

# USE OF IONIC LIQUIDS FOR PRODUCED WATER TREATMENT

by

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## **Dedication**

*I want to dedicate this work to Allah Almighty who Is my creator and source of my faith and strength. To my supervisor for guidance, inspiration, and assistance. To my family, parents, and friends for their support and motivation.*

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## Abstract

Produced water (PW) has adverse effects on human health and aquatic life. Finding a viable method for the efficient extraction of oil from PW is a challenging task for environmental researchers. In this work, various ionic liquids (ILs) having bis(trifluoromethylsulfonyl)imide (NTf<sub>2</sub>) anion with different cations such as imidazolium, ammonium, phosphonium, and pyridinium were employed for the removal of oil from PW through liquid-liquid extraction (LLE). Clay-alginate beads loaded with ILs were also applied as adsorbents via the adsorption process. The effect of ILs structure on the removal efficiency of ILs was examined. The effects of several process parameters such as initial concentration of oil, contact time, pH, phase ratio, and temperature on the removal efficiency of ILs were analyzed and optimized. Different characterization such as Fourier transform infrared spectrophotometer (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and thermal gravimetric analysis (TGA) were used to investigate the surface morphology, chemical bond structure and functional group, and thermal stability of the used materials, respectively. Results revealed that 1-decyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [C<sub>10</sub>Mim][NTf<sub>2</sub>] is the best ionic liquid (IL) among the studied ILs at optimum conditions (500 ppm initial oil concentration, 4 min contact time, 8 pH, and at room temperature) with a removal efficiency of 92.8% through LLE. However, clay-alginate-IL beads indicated a removal efficiency of 71.8 % at optimum conditions (600 ppm initial oil concentration, 70 min contact time, 10 pH, and at room temperature) with an adsorption capacity of 431 mg/g. FTIR analysis confirmed the successful chemical bond interaction of oil with IL and beads. SEM analysis verified that beads have a porous and rough surface which is appropriate for the adsorption of oil onto the bead's surface. TGA analysis provides the thermal degradation profile of clay-alginate-IL. Moreover, the beads used in the adsorption process were regenerated and used up to 4 cycles.

**Keywords:** *Produced Water, Emulsified Oil, Liquid-Liquid Extraction, Ionic Liquids, Adsorption, Clay-Alginate beads*

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## List of Abbreviations

ADNOC	Abu Dhabi National Oil Company
COD	Chemical Oxygen Demand
EDX	Energy Dispersive X-Ray
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectrophotometer
HCO	Heavy Crude Oil
ILs	Ionic Liquids
LLE	Liquid-Liquid Extraction
NPDES	National Pollution Discharge Elimination System
PAHs	Polycyclic, Aromatic Hydrocarbons
ppm	Parts Per Million
RO	Reverse Osmosis
SBRs	Sequencing Batch Reactors
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solids
TGA	Thermal Gravimetric Analysis
TOC	Total Organic Carbon
TPHs	Total Petroleum Hydrocarbons
VFAs	Volatile Fatty Acids

## **Chapter 1. Introduction**

This chapter provides an overview of produced water (PW), its treatment technologies, and the problems associated with them. It also gives an idea about the objective of the thesis and research contribution for PW treatment.

### **1.1. Overview**

Oil and gas play a key role in our daily life applications. Therefore, the consumption of oil and gas is increasing day by day [1]. Due to high consumption and demand for oil and gas, this industry has got a significant attraction in the present era. This significant demand for petroleum and related products has increased extraction processes in the oil and gas industries. The Arabian Gulf is considered the largest petroleum production area in the world [2]. During the extraction process of oil, a huge amount of wastewater streams is produced which is known as PW [3]. PW is 80 to 95 % of the total liquid waste obtained during the extraction process. It is estimated that almost 75 billion barrels of PW are being produced annually worldwide [4].

Alkaline surfactants and polymers are added for maximum recovery of oil because they lower the surface tension between the surface of crude oil and water [5]. PW consists of a huge amount of organic and inorganic compounds, including but not limited to, dissolved and dispersed oil, grease, heavy metals, waxes, chemicals, surfactants, salts, microorganisms, and gases [6]. However, the physical and chemical characteristics of PW may vary depending on the geographical location of oil reservoirs, the nature of the produced hydrocarbons, operating conditions, and added chemicals [7]. Moreover, the composition of PW can be changed according to different sources [3].

PW is being discharged into oceans and lakes without proper treatment which has caused serious environmental issues [8]. PW has become a major environmental concern due to its complex physiochemical nature, toxicity, variation in composition, bulk discharged amount, and contamination [9]. Water contaminated with oil and organic compounds showed an adverse negative effect on human health and marine life [10]. Therefore, oil and gas companies must treat PW before discharging it into the environment to reduce toxicity and mitigate its effects on soil, underground and surface water, and human health.

Multiple techniques have been used for the removal of different organic and inorganic pollutants such as dispersed oil, grease, gases, and heavy metals from aqueous solutions. These include physical, chemical, and biochemical methods, such as gravity separation, hydro-cyclones, membrane separation, filtration electro dialysis, precipitation, and adsorption [11]. Most techniques have some disadvantages, such as the involved cost, the toxicity of the material used, not being ecofriendly, and the lacking efficiency [11]. Ionic liquids (ILs) got more attraction due to their intrinsic properties of negligible vapor pressure, thermal stability, excellent solvation characteristics, and easy isolation from the aqueous stream for hydrophobic ILs [12]. These properties of ILs make them an environmentally friendly and potentially cost-effective alternative to other toxic solvents with high vapor pressure [13].

In this study, room temperature ILs were employed for the treatment of PW via Liquid-Liquid Extraction (LLE) and adsorption.

## **1.2. Thesis Objectives**

Multiple techniques have been developed for the treatment of PW to remove pollutants. These techniques are not economical and require the use of hazardous materials. In this study, room temperature ILs were examined and tested for their potential application as extraction solvents for the removal of emulsified oil from PW. The objective of this study was to remove emulsified oil from PW using appropriate ILs and examine the optimum operating condition for LLE and adsorption processes. Advanced analytical methods were applied to examine the changes in PW before and after treatment with ILs qualitatively and quantitatively.

## **1.3. Research Contribution**

The research contribution is summed up below:

- Characterization of PW and investigating appropriate treatment using ILs.
- Screening of the ILs for the PW treatment.
- Study the effect of ILs structures on removal efficiency of ILs.
- Evaluation of removal of the emulsified oil from PW using ILs via LLE and adsorption.

- Determination of the optimum conditions such as pH, initial concentration, contact time, phase ratio, temperature, and salt effect for LLE and adsorption.
- Analyzing the surface morphology, chemical bond structure and functional group interaction, and thermal stability of PW, IL, and beads using various characterization techniques such as SEM-EDX, FTIR, and TGA analysis.
- Thermodynamics study for the removal of oil from PW using pure ILs through LLE.
- Adsorption kinetics and isotherm study for the removal of oil from PW using clay-alginate-IL beads through adsorption.

#### **1.4. Thesis Organization**

Chapter 2 describes the introduction of PW with its characterization and properties. The composition of PW was discussed in detail in chapter 2. Technologies available for the treatment of PW were also discussed in this chapter. A brief introduction of ILs, their properties, and their applications are also included in chapter 2. Chapter 3 discusses the experimental methodology, chemicals, and instruments used in this work. Chapter 4 represents the results and discussion in detail for this work. Chapter 5 describes the conclusion, summary of the work with recommendations and suggestions.



## **Chapter 2. Background and Literature Review**

In this chapter PW sources, constituent chemical species, and characteristics will be discussed. Moreover, the techniques available for the treatment of PW are also discussed in detail. This chapter also highlights the introduction of ILs, their properties, and their application in various fields.

### **2.1. Produced Water and its Characteristics**

This section discussed the basic overview of PW including the introduction and basic sources of PW. Besides, this section discusses the nature, composition, and characteristics of PW.

#### **2.1.1 What is produced water?**

PW is wastewater that is generated when gas and oil are produced from offshore wells or onshore wells. The freshwater which has been confined with oil and natural gas for many years in a geological reservoir is called formation water [14]. It will emerge when a hydrocarbon reservoir accompanied by oil, natural gas is accessed by a well. However, to increase the recovery rate, freshwater, brine, and chemicals are pumped into the reservoir. The combination of pumped water and formation water is known as PW, which can consist of 80 % of the waste and residuals produced from the natural gas operation unit. Flow back water is another important term to be highlighted. Flow back water contains a major part of the fluid which is injected into the oil well in fracturing operation at high pressure. Although some amount of this water will be appearing again on the surface after some days of the fracturing operation. The re-appearance of water will have a higher amount of total dissolved solids (TDS) and chemicals [15].

#### **2.1.2 Characteristics of produced water.**

The main constituents of PW are organic and inorganic materials [8]. The physical and chemical characteristics of PW are determined by the following factors.

- The geographical location of the oil reservoir
- Existence of reservoir
- Nature of hydrocarbon produced

- Operating conditions and chemicals added

However, PW composition varies according to different sources, most are like the composition of oil/gas production. Major components present in PW are [16]:

- Dispersed and dissolved oil components
- Dissolved formation minerals
- Production chemical compound
- Dissolved gases
- Production solids such as waxes, bacteria, scale, and corrosion products

Dispersed and dissolved oil compounds consist mostly of hydrocarbons such as xylene, benzene, toluene, and polycyclic aromatic hydrocarbons [17]. These hydrocarbons are mostly dispersed into the water due to immiscibility and their amount depends on pH, salinity, TDS the oil/water ratio, temperature, and oil composition. Soluble organic compounds are also present in PW such as propionic acid and formic acid and their amount depends on the type of oil, pH, pressure, and temperature [18].

The oil present in PW consists of petroleum compounds, which can be hydrocarbons or heteroatoms. Hydrocarbons correspond to Total Petroleum Hydrocarbons (TPHs) which have only carbon and hydrogen [8]. Heteroatoms compounds include sulfur, oxygen, nitrogen in addition to carbon and hydrogen. These hydrocarbons can be classified into saturated, unsaturated, and aromatic hydrocarbons. The saturated hydrocarbons can be categorized into aliphatic and alicyclic. The unsaturated hydrocarbons can be divided into alkenes and alkynes. The unsaturated hydrocarbons are produced during the cracking process. Aromatic compounds consist of benzene rings [10]. Moreover, the most toxic hydrocarbons, such as aromatic hydrocarbons (PAHs), and aliphatic hydrocarbons are difficult to be separated from PW. The concentration of these hydrocarbons depends on the density of oil and interfacial tension between water and oil [19]]. The dissolved formation minerals, production solids, chemicals, and corrosion inhibitors are also present in PW, depending on the geological location of the reservoir.

Table 2-1: Summary of the parameters and heavy metals found in the PW

<b>Parameters</b>	<b>Values</b>	<b>Heavy Metals</b>	<b>Values (mg/L)</b>
Density (kg/m <sup>3</sup> )	1014-1140	Calcium	13-25800
Surface Tension (dynes/cm)	43-78	Sodium	132-9700
TOC (mg/L)	0-1500	Potassium	24-4300
COD (mg/L)	1220	Magnesium	8-6000
TSS (mg/L)	1.2-1000	Iron	<0.1-100
pH	4.3-10	Aluminum	310-410
Total Oil (mg/L)	2-556	Boron	5-95
Volatile (mg/L)	0.39-35	Barium	1.3-650
Base (mg/L)	<140	Cadmium	<0.005-0.2
Chloride (mg/L)	80-20,0000	Copper	<0.002-1.5
Bicarbonate (mg/L)	77-3990	Lithium	3-50
Sulfate (mg/L)	<2-1650	Manganese	<0.004-175
Ammoniacal Nitrogen (mg/L)	10-300	Lead	0.002-8.8
Sulfate (mg/L)	10	Strontium	0.02-1000
Total Polar (mg/L)	9.7-600	Titanium	<0.01-0.7
Higher Acids (mg/L)	<1-63	Zinc	0.01-35
Phenol (mg/L)	0.009-23	Arsenic	<0.005-0.3
VFAs (mg/L)	2-4900	Mercury	<0.001-0.002

The dissolved formation minerals mainly constitute heavy metals, anions, cations, and radioactive materials [8], [20]. Mercury, lead, silver, zinc, cadmium, copper, and nickel are examples of heavy metals [21]. The quantity of these heavy metals is directly associated with the age of the oil well. Cations may include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^+$ ,  $\text{Ba}^{+2}$ , whereas anions may include  $\text{SO}_3^{-2}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{-2}$  [21]. Radium isotopes,  $^{226}\text{Radium}$ , and  $^{228}\text{Radium}$  are the most abundant radioactive elements that are present in PW along with co-precipitated Barium Sulphate [22].

During the production of oil and gas, some chemicals are added which will alter the composition of the PW. These chemicals include emulsion breakers, corrosion inhibitors, water treatment chemicals, and biocides. PW also contains solids such as waxes, bacteria, asphaltenes, and corrosion products. Anaerobic bacteria also have been detected in PW which usually causes clogging and corrosion of equipment and pipelines. PW also contains some dissolved gases like carbon dioxide, oxygen, and hydrogen sulfide [11], [21]. Table (2-1) represents the summary of oil-field parameters such as total organic carbon (TOC), chemical oxygen demand (COD), total suspended solids (TSS), volatile fatty acids (VFAs), and heavy metals present in PW [5].

## **2.2. Technologies Available for Produced Water Treatment**

### **2.2.1 Physical treatment**

#### ***2.2.1.1. Adsorption***

Different compounds can be removed from PW via the adsorption process using different adsorbents [23]. Literature showed that different adsorbents such as kiwi peels, agriculture waste, tea waste biochar, boehmite nano powder have been used for the treatment of PW [24]–[27]. Dissolved organic compounds are attached to the surface of the adsorbent. After saturation desorption starts to take place by the air oxidation process. Activated carbon can remove many soluble organic components like benzene, toluene, ethylbenzene, and xylene [28]. However, Organoclay can remove insoluble hydrocarbons. The advantages of this method show high efficiency, no corrosion, and no scale decomposition. The disadvantages include the following factor which needs to be taken into consideration, such as high operating costs including all pre-treatment, disposal of spent material causing environmental pollution, and fouling of the used material such as the bed. Zeolite pellets also can be used as an absorbent in a fixed bed. A column filled with resin also removes soluble organic components. The efficiency of

the adsorption process can be affected by temperature, pH, Salinity, dispersed/suspended oil, dissolved organic chemicals, and heavy metals. Table (2-2) represents the results obtained for PW treatment using a packed column [6].

Table 2-2: Results obtained from a packed column adsorption system for PW

<b>Contents</b>	<b>Before treatment parts per million (ppm)</b>	<b>After treatment (ppm)</b>
Oil and Grease	148	1.1
Benzene	151	1.2
Toluene	3.14	<0.5
Ethylbenzene	4.97	<0.5
Xylene	4.95	<0.5

#### ***2.2.1.2. Sand filters***

Sand filters can be used for the PW treatment [7]. This technique is applied after pre-treatment where pH should be controlled to start the oxidation reaction and there should be enough oxygen in the aeration unit. There should be enough retention time for the separation of solid particles followed by a sand filter to separate suspended particles. A previous study in the literature reported more than 90 % removal of iron from PW [11].

#### ***2.2.1.3. Evaporation***

Another method that can be used to remove oil components from PW is evaporation [29], [30]. Different kinds of evaporators such as a vertical tube, falling film, and vapor condensation can be used for this process. In this method, no physical or chemical treatment is needed. This method requires less maintenance compared to other processes used in the PW treatment [31]–[33].

#### ***2.2.1.4. Dissolved air precipitation***

Dissolved air precipitation is another method for PW treatment [34]. This method involves the saturation of air in water in a packed column. The air will precipitate and form bubbles by releasing pressure in the column. It is found that implementation of this method shows removal efficiency of 95 %, 75 %, and 40 % for dissolved octane, micro-dispersed decane, and dissolved ethyl benzene respectively [11], [35].

### **2.2.1.5. C-TOUR**

PW can also be treated by this method [36]. C-Tour is a patented method that is used to remove dissolved components in PW by a solvent named liquid condensate. This method has the following factors.

- The condensate stream injected into the PW
- Equilibrium time between condensate and PW
- Separation of polluted condensate from water
- Recycling of polluted condensate

### **2.2.1.6. Electrodialysis**

Electrodialysis is another method that can be used for PW treatment. This method uses electrodes that attract the ions. The cations have a positive charge and are attracted to the negative electrodes and the anions have a negative charge and are attracted to the positive electrodes. In this way, cations and anions present in PW can be treated. This method shows good performance when the amount of TDS is low, but for High TDS or concentrated water, it is not suitable [37].

## **2.2.2 Chemical treatment**

### **2.2.2.1. Chemical Precipitation**

Coagulation and flocculation are used in this method to remove suspended particles especially heavy metals like arsenic and mercury [38]. PW with a high amount of TDS, sulfides, and oil can be treated so that it can be used as feed water for the steam generator. A study was carried to determine the efficiency of this method for PW obtained from oil and gas fields for treating hydrocarbons, arsenic, and mercury. It showed that after the treatment, the amount of mercury in PW is very small as compared to arsenic and TPH amounts [39].

### **2.2.2.2. Photocatalytic treatment**

Photocatalytic treatment can be applied for PW treatment. The literature showed that this method can be employed for the removal of different pollutants from PW [40]–[42]. Honda and Fujishima decomposed water on TiO<sub>2</sub> electrodes by using this method in 1972 which is known as Honda and Fujishima effect. This method was performed in an open reactor at constant pH followed by flocculation. After removing the filtrate,

TiO<sub>2</sub> was used as a catalyst at high pressure and room temperature. Results showed that this method has reduced the toxicity of PW [11].

#### ***2.2.2.3. Fenton Process***

In the literature, it is reported that the Fenton process is another process that has been tested for the PW treatment [43], [44]. There are two steps in this process, flocculation, and settlement. Employment of this method minimizes the COD and oil significantly. A study showed when poly ferric sulfate is used as a flocculent and it allows 30 minutes to settle down. The COD decreased from 2634 to 100 ppm and oil decreased from 93.1 to 5 ppm [11].

#### ***2.2.2.4. Treatment with ozone***

Another way to remove dissolved organic compounds from PW is the usage of ozone [45]–[47]. Literature reported that chemical oxidation has been widely used for the removal of effluents from an aqueous solution. The different groups demonstrated the effectiveness of this method eliminating (50-70 %) COD. The effectiveness of this method can be increased by combining the oxidants (H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>) [48].

#### ***2.2.2.5. Room-temperature ionic liquids***

Room-temperature ILs especially hydrophobic ILs can be used to remove oil from PW due to their unique properties. The literature showed that ILs can remove different pollutants, such as phenolic compounds [49], heavy metals [50], dyes [51], desulfurization [52], and aromatic compound [53] from aqueous solution.

### **2.2.3 Biological treatment**

PW can be treated by biological treatment method [54], [55] In this technique, aerobic and anaerobic microorganisms are used to remove organic compounds [56]. Activated sludge, trickling filter, sequencing batch reactors (SBRs), and lagoons are used in aerobic conditions [57]. A study shows that the use of different aerobic bacteria in an activated sludge removed 98-99% of the TPHs [58]. Various studies have also been done to remove the COD and TOC using SBRs and trickling filters [59].

### **2.2.4 Membrane treatment**

This method does not require chemicals therefore it is preferred over chemical and biological methods [60]. This method also requires less space for installation. This is a physical method for the treatment of water in which separation depends on the pore size

of the membranes [61]. It can be of different pore sizes and accordingly, they are categorized as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (RO) [62]. Microfiltration is used to separate suspended particles and ultrafiltration separates macromolecules. RO is used for the separation of dissolved particles as well as ionic constituents. These methods got great attention because they are competing with other complex methods. These methods are good with high oil content, small particle size, and flow rate of more than  $150 \text{ m}^3 \cdot \text{h}^{-1}$ . Moreover, they are also effective for medium and large offshore platforms [63]. The literature reported that different membranes such as Mxene composite membranes [64], adsorption membranes [65], coagulation membranes [66], polymeric membranes [67], and nanofiber membranes [68] have been reported for wastewater treatment.

Table 2-3: Summary of the major methods employed for treating PW

<b>Physical Treatment</b>	<b>Chemical treatment</b>	<b>Biological Treatment</b>	<b>Membrane Treatment</b>
Adsorption	Chemical Precipitation	Activated Sludge	RO
Sand filters	Electrochemical Process	Trickling filters	Ultrafiltration
Evaporation	Photochemical treatment	Sequencing batch reactor	Nanofiltration
Freeze-Thaw/Evaporation	Fenton Process		Microfiltration
Cyclones	Treatment with Ozone	Lagoons	-
Dissolved Air Precipitation	Room Temperature ILs	Chemo state reactors	-
Electrolysis	-	-	-
C-Tour	-	-	-



## **2.3. Produced Water Management Practice**

Different methods can be implemented for better-PW management which includes [69].

### **2.3.1 Water reduction**

It is very important to do try and minimize the water produced. It is commonly performed by three methods, Downhole Water Separation, and Injection, Advanced Production and Completion Techniques, Horizontal drilling. The first method resists the production of groundwater to the surface. The second method controls the unconfined fracture spreading. The horizontal method is considered a very good method to minimize the net water production and it enhances the resource recovery for every barrel of PW [70]. The amount of PW can also be decreased by injecting less amount of water into the well which can be done by placing some mechanical blocking device or adding any water shut-off chemical like polymer gel. Moreover, the volume of surface water can also be decreased by floor separation modules. The amount of water inserted during the fracturing process can also be minimized by material substitution.

### **2.3.2 Recycle**

If water quality is good and especially it has low TDS then it is acceptable for certain uses like recreational uses, irrigation, municipal water supplies, and even drinking water [71]. If we do recycle and reuse PW, it can be implemented for many uses which include re-injection for improved recovery or subsidence control.

### **2.3.3 Discharge management and quality control**

Most of the PW is inserted underground and the remainder is purified or discharged on the surface [72]. Whereas disposal is sometimes acceptable for offshore facilities, but onshore facilities treatment is required. If it is not disposed of it can be injected for underground water recharge, it can also be evaporated or disposed of commercially offsite. All the above methods highlight the importance of PW treatment, which is of great value, beneficial, and cost-effective. Offshore-PW is mostly discharged back into the ocean following the National Pollution Discharge Elimination System (NPDES) Act. According to the environmental protection agency (EPA) discharge limit for oil and grease is 29 ppm weekly on average and a maximum of 42 ppm daily [73].In Dubai,

the allowable discharge limit of oil and grease for offshore and onshore facilities is 40 ppm and 10 ppm respectively.

Therefore, Treatment of PW is necessary regarding environmental concerns [74]. In this work, ILs were applied for the PW treatment via LLE and adsorption.

#### **2.4. Introduction to Ionic Liquids**

ILs are compounds comprising of ions with melting points below 100 °C. The first IL (Ethyl ammonium nitrate) was reported by Paul Walden in 1914. In recent years, ILs got great attention due to their excellent properties [75]. ILs are considered as a substitute for traditional organic solvent which results in the formation of photochemical smog, ozone depletion, and global warmings. ILs are emerging as a green solvent due to the following properties, non-flammability, non-volatility, low vapor pressure, high ionic conductivity, high thermal and electrochemical stability, high solubility, design flexibility, and recyclability [76]. In addition, an unlimited number of possible ILs cation/anion combinations can be designed according to the desired application. ILs exhibited promising outcomes on a laboratory scale in various fields like synthesis, separation technologies, chemical catalysis, material science, and electrochemical processes [77].

#### **2.5. Introduction to Liquid-Liquid Extraction**

LLE is also known as solvent extraction. It is a separation technique that is used for the separation of the desired component (solute) from immiscible liquids (feed and extractant) based on the solubility of the solute in these liquids. The solvent which is used to extract the required component is called extractant and feed is the liquids from which solute needs to be extracted. The techniques follow the phase distribution principle which is defined as the solute can distribute itself between two immiscible liquids in a particular ratio depending upon the activity coefficient in each phase [78]. Extractant could be a mixture of more than one solvent designed for the separation of one or more solutes from feed [73]. Conventionally, LLE is used in solvent recovery, product recovery, or for increasing the solute concentration in the extractant. This technique is applied in case of non-availability of other viable or economic options because this technique required another separation after extraction. Separation of heat-

sensitive and non-volatile compounds, washing of acid or base media, removal of phenol, aniline, and aromatic compounds from water, are typical examples of LLE.

### **2.5.1 Solvent selection criteria**

Solvent selection mainly depends on solute nature which needs to be extracted and feed nature. The solvent is selected which has maximum solute transfer from feed to solvent. Characteristics of solute have been summarized

- Immiscible with feed
- High affinity towards solute
- Thermally stable
- Low viscosity
- Non-reactive towards other components of feed and equipment parts
- Non-toxic and non-flammable
- Non-corrosive to equipment's parts
- Economic and environment friendly

Different solvents need to be analyzed and compared before selecting a suitable solvent for the extraction of desired components.

### **2.5.2 Factors affecting LLE**

LLE depends on many factors including, but not limited to, interfacial area, mass transfer rate, viscosity, and affinity of extractant for the solute. Extraction efficiency can be increased by increasing interfacial area or reducing mass transfer resistance. An increment in temperature reduces viscosity which increases mass transfer between phases and reduced mass transfer resistance.

### **2.5.3 Distribution coefficient**

The removal efficiency and distribution coefficient can be calculated by using the following equations: [79]

$$R = \left( \frac{S_o - S}{S_o} \right) * 100 \quad (1)$$

Here,  $R$  is the removal efficiency of solute by extractant,  $S_o$  is initial concentration before extraction in ppm,  $S$  is final concentration after extraction in ppm

Molal distribution coefficient in the case of completely immiscible liquids is:

$$D = \left(\frac{\gamma_1}{\gamma_2}\right) * K \quad (2)$$

Here,  $K$  is constant for completely immiscible feed and extractant,  $\gamma$  is molal activity coefficient of solute in respective phase and  $D$  is activity coefficient for low concentration activity coefficient become unity and distribution coefficient become constant.

The extraction efficiency of solute and distribution coefficient can be represented as [79].

$$D = P * \left(\frac{R}{100 - R}\right) \quad (3)$$

Here,  $R$  is the percentage removal efficiency of solute from the feed,  $D$  is the distribution coefficient and  $P$  is the ratio of feed volume to extractant volume.

#### **2.5.4 Applications of LLE**

To remove organics from aqueous solutions multiple techniques have been reported including physical, chemical, biological, and membrane technology. These methods are quite expensive, toxic, and offer limited design flexibility [80], [81]. While, on the other hand, LLE Extraction is simple, less expensive but has some limitations depending on the selection of the solvent. Recently, LLE got the great attention of researchers. Multiple papers have reported the removal of dyes, phenol, and aromatic compounds using this method [82]–[84].

#### **2.5.5 Ionic liquids in solvent extraction**

Room temperature ILs got more attraction due to their intrinsic properties of negligible vapor pressure, thermal stability, excellent solvation characteristics, and easy isolation from the aqueous stream for hydrophobic ILs [85]. These properties make ILs environmentally friendly as compared to other toxic solvents with high vapor pressure [13]. In the literature it is reported that ILs can be used for the extraction of aromatic hydrocarbons [86], Sulphur [87], Uranium [88], Toluene [89], Lanthanide [90],

polyunsaturated fatty acids methyl esters [91], aromatic amines, phenols [92], and other compounds. Therefore, this suggests that ILs can be used for the removal of oil from PW.

## **Chapter 3. Materials and Methodology**

This chapter highlights the materials, instruments, and the adopted methodology for the PW treatment. Two different techniques, LLE, and adsorption were used for the removal of oil from PW. A detailed discussion of the solutions preparation, extraction methodology, and quantification of oil after treatment has been provided in this chapter for both LLE and adsorption study.

### **3.1. Liquid-Liquid Extraction with ILs**

#### **3.1.1 Chemicals and instruments**

Heavy crude oil (HCO) was provided by Abu Dhabi National Oil Company (ADNOC), UAE. The surfactant (ENDOR OCC9783) was received from Suez, UAE. ILs were received from Sigma Aldrich and Iolitec, Germany. All other chemicals were of analytical grade and were used without further purifications. Synthetic PW is prepared by mixing heavy oil, in a specified ratio of the surfactant, and deionized water (40:60). During the whole experiment, distilled water was used (Water Still Aquatron A4000D, UK). Stuart Vortex mixer (UK) was used for homogenous mixing at 2500 rpm. Oil and water layers were separated using a centrifuge (HERMLE Labortechnik, Germany). A pH meter (Okton pH 510 series, Malaysia) was used to perform PH measurements. To adjust the pH of all solutions 0.1 M HCl and 0.1 M NaOH were used. The concentration of oil in the different samples was determined spectrophotometrically using a UV-Vis spectrophotometer (Thermo Scientific Evolution 220). FTIR (Perkin Elmer, USA) was used to determine the presence of the functional groups in ILs before and after oil removal. Table (3-1) represents the list of tested ILs used in LLE. The selected  $\text{NTf}_2$  based ILs are nonflammable, less viscous, easy to handle and store, thermally stable, and non-toxic.

#### **3.1.2 Preparation of oil-hexane standard solution**

The oil-hexane solutions of different concentrations ranging from 3.125 ppm to 200 ppm were prepared by adding oil in hexane. Firstly, the oil-hexane solution of 200 ppm was prepared by adding 20 mg of heavy oil in 100 ml hexane. This oil-hexane solution of 200 ppm was diluted with hexane to prepare the oil-hexane solutions of 100 ppm, 50 ppm, 25 ppm, 12.5 ppm, 6.25 ppm, and 3.125 ppm concentration. The spectra of these solutions were recorded, and concentration was quantified at 275 nm.

Table 3-1: List of ILs used in LLE

N0.	Name	Symbols	MW (g/mol)
IL1	1-ethyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide	[C2Mim] [NTf2]	391.30
IL2	1-butyl-2-3-dimethylimidazolium bis (trifluoromethyl sulfonyl) imide	[C4Mim] [NTf2]	433.39
IL3	1-methyl-3-octyl-imidazolium bis (trifluoromethyl sulfonyl) imide	[C8Mim] [NTf2]	475.47
IL4	1-decyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide	[C10Mim] [NTf2]	503.50
IL5	1-butyl-4-methylpyridinium (trifluoromethyl sulfonyl) imide	bis [C4Mpy] [NTf2]	430.39
IL6	Tributyl methyl phosphonium bis (trifluoromethyl sulfonyl) imide	[P1,4,4,4] [NTf2]	497.50
IL7	Butyl trimethylammonium bis (trifluoromethyl sulfonyl) imide	[N1,1,1,4] [NTf2]	396.37

### 3.1.3 Preparation of surfactant-water solution

The surfactant-water solution with a surfactant-water ratio of 40:60 was prepared by mixing 40 ml of surfactant with 60 ml of de-ionized water [93]. The solution was then sonicated for 10 min for homogenous mixing. Then the spectra of this solution were recorded.

### 3.1.4 Preparation of synthetic produced water

The PW solutions of different concentrations were prepared by adding a specific mass of oil to the surfactant-water solution and sonicated for 10 minutes [94]. The concentration range of oil in surfactant-water solution was in the range of 100-700 ppm.

### 3.1.5 Treatment of produced water with IL

Treatment of PW was performed by using selected hydrophobic ILs. A known amount of IL was added to a certain volume of synthesized PW followed by vortex mixing at

speed of 2500 rpm for 5 min. The heterogeneous solution was then centrifuged at 3500 rpm for 10 min. The water layer was separated, and its oil content was determined by extraction with hexane and quantified spectrophotometrically. For this purpose, 1 ml of the water layer was extracted with hexane as explained below.

### **3.1.6 Extraction with hexane**

The surfactant-water solution with surfactant-water ratio (40:60) was prepared by mixing 40 ml of surfactant with 60 ml of di-ionized water. One ml from the water layer was mixed with 9 ml of hexane and mixed on a vortex mixer for 5 minutes at 2500 rpm. The sample was then centrifuged at 3500 rpm for 10 minutes. Two layers were formed with the hexane layer successfully removing all oil from the water layer. The oil content in the hexane layer was quantified spectrophotometrically. To confirm that the hexane is extracting all the oil from PW, a control experiment was performed for a different known concentration of oil in the PW solution. For this purpose, PW with the known concentration of oil was extracted with 9 ml hexane and extracted amount of oil in hexane was analyzed spectrophotometrically. After that, this result was compared with the known concentration and it was found that the hexane has extracted all the oil from the PW.

### **3.1.7 Liquid-liquid extraction**

Removal of oil from PW by various ILs was performed by LLE. A known amount of IL was added to a certain volume of synthesized PW followed by vortex mixing at speed of 2500 rpm for 5 minutes. The heterogeneous solution was then centrifuged at 3500 rpm for 10 min. The water layer was separated, and its oil content was determined by extraction with hexane and quantified spectrophotometrically. For this purpose, 1 ml of the water layer was extracted with 9 mL hexane. The removal efficiency was determined by using the following equation (4) [79].

$$R = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \quad (4)$$

Here,  $R$  represents the removal efficiency of ILs,  $C_i$  and  $C_f$  represents the concentration of oil in PW in mg/L before and after treatment.



### **3.1.8 Process optimization**

Oil extraction from PW using ILs depends on different parameters. Therefore, it is necessary to study the effect of these parameters. In this study, the effect of different initial concentrations of oil in PW (100-600 ppm), contact time (2-10 min), pH (2-12), temperature (25-65°C), salinity (0-2000 ppm), and phase ratio (PW: IL) ranging from 1 to 8 were studied on the removal efficiency of IL and process conditions were optimized to get the maximum removal efficiency.

## **3.2. Adsorption Study Using Clay -Na-Alginate-IL beads**

### **3.2.1 Chemicals and instruments**

HCO was supplied by Abu Dhabi Oil company (ADNOC), UAE, and the surfactant (ENDOR OCC9783) was provided by Suez, UAE. IL (1-Ethyl-3-Methylimidazolium acetate > 98%) was selected due to its attractive properties of low melting point, viscosity, toxicity, and corrosiveness [95]. Potassium bromide (FTIR grade >99%), and n-Hexane were obtained from Sigma Aldrich, Germany. Sodium alginate with the viscosity of 2000 cp was obtained from SFDCL, India. Raw clay was used during beads preparation. Sodium hydroxide (NaOH, 99%), Calcium chloride dihydrate, and hydrochloric acid (HCl, 37%) was obtained from Merck, Germany. All other chemicals were of analytical grade and were used without any purification. PW was prepared by adding HCO to the surfactant-water solution. The surfactant-water solution was prepared by mixing surfactant and water with a 40:60 ratio. Distilled water was used during the whole experiment. The solutions of 0.1 M HCl and 0.1 M NaOH were used to adjust the pH of the solution.

Water Still Aquatron A4000D, UK was used for distilled water. For homogenous mixing, a Stuart Vortex mixer (UK) was used. A centrifuge (HERMLE Labortechnik, Germany) was used to separate the oil and water layer. To perform pH measurements a pH meter (Oakton pH 510 series, Malaysia) was used. A UV-Vis spectrophotometer (Thermo Scientific Evolution 220) was used to determine the concentration of oil in PW. A magnetic stirrer (WiseStir MSH-20D) was used to prepare uniform beads. A heat stirrer (Stuart CB162, UK) was used at 50 °C to prepare an alginate-clay-IL solution. FTIR (Perkin Elmer, USA) was used to analyze the presence of functional groups and the chemical bond structure of oil with the beads. To study the surface

morphology of the beads, SEM (TESCAN Vega 3) equipped with EDX was used. Thermal degradation of beads was observed using TGA (SHIMADZU DTG-60AH).

### **3.2.2 Preparation of synthetic produced water**

Synthetic PW was prepared by using HCO, surfactant, and distilled water. Firstly, the solution of surfactant -water (40:60) was prepared by adding them together in a specific ratio of 40 ml surfactant and 60 ml of water and sonicated for 10 minutes. Then the solution of different concentrations of PW was prepared by adding a specific amount of oil in surfactant-water (40:60) solution and sonicated for 10 minutes to prepare a homogenous emulsion of oil in water. To prepare a 200-ppm solution of PW, 20 mg of HCO were added into the 100 ml solution of surfactant-water solution. Similarly, the different concentrations of PW ranging from 100 to 700 ppm were prepared by adding the respective amount of oil in surfactant-water solution which was used for further experiment.

### **3.2.3 Preparation of clay-alginate-IL beads**

Sodium alginate, calcium chloride dihydrate, raw clay, IL, 1-ethyl-3-methylimidazolium acetate [EMIM][Ac], and distilled water were used for beads preparation. First, 0.5 g of ILs were added to 25 ml of water to prepare the IL-water solution. Then 0.5 g of raw clay was mixed with 0.5 g of sodium alginate to get a mixture in a powder form. After that, the powder was added slowly into the already prepared IL-water solution at 50 °C using a heat stirrer (Stuart CB162, UK) to get an alginate-clay-IL solution. After 1 hour of continuous stirring, a viscous solution of alginate-clay-IL formed. This alginate-clay-IL solution was added drop by drop into the 5 % (w/w) solution of calcium chloride using a magnetic stirrer (WiseStir MSH-20D). Uniform solid beads started to form as this viscous solution was added into the calcium chloride solution. The beads were stirred for 2 hours in calcium chloride solution for better cross-linking and stability. After that, these beads were taken off from the calcium chloride solution and washed with distilled water for 15 minutes to remove all calcium ions on the surface of the beads. After that, the beads were kept in the open air for 15 hours to remove the moisture. Similarly, clay-alginate beads without IL were prepared. After that, both types of beads were tested for the removal of oil from PW. It was found the clay-alginate beads loaded with IL are highly efficient as

compared to the clay-alginate beads without IL. Therefore clay-alginate beads loaded with IL were employed for the removal of oil from PW via the adsorption process.

### 3.2.4 Adsorption study

The beads were prepared by immobilization of the ILs on a solid supporting surface to remove the oil from the PW. 10 mg of the beads were added to a 10 ml solution of PW and were placed into the shaker for 60 minutes for maximum mass transfer of oil into the beads. After the beads were separated from the PW, the PW was analyzed by UV-visible spectroscopy at the wavelength of 275 nm, for the remaining oil. Equations (5-6) were used to calculate the adsorption capacity  $q_e$  (mg/g) and removal efficiency, respectively [24], [79].

$$q_e = (C_i - C_f) * \frac{V}{m} \quad (5)$$

$$\% R = \left( \frac{C_i - C_f}{C_f} \right) * 100 \quad (6)$$

Here,  $C_i$  and  $C_f$  are initial and final concentrations (mg/L) of PW, respectively.  $V$  is the volume of PW used, and  $m$  is the mass of the beads used.

### 3.2.5 Process optimization.

To maximize the removal efficiency of the beads from PW, the effect of the different parameters such as pH, initial concentration of oil, contact time, and temperature was studied. To study the effect of pH, different solutions of PW with pH ranging from 2 to 14 were prepared. The effect of the initial concentration of oil on the removal efficiency of the beads was studied by preparing a solution of different concentrations ranging from 100 to 600 mg/L. The effect of contact time ranging from 10 min to 90 min on the removal efficiency of the beads was also studied. The effect of temperature on the removal efficiency of beads was also examined. The adsorption kinetics and isotherm study were performed for the adsorption of oil through beads.

### 3.2.6 Characterization of materials used in adsorption study

Different characterization techniques were performed to confirm the adsorption of oil by the beads. FTIR analysis ranging from 4000 to 400  $\text{cm}^{-1}$  was performed to identify the functional groups and chemical bond structure and interaction of oil with beads. SEM-EDX analysis was performed to study the surface morphology of the beads.

Thermal degradation of the beads was observed by TGA ranging from 50 to 500 °C with a heating rate of 10 °C /min in a nitrogen environment. The concentration of oil in PW was determined by UV-visible spectrophotometry.

### **3.2.7 Regeneration study of clay-alginate-IL beads**

Removal of oil from PW was done by adding 10 mg of beads in a 10 ml solution of PW. To use the same beads for the second cycle regeneration of these beads was done by washing the beads with ethyl acetate. For this purpose, 10 mg of beads was added to the ethyl acetate at 100 rpm for 30 min. After that, the beads were washed with distilled water for 10 min and were used for the second cycle after drying. A similar procedure was performed to use the beads for the 3<sup>rd</sup> and 4<sup>th</sup> cycles.

## Chapter 4. Results and Discussion

This chapter presents the results obtained for the treatment of synthesized PW using room temperature ILs via LLE and adsorption. The first part includes the LLE in which a detailed discussion of the effects of different process parameters on removal efficiency of the selected ILs was studied and removal efficiency was calculated at optimum parameters. Similarly, for adsorption, the parameter optimization study was performed, and samples were characterized using different techniques. Thermodynamic analysis was performed for LLE, and adsorption kinetics and isotherms studies were performed for adsorption. In the end, the results were compared.

### 4.1. Oil -Hexane Solution: Spectra and Calibration Curve

Oil -hexane solutions of different concentrations ranging from 3.125 ppm to 200 ppm were prepared by adding oil in hexane. Firstly, the oil-hexane solution of 200 ppm was prepared by adding 20 mg of heavy oil in 100 ml hexane. This oil-hexane solution of 200 ppm was diluted with hexane to prepare the oil-hexane solutions of 100 ppm, 50 ppm, 25 ppm, 12.5 ppm, 6.25 ppm, and 3.125 ppm concentration. The spectra of these solutions were recorded and were quantified at 275 nm using UV-spectroscopy.

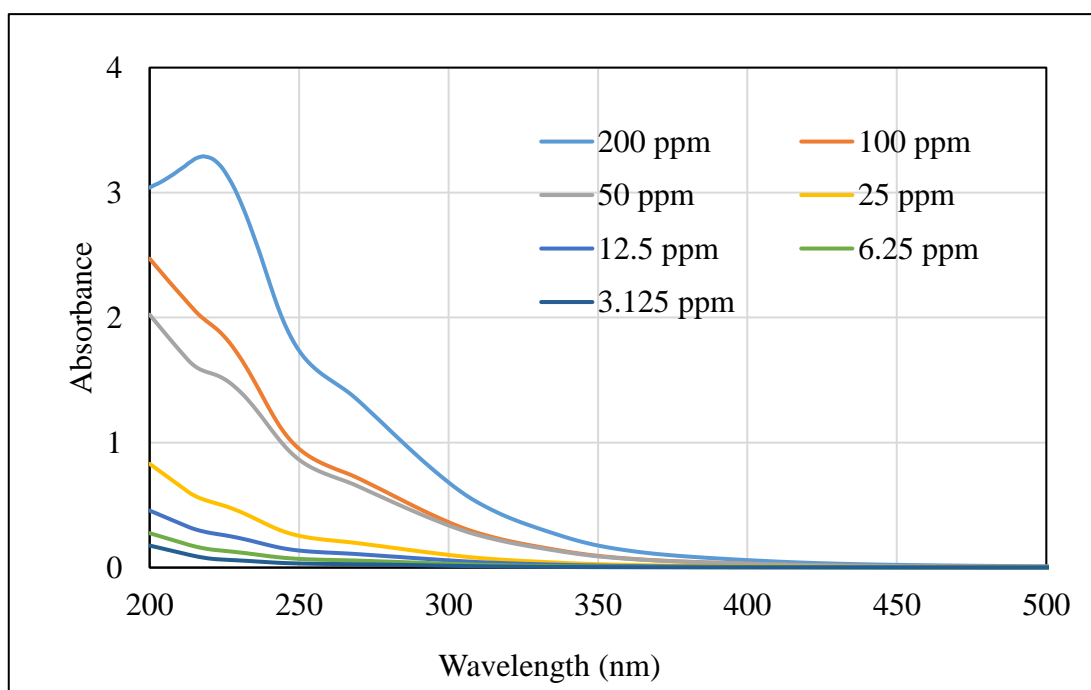


Figure 4-1: Spectra of standard solutions of oil in hexane

The absorbance was plotted against concentration to get the calibration curve, which showed a positive linear relationship. Figures (4-1) and (4-2) represent the spectra and calibration curve for different oil-hexane standard solutions, respectively.

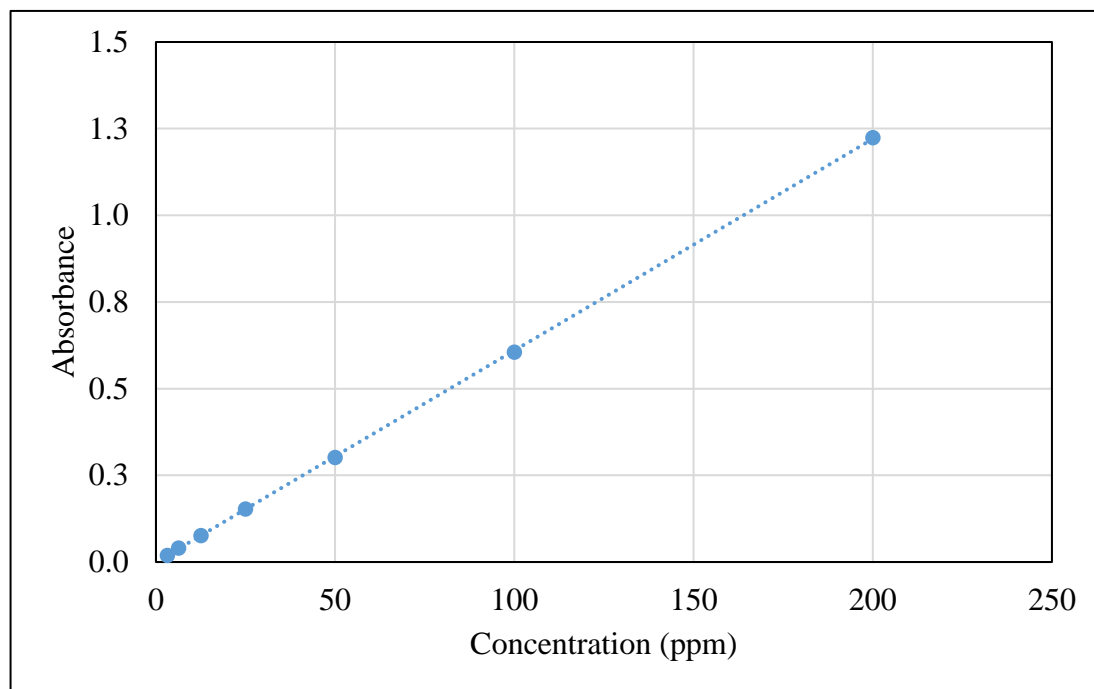


Figure 4-2: Calibration curve of oil in hexane at 275 nm

#### 4.2. Spectra of the Surfactant-Water Solution with Hexane Extraction

Figure (4-3) represents the spectra of the surfactant-water solution before (blue) and after (orange) extraction with hexane. Hexane spectra have a small contribution of surfactant with a minimum value at 275 nm. Hence, this wavelength is selected in the quantification of oil in hexane after extraction. For this purpose, surfactant-water solution 4:6 ratio was prepared followed by 10 minutes stirring. After that 1 ml of surfactant-water solution was extracted with 9 ml of hexane. Surfactant-water and hexane solution was mixed using vortex mixer at 2500 rpm for 5 minutes. After homogenous mixing two-layer was separated by centrifuging the mixture at 3500 rpm for 10 minutes. After that the spectra of the surfactant water solution before and after hexane extraction was recorded to check the surfactant concentration in hexane. It was found that there is no significant concentration of surfactant appearing in the hexane at 275 nm which concluded that at a wavelength of 275 nm there is no other peak

expected. So, this wavelength of 275 nm was chosen to make calibration for an oil-hexane solution. All the experiments were performed using this wavelength.

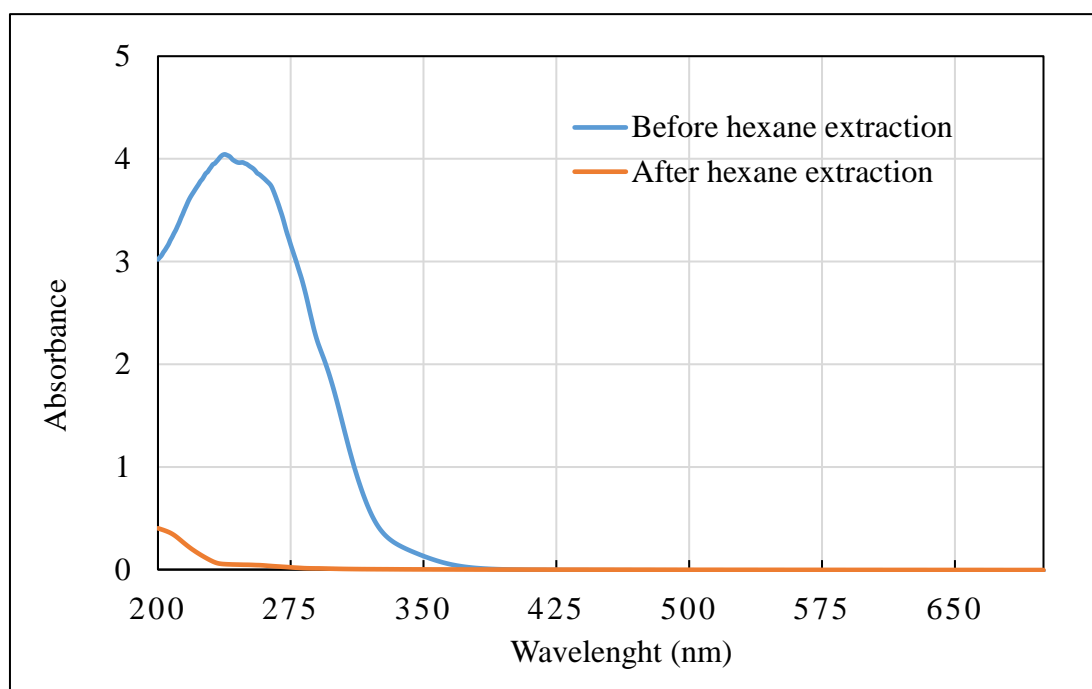


Figure 4-3: Spectra of surfactant-water before and after hexane extraction

### 4.3. Liquid-Liquid Extraction Using ILs

#### 4.3.1 Effect of alkyl chain length on removal efficiency of oil extraction

To study the effect of the alkyl chain length of cations, Imidazolium-based ILs with different carbon chain lengths C<sub>2</sub> (IL1), C<sub>4</sub> (IL2), C<sub>8</sub> (IL3), and C<sub>10</sub> (IL4) were employed for the removal of oil from PW. The results in Figures (4-4) show the effect of the carbon chain length in LLE of oil from PW and reveal that the removal efficiency is increasing with the increase in the carbon chain length. The removal efficiency of 80 %, 82%, 83%, and 85% was recorded for the carbon chain length of C<sub>2</sub> (IL1), C<sub>4</sub> (IL2), C<sub>8</sub> (IL3), and C<sub>10</sub> (IL4), respectively. IL4, [C<sub>10</sub>Mim][NTf<sub>2</sub>], showed maximum efficiency of 85 %. As alkyl chain length increases the interfacial surface tension (IFT) between oil and water decreases which leads to an increase in mass transfer between the two phases, which results in increasing the extraction efficiency of oil from PW [96]. Short alkyl chain lengths have lower mass transfer ability compared to higher alkyl chain lengths [96]. It was reported that the hydrophobicity increases with increasing alkyl chain length and thus leading to an increase in mass transfer between

the two phases [97]. Furthermore, a study by Zhu et.al, 2019 showed that imidazolium-based ILs with NTf<sub>2</sub> anions displayed lower extraction efficiency at lower alkyl chain lengths [98].

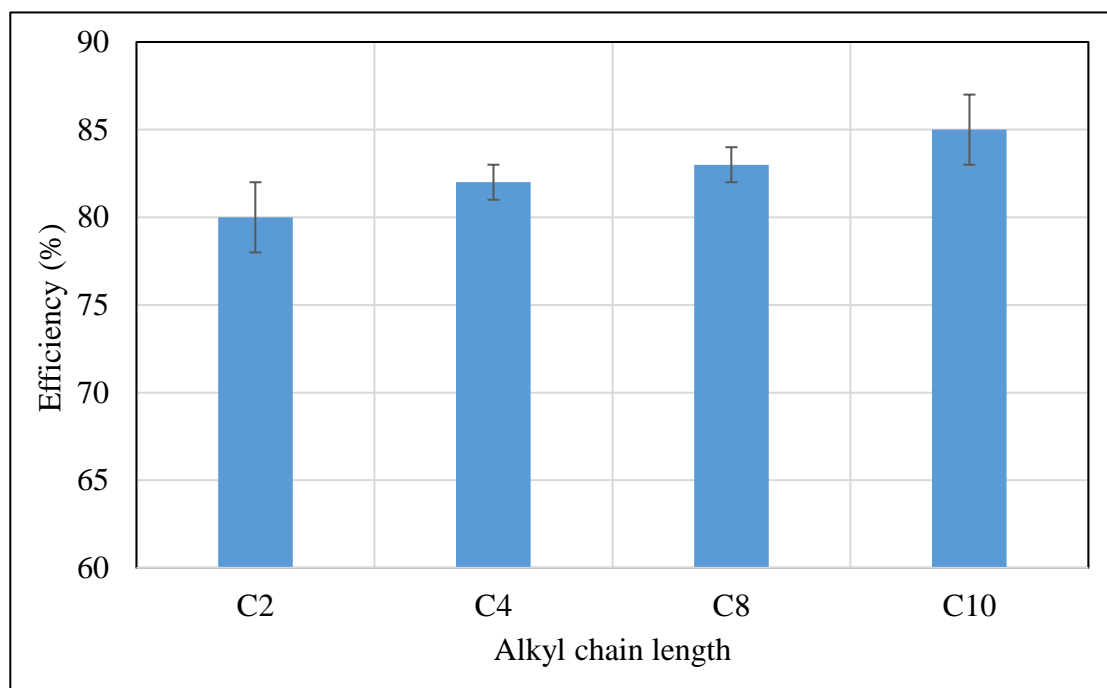


Figure 4-4: Effect of alkyl chain length on the removal efficiency of oil from PW using different ILs at initial concentration=500 ppm, contact time=5 min, phase ratio (IL: PW) =1:5, temperature=25 °C

#### 4.3.2 Effect of cation group on removal efficiency of oil extraction

The structure of ILs affects the extraction efficiency of ILs. To study the effect of cation nature, NTf<sub>2</sub> based ILs having different cations such as imidazolium, pyridinium, phosphonium, and ammonium were tested. The results in figure (4-5) show that the nature of the cation has a significant effect on oil extraction from PW. The results showed the IL with imidazolium cation is the best among all these ILs. The efficiency of these ILs with different cations is following the order: imidazolium 85% > Ammonium 70% > Phosphonium 69% and > Pyridinium 63%. This is due to the hydrophobicity of IL with higher alkyl chain length, which makes polar-polar interaction with the heteroatoms of crude oil due to the higher van der Waals forces [99]. The results are in parallel with the literature, it was reported that imidazolium-based NTf<sub>2</sub> ILs with long alkyl chain length are successfully separating the oil and



water emulsion [96]. In the literature, it has been reported that the imidazolium ILs are efficient to remove pollutants from contaminated water [98].

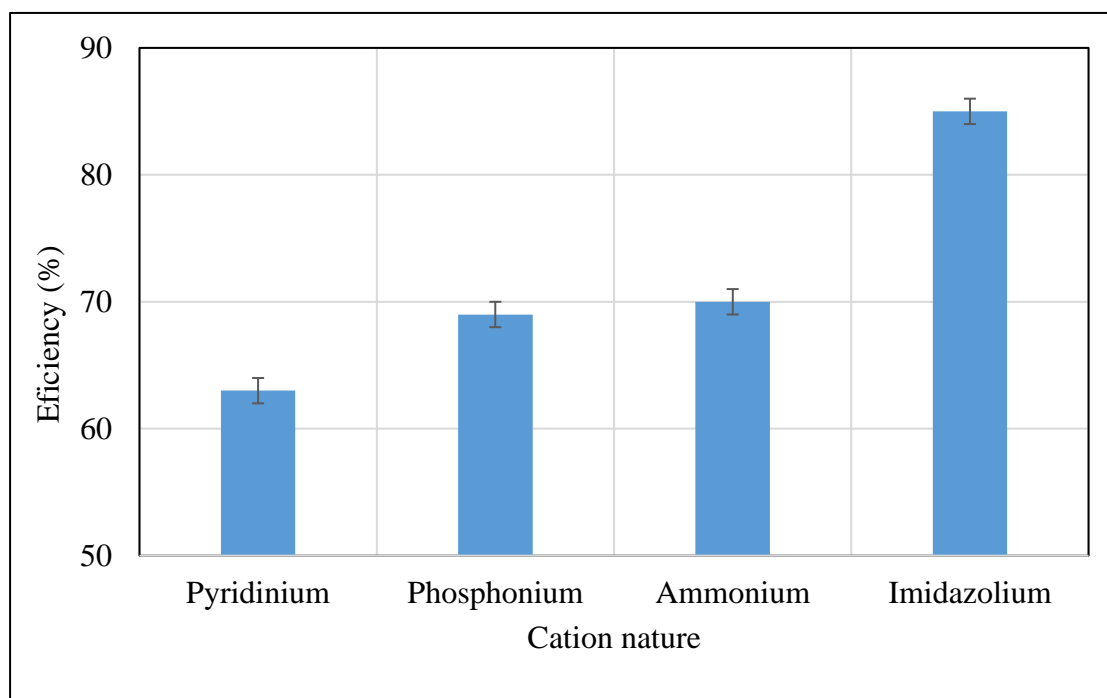


Figure 4-5: Effect of cation nature on the removal efficiency of oil from PW using different ILs at initial concentration=500 ppm, contact time=5 min, phase ratio (IL: PW) =1:5, temperature=25 °C

#### 4.3.3 Effect of the initial concentration of oil on removal efficiency of oil extraction

The initial concentration of oil in PW affects its removal efficiency by ILs. IL4 was selected in this work since it gave the best removal efficiency at the optimized conditions. Figure (4-6) displays the removal efficiency of oil from synthetic PW using IL4 as a function of initial oil concentration, and it shows that the removal efficiency increases with an increasing initial concentration of oil in PW. This increase in extraction efficiency could be attributed to the fact that as the concentration increases, the distribution equilibrium will shift to the IL phase according to Leshatlier's principle, thus leading to the observed increase in oil removal by the IL [100]. The removal efficiency becomes constant after 500 ppm which might be due to the reason that the IL has become saturated and reached its solubility limit. These results are in parallel with the literature which showed that ILs were used for the extraction of oil and phenol from the aqueous phase, the extraction efficiency of these ILs increased with an increase in oil and phenol concentration [96], [100].

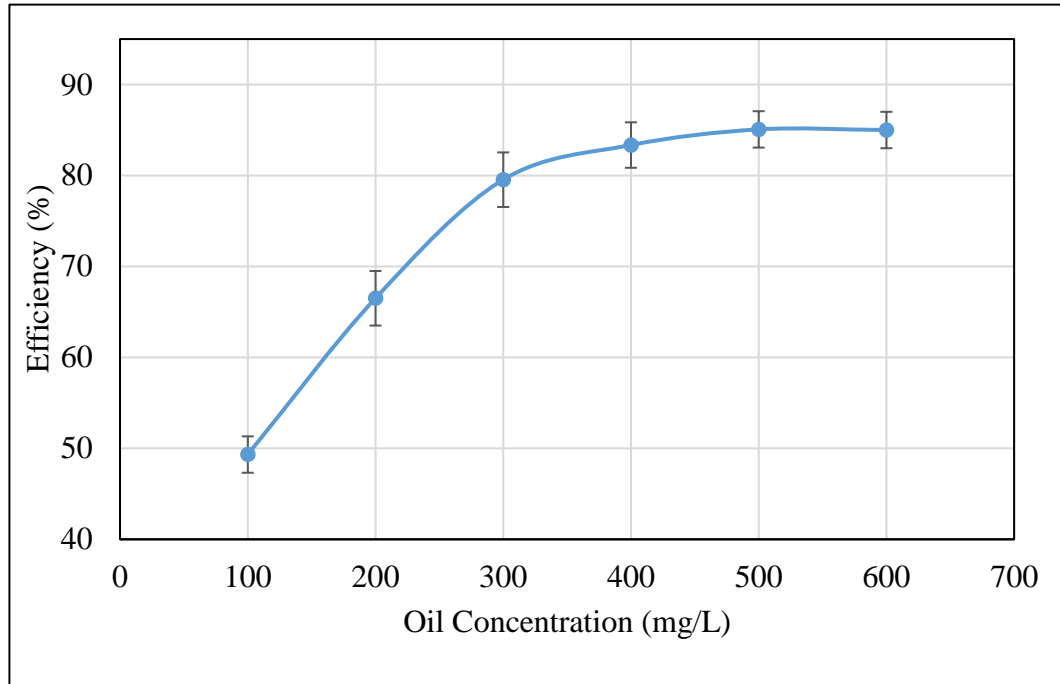


Figure 4-6: Effect of the initial concentration of oil in PW on its removal efficiency by IL4 at phase ratio (IL: PW) =1:5, time=5 min, temperature=25 °C

#### 4.3.4 Effect of contact time on removal efficiency of oil extraction

Contact time between PW and IL is an important factor for the LLE of oil from PW. Therefore, it is necessary to know the optimal contact time required for the efficient removal of oil from PW under a given set of conditions. Figure (4-7) displays the effect of contact time on the removal efficiency of oil from PW by IL4 and shows that the removal process is fast (< 2 minutes) with no significant effect of contact time on the removal efficiency. ILs which show good removal efficiency in a short time are most suitable and cost-effective for industrial applications. A plateau was observed after 4 min indicating no further mass transfer between the two phases and could be attributed to IL saturation at equilibrium. Hence 4 min was selected as the optimum contact time for the next experiments. It also shows that the transfer of oil into IL is fast and LLE is cost-effective in terms of time. Comparative studies for contact time between this IL and other adsorbents were also performed for the extraction of oil from PW. It represents that the removal of oil from PW using this IL is faster and it takes only 4 minutes for the PW treatment which is the smallest time as compared to all other adsorbents used for the PW.

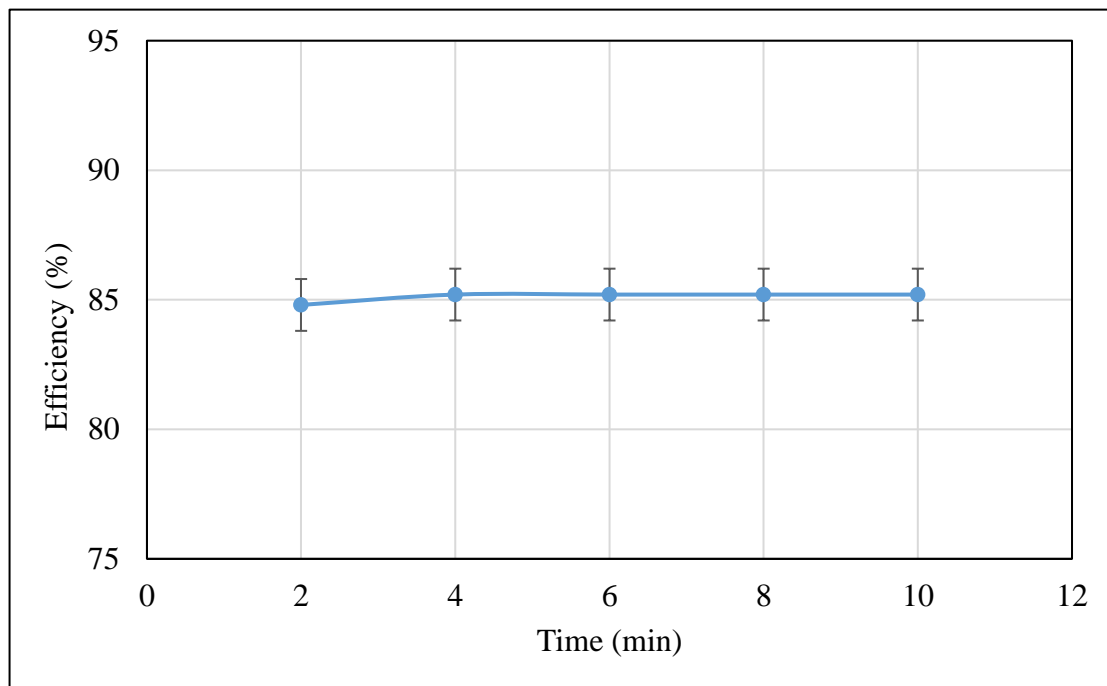


Figure 4-7: Effect of the contact time on the removal efficiency of oil by IL4. Initial concentration of oil=500 ppm, phase ratio (IL:PW) =1:5, temperature=25 °C

#### 4.3.5 Effect of pH of PW solution on removal efficiency of oil extraction

The pH of the solution is an important factor during the PW treatment through LLE, and it affects the removal efficiency of the oil from PW. Therefore, the effect of pH on oil extraction from PW was studied. For this purpose, PW solutions of different pH ranging from 2 to 12 were prepared and IL4 was employed for extraction. Figure (4-8) demonstrates that the removal efficiency is increasing with an increase in pH, until pH 8 where a plateau is observed. So, a pH value of 8 was selected as the optimal pH for the experiments. The basic region is the most favorable for the removal of oil from PW. It is well known that the pH affects the speciation of pollutants in oil, and this affects their distribution to the IL phase. At low pH, it is expected that pollutants exist in the molecular form whereas at high pH they undergo ionization giving charged ions that have stronger attraction and affinity towards the cations and anions of the IL, thus leading to the observed increase in the removal efficiency as a function of pH. A similar trend was observed for the effect of pH on removal efficiency in the aqueous phase [100]. The plateau at pH 8, indicates that maximum ionization was reached with no further increase in removal efficiency.

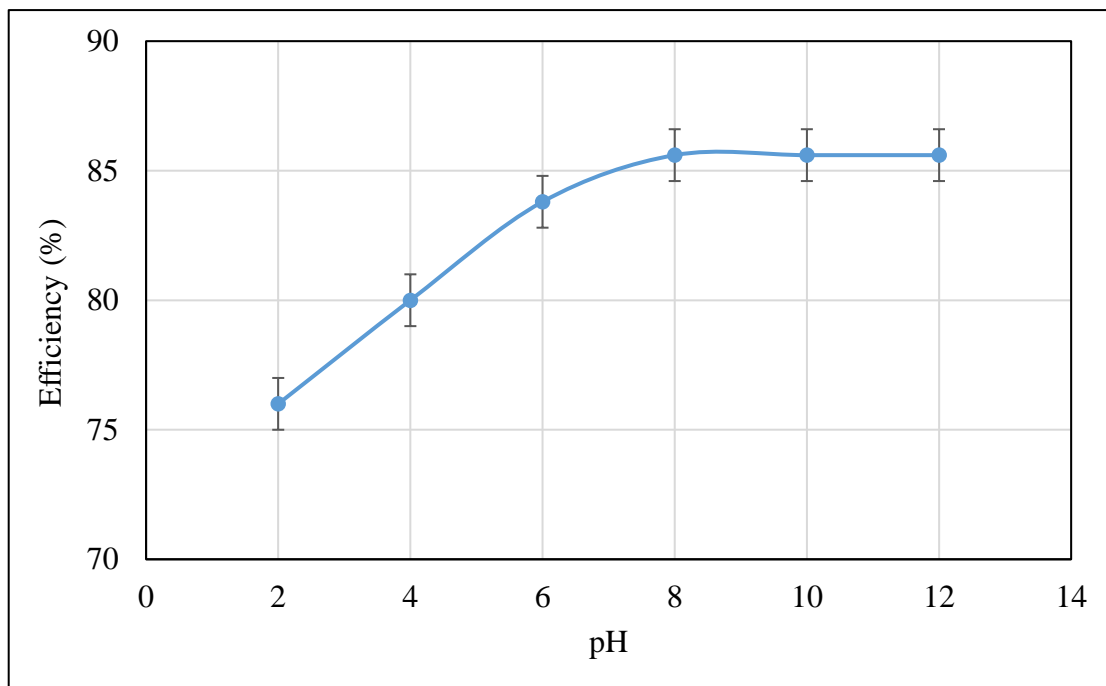


Figure 4-8: Effect of the pH on the removal efficiency of oil by IL4, Initial concentration of oil=500 ppm, phase ratio (IL: PW) =1:5, temperature=25 °C, and contact time=4 min

#### 4.3.6 Effect of phase ratio (PW: IL) on removal efficiency of oil extraction

The phase ratio is an important factor in LLE, and it has significant effects on the removal efficiency of oil by ILs. Therefore, the effect of the phase ratio (PW: IL) was also studied. For this purpose, IL4 was used with different values of phase ratios ranging from 1 to 8 and an initial oil concentration of 500 ppm, contact time of 4 min, and pH=8. Inspection of the figure (4-9) reveals that the removal efficiency of oil from PW by IL4 decreases with an increasing phase ratio. It is evident from the figure (4-9) that the maximum efficiency (92.8%) was achieved at phase ratio 1. As the phase ratio changes from 1 to 8, the removal efficiency has decreased significantly from 92.8 % to 79.44 %. This decrease in removal efficiency is due to the that, at a higher phase ratio, many molecules of oil are present for ILs to remove which leads to reduced extraction efficiency [101]. Similar behaviors for the removal of pollutants from the aqueous phase using ILs were reported in the literature [101]. A phase ratio of 4 was used for the further experiments to save the amount of IL because there is no significant change in extraction efficiency at the phase of 1 and 4.

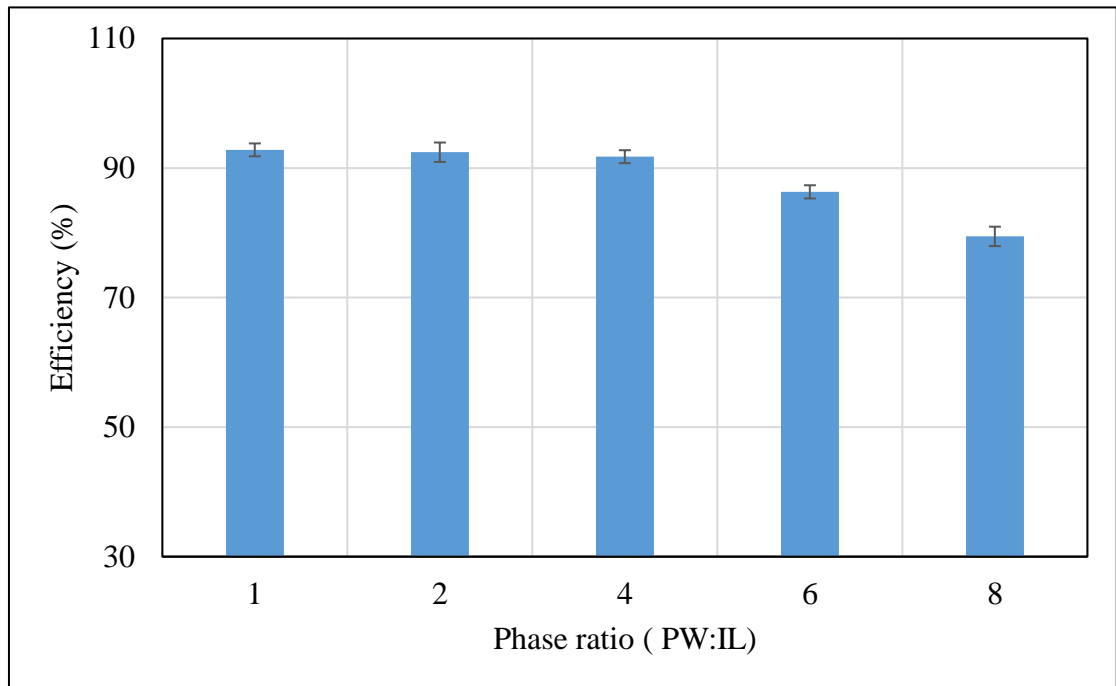


Figure 4-9: Effect of the phase ratio on removal efficiency of IL4. Initial oil concentration=500 ppm, contact time=4 min, pH=8, temperature=25 °C

#### 4.3.7 Effect of temperature on removal efficiency of oil extraction

Temperature affects the removal efficiency of oil from PW. It is highly recommended that an extraction process that leads to high efficiency at a wide temperature range is more desirable for industrial applications. Therefore, in this study, the effect of temperature on the extraction efficiency of oil from PW using IL4 was studied. As a result, the experiments were performed at different temperatures ranging from 25 to 65 °C at the optimum conditions of initial concentration of oil 500 ppm, contact time 4 min, pH 8, and phase ratio (PW: IL) of 4. Figure (4-10) demonstrates that the extraction efficiency was slightly increased with the increase in temperature. This observation indicates that the extraction process is endothermic as it requires more energy at higher extraction efficiency. Overall, there is no significant effect of temperature on the extraction efficiency of oil by IL4, hence, ambient temperature can be used to save energy and cost. A similar trend was reported in the literature for wastewater treatment using ILs [101]. It can be seen from the figure (4-10) that due to the negligible effect of temperature on the removal efficiency of the oil extraction process from PW the room temperature was selected for further studies and all other parameters were optimized using room temperature.

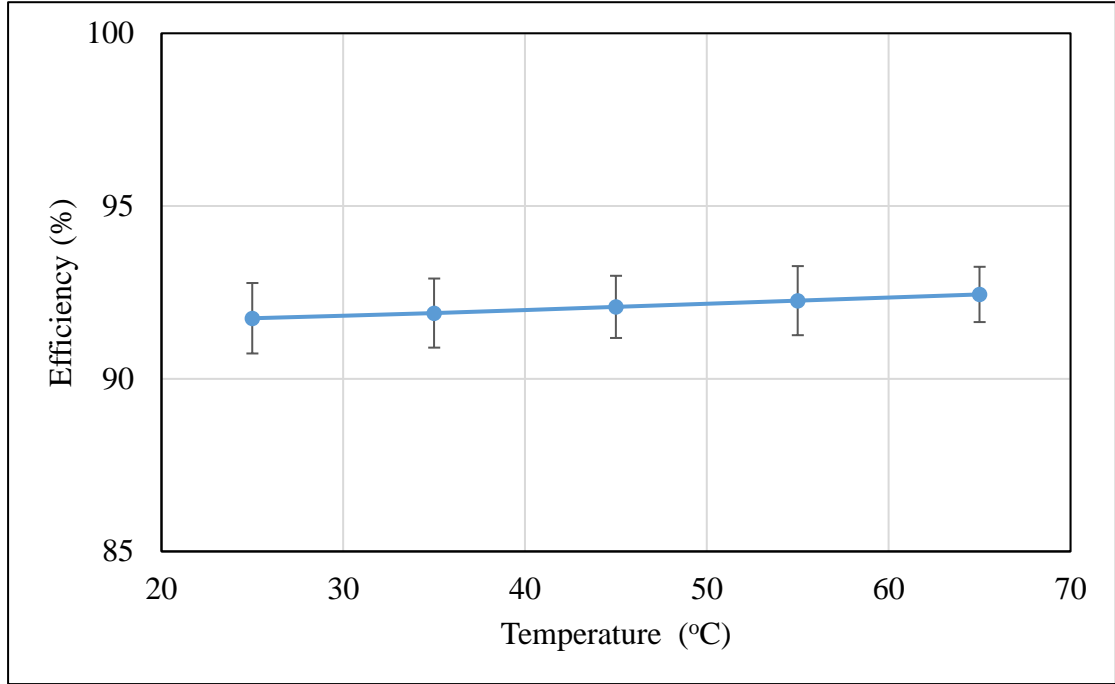
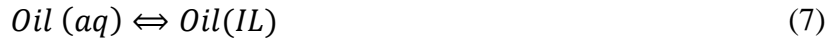


Figure 4-10: Effect of the Temperature on Removal efficiency of oil by IL4. Initial oil concentration=500 ppm, contact time=4 min, pH=8 phase ratio (IL:PW) =1:4

#### 4.3.8 Thermodynamic study of oil extraction from PW using IL

Oil distribution between the aqueous phase and IL and distribution coefficient can be represented by the following equations (7-9) [102].



The distribution coefficient can be found in the following equation (8).

$$D = \left( \frac{(Oil)_{IL}}{(Oil)_{aq}} \right) \quad (8)$$

And was calculated by using equation (9)

$$D = \left( \frac{C_i - C_f}{C_f} \right) * \left( \frac{V_{aq}}{V_o} \right) \quad (9)$$

Equations (11 –13) are used to calculate the thermodynamics parameters for the removal of oil from PW using IL4 [102]. Figure (4-11) shows the plot of the integrated vant' Hoff plot (equation 11) with an excellent correlation coefficient indicating that  $\Delta H$  is temperature independent and is equal to 2.0 kJ/mol.

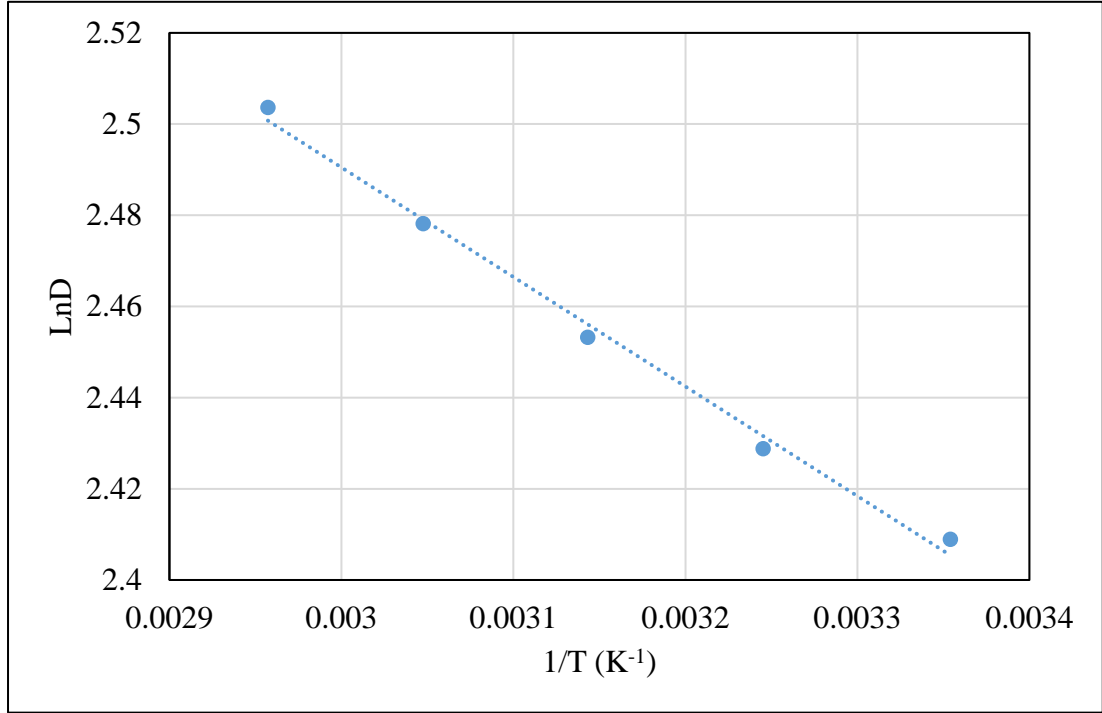


Figure 4-11: Van't Hoff plot for oil extraction from PW using IL4. Initial oil concentration=500 ppm, contact time=4 min, pH=8 phase ratio (IL:PW) =1:4 and temperature=25 °C

$$\frac{\partial \ln D}{\partial T} = \frac{\Delta H}{RT^2} \quad (10)$$

$$\ln D = -\frac{\Delta H}{R * T} + C \quad (11)$$

$$\Delta G = -RT \ln D \quad (12)$$

$$\Delta G = \Delta H - T \Delta S \quad (13)$$

Equation (12) was used to calculate Gibb's free energy ( $\Delta G$ ) at 298 K with  $D = 11.12$  which gave a value of  $-5.97$  kJ/mol indicating the spontaneously of the extraction process. The change in entropy ( $\Delta S$ ) was calculated using equation (13) and gave a value of  $26.7$  J mol<sup>-1</sup> K<sup>-1</sup> at 298 K indicating that the mass transfer from the aqueous phase to the IL phase results in an increase in entropy due to freeing water of hydration in aqueous phase upon transfer to the IL phase. The positive values of change in entropy ( $\Delta S$ ) represent that initially, the system was not at an equilibrium state and after the oil extraction equilibrium has been achieved.

#### 4.3.9 Effect of salinity of PW solution on removal efficiency of the oil extraction process

The removal of oil from water can be affected by the presence of dissolved material and the salt amount present in PW [8]. As a result, the effect of the amount of salt on the removal efficiency of IL4 was studied. For this purpose, solutions of different concentrations of salt were prepared in PW ranging from 250 ppm to 2000 ppm. IL4 was tested for each concentration of salt at the optimum conditions: initial concentration of oil 500 ppm, contact time for 4 min, pH 8, phase ratio of 4, and temperature at 25 °C. Figure (4-12) presents the effect of salinity on the extraction efficiency of oil from PW by IL4. The results showed that the removal efficiency decreases with the increase in salt concentration. Figure (4-12) displays that the extraction efficiency decreases with increasing salinity. This decrease in extraction efficiency could be attributed to the interaction of the constituents of oil with the sodium chloride ions in water which hinders their transfer to the IL phase [103]. Similar behavior has been previously reported for the removal of pollutants from the aqueous phase using ILs [103].

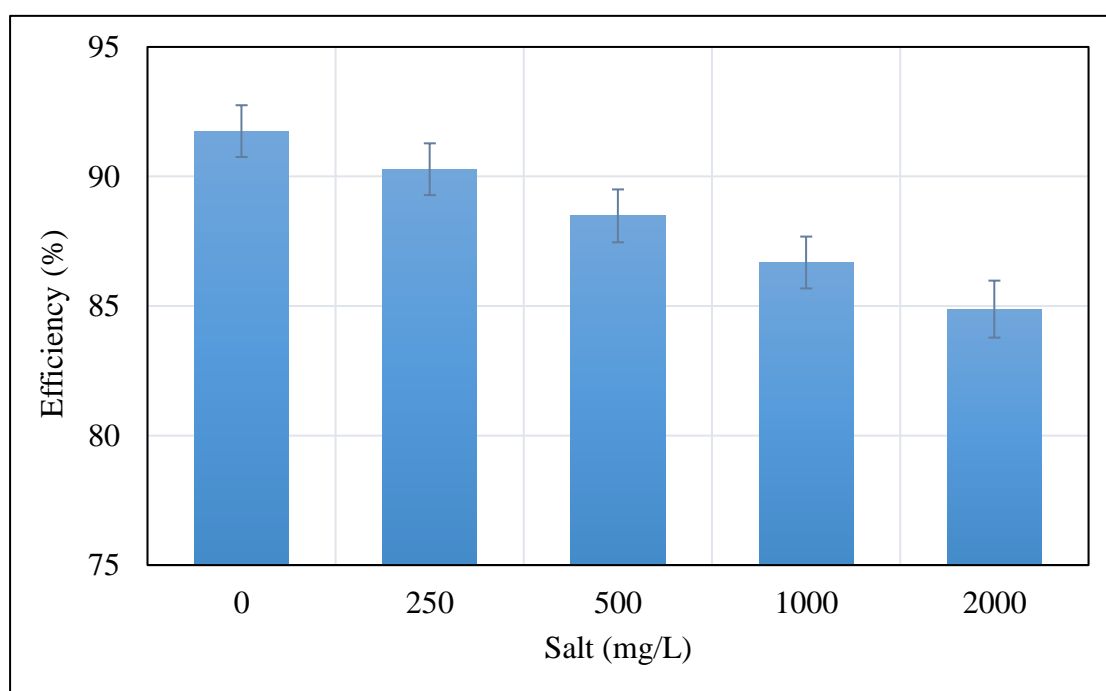


Figure 4-12: Effect of the Salinity on Removal efficiency of IL4. Initial oil concentration=500 ppm, contact time=4 min, pH=8 phase ratio (IL:PW) =1:4 and temperature=25 °C



#### 4.3.10 FTIR analysis of the oil, IL, and IL-oil used in LLE

FTIR analysis of the oil, IL, and IL-oil were recorded in the range of 500 to 4000  $\text{cm}^{-1}$  to study the chemical bond structure, function group peaks, and their interaction. The experimental results showed that the selected IL  $[\text{C}_{10}\text{Mim}][\text{NTf}_2]$  is successfully removing the oil from PW with a removal efficiency of 92.8 %. The following peaks in the IR can be identified as follows: single bond region (2500-4000  $\text{cm}^{-1}$ ), triple bond region (2000-2500  $\text{cm}^{-1}$ ), double bond region (1500-2000  $\text{cm}^{-1}$ ) and fingerprint region (600-1500  $\text{cm}^{-1}$ ) [104]. Figure (4-13) represents the FTIR analysis of oil, IL, and IL-oil. The peaks present in the region of 3500-3600  $\text{cm}^{-1}$ , 3050-3150  $\text{cm}^{-1}$ , and 2950-3000  $\text{cm}^{-1}$  are associated with C-H single bond whereas the peaks of the 2000-2100  $\text{cm}^{-1}$  region are due to the existence of the  $\text{C}\equiv\text{C}$  bond. The presence of  $\text{C}=\text{C}$  and  $\text{C}=\text{N}$  bonds is responsible for the peaks appearing in the 1500-1650  $\text{cm}^{-1}$  region. The region of 600-1500  $\text{cm}^{-1}$  is associated with the peaks of the fingerprint region. Figure (4-13) shows that the peaks of IL for C-H are shifted from 3030 to 3071  $\text{cm}^{-1}$ , and 3713 to 3734  $\text{cm}^{-1}$  which represents the successful absorption of oil into IL. There is also some vibration and stretching of molecules observed in the C-H single bond region at 3497  $\text{cm}^{-1}$  and 3272  $\text{cm}^{-1}$ .

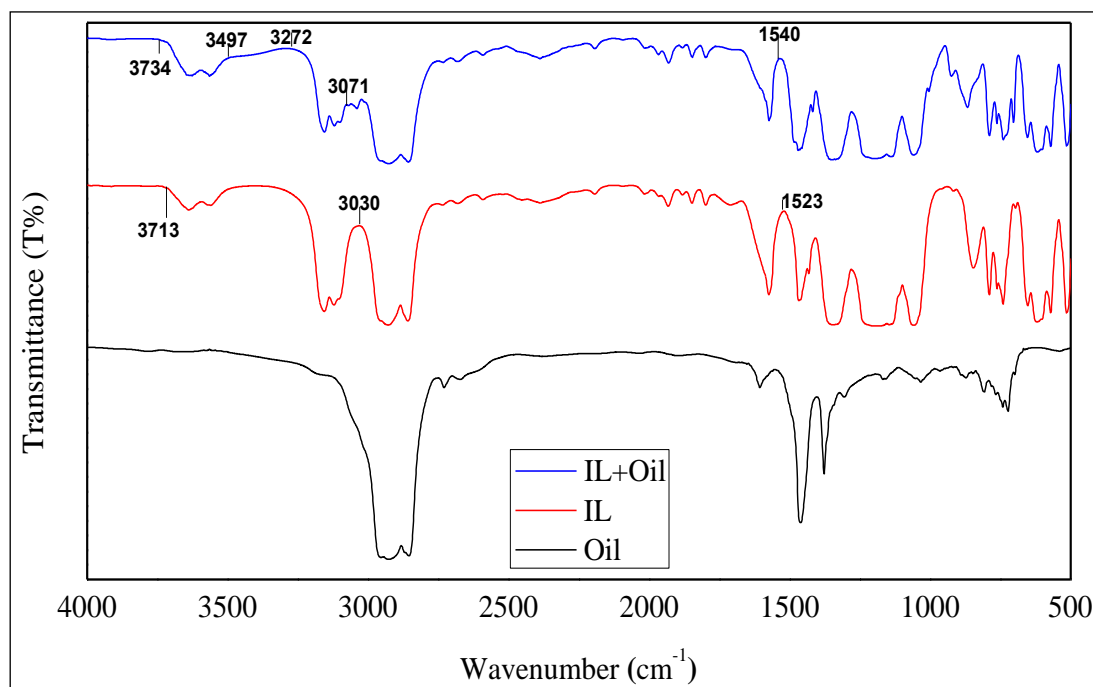


Figure 4-13: FTIR analysis of the oil, IL, and IL-oil used in LLE

The peak for the C≡C bond shifted from 1523 to 1540 cm<sup>-1</sup> which represents the absorption of oil into IL. FTIR spectra confirm the successful chemical bond interaction of IL-oil which represents successful extraction of oil from [105], [106].

#### 4.4. Adsorption Using Clay-Alginate-IL Beads

##### 4.4.1 FTIR analysis of materials used in the adsorption process

To study the chemical bond interaction between oil and the clay-alginate-IL beads, FTIR analysis was performed. The spectra of, oil, clay-alginate-IL beads, and clay-alginate-IL-oil beads were recorded in the range of 500 to 4000 cm<sup>-1</sup>. The experimental study revealed that the beads have a good ability to extract oil from the PW with an adsorption capacity of 431 mg/g. Figure (4-14) represents the FTIR analysis before and after the absorption of oil onto the surface of the bead.

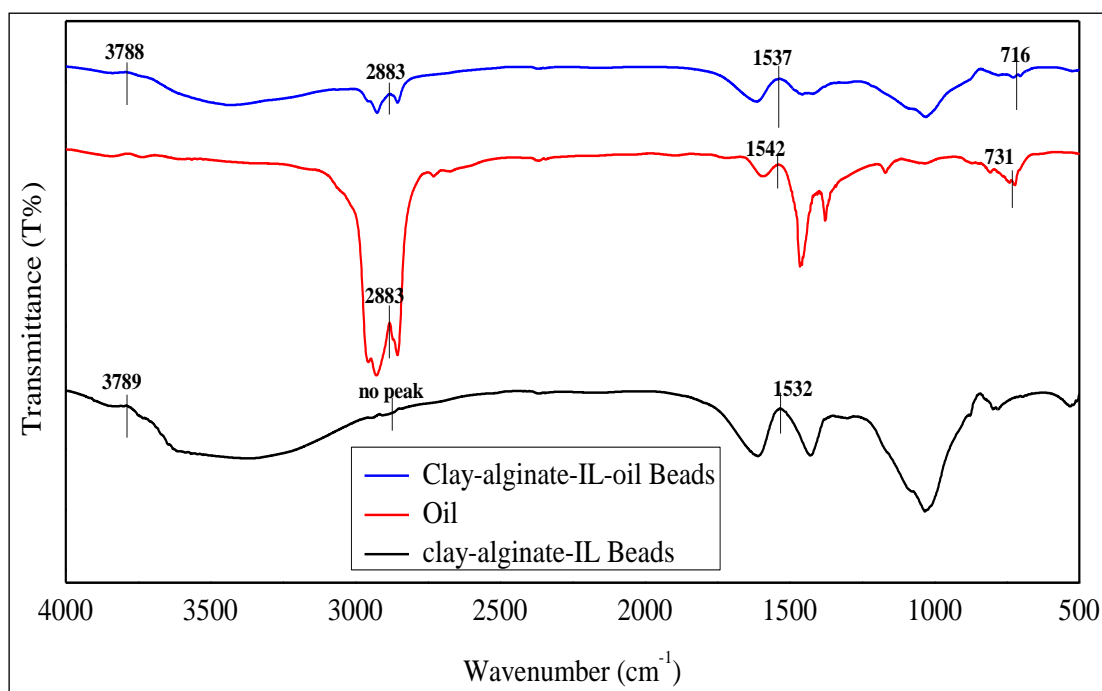


Figure 4-14: FTIR analysis of oil, IL, Na-alginate, clay, clay-alginate-IL beads, and clay-alginate-IL-oil beads used in the adsorption process

Inspection of Figure (4-14) shows that there is no peak for the beads in the region 2800-3000 cm<sup>-1</sup> before the implementation of beads for PW treatment. But after applying the beads for adsorption, a peak at 2883 cm<sup>-1</sup> appears which represents the successful adsorption of the oil on the active sites of the beads. A small peak shifting was also noticed at 3788 cm<sup>-1</sup> which also provides evidence of oil adsorption on the surface of

the bead. A peak shifting in the triple bond region was also noticed from 1542 to 1537 showing the stretching and vibration of molecules due to their interaction. Similar trends were found in the literature for the alginate beads loaded with ILs for decontamination of pollutants from the aqueous phase [68].

#### 4.4.2 TGA analysis of clay-alginate-IL beads and Na-alginate used in the adsorption process

The thermal degradation profile of beads and Na-alginate was recorded to study their behavior and thermal stability. For this purpose, TGA of the beads and Na-alginate was performed at a temperature range of 50 to 800 °C with a heating rate of 10 °C/min in an N<sub>2</sub> environment. Figure (4-15) represents the TGA analysis of beads and Na-alginate.

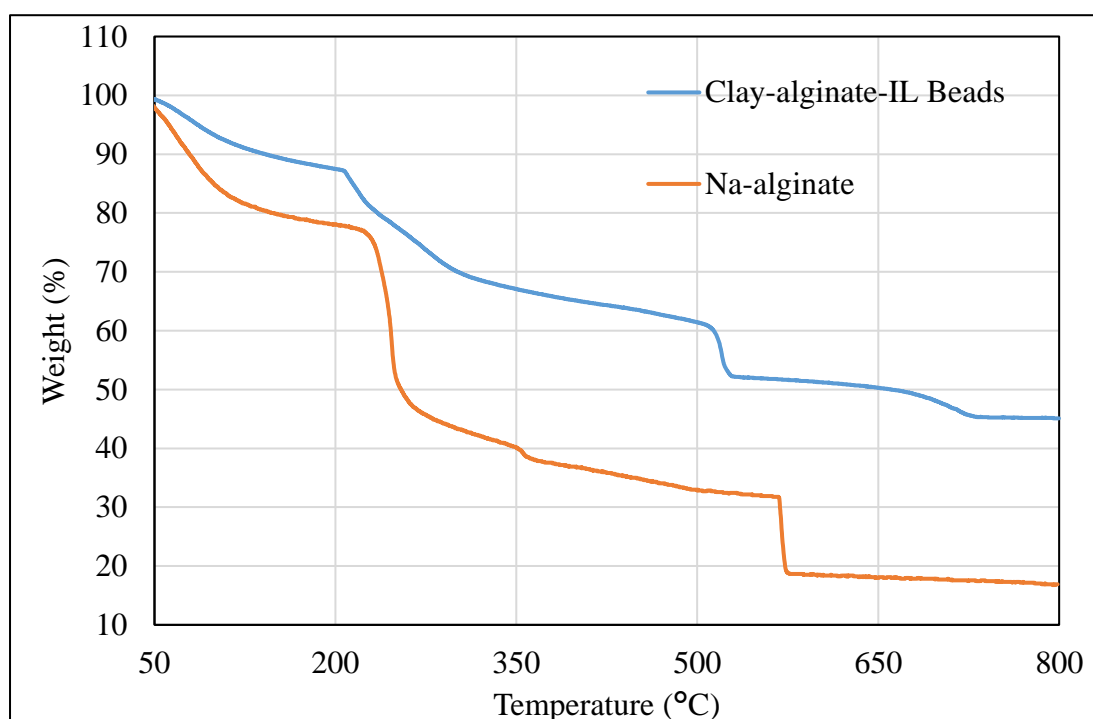


Figure 4-15: TGA analysis of clay-alginate-IL beads and Na-alginate used in adsorption process

Figure (4-15) represents the loss in weight with the increment in temperature. TGA profile showed that the thermal degradation of both beads and Na-alginate is increasing with temperature. There are three phases for the degradation of the beads and Na-alginate. The first phase lies between 50 to 120 °C where a small amount of mass was decreased which represents the removal of moisture content. After 200°C about 10 % weight loss has been observed for clay-alginate-IL beads. The second phase can be

observed between 200 and 400 °C which represents the pyrolysis of the beads where a significant amount of the weight loss can be observed due to degradation of the IL and sodium alginate. After 500 °C about 40 % weight of the clay-alginate-IL beads has been decreased. The third phase is called the passive region that lies between 400 to 550 °C where degradation of the component is occurring. After 800 °C about 50% weight of the clay-alginate-IL beads has been lost and it becomes constant which represents that only clay is left behind and IL and sodium-alginate already have been degraded. A similar degradation profile was reported in the literature for Na-alginate beads [107].

#### 4.4.3 SEM-EDX analysis of clay-alginate-IL beads

To study the surface morphology and texture of the beads, SEM-EDX analysis was performed. Figure (4-16 (a, b, c)) presents the SEM of clay- Na alginate-IL beads with different magnifications, and figure (4-16 (d)) displays the elemental analysis of beads.

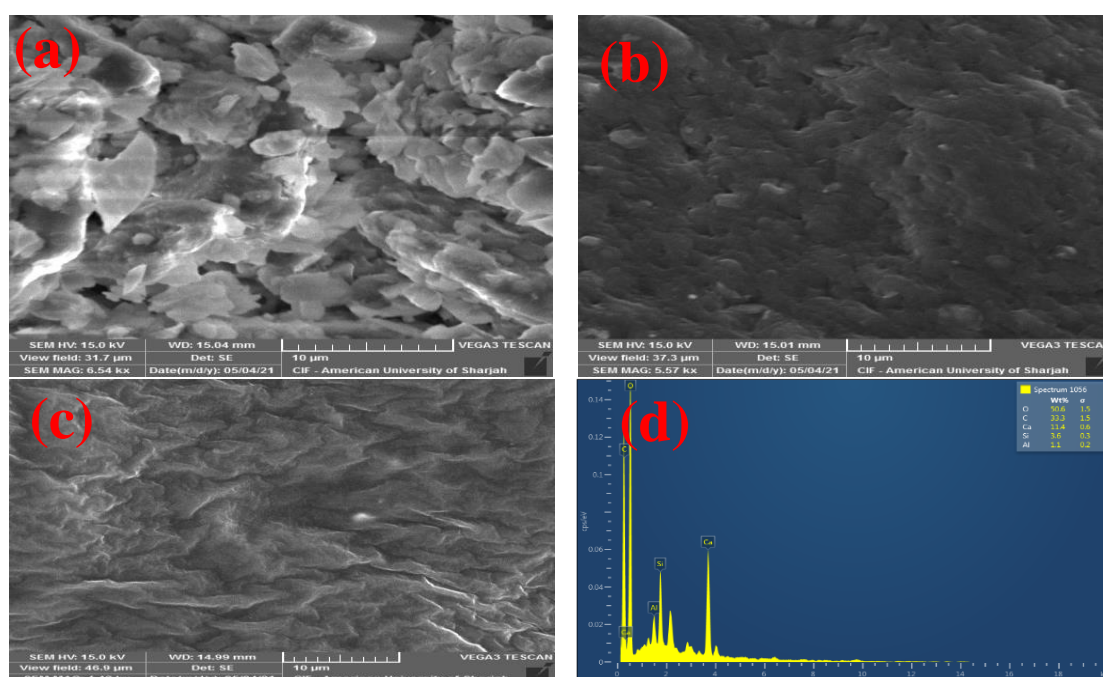


Figure 4-16: SEM image of clay-alginate-IL beads with different magnifications (a) 31.7 μm, (b) 37.3 μm, (c) 46.9 μm (d) EDX analysis of clay-alginate-IL beads

Figure (4-16) displays that the IL-based beads have a porous-rough surface which is helpful for the adsorption of oil into the surface of the bead [108], [109]. In the literature, it has been reported that the Na-alginate beads have a porous surface which is efficient

for the adsorption of oil into the beads. [110]. The EDX analysis showed the elemental composition of the major elements such as oxygen (O), calcium (Ca), and silicon (Si) present in beads.

#### 4.4.4 Effect of pH of PW solution on the adsorption capacity of the beads

The pH is an important factor during the adsorption of oil from PW using the beads. To study the effect of pH on the adsorption capacity of the beads, PW solutions of different pH ranging from 2 to 14 were prepared and the adsorption capacity for each pH solution was calculated at, initial concentration of oil 200 ppm, contact time 60 min, beads dosage of 10 mg, and PW volume 10 ml at room temperature and pressure. Figure (4-17) presents the effects of the pH on the adsorption capacity of beads, where the adsorption capacity was increased from 18.8 mg/g to 109.5 mg/g when pH was increased from 2 to 10.

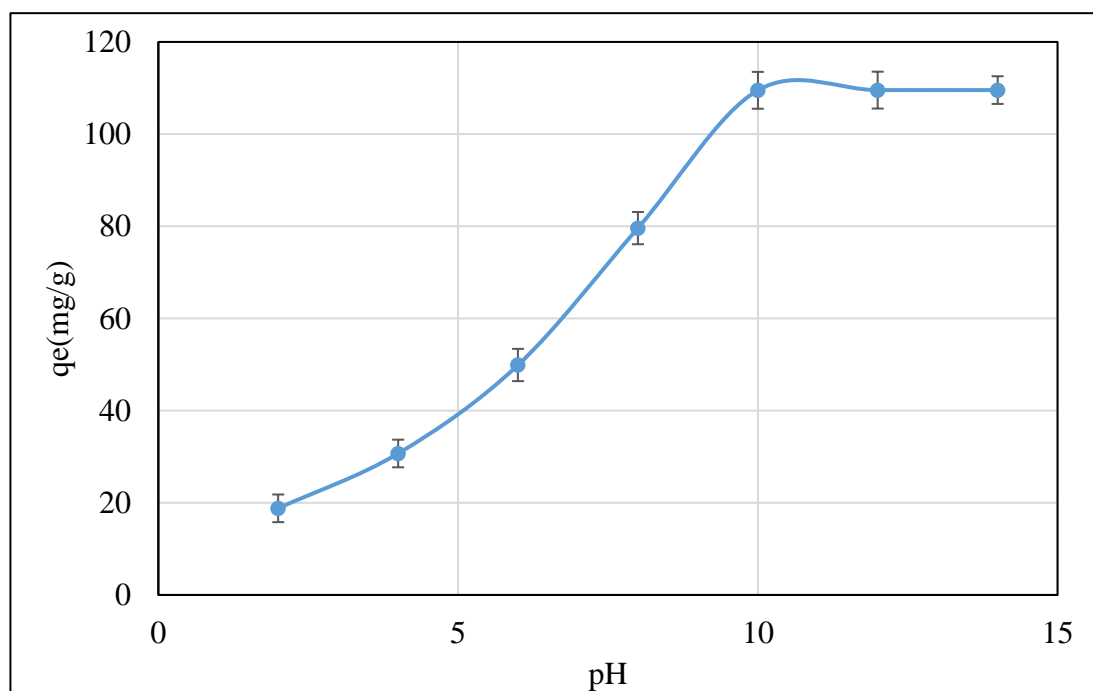


Figure 4-17: Effect of pH on adsorption capacity of beads at contact time=60 min, initial concentration=200 ppm, dosage=10 mg

The adsorption capacity did not change and became constant at the value of 109.5 mg/g when pH was changed from 10 to 14. The pH value of 10 was considered as the optimal value for further experiment. The adsorption capacity is low in the acidic region as

compared to the basic region. The adsorption capacity is low in the acidic region due to larger mass transfer resistance which minimizes the mass transfer between oil and the beads. In the basic region, mass transfer resistance decreases, and the driving force for mass transfer between oil and beads increases, which increases the adsorption capacity of the beads. A similar trend was reported in the literature for the adsorption of methylene blue dye [111].

#### 4.4.5 Effect of oil initial concentration on bead's adsorption capacity

The initial concentration of the oil in the PW solution can affect the adsorption capacity of the beads [112]. To study the effect of initial concentration on the adsorption capacity of solid-supported IL-beads, PW solutions of different initial concentrations ranging from 100 to 600 ppm were prepared. The adsorption capacity of IL-based beads was studied for each solution of PW at pH 10, contact time 60 min, beads dosage of 10 mg, and PW volume 10 ml at room temperature and pressure.

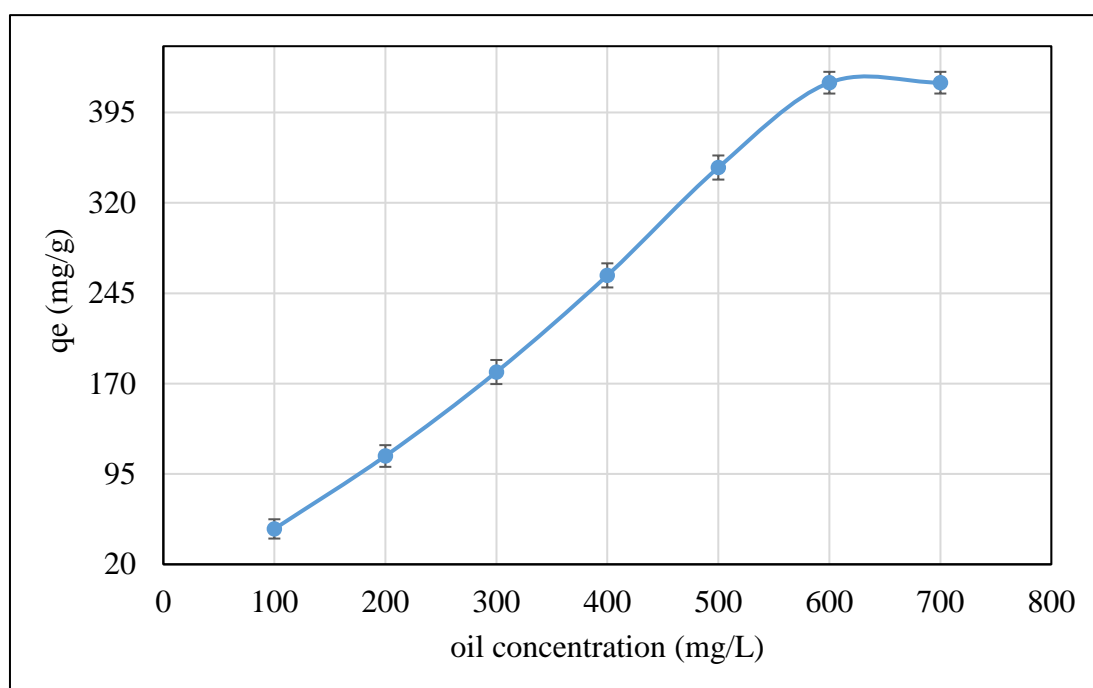


Figure 4-18: Effect of initial concentration of oil on adsorption capacity of beads at contact time=60 min, pH=10, dosage=10 mg

Figure (4-18) displays the effect of the initial concentration of oil in PW on the adsorption capacity of IL-based beads. Figure (4-18) showed that the adsorption

capacity of the beads followed an increasing trend with the initial concentration of oil in the PW solution. This increase in adsorption capacity is due to the transfer of more oil towards the beads at a higher initial concentration as compared to the small initial concentration. At higher initial concentration the driving force for mass transfer is higher and the mass transfer resistance is lower which causes the transfer of more oil towards the active site of the beads. An initial concentration of 600 ppm with a maximum adsorption capacity of 420 mg/g was taken as the optimum concentration for further experiments. A similar trend was reported in the literature for the alginate beads for the removal of pollutants from the aqueous phase [110].

#### 4.4.6 Effect of contact time on adsorption capacity of beads

Contact time is an important factor for the adsorption of oil from PW and it can affect the adsorption capacity of the beads.

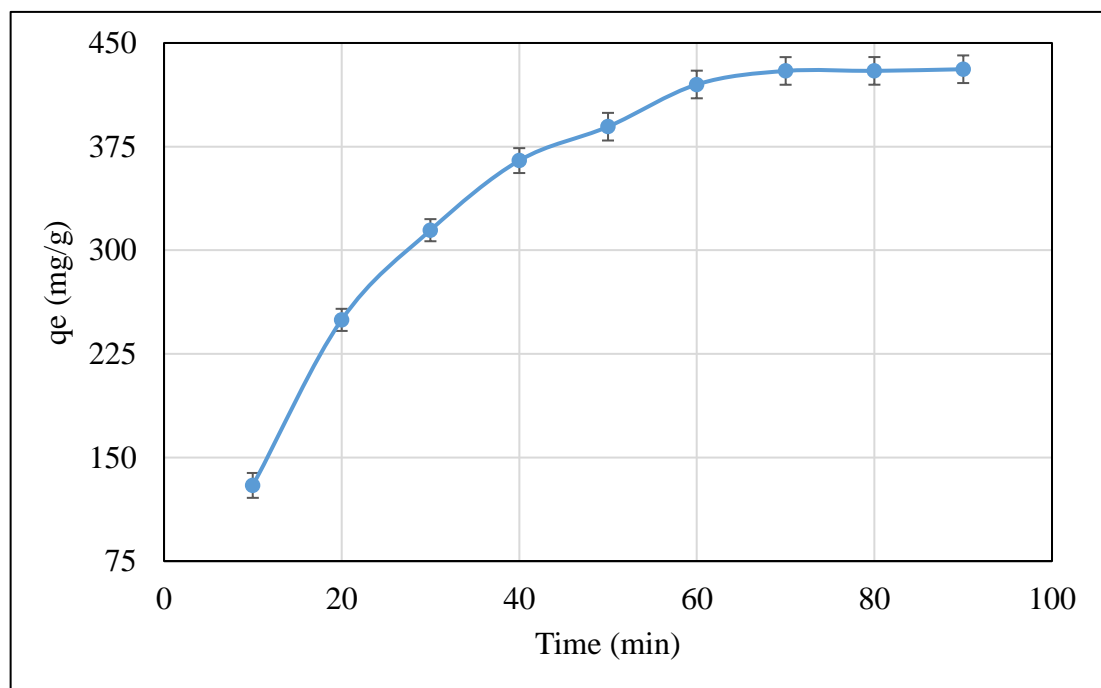


Figure 4-19: Effect of contact time on adsorption capacity of beads at initial concentration=600 ppm, pH=10, dosage=10 mg

Therefore, to study the effect of contact time on adsorption capacity, the beads were tested for different time intervals ranging from 10 to 90 min at pH 10, initial concentration 600 ppm, beads dosage of 10 mg, and PW volume 10 ml at room temperature and pressure Figure (4-19) represents the effect of contact time on the adsorption capacity of sodium-alginate-IL-based composite beads. Inspection of the

figure (4-19) reveals that the adsorption capacity is low at the start and started to increase with time and becomes constant (429.8 mg/g) after a specific time. This increase in adsorption capacity is due to the transfer of a greater number of molecules of oil towards sodium-alginate-IL-based beads at a higher contact time compared to less contact time. The adsorption capacity almost became constant at 429.8 mg/g after 70 min because the beads were saturated, and no mass transfer has occurred between the oil and beads. A contact time of 70 min with a maximum adsorption capacity of 429.8 mg/g was taken as the optimal time for further experiments. The literature also reported as the contact time was increased the adsorption capacity was also increased for alginate beads [110].

#### 4.4.7 Effect of temperature on adsorption capacity of beads

Temperature is an important factor during the adsorption of oil through solid beads and can affect the adsorption capacity of solid-supported IL-beads. Therefore, the effect of temperature on the adsorption capacity of IL-beads was studied.

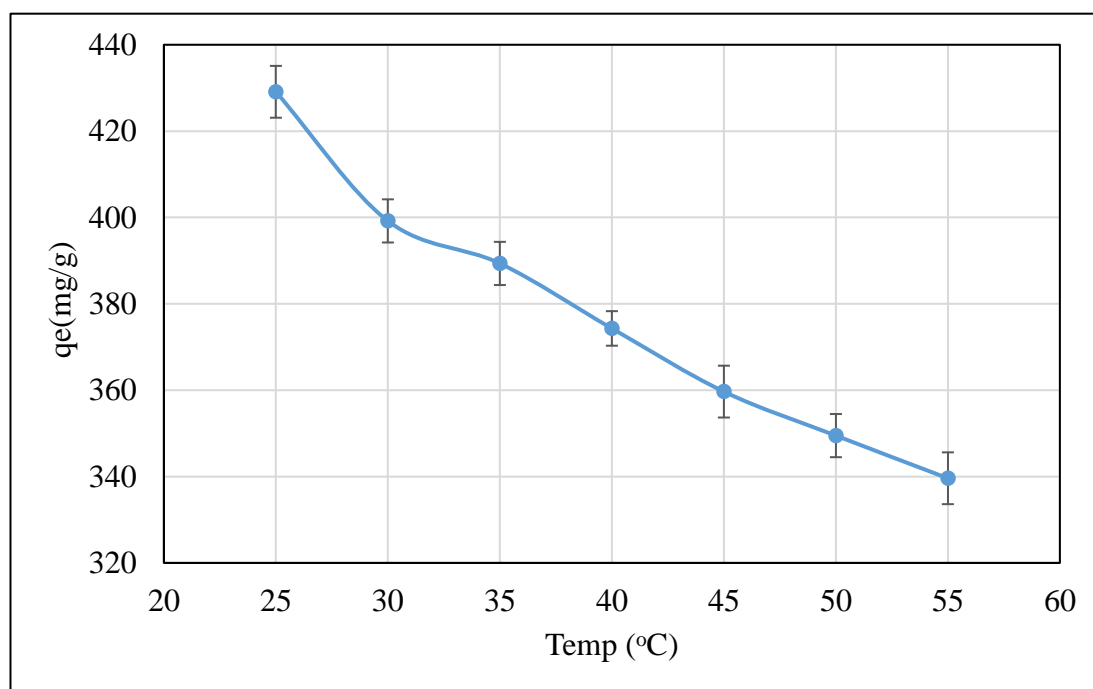


Figure 4-20: Effect of temperature on adsorption capacity of beads at initial concentration=600 ppm, pH=10, dosage=10 mg, contact time=70 min

The beads were tested at different temperatures ranging from 25 to 55 °C at the following optimum conditions, pH 10, initial concentration 600 ppm, beads dosage of 25 mg, and PW volume 10 ml at room pressure. Figure (4-20) presents the temperature



effect on the adsorption capacity of the beads. The figure (4-20) showed that adsorption capacity has an inverse relation with temperature. It is evident from the figure (4-20) that the adsorption capacity was decreased from 429.1 mg/g to 339.6 mg/g when the temperature was increased from 25 °C to 55 °C. This decrease in adsorption capacity is due to the decrease in driving force for mass transfer at a higher temperature compared to the lower temperature. Therefore, a higher number of oil molecules transfer from PW to the beads at a lower temperature. As a result, the room temperature was selected as an optimal temperature which is also economical in terms of energy and cost. A similar trend was reported in the literature for the adsorption of heavy metal from industrial wastewater on the clay-based adsorbent [113].

#### 4.4.8 Regeneration study of beads used in the adsorption process

Regeneration of the beads is very important from an economical point of view. The beads will be graded more efficiently if they can be reused for multiple cycles after regeneration.

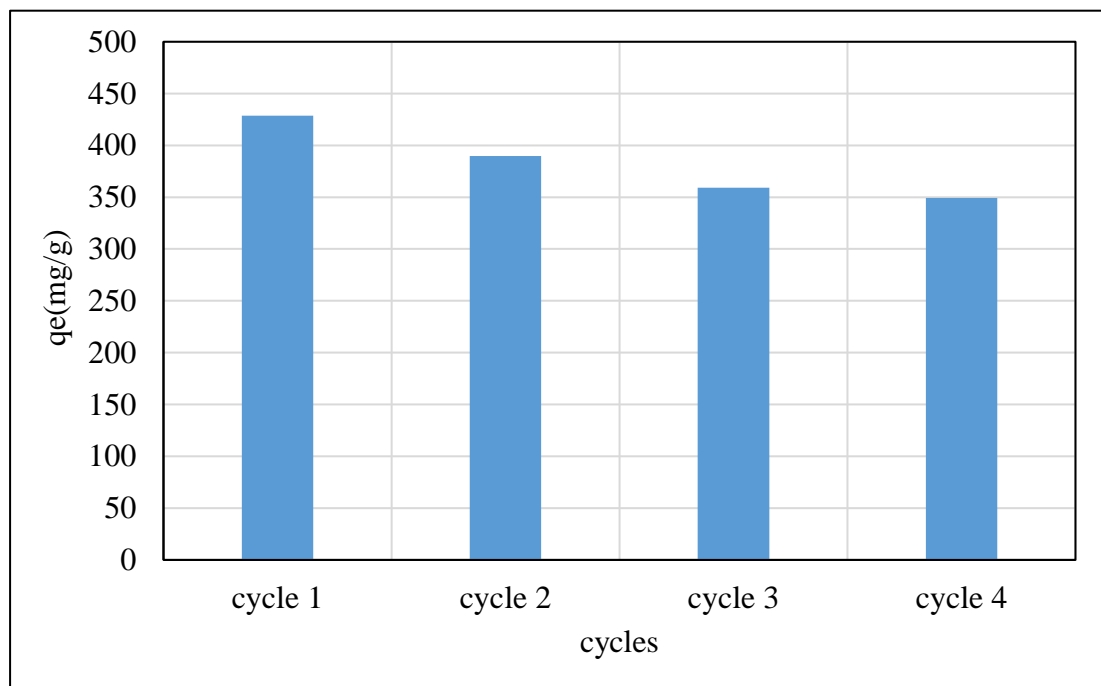


Figure 4-21: Regeneration study of clay-alginate-IL beads

Therefore, a regeneration study was also performed to regenerate and use the tested beads for further cycles. The regeneration of beads was done by keeping the beads in ethyl acetate for 30 min with continuous shaking of 100 rpm, so that, the oil can be

removed from the saturated beads, and as a result, more active sites would be available for further cycles. After that, the beads were washed with distilled water and dried before using them for the next cycles. A similar procedure was adopted for the 3<sup>rd</sup> and 4<sup>th</sup> cycles. Figure (4-21) represents the adsorption capacity for different cycles. Experimental results showed that beads were efficient to use up to the 4<sup>th</sup> cycle.

#### 4.4.9 Adsorption models

##### 4.4.9.1. Adsorption kinetics for the adsorption of oil onto clay-alginate-IL beads surface

Two kinetic models, pseudo-first order and pseudo-second order were applied to the experimental data to investigate the kinetics of oil adsorption onto the Na-alginate beads. Equations (14-15) were used to determine the kinetics parameters for pseudo-first-order and pseudo-second-order, respectively [94]. The rate constants of the pseudo-first order and pseudo-second orders are  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ), respectively.

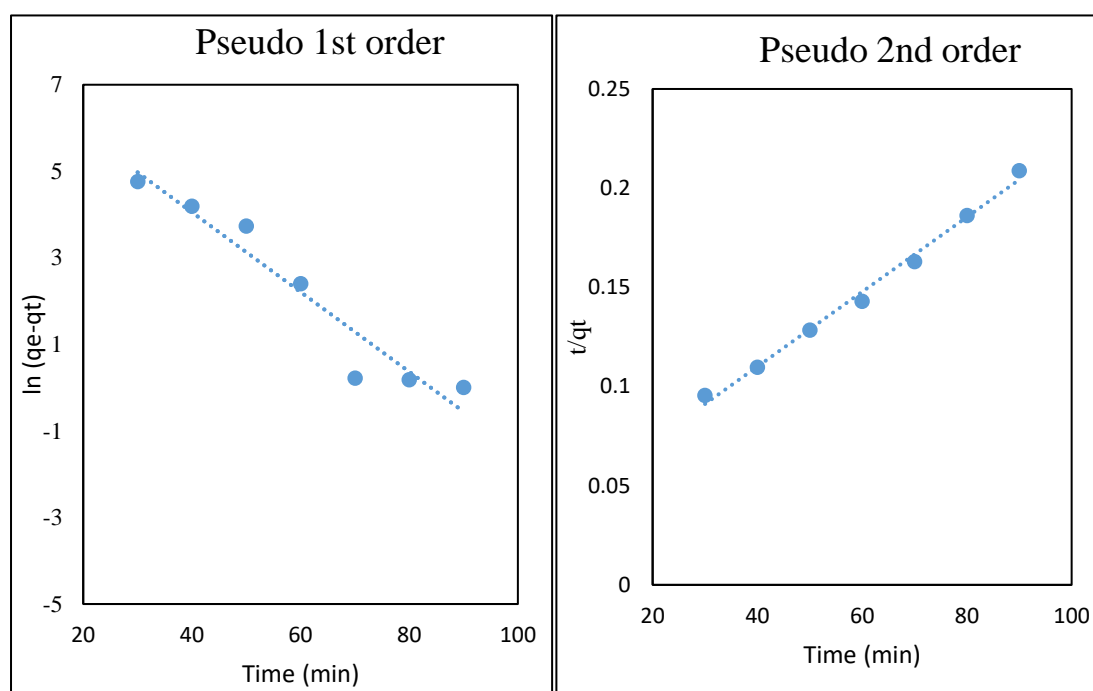


Figure 4-22: Adsorption kinetics study for pseudo first and second order

The regression coefficients for pseudo-first and pseudo-second order are  $R^2 = 0.92$  and  $R^2 = 0.99$ , respectively, which showed that the adsorption of oil into the beads follows the pseudo-second order. The pseudo-second order indicates that the chemisorption took place during the adsorption process. Figure (4-22) represents the plot of  $[t \text{ vs } \ln(q_e - q_t)]$

and  $[t/q_t]$  for pseudo-first order and pseudo-second order, respectively. Table (4-1) represents the kinetic parameters for both models.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (14)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (15)$$

Table 4-1: Adsorption kinetics parameters of oil into clay-alginate-IL beads

Kinetic models	Parameters	Values
Pseudo first order	$k_1$ ( $\text{min}^{-1}$ )	0.0922
	$R^2$	0.9241
Pseudo second order	$k_2$ ( $\text{g/mg min}^{-1}$ )	$7 \times 10^{-5}$
	$R^2$	0.9924

#### 4.4.9.2. Adsorption in a Pseudo-second order isotherm

Two isotherm models, Langmuir and Freundlich, were applied to the experimental data to study the adsorption isotherm of oil into the beads at room temperature. Equations (16-17) were used for these models respectively [94]. where  $C_e$  (mg/L) represents the remaining oil in the aqueous phase at equilibrium,  $q_m$  (mg/g) represents the maximum adsorption capacity of the beads,  $b$  ( $\text{L mg}^{-1}$ ), shows the Langmuir adsorption constant which is related to the free energy,  $k_f$  ( $\text{L mg}^{-1}$ ) and  $n$  represents the Freundlich constants and can be calculated by plotting  $\ln q_e$  against  $\ln C_e$ . Table (4-2) presents the calculated isotherm parameters. Figure (4-23) presents the Langmuir and Freundlich isotherm plots. The regression coefficients for the Langmuir model and Freundlich model are  $R^2=0.96$  and  $R^2=0.99$ , respectively which showed that experimental data of the oil adsorption into beads was fitted more accurately using the Freundlich isotherm model. The Freundlich isotherm model represents that the adsorption process is multilayer and adsorption capacity is the logarithmic function of the remaining concentration of oil in PW.

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (16)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (17)$$

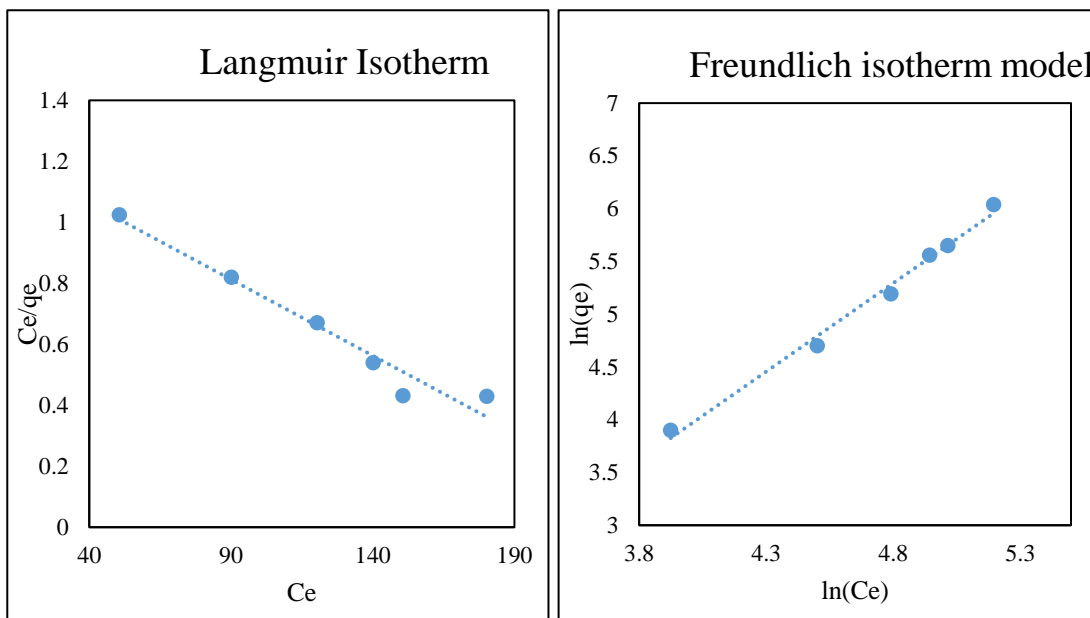


Figure 4-23: Adsorption isotherms study of oil onto clay-alginate-IL beads surface

Table 4-2: Adsorption isotherm parameters of oil adsorption into beads

Isotherm model	Parameters	Values (25 °C)
Langmuir model	$K_L$ (L/mg)	-0.0039
	$R^2$	0.9583
Freundlich model	$K_f$ (mg/g)(L/mg) <sup>1/n</sup>	0.2239
	$n$	0.5968
	$R^2$	0.99

#### 4.5. Comparison Between LLE and Adsorption Process

Different ILs were applied for LLE, and the process parameters were optimized for the best selected IL [C<sub>10</sub>Mim][NTf<sub>2</sub>]. Experimental results showed that our selected IL can remove up to 92.8 % oil from the PW at optimum conditions within a short time, but

the used IL cannot be recovered in LLE. On the other hand, the sodium alginate-clay beads loaded with IL showed a removal efficiency of 71.8 % at optimum conditions. Although the removal efficiency was decreased a little bit in absorption, the beads were regenerated successfully and were used up to 4 cycles. According to the experimental results, it can be suggested that the adsorption of oil on the surface of the bead is more economical and feasible as compared to LLE, but it requires a longer time.

#### 4.6. Comparison with Literature Values

Table (4-3) represents the comparison between the reported equilibrium time for already reported adsorbents and materials used in this study for the removal of oil from PW. Table (4-3) shows that the time required for the IL, tested in this study is the smallest as compared to other reported adsorbents with the highest efficiency of 92.8 %. Beads tested in this study showed comparatively low efficiency (71.8 %) within 70 minutes.

Table 4-3: A comparison between the reported equilibrium time and efficiency of the extraction of oil by different adsorbents and ILs and beads used in this study

<b>Material Used</b>	<b>Removal Efficiency (%)</b>	<b>Equilibrium Time (min)</b>	<b>Reference</b>
Kiwi peels	90	150	[24]
Walnut shell	87	-	[114]
Date pits	80	-	[114]
Graphene	80	60	[93]
Graphene magnetite	75	30	[93]
olive leaves	80	80	[94]
pomegranate peel	92	50	[115]
multiwalled carbon nanotubes and their derivates	85	20	[116]
eggplant peels	95	40	[117]
Iron oxide nano adsorbents	67	90	[118]
ILs	92.8	4	This work
Na-alginate -IL beads	71.8	70	This work

## Chapter 5. Conclusion

The objective of this study was to test ILs (NTf<sub>2</sub> based) and clay-alginate-IL beads for oil removal from PW via LLE and adsorption processes, respectively. In LLE, the effect of ILs structure on the oil removal was investigated. It was found that the removal efficiency of the ILs increases with the alkyl chain length. Moreover, Imidazolium-based IL has higher efficiency as compared to ILs having ammonium, phosphonium, and pyridinium cations. In process parameter optimization for LLE, it was found that the removal efficiency of ILs is the strong function of the initial concentration, phase ratio (PW: IL), and pH of PW solution. However, there is no significant effect of contact time and temperature on its removal efficiency. The removal efficiency of ILs increases with increasing the initial concentration and pH of the solution. An increase in PW to IL phase ratio adversely affected the removal efficiency. On the other end, during process parameter optimization for adsorption, it was examined that the adsorption capacity of the beads is the strong function of pH of PW, initial concentration of oil in PW, contact time, and temperature. The adsorption capacity followed an increasing trend with the initial concentration of oil, pH of PW, and contact time and began to decrease with temperature.

The extraction efficiency of 92.8 % was achieved at optimum conditions (500 ppm initial concentration of oil, 4 min contact time, 1:4 phase ratio (PW: IL), 8 pH, and at room temperature) for LLE. However, the adsorption capacity of 431 mg/g was achieved with clay-alginate-IL beads at optimum process conditions (600 ppm initial concentration of oil, 70 min contact time, 10 pH, and at room temperature). Different characterization techniques such as FTIR, SEM-EDX, and TGA were applied to investigate the chemical bond interaction and functional groups, surface morphology, and thermal stability of the used materials. FTIR analysis validated the successful chemical bonding of oil with pure IL and beads. SEM analysis demonstrated that clay-alginate-IL beads have a porous and rough surface which is appropriate for the adsorption of oil into the bead's surface. TGA analysis showed the thermal degradation profile of the clay-alginate-IL beads indicating the weight loss with temperature. Moreover, the clay-alginate-IL beads utilized in the adsorption process were regenerated and used up to the 4<sup>th</sup> cycle.

It can be concluded that pure ILs demonstrated good removal efficiency (92.8%) within a short time of 4 minutes at optimum parameters. However, regeneration of ILs was not possible. On the other hand, clay-alginate-ILs beads showed an adsorption capacity of (431 mg/g) or removal efficiency of (71.8 %) within 70 min. Meanwhile, beads can be and were regenerated and reused. It is suggested that the employing of clay-alginate-IL beads through adsorption is a more suitable and economical method as compared to the implementation of ILs through LLE for the removal of oil from PW. Further research regarding cost and regeneration can be performed to make the process more economical and feasible.

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