salt (**Fig. 13)**. The increased ion concentration in the solution due to the addition of NaCl resulted in more calcium and magnesium being extracted by the PIM system. This process is referred to as salting in. In this case, increased ionic strength in solution favours the reaction of calcium and magnesium solvated ions with the carriers in the membrane.

PIM can be used for the transportation of the analytes with low influence or no matrix effect. However, a selective carrier is recommended for good recoveries [34]. In this study, during the extraction of the spiked seawater samples with pure salt to induce the matrix effect, the experiments were carried out in triplicates to minimise errors. Additionally, dilutions were created before ICP-OES testing on the samples. The origin of the matrix effect in seawater includes salinity. A few years ago, the analysis of several metals in seawater showed that they were less affected by salinity known as the salt effect. This has shifted the focus of many researchers to pay more attention to the matrix effect generated by the instruments. The researchers concluded that salinity is not affected by the other matrix which can negatively affect the outcome of the results [40].

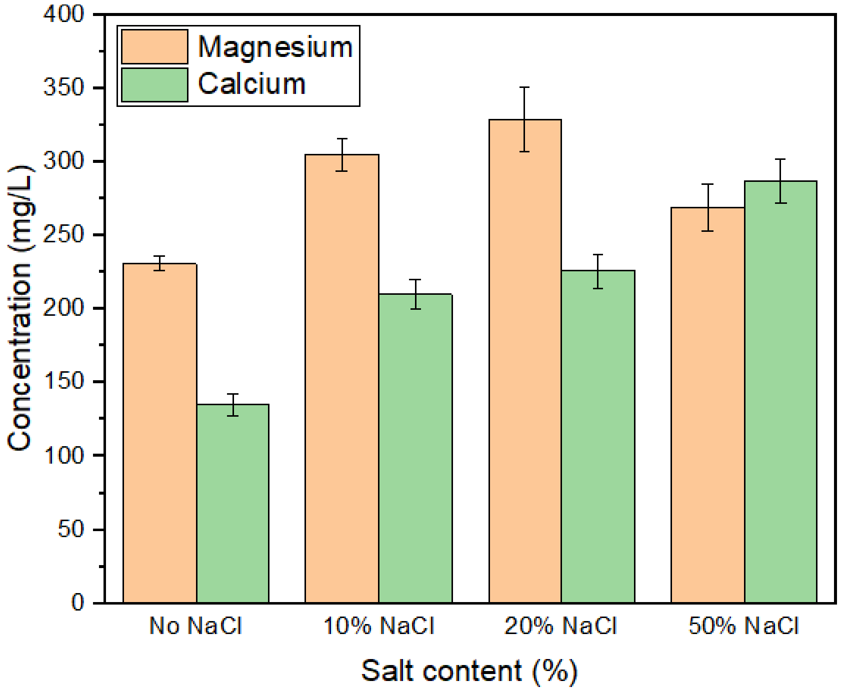


Fig. 13. The analysis of seawater samples spiked with pure NaCl for the extraction of magnesium and calcium.

4.4.5 The physical parameters of seawater tested during sample collection

Seawater samples were collected from the Indian Ocean at Blue Lagoon Beach in the city of (Durban, South Africa) (29°48'47.1"S 31°02'30.0"E). During the sampling, the testing of several parameters was conducted in the ocean with the results depicted in **Table 4**. Seawater samples were transported to the laboratory at the University of the Witwatersrand where the extraction and analyses were performed.

The physical and chemical factors that affect the aquatic environment include salinity, pH, temperature, dissolved oxygen (DO) and carbon dioxide. These factors need to be monitored to determine how contaminated seawater is as they have an impact on water quality [23]. In this study, the measured total dissolved solids (TDS) are low compared to salinity. This is because they are known to be proportional to each other and are not necessarily the same. Numerous factors including location, seawater depth and environmental concerns might contribute to low TDS [23].

Table 4

Physicochemical parameters of seawater at Blue Lagoon Beach, Durban.

pH	**Conductivity (mS/cm)**	**Dissolved oxygen (mg/L)**	**Total dissolved solids (ng/L)**	**Salinity (PSU)**	**Resistivity (mΩ/cm)**	**Redox potential (mV)**
8,52	46,76	0,520	23,38	30,46	0	5,1809

4.4.6 The application of the PIM-based statics experiment sampling to real seawater samples

In **Fig. 14**, when comparing the receiver solution concentrations, it shows that metal ions were transported to the acceptor phase from days 1 to 13 using 0.05 M HCl and 0.1 M HCl receiver solutions. It was observed that as the number of days increased, the uptake of the mineral salts also increased. However, the uptake at 0.05 M HCl was the minerals much better compared to the 0.1 M HCl. Between days 1 and 8 the linear uptake of calcium and magnesium was observed with 0.05M HCl as the acceptor solution [9]. The two concentrations were studied again in real seawater samples to validate that the method is comprehensive and reliable and to investigate the trend in the results obtained from artificial and real seawater samples. Lithium is not included in **Fig. 14** because it was not detected in real seawater extracted samples. The results indicated that the membrane was not selective towards potassium and sodium found in seawater as lithium was below the detection limit of the instrument used**.** This could be influenced by the ionic radius [41]. Lithium has a smaller radius (69 pm) than other ions which include Na^+ (102 pm), K^+ (138 pm), Ca^{2+} (100 pm) and Mg^{2+} (72 pm). Even though Li^+ and Mg^{2+} have almost similar ionic radii, Mg^{2+} has higher hydration which makes it less prone to deintercalation compared to Li^+. Hydrated ionic sizes also play a huge role in the transportation of the cations passing through the membrane. Therefore, Mg^{2+} and Ca^{2+} have relatively small radii with larger hydration values as a result, it is not easy for them to undergo dehydration. Whereas alkali metal ions such as Li^+ and Na^+ have weak hydration layers [39].

Furthermore, the low concentration of lithium obtained in the receiver solution might be the result of the diffusion of other ions which resulted in slowing down its diffusion rate [41]. The high uptake of Mg^{2+} and Ca^{2+} compared to the other metals is evidence of the formation of the strong complex between these target analytes with the carriers used in this study. The possible factor that can result in a strong interaction of the targeted cations with the carriers includes hydration energy. This is because for a metal ion to be extracted by the PIM, it should lose some water molecules and interact with the functional groups within the PIM [42]. Previous researchers have reported similar results to the ones that were obtained in this study whereby the binding strength of the targeted cations such as Mg^{2+} and Ca^{2+} with carriers used was found to be higher compared to Li^+ using DFT [42]. Therefore, it is much easier for them to leave the hydration shell during their transportation across the membrane pores [39]. In this study, the extraction of metal ions using a membrane increases with time. However, the PIM shows excellent selectivity for Mg^{2+} in both optimized and real seawater analysis. Based on the findings of this study, the PIMs technology has proved to be a promising approach for the uptake of Ca^{2+} and Mg^{2+} ions in seawater.

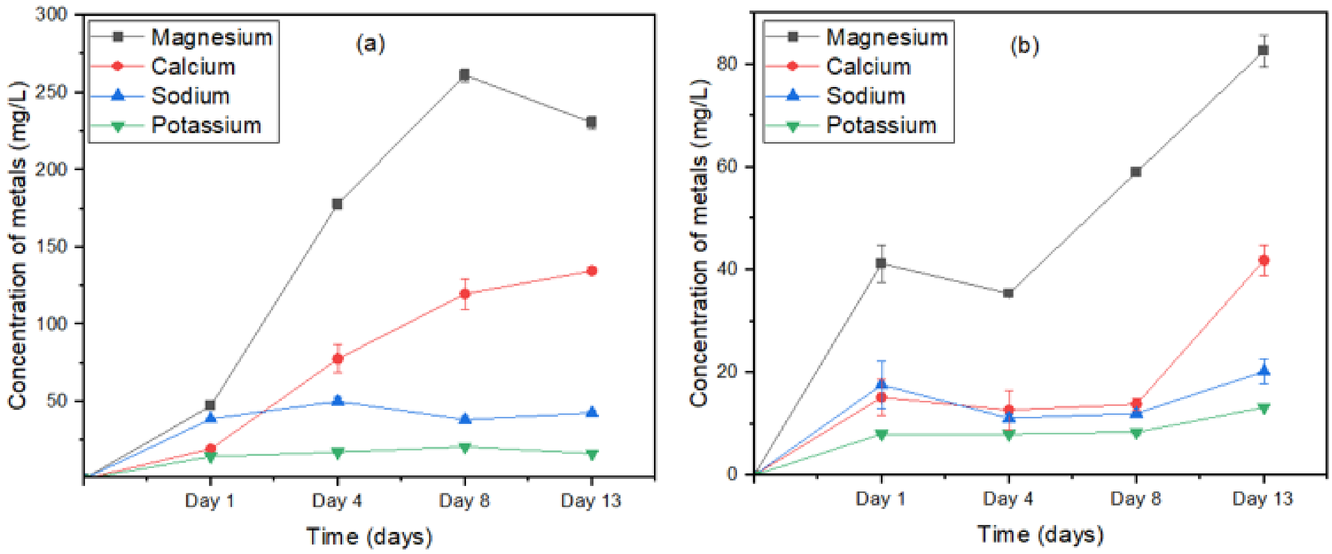


Fig. 14. Transport of calcium and magnesium using (experimental conditions: receiver solution- (a) 0,05M HCl and (b) 0,1M HCl. Both experiments were carried out at a pH of 8,5. Membrane composition: 60 wt.% (TTA+TOPO): 30 wt.% (CTA): 10 wt.% (2-NPOE). The error bars are ± SD (standard deviation).

4.5 Conclusion and recommendations

This study has successfully demonstrated the ability to utilize membrane technology for the uptake of minerals in seawater. The findings of the study revealed that the composition and components of the PIM have a substantial impact on both its performance and its ability to extract certain mineral ions. This was demonstrated through the application of different PIM component compositions for the uptake of mineral ions in seawater. The computational investigations demonstrated that the carriers used in the PIM synthesis had preferential selectivity towards magnesium and calcium. These findings were in agreement with the experiments performed in the laboratory setting where the selectivity was tested in the presence of alkali metals such as lithium, potassium, and sodium. Interestingly, the PIM extraction occurred better when the pH of the feed solution was 8.5 which falls within the region of seawater. This means the synthesized PIM has the potential to extract the investigated minerals in natural seawater conditions. Although the membrane is promising, further analysis of the PIM surface could be performed using contact angle measurements. This will give an idea of the effect of the carries and plasticizer when added to the polymeric matrix as well as check if the membrane is hydrophobic or hydrophilic. Further studies can also be carried out to investigate the membrane characterization using atomic force microscopy (AFM) to better understand the surface properties including hydrophobicity, hydrophilicity and texture. Further investigation can be done by introducing new carriers to identify those with higher selectivity for specific ions or improved performance in various environmental conditions. The membrane's stability can also be assessed within seawater by taking into account its resistance to fouling and degradation.

Acknowledgments

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Conflicts of Interest

The authors declare they have no conflict of interest.

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4 Paper 2

This paper titled ‘Behaviour of major cations in optimisation of polymer inclusion membrane (PIM) for the transport of Lithium from seawater’ This part of the work presents the optimisation of the PIM for the extraction of lithium in spiked ultrapure water followed by the application of the optimised method to real seawater samples. Land mining has been reported as not environmentally sustainable due to the pollution and the large waste generated during and after the extraction of minerals. So as the lithium demand is continually rising, seawater has been reported as a promising source of minerals. However, there is still a challenge with lithium extraction since it is found at very low concentrations in seawater. Therefore, this study aims to develop and optimize the PIMs method for the extraction of minerals in seawater by introducing a new carrier molecule to enhance the metal uptake.

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Behaviour of major cations in optimisation of polymer inclusion membrane (PIM) for the transport of Lithium from seawater

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ABSTRACT

Recovery of lithium from seawater remains a difficult problem because of its low concentration compared to other metals. In this study, the extraction of lithium was carried out in both spiked and real seawater samples. The PIM was synthesized using cellulose triacetate as a base polymer, dibenzoylmethane and trioctylphosphine oxide as carriers as well as 2-nitrophenyloctyl ether as a plasticizer. The composition of the membrane, the effect of the pH and the concentration of the receiver solution were optimised. Six different membrane compositions were tested during the optimisation process. The pH of the feed source was adjusted from 8.5 to 12. The findings demonstrated that lithium uptake was much higher than the other metals when the pH was increased to pH 12. The concentration of the receiver solution varied between 0,05 M HCl, 0,1 M HCl and 1 M HCl. The combination of 60 wt % DBM: TOPO: 30 wt % CTA: 10 wt % 2-NPOE in a (1:1) and (2:1) ratio of carriers performed well towards lithium. $Li^+ > Na^+ > Ca^{2+} > Mg^{2+}$ was the selectivity achieved using 0,05 M HCl in this composition at a 1:1 ratio. On the other hand, the selectivity from the same membrane components but in a 2:1 ratio was $Li^+ > Ca^{2+} > Na^+ > Mg^{2+}$. In the real seawater samples, the two PIMs were further utilised for metal ion extraction. The 1:1 ratio resulted in a selectivity of $Ca^{2+} > Na^+ > K^+$ and the 2:1 ratio membrane produced a selectivity of $Ca^{2+} > Na^+ > K^+ > Mg^{2+}$.

Keywords:

Lithium; Seawater; Cellulose triacetate; Extraction; Metals; Optimisation

4.1 Introduction

Lithium is known to be a very crucial element due to its diverse applications. Lithium plays a huge role in the ceramics and glass industries. This is because incorporating lithium into the glass batch during production can lower the glass's viscosity, melting point and thermal expansion thereby reducing energy consumption [1]. It is also used in ion batteries as a very good energy storage for electric cars [2]. Lithium extraction from seawater is still a challenge due to the presence of several metals in high concentrations including Na^+, Mg^{2+}, Ca^{2+}, K^+ and Sr^{2-} [2,3]. Seawater contains significant anions such as Cl^-, SO_4^{2-} and Br^-. All these compounds are very useful for several applications which include the pharmaceutical and agricultural sectors [4,5]. The estimated concentration of lithium in seawater is approximately 0,17 mg/L. Furthermore, the other major ions such as sodium, magnesium, calcium and potassium are known to be approximately 10800 mg/L, 1290 mg/L, 411 mg/L and 380 mg/L respectively [6,7].

Several techniques have been attempted to recover lithium from seawater such as supported liquid membranes (SLMs), bulk liquid membranes (BLMs), nanofiltration (NF), reverse osmosis (RO) and electrochemical-based processes [8]. Nevertheless, there are several drawbacks to these techniques including the need for harsh chemicals for their synthesis and their heavy reliance on organic solvents [2]. The major drawback is that no one has managed to selectively extract lithium in quantitative amounts that are of commercial interest. Therefore, it is highly desirable to create an analytical method that can selectively extract lithium from seawater samples. PIMs are regarded as the more attractive method than liquid membranes due to their high stability. Furthermore, PIMs are considered environmentally sustainable because they are also being applied during the extraction of heavy metals [9,10].

Polymer inclusion membranes (PIMs) have been studied for the extraction of metal ions, anions, medication and other environmental pollutants in seawater [11]. PIMs are made of base polymers,carriers and plasticizers The two most widely used base polymers are cellulose triacetate (CTA) and polyvinyl chloride (PVC) and they have similar properties [12]. Base polymers are known to provide a foundation as they are responsible for the mechanical support of the membrane. Carriers are responsible for the binding and transportation of targeted metal ions across the membrane. Furthermore, without the existence of carriers the transport of metal ions cannot be possible [13]. Plasticizers are an additional component that is used in the production of PIMs. They are employed to increase the membrane's elasticity and softness which increase the PIM's permeability and flexibility. Plasticizers work as a solvent to enable the carriers to pass across the membrane and form a complex with metal ions from the feed to the receiver phase [10,14]. However, some carriers also have plasticizing qualities as a result other membranes such as Aliquat 336 do not contain plasticizers [10,13]. Moreover, in recent studies it has been observed that PIM transport efficiency decreases with frequent use of the same PIMs. This is a result of membrane components leaching from PIM to the feed or receiver solution [9].

PIMs are reported to be hydrophobic which then results in slow mass tranfer during the transit of targeted analytes and increases extraction time. Fouling is the term for this phenomenon, which is caused by various undesirable solutes that tend to clog the pores on the membrane surface [11,15]. The mechanism of transport depends on the type of carrier, donor and acceptor solution. One type of carrier-mediated transport is called counter-coupled transport. An appropriate carrier molecule is selected based on its capacity to bind to the target ion or molecule to be extracted as well as to enhance the transfer. After that, the chosen carrier molecule is added to a polymer matrix. The extractant is usually an organic complexing reagent that is combined with the membrane liquid. So, either a basic extractant (RA) or an acidic extractant (RH) mediates the target analyte's transition from the membrane's donor phase to the receiver phase. The carrier reacts with the target metal from the feed source releasing H^+ to form a metal complex. The formed complex passes across the membrane and reaches the receiver region. Eventually, the target species are released on the other side of the membrane into a receiving solution. The extractant is regenerated and the procedure starts over [16]. Therefore, during the transportation of metal ions across the membrane the targeted analytes will migrate from the high pH feed solution to the low pH region (receiver phase). The carrier interacts with either an anion in the acceptor phase such as (Cl^-) or a proton (H^+). After that reaction the anion is released in the acceptor phase and the carrier diffuses back to the donor phase. The anion from the acceptor solution is the driving force in this situation [9,17,18]. The concentration gradient of the cations and anions is known as the coupled transport across the membrane system [12].

In this work, CTA was used as a base polymer whereas dibenzoylmethane (DBM) shown in **Fig.1** and trioctylphosphine oxide (TOPO) were used as carriers. The previous study attempted to extract lithium using a liquid-liquid extraction (LLE) approach with high selectivity [19]. However, only lithium was extracted from spiked water samples and the study assumed that major ions were removed first before performing the extraction. Then, in our study we attempt to show how lithium extraction can be influenced by other ions in spiked and real seawater samples. This is important to understand how selective extraction of lithium can be achieved and gives an idea of which metals must be removed most in seawater before PIM application to remove lithium.

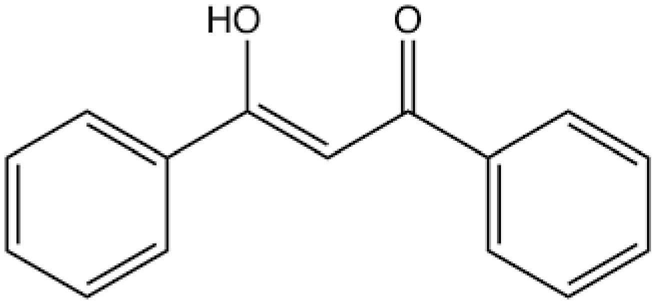


Fig. 1. One of the carriers used for PIM synthesis (dibenzoylmethane (DBM)). The structures of the other components are shown in **paper 1**.

4.2 Materials and methods

4.2.1 Reagents and chemicals

Dichloromethane (DCM) (99, 9%) HPLC grade, hydrochloric acid (HCl) (32%) and nitric acid (NH_3) (55%), the base polymer, carrier and plasticizer such as cellulose triacetate (CTA), trioctylphosphine oxide (TOPO) and 2-nitrophenyloctyl ether (2-NPOE), mineral salts such as Li_2CO_3, $MgCO_3$, $CaCO_3$, Na_2CO_3 and K_2CO_3 were purchased from Sigma Aldrich (Johannesburg, South Africa). Carrier dibenzoylmethane (DBM, 98 %) was purchased from Sigma Aldrich (Steinheim, Germany).

4.2.2 Instrumentation

A scanning electron microscope (SEM) (Zeiss Evo 50, Oberkochen, Germany) was used to study the morphology of the membrane. Fourier transformed infrared spectrometry (FTIR) from Bruker (Johannesburg, South Africa) was used to investigate the functional groups of the PIM components the range of 4000–400 cm-1. The Five Easy FE20 pH meter from Mettler Toledo (Johannesburg, South Africa) was used for the pH adjustment of the aqueous solutions. All the PIM components were accurately weighed using an analytical top balance from Ohaus (Johannesburg, South Africa). The distilled water was further purified by the Millipore Milli-Q water system from (Millipore, Bedford, Massachusetts, USA). Metal concentration was investigated using inductively coupled plasma optical emission spectrometry (ICP-OES) from

Spectro Genesis (Kleve, Germany). The ICP-OES plasma torch was orientated axially, and a crossflow nebuliser was used with a flow rate of 1 ml/min. The argon pressure was 6,48 bar, the coolant flow was 14 ml/min, the auxiliary flow rate was 1 ml/min, the plasma power was 1400 W and the pump speed was 2 rpm.

4.2.3 Polymer inclusion membrane preparation

Polymer inclusion membranes were prepared following the procedure previously described by Fernández-Escalante et al. [19]. The composition of the membrane was investigated by forming a combination of different PIMs. The PIM components with a total of 2 g were dissolved in 20 mL DCM and stirred at room temperature to improve the dissolution of the components. The resulting mixture was transferred into a glass Petri dish with a diameter of 9 cm purchased from Sigma Aldrich (Johannesburg, South Africa) and was covered with filter paper to avoid contamination. The solution was allowed to evaporate overnight shown in **Fig. 1.** The resulting film was peeled off from the Petri dish and small circular pieces were cut out and used for the static experiments. The investigated ratios for carrier molecules; (DBM: TOPO) were 1:1 and 2:1. Other PIMs contained a plasticizer (2-NPOE) with a concentration of 10 wt%.

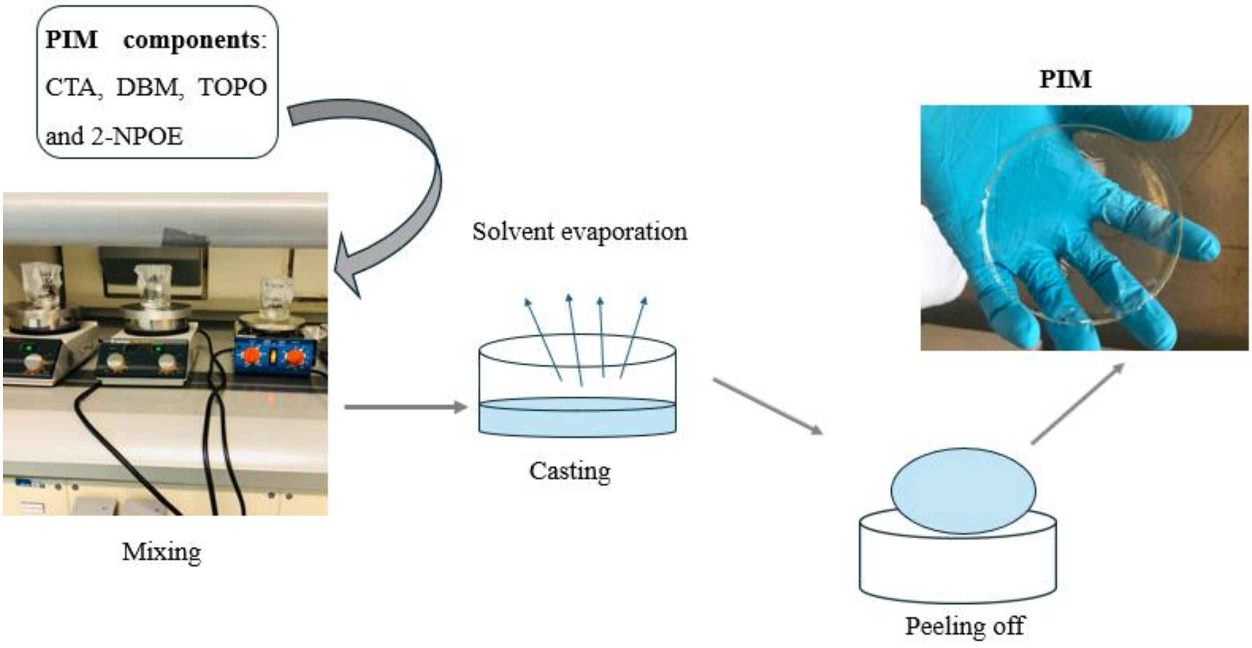


Fig. 1. Schematic diagram showing the PIM preparation process.

Table 1

PIMs with different compositions containing carrier molecules, base and plasticizer

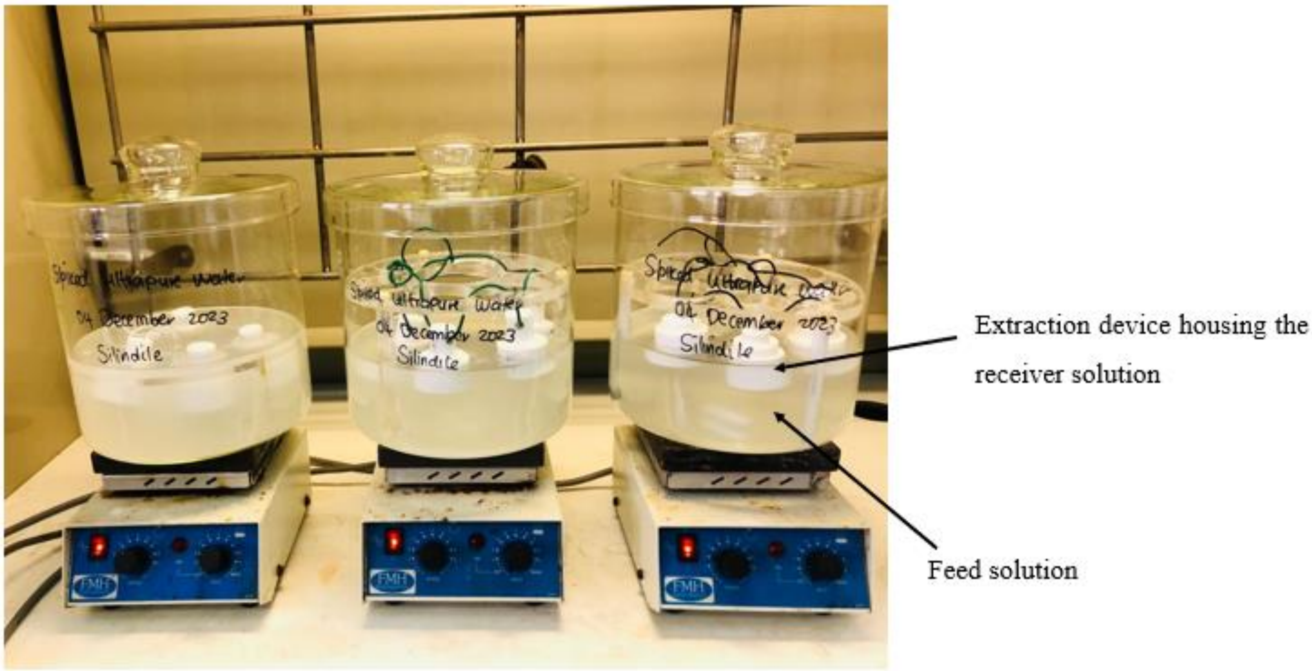
Experiment number	**Carrier amount (g)**	**Ratio (DBM: TOPO)**	**Base amount (g)**	**Plasticizer amount (g)**	**Composition (wt.%) (Carrier: Base: Plasticizer)**
1	1,2	1:1	0,8	0	60:40:0
2	1,2	1:1	0,6	0,2	60:30:10
3	1,2	2:1	0,8	0	60:40:0
4	1,2	2:1	0,6	0,2	60:30:10
5	1	1:1	1	0	50:50:0
6	1,1	1:1	0,9	0	65:35:0

4.2.4 Sample preparation before SEM analysis

The membrane samples were prepared for SEM analysis. For cross section, the membrane was teared to expose a clean cross section. The torn membrane was placed on the SEM stub using carbon tape with the torn edge facing upwards. This was to ensure that the area of interest is easily accessible for the electron beam. The coating was done using gold and palladium to prevent charging under the electron beam during SEM analysis.

4.2.5 Static experiment for the optimisation of polymer inclusion membrane extraction

The resulting membrane composition which was found to be optimal was used to study its performance in both spiked and real seawater. The feed solution of 2 L was spiked with 15 mg/L of the salts containing the metal of interest as well as other competing metals. These salts include $MgCO_3$, $CaCO_3$, Li_2CO_3, K_2CO_3 and Na_2CO_3. The experiments were carried out for 4 days during which the extraction devices shown in **Fig. 2** were deployed into a 5 L glass beaker containing seawater. The receiver phase contained 5 mL of dilute HCL as a stripping solution. The pH was investigated at 8,5, 10 and 12 while keeping the other parameters constant which include PIM composition and concentration of the receiver solution. The samples were analysed using the ICP-OES analysis.



Extraction device housing the receiver solution

Feed solution

Fig. 2. Experimental setup for the extraction of lithium and other metals in seawater. The sample solution was stirred at 200 rpm at room temperature.

4.3 Results and discussion

4.3.1 Characterisation of the PIM

4.3.1.1 FTIR for functional groups interpretation

The functional groups of the PIM were investigated using FTIR in the range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1}. The FTIR spectrum illustrated in **Fig. 3** represents the pure components as well as the prepared PIM before static experiments with metal ions. The observed characteristic bands of the carbonyl group (C=O) at approximately 1735 cm^{-1} represent CTA [20]. The main functional group of the plasticizer (2-NPOE) is observed at approximately 1526 cm^{-1} which represents the nitro group (NO_2). The peaks observed at 2923 cm^{-1} and 2856 cm^{-1} are attributed to the stretching vibrations of the asymmetric and symmetric stretching vibrations of (CH_2) for TOPO [20]. The phosphorus group (P=O) from TOPO was observed at 1154 cm^{-1}. The synthesized membrane displayed a very intense peak representing TOPO before extraction. Meanwhile, the height of the peak after extraction showed a decrease. This might be an indication that the carrier is the main component that can move around and interact with other components within the polymeric matrix [20]. The absorption at 3060 cm^{-1} of stretching is assigned to the (-OH) group in the enol form of diketones representing the DBM molecule. Whereas the vibrations observed at around 1590 cm^{-1} correspond to the DBM (C=O) carbonyl group [21]. The vibrational band observed around 1454 cm^{-1} which represents DBM is the combination of (C=C) stretching with TOPO [21]. The (C-H) groups at 746 cm^{-1}, 675 cm^{-1} and 610 cm^{-1} are the stretching groups involving mainly phenyl groups from the DBM carrier [21].

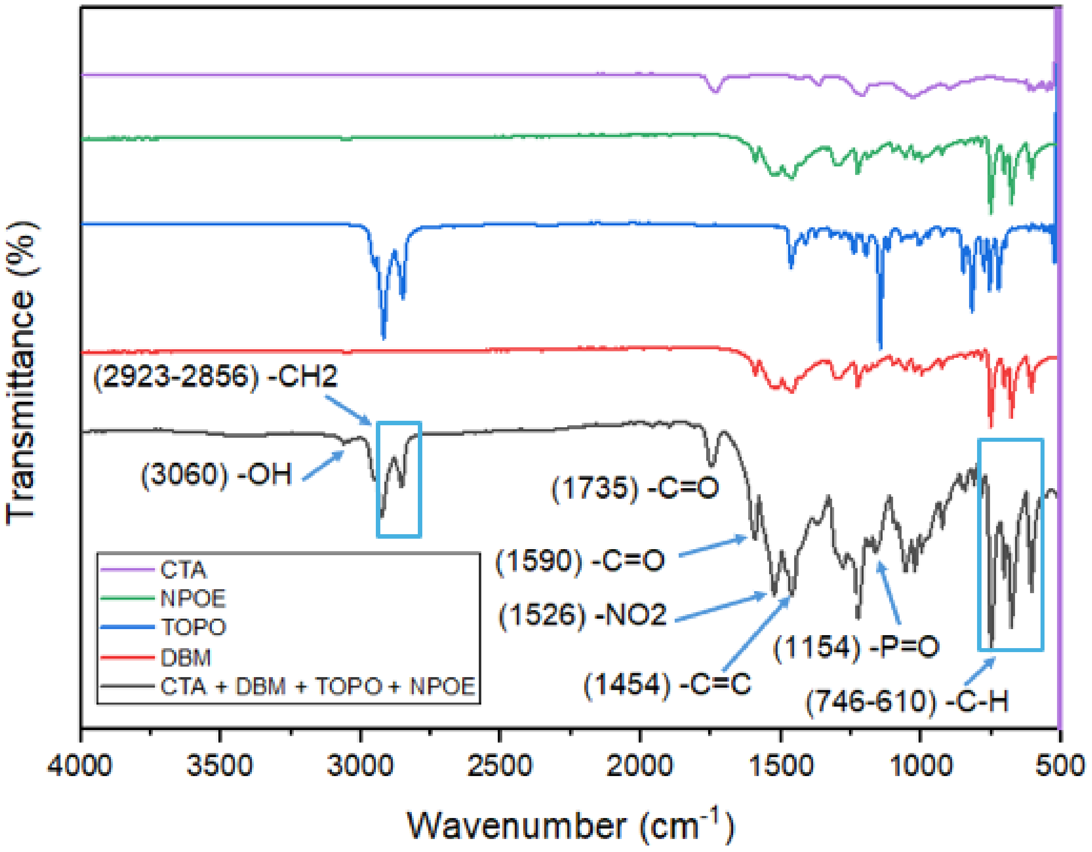


Fig. 3. FT-IR spectrum of the PIM before the extraction of metal ions. Composition: 60 wt % of the carriers, DBM and TOPO (1: 1): 30 wt % (CTA): 10 wt % (NPOE) plasticizer.

4.3.1.2 Scanning electron microscopy analysis of the membrane morphology

The scanning electron microscope (SEM) was used to examine the membrane's surface morphology. To prevent electrical conductivity, membranes were cut into strips and sputter-coated with gold-palladium [22]. The SEM photomicrographs shown in **Fig. 4 (a)** at 200x magnification, the membrane is showing some wrinkles and roughness. Moreover, in **Fig. 4 (b)** the wrinkles are more visible and pronounced on the surface of the PIM when the magnification was increased to 2000x. CTA is known to be soluble in dichloromethane although it precipitates in water [23]. However, the membrane did not show any visible pores in the images. The surface and the cross-sectional images of the membranes were also studied as shown in **Fig. 4 (c)**. The cross-sectional images were observed to have a dense structure. This was also observed in one of the previous studies conducted by Mahmoud et al. [24]. The morphology of another membrane composition of 65:35 (1:1) was tested to investigate the trend as the composition of the PIM was changed. **Fig.4 (d)** at 200x magnification, the roughness of the PIM was more pronounced as the amount of the carriers and the base was increased. In **Fig. 4 (e)** shows the PIM surface that was increased from 200x to 2000x. The surface displayed a lot of defects with no proper explanation.

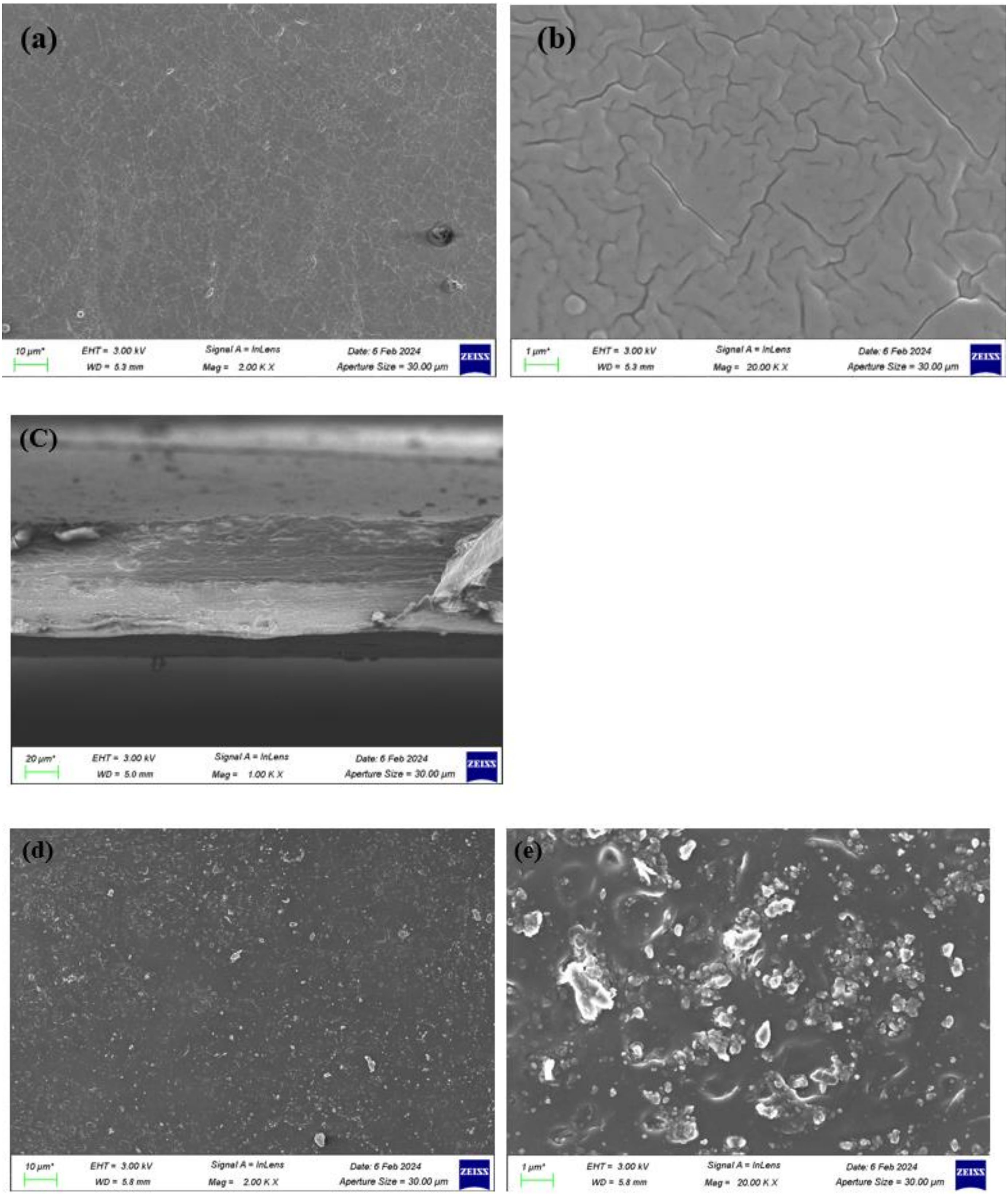


Fig. 4. Characterization of PIM surface composition: 60 wt % of DBM and TOPO (1: 1): 30 wt % (CTA): 10 wt % (NPOE) before extraction of metal ions (a), (b) and (c) cross-section PIM surface composition: 65 wt% DBM and TOPO (1: 1): 35 wt% CTA (d) and (e).

4.4 Polymer inclusion membrane studies

4.4.1 Optimisation of PIM composition and pH effect

The results on the investigation of PIM composition conducted using six different combinations ratios is shown in (**Fig. 5)**. Based on the results, the optimum composition was found to be 60 wt % of the carriers, DBM, and TOPO (1: 1): 30 wt % (CTA): 10 wt % (2-NPOE) plasticizer followed by one with 2:1 ratio of carriers and same composition. Based on the results obtained as shown in (**Fig. 5)**, this composition showed very excellent selectivity for lithium compared to calcium, magnesium, sodium and potassium. The increase of the base polymer (CTA) to 50 wt % in all the graphs showed a decrease in metal uptake of lithium, calcium, magnesium and sodium. Based on the previous studies, the increase of the base concentration causes the membrane to be thicker. As a result, this affects the transport rate thus decreasing the transfer of the ion-carrier complexes across the membrane [25]. The base polymer (CTA) was used due to its high strength and being less prone to hydration [9]. The 2-NPOE plasticizer was chosen in this study because it is the most used plasticizer in PIMs due to its high dielectric constant and low viscosity [10].

The effect of sample pH was studied at 8,5, 10 and 12 for the extraction of metal ions from seawater (**Fig. 5**). Lithium was not detected at pH 8,5 and pH 10 whereas other metals such as Ca^{2+}, Mg^{2+}, Na^{2+} and K^+ were detected at very low concentrations in all the prepared PIMs. However, at pH 12, lithium was detected at very high concentrations compared to the rest of the metal ions in different PIMs. This suggests that the uptake of lithium is good at the high pH of the feed solution. An increase in pH in the feed phase is known to enhance the transportation of targeted analytes in counter coupled transport with low pH of the acceptor solution. This is due to the increase in the gradient between the feed phase and receiver phase which is a driving force for the complexation and release of the metal in the extraction process. High pH also increase the stability of PIMs as are known to undergo dehydration in too acidic conditions compared to alkaline solutions [26]. Thus, pH 12 was selected as the optimum pH. Thus, at pH 12, the extraction process followed $Li^+ > Na^+ > Ca^{2+} > Mg^{2+}$ with the 60:30:10 (1:1) membrane composition towards the metal ions. Whereas the second-best performing membrane composition of a 60:30:10 (2:1) ratio showed extraction process of $Li^+ > Ca^{2+} > Na^+ > Mg^{2+}$. These results are supported by a study where these carriers were used to extract lithium in spiked samples with LLE where almost all the lithium was extracted. So the previous study employed the same carrier achieving high extraction efficiencies [19]. This supports the validity of our findings since they show similarly high extraction efficiency of lithium from the spiked samples. As a result, both membranes were utilised for further testing in seawater.

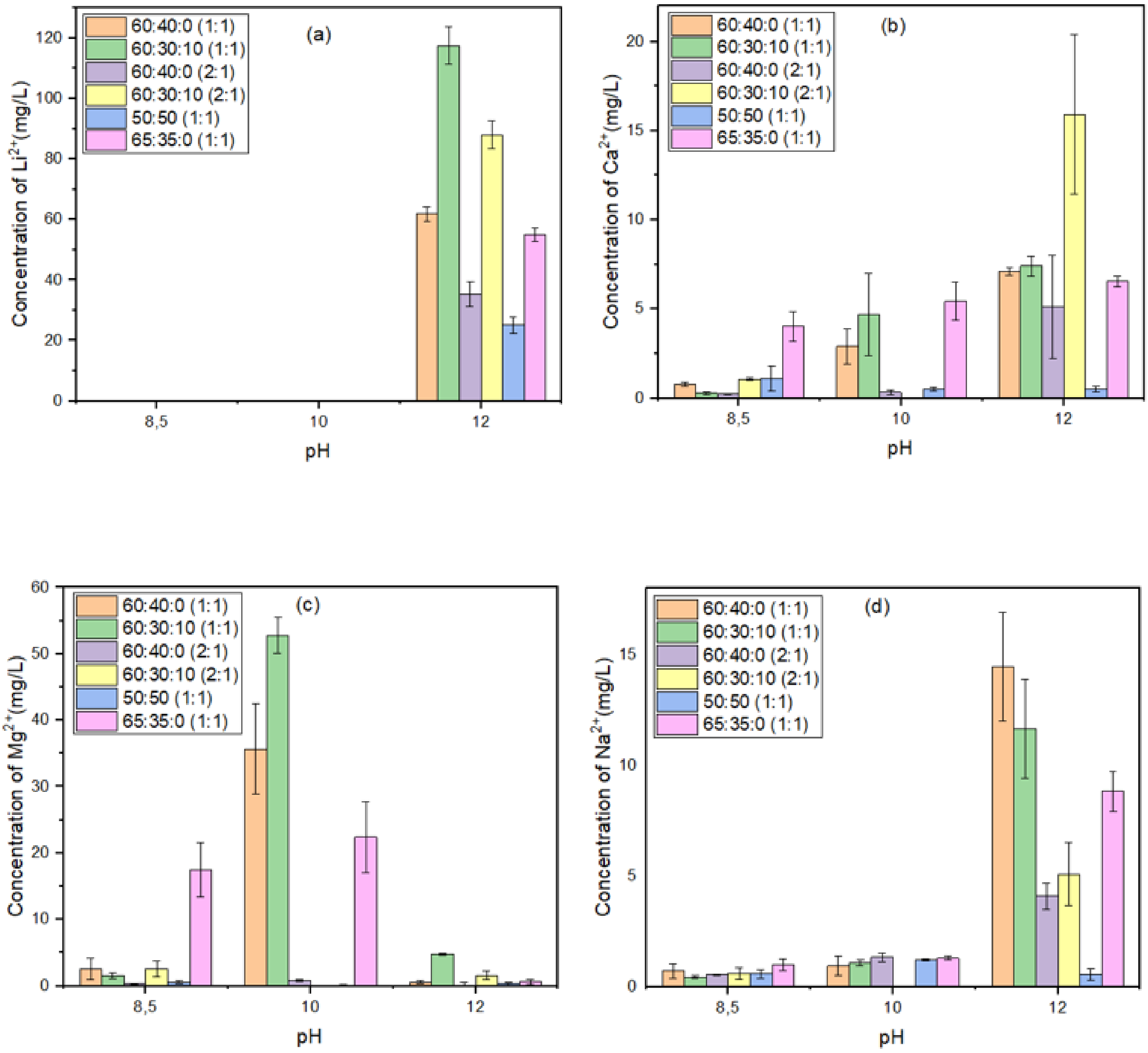


Fig. 5. The effect of PIM composition and pH on the extraction of metal ions (a) lithium, (b) calcium, (c) magnesium and (d) sodium. Feed solution: ultrapure water spiked with 15 mg/L of targeted metals. Extraction time: 4 days. The error bars are: ± SD (standard deviation), (n = 3).

4.4.2 Optimisation of the receiver solution concentration

The investigation was carried out using 60 wt % DBM and TOPO: 30 wt % CTA: 10 wt % 2-NPOE (**Fig 6**). For comparison, the same PIMs were prepared: one in a 1:1 ratio and another in a 2:1 ratio of the carriers. The extraction of lithium at the compositions of 60 wt % DBM: TOPO (1:1): 30 wt % CTA: 10 wt % 2-NPOE using 0,05 M HCl receiver solution was detected at high concentrations compared to the other competing metal ions. The trend was $Li^+ > Na^+ > Ca^{2+} > Mg^{2+}$. When the concentration of the receiver solution was increased to 0,1 M HCl, the concentration of lithium extracted remained high compared to the other competing metals. However, overall, the metal concentration extraction was decreasing. Moreover, the concentration of the receiver solution at 1 M HCl also gave results extraction with more lithium extracted than other metal ions. The concentration of lithium remained high compared to the other metal ions although the concentration was further decreasing. At this concentration magnesium was not detected. The second membrane of 60 wt % DBM: TOPO (2:1): 30 wt % CTA: 10 wt % 2-NPOE using 0,05 M HCl receiver solution was also tested as shown in (**Fig. 6 (b))**. The results obtained were still showing the same pattern because when the concentration of the stripping solution was increased, the metal ion uptake was reduced. The extraction of metals was $Li^+ > Ca^{2+} > Na^+ > Mg^{2+}$ in 0.05M HCl whereas the 0,1 M HCl receiver solution gave $Li^+ > Ca^{2+} > Na^+ > K^+$ and Mg^{2+} was not detected. A similar trend was observed in 1 M HCl receiver solution whereby the extraction followed $Li^+ > Ca^{2+} > Na^+ > K^+$ and Mg^{2+} was not detected. By looking at both membranes, there is not much of a significant difference when it comes to metal ion uptake. The increase in the concentration of the receiver solution resulted in low extraction. Dilute acid concentrations of the receiver tend to give higher extraction due to high ionization of the proton used in extraction process [26, 27, 28]. In one of the studies reported [28], different concentrations of HCl were tested as acceptor solutions and observed that when they increased the concentration of the HCl in the receiver solution it resulted in a decrease in the permeability of the PIM. There are several factors that contribute to the decrease in permeability when the HCl concentration is increased in the receiver solution. These include protonation of functional groups in PIM. As the concentration of HCl increases, more hydrogen ions (H^+) are present. As a result the functional groups present in the PIM will get protonated which then reduces the membrane's permeability [28].

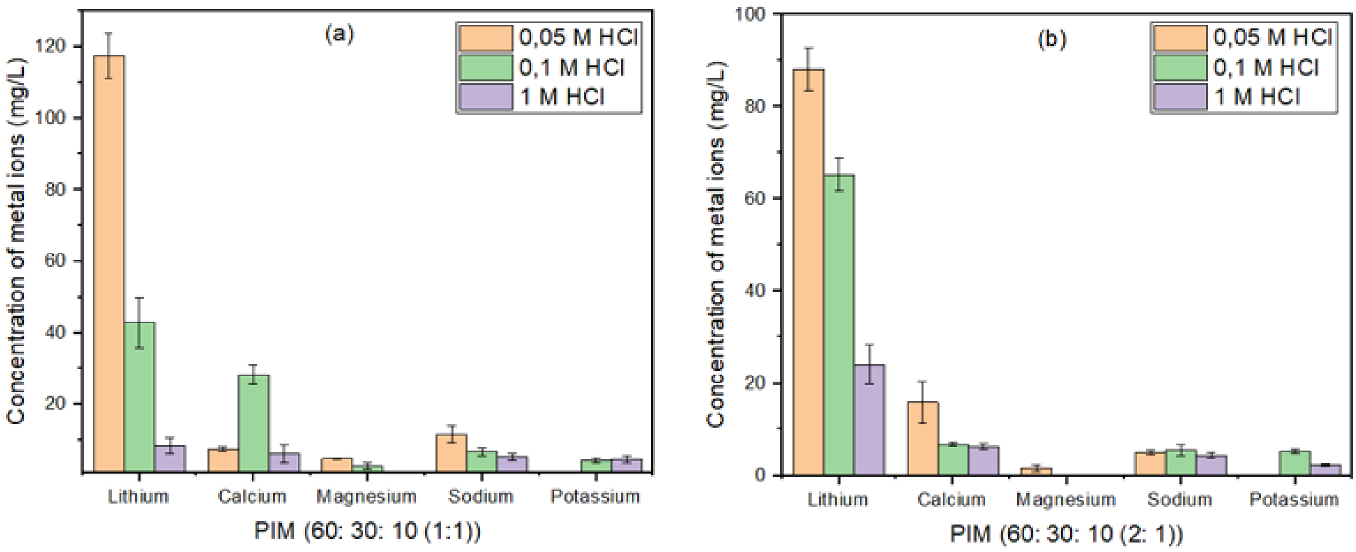


Fig. 6. The influence of the receiver concentration during the extraction of minerals lithium, calcium, sodium and potassium in spiked (15 mg/L) ultrapure water. The receiver solution contained 0,05 M HCl, 0,1 M HCl and 1 M HCl. Error bars represent ± SD (standard deviation), (n = 3).

4.4.3 Studying the performance of the PIM-based statics experiments in real seawater

The optimised parameters such as PIM composition, pH effect and receiver solution concentration were further tested in real seawater samples (**Fig. 7**). The pH of the seawater was adjusted from 8,5 to 12 as per our optimised method. The composition of the membrane with different ratios 60 wt % DBM: TOPO (1:1): 30 wt % CTA: 10 wt % 2-NPOE and 60 wt % DBM: TOPO (2:1): 30 wt % CTA: 10 wt % 2-NPOE were tested in seawater. The ratio of PIM 1:1 at 0,05 M HCl, 0,1 M HCl and 1 M HCl of the receiver solution resulted in the same selectivity of $Ca^{2+} > Na^{+} > K^{+}$. However, the concentration of the metal ions such as Ca^{2+} seemed to increase from 0,05 M HCl to 0,1 M HCl while it showed a slight decrease at 1 M HCl. However, for PIM in a 1:1 ratio, Na^{+} and K^{+} the concentration was almost similar to the concentration of 0,05 M HCl in the receiver solution. Moreover, for both PIMs in a 1:1 and 2:1 ratio the trend is slightly the same. Although, the selectivity of the PIM is largely affected by the ratio of the carriers. Subsequently, there was no significant change in calcium and potassium uptake in all the concentrations for both PIMs. According to the results, there was no detection of lithium from seawater. This is because seawater contains extremely low concentrations of lithium thus, other matrix components have higher concentrations which suppress the lithium since they are in different concentrations [29]. Comparing these results with the spiked samples, at 0,05 M HCl the trend is different despite that lithium was not detected. However, at 0,1 M HCl the selectivity is the same and at 1 M HCl the selectivity changed. Furthermore, the same PIM with a 2:1 ratio was tested. The results obtained at 0,05 M HCl receiver solution gave the selectivity of $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$. Whereas in 0,1 M HCl receiver solution the selectivity was $Ca^{2+} > Na^{+} > K^{+}$. In this case Mg^{2+} was not detected. As the concentration of the receiver solution was further increased to 1 M HCl, the selectivity was $Na^{+} > K^{+}$. The observation was that most of the metal ions were not detected as the concentration of the receiver solution was increased further. The selectivity of the two membranes differs completely in seawater. As would be expected, the concentration of competing species is significantly higher in the real seawater sample than it is in the spiked one. The lithium may be suppressed by these large quantities. In the previous study, the impact of these metal ions on the extraction efficiency of lithium ions was reported [29]. The seawater composition of the targeted analyte of interest such as lithium is estimated to be 0,17 mg/L. Whereas the concentrations of the competing species that were being analysed in the study such as calcium, magnesium, sodium and potassium are 411 mg/L, 1290 mg/L, 10800 mg/L and 392 mg/L respectively **(Table 1)**.

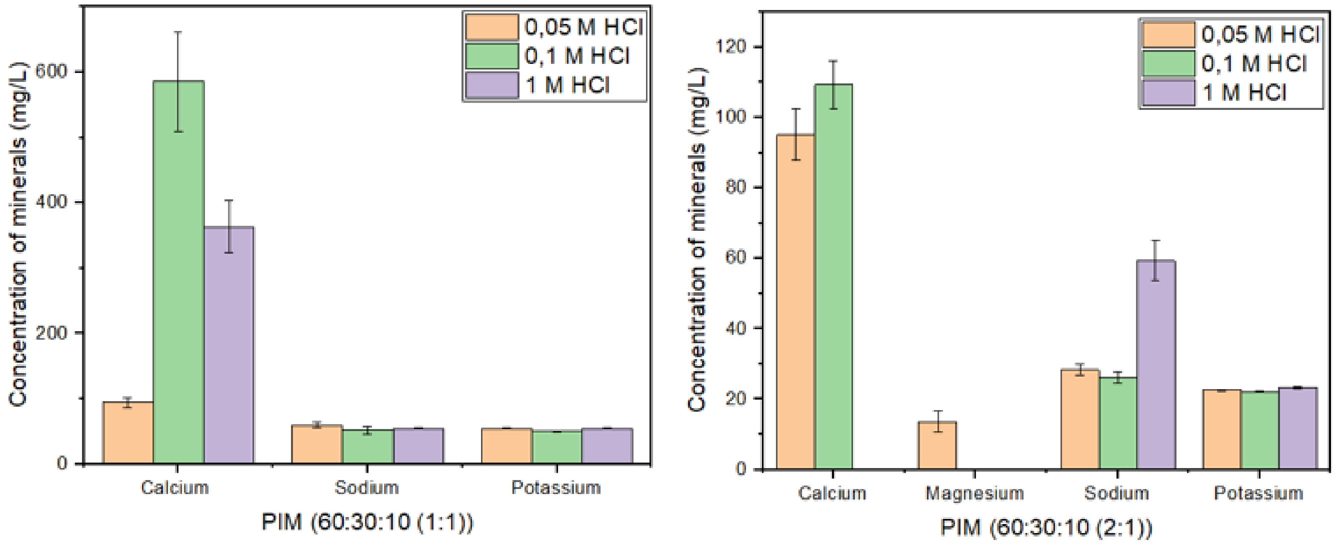


Fig. 7. Extraction of metal ions in seawater samples. Error bars represent ± SD (standard deviation), (n = 3).

Table 1

The estimated concentrations of metal ions in seawater from the previous study [6] were compared with the concentrations that were analysed in this study.

Metal	Concentration from the previous study (mg/L)	Concentration (mg/L) and % RSD found in this study
Na^+	10800	6368 ± 1,15
Mg^{2+}	1290	1002 ± 10,08
Ca^{2+}	411	390 ± 12,54
K^+	392	347 ± 12,38
Li^+	0,17	$0{,}14^*$ ± 2,72

* - reading near the detection limit of the ICP-OES

4.4.4 Enrichment factors

The enrichment factor (EF) was calculated to compare the measured concentration of metal ions to the actual concentration of these metal ions in seawater (32). The obtained EF is shown in **Table 2.** First, all metals were not enriched as values were not above 1 except for Ca^{2+} in PIM 1 at 0.1M HCl acceptor solution. The selectivity in PIM 1 is thus $Ca^{2+} > K^+ > Na^+$. In PIM 2 $Ca^{2+} > K^+ > Na^+$. Magnesium detection in PIM 2 cannot be concluded without error bars. These results imply that tested PIM compositions are highly able to exclude the extraction of major metals in seawater even though lithium is not extracted to detectable levels in ordinary ICP-MS/ICP-OES analysis. This suggests that if seawater is precipitated first with major cations and then the resulting solution is extracted by PIM, perhaps lithium can be quantitatively extracted from seawater.

Table 2

The seawater enrichment factors of the metal ions under examination utilise two distinct PIMs and varying receiver solution concentrations.

	PIM 1			**PIM 2**		
Metals	**0.05 M HCl**	**0.1 M HCl**	**1 M HCl**	**0.05 M HCl**	**0,1 M HCl**	**1 M HCl**
Calcium	0,229	1,43	0,884	0,232	0,266	nd
Magnesium	nd	nd	nd	0,0150	nd	nd
Sodium	0,00549	0,00475	0,00501	0,000148	0,00242	0,00550
Potassium	0,137	0,128	0,138	0,000510	0,0565	0,0594

PIM 1: 60 wt % DBM: TOPO (1:1): 30 wt % CTA: 10 wt % 2-NPOE; **PIM 2**: 60 wt % DBM: TOPO (2:1): 30 wt % CTA: 10 wt % 2-NPOE

4.5 Conclusion and recommendation

In this work, the optimized membrane is very selective towards lithium. However, in seawater samples, lithium could not be extracted enough to be detected because of high concentration of other metals. Subsequently, this could mean that if the other major ions are to be precipitated from seawater followed by the PIM approach using the optimised conditions, then lithium may be recovered from seawater. Thus, this work has laid the foundation for possible extraction of lithium from seawater by precipitation approach first followed by polymer inclusion membrane.

Conflicts of interest

The authors declare that there is no conflict of interest.

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4 Paper 3

The last paper entitled ‘Semi upscaled pilot study of polymer inclusion membrane for the extraction of minerals in seawater’ This part of the work presents the application of the optimised conditions that were obtained from paper 1. The membrane was tested for a period of 39 days while collecting the samples in between. The traditional methods remain a challenge for the extraction of minerals in seawater. This is because of the stability of the membrane. In most previous studies the scaling up of the membrane was not conducted. So, this study aims to upscale this method which is introduced in **paper 1**. This is to investigate if the membrane will be stable enough when deployed for longer extraction times on a larger scale.

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Semi-upscaled pilot study of polymer inclusion membrane for the extraction of minerals in seawater

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ABSTRACT

Polymer inclusion membrane (PIM) is one of the attractive methods for the removal of valuable metals from aqueous solutions. This is because it doesn’t require the use of harsh solvents and it is associated with low separation costs. In this work, the optimised PIM composition of (60 wt % of the carriers, thenoyltrifluoroacetone and trioctylphosphine oxide (1: 1): 30 wt % (CTA): 10 wt % 2-NPOE was further studied for semi pilot upscaled extraction. Then, actual seawater samples were treated using the upscaled methodology. The sample pH of 8.5 was used for the seawater, 0.1 and 0.05M HCl acceptor solutions with a deployment time of up to 39 days. The volume of the receiver solution was tested in both 1 and 2 L. The selectivity of extraction was different from previously optimised conditions with a small system. Thus, the selectivity was found to be $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ for 0.05 M HCl in both 1 L and 2 L of the receiver solution. In contrast, a receiver concentration of 0.1 M HCl in both 1 L and 2 L had a selectivity of $Mg^{2+} > Ca^{2+} > K^+$. The concentration trend of sodium at 0,1 M HCl receiver solution was not clear which is why it was never added to the selectivity trend. The reason for the deviation in selectivity from previous optimisation in smaller system is not very clear and further studies are needed to investigate this.

Keywords:

Polymer inclusion membrane; Extraction; Thenoyltrifluoroacetone; Seawater; Valuable metals

4.1 Introduction

Extracting minerals from seawater has become economically attractive. This is because seawater contains a wide range of minerals which include common major metal ions such as Na^+, Mg^{2+}, K^+, Ca^{2+}. The extraction of these metal ions from seawater is considered cheap as is the benefit of having the targeted analyte readily dissolved in the solution [1]. In this regard, seawater could be considered as an option to fight against the depletion of high-grade ores and maintain long-term stability. Minerals such as sodium known as common table salt are found in seawater at very high concentrations followed by magnesium, calcium, and potassium and lithium comes after potassium with a very low concentration of 0.17 mg/L. These minerals have been commercially extracted from seawater several times [2]. Extraction methods that have been developed for mineral extraction from seawater include chemical precipitation, solar evaporation and solvent extraction [3–5]. However, further investigation is required to identify feasible methods of extracting these essential minerals mainly lithium [4,5].

Polymer inclusion membranes (PIMs) are a non-porous physical barrier that comprises a carrier trapped inside a polymeric matrix providing the membrane with increased stability [1,6]. Furthermore, the use of PIMs has grown in recent years due to their properties which include high selectivity, strength and reusability [7]. The advantage of using PIMs is that they are environmentally sustainable since they are not associated with the use of harsh solvents, and they require a very small amount of solvent. The carrier leaching into the aqueous phase is very minimal because the membrane liquid phase is immobilized in a network of nanoscale channels [8]. Another advantage of using a PIM as the semipermeable membrane barrier in an extraction process tool is the ability to use solutions such as hydrochloric acid (HCl) or sodium chloride (NaCl) instead of an organic solvent or a solid sorbent/resin as the receiving phase [8]. The two most popular polymers that are frequently used to synthesize PIMs are polyvinyl chloride (PVC) and cellulose triacetate (CTA). However, membranes made of PVC are known to withstand highly acidic conditions compared to CTA membranes [9]. PIMs can also be carried out by using similar extractants which are also employed in solvent extraction. In addition, a plasticizer added to the membrane polymer can increase its flexibility and promote the complex formed to disperse [6]. The most interesting part of PIMs is that when they are incorporated into the extraction tool it allows for both extraction and back-extraction to occur simultaneously. This saves a lot of time unlike other conventional methods such as ion exchange resins which are time-consuming [9]. PIMs serve as semipermeable membranes in extraction devices by dividing a receiving solution from the aquatic medium such as lake or river samples. During the deployment of an extraction device, the target analyte contained in the feed source is thereby continually carried across the PIM and accumulates inside the receiving solution. These targeted analytes move to the receiver solution through a variety of transport mechanisms depending on the system [8].

In the previous work that was conducted in this study, a similar system was optimised, and the optimum parameters were used for a semi-upscaled version. The main aim was to investigate the behaviour of the system as the sample volume of the feed was increased from 5 L to 10 L and the acceptor solution volume was increased from 5 mL to 2 L.

4.2 Research methodology

4.2.1 Materials and reagents

The commercial extractants, thenoyltrifluoroacetone (TTA) and trioctylphosphine oxide (TOPO) were supplied by Sigma Aldrich (Johannesburg, South Africa) and used as received for the preparation of PIM. Cellulose triacetate (CTA) base was supplied by Sigma Aldrich. Chemicals such as nitric acid (55%), dichloromethane (DCM) (99, 9%) HPLC grade and hydrochloric acid (HCl) (32%) were also supplied by Sigma Aldrich.

4.2.2 Instrumentation

The functional groups of the components were studied before and after extractions using Fourier-transformed infrared spectrometry (FTIR) from Bruker (Johannesburg, South Africa). All the pH measurements were conducted with a Five Easy FE20 pH meter from Mettler Toledo (Johannesburg, South Africa). A top balance from Ohaus (Johannesburg, South Africa) was employed for weighing all the PIM components. The ultrapure water from the Milli-Q-RO4 water system purchased from Millipore (Bedford Massachusetts, USA) was used for the preparation of all solutions. The flat sheet membranes were made by casting the membrane using a 4340 Automatic Film Applicator purchased from Elcometer (Manchester, UK). The concentration of metal ions in the solutions was quantified by ICP-OES from Spectro Genesis (Kleve, Germany). The morphology of the PIM was studied using the scanning electron microscope (SEM) coupled with energy-dispersive spectroscopy (EDS) from (Zeiss Evo 50, Oberkochen, Germany). The samples were cut into small pieces for the surface and cross section analysis. The small piece of PIM was torn so that the cross-section images would be visible. The samples were further coated with gold palladium prior SEM analysis.

4.2.3 Preparation of semi-upscaled polymer inclusion membrane (PIM)

PIMs were created by weighing the CTA, TTA, TOPO, and 2-NPOE components of the membrane and then further dissolving them in DCM. The mixture was then poured into the casting machine shown in **Fig. 1** to obtain a flat sheet. The DCM was left to evaporate overnight at room temperature to produce a uniform, transparent, flexible, and mechanically strong membrane. After that, the membrane was removed from the glass plate by placing the glass into the container with ultrapure water. The resulting membrane was left to dry at room temperature. A round piece with a diameter of 260 mm was removed from its central section and subsequently used for the extraction experiments.

Fig. 1. Casting machine for PIM preparation

4.2.4 The semi-upscaled design and static experimental setup

The static experiments were carried out using the previously optimised method which in this study was further semi-upscaled for the extraction of minerals in seawater using the bigger extraction devices shown in **Fig. 2**. This device is a version of the small device used for optimisation which was made by the Department of Physics at Witwatersrand University (Johannesburg, South Africa). The feed solution in the 25 L plastic container had 10 L of seawater shown in **Fig. 3**. The concentration of the receiver solution varied between 0,05 M HCl and 0,1 M HCl. This extraction device has about a 5 L acceptor volume, but during the experiments, 1 and 2 L volumes of the receiver solution were used. The extraction time was up to 39 days. The pH of the feed solutions was 8.5 which was the optimum pH adopted during the optimisation. Sample collection of 10 mL of the receiving phase was carried out every 13 days until day 39 for the analysis of metal ions using the ICP-OES instrument. The first sample collection of 10 mL was made after 13 days, and additional collections were made until day 39.

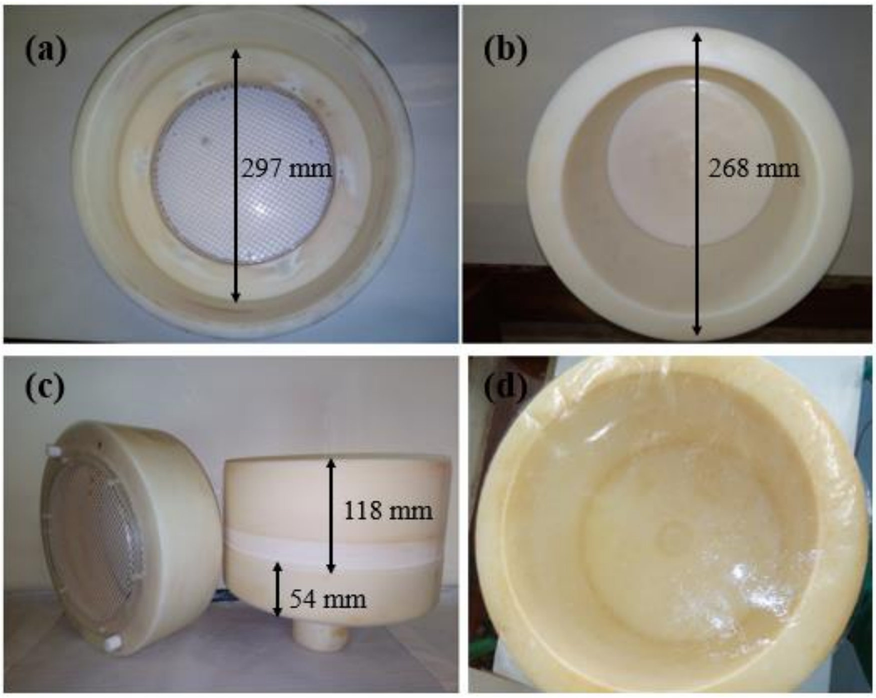

Fig. 2. A representation showing (a) the screw cap with an opening window, (b) the receiver solution chamber, (c) the extraction device and d) shows how the synthesized PIM was placed in the opening of the receiver solution chamber.

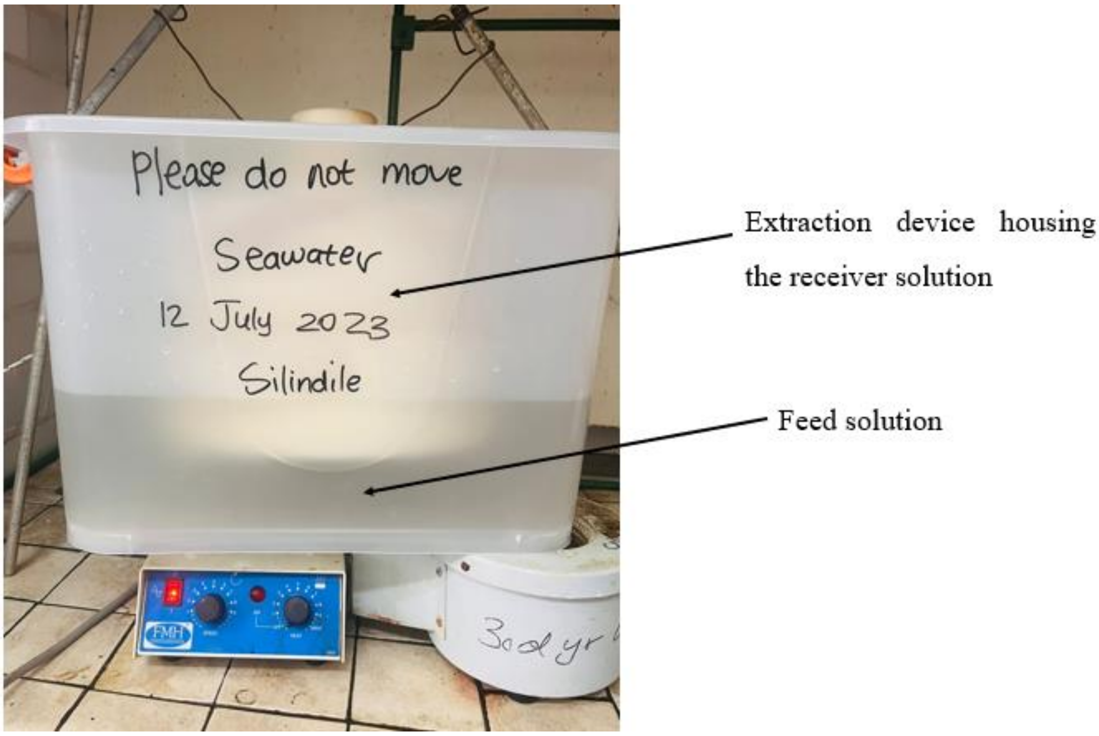

Fig. 3. Laboratory experimental setup for a semi-upscaled extraction device.

4.3 Results and discussion

4.3.1 FTIR spectroscopy studies

The FTIR spectroscopy studies were conducted to investigate the functional groups of the PIM components. The obtained spectra of the membrane before and after extraction are shown in **Fig. 4**. The PIM before extraction shows stretching observed at 2923 cm^{-1} and 2856 cm^{-1} corresponding to the asymmetric and symmetric stretching bands of (CH_2) for TOPO. The band observed at 1745 cm^{-1} is the stretching vibration of the (C=O) group in CTA [10]. Another band representing the (C=O) was observed around 1641 cm^{-1} corresponding to TTA which was used as a carrier during the preparation of PIM [11]. The vibrational bands shown at around 1224 cm^{-1} and 1041 cm^{-1} represent the (C-O-C) for both asymmetric and symmetric single bonds of the CTA and the peak at 1359 cm^{-1} is attributed to the (C-H) bonds. These vibrational bands for CTA correspond to what was observed by [10,11]. The main functional group of the plasticizer such as (NO_2) is observed in all the spectra at approximately 1526 cm^{-1}. The stretching observed in all the spectra at 1149 cm^{-1} corresponds to the (P=O) group for TOPO. Moreover, the (C-H) band appearing at 721 cm^{-1} corresponds to the TTA carrier molecule [11]. This vibrational band was weakened after the exposure of the membrane to seawater after 39 days of extraction. In addition, the extraction was conducted for 39 days in real seawater samples. After the extraction, the functional groups remained attached to the PIM. No chemical shift was observed but this is qualitative information, and it was difficult to tell whether the membrane composition itself was still the same. However, the (P=O) group from the (TOPO) carrier formed one weak band with the peak observed at 1108 cm^{-1}. This would mean that (P=O) is one of the main functional groups that plays a huge role in the transport mechanism [12]. The FTIR results from the PIM exposed to both 0,05 M HCl and 0,1 M HCl as acceptor solutions were the same. The slight change in some of the peaks after extraction might be the result of a longer exposure resulting in degradation brought on by the partial elimination of acetyl groups [13].

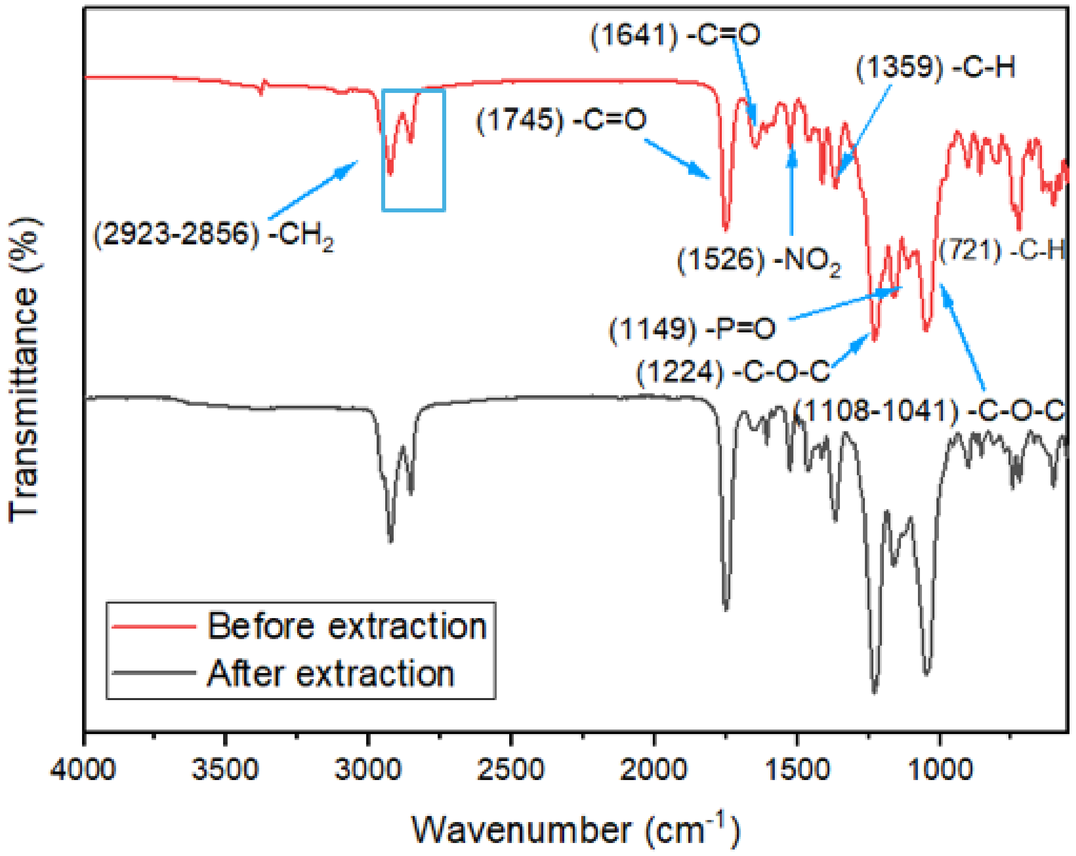

Fig. 4. FT-IR spectra of the PIM before and after the removal of metal ions from seawater. The extraction in seawater was conducted for 39 days using the synthesized PIM.

4.3.2 SEM study

The quality of the membrane is largely determined by the morphology of the membrane [10]. Before the PIM morphological studies, the synthesized membrane obtained was homogeneous, dense, and soft. The surface of the membrane in **Fig. 5 (a)** represents the membrane base (CTA) before extraction. The membrane shows a smooth surface with small defects in it. In **Fig. 5 (b),** the surface of the PIM was rough with spherical shaped particles. In **Fig. 5 (c)**, the PIM showed small deposits and visible possible pores after the addition of all components (CTA: TTA: TOPO: NPOE). SEM was used in one of the studies that [14] reported to characterize their CTA-based membrane. Before the incorporation of additional components into the CTA basis, they noticed that the membrane's surface displayed apparent pores. The cross-section shown in **Fig. 5 (d)** reveals finger-like structures. The surface of the PIM shown in **Fig. 5 (e)** shows a drastic change in the morphology as the spherical shapes that were observed before analysis completely disappeared after the extraction of metal ions from seawater. This could be due to the large number of metal ions and anions with high concentrations constantly bombarding the PIM [13]. The cross section in **Fig. 5 (f)** also changed because the finger-like structures deteriorated. The section is evidence that there were a lot of matrices deposited on the surface of the membrane and were not lost as they can be observed under the EDS analysis. The membrane’s alteration after extraction of metal ions in seawater may be related to the lack of selectivity or membrane’s composition.

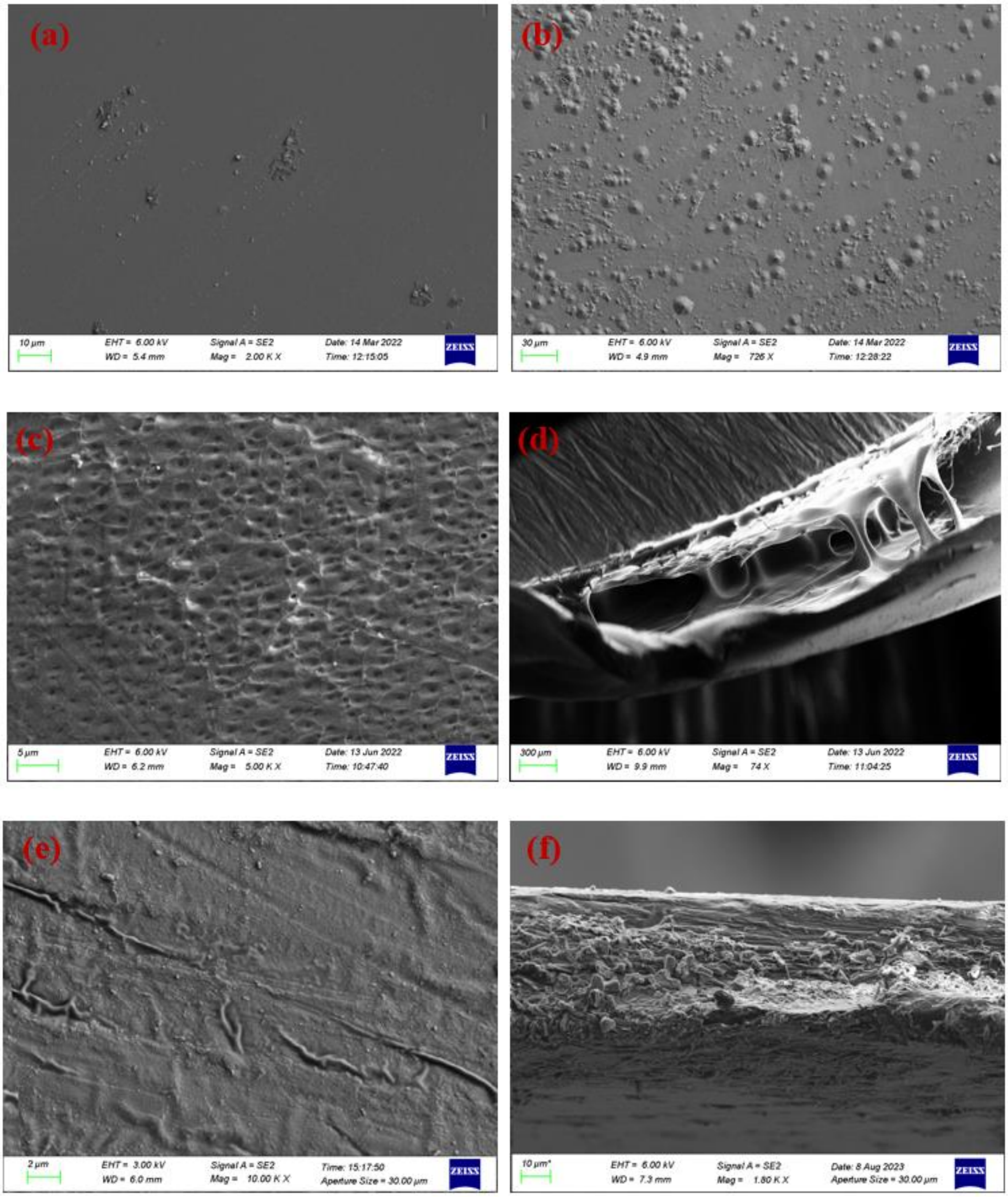

Fig. 5. SEM images of the PIM using 0,05 M HCl receiver solution. (a) is the surface of the CTA before extraction, (b) the surface of CTA after the addition of 2-NPOE, (c) the surface containing CTA: TTA: TOPO: 2-NPOE before extraction, (d) the cross-section containing CTA: TTA: TOPO: NPOE before extraction, (e) surface of the membrane after 39 days of extraction and its cross-section (f).

4.3.3 Energy dispersive spectroscopy (EDS)

Energy dispersive spectroscopy (EDS) was carried out to investigate the metals that remain attached to the surface of the membrane after extraction. The spectra from **Fig. 6 (a)** showed an enhanced potassium peak 0,1 KeV. Whereas in **Fig. 6 (b)** the big defect indicated by the circle shows the targeted analyte such as calcium with the other non-targeted analytes such as chlorides peak at 0,5-0,8 KeV, iron peaks at 0,1 KeV and 5,3 KeV, sulphur peak at 0,5 KeV, titanium peaks at 0,1 KeV and 0,9 KeV, and phosphorus peak at 0,4 KeV. The appearance of calcium as a possible precipitate on the surface of the membrane might be an indication of why calcium was less extracted than magnesium because most of it was blocked by other competing metal ions. Most of these non-targeted analytes such as iron, sulphur, phosphorus and titanium were not detected on the ICP-OES instrument. **Fig. 6 (c)** shows chlorides and some sodium. The EDS for 0,1 M HCl receiver solution had few non-metals such as carbon, sulphur, oxygen and chlorides which is why it was not included in this section because they didn't include many interesting metal ions.

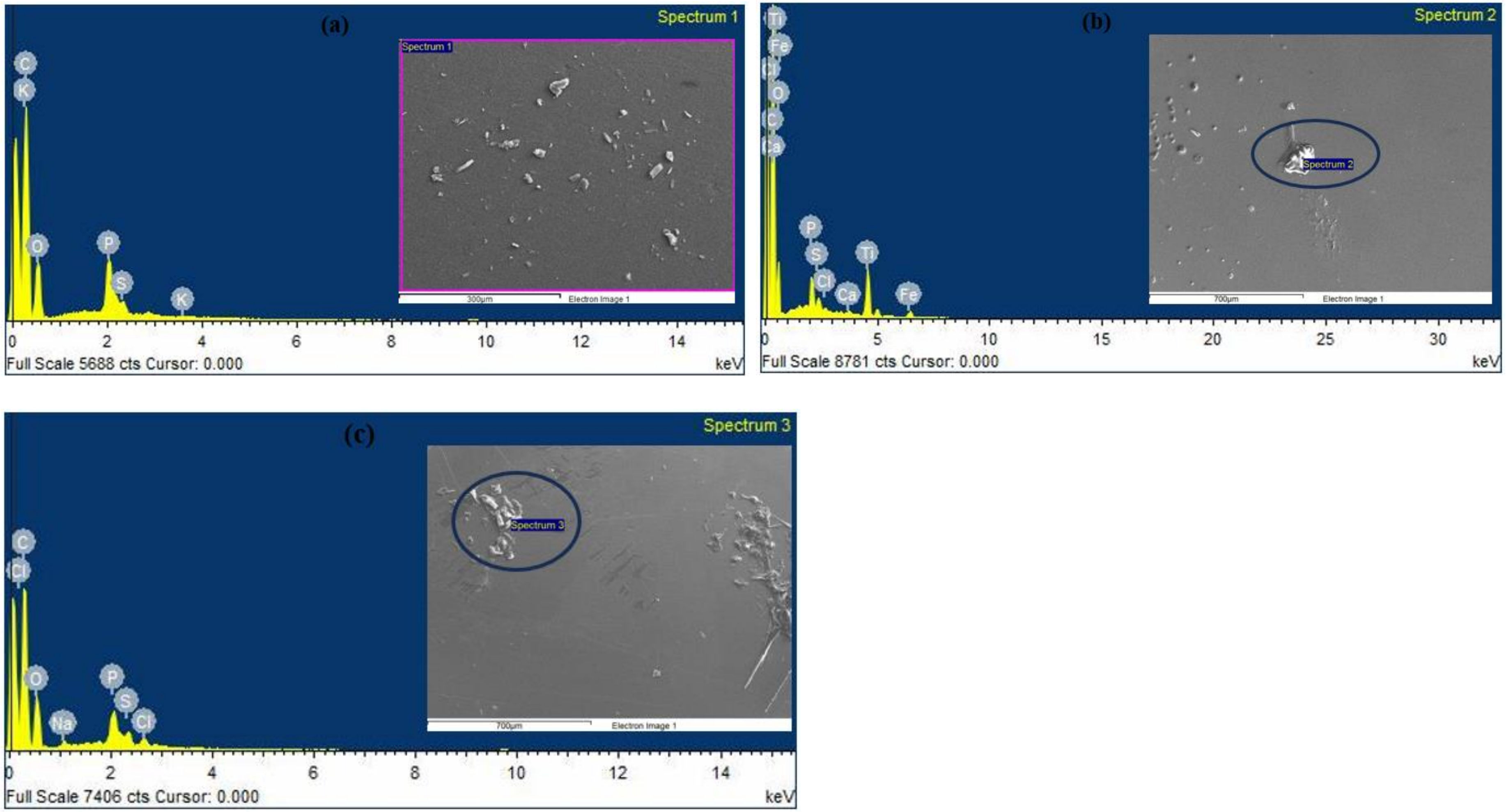

Fig. 6. EDS spectrum of the upscaled PIM with 60 wt % of the carriers, TTA and TOPO (1: 1): 30 wt % (CTA): 10 wt % (NPOE) plasticizer. Receiver solution at 0,05 M HCl. The spectra that are shown in a, b and c reveal metal ions that remained attached to the surface of the PIM after extraction.

4.3.4 Application of semi-upscaled PIM extraction device to seawater

The optimum composition from previous studies which was found to be 60 wt % of the carriers, TTA and TOPO (1: 1): 30 wt % (CTA): 10 wt % (2-NPOE) plasticizer was applied to seawater with a semi-upscaled extraction device. The PIM was semi-upscaled from its smaller-scale version. The semi-upscaled acceptor volumes of 1 L and 2 L were as compared to 5mL in the first paper. These two different receiver volumes are used for comparison with uptake amounts and the resulting selectivity of extraction. The findings of this investigation are displayed in **Table 1** and **Fig. 7**. The receiver solution of 0,05 M HCl with both 1 L and 2 L had the same selectivity which was $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ with no significant difference. When the PIM was deployed in 0,1 M HCl of receiver solution, the selectivity obtained for 1 L and 2 L receiver volumes was $Mg^{2+} > Ca^{2+} > K^+$ and K^+. The concentration of sodium did not show clear trend, therefore it was not reported. So, comparing these results with what was obtained from the first paper for the application of the optimised membrane in seawater, the selectivity was $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. The uptake of sodium was very low as was the uptake of potassium and lithium was not detected. With regards to the DFT studies, the selectivity $Mg^{2+} > Ca^{2+} > Li^+ \approx Na^+ > K^+$ was nearly the same compared to the small system presented in **paper 1**. Moreover, this selectivity is different from the semi-upscaled system. The small PIM system strongly preferred magnesium than the rest of the metal ions. There was a deviation in the selectivity on the semi-upscaled PIM since the system was taking more sodium than the rest of the tested metals. The sudden change in selectivity is not known. However, given that the same seawater was used throughout, it's possible that because the feed solution was in an open container during the extraction, some of the seawater may have evaporated and turned into brine. In that case, the concentration of sodium might have increased drastically. Another possible reason might be the loss of the carrier ratio during the upscaling. According to the reports, $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ is the primary metal ions that make up 99.9% of the salts in seawater in decreasing order [15]. The extraction of sodium was greater than that of magnesium, calcium and potassium. The trend obtained from the semi-upscaled method is exactly what is estimated from seawater and does not take into account the selectivity of the carriers as given by DFT studies.

The concentration of the metal ions showed a decrease when the concentration of the receiver solution was increased to 0,1 M HCl. A similar trend was discovered in a previous study whereby they noticed that increasing the concentration of the receiver solution (HCl) reduced the extraction percentages of their target metal ion [18]. In the previous study, it was reported that the mechanism of transport of metal ions from the feed phase was said to be a counter-coupled transport of H^+ in the opposite direction [19].

Table 1

Summary of selectivity of extraction between 0.05 M HCl and 0.1 M HCl at 1 L and 2 L of the receiver solution.

Receiver solution		**Receiver solution**	
0,05 M HCl (1 L)	**0,05 M HCl (2 L)**	**0,1 M HCl (1 L)**	**0,1 M HCl (2 L)**
$Na^+ > Mg^{2+} > Ca^{2+} > K^+$	$Na^+ > Mg^{2+} > Ca^{2+} > K^+$	$Mg^{2+} > Ca^{2+} > K^+$	$Mg^{2+} > Ca^{2+} > K^+$

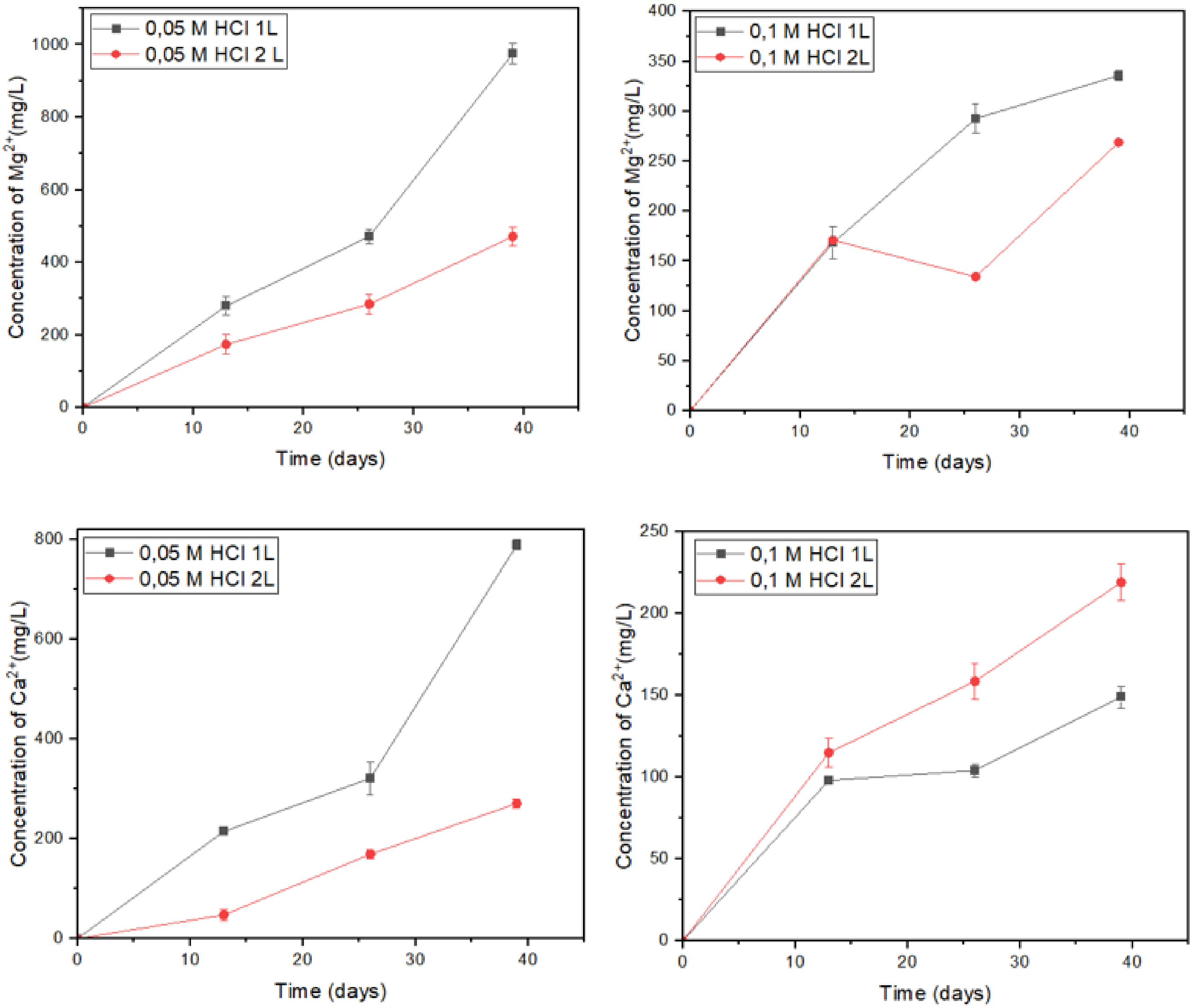

Fig. 7. Transport of minerals across the membrane using a bigger passive sampler device. Conditions: the upscaled membrane composition: 60 wt % of the carriers, TTA and TOPO (1: 1): 30 wt % (CTA): 10 wt % (NPOE) plasticizer, pH 8,5, the concentration of receiver solution - 0,05 M HCl and 0,1 M HCl, 39 days of extraction. The error bars are ±SD (standard deviation).

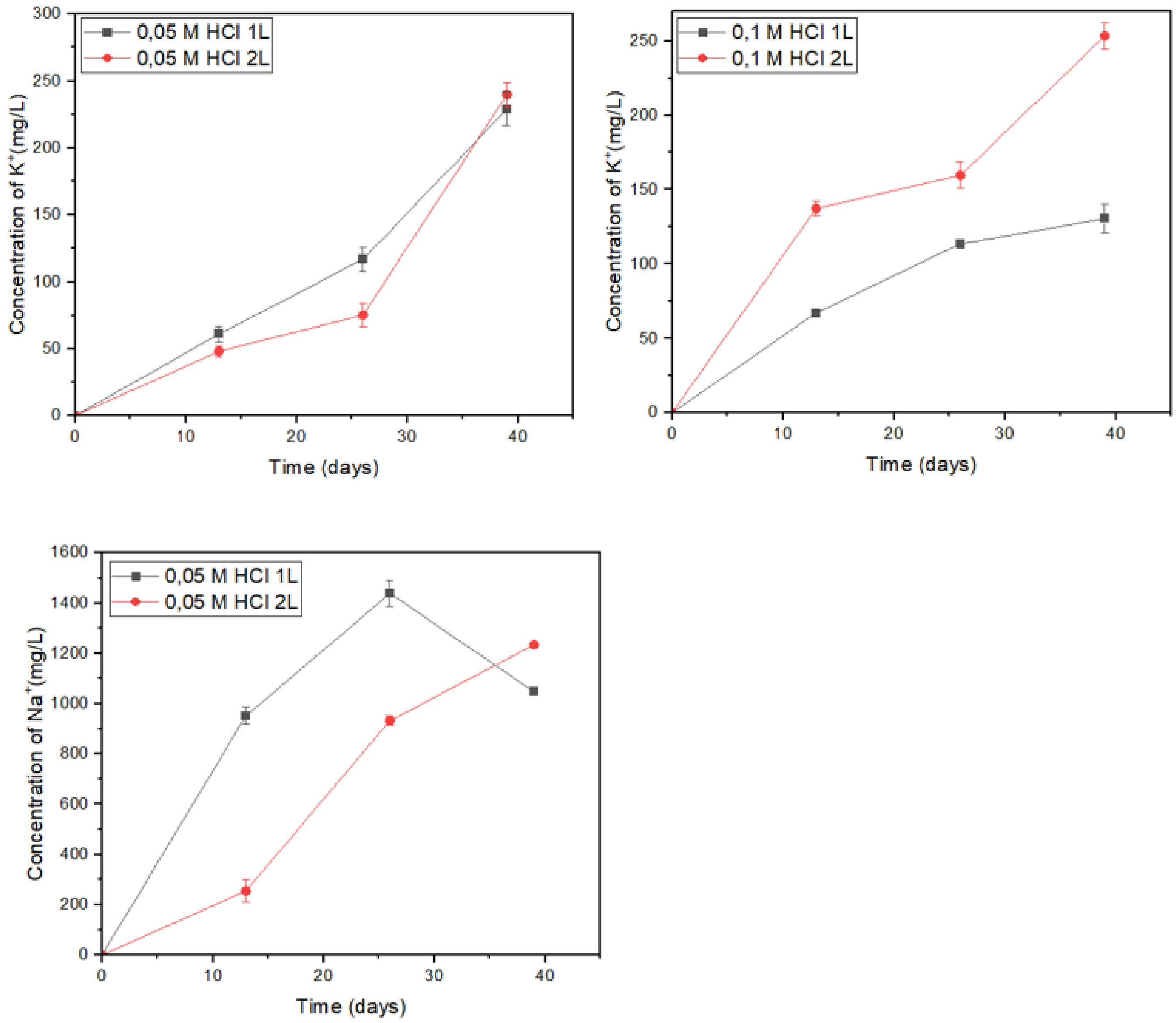

Fig. 7. Transport of minerals across the membrane using a bigger passive sampler device. Conditions: the upscaled membrane composition: 60 wt % of the carriers, TTA and TOPO (1: 1): 30 wt % (CTA): 10 wt % (NPOE) plasticizer, pH 8,5, the concentration of receiver solution - 0,05 M HCl and 0,1 M HCl, 39 days of extraction. The error bars are ±SD (standard deviation) **(Continues).**

4.4 Conclusion and recommendations

Previous optimised small PIM system was semi-upscaled and applied to seawater. The semi-upscaled system worked well but lacked selectivity. The results obtained gave the selectivity of $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ but all these metals were sufficiently extracted. When comparing this selectivity to that of the small extraction device, which yielded the selectivity of $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$ is not the same. The small PIM system strongly preferred magnesium as its uptake was higher compared to the rest of the metal ions. This deviation requires further investigation to determine whether the upscaling may have affected the composition of the membrane leading to a change in selectivity.

Declaration of Competing Interest

The authors declare that none of the work reported in this study could have been influenced by any known competing financial interests or personal relationships.

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CHAPTER 5

This chapter highlights the development and application of polymer inclusion membrane in all three papers presented for the extraction of minerals from seawater.

5. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 CONCLUSIONS

The demand for essential minerals which include lithium, calcium and magnesium has increased due to their chemical properties which are very useful in many applications. Based on the literature review discussed, it was highlighted that the traditional methods have disadvantages which include the usage of large amounts of organic solvents, and they are not environmentally friendly. PIMs offer several advantages such as high selectivity and the potential for reuse. This study sought to develop and optimise extraction techniques such as polymer inclusion membrane (PIM) for the extraction of essential minerals in seawater samples. Then to investigate the performance of the synthesized PIM in spiked ultrapure water and in real seawater samples.

Based on the results obtained in this research work, the synthesized PIM was successfully tested for possible extraction of metal ions in seawater. Metals that were tested in this study include lithium, magnesium, and calcium as well as sodium and potassium, since their concentrations are also high in seawater. The PIM was tested in spiked ultrapure water and the selectivity obtained from the spiked samples for the optimised parameters of the small PIM system was $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+} > Li^{+}$. Whereas the application in the actual seawater resulted in a selectivity of $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$. However, the selectivity obtained from the DFT studies was $Mg^{2+} > Ca^{2+} > Li^{+} \approx Na^{+} > K^{+}$. The DFT studies agreed with the results obtained in real seawater samples. This is an indication that the components and composition used had a great impact on the selectivity of the target metals. This was also in agreement with the computational studies conducted.

In the second approach, another PIM composition was developed for the possible selective extraction of lithium. The previous reported method by Fernandez-Escalante was used as a guide although the researchers used a liquid-liquid extraction approach for the extraction of lithium. So, the same components such as dibenzyl methane (DBM) and trioctylphosphine oxide (TOPO) were used in this study and on the spiked samples, the PIM preferred lithium. However, in their study only spiked samples for lithium was tested. Therefore, in our study we first optimised the system in the presence of all other major metal ions found in seawater and then applied to real seawater to investigate how the uptake of lithium is influenced by other metals. The optimised membrane composition with carrier ratios of 1:1 (DBM: TOPO) and 2:1 (DBM: TOPO) were employed. The selectivity obtained for a 1:1 ratio using different concentrations of the receiver solutions such as 0,05 M HCl, 0,1 M HCl and 1 M HCl were $Li^+ > Na^+ > Ca^{2+} > Mg^{2+}$, $Li^+ > Ca^{2+} > Na^+ > K^+ > Mg^{2+}$ and $Li^+ > Ca^{2+} > Na^+ > K^+$, respectively in spiked samples. The selectivity obtained after the extraction of metals from seawater was $Ca^{2+} > Na^+ > K^+$ as lithium was not detected. The second membrane in a 2:1 ratio was also tested in spiked samples and the selectivity obtained was $Li^+ > Ca^{2+} > Na^+ > Mg^{2+}$ for 0,05 M HCl of the receiver solution. However, when the concentration of the stripping solution was changed to 0,1 M and 1 M HCl the selectivity was $Li^+ > Ca^{2+} > Na^+ > K^+$ for both concentrations. The PIM composition was further tested in seawater resulting in the selectivity of $Ca^{2+} > Na^+ > K^+ > Mg^{2+}$ for the 0,05 M HCl receiver solution and $Ca^{2+} > Na^+ > K^+$ when the concentration was increased to 0,1 M HCl. The membrane was further tested in seawater with the concentration of the receiver solution increased to 1 M HCl giving a selectivity of $Na^+ > K^+$.

The third approach was based in semi-upscaled which was conducted on seawater samples using the bigger extraction device. The optimised parameters obtained in **paper 1** were then applied for semi-upscaling. The main idea was to investigate the behaviour of the system as the sample volume of the feed was increased from 5 L to 10 L while the acceptor solution volume was increased from 5 mL to 2 L. Therefore, the volume of the receiver solution was tested in 1 L and 2 L. Whereas, different concentrations of the receiver solution were also tested in both 0,05 M HCl and 0,1 M HCl. The selectivity obtained was $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ for 0.05 M HCl in both 1 L and 2 L of the receiver solution. When the membrane was tested in 0,1 M HCl of the receiver solution exhibited a selectivity of $Mg^{2+} > Ca^{2+} > K^+$ for both 1 L and 2 L of the receiver solution. The trend was not clear for 0,1 M HCl receiver solution for both volumes when it comes to sodium.

The membranes were successfully characterized using FTIR, SEM equipped with EDS. The functional groups present in the PIM were confirmed using FTIR spectroscopy. These functional groups include -C=O, -C-O-C, $-NO_2$, -OH, $-CH_3$, $-CH_2$ and P=O.

The synthesized PIM has demonstrated the ability to extract lithium, calcium, magnesium, potassium and sodium in spiked ultrapure water. Whereas, in real seawater it was able to extract magnesium, calcium, potassium and sodium. However, the overall approach was observed to have high selectivity in laboratory scale using synthetic seawater, but their selectivity increased further when the PIM was exposed to the actual seawater which is known to have complex matrices. This indicated that the optimization process successfully demonstrated to real-world scenarios. The proposed membrane was deployed over a period of 39 days indicating its potential for long-term use in practical applications.

5.2 RECOMMENDATIONS FOR FUTURE WORK

The study’s aim and objectives were successfully achieved. However, the following recommendations can be considered for future work in order to improve the findings obtained from this study:

- The proposed membrane was observed to have the ability to extract the metals of interest both in spiked ultrapure water and real seawater samples. However, the extraction of metals can be improved by combining both the PIM approach and the precipitation method. Thus, the approach involves first precipitating out some metal ions followed by extracting what is remaining using the PIM approach. This is because the selectivity towards lithium was enhanced on the spiked samples which is evidence that lithium is extracted better when the matrix has the same concentration. The system changed when the membrane was tested on real seawater samples.
- PIM stability and reusability can be further investigated to ensure consistent performance over multiple cycles in real seawater samples.
- The proposed PIM may also be deployed in the ocean to investigate if the extraction processes are both environmentally benign and economically viable. These tests will help identify any challenges that arise from pilot-scale setting in terms of membrane consistency and cost to assess its potential as a promising technology.