

**PRETREATMENT OF OILFIELD PRODUCED WATER  
USING IONIC LIQUIDS FOR DISSOLVED AIR  
FLOATATION**

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By

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## ABSTRACT

Energy consumption is rising due to population increase and industry development. There will be an increase of nearly 66% of energy consumption related to fossil fuel such as oil and gas between 2003 and 2030 from  $7.6 \times 10^{13}$  to  $12.6 \times 10^{13}$  kilowatt-hours worldwide. With the increase in the production of oil and gas, a larger amount of produced water (PW) will be generated. Produced water poses a risk to the environment, because it contains persistent toxic and carcinogenic constituents. The dissolved air floatation (DAF) process is the most widely used technique in the world for produced water treatment. In order to reach better experimental results, different coagulants are added as a pretreatment process.

In this research, as a pretreatment to the DAF process, three similarly structured ionic liquids (n-methylpyridinium tosylate, 1,3-dimethylimidazolium tosylate, and 1-benzyl-3-methylimidazolium tosylate) were used to improve the efficiency of treatment. An orthogonal experimental design (OED) with different factors and levels was designed to determine the most effective ionic liquid, the best operation conditions, and the influence strength order of different factors. Two blank columns were designed for error estimate. Range analysis and variance analysis (ANOVA) were used to understand factor influence and determine the best operating conditions. The results of the experiments indicate that, with the same operation conditions (concentration, speed, and reflux ratio), 1-benzyl-3-methylimidazolium tosylate had the highest oil and turbidity removal efficiency when compared to the other two ionic liquids. According to range analysis and variance analysis (ANOVA), the three ionic

liquids have the same influential order for the three factors considered with an ionic liquid concentration influence greater than that of both speed (RPM) and the reflux ratio (RR). The best operating conditions for the three ionic liquids were 300 mg/l for ionic liquid concentration, 200 for RPM, and 20% for RR, respectively. At the best operating conditions, the percentages of the removal of oil content were  $75.4\% \pm 0.7\%$  for n-methylpyridinium tosylate,  $71.0\% \pm 0.2\%$  for 1,3-dimethylimidazolium tosylate, and  $81.6\% \pm 0.3\%$  for 1-benzyl-3-methylimidazolium tosylate, respectively.

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## NOMENCLATURE

|             |   |
|-------------|---|
| ANOVA       | Variance Analysis                             |
| API         | American Petroleum Institute                  |
| BAF         | Biological Aerated Filters                    |
| bbbl        | Barrel (unit of volume)                       |
| BOD         | Biochemical Oxygen Demand                     |
| BTEX        | Benzene, Toluene,<br>Ethylbenzene, Xylenes    |
| Btu         | British thermal unit                          |
| CFU         | Colony Forming Unit                           |
| COD         | Chemical Oxygen Demand                        |
| d           | Diameter of drop/agglomerate                  |
| DAF         | Dissolved Air Flotation                       |
| DAP         | Dissolved Air Precipitation                   |
| DI          | Deionized water                               |
| DLVO Theory | Derjaguin, Landau, Verwey,<br>Overbeek Theory |
| DNA         | Deoxyribonucleic acid                         |
| ED          | Electrodialysis                               |
| EOR         | Enhanced Oil Recovery                         |
| IL          | Ionic Liquids                                 |
| kWh         | kilo-Watt-hours                               |
| NEB         | National Energy Board                         |

|      |  |
|------|--|
| NORM | Naturally Occurring Radioactive Material           |
| NTU  | Nephelometric Turbidity Unit                       |
| OADT | Orthogonal Array Design Table                      |
| OED  | Orthogonal Experimental Design                     |
| OGP  | International Association of Oil and Gas Producers |
| PAH  | Polycyclic Aromatic Hydrocarbons                   |
| PW   | Produced Water                                     |
| RR   | Recycle Ratio                                      |
| SBRs | Sequencing Batch Reactors                          |
| TDS  | Total Dissolved Solids                             |
| TOC  | Total Organic Carbon                               |
| TOG  | Total Oil-Grease                                   |
| TSS  | Total Suspended Solid                              |
| ZP   | Zeta Potential                                     |

## CHAPTER 1: INTRODUCTION

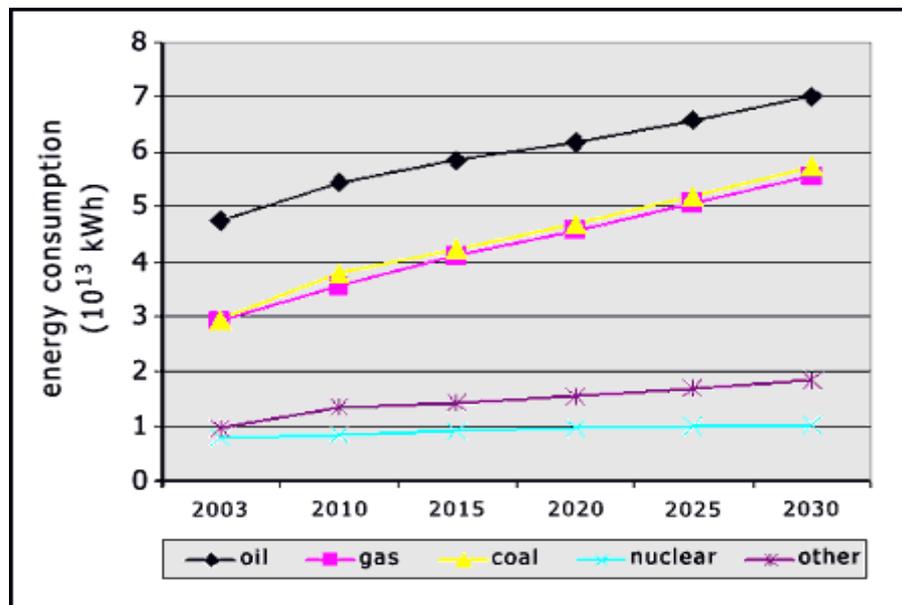
### 1.1 Background

With the growth of population and development of modern civilization, the consumption of energy around the world is increasing dramatically. As Figure 1.1 shows, in 2030, the energy consumption related to oil and gas is estimated to reach  $7 \times 10^{13}$  and  $5.6 \times 10^{13}$  kilowatt-hours, respectively.

Produced water is a large part of the effluent generated in the oil and gas production process. It is an integral part of hydrocarbon production and it contains organic materials, salts, heavy metals, and other toxic compounds. Produced water can cause serious environmental problems, such as soil degradation and water pollution, and therefore, affect human and animal survival (Lee et al., 2003). The volume of produced water in the world is over 25 million barrels per day (Fakhru'l-Razi et al., 2009), and Figure 1.2 shows the onshore and offshore volumes of produced water from 1990 to 2014. Many countries have imposed strict produced water discharge limits.

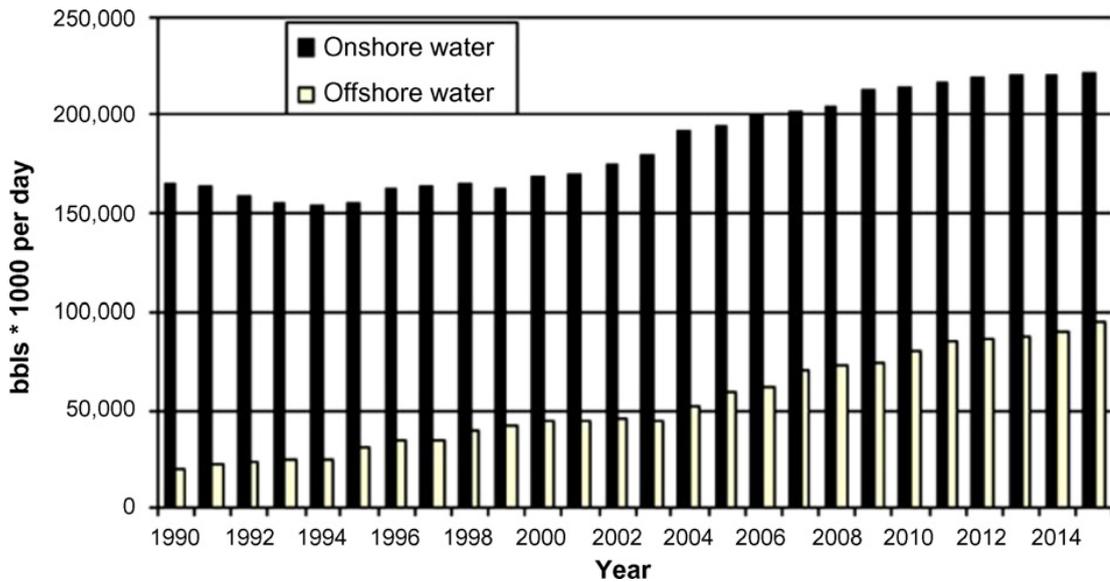
The cost of management and treatment of produced water is estimated at 40 billion U.S. dollars per year (Mastouri, Nadim, & Kargari, 2010). The dissolved air floatation (DAF) process, which is recognized as an effective and economic technique for oily wastewater treatment, is widely used worldwide. Compared to other physical techniques such as gravity separation and centrifugal segregation, DAF is efficient in separating similar density materials because air bubbles can increase the buoyancy of the oil droplets (Al-Shamrani, James, & Xiao, 2002; Wang, Fahey, & Wu, 2005).

However, DAF alone sometimes cannot achieve the required environmental standards for oil content. Adding a coagulant as a pretreatment is a common occurrence. Among the large number of physical, chemical, and biological additions for effluent pretreatment available (Baldoni-Andrey, Pedenaud, Dehaene, & Segues, 2006), ionic liquid stands out due to its excellent performance. When compared to traditional aluminum or iron coagulants, ionic liquid is an eco-friendly solvent and has no restriction concerning the pH (Guzmán-Lucero, Flores, Rojo, & Martínez-Palou, 2010).



**Figure 1.1:** Estimation of energy consumption from 2003 to 2030.

(Source: <http://www.eia.gov/>)



**Figure 1.2:** The volume of onshore and offshore produced water from 1990 to 2014.

(Source: Fakhru'l-Razi et al., 2009)

## 1.2 Objectives

Three similarly structured ionic liquids were selected as a pretreatment for produced water with the DAF process in this research: (1) n-methylpyridinium tosylate, (2) 1,3-dimethyl imidazolium tosylate, and (3) 1-benzyl-3-methylimidazolium tosylate. The orthogonal experimental design (OED) was applied as a guideline for the experimental procedure. The objectives of the research are:

1. Obtain the influence strength order of the different operating variables (factors).
2. Find the best operating conditions.
3. Determine the optimal combination of experimental conditions.
4. Find the best ionic liquid for produced water treatment.
5. Correlate differences of experimental results with structure differences of the ionic liquids.

### 1.3 Originality of research

Adding coagulants as a pretreatment to the DAF process for produced water has been reported in several papers. Most researches have focused on aluminum and ferric salts. However, these heavy metal salts cause chronic hazards to plants and animals, which leads to a severe negative influence on human beings (Tchounwou, Yedjou, Patlolla, & Sutton, 2012). Ionic liquids are considered green solvents and are in the process of finding wide application in enhanced oil recovery (EOR) research. However, they have not yet been reported in produced water treatment. In addition, in research on the DAF process, researchers generally focus on one or two key elements for the improvement of DAF efficiency, such as pressure, RR, or concentration. In other words, they consider the conditions independently. A systematic study examining the influencing factors simultaneously has not yet been published. In this research, three key elements (factors) are considered simultaneously for the first time: concentration, RR, and RPM.

This research studies the influence of similarly structured ionic liquids with the same anion on the DAF process. N-methylpyridinium tosylate and 1,3-dimethylimidazolium tosylate have the same ring number but different functional groups. 1-Benzyl-3-methylimidazolium tosylate has the highest number of rings, which is three, and the same imidazole function group as 1,3-dimethyl imidazolium tosylate. The results of the comparison and the conclusion can be used as a guideline for the selection of other ionic liquids in future studies.

In addition, this experiment selected an efficient and economic experimental method.

An orthogonal array design table (OADT) has two advantages: uniform dispersion and regular comparison (Zhu, Chew, & Wu, 2013). Three factors (concentration, RR, and RPM) with different levels are studied in this research simultaneously according to OED. Applying range analysis and variance analysis (ANOVA) gives assurances for the consistency of the results. Moreover, ANOVA can mitigate the influence of experimental errors.

## **CHAPTER 2: LITERATURE REVIEW**

### **2.1 Produced water**

Produced water is the largest volume waste stream generated during oil and gas exploration and production processes (Tibbetts, Buchanan, Gawel, & Large, 1992). In onshore and offshore fields, hydrocarbon production may be only one-tenth of the produced water production. In the end period of production for a well, the amount of produced water can reach 98% of the total output (Stephenson, 1992).

The formation of produced water can be divided into three categories. The first type is natural water such as fresh water or seawater, which was trapped in a reservoir. That water has accompanied hydrocarbons for million years in the liquid phase (Collins, 1975). The second type is condensed water, which was produced in the oil and gas exploitation process. The condensation is caused by pressure change (Clark & Veil, 2009). The third type is artificially produced water, which refers to the injected water or steam in the enhanced oil recovery (EOR) process (Neff, 2002).

Produced water production reached 77 billion barrels per year in 2002. (Khatib & Verbeek, 2003). In 2003, as reported by the International Association of Oil and Gas Producers (OGP), the amount of produced water discharged into the ocean was evaluated as 21.1 million tons in North America and 388 million tons in Europe. In addition, worldwide, the discharge amount was estimated as 667 million tons (OGP, 2004).

#### **2.1.1 Characteristics of produced water**

The content of produced water is complex. In addition to water, a large amount of organic and inorganic materials are dissolved and suspended in produced water. The content of produced water varies widely according to reservoir location, formation time, hydrocarbon component, and injection media (Neff, Lee, & DeBlois, 2011). The components of produced water can be grouped into seven categories: (1) organic material, (2) salts, (3) metals, (4) radionuclides, (5) particulate solids, (6) injection chemical substances, and (7) dissolved gas.

1. Organic material:

Overall, the organic material in produced water can be summarized as oil and grease content. It can be categorized into two types: petroleum hydrocarbons and hydrocarbon derivatives (Faksness, Grini, & Daling, 2004). The contents of petroleum hydrocarbons are only carbon and hydrogen. Petroleum hydrocarbons are divided into two categories: aliphatic and aromatic compounds. Common petroleum hydrocarbons include straight chain hydrocarbons; benzene, toluene, ethylbenzene, and xylenes (BTEX); polycyclic aromatic hydrocarbons (PAH); phenols; etc. (Johnsen, Røe Utvik, Garland, E., de Vals, B., & Campbell, 2004). Hydrocarbon derivatives are hydrocarbon compounds whose hydrogen atoms have been replaced by different functional groups. The most common hydrocarbon derivatives are alkyl halides, alcohols, and mono- and di-carboxylic acids (Skaare, Wilkes, Vieth, Rein, & Barth, 2007).

2. Salts:

Salts dissolve in water in the form of ions. Sodium and chloride are the most abundant ions in produced water. The other important inorganic ions are calcium, magnesium, potassium, sulphate, bromide, strontium, ammonium, bicarbonate, iodide, boron, carbonate, and lithium (Collins, 1975).

### 3. Metals:

Metals in produced water are present in dissolved or micro particulate forms. The type, concentration, and chemical properties of metals vary depending on the reservoir location and depth. The most common metals in produced water are arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, vanadium, and zinc (Neff, 1987).

### 4. Radionuclides:

It has been known that produced water in many places of the world contain naturally occurring radioactive material (NORM). Radium produced from the radioactive decay of uranium-238 and thorium-232 can be found in some special reservoirs. Radium-226 ( $^{226}\text{Ra}$ ) and radium-228 ( $^{228}\text{Ra}$ ) are the most abundant radionuclides (Michel, 1990; Utvik, 2003).

### 5. Particulate solids:

Particulate solids include bacteria, waxes, sand, and stone chips that are suspended in produced water systems. Particulate solids are harmful to the transportation devices of produced water (Veil, Puder, Elcock, & Redweik, 2004).

### 6. Injection chemical substances:

Chemical compounds such as biocide, emulsion breaker, scale inhibitor, corrosion inhibitor, gas treatment chemicals, coagulants and flocculants, and H<sub>2</sub>O/O<sub>2</sub> scavenger are injected into production wells and pipelines. The purposes of using these chemical solvents are multiple. Some are used to increase the EOR, others are used to protect devices from corrosion, and some are selected to decrease the separation time of oil, gas, and water (Johnsen et al., 2004).

7. Dissolved gas:

Produced water has a certain amount of dissolved gas (for example, CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>S). A trace of dissolved gas is normal; however, a huge number of gas bubbles in pipeline transportation can be dangerous and can cause much damage (Hansen & Davies, 1994).

Table 2.1 shows the typical characteristics of oilfield produced water parameters in the world, while Table 2.2 contains a summary of gas field produced water constituents in the world.

**Table 2.1:** Typical characteristics of oilfield produced water parameters in the world.

| Parameter   | Values (mg/l) |
|-------------|---------------|
| Total oil   | 2-565         |
| BTEX        | 0.39-35       |
| Phenols     | 0.009-23      |
| Chloride    | 80-200000     |
| Bicarbonate | 77-3990       |
| Sulphate    | 2-1650        |

|                     |        |
|---------------------|--------|
| Sulphite            | 10-15  |
| Ammoniacal nitrogen | 10-300 |

(Source: Tibbetts et al., 1992)

**Table 2.2:** Summary of gas field produced water constituents in the world.

| Parameter | Values(mg/l) |
|-----------|--------------|
| Aluminum  | 0-83         |
| Arsenic   | 0.004-151    |
| Barium    | 0-1740       |
| Boron     | 0-56         |
| Bromide   | 150-1149     |
| Cadmium   | 0-1.21       |
| Calcium   | 0-25000      |
| Chloride  | 1400-190000  |
| Chromium  | 0-0.03       |
| Copper    | 0-5          |

(Source: Johnson, Kanagy, Rodgers Jr, & Castle, 2008)

### 2.1.2 Environmental hazards of produced water

Produced water can have acute or/and chronic impacts on offshore and onshore environments. Generally, produced water, which includes acute toxicity materials, only influences the vicinity of the area where the discharging happens. The long-term ecological impacts are respiratory problems, endocrine disruption, genetic pollution, fecundity decrease, etc. (Lee et al., 2003; Holdway, 2002).

Organic materials increase biochemical oxygen demand (BOD) in water and thus endanger aquatic organisms. Light hydrocarbons floating on the surface of the water influence the light penetration rate and cause toxic compounds evaporation. Some non-polar organics are persistently toxic, and BTEX are recognized carcinogenic organics (Elias-Samlalsingh & Agard, 2003).

Salts are considered a main contributor to toxicity. In addition, high salt content leads to soil degradation and landscape destruction, which decreases grain output (Fakhru'l-Razi et al., 2009).

Produced water often has a higher concentration of metals than seawater. Heavy metals will accumulate in the top of the food chain through the distribution chain. The toxicity of metals is less than that of non-polar organics (Wake, 2005).

Chemical compounds, which are injected into a reservoir, may precipitate and accumulate in marine or inland sediments. Generally, oil soluble chemicals have a higher environmental risk than water-soluble chemicals (Grigson, Wilkinson, Johnson, Moffat, & McIntosh, 2000).

The other components of produced water, such as radionuclide and suspended solids, have a very small influence on the environment (Meinhold, Holtzman, & Hamilton, 1995).

### 2.1.3 Management methods of produced water

#### 2.1.3.1 Regular limits

Oil and grease compounds are regulated in both onshore and offshore production. For offshore production, salinity is not a regulated parameter because seawater already

has a high salt content. However, for onshore production, salinity must be controlled except for underground injection (National Petroleum Council, 2011). Table 2.3 shows the national discharge limits of oil and grease in water in some countries. In Canada, the regulatory standard of the amount of oil in offshore water is set by the National Energy Board (NEB) in its “Offshore Waste Treatment Guidelines” (2010), which indicates that discharged produced water should not exceed 30 mg/l average oil in water concentration per month and 44 mg/l average oil in water per day (NEB, 2010). In addition, environmental regulatory agencies such as Fisheries and Oceans Canada are applying continual chronic toxicity studies to support the development of advanced monitoring and environmental evaluation protocols (Neff et al., 2011).

**Table 2.3:** Summary of national discharge limits of oil and grease in water.

| <b>Country</b> | <b>Legal Instrument</b> | <b>Oil in Water Limit</b>   |
|----------------|-------------------------|-----------------------------|
| America        | 40 CFR 435              | 29 mg/l avg. 42 mg/l max    |
| China          | GB 4914-85              | 30-50 mg/l avg. 75 mg/l max |
| Canada         | Act RSC 1987            | 40 mg/l avg. 80 mg/l max    |
| UK             | OSPAR Convention        | 40 mg/l avg. 100 mg/l max   |
| UAE            | KUWAIT Convention       | 40 mg/l avg. 100 mg/l max   |

#### 2.1.3.2 Management methods

There are three hierarchical ways to prevent environmental risk caused by produced water (Fakhru’l-Razi et al., 2009):

1. Minimize:

Minimization means applying technologies to minimize produced water production, which is the best way to control the amount of effluent. It can be achieved by using CO<sub>2</sub> or propane instead of water to enhance oil recovery.

## 2. Reuse/recycle:

In order to reuse or recycle produced water, treatments may be required to meet qualifications. Produced water may be used for different aspects such as re-injection into the same field, agricultural utilization, industry purpose, etc. (Boysen, Boysen, & Boysen, 2002; Tao et al., 1993).

## 3. Discharge:

If neither of these two ways is practical, discharge of the water is the final option (Veil, 2007). Most of the time, discharge happens on offshore reservoirs.

### 2.1.4 Treatment technologies of produced water

Produced water is considered as a waste product in oil and gas production; however, after treatment, it has the potential to be a harmless and valuable resource. The common objectives for produced water treatment are (Arthur, Langhus, & Patel, 2005):

1. Removing dispersed oil and grease
2. Removing dispersed salts
3. Removing heavy metals
4. Removing suspended solids
5. Removing dissolved gases
6. Removing NORM

## 7. Removing organics such as BTEX and PAH

In general, the treatment of produced water can be divided into three categories: (1) physical, (2) chemical, and (3) biological.

Physical treatments use physics such as adsorption, evaporation, and physical precipitation. The physical treatment technologies are (Doyle & Brown, 2000; Carvalho, Clarisse, Lucas, Barbosa, & Barbosa, 2002; Liu, Zhang, Dong, Zhao, & Du, 2005; Plebon, Saad, & Fraser, 2005; Li, Wu, Wu, Xu, & Ma, 2008; Lefebvre & Moletta, 2006; Dallbauman & Sirivedhin, 2005; Knudsen et al., 2004; Janks & Cadena, 1992; Thoma, Bowen, & Hollensworth, 1999):

- Dissolved air floatation (DAF)
- Activated carbon, organoclay, copolymers, zeolite, and resins
- Sand filters
- Cyclones
- Dissolved air precipitation (DAP)
- C-TOUR
- Electrodialysis (ED)
- Membranes
- Physical separation

Chemical treatment technologies include (Holloway, 1977; Renou, Givaudan, Poulain, Dirassouyan, & Moulin, 2008; Ma & Wang, 2006; Bessa, Sant'Anna, & Dezotti, 2001; Li et al., 2006; Adams, Campbell, & Robertson, 2008; Li et al., 2007; Yang & Zhang,

2005; Morrow, Martir, Aghazeynali, & Wright, 1999; McFarlane et al., 2005; Klasson et al., 2002):

- Ionic liquids
- Chemical precipitation
- Chemical oxidation
- Electrochemical treatment
- Photocatalytic process
- Fenton process
- Ozone treatment
- Demulsifier

Biological treatments generally use aerobic and anaerobic microorganisms. These technologies are (Freire, Cammarota, & Sant'Anna, 2001; Baldoni-Andrey et al., 2006; Palmer, Beyer, & Stock, 1981; Jackson & Myers, 2003; Beyer, Palmer, & Stock, 1979; Gurden & Cramwinckel, 2000; Al Mahruki, Alloway, & Patzelt, 2006):

- Activated sludge
- Trickling filters
- Sequencing batch reactors (SBRs)
- Chemostate reactors
- Biological aerated filters (BAF)
- Lagoons

Recently, increasingly more researchers have focused on using a combined system of physical, chemical, and biological methods because of their outstanding performance.

In addition, the removal of oil and salt from produced water are the first consideration for scientists. The commonly used oil removal technologies include physical separation, adsorption, floatation, and coagulation. Salt removal methods mainly use membrane filtration, thermal treatment, and ion exchange (Mastouri et al., 2010; Hayes & Arthur, 2004; Casaday, 1993; Guerra, Dahm, & Dunderf, 2011; Lefebvre & Moletta, 2006).

Some important water quality indicators are: oil content, pH, conductivity, salinity, turbidity, zeta potential, chemical oxygen demand (COD), BOD, total organic carbon (TOC), total dissolved solids (TDS), and total suspended solids (TSS), which are commonly applied in the wastewater treatment process. Table 2.4 shows a typical range of these indicators of produced water around the world.

**Table 2.4:** Typical range of water quality indicators of produced water.

| <b>Parameters</b>  | <b>Typical Range</b> |
|--------------------|----------------------|
| Oil content (mg/l) | 220-2,000            |
| pH                 | 7.0-8.6              |
| TDS (mg/l)         | 6,015-31,349         |
| TSS (mg/l)         | 68-447               |

(Source: Environment Canada, 1983)

## 2.2 Dissolved air flotation

The flotation technique has proven to be a reliable, practical, and efficient separation method for the removal of contaminants in produced water. The mechanism of the flotation technique is by generating bubbles to contact the dissolved and suspended

particles such as oil droplets, fats, ions, heavy metals, solids, and biomolecules to bring them to the surface of water (Bremmell, Jameson, & Farrugia, 1994). The advantages of the flotation technique are high separation (selection) efficiency, low sludge generation, and the excellent throughput of devices (Parekh & Miller, 1999; Rubio, Souza, & Smith, 2002). The flotation technique was first applied in the mineral and metallurgical process for solid/solid separation. Now this technique is practiced in other fields, especially pollutant water treatment, which is a solid/liquid separation. The main differences between solid/solid and solid/liquid separation are the bubble size and shear rate. The solid/liquid separation process requires smaller bubble and lower shear speed (Mavros & Matis, 1992). The four most conventional flotation techniques are dissolved air (pressure) flotation (DAF), electro-flotation (EF), dispersed (induced) air flotation (IAF), and vacuum flotation (VF). In addition, many new flotation techniques have recently emerged, such as nozzle flotation (NF), centrifugal flotation (CF), jet flotation (JF), and cavitation air flotation (CAF) (Zouboulis, Kydros, & Matis, 1992a, 1992b; Zheng & Zhao, 1993; Lazaridis, Matis, Stalidis, & Mavros, 1992; Gopalratnam, Bennett, & Peters, 1988; Finch, 1995; Beeby & Nicol, 1993; Jameson, 2004; Zouboulis & Avranas, 2000).

Dissolved air (pressure) flotation is by far the most widely used flotation technique in the world for produced water treatment. This physical process removes dissolved and suspended particles from the water by carrying those particles to the surface of the water. Oil is generally removed from waste effluent mainly by DAF. In addition, DAF

is also used for clarification and sludge wipe-off of wastewater (Al-Shamrani et al., 2002).

The normal operation procedure of DAF is as follows: First, air is dissolved in a saturator over the atmospheric pressure. Second, the saturated water is released into a flotation cell, which is under atmospheric pressure to create micro bubbles. The bubbles attach to the fine grains in the water and carry them to the surface.

The bubble formation process has two steps: nucleation and growth. Nucleation happens almost simultaneous with pressure reduction. After the dissolved air reaches saturation in the floatation cell, bubbles grow because of coalescence, hydrostatic decrease, and gas uptake action. Finally, after a certain retention time, the bottom level of the cell is considered clean water while the top level is considered the effluent (Wang et al., 2005).

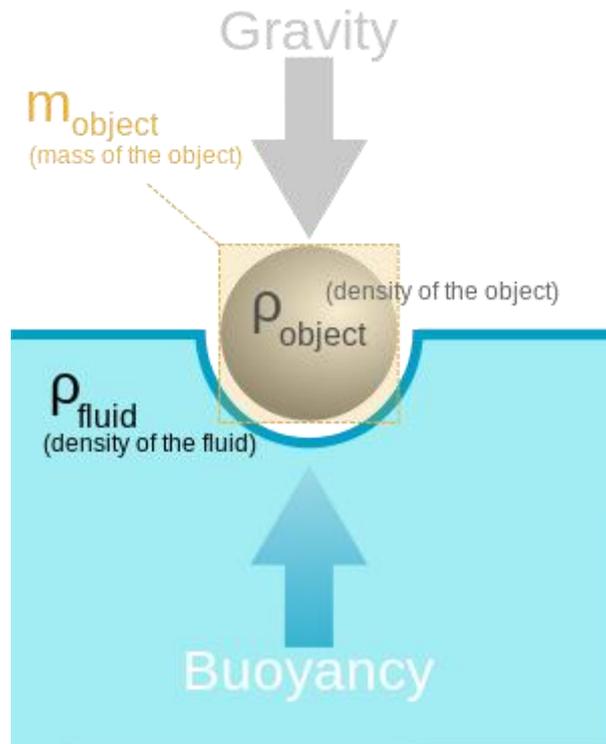
Dissolved air (pressure) flotation can be divided into three operating configurations: (1) full-flow pressure flotation, (2) part-flow pressure flotation, and (3) recycle-flow pressure flotation. The difference between these three configurations is the amount of effluent that is used to generate the saturated water. It has been proven that recycle-flow pressure flotation can generate the smallest bubbles (less than 100 micrometers) (Haarhoff & Edzwald, 2004; De Rijk & den Blanken, 1994).

### 2.2.1 Principles of Dissolved Air (Pressure) Flotation

- Buoyancy

Buoyancy, also known as up-thrust, is an upward force that exists in the fluid, which opposes the gravity force. Buoyancy is the reason why objects float on the surface of

liquids. The DAF process can increase the buoyancy of particles by way of small air bubbles contact. The contact causes a further decrease in density between particles and water. This will result in a faster rise process than normal gravity separation (Bremmell et al., 1994). Figure 2.1 contains a schematic diagram of buoyancy.



**Figure 2.1:** Schematic diagram of buoyancy.

(Source: <https://en.wikipedia.org/wiki/Buoyancy>)

- Air solubility

Solubility refers to the ability of a substance to dissolve in a standard amount of another substance. The standard amount of substance is called the solvent while the other substance is called the solute (Nitsche, 1991). Air is a solute and water is a solvent in the DAF process. Air solubility depends on temperature and pressure. High temperature accelerates gas molecular motion and thereby decreases air solubility in water. In a constant temperature, air

solubility follows Henry's law, as shown in Eq.(1), which states that the amount of a gas that dissolves in a liquid is directly proportional to the partial pressure of that gas in equalization with that liquid (Henry, 1803).

$$C = \frac{P}{k_H} \quad (1)$$

Where, C is the gas concentration in water; P is the gas partial pressure; and  $k_H$  is the Henry's law constant.

- Bubble quantity, size, and shape

The production of micro bubbles is critical in the DAF process. Bubble quantity, size, and shape are closely related to saturated pressure and the recycle ratio (RR) (Fukushi, Matsui, & Tambo, 1998). A low enough saturated pressure and RR will cause back flow, which has an effect on bubble generation (Ives, 2012). A Bubble size study applies video micrographs and proves that saturator pressure and a release valve have a significant effect on bubble size. A minimum of 392 kPa is the suggested saturator pressure (Haarhoff & Rykaart, 1995). It has been verified that the shape of a small bubble (<100 micrometers) is spherical and the shape of a large bubble (>1 millimeter) is ellipsoid (Edzwald, 2010). Bubble quantity, size, and shape influence the effective contact area between bubbles and particles (Takahashi, Miyahara, & Nishizaki, 1979).

- Lift velocity:

The lift velocity of bubbles follows Stoke's equation (shown in Eq. (2)), which indicates that the rise velocity of bubbles in a fluid by way of gravitational

force mainly depends on the bubble size and the density difference between the bubble and the fluid (Work & Work, 1969).

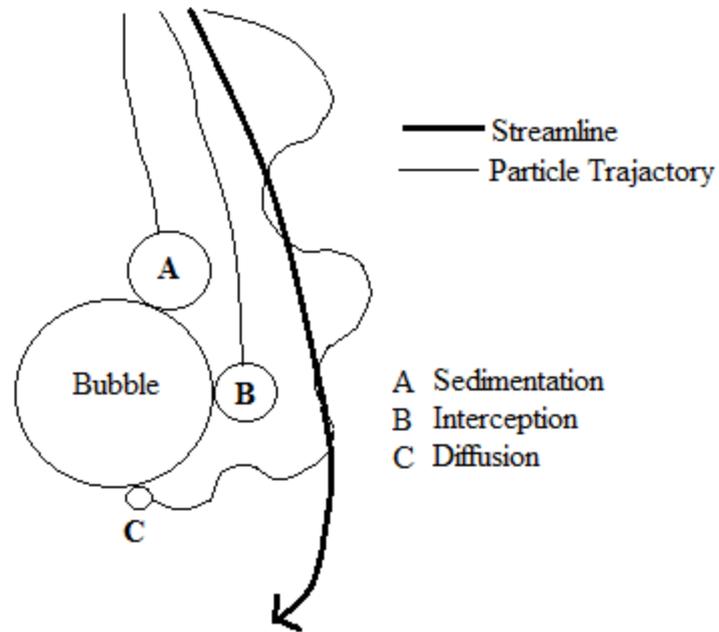
$$v = \frac{d^2(p-l) \times g}{18n} \quad (2)$$

, where  $v$  is the lift velocity of a bubble;  $d$  is the diameter of the bubble;  $p$  is fluid density;  $l$  is bubble density;  $g$  is gravitational acceleration; and  $n$  is the dynamic viscosity of fluid.

Based on Stoke's equation, a larger bubble has a high speed and a smaller bubble has a low speed in fluid. Low velocity extends the residence time in the floatation cell; thus allowing more chances for collisions between bubbles and particles (Moosai & Dawe, 2003).

- Interaction:

The bubble-particle and bubble-bubble interaction forces are hydrophobic, hydrodynamic, and van der Waals (Edzwald, 2010). In order to increase oil removal efficiency in the DAF process, a large oil droplet and a small bubble size are required to increase the impact area and residence time. Based on the white water blanket model, the collision between bubbles and particles has three types, which are shown in Figure 2.2.



**Figure 2.2:** Structure of collision types.

(Source: Faisal, 2015)

### 2.2.2 Removing dissolved oil from produced water by dissolved air flotation

Oil pollution is caused by the continuous expansion of the hydrocarbon production industry and the extensive utilization of oil-related products. Oil concentration in produced water varies from 220 to 2000 mg/l. Generally, oil exists in produced water in a colloidal and emulsified status, which makes oil separation by simple gravity impossible (Schuster, 1996). Dissolved air flotation is the main technique used to remove oil from produced water. Compared to gravity separation, DAF enhances the buoyancy of small oil droplets by using air bubbles, and thus, increases oil removal efficiency (Zouboulis & Avranas, 2000).

Multon and Viraraghavan (2008) reported a 72% average oil removal in a solo DAF system. Bayati, Shayegan, and Noorjahan (2011) had a similar conclusion by applying a dissolved air device to separate total oil-grease (TOG) from produced water (the

removal percentage of TOG achieved 70%). Without any other process, Thoma et al. (1999) indicated that using the DAF process can remove up to 95% of dissolved octane and 75% of decane.

Sometimes, the DAF process cannot reach the oil limit standard alone. In these circumstances, physical additions such as activated carbon and organoclay, chemical reagents such as coagulation and flocculation, and biological materials such as activated sludge are added as a pre-treatment or late treatment process to increase oil removal efficiency (Liu et al., 2007; Tansel & Pascual, 2004; Al-Shamrani et al., 2002; Baldoni-Andrey et al., 2006).

### 2.3 Zeta potential

The zeta ( $\zeta$ ) potential is a physical index that is exhibited by any particle in a colloidal dispersion system. The magnitude of the zeta potential reflects the stability of a colloidal system. The general boundary between stable and unstable suspensions is either +30 mV or -30 mV. Thus, a colloid system with a zeta potential between +30 mV and -30 mV is generally considered an unstable system. The 0 mV zeta potential generally is the most unstable status for a colloid system. In contrast, when a colloid system has a zeta potential that is not within that range (more positive than +30 mV or more negative than -30 mV), the system is commonly considered stable. Cognition of the zeta potential can identify the stability of a colloid system and reduce the time to derive an empirical equation (Derjaguin & Landau, 1941; Verway & Overbeek, 1948; Hunter, 2013).

### 2.3.1 The Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory and the double layer theory

In a colloid system, solid, liquid and gas are the three fundamental states of substance.

Derjaguin, Landau, Verwey, and Overbeek proposed a new theory named the “DLVO” theory, which refers to the stability of a colloidal system. The theory can be represented as shown in Eqs. (3)–(5) (Israelachvili, 2011).

$$V_T = V_A + V_R + V_S \quad (3)$$

$$V_A = -A/(12 \pi D^2) \quad (4)$$

$$V_R = 2\pi\epsilon a\zeta\exp(-\kappa D) \quad (5)$$

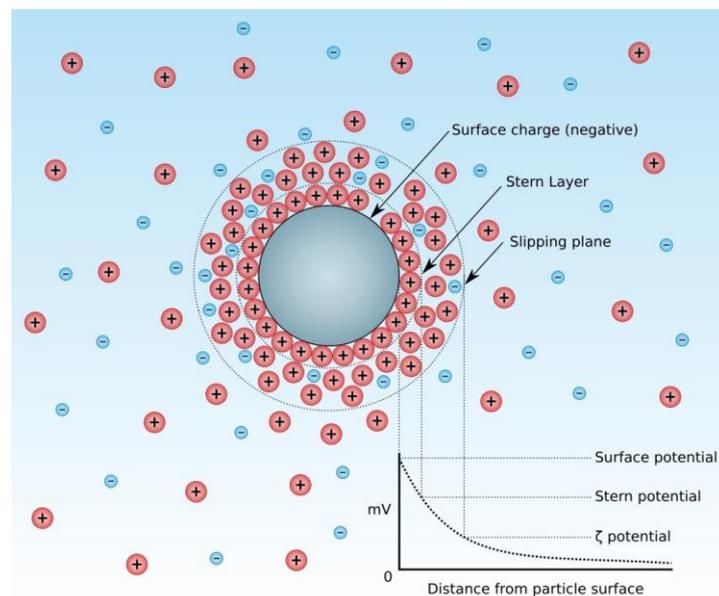
, where  $V_T$  is the total potential energy;  $V_A$  is the attractive energy;  $V_R$  is the repulsive energy;  $V_S$  is the potential energy due to solvent;  $A$  is the Hamaker constant;  $D$  is particle separation;  $\epsilon$  is solvent permeability;  $a$  is particle radius;  $\zeta$  is zeta potential; and

$\kappa$  is a function of ionic composition.

In this theory,  $V_S$  is often ignored because of its very small magnitude. The contribution of  $V_A$  and  $V_R$  decides the amount of  $V_T$ .  $V_A$  is determined by the van der Waals attractive force, and  $V_R$  is decided by electrical double layer repulsive.

A double layer theory is proposed for the repulsive energy. The formation mechanism of the double layer is that the surface charge of a particle is negative and attracts positive charges. The development of positive charges at the surface influences the distribution of ions in the nearby interfacial region, which means the negative charge ions will concentrate around the particle surface. The double layer contains two layers:

(1) a stern layer (inner layer) where the ions are associated firmly, and (2) a diffuse (outer) region where the ions are less strongly bound. The slipping plane belongs to the diffuse region, which is a notional boundary to describe the ions within and forms a stable status. The diffuse region corresponds to the zeta potential (Qasim, Motley, & Zhu, 2000; Gregory, 2005). Figure 2.3 contains a diagram of the distribution of ions around a particle.



**Figure 2.3:** Distribution of ions around a particle.

(Source: [https://en.wikipedia.org/wiki/Zeta\\_potential](https://en.wikipedia.org/wiki/Zeta_potential))

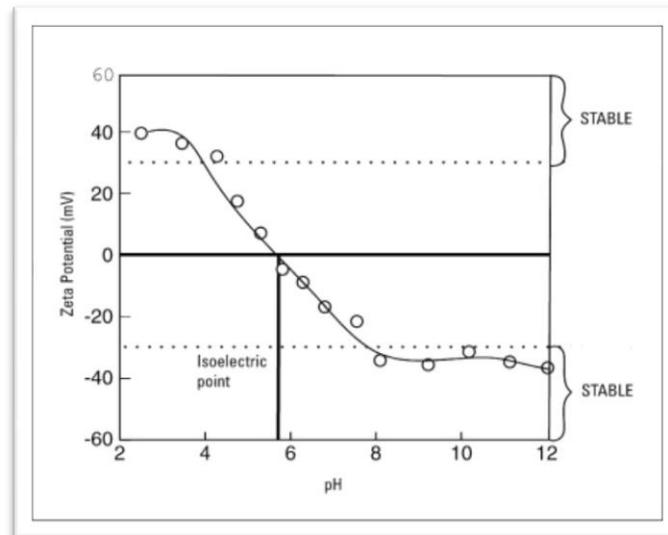
The DLVO theory proposes that the sum of  $V_A$  and  $V_R$  decides the stability of a colloidal system. Particles in the solution keep approaching each other by the Brownian motion. A notion of energy barrier is defined, which is actually the repulsive force. Coagulation and flocculation happens if some particles have enough energy to overcome the barrier by decreasing the repulsive force or increasing the particle energy. Those particles will combine with each other by the attractive force. On the contrary, if the barrier energy is too strong to cross, the particles will keep their

distance and the colloidal system is stable (Bhattacharjee, Elimelech, & Borkovec, 1998).

### 2.3.2 Influencing factors of the zeta potential

- pH

The potential of hydrogen (pH) is an important influence factor on the zeta potential. Figure 2.4 shows a typical plot of the zeta potential versus pH. The zeta potential is positive at low pH and negative at high pH because pH is decided by the relationship of  $H^+$  and  $OH^-$ . There is a point where the plot passes through the zero zeta potential value, which is called the isoelectric point. The isoelectric point is a very important indicator for practical application because generally the colloid system is the least stable at that point (Talero, Pedrajas, & Rahhal, 2013).



**Figure 2.4:** Typical plot of zeta potential versus pH.

(Source: <http://www.silver-colloids.com>)

- Ions

The quantity and the valency of ions decide the thickness of the double layer. Generally, ionic strength represents the amount of ions in a solution. The higher the ionic strength, the thinner the formation of the double layer. A high valency of ions has a compacted double layer compared to a low valency of ions. In addition, inorganic ions have selective zeta potential. Some specific inorganic ions can lead to a change in the isoelectric point even at low concentration. Some inorganic ions can cause a charge reversal on the surface (Malvern Instruments, 2012).

### 2.3.3 Coagulant

A coagulant is a chemical compound that is added to an effluent to destabilize the colloidal system, and coagulation is the process of coagulant in action. The difference between coagulation and flocculation is that coagulation is an irreversible process. The critical influences of a coagulant include (Bunker, Edzwald, Dahlquist, & Gillberg, 1995; Metcalf, 2003):

- dosage
- molecular weight
- stir rate
- time of coagulation
- charge density

In a published book, Bratby (2006) mentioned that the Egyptians were the first to use almonds as a flocculant for water treatment in 2000 BC, and the Romans first applied alum as a coagulant in 77 AC. Bratby also concluded that coagulation and flocculation are the most widely used techniques in water treatment around the world.

According to Duan and Gregory (2003), aluminum and ferric salts are the most common coagulants used in wastewater treatment. They have two functions: charge neutralization and hydroxide precipitation. Duan and Gregory selected aluminum and ferric salts as coagulants in their study and tested them at different pH values and dosage concentrations. The results showed that aluminum and ferric coagulants have to stay in a specific pH range to achieve charge neutralization (Duan & Gregory, 2003). For aluminum salts, the pH range was 8-9; while for ferric salts, the pH range was 5-8. The closer the pH approached the isoelectric point, the higher the amount of coagulant needed. However, a superfluous coagulant dosage leads to a charge reversal and leads to the stability of the colloid system again. Moreover, adding too much coagulant caused hydroxide precipitation in many cases.

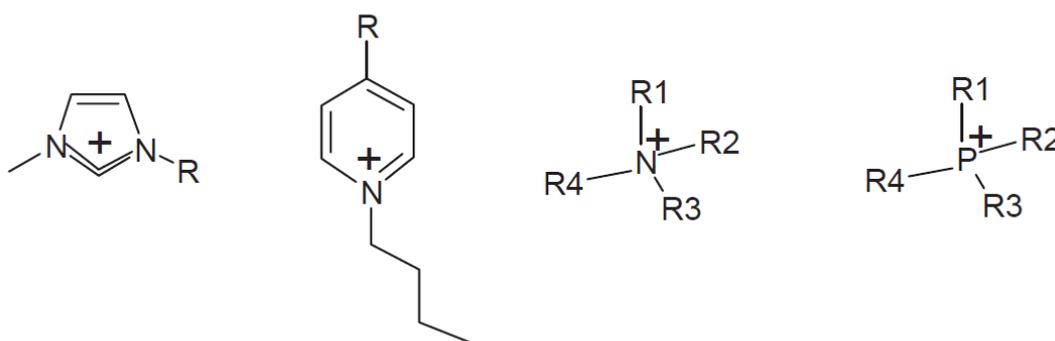
Jaji (2012) selected iron salt and powdered activated carbon (PAC) as a pretreatment for wastewater. The results showed that iron salt ( $\text{FeCl}_3$ ) of 20 mg/l as a coagulant had 70.6% oil removal efficiency at a pH of 8. Powdered activated carbon as a physical addition showed 77.5% and 78.1% oil removal of the dosage concentration of 100 mg/l and 300 mg/l, respectively. The original oil content was 300 mg/l.

Zouboulis and Avranas (2000) conducted research on the removal of oil from wastewater by the DAF process using a surfactant and a coagulant. Several factors were considered such as pH, RR, coagulant concentration, and surfactant dosage. The results showed that the best oil removal efficiency was 95% (475 mg/l oil was removed from 500 mg/l original content), and the optimal operating conditions were a

pH of 6, a RR of 30%, an iron salt (coagulant) concentration of 100 mg/l, and a sodium sulphate (surfactant) of 50 mg/l.

#### 2.4 Ionic liquid (IL)

Ionic liquid is a generic name for an organic salt, which has a weak chemical bond between its cation and anion. Because of the poor bond, ionic liquids (ILs) are liquids at a temperature below 100 °C, sometimes even at room temperature. Ionic liquids can be formed by a combination of organic cations and anions. The cationic type of ionic liquids can be divided into four general categories as shown in Figure 2.5: imidazolium, pyridinium, ammonium, and phosphonium. In addition, the R group of the cations in each category can vary from methyl to any other organic group. Anions include inorganic or organic groups such as chloride, bromide, nitrate, sulphate, aluminum chloride, hexafluorophosphate, tetrafluoroborate, alkyl sulphates, alkyl sulphonates, triflate ( $\text{CF}_3\text{SO}_3^-$ ), bis(triflyl)imide ( $((\text{CF}_3\text{SO}_2)_2\text{N}^-\text{Tf}_2\text{N})$ ), etc. Actually, the types of ILs appear to be almost unlimited (Meindersma et al., 2005).



**Figure 2.5:** Structure of 1-R-3-methylimidazolium, 4-R-n-butylpyridinium, quaternary ammonium, and quaternary phosphonium cations.

As new solvents, ionic liquids are widely applied in various domains such as chromatography, extraction, electro-analytical chemistry, sensing, and spectrometry (Pandey, 2006).

The advantages and disadvantages of ionic liquids are as follows.

Advantages:

- High thermal stability
- High ionic conductivity
- Better kinetic control on reactions
- Non-flammable
- Negligible vapor pressure
- Good electrochemical stability
- Recyclable solvent
- Environment-friendly production

Disadvantages:

- Unclear physical properties
- High viscosity
- Unknown toxicity
- High price

Pereira, Costa, Foios, & Coutinho (2014) worked with a couple of ionic liquids in enhanced oil recovery in sand-pack columns. Pilot experiments were performed to select the best performing ionic liquid. 1-ethyl-3-methylimidazolium tosylate ([C2mim][OTs]) was chosen for further testing. The results showed that the injection

of a diluted solution of ionic liquid increased the oil recovery compared to the injection of brine alone. Two mechanisms, electrostatic and  $\pi - \pi$  interaction, were used to explain the increase in oil recovery. Another conclusion was that this type of ionic liquid did not decrease the interfacial tension (IFT) between crude oil and an aqueous solution.

Lemos et al. (2010) used two imidazolium group ILs (omimBF<sub>4</sub> and omimPF<sub>6</sub>) in a demulsification process of a water-in-crude oil emulsion. OmimPF<sub>6</sub> was shown to be significantly more efficient than omimBF<sub>4</sub>. Further research into the molecular structure of ILs in the destabilization process was recommended. Unlike Pereira's conclusion, a decrease of the IFT of the oil/aqueous phase occurred after the addition of both ILs.

McFarlane et al. (2005) investigated the use of nine different ILs in produced water treatment. Distribution coefficients were determined as the most important indicator. The results of the research indicated that ILs were very selective in the removal of particular organic contaminants in produced water.

## 2.5 Orthogonal experimental design (OED)

### 2.5.1 Introduction

The design of experiments (DOE) is a statistical technique used to reveal the process of determination of the relationships between factors as well as to output the experimental steps systematically. The DOE can be divided into several statistical methods such as full factorial, fractional factorial, central composite, etc. The basic theories of statistical methods in DOE are repetition, randomization, and blocking.

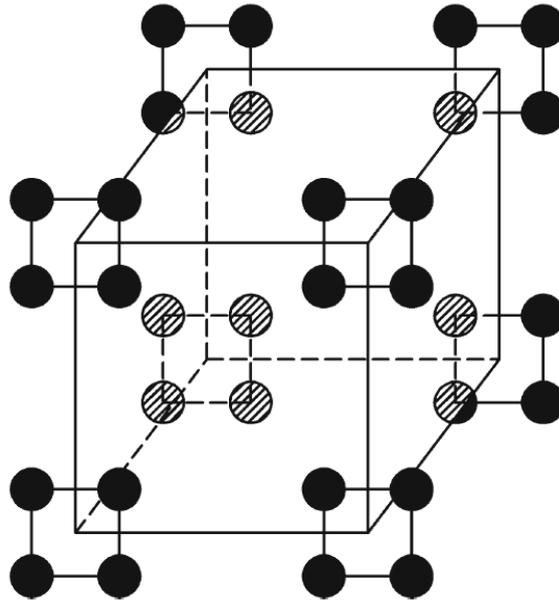
Repetition means replication of the experiment several times to acquire a more accurate result, as reflected for example in the mean value. Another function of repetition is to estimate the experimental error and report it as standard deviation and standard error. Randomization indicates the experimental steps are conducted in random order. Neither the previous step nor the subsequent step has any effect on the experimental step performance. Blocking aims at isolating the influence of other factors on one factor. The developments of DOE can generally be divided into three phases. In the 1920s, Fisher was the first statistician to apply statistical science in DOE. Box and Wilson developed the response surface method in 1951, which was considered the second era in DOE development. In the 1980s, a Japanese statistician, Taguchi, based on the foundations of modern statistical science, created a convenient and efficient DOE method, which is an orthogonal experimental design (OED) and is also known as the Taguchi method (Cavazzuti, 2012).

Orthogonal experimental design is an effective DOE technique, which can simplify experimental procedures and achieve significant results. It has been used widely and rapidly in various domains such as manufacturing, agriculture, medicine, and economic analysis. The Taguchi method was considered as a main motivation for the competitive position of the Japanese industry, because it implemented the improvement of off-line total quality control (Zhu et al., 2013). In OED, a factor (also known as the independent variable) is an explanatory variable handled by the tester. The “level” is the number of different values for a factor. The level is decided

according to the discretization of factors. The purpose of OED is to find the best level and compare the significant influence of each factor.

### 2.5.2 Mechanism

Orthogonal experimental design is based on mixed levels, fractional factorial designs, and orthogonality. It includes two parts: control factors and noise factors. Control factors can be controlled and are considered the main factors. Noise factors cannot be controlled except during experiments in the test. Different orthogonal designs are applied for these two types of factors. A full factorial design of inner array is chosen for control factors, and a full factorial design of outer array is designed for noise factors. Combination of the inner and outer array is called a crossed array. Each sample in the inner array performs the full set of experiments of the outer array. Crossed array represents the interaction between the control factors and noise factors, which is important for OED. For example, in a five factor experiment, if each factor has two levels, three factors are considered as inner array factors (control factors) and two factors are outer array factors (noise factors). Figure 2.6 displays the inner and outer array design for this example, graphically.



**Figure 2.6:** Example of OED for a combination of inner array and outer array factors.

The design of the combination of inner array and outer array factors has a huge advantage, which is distinction between control factors and noise factors. Estimation of the mean value and standard deviation for inner array samples are allowed because inner array points are surrounded, symmetrically, by outer array points. In other words, the combination simplifies the experimental procedure. Now the purpose of change is to increase the average performance of factors while keeping standard deviation low.

A full factorial design table is shown in Table 2.5, where  $X_{in}$  represents the factors of inner array, and similarly,  $X_{out}$  represents the factors of outer array.

**Table 2.5:** Example of OED for full factorial inner array and outer array.

| Exp. No. | Inner Array |            |             | Outer Array |    |    |    | Output |                |
|----------|-------------|------------|-------------|-------------|----|----|----|--------|----------------|
|          | $X_{in,1}$  | $X_{in,2}$ | $X_{in,3}$  | 1           | 2  | 3  | 4  | Mean   | Std. Deviation |
|          |             |            | $X_{out,1}$ | -1          | -1 | +1 | +1 |        |                |
|          |             |            | $X_{out,2}$ | -1          | +1 | -1 | +1 |        |                |

|          |    |    |    |           |           |           |           |          |                     |
|----------|----|----|----|-----------|-----------|-----------|-----------|----------|---------------------|
| <b>1</b> | -1 | -1 | -1 | $y_{1,1}$ | $y_{1,2}$ | $y_{1,3}$ | $y_{1,4}$ | $E[y_1]$ | $E[(y_1-E[y_1])^2]$ |
| <b>2</b> | -1 | -1 | +1 | $y_{2,1}$ | $y_{2,2}$ | $y_{2,3}$ | $y_{2,4}$ | $E[y_2]$ | $E[(y_2-E[y_2])^2]$ |
| <b>3</b> | -1 | +1 | -1 | $y_{3,1}$ | $y_{3,2}$ | $y_{3,3}$ | $y_{3,4}$ | $E[y_3]$ | $E[(y_3-E[y_3])^2]$ |
| <b>4</b> | -1 | +1 | +1 | $y_{4,1}$ | $y_{4,2}$ | $y_{4,3}$ | $y_{4,4}$ | $E[y_4]$ | $E[(y_4-E[y_4])^2]$ |
| <b>5</b> | +1 | -1 | -1 | $y_{5,1}$ | $y_{5,2}$ | $y_{5,3}$ | $y_{5,4}$ | $E[y_5]$ | $E[(y_5-E[y_5])^2]$ |
| <b>6</b> | +1 | -1 | +1 | $y_{6,1}$ | $y_{6,2}$ | $y_{6,3}$ | $y_{6,4}$ | $E[y_6]$ | $E[(y_6-E[y_6])^2]$ |
| <b>7</b> | +1 | +1 | -1 | $y_{7,1}$ | $y_{7,2}$ | $y_{7,3}$ | $y_{7,4}$ | $E[y_7]$ | $E[(y_7-E[y_7])^2]$ |
| <b>8</b> | +1 | +1 | +1 | $y_{8,1}$ | $y_{8,2}$ | $y_{8,3}$ | $y_{8,4}$ | $E[y_8]$ | $E[(y_8-E[y_8])^2]$ |

Taguchi did not design the OED as a mean response value and its standard deviation, as listed in the table. He introduced a concept called the signal-to-noise ratio (SN). This ratio is an appropriate ratio that is proposed based on the nature of the investigated problem. The most famous ratios are:

- Smaller-the-better:  $SN_{stb} = -10 \log_{10} E[y_i^2]$
- Larger-the-better:  $SN_{ltb} = -10 \log_{10} E[1/y_i^2]$
- Nominal-the-better:  $SN_{ntb} = -10 \log_{10} \frac{\{E^2[y_i]\}}{(E[(y_i - E[y_i])^2])}$

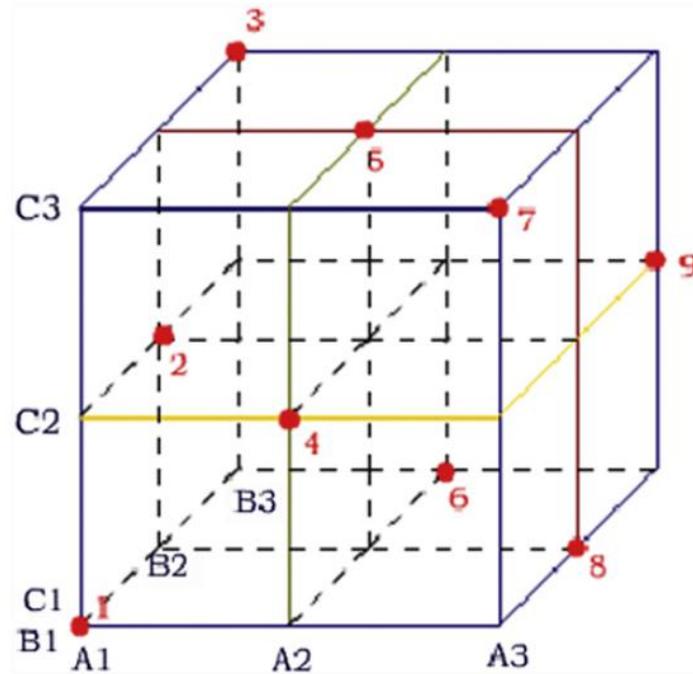
In these ratios, E stands for expected value; smaller-the-better and larger-the-better apply when the response variable is to be minimized and maximized; and nominal-the-best is used when a target value is pursued for the response variable (Cavazzuti, 2012).

### 2.5.3 Orthogonal array design table (OADT)

According to OED, the inner and outer arrays are applied by a list of published orthogonal array design tables (OADTs). The OADT is individuated as  $L_n(m^k)$  in the

literature, in which L indicates the orthogonal array, n means the time of experiments, m is the number of factor levels, and k represents the amount of factors. The OADT chooses representative points from a full factorial experiment based on a set of rules to make sure those points are uniformly dispersed within the experimental range (Leyton, 2016). Take the OADT  $L_9(3^3)$  as an example. As shown in Figure 2.7, 27 intersection points of the three-dimensional (3D) space indicate 27 tests of a full factorial experiment. Nine numbered points in the cube represent the chosen points. This means nine experiments are used on behalf of 27 full experiments. Two principles support the rationality of the OADT. First, there is only one point on each side of the cube. Second, when dividing the cube into three planes from any directions uniformly, such as A1 to A3, B1 to B3, and C1 to C3, it is not hard to find that any plane contains three points only. This proves that the nine points are distributed in the cube homogeneously, and thus they represent all 27 tests adequately.

Table 2.6 shows the  $L_9(3^4)$  OADT, which is followed by two conditions. First, each factor has the same occurrences of all different levels (one column). Second, any two factors have the same occurrences of any different level combinations (two columns). Statisticians have invented different types of OADTs for practical application. In general, there are two types of OADTs. In one type, each factor has the same level, for example,  $L_8(2^7)$ ,  $L_9(3^4)$ , and  $L_{16}(4^5)$ . For this type of OADT, different numbers of factors and levels have a corresponding OADT, which is shown in Table 2.7. The other type of OADT is a hybrid OADT, which means different factors have different levels such as  $L_8(4^1 \times 2^4)$  (Tang, 2007).



**Figure 2.7:** Cube model of nine test points representing 27 test points.

**Table 2.6:** The  $L_9(3^4)$  orthogonal array design table.

| Exp. No. | Factors |   |   |   |
|----------|---------|---|---|---|
|          | A       | B | C | D |
| 1        | 1       | 1 | 1 | 1 |
| 2        | 1       | 2 | 2 | 2 |
| 3        | 1       | 3 | 3 | 3 |
| 4        | 2       | 1 | 2 | 3 |
| 5        | 2       | 2 | 3 | 1 |
| 6        | 2       | 3 | 1 | 2 |
| 7        | 3       | 1 | 3 | 2 |
| 8        | 3       | 2 | 1 | 3 |
| 9        | 3       | 3 | 2 | 1 |

**Table 2.7:** Orthogonal experimental design synoptic table.

| Number of Factors | Number of Levels |                 |                 |                 |
|-------------------|------------------|-----------------|-----------------|-----------------|
|                   | 2                | 3               | 4               | 5               |
| 2                 | L <sub>4</sub>   | L <sub>9</sub>  | L <sub>16</sub> | L <sub>25</sub> |
| 3                 | L <sub>4</sub>   | L <sub>9</sub>  | L <sub>16</sub> | L <sub>25</sub> |
| 4                 | L <sub>8</sub>   | L <sub>9</sub>  | L <sub>16</sub> | L <sub>25</sub> |
| 5                 | L <sub>8</sub>   | L <sub>18</sub> | L <sub>16</sub> | L <sub>25</sub> |
| 6                 | L <sub>8</sub>   | L <sub>18</sub> | L <sub>32</sub> | L <sub>25</sub> |
| 7                 | L <sub>8</sub>   | L <sub>18</sub> | L <sub>32</sub> | L <sub>50</sub> |
| 8                 | L <sub>12</sub>  | L <sub>18</sub> | L <sub>32</sub> | L <sub>50</sub> |
| 9                 | L <sub>12</sub>  | L <sub>27</sub> | L <sub>32</sub> | L <sub>50</sub> |
| 10                | L <sub>12</sub>  | L <sub>27</sub> | L <sub>32</sub> | L <sub>50</sub> |

#### 2.5.4 Range analysis

Range analysis is the most common analysis used in OED. It has three advantages:

- Convenient calculation
- Visualized comparison
- Easy comprehension

In range analysis, because of the orthogonality, the influence of other factors on the experimental result is balanced.  $K$  is individuated as a sum of the results in the same level.  $K_{avg}$  is individuated as an average value of  $K$  based on the test times in the same level (Cui, Li, Zhou, & Weng, 2007). For example, concerning four factors

from A to D, each factor has two levels. A  $L_8$  OADT is chosen, which means that, corresponding to each factor column, there are eight results, and each level is related to two results.  $K_1$  is equal to the sum of two results related to Level 1.  $K_{avg1}$  is  $K_1$  divided by two. The calculation of  $K_2$  to  $K_4$  and  $K_{avg2}$  to  $K_{avg4}$  is conducted in a similar way. If Factor A has no effect on the experimental results,  $K_{avg1}$  should be the same as  $K_{avg2}$ ,  $K_{avg3}$ , and  $K_{avg4}$ . Actually, most often, different levels have different  $K_{avg}$  for the same Factor A, for example, which can prove that the change of level value of Factor A has an influence on the experimental results. The range of each factor, which is represented as  $R$ , is decided by the gap between the largest and smallest  $K_{avg}$  values ( $R = \max(K_{avg_i}) - \min(K_{avg_i})$ ). A large  $R$  value among the factors means a significant influence on this experiment. Range analysis includes the following parts:

1. Sorting the range value  $R$  in a descending order and deciding the influence ability order of each factor.
2. Deciding the optimal operating level for each factor.
3. Deciding the optimum operating combination for the experiment.
4. Discussing future research directions.

Sometimes, the best optimum operating combination is not shown in an OADT. A verification test may be required (Wang et al., 2014). In addition, in a hybrid OADT, because the level numbers of different factors are different, an adjusted range ( $R'$ ) is applied. The adjustment equation is shown in Eq. (6).

$$R' = dR\sqrt{r} \tag{6}$$

, where  $R'$  is the adjusted range;  $D$  is the convert coefficient;  $R$  is the range; and  $R$  is the time of repetition for each factor of each level.

The relationship between the number of level ( $m$ ) and convert coefficient ( $d$ ) is shown in Table 2.8.

**Table 2.8:** Covert coefficient table.

|   |      |      |      |     |      |      |      |      |      |
|---|------|------|------|-----|------|------|------|------|------|
| m | 2    | 3    | 4    | 5   | 6    | 7    | 8    | 9    | 10   |
| d | 0.71 | 0.52 | 0.45 | 0.4 | 0.37 | 0.35 | 0.34 | 0.32 | 0.31 |

#### 2.5.5 Variance analysis (ANOVA)

Range analysis is concise and explicit in result analysis; however, it cannot distinguish data fluctuation, which is caused by test condition change or experimental error. In other words, the range analysis cannot identify the corresponding differences of trial results created by factors and level differences or test errors. Range analysis is also unable to assess the size of experimental errors. In addition, range analysis cannot propose a standard or accurate number to judge whether experimental factors vary significantly or not because the level of influence caused by each factor cannot be evaluated. In order to remedy the defects of range analysis, variance analysis is applied. The basic principle of ANOVA is dividing the variation of data into two parts (variation caused by factors and variation caused by error) to structure the F statistic and conduct F inspection, thereby evaluating the significance of factor influence (Ye, Liu, Yang, Peng, & Xu, 2011). Generally, one or two blank columns exist in an OADT to estimate experimental errors. Table 2.9 shows the calculation of ANOVA, while the concept definitions and calculation steps are as follows:

- a.  $SS_T = SS_{\text{factor}} + SS_{\text{error}}$
- b.  $DF_{\text{Total}} = DF_{\text{factor}} + DF_{\text{error}}$
- c.  $MS_{\text{factor}} = SS_{\text{factor}} / DF_{\text{factor}}$
- d.  $MS_{\text{error}} = SS_{\text{error}} / DF_{\text{error}}$
- e.  $F_{\text{factor}} = MS_{\text{factor}} / MS_{\text{error}}$
- f. Compare  $F_{\text{factor}}$  with  $F_{\text{theory}}$ . If  $F_{\text{factor}} > F_{\text{theory}}$ , the factor has a significant influence to experimental results; on the contrary, if  $F_{\text{factor}} < F_{\text{theory}}$ , the factor has a non-significant influence to experimental results.
- g. Generally,  $DF_{\text{error}}$  should not be smaller than two in case inspection sensitivity is too low. In addition, it is necessary to compare MS for each factor with  $MS_{\text{error}}$ . If  $MS_{\text{factor}} < 2 MS_{\text{error}}$ , the SS and DF of this factor or these factors can combine with  $SS_{\text{error}}$  and  $DF_{\text{error}}$  to improve F inspection sensitivity.
- h. If an OADT does not arrange blank columns, duplicate tests should apply to evaluate errors.

**Table 2.9:** Calculation of ANOVA.

| Factors  | A   | B   | ... | ... | Results |         |
|----------|-----|-----|-----|-----|---------|---------|
| Columns  | 1   | 2   | ... | k   | $x_i$   | $x_i^2$ |
| Exp. No. |     |     |     |     |         |         |
| 1        | 1   | ... | ... | ... | $x_1$   | $x_1^2$ |
| 2        | 1   | ... | ... | ... | $x_2$   | $x_2^2$ |
| ...      | ... | ... | ... | ... | ...     | ...     |

|            |            |            |     |            |  |   |  |
|------------|------------|------------|-----|------------|--|---|--|
| n          | m          | ...        | ... | ...        | $x_n$  | $x_n^2$                                     |  |
|            |            |            |     |            |  | $DF_{Total} = n - 1$<br>$DF_j = m - 1$      |  |
|            |            |            |     |            |  | $T = \sum_{i=1}^n x_i$ $CT = \frac{T^2}{n}$ |  |
| $K_{1j}$   | $K_{11}$   | $K_{12}$   | ... | $K_{1k}$   | $Q_T = \sum_{i=1}^n x_i^2$<br>$SS_T = Q_T - CT$  |   |  |
| $K_{2j}$   | $K_{21}$   | $K_{22}$   | ... | $K_{2k}$   |  |   |  |
| ...        | ...        | ...        | ... | ...        | $Q_j = \frac{1}{r} \sum_{i=1}^m K_{ij}^2$<br>$SS_j = Q_j - CT$   |   |  |
| $K_{mj}$   | $K_{m1}$   | $K_{m2}$   | ... | $K_{mk}$   |  |   |  |
|            |            |            |     |            |  | $SS_j = Q_j - CT$                           |  |
|            |            |            |     |            |  | $SS_j = Q_j - CT$                           |  |
| $K_{1j}^2$ | $K_{11}^2$ | $K_{12}^2$ | ... | $K_{1k}^2$ | $SS_j = \frac{1}{n} (K_{1j} - K_{2j})^2$   |   |  |
| $K_{2j}^2$ | $K_{21}^2$ | $K_{22}^2$ | ... | $K_{2k}^2$ |  |   |  |
| ...        | ...        | ...        | ... | ...        | <p>, where SS is the sum of square, DF is the degree of freedom, MS is the mean of square, and F is the F-value.</p> |   |  |
| $K_{mj}^2$ | $K_{m1}^2$ | $K_{m2}^2$ | ... | $K_{mk}^2$ |  |   |  |
| $SS_j$     | $SS_1$     | $SS_2$     | ... | $SS_k$     |  |   |  |

Notes. i = the row number, j = the column number, n = the number of experiments, m = the number of factor levels, k = the number of factors, and r = the number of repetition for each factor of each level.

Multon and Viraraghavan (2008) designed a full factorial experiment for DAF. Two factors (pressure and RR) were selected. Each factor had three levels. The experimental results were analyzed statistically to decide if these two factors had a significant influence on oil removal efficiency. The analysis results show that neither pressure nor RR had a significant influence on effluent oil removal efficiency. In addition, there was no interaction effect between the two factors.

In a set of factorial experiments, Gehr, Swartz, and Offringa (1993) mentioned that five factors were selected. Each factor had two levels. The results showed that RR had no significant influence on the removal of trihalomethane precursors (THMPs), which are an organic solvent. The significant influence factors were identified as inorganic coagulant dose, pH, and polymer addition in order.

Adlan, Palaniandy, & Aziz (2011) inspected five factors (pressure, flow rate, coagulant dose, pH, and injection time) by using response surface methodology (RSM) to optimize the improvement of four response variables (turbidity, COD, colour, and  $\text{NH}_3\text{-N}$ ). His conclusion was that flow rate and pressure had less impact than the other three factors.

## CHAPTER 3: MATERIALS AND METHODS

### 3.1 Synthetic produced water

Synthetic produced water was produced and used in this study to keep consistency in the experiments. Compared to actual field produced water, synthetic produced water was more convenient in terms of controlling the indicators. In addition, the contaminant content of field produced water changes with time. It is also expensive to transport and store large quantities of field produced water.

Only one kind of salt (sodium chloride with 99% purity from EMD Chemicals Inc., Germany) was used in this research. This design removed the interaction influence from other salts and thereby simplified the experimental procedures. Fourteen (14) grams of NaCl were added into a conical flask with a stir bar. Two litres of ultrapure water were added as measured in a graduated cylinder and poured into the same conical flask. The flask was then placed on an electric magnetic stirrer at 1200 rpm for 15 minutes. Oil from Crescent Point region, which is located in Bakken area(Saskatchewan), has a density of  $0.81 \text{ g/cm}^3$  and an API of 43.14 degrees. An amount equivalent to 0.9 ml oil was injected into the blender by a syringe with a 1 millilitre range. It should be noted that half of the previously prepared brine was transferred to the blender before adding the oil to avoid oil depletion. After adding the other half of brine, the blender was capped, and the blender speed was set to 18,000 rpm (the sixth level) for two minutes. The synthetic produced water was used immediately in all experiments.

The oil content of produced water in Saskatchewan is 260 mg/l, as reported in a literature review (Environment Canada, 1983). It was hard to control artificial error in

the experiments, such as oil injection speed and the time intervals between transferring solutions. As a result, two sets of synthetic produced water were prepared and tested in a similar manner at the same time. The parameters of the tests included oil content, zeta potential, turbidity, conductivity, TDS, and sanity. An average standard deviation method was applied and the results are displayed in Chapter 4.

### 3.2 Ionic liquids

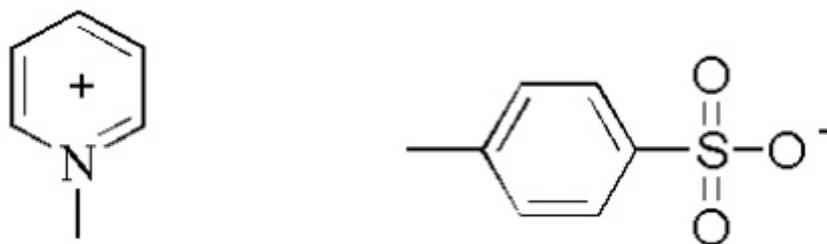
All ionic liquids used in this research were purchased from Shanghai Cheng Jie Chemical Co. LTD. (Shanghai, China). Table 3.1 shows a few parameters for the three kinds of ionic liquids used. It should be mentioned that the status of 1-benzyl-3-methylimidazolium tosylate was liquid in the certificate of analysis from the manufacturer. However, it was a solid crystal in the lab environment. This was due to a condensation phenomenon, which was a normal situation that happened to the ionic liquid as explained by the manufacturer.

**Table 3.1:** Parameters of the ionic liquids used in the study.

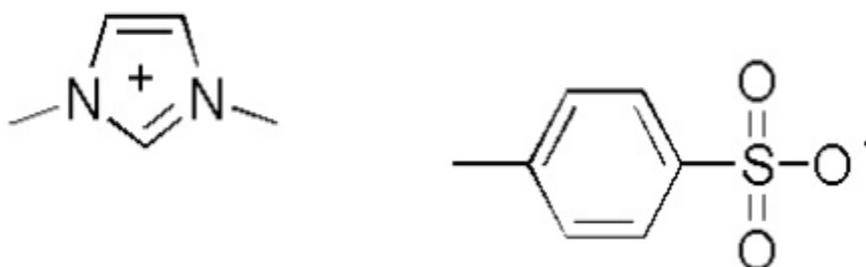
| <b>Parameter</b>     | <b>N-methylpyridinium tosylate</b> | <b>1,3-Dimethylimidazolium tosylate</b> | <b>1-Benzyl-3-methylimidazolium tosylate</b> |
|----------------------|------------------------------------|---|--|
| <b>Colour</b>        | Off-white                          | Off-white                               | Deep yellow                                  |
| <b>Status</b>        | Solid powder                       | Solid powder                            | Solid crystal                                |
| <b>Purity</b>        | 99.3%                              | 99.5%                                   | 99.1%  |
| <b>Water content</b> | 0.13%                              | 0.15%                                   | 0.18%  |

The molecular structure representations of the three ionic liquids are shown in Figures 3.1–3.3. All of the ionic liquids have very similar molecular structures. Each ionic liquid had a tosylate anion. The cations were different, but at least one ring was

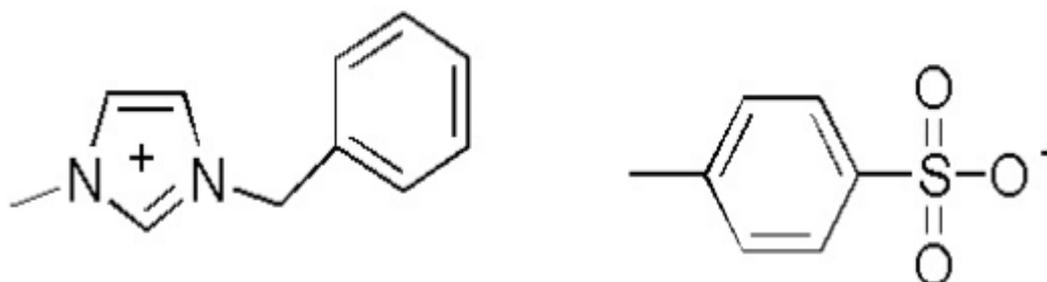
present. The numbers of rings for n-methylpyridinium tosylate, 1,3-dimethylimidazolium tosylate, and 1-benzyl-3-methylimidazolium tosylate were two, two, and three, respectively. The main difference between n-methylpyridinium tosylate and 1,3-dimethylimidazolium tosylate is that one is a pyridine functional group and the other is a glyoxaline (imidazole) functional group.



**Figure 3.1:** The molecular structure of n-methylpyridinium tosylate.



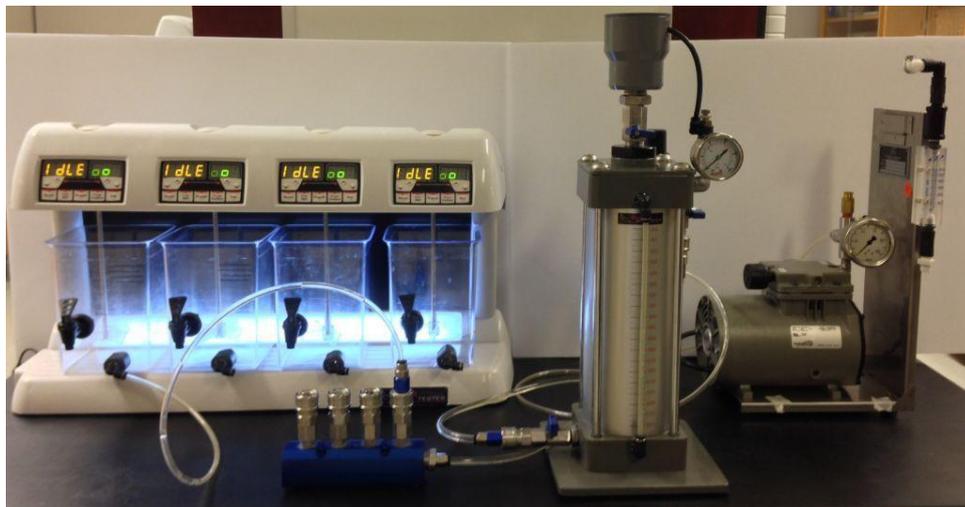
**Figure 3.2:** The molecular structure of 1,3-dimethylimidazolium tosylate.



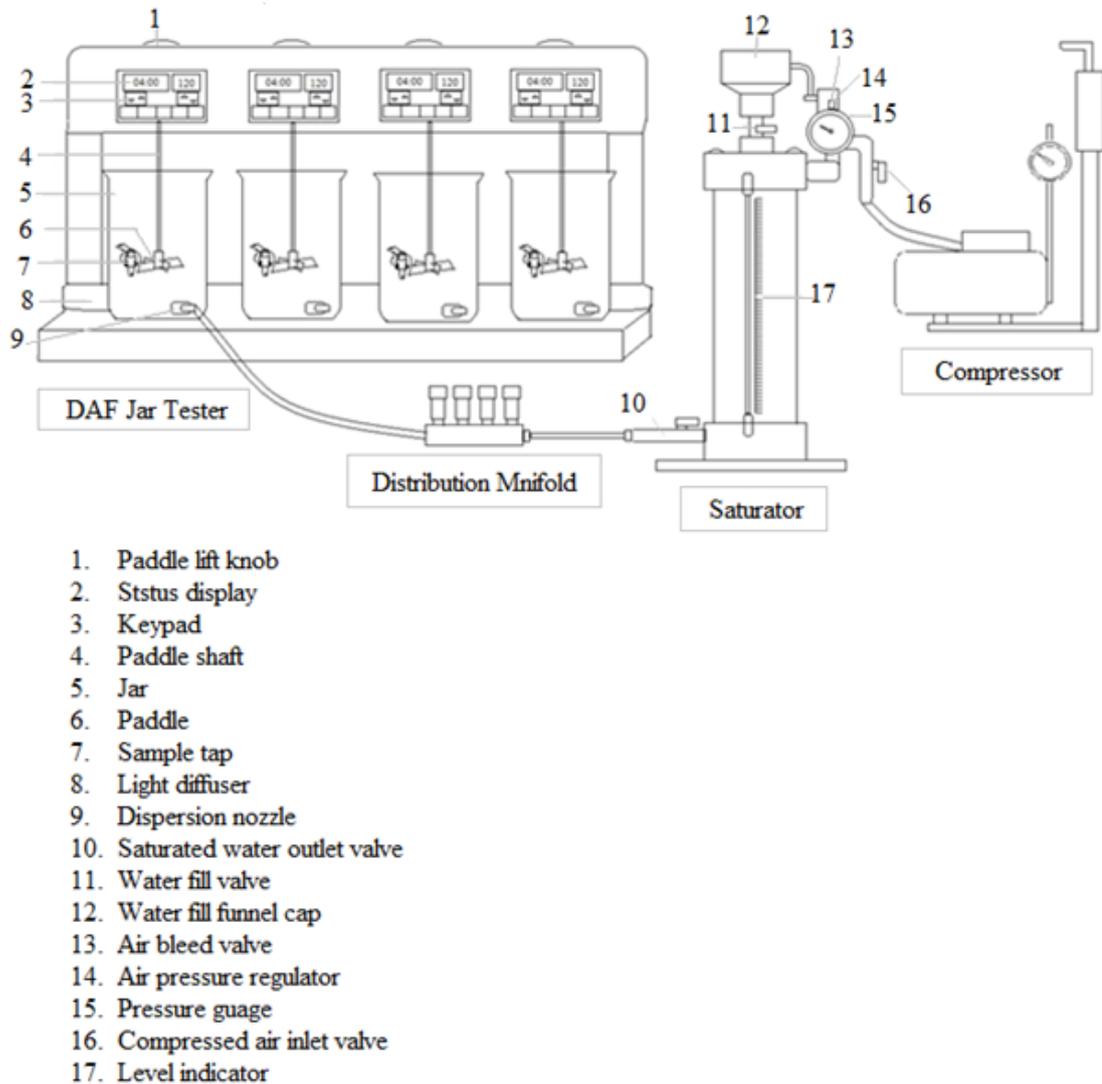
**Figure 3.3:** The molecular structure of 1-benzyl-3-methylimidazolium tosylate.

### 3.3 Dissolved air floatation system

The dissolved air flotation system in this research can be divided into five parts: (1) the compressor, (2) the saturator, (3) the manifold, (4) the jar tester, and (5) the jars. All parts were connected through a transparent plastic tube with a quick disconnect and push-in fittings. Spherical valves were used to ensure the system was opened or closed immediately. As shown in the photograph in Figure 3.4, the jars were connected with a manifold. The manifold was connected to the saturator, which was connected to the compressor. Figure 3.5 contains a detailed schematic of the dissolved air flotation system.



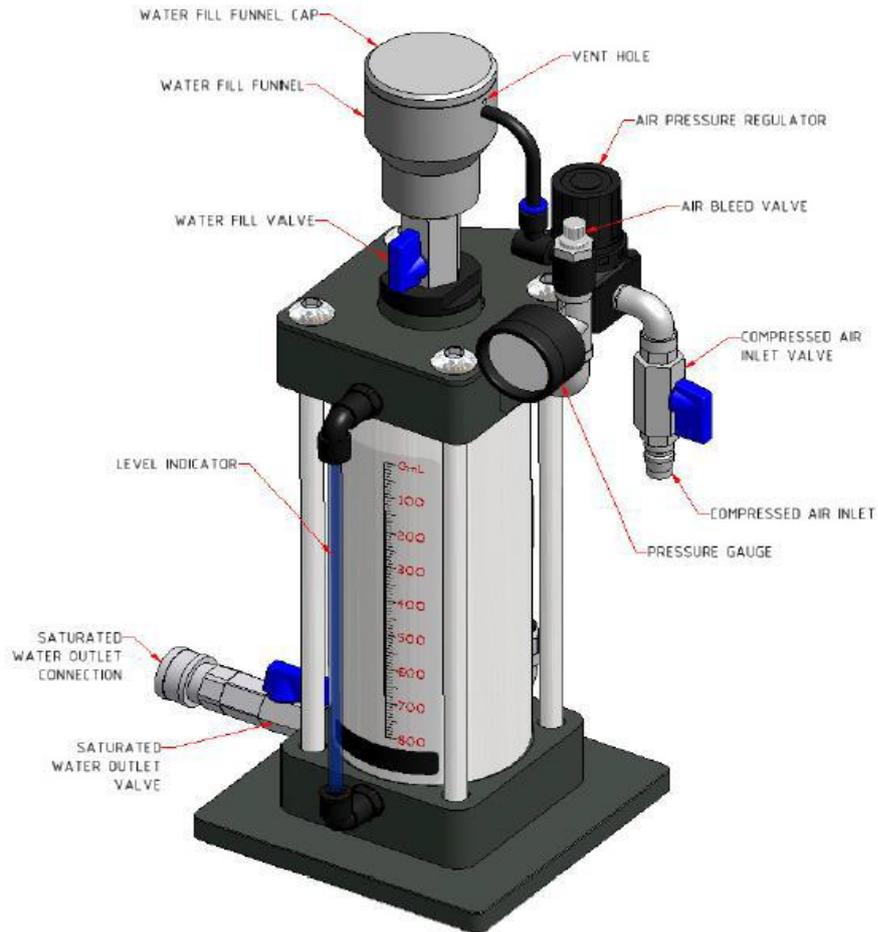
**Figure 3.4:** Photograph of dissolved air flotation system.



**Figure 3.5:** Detailed diagram of the DAF system.

A compressor was used to increase the pressure of the air transferred to the saturator. The compressor had a transducer to show the actual pressure. The saturator is a two-litre aluminum tank. Figure 3.6 is a representation of the saturator. On the top of the tank, there is a water fill funnel system. Ultrapure water was added by opening the cap and valve. An air pressure regulation system was designed to release the extra pressure. It included an air pressure regulator, air bleed valve, and pressure gauge. Compressed air from the compressor was supplied to the tank using the air inlet valve. A pressure gauge displayed the pressure of the saturator. The saturated water level can

be read using a level indicator. A saturated water outlet was connected to the manifold and controlled the flow using a valve.

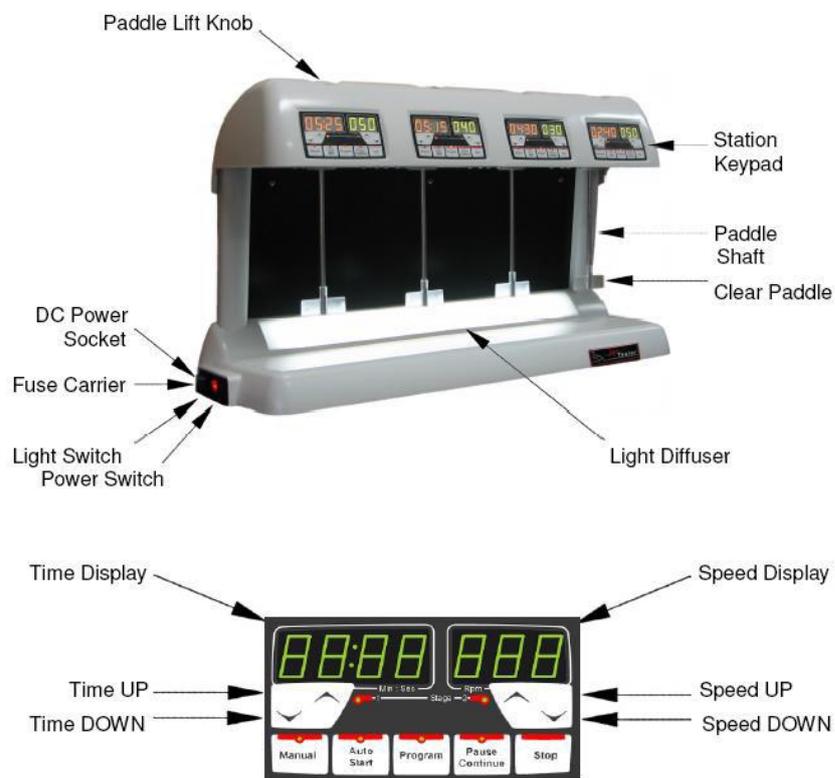


**Figure 3.6:** Structural representation of the saturator.

The function of the manifold was to distribute the saturated water to different jars. It has one inlet and four outlets, which can transfer the saturated water to four jars simultaneously and evenly.

Figure 3.7 shows the jar tester, which is actually a mixing platform. The three types of paddles available for stirring are presented in Figure 3.8. The butterfly paddle was selected for this study, because it was proven, in an earlier study in our lab, to be the most efficient. The jar tester had two types of stirring modes that can fit different

requirements: a manual mode and an automatic mode. The mixing speed can be digitally controlled through water resistant keypads and it was clearly displayed on the LED screen. Real time Hall Effect sensor feedback was used to maintain the paddle speed. Each paddle was controlled by a component to maintain axial flow. A bright white LED light shone through the jar tester to illuminate the jars uniformly, which was helpful for observation during operation. The power switch for the light was on the left side near the bottom.



**Figure 3.7:** Representation of jar tester.



**Figure 3.8:** Different types of paddles.

The jars are four lucid cubic plastic boxes with volumes of 2 litres. There is a tap for sampling in the middle of the box and an inlet tube for connecting on the bottom of the box.

The DAF system had two disadvantages: (1) the saturated water flow rate could not be controlled, and (2) the sample tap location was too high, and hence, not very suitable for this kind of experiment.

### 3.4 Experimental design

Orthogonal experimental design (OED) was applied in this study. An  $L_8 (4^1 \times 2^4)$  orthogonal array design table (OADT) was selected for each ionic liquid. Table 3.2 represented the factors and levels. Factor A was the ionic liquid concentration with four levels from 100 to 700 mg/l. Factors B and C were the stirring speed and recycle ratio with two levels each (100-200 rpm and 10-20%). Table 3.3 shows the orthogonal array design. Two blank columns were set for error estimation. In each column, the numbers of occurrences of the different levels were equal. In any two columns, the arrangement of numbers was complete and balanced. This denoted OAD table can be considered as a full factorial experiment because of uniform dispersion and regular comparables.

**Table 3.2:** Design of factors and levels.

| <b>Factor</b> |                      |              |            |
|---------------|----------------------|--------------|------------|
|               | <b>A</b>             | <b>B</b>     | <b>C</b>   |
| <b>Levels</b> | <b>Concentration</b> | <b>RPM</b>   | <b>RR</b>  |
|               | <b>(mg/l)</b>        | <b>(rpm)</b> | <b>(%)</b> |
| <b>1</b>      | 100                  | 100          | 10         |
| <b>2</b>      | 300                  | 200          | 20         |
| <b>3</b>      | 500                  |              |            |
| <b>4</b>      | 700                  |              |            |

**Table 3.3:** Orthogonal array design table.

| Group | No. | Content | RPM | RR | Empty | Empty |
|-------|-----|---------|-----|----|-------|-------|
|       | 1   | 1       | 1   | 1  | 1     | 1     |
|       | 2   | 1       | 2   | 2  | 2     | 2     |
|       | 3   | 2       | 1   | 1  | 2     | 2     |
|       | 4   | 2       | 2   | 2  | 1     | 1     |
|       | 5   | 3       | 1   | 2  | 1     | 2     |
|       | 6   | 3       | 2   | 1  | 2     | 1     |
|       | 7   | 4       | 1   | 2  | 2     | 1     |
|       | 8   | 4       | 2   | 1  | 1     | 2     |

### 3.5 Experimental procedure

#### 1. Saturator

In the beginning, the saturator was sealed by closing all inlet and outlet valves. Ultrapure water was filled using the funnel after opening the cap and water fill valve. Then the water fill valve was closed, the compressor was turned on, and the gas inlet valve was opened. The compressor was run for at least 30 minutes before saturated water was released to the manifold to keep a stable flow of air bubbles, as recommended by the manufacturer. The tank pressure was adjusted by rotating the air bleed valve. The maximum pressure, which was 100 psi, was used in all the experiments. An air bleed valve was also used to release the saturator pressure when the refilling of ultrapure water was required.

#### 2. Jars

After setting up the DAF system and checking the connection of each part, two different levels of concentration for the same ionic liquid were weighed and added into the two jars. In order to facilitate the experimental procedure and decrease any error, each ionic liquid was added in eight experiments divided into four groups, as shown in Table 3.3. Based on the  $L_8 (4^1 \times 2^4)$  OAD table, the experiment of the same

recycle ratio level will be in one group. For example, 100 mg/l, 100 rpm with 10% RR (Experiment No.1) and 300mg/l, 100 rpm with 10% RR (Experiment No. 3) is one group. Correspondingly, 100 mg/l, 200 rpm with 20% RR (Experiment No. 2) and 300mg/l, 200 rpm with 20% RR (Experiment No. 4) is another group. Two litres of prepared feed water were divided into the same two jars evenly (1 litre per jar). An rpm of 200 was used for 10 minutes at the beginning of the DAF process to mix the ionic liquid and feed water.

### 3. Dissolved air floatation

The DAF process started when we opened the saturated water outlet valve fully. Corresponding volumes of saturated water, which were measured by the level indicator, were released to the jars. For 10% RR, the volume of water was 200 ml. For 20% RR, the volume of water was 400 ml. The recycle ratio was calculated by Eq. (7).

$$\text{Recycle ratio} = \text{Volume of saturated water} / \text{Volume of feed water} \quad (7)$$

The stirring speed was controlled by the jar tester. The same group has the same RPM: either 100 rpm or 200 rpm. It can be observed that the air bubble size was large at first. As time passed, it became much smaller. When it reached the volume of saturated water, the outlet valve was immediately closed and the flotation process started. We selected two flotation times (20 minutes and 3 hours) based on the literature.

### 4. Sampling

After the flotation process ended, sampling was done by using a pipette injected into the bottom of jar. Because of buoyancy, the bottom layer water was cleaner. In

contrast, the top layer water had high oil and grease content. The sample tap was not suitable because of its location, as mentioned earlier. After both jars were sampled, the parameters of oil content, zeta potential, turbidity, conductivity, TDS, and salinity were measured. The same time intervals for each step were used to reduce error. All the experiments were repeated once. Average value  $\pm$  standard deviation was represented in results.

### 3.6 Instrumentation

#### 3.6.1 Digital balance

- a. Objective: A digital balance was used for weighting the sodium chloride and the ionic liquids precisely.
- b. Company: Mettler Toledo.
- c. Units: Digital balance (Model: MS4002S), aluminum container.
- d. Procedure: A clean container was used for each different agent. The container was placed on the pan and then set up to zero. The agent was added slowly and carefully. The result was read after the digital number became stable. The instrument was calibrated to zero before the power was shut off (Faisal, 2015).



**Figure 3.9:** Digital balance.

(Source: [www.mt.com](http://www.mt.com))

#### 3.6.2 Electric magnetic stirrer

- a. Objective: An electric magnetic stirrer was used to dissolve brine into water.
- b. Company: Cole-Parmer.
- c. Units: Electric stirrer (Model: DLM1921X1), stir bar, conical flask.
- d. Procedure: Sodium chloride (14 grams) and a stir bar were added into a conical flask. Later, 2 litres of ultrapure water were poured into the same flask. The right knob was turned on to 1200 rpm. After 15 minutes of mixing, the instrument was turned off (Cole-Parmer, 2007).



**Figure 3.10:** Electric magnetic stirrer.

### 3.6.3 Blender

- a. Objective: A blender was used for stirring and emulsifying the oil with water.
- b. Company: Waring Commercial.
- c. Units: Blender base (Model: MX1200XTS), stainless steel container.
- d. Procedure: The previously prepared 2 litres of brine were added to a stainless steel container. 0.9 millilitre of oil was injected into the brine slowly by syringe with a 1 millilitre range. The container was placed on the blender base. The switch was turned on and the speed was increased step-by-step to Level 6, which was 18000 rpm. This stirring speed was maintained for 2 minutes. Then

the speed was decreased slowly to Level 0 and the blender turned off (Abbasi, 2014).



**Figure 3.11:** Blender.

#### 3.6.4 Simplicity UV water purification system

- a. Objective: This instrument produced ultrapure water, which is also called deionized (DI) water.
- b. Company: EMD Millipore.
- c. Units: Tank, cartridge, filter, UV lamp, distribution pump.
- d. Procedure: Reverse osmosis water was added into the tank and then pumped into the ultraviolet (UV) lamp. The function of the UV lamp was to remove organic molecules in the water. Later on, the pretreated water was moved to the cartridge and membrane filter for deionization and filtration, respectively. The ultrapure water qualification can reach  $\text{TOC} < 5$  ppb and micro organism  $< 0.1$  CFU/ml (EMD Millipore, 2012).



**Figure 3.12:** Simplicity UV water purification system.

### 3.6.5 Oil content analyzer

- a. Objective: An oil content analyzer was used to detect the amount of oil in a sample.
- b. Company: Horiba.
- c. Units: Oil content analyzer (OCMA-350), solvent (S-316), cell, solvent reclaimer unit (SR-305).
- d. Mechanism: The Horiba oil content analyzer uses infrared spectroscopic analysis. The absorbed wavelength of oil and grease particles was in the range of 3.4 and 3.5 micrometers, which can be measured and calculated by the analyzer to determine the oil amount. A solvent extraction technique was used to wipe off interaction. The principle of solvent extraction is based on the solubility difference of different liquids. Oil drops are easily extracted by organic solvent from water because of specific gravity distinction. The organic extraction solvent S-316 was selected due to the fact that its absorb wavelength has no influence on oil. The content of the S-316 solvent was chlorotrifluoroethylene polymers (Horiba, 2005).

- e. Procedure: The Horiba oil content analyzer was turned on for 30 minutes for warm up before any test. According to the manufacturer's instructions, the calibration of the instrument should be adjusted every 2-4 weeks. Zero calibration uses pure S-316 solvent to obtain a zero oil content point. Span calibration uses B-heavy oil, which is solved into pure solvent, to find the 200 mg/l oil content point. Each measurement should follow the same procedure to keep the consistency in every sample solution.

Around a 10 millilitre test sample was prepared in a tube to test the amount of oil. First, 2 molar hydrochloric acid were added in order to reduce the pH to below 2. Second, 8 millilitres of pH-reduced liquid were transferred to a vial by a pipette. Third, 8 millilitres of pure S-316 solvent were added to the same vial according to the pipette. Fourth, the tube was shaken violently for 30 seconds for the extraction process. Fifth, the vial was set down for 1 minute. The solution separated as two layers. The top layer was water, and the bottom layer was oil with a S-316 solvent. Sixth, using the pipette, around 7 millilitres bottom layer liquid was transferred to the cell and covered with a cap. Seventh, the Horiba oil content analyzer lid was opened and the cell placed into the right position. In the end, the lid was closed and the number read after 10 seconds. S-316 solvent is expensive and it is environmentally hazardous if directly discharged; hence the used S-316 was collected and reclaimed with the help of a reclaimer unit (SR-305). The structure of the reclaimer unit consists of a separation filter, an activated carbon layer, and an aluminum

oxide layer to eliminate small particles, oil content, and water, respectively. The used solvent drive by gravity and the regenerate procedure takes 7 to 8 hours (Horiba, 2005).



**Figure 3.13:** Solvent reclaimer, S-316, and OCMA-350.

#### 3.6.6 Turbidity meter

- a. Objective: The turbidity meter was used to measure the turbidity of the solution.
- b. Company: Hanna Instruments.
- c. Units: Turbidity and free/total chlorine meter (HI 83414), test vial, standard solution vial.
- d. Mechanism: Liquid loses transparency due to suspended particles. The particle amount, size, shape, and refractive index will affect light scatter. As a result, turbidity can be measured by the amount of light that is scattered and transmitted across a sample solution. A turbidity meter is composed of a tungsten filament lamp with a 525 nm infrared filter for light generation, a scattered light detector and a transmitted light detector for light detection, and a microprocessor for signal transmission and turbidity calculation. A large

amount of suspended particles cause high scattered light, which lead to high turbidity value (Hanna, 2006).

- e. Procedure: The turbidity meter should be calibrated every month with standard solution from 0 to 2000 Nephelometric Turbidity Units (NTU). A sample solution was added to the test cuvet to the corresponding level and covered with a cap. After that, the test cuvet was placed in the equipment and the lid was closed. The measurement button was pushed to read the result. Silicone oil was used when the inner and outer glass wall of the vial had scratches (Hanna, 2006).



**Figure 3.14:** Standard solution, test vial, and turbidity meter.

### 3.6.7 Total dissolved solids/salinity/conductivity/resistivity meter

- a. Objective: This equipment was used to measure the conductivity, total dissolved solids (TDS), salinity, and resistivity of the sample solution.
- b. Company: Hanna Instruments.
- c. Units: TDS/salinity/conductivity/resistivity Meter (HI 4522), probe.

- d. Mechanism: There are many charge particles in produced water, such as ions and emulsified oil. When a voltage potential difference was applied between two electrodes of probe, charged particles movement toward electrodes happened. Based on the measurement of current intensity between two electrodes and the corresponding relation between each parameter, the expected measurement results were calculated (Hanna, 2006).
- e. Procedure: New calibration should be finished every 3 months with a standard solution, which has a conductivity of 24.82 mS. At the beginning of use, a probe clean by acetone and ultrapure water was required. There are two types of probe on this instrument. The same type of probe was inserted for each measurement. The data of conductivity was read until it was showed steadily on the screen and the channel was changed by pressing the button to read other parameters. After each test, the probe was cleaned by ultrapure water (Hanna, 2006).



**Figure 3.15:** The TDS/salinity/conductivity/resistivity meter.  
(Source: [www.hannainst.com](http://www.hannainst.com)).

### 3.6.8 pH Meter

- a. Objective: A pH meter was used to measure the pH.
- b. Company: Horiba,
- c. Units: pH instrument (F-55), probe.
- d. Mechanism: The concept of pH is a measurement of the hydrogen ion concentration in a solution. This instrument has two glass electrodes. The outside electrode was a measurable electrode, which has ion exchange with the sample solution. The inside electrode was a reference electrode which remains the same as the standard solution. When the probe was applied to the sample solution, there was a voltage difference between the outside and inside electrode because of movement of the hydrogen ions. The difference was amplified and translated by corresponding microprocessors and then shown on a digital screen (Horiba, 2003).
- e. Procedure: Three kinds of standard solutions (pH 4, pH 7, and pH 10) were used for monthly calibration. Before the first test, the probe was cleaned by acetone and ultrapure water. The probe was injected into the sample solution, and then the number read once it was stabilized. After each measurement, ultrapure water was used to clean it. In order to extend service life, the glass electrode was always kept in the cover when not in use (Horiba, 2003).



**Figure 3.16:** pH meter.

(Source: [www.horiba.com](http://www.horiba.com))

### 3.6.9 Zetasizer

- a. Objective: The function of the zetasizer system was the zeta potential measurement for the sample solution.
- b. Company: Malvern.
- c. Units: Zetasizer Nano ZS (ZEN3600), corresponding software, cell/cuvette.
- d. Mechanism: The zeta potential is a potential at the slipping plane. It indicates the potential difference existing between the particle surface and the dispersing liquid. The solution was regarded as being in an unstable condition with a zeta potential between -30 mV to +30 mV. Outside this range, the solution was considered as a stable situation. In other words, a large negative or positive zeta potential value means a strong repulsive force between particles. As a result, particles cannot approximate each other. Electrophoresis and laser Doppler anemometry are two principles utilized in the Zetasizer Nano ZS (ZEN3600). Electrophoresis is the motion of dispersed particles relative to a fluid under the influence of an electric field. Laser Doppler

anemometry, also known as laser Doppler velocimetry, is the technique of using Doppler shift to measure the velocity of particles.

633 nm red laser was passed through the sample cuvette and the light scattered was detected at 13 degrees. Later on, the electric field was applied according to electrodes. Because the electric field changed the speed of particles, the intensity of the light scattered changed correspondingly. A frequency spectrum was produced after those changes were sent to the software by a digital signal processor. When these techniques are taken together, the zeta potential can be determined (Malvern, 2009).

- e. Procedure: There are three kinds of cells for different solutions. In order to obtain accurate results, a polycarbonate folded capillary cuvette was applied in this research. Bakken area oil was selected as the material whose specific gravity and density needs to be measured because water is the dispersant. Every test should follow the same procedure to keep the consistency of the experiment. A sample solution was injected into the cuvette slowly and fully by syringe so that no air bubbles were created in the cell. After being covered with small plastic caps, the cell was placed into the right position in the instrument. The lid was closed, and the start button on the computer was clicked to start the measurement. For each sample, the zeta potential results were obtained in triplicate. These results were stored in a corresponding file (Malvern, 2009).



**Figure 3.17:** Malvern Zetasizer.

### 3.6.10 Mastersizer

- a. Objective: The Mastersizer was used to measure the distribution of particles size in the sample solution.
- b. Company: Malvern.
- c. Units: Mastersizer optical unit (MAZ3000), automatic wet dispersion unit (MAZ3300), corresponding software.
- d. Mechanism: This device uses the light (laser) diffraction method. Figure 3.18 is a schematic diagram of the scattered principle to different particle size. When 633 nm red light and 470 nm blue light passed through the particles, scattered and unscattered light were detected by a light sensor. An automatic wet dispersion unit (MAZ3300) was used to circulate the sample solution through a cell, which was located within the optical unit. The function of the optimal unit was to generate and direct light through a sample solution cell. All signals and information were transferred to corresponding software to obtain results. Software also controlled the optical unit and wet dispersion unit (Malvern, 2011).

e. Procedure: At the beginning of the measurement, Bakken area oil was selected as the material and water was selected as the dispersant. The reflective index of 1.45 and density of 0.8 g/cc were inputted into the software as properties values. It was necessary to pick up the suitable obstruction, which was 5-15% in this research. Obstruction is the amount of light that is blocked or scattered in the sample solution. Obstruction has an influence on the accuracy of the experimental results. A light scattered graph can be observed in the measurement window according to professional software.

First, the background situation (without sample solution) was measured. Second, the sample solution was slowly added to the automatic wet dispersion unit (MAZ3300) with the mentioned obscuration range. Comparison was made and transferred to a colourful line graph represented by DV 10, DV 50, and DV 90. DV 10, DV 50, and DV 90 indicate that 10%, 50%, and 90% of the particles were smaller than the corresponding size. At the end of the test, a micro 90 solution and ultrapure water were used to drain the sample solution out and clean the instrument (Malvern, 2011).



**Figure 3.18:** Malvern Mastersizer.

## CHAPTER 4: RESULTS AND DISCUSSION

### 4.1 Characteristics of synthetic produced water

Synthetic produced water was made by the procedure mentioned in Chapter 3. Fourteen grams of sodium chloride were dissolved in 2 litres of ultrapure water, and 0.9 millilitre oil was added to the brine water. All synthetic produced waters had to be used immediately to keep the integrity of the experiments. The instruments were calibrated by standard solution twice to keep accuracy. Fresh synthetic produced water was prepared twice and then used immediately. The measurement results were presented as average  $\pm$  standard deviation as shown in Table 4.1.

**Table 4.1:** Characteristics of synthetic produced water.

| <b>Parameter</b>           | <b>Feed</b>     |
|----------------------------|-----------------|
| <b>Oil Content (mg/l)</b>  | 262.0 $\pm$ 2.8 |
| <b>Zeta potential (mV)</b> | -29.2 $\pm$ 0.6 |
| <b>Turbidity (NTU)</b>     | 500 $\pm$ 0     |
| <b>Conductivity (mS)</b>   | 7.02 $\pm$ 0.02 |
| <b>TDS (ppt)</b>           | 6.72 $\pm$ 0.02 |
| <b>Salinity (%)</b>        | 25.0 $\pm$ 0.1  |

Based on Canada offshore water treatment guidelines, the discharge limits for average volume weighted oil and grease content is 30 mg/l for 30 days and 44 mg/l for 24 hours in water concentration (CNSOPB, 2010). Feed water has almost nine times the oil content than recommended by the treatment guidelines. Thus, it is necessary to control the indicator of oil content before discharging the feed water into the

environment. In addition, the typical produced water characteristics adopted by Environment Canada, which were listed in Chapter 2, mention that the range of oil content and TDS are 220-2000 mg/l and 6–31 ppt, respectively. This illustrates that the synthetic produced water used in this study was a good presentation of real produced water.

The zeta potential of the feed water has a negative value close to -30 mV. A negative zeta potential value in oil content produced water was observed in many published studies. A value close to -30 mV means the solution is stable and it is not easy to remove dissolved particles from it. The turbidity of the synthetic produced water was  $500 \pm 0$  NTU because of its high dissolved oil and solid content. Dissolved oil droplets in produced water also affect water conductivity. The salinity of the feed water is lower than the average ocean salinity level. In offshore production, it is not a considerable factor; however, in onshore production, for different usage types, salinity may have to be controlled.

Figure A.1 in the appendix shows particle size distribution in the synthetic produced water. Particle size distribution has an influence on the settling velocities of particles and the colloidal properties of the solution.  $D_v 90$  (50 and 10) indicates 90% (50% and 10%) particles by volume exist in this solution and have a diameter under a measured value of number. From Figure A.1, 90% of the particles' diameters were below the size of 15.200  $\mu\text{m}$ , 50% of the particles were smaller than 3.45  $\mu\text{m}$ , and 10% of the particles were less than 0.0643  $\mu\text{m}$ . These values proved that this synthetic

produced water was in a colloidal status. However, most of the particle sizes were above the colloidal range (1-0.001  $\mu\text{m}$ ).

## 4.2 Results

### 4.2.1 Results for n-methylpyridinium tosylate

Table 4.2 shows the factors and levels of design of an orthogonal experimental design (OED) for n-methylpyridinium tosylate. The three factors are (1) concentration of the ionic liquid, (2) the RPM of the DAF process, and (3) the recycle ratio (RR). Boundary values for the levels were determined by a pilot experiment and a review of the literature. Factor A had four levels from 100 mg/l to 700 mg/l. Factors B and C had two levels each. 200 rpm is the maximum stir speed in this DAF unit. The most frequently used recycle ratios were set as 10% and 20%, as commonly mentioned in the literature.

Table 4.3 is the orthogonal array design table (OADT) for n-methylpyridinium tosylate. Factors A and B and C have different levels, and an  $L_8 (4^1 \times 2^4)$  OADT was used. Because oil content is the most important indicator in produced water treatment, the OED in Table 4.3 only shows the oil content results. After correlating the R value to the R' value, the range analysis results (summarized in Table 4.4) reflected the order of significance factors as ionic liquid concentration > RPM > recycle ratio. The optimum levels for each factor were 300mg/l for Factor A, 200 rpm for Factor B, and 20% for Factor C. The optimal oil content removal combination for n-methylpyridinium tosylate was  $A_2-B_2-C_2$ .

Analysis of variance (ANOVA) was later utilized to assess the OADT results. Two blank columns were designated for error evaluation. The sum of square of deviations (SS), degree of freedom (DF), mean of square of deviation (MS), and F-value (F) for oil content were calculated and summarized in Table 4.5. The obtained F-values in this experiment were compared with the theoretical ones in the appendix (A.2 & A.3). Factors A and B (representing the ionic liquid concentration and RPM, respectively) have statistical significance to oil content ( $p < 0.01$ ). The recycle ratio shows an indistinctive effect. The F-value in ANOVA is in agreement with the order of significance factors obtained from the range analysis. Figure 4.1 shows the turbidity removal versus oil removal. A high coefficient of determination ( $R^2 = 0.99$ ) indicates that turbidity removal has a high relation with oil removal.

**Table 4.2:** N-methylpyridinium tosylate factors and levels design.

| Levels | Factor        |       |     |
|--------|---------------|-------|-----|
|        | A             | B     | C   |
|        | Concentration | RPM   | RR  |
|        | (mg/l)        | (rpm) | (%) |
| 1      | 100           | 100   | 10  |
| 2      | 300           | 200   | 20  |
| 3      | 500           |       |     |
| 4      | 700           |       |     |

**Table 4.3:** N-methylpyridinium tosylate OADT.

| Exp. No. | A | B | C | Blank Column | Blank Column | Oil Content (mg/l) |
|----------|---|---|---|--------------|--------------|--------------------|
| 1        | 1 | 1 | 1 | 1            | 1            | 119.0 ± 3.2        |
| 2        | 1 | 2 | 2 | 2            | 2            | 103.0 ± 1.9        |
| 3        | 2 | 1 | 1 | 2            | 2            | 74.6 ± 2.4         |
| 4        | 2 | 2 | 2 | 1            | 1            | 64.5 ± 1.8         |
| 5        | 3 | 1 | 2 | 1            | 2            | 87.0 ± 2.0         |
| 6        | 3 | 2 | 1 | 2            | 1            | 76.1 ± 1.7         |

|                         |       |       |       |       |       |             |
|-------------------------|-------|-------|-------|-------|-------|-------------|
| <b>7</b>                | 4     | 1     | 2     | 2     | 1     | 118.0 ± 2.5 |
| <b>8</b>                | 4     | 2     | 1     | 1     | 2     | 111.0 ± 3.1 |
| <b>K<sub>1</sub></b>    | 222.0 | 398.6 | 380.7 | 381.5 | 377.6 |             |
| <b>K<sub>2</sub></b>    | 139.1 | 354.6 | 372.5 | 371.7 | 375.6 |             |
| <b>K<sub>3</sub></b>    | 163.1 |       |       |       |       |             |
| <b>K<sub>4</sub></b>    | 229.0 |       |       |       |       |             |
| <b>K<sub>avg1</sub></b> | 111.0 | 99.7  | 95.2  | 95.4  | 94.4  |             |
| <b>K<sub>avg2</sub></b> | 69.6  | 88.7  | 93.1  | 92.9  | 93.9  |             |
| <b>K<sub>avg3</sub></b> | 81.6  |       |       |       |       |             |
| <b>K<sub>avg4</sub></b> | 114.5 |       |       |       |       |             |
| <b>R</b>                | 45.0  | 11.0  | 2.1   | 2.5   | 0.5   |             |
| <b>R'</b>               | 28.6  | 15.6  | 2.9   | 3.5   | 0.7   |             |

**Table 4.4:** N-methylpyridinium tosylate range analysis results.

| <b>Order</b>               | <b>A&gt;B&gt;C</b>                               |                      |                      |
|----------------------------|--|----------------------|----------------------|
| <b>Optimal Level</b>       | <b>A<sub>2</sub></b>                             | <b>B<sub>2</sub></b> | <b>C<sub>2</sub></b> |
| <b>Optimal Combination</b> | <b>A<sub>2</sub>-B<sub>2</sub>-C<sub>2</sub></b> |                      |                      |

**Table 4.5:** N-methylpyridinium tosylate variance analysis (ANOVA).

| <b>Factors</b> | <b>SS</b> | <b>DF</b> | <b>MS</b> | <b>F</b> | <b>Significant</b> |
|----------------|-----------|-----------|-----------|----------|--------------------|
| <b>A</b>       | 2923.9    | 3         | 974.6     | 139.8    | **                 |
| <b>B</b>       | 242.0     | 1         | 242.0     | 34.7     | **                 |
| <b>CΔ</b>      | 8.4       | 1         | 8.4       | 1.2      | -                  |
| <b>Error</b>   | 12.5      | 2         | 6.3       | -        | -                  |
| <b>ErrorΔ</b>  | 20.9      | 3         | 7.0       | -        | -                  |
| <b>Total</b>   | 3186.8    | 7         | -         | -        | -                  |

Notes:  $F_{0.05}(3,3)=9.28$

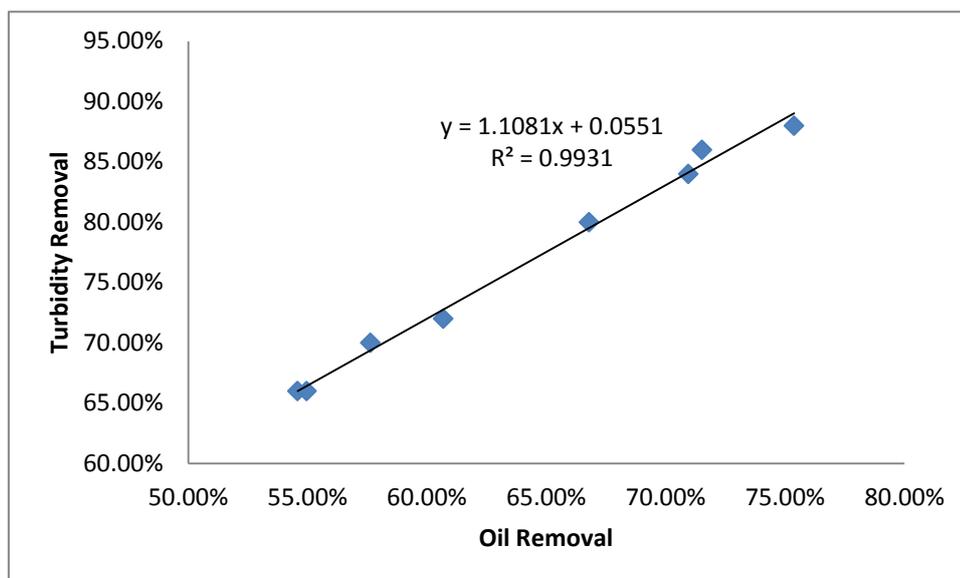
$F_{0.01}(3,3)=29.46$

$F_{0.05}(1,3)=10.13$

$F_{0.01}(1,3)=34.12$

SS= Sum of square; DF=Degree of freedom; MS=Mean of square; F=F-value;

\*\* :  $p < 0.01(F > F_{0.01}(3,3) \text{ or } F > F_{0.01}(1,3))$ ; \* :  $p < 0.05(F > F_{0.05}(3,3) \text{ or } F > F_{0.05}(1,3))$ .



**Figure 4.1:** N-methylpyridinium tosylate oil removal versus turbidity removal.

#### 4.2.2 Results for 1,3-dimethylimidazolium tosylate

Table 4.6 shows the factors and levels of design of the OED for 1,3-dimethylimidazolium tosylate. The design of factors and levels are the same as those for n-methylpyridinium tosylate. Boundary values for the levels were determined by a pilot experiment and a review of the literature.

Table 4.7 is the OADT for 1,3-dimethylimidazolium tosylate. Similar to n-methylpyridinium tosylate, an  $L_8 (4^1 \times 2^4)$  OADT was used. Oil content is the most important indicator in produced water treatment. As a result, the OED in Table 4.7 only reports the oil content value. After the correlation of the R value to the R' value, the range analysis results, summarized in Table 4.8, suggest that the order of significance factor is ionic liquid concentration > RPM > recycle ratio. The optimum levels for each factor were 300mg/l for Factor A, 200 rpm for Factor B, and 20% for Factor C. The optimal oil content removal combination for 1,3-dimethylimidazolium tosylate was  $A_2-B_2-C_2$ .

Analysis of variance (ANOVA) was further utilized to assess the OED results. Two blank columns were designated for error evaluation. The sum of square of deviation (SS), degree of freedom (DF), mean of square of deviation (MS), and F-value (F) for oil content were calculated and summarized in Table 4.8. According to the obtained F-value in this experiment, and when compared with the theoretical one in the appendix (A.2 & A.3), Factors A and B (representing the ionic liquid concentration and RPM, respectively) have statistical significance on the removal of oil content ( $p < 0.01$ ). The recycle ratio shows an indistinctive effect. The F-value in ANOVA is in agreement with the order obtained from the range analysis.

Figure 4.9 shows the turbidity removal versus the oil removal. A high coefficient of determination ( $R^2 = 0.87$ ) means the turbidity removal has a linear relation with oil removal.

**Table 4.6:** 1,3-dimethylimidazolium tosylate factors and levels design.

| Levels | Factor                  |              |           |
|--------|-------------------------|--------------|-----------|
|        | A                       | B            | C         |
|        | Concentration<br>(mg/L) | RPM<br>(rpm) | RR<br>(%) |
| 1      | 100                     | 100          | 10        |
| 2      | 300                     | 200          | 20        |
| 3      | 500                     |              |           |
| 4      | 700                     |              |           |

**Table 4.7:** 1,3-dimethylimidazolium tosylate OADT.

| Exp. No. | A | B | C | Blank Column | Blank Column | Oil Content (mg/l) |
|----------|---|---|---|--------------|--------------|--------------------|
| 1        | 1 | 1 | 1 | 1            | 1            | 113.0 ± 0.6        |
| 2        | 1 | 2 | 2 | 2            | 2            | 100.2 ± 0.5        |
| 3        | 2 | 1 | 1 | 2            | 2            | 84.4 ± 0.3         |
| 4        | 2 | 2 | 2 | 1            | 1            | 76.0 ± 0.4         |
| 5        | 3 | 1 | 2 | 1            | 2            | 90.0 ± 0.5         |

|                         |       |       |       |       |       |             |
|-------------------------|-------|-------|-------|-------|-------|-------------|
| <b>6</b>                | 3     | 2     | 1     | 2     | 1     | 81.6 ± 0.3  |
| <b>7</b>                | 4     | 1     | 2     | 2     | 1     | 112.0 ± 0.6 |
| <b>8</b>                | 4     | 2     | 1     | 1     | 2     | 100.5 ± 0.4 |
| <b>K<sub>1</sub></b>    | 213.2 | 399.4 | 379.5 | 379.5 | 382.6 |             |
| <b>K<sub>2</sub></b>    | 160.4 | 358.3 | 378.2 | 378.2 | 375.1 |             |
| <b>K<sub>3</sub></b>    | 171.6 |       |       |       |       |             |
| <b>K<sub>4</sub></b>    | 212.5 |       |       |       |       |             |
| <b>K<sub>avg1</sub></b> | 106.6 | 99.9  | 94.9  | 94.9  | 95.7  |             |
| <b>K<sub>avg2</sub></b> | 80.2  | 89.6  | 94.6  | 94.6  | 93.8  |             |
| <b>K<sub>avg3</sub></b> | 85.8  |       |       |       |       |             |
| <b>K<sub>avg4</sub></b> | 106.3 |       |       |       |       |             |
| <b>R</b>                | 26.1  | 10.3  | 0.3   | 0.3   | 1.9   |             |
| <b>R'</b>               | 16.6  | 14.6  | 0.5   | 0.5   | 2.7   |             |

**Table 4.8:** 1,3-dimethylimidazolium tosylate range analysis results.

| <b>Order</b>               | <b>A&gt;B&gt;C</b>                               |                      |                      |
|----------------------------|--|----------------------|----------------------|
| <b>Optimal Level</b>       | <b>A<sub>2</sub></b>                             | <b>B<sub>2</sub></b> | <b>C<sub>2</sub></b> |
| <b>Optimal Combination</b> | <b>A<sub>2</sub>-B<sub>2</sub>-C<sub>2</sub></b> |                      |                      |

**Table 4.9:** 1,3-dimethylimidazolium tosylate variance analysis (ANOVA).

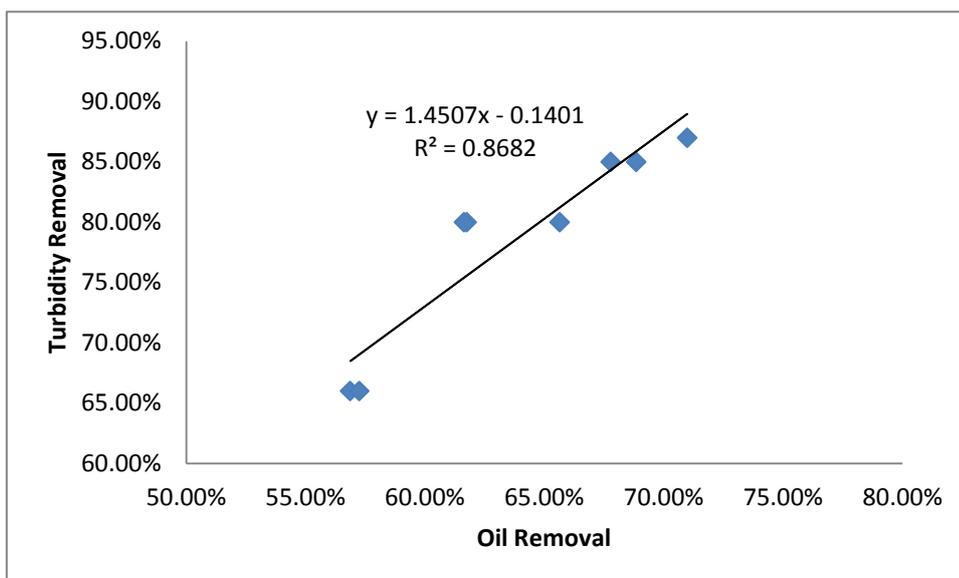
| <b>Factors</b>                  | <b>SS</b> | <b>DF</b> | <b>MS</b> | <b>F</b> | <b>Significant</b> |
|---------------------------------|-----------|-----------|-----------|----------|--------------------|
| <b>A</b>                        | 1128.9    | 3         | 376.3     | 151.5    | **                 |
| <b>B</b>                        | 211.2     | 1         | 211.2     | 85.0     | **                 |
| <b>C<math>\Delta</math></b>     | 0.2       | 1         | 0.2       | 0.1      | -                  |
| <b>Error</b>                    | 7.2       | 2         | 3.6       | -        | -                  |
| <b>Error<math>\Delta</math></b> | 7.5       | 3         | 2.5       | -        | -                  |
| <b>Total</b>                    | 1347.5    | 7         | -         | -        | -                  |

Notes:  $F_{0.05}(3,3)=9.28$   $F_{0.01}(3,3)=29.46$

$F_{0.05}(1,3)=10.13$   $F_{0.01}(1,3)=34.12$

SS=Sum of square; DF=Degree of freedom; MS=Mean of square; F=F-value;

\*\* :  $p < 0.01(F > F_{0.01}(3,3)$  or  $F > F_{0.01}(1,3)$ ); \* :  $p < 0.05(F > F_{0.05}(3,3)$  or  $F > F_{0.05}(1,3)$ ).



**Figure 4.2:** 1,3-dimethylimidazolium tosylate oil removal versus turbidity removal.

#### 4.2.3 Results for 1-benzyl-3-methylimidazolium tosylate.

Table 4.10 illustrates the factors and levels design for the OED for 1-benzyl-3-methylimidazolium tosylate. The design of factors and levels are the same as the design for the other two ionic liquids. Boundary values for the levels were determined by a pilot experiment and a review of the literature. Table 4.11 is the OADT for 1-benzyl-3-methylimidazolium tosylate. Similar to the previous experimental design, an  $L_8 (4^1 \times 2^4)$  OADT was used. Oil content is the most important indicator in produced water treatment; therefore, the OED in Table 4.11 only reports the oil content value.

After using the correlation equation and sorting the R' value, the range analysis results, which are listed in Table 4.12, state the order of significance factors as ionic liquid concentration > RPM > recycle ratio. The optimum levels for each factor were 300mg/l for Factor A, 200 rpm for Factor B, and 20% for Factor C. The optimal oil content removal combination for 1-benzyl-3-methylimidazolium tosylate was  $A_2-B_2-C_2$ .

Analysis of variance (ANOVA) was utilized to assess the OED results in the next step. The sum of the square of deviation (SS), degree of freedom (DF), mean of the square of deviation (MS), and F-value (F) for the oil content were calculated and are summarized in Table 4.13. According to a comparison of the obtained F-value in this experiment with the theoretical one in the appendix (A.2 & A.3), Factors A and B (representing the ionic liquid concentration and RPM, respectively) have statistical significance on the removal of oil content ( $p < 0.01$ ). The recycle ratio shows a non-significant effect. The F-value in ANOVA is in agreement with the order obtained from range analysis. Figure 4.3 shows the turbidity removal versus oil removal. A high coefficient of determination ( $R^2 = 0.97$ ) signifies that turbidity removal has a direct relation with oil removal.

**Table 4.10:** 1-benzyl-3-methylimidazolium tosylate factors and levels design.

| Levels | Factor                  |     |           |
|--------|-------------------------|-----|-----------|
|        | A                       | B   | C         |
|        | Concentration<br>(mg/L) | RPM | RR<br>(%) |
| 1      | 100                     | 100 | 10        |
| 2      | 300                     | 200 | 20        |
| 3      | 500                     |     |           |
| 4      | 700                     |     |           |

**Table 4.11:** 1-benzyl-3-methylimidazolium tosylate orthogonal array design.

| Exp. No. | A | B | C | Blank Column | Blank Column | Oil Content (mg/l) |
|----------|---|---|---|--------------|--------------|--------------------|
| 1        | 1 | 1 | 1 | 1            | 1            | 119 ± 1.2          |
| 2        | 1 | 2 | 2 | 2            | 2            | 100.4 ± 0.9        |
| 3        | 2 | 1 | 1 | 2            | 2            | 62.6 ± 0.8         |
| 4        | 2 | 2 | 2 | 1            | 1            | 48.1 ± 0.8         |
| 5        | 3 | 1 | 2 | 1            | 2            | 74.4 ± 1.1         |
| 6        | 3 | 2 | 1 | 2            | 1            | 65.4 ± 0.7         |
| 7        | 4 | 1 | 2 | 2            | 1            | 119.4 ± 1.1        |

|                         |       |       |       |       |       |             |
|-------------------------|-------|-------|-------|-------|-------|-------------|
| <b>8</b>                | 4     | 2     | 1     | 1     | 2     | 100.7 ± 1.0 |
| <b>K<sub>1</sub></b>    | 219.4 | 375.4 | 347.7 | 342.2 | 351.9 |             |
| <b>K<sub>2</sub></b>    | 110.7 | 314.6 | 342.3 | 347.8 | 338.1 |             |
| <b>K<sub>3</sub></b>    | 139.8 |       |       |       |       |             |
| <b>K<sub>4</sub></b>    | 220.1 |       |       |       |       |             |
| <b>K<sub>avg1</sub></b> | 109.7 | 93.9  | 86.9  | 85.6  | 88.0  |             |
| <b>K<sub>avg2</sub></b> | 55.4  | 78.7  | 85.6  | 87.0  | 84.5  |             |
| <b>K<sub>avg3</sub></b> | 69.9  |       |       |       |       |             |
| <b>K<sub>avg4</sub></b> | 110.1 |       |       |       |       |             |
| <b>R</b>                | 54.7  | 15.2  | 1.3   | 1.4   | 3.4   |             |
| <b>R'</b>               | 34.8  | 21.6  | 1.9   | 2.0   | 4.9   |             |

**Table 4.12:** 1-benzyl-3-methylimidazolium tosylate range analysis results.

| <b>Order</b>               | <b>A&gt;B&gt;C</b>                               |                      |                      |
|----------------------------|--|----------------------|----------------------|
| <b>Optimal Level</b>       | <b>A<sub>2</sub></b>                             | <b>B<sub>2</sub></b> | <b>C<sub>2</sub></b> |
| <b>Optimal Combination</b> | <b>A<sub>2</sub>-B<sub>2</sub>-C<sub>2</sub></b> |                      |                      |

**Table 4.13:** 1-benzyl-3-methylimidazolium tosylate variance analysis (ANOVA).

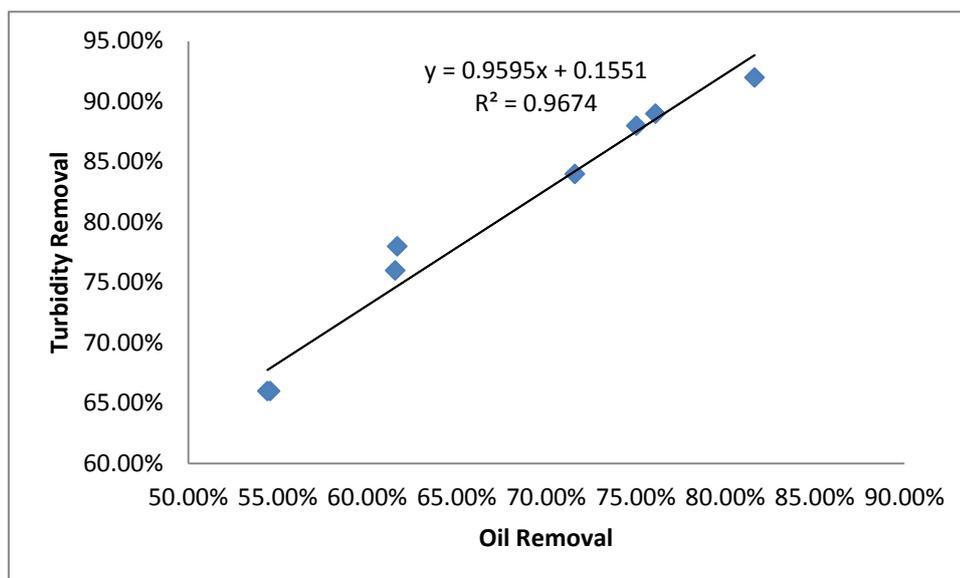
| <b>Factors</b> | <b>SS</b> | <b>DF</b> | <b>MS</b> | <b>F</b> | <b>Significant</b> |
|----------------|-----------|-----------|-----------|----------|--------------------|
| <b>A</b>       | 4677.0    | 3         | 1559.0    | 149.1    | **                 |
| <b>B</b>       | 462.1     | 1         | 462.1     | 44.2     | **                 |
| <b>CΔ</b>      | 3.6       | 1         | 3.6       | 0.3      | -                  |
| <b>Error</b>   | 27.7      | 2         | 13.9      | -        | -                  |
| <b>ErrorΔ</b>  | 31.4      | 3         | 10.5      | -        | -                  |
| <b>Total</b>   | 5170.4    | 7         | -         | -        | -                  |

Notes:  $F_{0.05}(3,3)=9.28$        $F_{0.01}(3,3)=29.46$

$F_{0.05}(1,3)=0.13$        $F_{0.01}(1,3)=34.12$

SS=Sum of square; DF=Degree of freedom; MS=Mean of square; F=F-value;

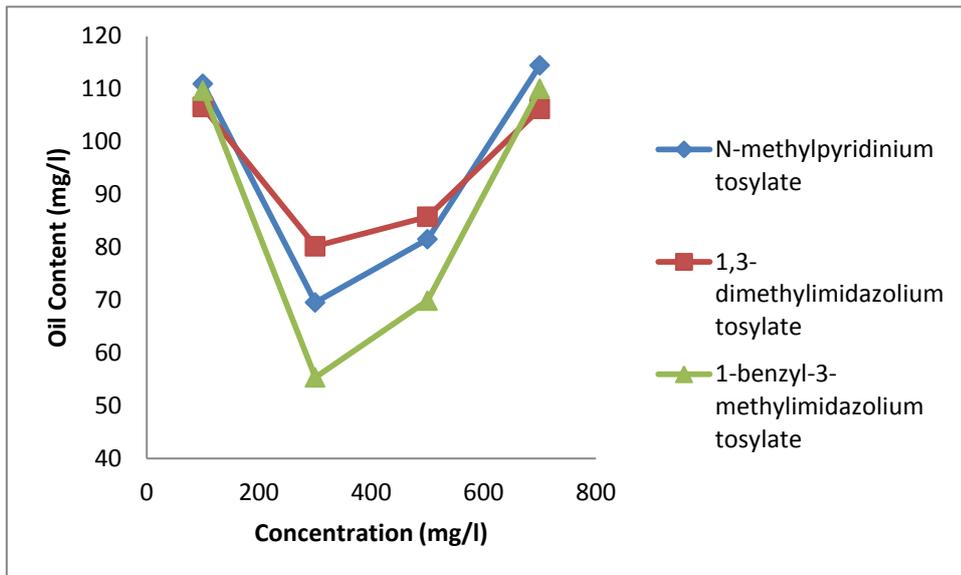
\*\* :  $p < 0.01(F > F_{0.01}(3,3) \text{ or } F > F_{0.01}(1,3))$ ; \* :  $p < 0.05(F > F_{0.05}(3,3) \text{ or } F > F_{0.05}(1,3))$ .



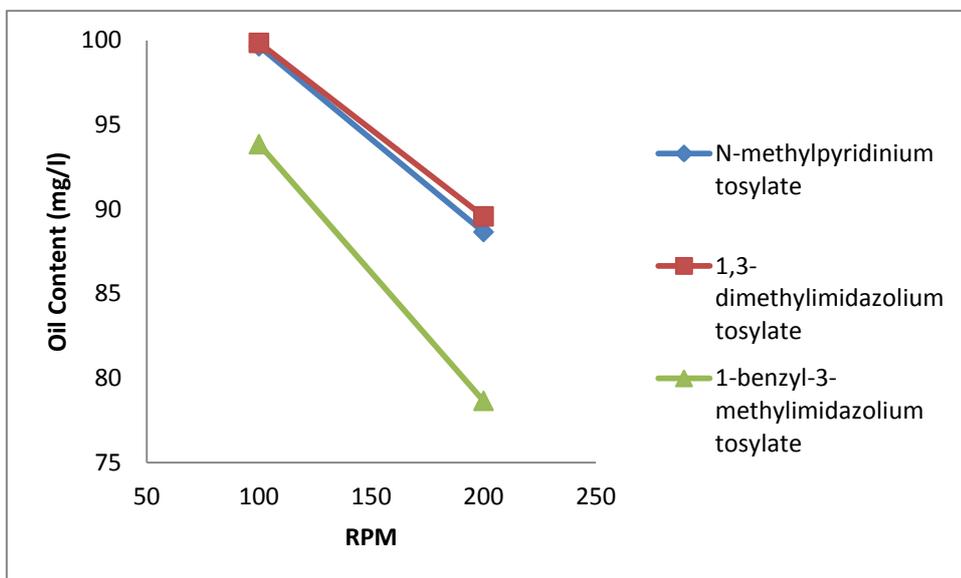
**Figure 4.3:** 1-benzyl-3-methylimidazolium tosylate oil removal versus turbidity removal.

#### 4.2.4 Effects of each factor on ionic liquid with a dissolved air flotation experiment using orthogonal experimental design

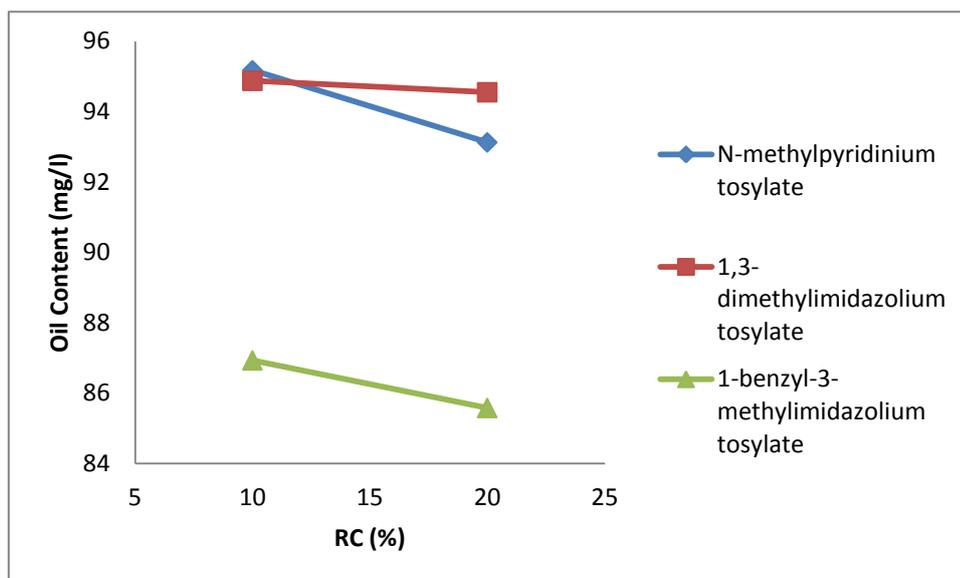
In order to evaluate the influence of each factor's level on synthetic produced water treatment directly, the average oil content in terms of the same level in the OADT are depicted in Figures 4.4–4.6. In Figure 4.4, three kinds of ionic liquid effect of feed water on the oil content are shown. When the concentration was increased from 100 to 300 mg/l, the oil content dropped dramatically. After 300 mg/l, with increasing concentration, the corresponding oil content increased. Figure 4.5 shows that the oil content decreased clearly when RPM was increased. As observed in Figure 4.6, with the increase of RR from 10 to 20%, the oil content decreased. The trends of oil content variance from Figures 4.4–4.6 coincide with the range analysis and ANOVA results for each ionic liquid, which have reported that 300 mg/l, 200 rpm, and 20% are the optimal levels for ionic concentration, RPM, and RR, respectively.



**Figure 4.4:** Effect of ionic liquid concentration.



**Figure 4.5:** Effect of RPM on oil content removal.



**Figure 4.6:** Effect of recycle ratio on oil content removal.

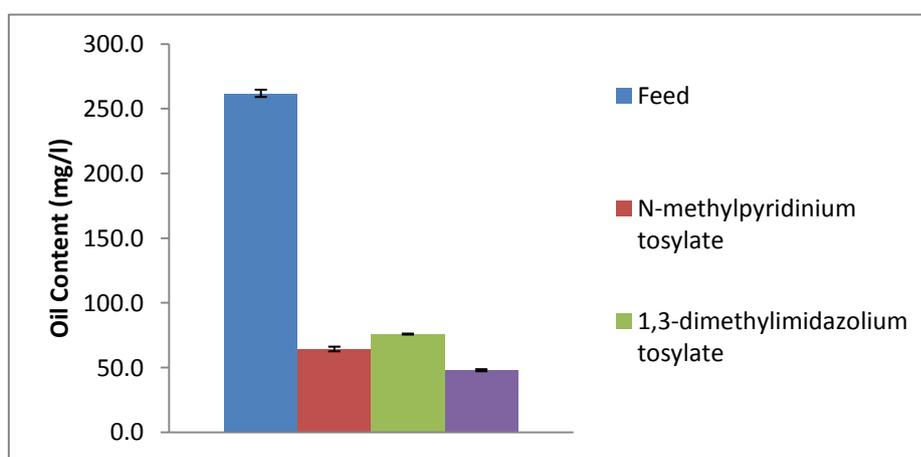
#### 4.2.5 Comparison of different ionic liquids results

The results of the characteristics of feed water and the different ionic liquids results are presented in Table 4.14. The removal percentages of different ionic liquids results are shown in Table 4.15. The combination of best oil removal results for three ionic liquids were concentrations of 300 mg/l, a RPM of 200, and a RR of 20%, respectively. The results indicate that 1-benzyl-3-methylimidazolium tosylate has the best performance compared to the other ionic liquids. N-methylpyridinium tosylate provides better produced water treatment results than 1,3-dimethylimidazolium tosylate in terms of oil and turbidity removal.

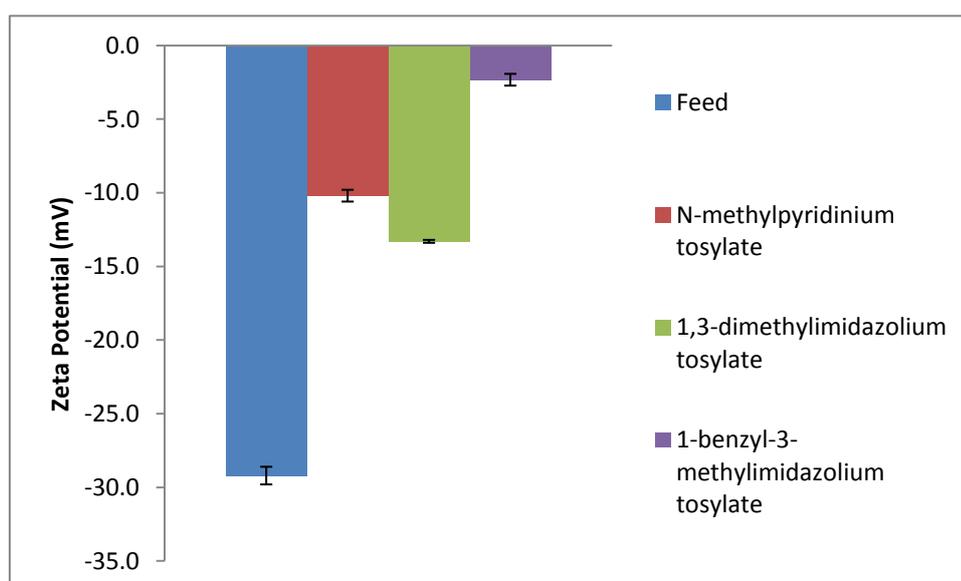
**Table 4.14:** Characteristics of feed water and different ionic liquids results.

| Parameter           | Feed        | N-methylpyridinium tosylate | 1,3-dimethylimidazolium tosylate | 1-benzyl-3-methylimidazolium tosylate |
|---------------------|-------------|-----------------------------|----------------------------------|---------------------------------------|
| Oil Content (mg/l)  | 262.0 ± 2.8 | 64.5±1.8                    | 76.0 ± 0.4                       | 48.1 ± 0.8                            |
| Zeta potential (mV) | -29.2 ± 0.6 | -10.2 ± 0.4                 | -13.3 ± 0.1                      | -2.3 ± 0.4                            |
| Turbidity (NTU)     | 500.0 ± 0.0 | 60.0 ± 3.5                  | 65.0 ± 3.5                       | 40.0 ± 0.0                            |
| Conductivity (mS)   | 7.02 ± 0.02 | 11.93 ± 0.02                | 11.14 ± 0.04                     | 11.61 ± 0.08                          |
| TDS (ppt)           | 6.72 ± 0.02 | 4.31 ± 0.01                 | 4.40 ± 0.01                      | 4.60 ± 0.02                           |
| Salinity (%)        | 25.0 ± 0.1  | 20.8 ± 0.1                  | 20.9 ± 0.4                       | 20.5 ± 0.6                            |

The oil contents were 64.5±1.8 mg/l, 76.0 ± 0.4 mg/l, and 48.1 ± 0.8 mg/l for the ionic liquids n-methylpyridinium tosylate, 1,3-dimethylimidazolium tosylate, and 1-benzyl-3-methylimidazolium tosylate, respectively. The daily discharge limit in Canada from the literature review was 44 mg/l. Ionic liquid 1-benzyl-3-methylimidazolium tosylate with DAF is the best method to reach the rejection standard compared to the other two ionic liquids. Graphical representation of the oil content is presented in Figure 4.7.

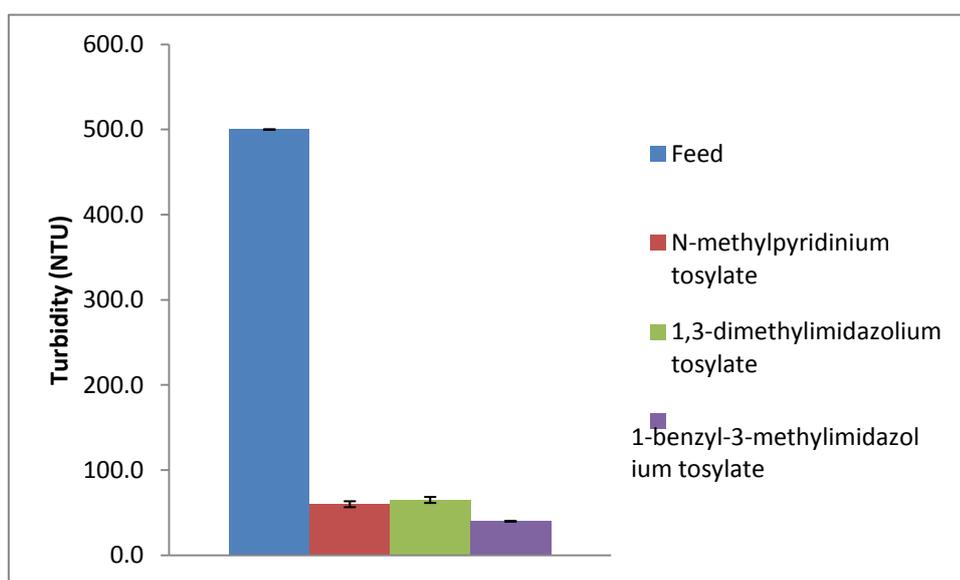
**Figure 4.7:** Comparison of oil content removal for different ionic liquids.

As shown in Figure 4.8, the zeta potential increased from  $-29.2 \pm 0.6$  mV (feed water) to  $-10.2 \pm 0.4$  mV (n-methylpyridinium tosylate),  $-13.3 \pm 0.1$  mV (1,3-dimethylimidazolium tosylate), and  $-2.3 \pm 0.4$  mV (1-benzyl-3-methylimidazolium tosylate), respectively. It was observed that the least oil content has a zeta potential that approached zero. The zeta potential value changed from around -30 mV, which is considered as a stable status, to -2.3 mV, which is considered as a non-stable emulsion. These data suggest that ionic liquid dissolved in feed water can break the stable colloidal solution. The reason may be that: first, adding ionic liquids increased the amount of ions in the produced water which has effect on double layer structure of colloid solution; second, these three ionic liquids have a strong acid group and a weak base group, which will increase the number of cations in the produced water. In addition, oil droplets have negative charges, and the removal of oil content by DAF will increase the zeta potential.



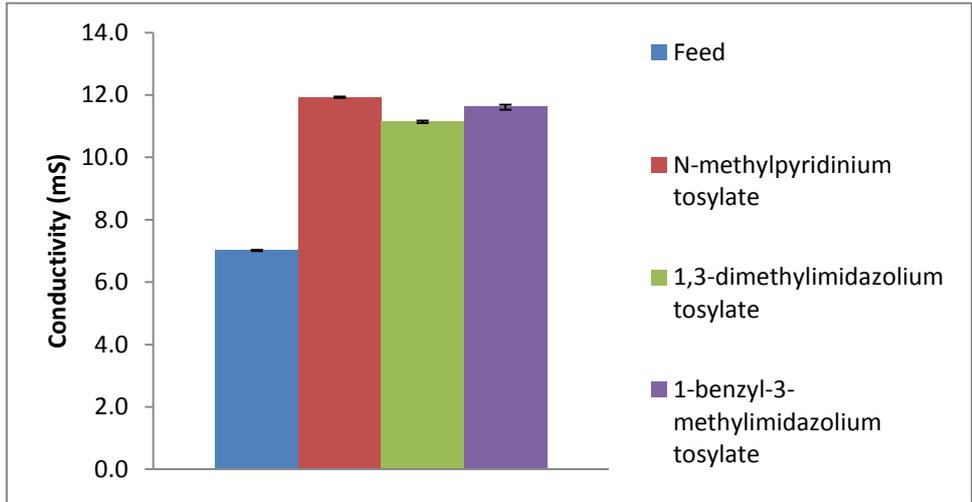
**Figure 4.8:** Comparison of the zeta potential for different ionic liquids.

The turbidity decreased dramatically from  $500.0 \pm 0.0$  NTU of synthetic produced water to  $60.0 \pm 3.5$  NTU of n-methylpyridinium tosylate,  $65.0 \pm 3.5$  NTU of 1,3-dimethyl imidazolium tosylate, and  $40.0 \pm 0.0$  NTU of 1-benzyl-3-methylimidazolium tosylate. The lower the oil content, the lower the turbidity concluded from the data. The corresponding graphic display is shown in Figure 4.9.



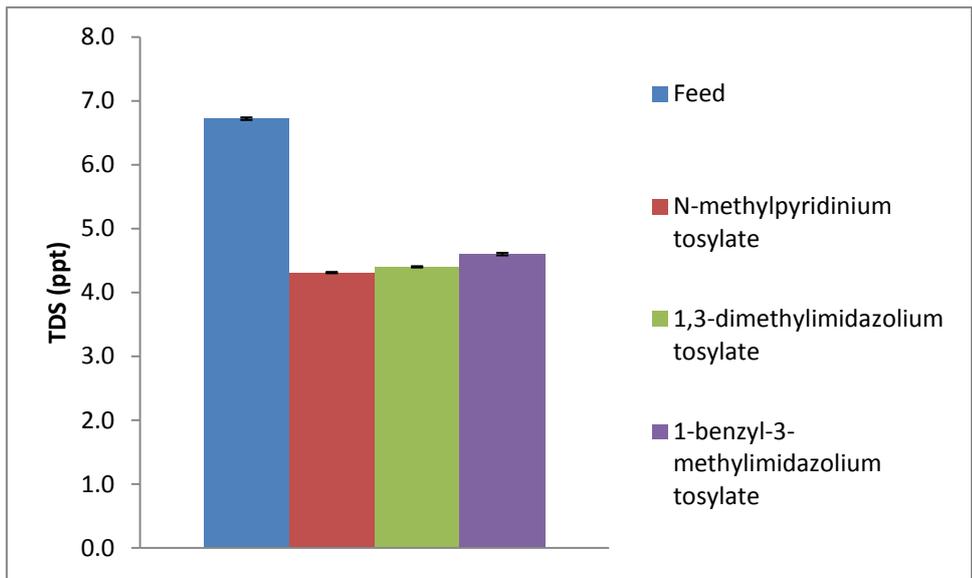
**Figure 4.9:** Comparison of the turbidity levels for different ionic liquids.

The conductivity increased from  $7.02 \pm 0.02$  mS for feed water to  $11.93 \pm 0.02$  mS,  $11.14 \pm 0.04$  mS, and  $11.61 \pm 0.08$  mS for n-methylpyridinium tosylate, 1,3-dimethyl-imidazolium tosylate, and 1-benzyl-3-methylimidazolium tosylate, respectively. Figure 4.10 shows the obtained results. Dissolved oil droplets in feed water have an effect on conductivity. Degradation of the oil content will increase water conductivity. Moreover, adding ionic liquids increased the concentration of ions in produced water. This is another reason that can explain why the conductivity increased.



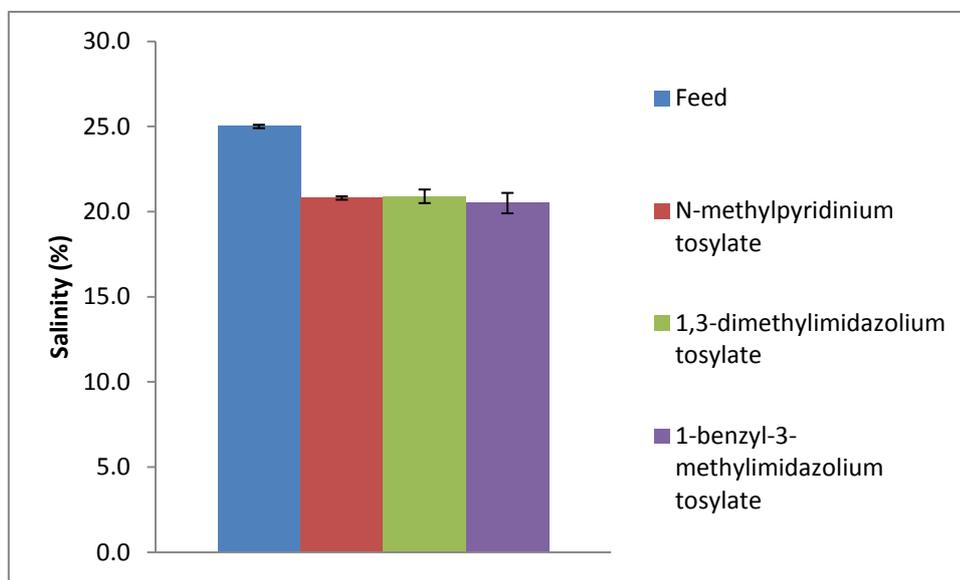
**Figure 4.10:** Comparison of conductivity after the addition of different ionic liquids.

The TDS value decreased because the DAF process dislodged solid particles, which dissolved in the feed water. The TDS decreased slightly from  $6.72 \pm 0.02$  ppt of feed water to  $4.31 \pm 0.01$  ppt of n-methylpyridinium tosylate,  $4.40 \pm 0.01$  ppt of 1,3-dimethylimidazolium tosylate, and  $4.60 \pm 0.02$  ppt of 1-benzyl-3-methylimidazolium tosylate. The comparison of the TDS results is reported in Figure 4.11.



**Figure 4.11:** Comparison of TDS levels after the addition of different ionic liquids.

As Figure 4.12 shows, a small reduction was observed for salinity due to the fact that the recycle ratio was 20%. It was clearly found that, for all ionic liquids, the same salinity was reached around 20.5% after DAF.



**Figure 4.12:** Comparison of salinity after the addition of different ionic liquids.

The removal percentages of parameters for different ionic liquids are presented in Table 4.15. High removal percentages represent high efficiency in removing contaminants from feed water. After ionic liquid and DAF treatment, the zeta potential and conductivity increased. The definition of percentage changes is given as Eq.(8) shows:

$$\text{Removal Percentage (\%)} = (F_c - T_c) / F_c \times 100 \quad (8)$$

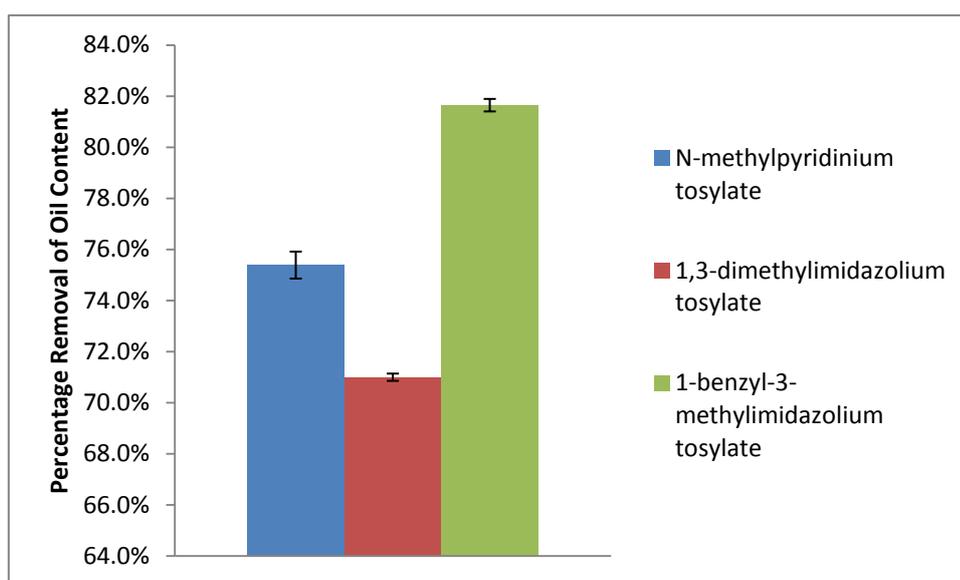
Where,  $F_c$  is the feed water concentration and  $T_c$  is the treatment water concentration.

**Table 4.15:** Percentage removal or percentage increase of different ionic liquids results.

| Parameter | N-methylpyridinium tosylate | 1,3-Dimethylimidazolium tosylate | 1-Benzyl-3-methylimidazolium tosylate |
|-----------|-----------------------------|----------------------------------|---------------------------------------|
|           |                             |                                  |                                       |

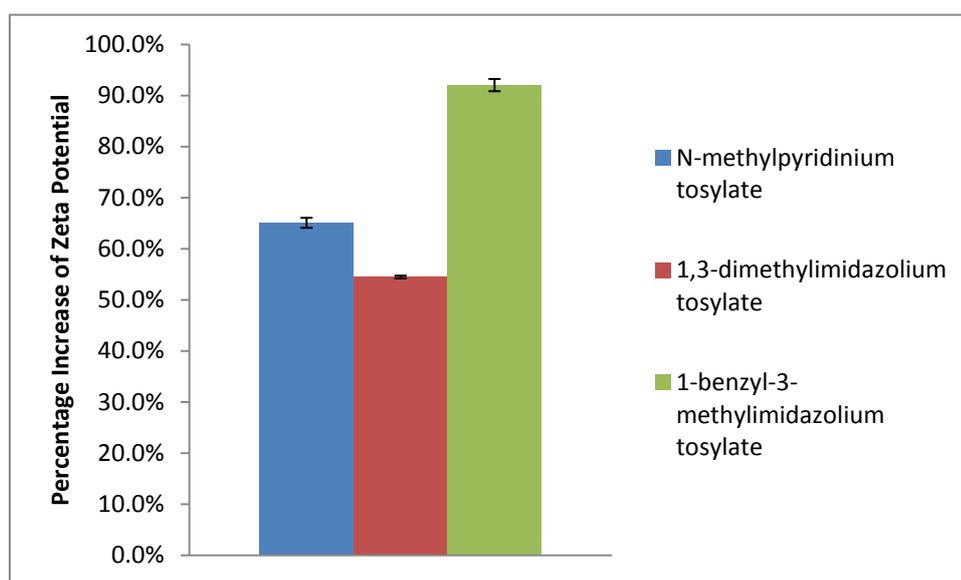
|  |              |              |              |
|--|--------------|--------------|--------------|
| <b>Percentage removal of oil content</b>     | 75.4% ± 0.7% | 71.0% ± 0.2% | 81.6% ± 0.3% |
| <b>Percentage increase of zeta potential</b> | 65.1% ± 1.5% | 54.5% ± 0.5% | 92.0% ± 1.3% |
| <b>Percentage removal of turbidity</b>       | 88.0% ± 0.7% | 87.0% ± 0.7% | 92.0% ± 0.0% |
| <b>Percentage increase of conductivity</b>   | 70.4% ± 0.3% | 59.1% ± 0.5% | 65.9% ± 1.3% |
| <b>Percentage removal of TDS</b>             | 35.7% ± 0.1% | 34.3% ± 0.1% | 31.3% ± 0.4% |
| <b>Percentage removal of salinity</b>        | 16.8% ± 0.6% | 16.4% ± 1.7% | 18.0% ± 2.3% |

The percentages of the removal of oil content were 75.4% ± 0.7%, 71.0% ± 0.2%, and 81.6% ± 0.3% for n-methylpyridinium tosylate, 1,3-dimethylimidazolium tosylate, and 1-benzyl-3-methylimidazolium tosylate, respectively. It is easy to conclude that 1-benzyl-3-methylimidazolium tosylate had the highest oil content removal ability. Graphical representations of oil content removal percentages are shown in Figure 4.13.



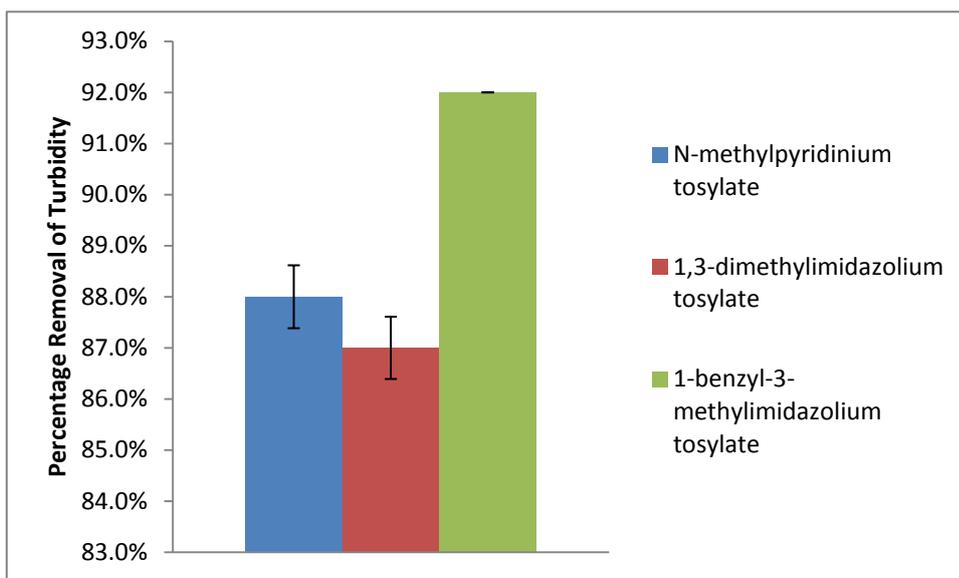
**Figure 4.13:** Percentages of the removal of oil content for the three ionic liquids.

Figure 4.14 displays the percentage increase of the zeta potential as  $65.1\% \pm 1.5\%$  for n-methyl pyridinium tosylate ,  $54.5\% \pm 0.5\%$  for 1,3-dimethylimidazolium tosylate, and  $92.0\% \pm 1.3\%$  for 1-benzyl-3-methylimidazolium tosylate. The highest percentage increase of the zeta potential implies that 1-benzyl-3-methylimidazolium tosylate decreased the stability of particles in the produced water further than the other two ionic liquids.



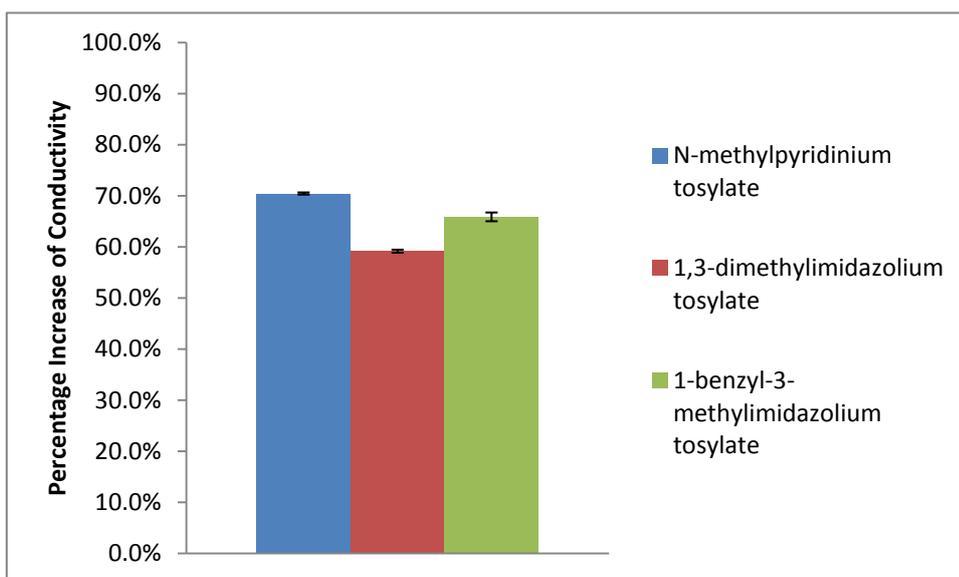
**Figure 4.14:** Percentage increase of the zeta potential for three ionic liquids.

The finding that turbidity removal has a high relation with oil removal was proved in the previous paragraph. The percentage removal of turbidity also conforms to the percentage removal of oil content. The order was 1-benzyl-3-methylimidazolium tosylate > n-methylpyridinium tosylate > 1,3-dimethylimidazolium tosylate, which is graphically presented in Figure 4.15.



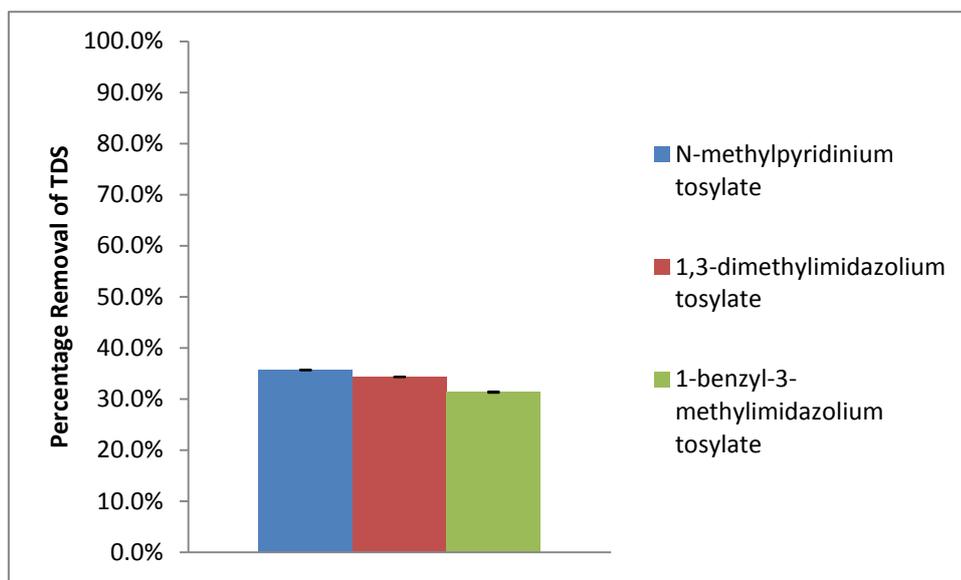
**Figure 4.15:** Percentage removal of turbidity for three ionic liquids.

The percentage increases of conductivity were  $70.4\% \pm 0.3\%$  for n-methylpyridinium tosylate,  $59.1\% \pm 0.5\%$  for 1,3-dimethylimidazolium tosylate, and  $65.9\% \pm 1.3\%$  for 1-benzyl-3-methylimidazolium tosylate. Conductivity is a complicated index, which is related to the concentration of ions and oil particles in water. For this research, these three ionic liquids have similar conductivity increase percentages. Figure 4.16 shows the percentage increase of conductivity for the 3 ionic liquids.

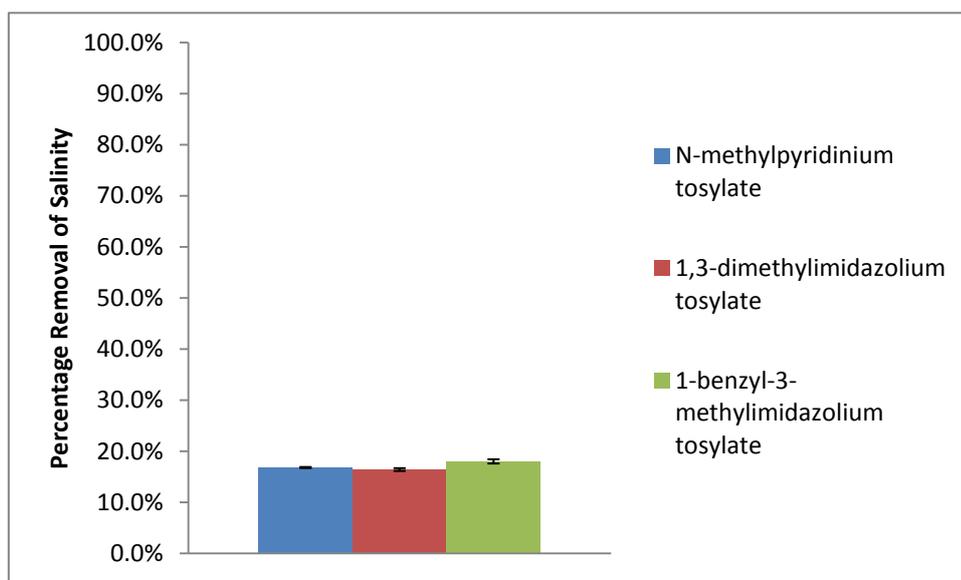


**Figure 4.16:** Percentage increase of conductivity for three ionic liquids.

The percentages of the removal of TDS and salinity for each ionic liquid are the same (around 33% and 16%, respectively). This proves that different ionic liquids with DAF treatment have the same capacity to remove dissolved solid and ions. Figures 4.17 and 4.18 illustrate the TDS and salinity percentage removal.

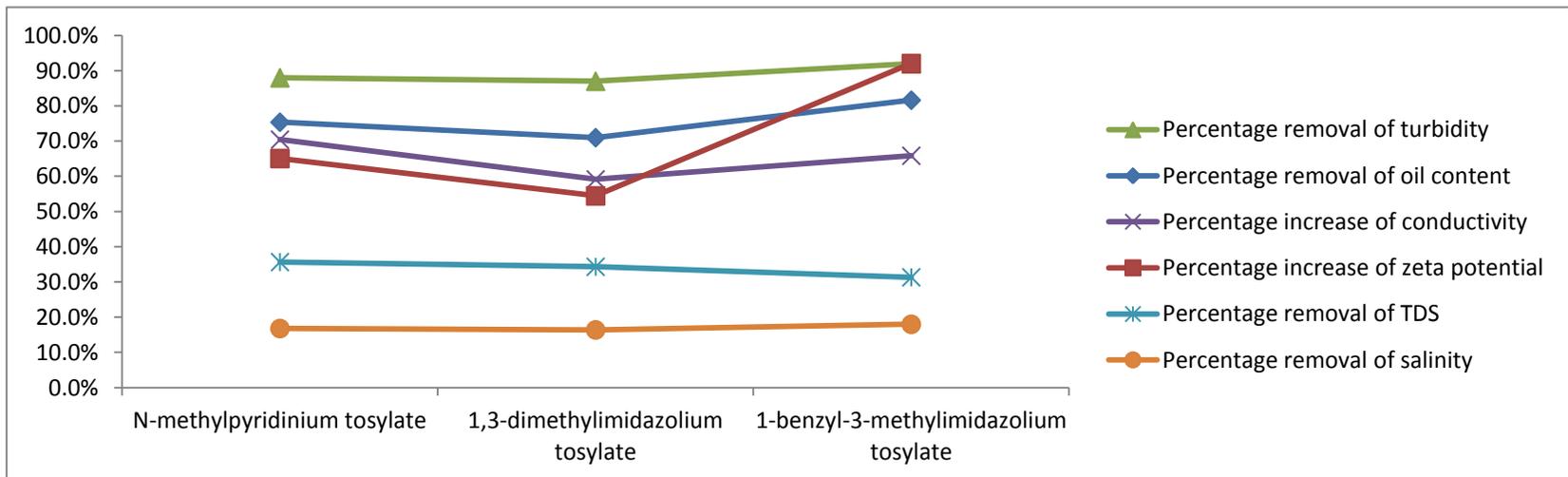


**Figure 4.17:** Percentage of removal of TDS for three ionic liquids.



**Figure 4.18:** Percentage of removal of salinity for the three ionic liquids.

The percentages of removal (increase) of different parameters in this research are shown in Figure 4.19. Comparing the result indicators, a high percentage of removal (or increase) can be observed for turbidity, oil content, zeta potential, and conductivity ranging from  $59.1\% \pm 0.5\%$  to  $92.0\% \pm 1.3\%$ . At the same time, a low percentage of removal can be found by TDS and salinity ranging from  $16.4\% \pm 1.7\%$  to  $35.7\% \pm 0.1\%$ . Taken together, these results suggest that turbidity and oil content have the highest percentage removal, which is over 70%. The TDS and salinity removal percentages were small (16-35%). Medium percentage changes (around 60%) were indicated by the parameters of conductivity and zeta potential. According to these comparisons, ionic liquids as a pretreatment to DAF is effective in removing suspended and dispersed particles such as oil droplets; however, they are ineffective in the removal of dissolved particles, such as salt ions, which was expected.



**Figure 4.19:** Percentage change of different parameters for the three ionic liquids.

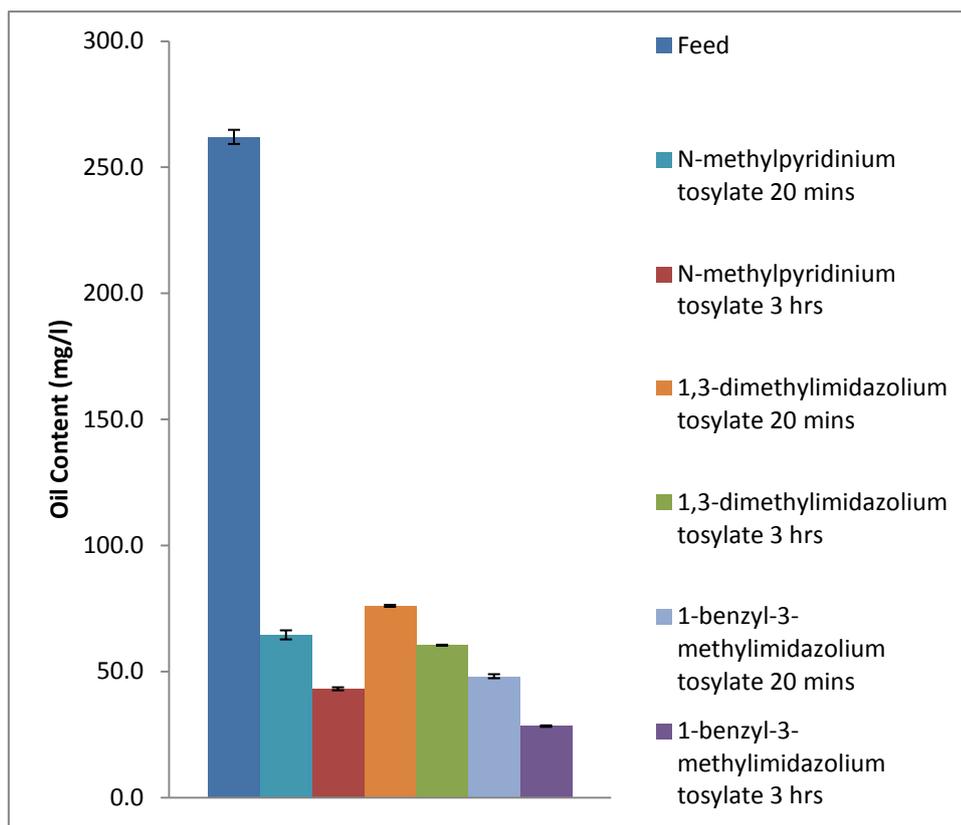
#### 4.2.6 Different flotation times

Tables 4.16 and 4.17 display, after 3 hours of flotation time, the oil content and removal percentage of the oil content for the three kinds of ionic liquids. It can be observed that 1-benzyl-3-methylimidazolium tosylate still has the lowest oil content and highest oil removal efficiency. 1-benzyl-3-methylimidazolium tosylate has an oil content of  $28.3 \pm 0.3$  mg/l, which is below the Canada discharge standard (the maximum monthly average standard discharge of oil and grease content is 30 mg/l). The oil content of n-methylpyridinium tosylate is  $43.1 \pm 0.6$  mg/l, which is also below the daily discharge limit of 44 mg/l in Canada.

**Table 4.16:** Oil content after 3 hours of flotation.

| <b>Parameter</b>              | <b>Feed</b>   | <b>n-methyl<br/>pyridinium<br/>tosylate</b> | <b>1,3-dimethylimi<br/>dazolium<br/>tosylate</b> | <b>1-benzyl-3-methyl<br/>imidazolium<br/>tosylate</b> |
|-------------------------------|---------------|---|--|---|
| <b>Oil Content<br/>(mg/l)</b> | $262 \pm 2.8$ | $43.1 \pm 0.6$                              | $60.4 \pm 0.2$                                   | $28.3 \pm 0.3$  |

Graphical representation of the oil content of feed water and three kinds of ionic liquids with two different flotation times is presented in Figure 4.20. The three hour floatation time had a lower oil content than the 20 minute floatation time on the whole. These data are consistent with the notion that oil droplets will segregate with water automatically by gravity.

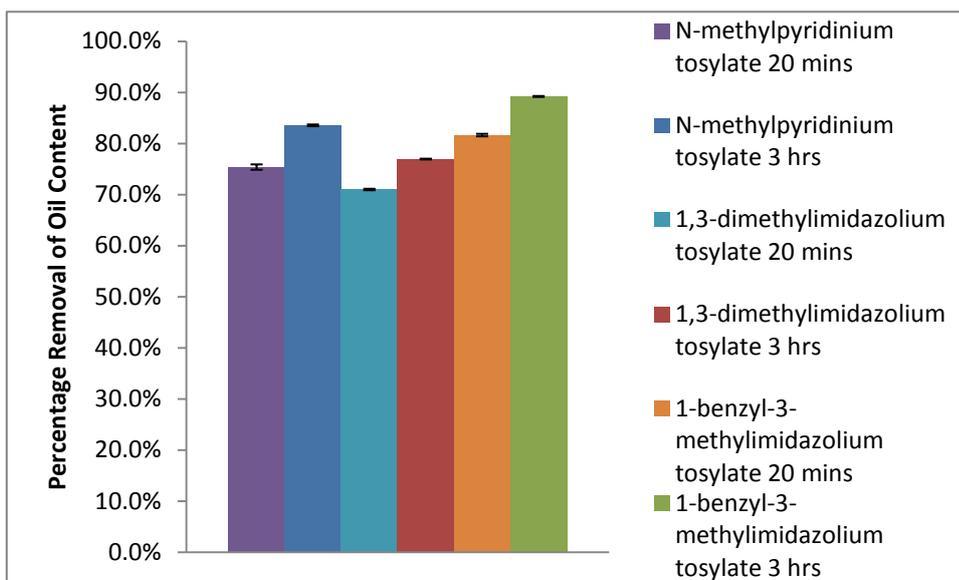


**Figure 4.20:** Comparison of oil content.

**Table 4.17:** Percentage removal of oil content after 3 hours of flotation.

| Parameter                         | n-methylpyridinium tosylate | 1,3-Dimethyl imidazolium tosylate | 1-benzyl-3-methyl imidazolium tosylate |
|-----------------------------------|-----------------------------|-----------------------------------|--|
| Percentage removal of oil content | 83.6% ± 0.2%                | 77.0% ± 0.1%                      | 89.2% ± 0.1%                           |

Figure 4.21 shows the oil removal percentage of the three kinds of ionic liquids with two different flotation times. Generally, after three hours of flotation time, the liquids had a higher oil removal efficiency. The percentage variances between different flotation times for each ionic liquid were similar (around 7%).



**Figure 4.21:** Percentage removal of oil content.

## CHAPTER 5: SUMMARY AND CONCLUSION

### 5.1 Summary

In this research, ionic liquids were used as pretreatment step to the dissolved air flotation (DAF) technique for synthetic produced water treatment. Dissolved air flotation is a recognized method in produced water treatment; however, it was not capable of removing oil content to the level required by regulatory standards. Based on literature review, the most common water treatment coagulants are aluminous and ferric salts. However iron salts are very sensitive to pH and will cause serious environmental problems. Comparing to those coagulants, ionic liquids has a tremendous advantage which is environmentally harmless. Flocculants can be added before the process of coagulant mixing in order to get better results, but the treatment process, time and cost will accordingly increase.

In this study, Ionic liquid as an eco-friendly coagulant was added. Three ionic liquids were selected with the same anion and similar cations. In order to maintain consistency in the experiments, synthetic produced water was prepared following the same procedure and it was used immediately. An  $L_8(4^1 \times 2^4)$  orthogonal array design table (OADT) was used to guide the different experiments. Two blank columns were set up for error estimation. Orthogonal experimental design (OED) is a fast, efficient, and economic experimental design method.

In this research, three factors were studied simultaneously. Different factors arranged in different levels can save reagent and energy. Range analysis and variance analysis (ANOVA) were applied to understand factor influence and determine the best

operating conditions. According to the OADT, the ionic liquid concentration, stirring RPM, and recycle ratio (RR) with corresponding levels were investigated in this study. Several parameters such as oil content, zeta potential, turbidity, conductivity, total dissolved solid (TDS), and salinity were measured for feed water in the different experiments to find the optimal coagulant and operation conditions. Three analogous ionic liquids were compared to understand the structure and cation effects on oil removal.

The results obtained in this research can be summarized as follows:

- Among the three ionic liquids used, in 20 minutes of floatation time, the highest oil removal efficiency was  $81.6\% \pm 0.3\%$  for 1-benzyl-3-methylimidazolium tosylate at the concentration of 300 mg/l, the RPM of 200, and the recycle ratio (RR) of 20%. The corresponding turbidity removal efficiency was  $92.0\% \pm 0.1\%$ .
- After 3 hours of flotation time, the oil removal efficiency of all ionic liquids increased to almost the same percentage. 1-Benzyl-3-methylimidazolium tosylate still showed the best result with  $28.3 \pm 0.3$  mg/l oil content and with an oil removal percentage of  $89.2\% \pm 0.1\%$ . The final concentration was below the monthly oil and grease discharge limit in Canada (30 mg/l). Comparing the percentage removal of oil content with other research studies, this study shows a similar performance. Using another pretreatment technique, a total of 79.5% of oil was removed using organic clay adsorption combined with DAF with an organic clay dose of 300 mg/l and a RR of 10% (Jaji, 2012). A total of 81% of

oil was removed when DAF was combined with polymer addition with a cationic polymer of 5 mg/l and a RR of 30% (Lance, 2008).

- In the same research group, Abbasi (2014) applied five types of coagulants (one iron salt and four ionic liquids) in produced water treatment with DAF system. The results showed the best removal efficiency of oil was aluminous salts (93.83%). The best result of four types of ionic liquids was 1-methyl-3-ctylimidazolium hexafluorophosphate (93.26%), which is better than this research ( $89.2\% \pm 0.1\%$ ). The reasons could be the used oil elements are different.
- According to the range analysis of OED, all three ionic liquids have the same influential order of the three factors on the oil content: ionic liquid concentration>RPM>RR. The optimum operation conditions of oil removal efficiency for all ionic liquids in this study were deduced as 300 mg/l for ionic liquid concentration, 200 for RPM, and 20% for RR, respectively.
- The variance analysis (ANOVA) is in agreement with the range analysis. Ionic liquid concentration and RPM had a significant effect on oil content removal ( $p<0.01$ ) for the three ionic liquids. The F value of concentration was higher than the RPM. The recycle ratio (RR) has no effect on the oil content indicator. For all ionic liquids, turbidity removal versus oil removal has a high coefficient of determination ( $R^2$ ), which indicates that these parameters are directly related to each other. For example, an increase in oil removal caused an increase in turbidity removal and vice versa.

- Compared to the feed water, after ionic liquids were used in the DAF treatment, parameters such as oil content, turbidity, TDS, and salinity decreased. The parameters of zeta potential and conductivity increased. These parameters have similar trends and vary in accordance with each other. In other words, these parameters have a relation with each other.
- As expected, a low percentage of removal was found in TDS removal and salinity removal (less than  $35.7\% \pm 0.1\%$ ). A high percentage of removal was observed for oil content removal and turbidity removal (up to  $92.0\% \pm 1.3\%$ ). This proves that ionic liquid with DAF was ineffective in dissolved particles removal and it was effective in the removal of suspended as well as dispersed particle removal.
- For the three kinds of ionic liquids, an increase ionic liquid concentration from 100 to 300 mg/l increased the oil removal efficiency. Further increasing the concentration will decrease the oil removal efficiency. As RPM and RR increased, the oil removal efficiency increased.
- At the same operating conditions, n-methylpyridinium tosylate had better oil removal results and high zeta potential than 1,3-dimethylimidazolium tosylate. This can be explained as n-methylpyridinium tosylate and 1,3-dimethylimidazolium tosylate have the same tosylate anion, which is a strong acid group. N-methylpyridinium tosylate has a pyridine base and 1,3-dimethylimidazolium tosylate has an imidazole base. Imidazole has a

stronger alkalinity than pyridine, which means imidazole has a higher value of  $K_b$ . The relationship of  $K_b$  and  $pK_b$  is shown in Eq. (9):

$$pK_b = -\log_{10}K_b \quad (9)$$

The equation indicates that 1,3-dimethylimidazolium tosylate has a lower  $pK_b$ , which means 1,3-dimethylimidazolium tosylate has a higher pH than n-methylpyridinium tosylate when solved in feed water. As mentioned in Chapter 3, pH has a direct influence on the zeta potential. A stronger  $pK_b$  has a better zeta potential improvement.

- Note that, when comparing the structures of 1-benzyl-3-methylimidazolium tosylate with n-methylpyridinium tosylate and 1,3-dimethylimidazolium tosylate, the first ionic liquid has one more ring. In other words, 1-benzyl-3-methyl imidazolium tosylate has a bigger structure and a heavier weight molecular structure. As detailed in Chapter 3, the reason the DAF system works well for small particles is due to buoyancy. Larger particles will slow bubble speed and increase the attach time. Consequently, larger particles will increase DAF efficiency.
- Orthogonal array design proved to be efficient in this study, as similar structures of ionic liquids lead to the same factor influence order and the same ANOVA results.

## 5.2 Conclusion

The experimental results indicate that, within the same operating conditions (concentration, RPM, and RR), 1-benzyl-3-methylimidazolium tosylate had the

highest oil and turbidity removal efficiency compared to n-methylpyridinium tosylate and 1,3-dimethylimidazolium tosylate. In terms of structure, 1-benzyl-3-methylimidazolium tosylate has one more carbon ring than the two other ILs. For similarly structured ionic liquids, the one with the “bigger” structure and heavier molecular mass will achieve better oil removal results.

The influential order for the three factors was studied in this research simultaneously. According to the variance analysis (ANOVA) and range analysis, the three ionic liquids have the same influential order for the three factors. The order is ionic liquid concentration>RPM>RR.

The best operation conditions for three ionic liquids are 300 mg/l for ionic liquid concentration, 200 for RPM, and 20% for RR.

At the best operating conditions, the percentage of removal of oil content were  $75.4\% \pm 0.7\%$ ,  $71.0\% \pm 0.2\%$ , and  $81.6\% \pm 0.3\%$  for n-methylpyridinium tosylate, 1,3-dimethylimidazolium tosylate, and 1-benzyl-3-methylimidazolium tosylate, respectively. The corresponding turbidity removal percentages were  $88.0\% \pm 0.7\%$ ,  $87.0\% \pm 0.7\%$ , and  $92.0\% \pm 0.0\%$ , respectively. Ionic liquids can therefore be considered as promising solvents for the pretreatment of produced water for produced water treatment.

Increasing RPM and RR will increase oil removal efficiency in this study. At low concentration, increasing ionic liquid concentration will help decrease oil content in synthetic produced water; however, a high concentration of ionic liquid will improve oil content by comparing low ionic liquid concentration.

It can be concluded that, after analysis of the results for the three ionic liquids, oil removal has a linear relationship with turbidity removal.

Comparing the result indicators, a high percentage of removal (or increase) can be observed by turbidity, oil content, zeta potential, and conductivity, and a low percentage of removal can be found for TDS and salinity. This indicates that ionic liquid as a pretreatment with the DAF system is effective in removing particles that are suspended in the produced water rather than dissolved in the produced water.

In this study, ionic liquid can increase zeta potential and break the stable status of oil colloid solution. Produced water treated by 1-benzyl-3-methylimidazolium tosylate for 20 minutes retention time has a zeta potential close to zero ( $-2.3 \pm 0.4$  mV) which is the most unstable status.

After 3 hours flotation time, the oil content of produced water decreased around 7% for all of the ionic liquids, comparing 20 minutes flotation time. The oil decline is caused by gravity separation. 1-benzyl-3-methylimidazolium tosylate still has the lowest oil content of  $28.3 \pm 0.3$  mg/l and the highest oil removal efficiency of  $89.2\% \pm 0.1\%$ .

Finally, based on this and group member's study, the use of ionic liquid as a pretreatment to DAF system is an environmentally friendly and effective method in removing oil but also suspended particles in produced water.

## CHAPTER 6: RECOMMENDATIONS

The following recommendations are suggested for future work:

- Designing four or five factors in OADT simultaneously. In addition to the factors used in this study, factors such as pressure, paddle type, etc., can be studied.
- Setting each factor at the same level to compare the results to those obtained for factors at different levels.
- Applying other DOE techniques (such as factorial design and fractional factorial design) to the same ionic liquids.
- Designing factors interaction OED to observe the interaction between each factor. Technically, each factor will affect another, and some interaction influence might be even stronger than single factor influence.
- Combining ionic liquid and the DAF treatment technique with other methods such as organic clay, active carbon, and membrane technology.
- Preparing the feed water with different salts to determine the effect of each salt.
- Using different oil types to make produced water such as heavy oil with more or less aromaticity.
- Scaling up the laboratory scale to plant scale.
- Trying different ionic liquids. For example, ionic liquids have the same cations but different anions.
- Using actual field produced water and comparing the results with synthetic produced water.
- Using nitrogen as a gas in the DAF instead of air.

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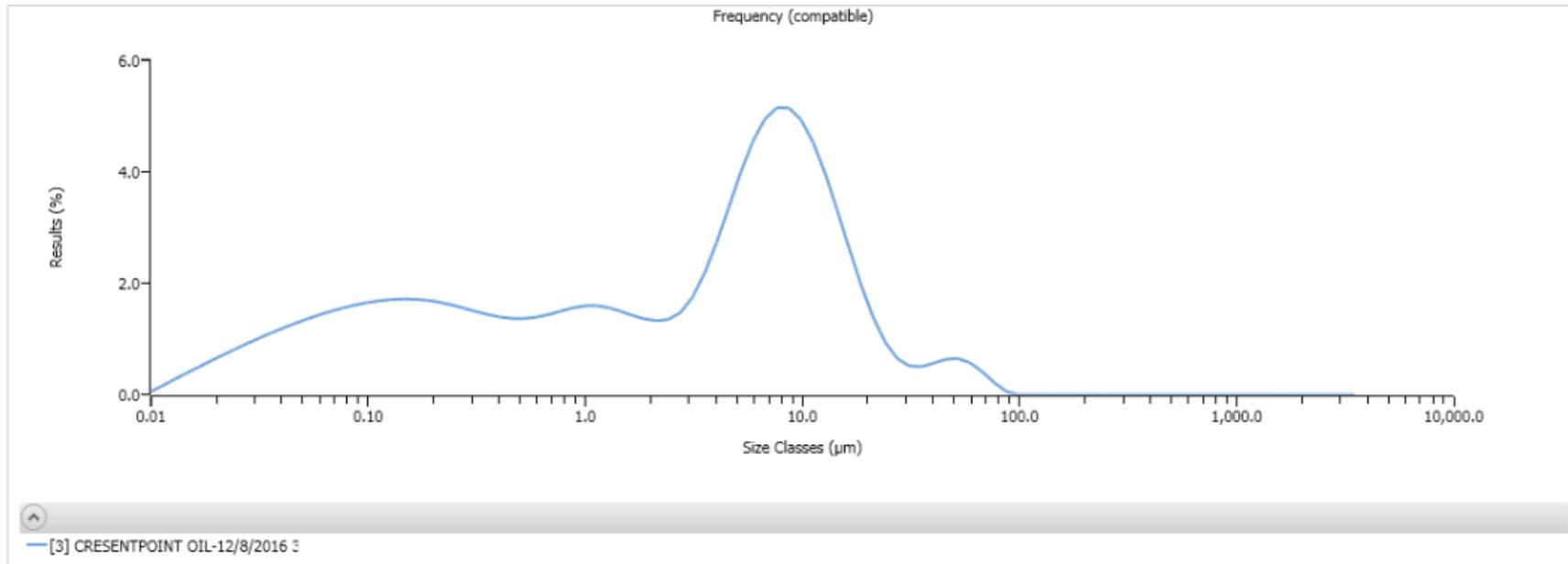
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## APPENDIX



|                  | Record Number | Sample Name      | Dv 10 (µm)    | Dv 50 (µm)  | Dv 90 (µm)  | Laser Obscuration (%) |
|------------------|---------------|------------------|---------------|-------------|-------------|-----------------------|
|                  | 3             | CRESENTPOINT OIL | 0.0643        | 3.45        | 15.2        | 9.46                  |
| <b>Mean</b>      |               |                  | <b>0.0643</b> | <b>3.45</b> | <b>15.2</b> | <b>9.46</b>           |
| <b>1xStd Dev</b> |               |                  | <b>0.00</b>   | <b>0.00</b> | <b>0.00</b> | <b>0.00</b>           |
| <b>1xRSD (%)</b> |               |                  | <b>0.00</b>   | <b>0.00</b> | <b>0.00</b> | <b>0.00</b>           |

**Figure A.1:** Oil particle size distribution in synthetic produced water.

F - Distribution ( $\alpha = 0.05$  in the Right Tail)

| df <sub>2</sub> \ df <sub>1</sub> |   | Numerator Degrees of Freedom |        |        |        |        |        |        |        |        |
|-----------------------------------|---|------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
|                                   |   | 1                            | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      |
| 1                                 | 1 | 161.45                       | 199.50 | 215.71 | 224.58 | 230.16 | 233.99 | 236.77 | 238.88 | 240.54 |
| 2                                 | 1 | 18.513                       | 19.000 | 19.164 | 19.247 | 19.296 | 19.330 | 19.353 | 19.371 | 19.385 |
| 3                                 | 1 | 10.128                       | 9.5521 | 9.2766 | 9.1172 | 9.0135 | 8.9406 | 8.8867 | 8.8452 | 8.8123 |
| 4                                 | 1 | 7.7086                       | 7.9443 | 6.5914 | 6.3882 | 6.2561 | 6.1631 | 6.0942 | 6.0410 | 6.9988 |
| 5                                 | 1 | 6.6079                       | 5.7861 | 5.4095 | 5.1922 | 5.0503 | 4.9503 | 4.8759 | 4.8183 | 4.7725 |
| 6                                 | 1 | 5.9874                       | 5.1433 | 4.7571 | 4.5337 | 4.3874 | 4.2839 | 4.2067 | 4.1468 | 4.0990 |
| 7                                 | 1 | 5.5914                       | 4.7374 | 4.3468 | 4.1203 | 3.9715 | 3.8660 | 3.7870 | 3.7257 | 3.6767 |
| 8                                 | 1 | 5.3177                       | 4.4590 | 4.0662 | 3.8379 | 3.6875 | 3.5806 | 3.5005 | 3.4381 | 3.3881 |
| 9                                 | 1 | 5.1174                       | 4.2565 | 3.8625 | 3.6331 | 3.4817 | 3.3738 | 3.2927 | 3.2296 | 3.1789 |
| 10                                | 1 | 4.9646                       | 4.1028 | 3.7083 | 3.4780 | 3.3258 | 3.2172 | 3.1355 | 3.0717 | 3.0204 |
| 11                                | 1 | 4.8443                       | 3.9823 | 3.5874 | 3.3567 | 3.2039 | 3.0946 | 3.0123 | 2.9480 | 2.8962 |
| 12                                | 1 | 4.7472                       | 3.8853 | 3.4903 | 3.2592 | 3.1059 | 2.9961 | 2.9134 | 2.8486 | 2.7964 |
| 13                                | 1 | 4.6672                       | 3.8056 | 3.4105 | 3.1791 | 3.0254 | 2.9153 | 2.8321 | 2.7669 | 2.7144 |
| 14                                | 1 | 4.6001                       | 3.7389 | 3.3439 | 3.1122 | 2.9582 | 2.8477 | 2.7642 | 2.6987 | 2.6458 |
| 15                                | 1 | 4.5431                       | 3.6823 | 3.2874 | 3.0556 | 2.9013 | 2.7905 | 2.7066 | 2.6408 | 2.5876 |
| 16                                | 1 | 4.4940                       | 3.6337 | 3.2389 | 3.0069 | 2.8524 | 2.7413 | 2.6572 | 2.5911 | 2.5377 |
| 17                                | 1 | 4.4513                       | 3.5915 | 3.1968 | 2.9647 | 2.8100 | 2.6987 | 2.6143 | 2.5480 | 2.4943 |
| 18                                | 1 | 4.4139                       | 3.5546 | 3.1599 | 2.9277 | 2.7729 | 2.6613 | 2.5767 | 2.5102 | 2.4563 |
| 19                                | 1 | 4.3807                       | 3.5219 | 3.1274 | 2.8951 | 2.7401 | 2.6283 | 2.5435 | 2.4768 | 2.4227 |
| 20                                | 1 | 4.3512                       | 3.4928 | 3.0984 | 2.8661 | 2.7109 | 2.5990 | 2.5140 | 2.4471 | 2.3928 |
| 21                                | 1 | 4.3248                       | 3.4668 | 3.0725 | 2.8401 | 2.6848 | 2.5727 | 2.4876 | 2.4205 | 2.3660 |
| 22                                | 1 | 4.3009                       | 3.4434 | 3.0491 | 2.8167 | 2.6613 | 2.5491 | 2.4638 | 2.3965 | 2.3419 |
| 23                                | 1 | 4.2793                       | 3.4221 | 3.0280 | 2.7955 | 2.6400 | 2.5277 | 2.4422 | 2.3748 | 2.3201 |
| 24                                | 1 | 4.2597                       | 3.4028 | 3.0088 | 2.7763 | 2.6207 | 2.5082 | 2.4226 | 2.3551 | 2.3002 |
| 25                                | 1 | 4.2417                       | 3.3852 | 2.9912 | 2.7587 | 2.6030 | 2.4904 | 2.4047 | 2.3371 | 2.2821 |
| 26                                | 1 | 4.2252                       | 3.3690 | 2.9752 | 2.7426 | 2.5868 | 2.4741 | 2.3883 | 2.3205 | 2.2655 |
| 27                                | 1 | 4.2100                       | 3.3541 | 2.9604 | 2.7278 | 2.5719 | 2.4591 | 2.3732 | 2.3053 | 2.2501 |
| 28                                | 1 | 4.1960                       | 3.3404 | 2.9467 | 2.7141 | 2.5581 | 2.4453 | 2.3593 | 2.2913 | 2.2360 |
| 29                                | 1 | 4.1830                       | 3.3277 | 2.9340 | 2.7014 | 2.5454 | 2.4324 | 2.3463 | 2.2783 | 2.2229 |
| 30                                | 1 | 4.1709                       | 3.3158 | 2.9223 | 2.6896 | 2.5336 | 2.4205 | 2.3343 | 2.2662 | 2.2107 |
| 40                                | 1 | 4.0847                       | 3.2317 | 2.8387 | 2.6060 | 2.4495 | 2.3359 | 2.2490 | 2.1802 | 2.1240 |
| 60                                | 1 | 4.0012                       | 3.1504 | 2.7581 | 2.5252 | 2.3683 | 2.2541 | 2.1665 | 2.0970 | 2.0401 |
| 120                               | 1 | 3.9201                       | 3.0718 | 2.6802 | 2.4472 | 2.2899 | 2.1750 | 2.0868 | 2.0164 | 1.9588 |
| ∞                                 | 1 | 3.8415                       | 2.9957 | 2.6049 | 2.3719 | 2.2141 | 2.0986 | 2.0096 | 1.9384 | 1.8799 |

Figure A.2: F-distribution for 0.05

F - Distribution ( $\alpha = 0.01$  in the Right Tail)

| df <sub>2</sub> | df <sub>1</sub> | Numerator Degrees of Freedom |        |        |        |        |        |        |        |        |
|-----------------|-----------------|------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
|                 |                 | 1                            | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      |
| 1               |                 | 4052.2                       | 4999.5 | 5403.4 | 5624.6 | 5763.6 | 5859.0 | 5928.4 | 5981.1 | 6022.5 |
| 2               |                 | 98.503                       | 99.000 | 99.166 | 99.249 | 99.299 | 99.333 | 99.356 | 99.374 | 99.388 |
| 3               |                 | 34.116                       | 30.817 | 29.457 | 28.710 | 28.237 | 27.911 | 27.672 | 27.489 | 27.345 |
| 4               |                 | 21.198                       | 18.000 | 16.694 | 15.977 | 15.522 | 15.207 | 14.976 | 14.799 | 14.659 |
| 5               |                 | 16.258                       | 13.274 | 12.060 | 11.392 | 10.967 | 10.672 | 10.456 | 10.289 | 10.158 |
| 6               |                 | 13.745                       | 10.925 | 9.7795 | 9.1483 | 8.7459 | 8.4661 | 8.2600 | 8.1017 | 7.9761 |
| 7               |                 | 12.246                       | 9.5466 | 8.4513 | 7.8466 | 7.4604 | 7.1914 | 6.9928 | 6.8400 | 6.7188 |
| 8               |                 | 11.259                       | 8.6491 | 7.5910 | 7.0061 | 6.6318 | 6.3707 | 6.1776 | 6.0289 | 5.9106 |
| 9               |                 | 10.561                       | 8.0215 | 6.9919 | 6.4221 | 6.0569 | 5.8018 | 5.6129 | 5.4671 | 5.3511 |
| 10              |                 | 10.044                       | 7.5594 | 6.5523 | 5.9943 | 5.6363 | 5.3858 | 5.2001 | 5.0567 | 4.9424 |
| 11              |                 | 9.6460                       | 7.2057 | 6.2167 | 5.6683 | 5.3160 | 5.0692 | 4.8861 | 4.7445 | 4.6315 |
| 12              |                 | 9.3302                       | 6.9266 | 5.9525 | 5.4120 | 5.0643 | 4.8206 | 4.6395 | 4.4994 | 4.3875 |
| 13              |                 | 9.0738                       | 6.7010 | 5.7394 | 5.2053 | 4.8616 | 4.6204 | 4.4410 | 4.3021 | 4.1911 |
| 14              |                 | 8.8616                       | 6.5149 | 5.5639 | 5.0354 | 4.6950 | 4.4558 | 4.2779 | 4.1399 | 4.0297 |
| 15              |                 | 8.6831                       | 6.3589 | 5.4170 | 4.8932 | 4.5556 | 4.3183 | 4.1415 | 4.0045 | 3.8948 |
| 16              |                 | 8.5310                       | 6.2262 | 5.2922 | 4.7726 | 4.4374 | 4.2016 | 4.0259 | 3.8896 | 3.7804 |
| 17              |                 | 8.3997                       | 6.1121 | 5.1850 | 4.6690 | 4.3359 | 4.1015 | 3.9267 | 3.7910 | 3.6822 |
| 18              |                 | 8.2854                       | 6.0129 | 5.0919 | 4.5790 | 4.2479 | 4.0146 | 3.8406 | 3.7054 | 3.5971 |
| 19              |                 | 8.1849                       | 5.9259 | 5.0103 | 4.5003 | 4.1708 | 3.9386 | 3.7653 | 3.6305 | 3.5225 |
| 20              |                 | 8.0960                       | 5.8489 | 4.9382 | 4.4307 | 4.1027 | 3.8714 | 3.6987 | 3.5644 | 3.4567 |
| 21              |                 | 8.0166                       | 5.7804 | 4.8740 | 4.3688 | 4.0421 | 3.8117 | 3.6396 | 3.5056 | 3.3981 |
| 22              |                 | 7.9454                       | 5.7190 | 4.8166 | 4.3134 | 3.9880 | 3.7583 | 3.5867 | 3.4530 | 3.3458 |
| 23              |                 | 7.8811                       | 5.6637 | 4.7649 | 4.2636 | 3.9392 | 3.7102 | 3.5390 | 3.4057 | 3.2986 |
| 24              |                 | 7.8229                       | 5.6136 | 4.7181 | 4.2184 | 3.8951 | 3.6667 | 3.4959 | 3.3629 | 3.2560 |
| 25              |                 | 7.7698                       | 5.5680 | 4.6755 | 4.1774 | 3.8550 | 3.6272 | 3.4568 | 3.3239 | 3.2172 |
| 26              |                 | 7.7213                       | 5.5263 | 4.6366 | 4.1400 | 3.8183 | 3.5911 | 3.4210 | 3.2884 | 3.1818 |
| 27              |                 | 7.6767                       | 5.4881 | 4.6009 | 4.1056 | 3.7848 | 3.5580 | 3.3882 | 3.2558 | 3.1494 |
| 28              |                 | 7.6356                       | 5.4529 | 4.5681 | 4.0740 | 3.7539 | 3.5276 | 3.3581 | 3.2259 | 3.1195 |
| 29              |                 | 7.5977                       | 5.4204 | 4.5378 | 4.0449 | 3.7254 | 3.4995 | 3.3303 | 3.1982 | 3.0920 |
| 30              |                 | 7.5625                       | 5.3903 | 4.5097 | 4.0179 | 3.6990 | 3.4735 | 3.3045 | 3.1726 | 3.0665 |
| 40              |                 | 7.3141                       | 5.1785 | 4.3126 | 3.8283 | 3.5138 | 3.2910 | 3.1238 | 2.9930 | 2.8876 |
| 60              |                 | 7.0771                       | 4.9774 | 4.1259 | 3.6490 | 3.3389 | 3.1187 | 2.9530 | 2.8233 | 2.7185 |
| 120             |                 | 6.8509                       | 4.7865 | 3.9491 | 3.4795 | 3.1735 | 2.9559 | 2.7918 | 2.6629 | 2.5586 |
| ∞               |                 | 6.6349                       | 4.6052 | 3.7816 | 3.3192 | 3.0173 | 2.8020 | 2.6393 | 2.5113 | 2.4073 |

Figure A.3: F-distribution for 0.01