

Okpala Chukwubuike

Flocculants in produced water

Master's thesis in Polymer Technology

Supervisor: Professor Gisle Oye

June 2020

NTNU
Norwegian University of Science and Technology
Faculty of Engineering
Department of Chemical Engineering



Norwegian University of
Science and Technology

Abstract

Produced water as the major by-product of oil and gas explorations contains high amounts of oil that are not safe for disposal into aquatic environment. With the increasing need for oil and gas across the globe, one of the major problems encountered is developing effective measures to properly treat and meet the regulation for reuse or disposal of produced water. Flocculation is an essential process in the treatment of produced water and involves the addition of flocculants during treatments to enhance effective separation of oil drops from water. Flocculation is however affected by the molecular weight of the flocculants, pH and salinity of the water. This work studied the effects of these factors on aggregation of flocculants in water.

Different concentrations of four flocculants of Polydiallyldimethylammonium chloride (PolyDADMAC) F100k, F200k, F350k and F500k having different molecular weights were prepared in varying pH and salt concentrations and tested. The aggregate size distribution, Polydispersity Index (PDI) and Zeta potential (ZP) were characterized with a zeta sizer. Adsorption to Silica surfaces using Quartz Crystal Microbalance with Dissipation (QCM-D) was also determined. It was found that the aggregate size distribution, PDI and ZP varied from one flocculant to another at different concentrations, indicating that the choice of flocculants for produced water treatment depends specifically on the water pH and salinity in addition to the flocculant's molecular weight. More mass was adsorbed at higher salinities and pH values and also depended on the type and concentration of the flocculant.

Sammendrag

Produsert vann som det viktigste biproduktet av leting etter olje og gass inneholder høye mengder olje som ikke er trygt for avhending i vannmiljøet. Med det økende behovet for olje og gass over hele kloden, er et av de største problemene som oppstår å utvikle effektive tiltak for å behandle og oppfylle forskriften for gjenbruk eller avhending av produsert vann riktig. Flokkulering er en essensiell prosess i behandlingen av produsert vann og innebærer tilsetning av flokkuleringsmidler under behandlinger for å forbedre effektiv separasjon av oljedråper fra vann. Flokkulering er imidlertid påvirket av pH og saltholdighet, og dette arbeidet studerte effekten av disse faktorene på aggregering av flokkuleringsmidler i vann.

Ulike konsentrasjoner av fire flokkuleringsmidler av Polydialldimetylammoniumklorid (PolyDADMAC) F100k, F200k, F350k og F500k med forskjellige molekylvekter ble fremstilt i varierende pH og saltkonsentrasjoner og testet. Flokkstørrelsesfordelingen, Polydispersity Index (PDI) og Zeta potensial (ZP) ble karakterisert med en zeta-størrelse. Adsorpsjon til silikondioksidoverflater ved bruk av Quartz Crystal Microbalance with Dissipation (QCM-D) ble også bestemt. Det ble funnet at fordelingen av flokkulasjonsstørrelsen, PDI og ZP varierte fra en flokkuleringsmiddel til en annen ved forskjellige konsentrasjoner som viser at valget av flokkuleringsmidler spesifikt avhenger av vannets pH og saltholdighet. Mer masse ble adsorbent ved høyere saltinnhold og pH-verdier og var også avhengig av typen og konsentrasjonen av flokkuleringsmiddelet.

Preface

This master thesis was carried out at the Department of Chemical Engineering in Norwegian University of Science and Technology (NTNU) for the fulfilment of a master's degrees in the Nordic five Technology after a one year studies in Aalto University Finland. The thesis studied flocculation of produced water and was written in spring 2020. Due to the pandemic caused by COVID-19 from March 2020, parts of the required experiments were skipped and replaced with theoretical reviews.

Acknowledgement

I wish to acknowledge my supervisor Professor Gisle øye for the success of this thesis work, also a huge thank you to my thesis co-supervisor Marcin Dudek (PhD.) for the tireless effort and advice towards making the technical and report aspects of this work a success. Gratitude all members of the Ugelstad Laboratory especially Jens Norman and Sebastien Simon for their guidance during the experimental part of this thesis.

Table of Contents

List of Figures	xii
List of Tables.....	xii
List of Abbreviations (or Symbols)	xiii
1 Introduction	14
2 Background.....	16
2.1 Petroleum production.....	16
2.2 Produced water.....	17
2.2.1 Produced water composition.	18
2.2.2 Produced water treatment.....	19
3 Produced water from polymer flooding.....	23
3.1 Polymer flooding.	23
3.2 Polymer flooding produced water (PFPW)	24
3.3 Treatment of PFPW.....	25
3.3.1 Water treatment	26
3.3.2 Water treatment strategies.....	26
3.3.2.1 Filtration	26
3.3.2.2 Gravity separators	29
3.3.2.3 Hydrocyclones	29
3.3.2.4 Centrifugation.....	29
3.3.2.5 Gas flotation.....	30
4 Emulsions and polymers in solution	31
4.1 Emulsion theory	31
4.1.1 Emulsion stability	31
4.1.2 Breakdown mechanism	31
4.1.3 Produced water as an emulsion.....	32
4.2 Flocculation mechanism	34
4.2.1 Polymer bridging.....	35
4.2.2 Electrostatic patch mechanism.....	36
4.3 Flocculants	37
4.3.1 Polymers in aqueous solution.....	37
4.3.2 Types of flocculants typical for produced water treatment	39
4.3.2.1 Non-Ionic flocculants	39
4.3.2.2 Anionic flocculants.....	40
4.3.2.3 Cationic flocculants	40
4.3.2.4 Amphoteric flocculants.....	41

4.3.3	Effects of different factors on flocculants.	41
4.3.3.1	Effects of pH.....	41
4.3.3.2	Salinity	43
4.3.3.3	Size and shape of polymers in water.	43
5	Experiments.....	45
5.1	Techniques.....	45
5.1.1	Zeta potential and size Characterization.....	45
5.1.2	Polydispersity Index determination.....	46
5.1.3	Adsorption to solid surfaces.....	46
5.2	Materials.....	47
5.2.1	Water solutions.....	47
5.2.2	Flocculants	47
5.3	Methods and Procedures	48
5.3.1	Size measurement in salt water	48
5.3.2	Zeta potential and size measurements.....	49
5.3.3	Adsorption on solid surface.....	49
6	Results	50
6.1	Size distribution	50
6.1.1	Effect of concentration	50
6.1.2	Effect of salinity	51
6.1.3	Effect of pH	52
6.2	Adsorption on solid surface.....	53
6.2.1	Effects of varying Varying salt concentrations.	53
6.2.2	Effects of pH.....	55
6.3	Adsorptions of each flocculant type at varying pH and salt.....	56
6.3.1	Effects of varying pH and salts on flocculant F500k.....	56
6.3.2	Effects of varying pH and salts on flocculant F350k.	56
6.3.3	Effects of varying pH and salts on flocculant F200k.	57
6.3.4	Effects of varying pH and salts on flocculant F100k.	58
7	Discussions	59
7.1	Influence on the size distribution and PDI.....	59
7.2	Influence on mass adsorbed	59
8	Conclusion	61
	Bibliography	63
	Appendices	67

List of Figures

Figure 2.1: Global daily demand for crude oil. (Sönnichsen, 2020).....	16
Figure 2.2: Volume of produced water in the NCS. (Norsk Olje and gass, 2017).	17
Figure 3.1: Oil recovery by polymer flooding. (Ahmed and Meehan, 2012).....	24
Figure 3.2: Breaking PFPW emulsions. (Huang <i>et al.</i> , 2019).....	26
Figure 3.3: Dead-end and cross-flow filtrations (left to right).(Igunnu and Chen, 2012)	28
Figure 3.4: PFPW desalination by electrodialysis. (Sosa-Fernandez <i>et al.</i> , 2018).....	29
Figure 4.1: Schematic illustration of coalescence process	32
Figure 4.2: PW emulsion stabilization. (McLean and Kilpatrick, 1997).....	34
Figure 4.3: Dispersion of polymer around the droplets	35
Figure 4.4: Adsorption of polymer chain unto droplet.	36
Figure 4.5: Polymer bridging of droplets.....	36
Figure 4.6: Schematic of a flocculation process. Deduced from (Pillai, 1997).....	37
Figure 4.7: Adsorption of different molecular weight polymers. (Kronberg, 2014)	38
Figure 4.8: Typical structure of a non-ionic polymer flocculants.....	40
Figure 4.9: Typical examples of anionic polymer flocculants.	40
Figure 4.10: Typical examples of cationic polymer flocculants.	41
Figure 4.11: Adsorption of cationic polymers at different pH values	42
Figure 4.12: Adsorption of polyacrylamide on silica at varying pH.(Kronberg, 2014)	42
Figure 5.1: Schematic of the DLS working principle. (Eberhard, 2012).	45
Figure 5.2: Folded capillary cell and Zeta Potential measurement. (Lazaro, 2014)	46
Figure 5.3: Schematic representation of the QCM-D setup.	47
Figure 5.4: Structure of Polydiallyldimethylammonium chloride.	48
Figure 6.1: Size distribution of the flocculants and their PDI.	50
Figure 6.2: Size distributions of the flocculants at varying salt concentrations.	51
Figure 6.3: PDI of the flocculants at varying salt concentrations.	52
Figure 6.4: Size distributions of the flocculants at varying pH levels.....	52
Figure 6.5: Zeta potentials of the flocculants.	53
Figure 6.6: Adsorption of the flocculants at 1000ppm NaCl concentration.	54
Figure 6.7: Adsorption of the flocculants at 35000ppm NaCl concentration.	54
Figure 6.8: Adsorption of the flocculants at pH3.	55
Figure 6.9: Adsorption of the flocculants at pH10	55
Figure 6.10: Effects of varying pH and NaCl on flocculant F500k.....	56
Figure 6.11: Effects of varying pH and NaCl on flocculant F350k.....	57
Figure 6.12: Effects of varying pH and NaCl on flocculant F200k.....	57
Figure 6.13: Effects of varying pH and NaCl on flocculant F100k.....	58

List of Tables

Table 2.1: Production chemicals used in North Sea. (Lee, 2011).....	19
Table 2.2: Oil and grease allowed for disposal in some countries. (Lee, 2011).....	20
Table 2.3: Produced water treatment Methods. (Arnold and Stewart, 1999).....	21
Table 5.1: Properties of Polydiallyldimethylammonium chloride.	48

List of Abbreviations (or Symbols)

NSC	Norwegian Continental shelf
TOC	Total Organic Carbon
EOR	Enhanced Oil Recovery
PFPW	Polymer flooding Produced water
NaCl	Sodium Chloride
PDI	Poly Dispersity Index
PPM	Parts Per Million
O/W	Oil in Water
W/O	Water in Oil
ZP	Zeta Potential
F100k	Flocculant 100 thousand MW (maximum)
F200k	Flocculant 200 thousand MW (maximum)
F350k	Flocculant 350 thousand MW (maximum)
F500k	Flocculant 500 thousand MW (maximum)
DLS	Dynamic Light Scattering
dH	Hydrodynamic diameter
K	Kelvin
API	American Petroleum Institute
TDS	Total dissolved salts
PolyDADMAC	Poly-Diallyldimethylammonium chloride
PW	Produced water
SARA	Saturate Aromatic Resin Asphaltene
Nm	Nano meters
ATBS	2-Acrylamide-2-methylpropane sulfonic acid
ELS	Electrophoretic Light Scattering

1 Introduction

Petroleum is one of the most important substances consumed largely on a global scale. It is used as source of fuel and energy for transportation in addition to wide applications in plastics, paints, medicine, fertilizers, cosmetics, insecticides, cooking and much more areas of our daily live sustenance. The source of petroleum is dead remaining of plants and animals buried underground over a long period of time where the activities of heat and pressure transform these remains into crude oil. Crude oil trapped underground in formations known as reservoirs is brought to the surface during recovery processes together with large volumes of water called produced water. In the beginning, the pressure of oil and gas from the reservoir is enough to bring them to the surface, but this pressure continues to drop as the well ages, leading to the use of Enhanced Oil Recovery techniques (EOR) to force the oil and gas to the surface. EOR uses production chemicals and large volumes of water to push the petroleum to the surface.

The large volumes and contents of the produced water generated during oil recovery is of huge concern to the world. The water is toxic to the environment and ecosystem at large due to the presence of components that are classified as harmful by Environmental protection agencies. Treatments requiring equipment and chemicals are used all over the world to reduce these components to the required or tolerable amounts that could be discharged into the environment or reused in the oil industries for further recovery.

The flocculants used in produced water treatment is mostly in the form of polymers in solution. These synthetic water-soluble polymers have high molecular weight distributions that make them excellent choice for bridging oil droplets and enhancing flocculation. Polyelectrolytes also reduce the potential energy of repulsion of oil droplets through charge interactions, thus making them essential in treatments of different types of charged produced water. Though different types of polymers exist for produced water treatment, the majority are from water-soluble ionic polymers (polyelectrolytes) with high molecular weights.

There are different techniques available for treating produced water, they mostly involve the use of chemical coagulants and flocculants to increase the phase separation of the oil from water before using equipment to remove the oil and other solids. In Oil and gas Industries the aim of the treatment is to reduce dispersed components of the water. The choice of chemical and equipment to use for produced water treatment depends on the required outcome, for instance generating 30 mg/L of oil drops in water as required by most Legislations.

Produced water components like salinity and pH affects the choice of chemical substance used for flocculation and the overall outcome of the treatment of produce water. The choice for the flocculant to use therefore depends greatly on the extent these factors affect the flocculant. This study involved the experimental analysis of the effects of these factors on flocculation in produced water treatment. The theoretical parts of this work review produced water, treatment strategies and components, emulsions and flocculation, PFPW and the various methods for characterizing produced water. The practical part of this work consists of analysis of a polymeric flocculant in water at

varying concentrations of salt and pH as a means for testing the effects of these factors on flocculation of produced water.

2 Background.

2.1 Petroleum production

The growing need for petroleum and its resources all over the world has necessitated the building of more rigs and expansion of the petroleum industries to meet these needs. The major elements that constitute petroleum include Carbon (87%), Oxygen (0.5%), Sulphur (6%), Nitrogen (2%), Hydrogen (14%) and metals (0.1%) at their maximum values. (Ancheyta and Ancheyta, 2011) Petroleum could be grouped into Heavy and light crude oils depending on the amounts of these elements measured in terms of Hydrocarbons and impurities in addition to the API gravity. Records show that these substances vary in heavy and light crude oils, hence the difference in crude oil types around the world. The hydrocarbon contents of petroleum are in the form of Saturates, Aromatics, Resins, and Asphaltenes (SARA) arranged in order of their increasing polarity, density, and aromaticity.

Petroleum production is continually increasing all over the world each year, report shows that in 2016, 1.5 billion barrels of oil was sold in the Norwegian Continental shelf (NCS) alone with an increase of 1.1% as compared to the previous year (2015).(Gass, 2017) The global energy demand is set to increase by 0.7-1.4% each year from 2008 to 2035 with Hydrocarbons being the essential part. (Nabzar, 2011) While more than 4 billion tons of petroleum is produced annually all over the world (Shvets *et al.*, 2016) with a value of \$1619 billion in 2017, it is anticipated to continue growing to \$2141.50 billion in 2026 (Presswire, 2018). The increasing demand (Figure 2.1) of petroleum is so high that more wells and rigs are set up by oil and gas industries yearly to meet up with the demands.

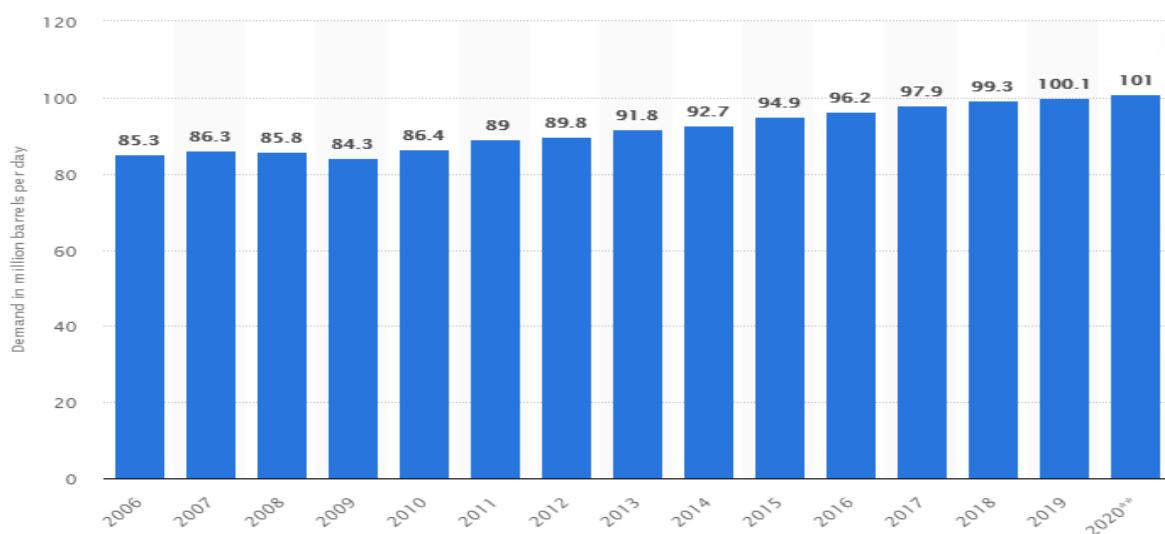


Figure 2.1: Global daily demand for crude oil. (Sönnichsen, 2020)

2.2 Produced water

Produced water is any water trapped or pumped into formations which are brought to the surface along with oil and gas from underground reservoirs during crude oil explorations. The water is a combination of salt and sea waters trapped in reservoirs, injected water containing production chemicals and any other water used in the oil exploration. They usually contain large volumes of dispersed oil, heavy metals, dissolved organic matter, radioactive isotopes, production chemicals, microbes and dispersed particles.

By volume, produced water is about 2 to 4 times the volume of oil when removed from reservoirs. Due to oil recovery processes when wells mature, the volume grows even more and might reach a volume of 98% depending on the formation.(Neff, 2002). Studies show that about 210-250 million barrels of produced water is generated daily all over the world, this amounts to a total of 77 billion barrels yearly, and accounts for about 80% of all the wastes generated in the exploration. (Neff, 2002; Veil *et al.*, 2004). Information from the Norwegian Continental shelf (NCS) shows that there is growth in the volumes of produced water, for instance, between 2003 and 2015 the volume of produced water rose from 943.5 million barrels to 1.2 billion barrels as shown in Figure 2.2 (Gass, 2017). From all volumes of produced water generated during oil and gas production daily, 40% of the water is discharged into the environment globally.(Igunnu and Chen, 2012) In the NCS volume difference of reused water could be as low as 14% - 24% of the total water volume, the rest is discharged into the sea (Figure 2.2). The Convention for the Protection of the Marine Environment of the North-East Atlantic or **OSPAR** convention set the discharge oil limit in produced water to be 30mg/L due to the toxic nature of the waste.

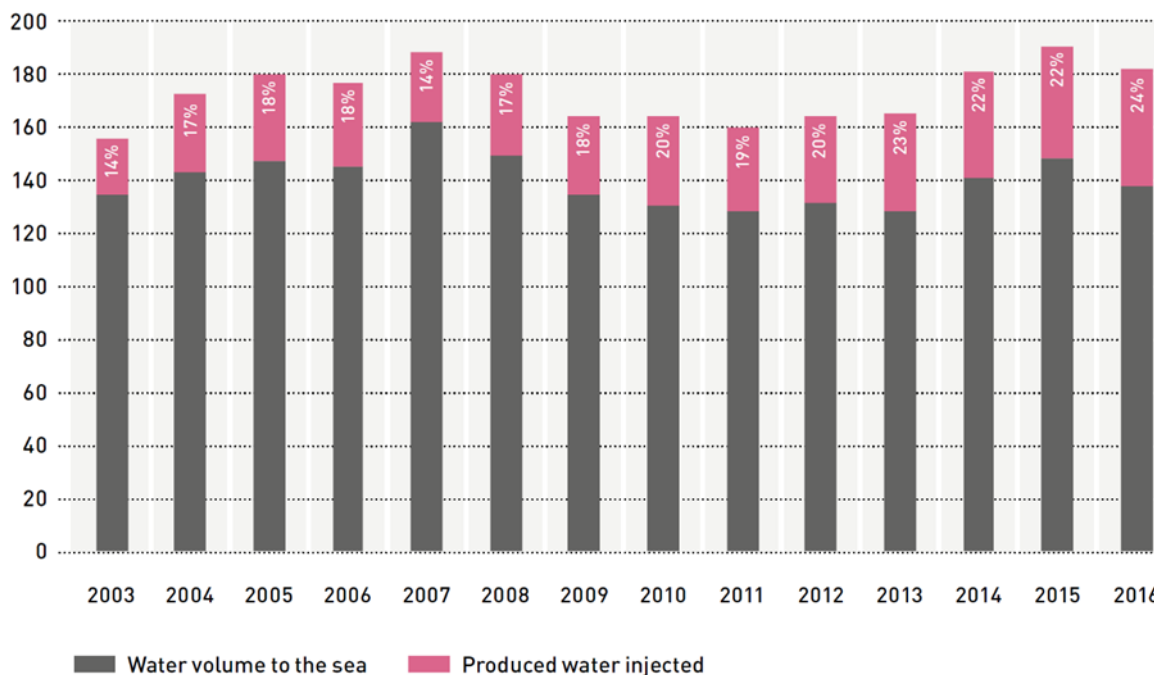


Figure 2.2: Volume of produced water in the NCS. (Norsk Olje and gass, 2017).

2.2.1 Produced water composition.

Produced water is made up of several compositions which range from a great number of dissolved organic and inorganic substances to dispersed chemicals in form of emulsions. The main sources of these components are production chemicals injected into the stream to enhance recovery and other naturally occurring compounds that have been buried underground over a large period of time. The quality of produced water is generally influenced by factors like; well location, age of reservoir and type of hydrocarbon product being produced. (Panneer Selvam, 2018) These components of produced water have great effects on both the chemical and physical properties of the water depending on the source and location. In the North Sea for instance, the water density could range from 1014 kg/m³ to 1085 kg/m³ with a temperature of about 3°C to 80°C and maximum TOC of 1500.(Dudek, 2018) For a better understanding of these components, they are best categorised into; *Dispersed and dissolved hydrocarbons, Inorganics, Production chemicals, Dissolved gases, Solid particles, and Other substances.*

Dispersed and dissolved hydrocarbons: The main hydrocarbon in produced water is in the form of crude oil in dissolved or dispersed state depending on their sizes and states. The dissolved forms occur naturally over time while the dispersed forms are created from shear forces generated during mixing to form emulsions.(Dudek, 2018) There are two major types of hydrocarbon in produced water; saturates and aromatic hydrocarbons.(Neff, 2002) Saturates refers to all straight and branched chain hydrocarbons, while the aromatic ones refer to phenols, phenanthrene, naphthalene, polyaromatic hydrocarbons, dibenzothiophene, xylenes, ethylbenzene, toluene, benzene and more. Polyaromatic hydrocarbons in produced water range from 0.040mg/L to 3mg/L and are mainly from congeners like naphthalene and alkyl homologues of 2- and 3- rings.(Neff, Boesch and Rabalais, 1987; Neff, 2002) One-ringed hydrocarbons like those of benzene, toluene, ethylbenzene and xylene are present in amounts ranging from 0.01mg/L to about 600 mg/L with benzene being the most abundant. Organic acids are also present in produced water in the form of short chains of mono- and di-carboxylic acids of saturated and aromatic hydrocarbons. Studies show that the amount of these substance in produced water is affected by location, volume, type, well maturation, water cut and process conditions such as temperature, pH, and pressure (Dudek, 2018; Zheng *et al.*, 2016).

Inorganics: Produced water contains dissolved inorganic components in form of ions, metals and radioactive materials. They affect the salinity of the water by influencing salt formation and its chemical properties. The salt content for sea water may range from 32-35‰ causing a variation in density of produced water from different geographical locations.(Neff, 2002) The brine concentration of produced water is affected by Cations like Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Fe²⁺ and Anions like Cl⁻, (CO₃)²⁻, (HCO₃)²⁻, (SO₄)²⁻.(Panneer Selvam, 2018) Metals present in produced water include; Barium, Cadmium, chromium, Copper, Mercury, Lead, Zinc, Nickel, Iron, Manganese, and Silver are some of the metals found in produced water.(Neff, Boesch and Rabalais, 1987; Panneer Selvam, 2018). Traces of radio isotopes of Radium like Ra²²⁶ and Ra²²⁸ are present in amounts ranging from 0.027pg/L - 0.04 pg/L and 0.005pg/L - 0.012pg/L in produced water respectively. Besides Radium, other elements like Lead, Uranium, Polonium and Thorium are also present in produced water.(Neff, 2002; NRPA, 2004).

Production chemicals: Great number of special additives known as production chemicals are added to aid recovery and pumping of petroleum from the wells to the storage tanks as well as prevent corrosion and hydrate formation. Production chemicals

contain biocides, scavengers for oxygen and hydrogen sulphide, scale and hydrate inhibitors, emulsion-breakers and flocculants, corrosion inhibitors, and gas treatment chemicals (glycol and methanol). Some of these chemicals are soluble in oil than water and therefore remain in the oil phase while those soluble in water and not oil remain in the water phase and are disposed with the produced water. (Lee, 2011). Due to the toxic nature of these chemicals, their disposal follows strong regulations where only chemicals marked as "Green" or "Yellow" are allowed for disposal without concern. (Kelland, 2014) The concentration of production chemicals in produced water vary from place to place and the mounts depends on the point in the production stream where they are added. An outline of common production chemicals used in the North Sea is shown in Table 1.1. Flocculants like polydimethyl diallylammonium chloride is added as production chemical to enhance oil recovery, these chemicals remain in the water phase and also aid in treatment of produced water.(Kelland, 2014)

Phase	Chemicals	Concentration in use (ppm)	Amount discharged in North sea (ton/year)
water	Scale inhibitor	3–10	1,143
	H ₂ O/O ₂ scavenger	5–15	22
	Biocide	10–200	81
	Coagulants and flocculants	<3	197
	Gas treatment chemicals	Variable amounts	2,846

Table 2.1: Production chemicals used in North Sea. (Lee, 2011)

Dissolved gases: Gases like carbon dioxide, oxygen and hydrogen sulphide which are formed naturally from the activities of micro-organisms and chemical reactions in water are also found in produced water. (Igunnu and Chen, 2012).

Particles: Clays, precipitated solids, waxes, bacteria, carbonates, sand and silt, corrosion and scale products, proppants and other formation solids like inorganic crystalline substances (SiO₂, Fe₂O₃, Fe₃O₄, and BaSO₄) are the major particles present in PW. Particles are normally dispersed in oil and water interfaces where they contribute in the stabilization of the emulsion depending on the type of particle. (Dudek, 2018; Igunnu and Chen, 2012; Panneer Selvam, 2018)

2.2.2 Produced water treatment

Need and objectives of produced water treatment

There is growing need for produced water treatment due to the toxic nature of the different components of this water. As shown in Figure 2.2, the quantity of produced water discharged into the environment is very high when compared to the amounts reused in production, hence the need for treatment before disposal. The effects of PW components could have strong effects on both aquatic lives and the ecosystem in addition to diseases considered fatal to humans like cancer, respiratory problems, irritation, and death in cases of over exposure. Depending on concentration, relative toxicity, predicted dispersion and biodegradation rates in receiving water, it is likely that the toxic effects is limited to the immediate vicinity of discharge. (Lee, Robinson and Chong, 2014). High salinity in produced water could lead to acute toxicity and death of

marine organisms, while increased oil in dissolved or dispersed phase can lead to increased biochemical oxygen demand, rise to water surface and evaporation of volatile droplet components in addition to accumulation and coverage of water bodies. Heavy metals could accumulate and eventually lead to death of an organism when strongly exposed to them. Radioactive materials in produced water are very toxic and dangerous, with potential effect of causing cancer and other fatal infections. The effect of production chemicals could range from accumulation in marine bodies to change in aquatic environment's properties which could eventually lead to death of organisms. It is for these reasons and more that strong regulations have been enacted to control the disposal of produced water. (Kelland, 2014; Panneer Selvam, 2018).

The treatment objective is usually removal of free dispersed oil and grease, dissolved organics, bacteria, algae and other micro-organisms, suspended particles, sand, and turbidity. The treatment also targets the removal of dissolved gases from light hydrocarbons, carbon dioxide and hydrogen sulphide. Dissolved salts, sulphates, nitrates, scaling agents and water hardness are also removed. There is also adjustment of sodium concentrations and removal of some radioactive materials. (Panneer Selvam, 2018).

Legislation

There are strong regulations and legislations all over the world restricting the disposal of effluents into aquatic environments. In oil producing countries, environmental regulatory agencies place limits to the concentration of petroleum that is disposable in produced water destined for seas and oceans. (Kelland, 2014) Depending on the country and regulation, the required amount of petroleum hydrocarbon content could range from 15mg/L to 50 mg/L. In the Northeast Atlantic (OSPAR) and North Sea areas for instance, the required standard for oil and grease discharge is about 30 ppm (30 mg/L, previously 40 mg/L). Studies also show that since January 1, 2007 the NCS is working hard on reducing this value to about 12mg/L, a value so low that strong treatment strategies will be needed to achieve it. As these numbers vary from one region to another, it might get as low as 5-10 mg/L depending on the country's regulations. (Gass, 2017) The oil operators in Norway agreed in 2005 to implement a zero environmental harmful discharge policy by developing environmental impact factor for the regulation. (Lee, 2011).

<i>Country</i>	<i>Monthly average (mg/L)</i>	<i>Daily maximum average(mg/L)</i>
Canada	30	60
USA	29	42
OSPAR (NE Atlantic)	30	Not specified
Mediterranean Sea	40	100
Western Australia	30	50
Nigeria	40	72
Brazil	Not specified	20

Table 2.2: Oil and grease allowed for disposal in some countries. (Lee, 2011)

Produced water treatment methods

There are different treatment techniques available for treating produced water, the selection of the appropriate technique and method depends on the components of the produced water and the available regulations in the country, in addition to other factors like cost, availability of equipment, and plan. The common treatment techniques include, Gravity separation, Hydrocyclone and centrifugation, use of coalescers and filtration. These physical separation methods alone are not enough in achieving the required level of purity due to the stability of produced water emulsion and the ability of these methods to recover only free and dispersed oil effectively but not the finely dispersed droplets. Addition of chemical substances like flocculants is therefore necessary to achieve proper separation of the emulsion components when using the equipment. (Ottaviano, Cai and Murphy, 2014).

Produced water treatment methods are best categorized into Primary, secondary and tertiary depending on area of application and final size of droplets desired. The primary treatment by gravity separation could remove oil droplets of size range 100-150 μ m using skimmer tanks and vessels, API separators, Disposal piles and skim piles. Plate coalescence is also another primary method of treatment that uses parallel plate interceptors, corrugated plate interceptors, cross flow separators and mixed flow separators to separate oil droplets up to size 30-50 μ m. Plate coalescence is mostly applied in addition to gravity separation to achieve efficient separation. Secondary separation uses enhanced coalescence, gas floatation and enhanced gravity separation methods to separate oil drops of sizes 5 - 20 μ m. The secondary separation methods are usually enough to generate produced water that meet most countries disposal regulations, for better treatment of produced water into higher quality usable for other purposes like irrigation, tertiary methods are used. The tertiary method involves the use of multi-media membrane filtration techniques to completely remove oil drops from produced water.(Arnold and Stewart, 1999). The Tertiary technique is also important in treatment of highly stabilized produced water like polymer flooding produced water which cannot be treated satisfactorily with these conventional treatment techniques. (Chen *et al.*, 2015).

Category	Method	equipment	Size(μm)
Primary	Gravity Separation	Skimmer Tanks and Vessels API Separators, Disposal Piles Skim	100-150
Primary	Plate Coalescence	Parallel Plate Interceptors, Corrugated Plate Interceptors, Crossflow Separators Mixed-Flow Separators	30-50
Secondary	Enhanced Coalescence	Precipitators Filter/Coalescers, Free-Flow Turbulent Coalescers	10-15
Secondary	Gas floatation	Dissolved Gas Hydraulic Dispersed Gas Mechanical Dispersed Gas	15-20
secondary	Enhanced Gravity separation	Hydrocyclone, Centrifuge	5-15
tertiary	Filtration	Multi-Media Membrane	1+

Table 2.3: Produced water treatment Methods. (Arnold and Stewart, 1999).

Gravity separators

This primary technique of separating oil from water removes high oil droplets sizes coming from the first produced water during explorations. Oil droplets dispersed in continuous water phase slowly rises to the surface by density differences at the start of separation. They are then separated into oil and water components leaving produced water of about 100 to 150 microns droplets. Large particles also settle to the bottom of the separator and are removed through valves in the tank. Gravity separators like skimmer tanks and vessels, API separators, disposal piles and skim piles are the commonly used equipment for this purpose. Plate coalescers like parallel plate interceptors (PPI) and corrugated plate interceptors (CPI) are usually added to gravity separators to improve separation to about 30-50 microns. In this case plate coalescers added to skim tanks or vessels and inclined at angles to the horizontal cause the oil droplets to coalesce and move to the surface faster.

Hydrocyclones

Hydrocyclones are also known as enhanced gravity separators. They are made up of cylindrical swirl chambers, concentric reduction sections, fine tapered section and a cylindrical tail. The produced water enters the equipment from the swirl chambers creating a high velocity vortex with reverse flowing central core. The speeding fluids passes through the concentric reducing section and fine tapered section, removing the oil at the tail section. The mechanism of operation of a hydrocyclone is that, it uses spinning motion of the fluids generated from centrifugal force to push heavier water outward and lighter oil into the middle core of the cones. Despite the high efficiency of this method, the larger pressure drops across the device, inability to remove particles, high cost of maintenance and ease of blockage seem to be problematic with the technique. (Arnold and Stewart, 1999; Arthur *et al.*, 2005).

Gas floatation

The gas floatation units use air or gases to float out oil more rapidly from produced water by bubbling gases that cause the density of oil drops to reduce as they attach to the bubbles. This reduction in density speeds up the movement of the oil to the surface from where they are skimmed off. The added air could either be induced or dissolved. In the dissolved gas floatation, air compressors inject and cause air to dissolve in the produced water. In induced gas floatation however, fine bubbles are created through mechanical hydraulic or sparging systems where improved efficiency and faster separation of oil from water due to smaller bubble sizes created than.

3 Produced water from polymer flooding.

3.1 Polymer flooding.

Enhanced oil recovery by water flooding could ensure oil recovery to limits where the viscosity of the oil slows down or even stops the recovery. Chemical enhanced oil recovery process like polymer flooding is then applied to improve the recovery by overcoming the oil viscosity. Polymer flooding could be defined as any chemical enhanced oil recovery method where polymer solutions are used to increase recovery of oil by decreasing the water-oil mobility ratio through increase in the viscosity of the displacing water. This recovery method is applicable to wells where water flooding is inefficient due to fractures and high permeability that channel the flow of injected water or even oil that is resistant to flow. (Speight, 2013) when the mobility ratio during water flooding is unfavourable and the reservoir is heterogenous, polymer injection improves the recovery (Thomas, 2019). The oil left behind after water flooding is usually as a result of capillary forces or due to bypass from the water flood. The addition of water-soluble polymers to water flood during EOR process increases viscosity of the water and improves oil recovery up to 50%. (Ahmed and Meehan, 2012) Besides increasing the viscosity of injection water, some polymers also adhere to reservoir rocks and decrease the water phase permeability resulting to higher sweep efficiency.(Thomas, 2019) Figure 3.1 shows the effect of polymer flooding in oil recovery as compared to water flooding.

Polymers used in water flooding are selected based on the injected water's temperature, permeability and salinity. Polymers commonly used in oil and gas industries for polymer flooding are mainly biopolymers like polysaccharides and synthetic polymers like polyacrylamides. Copolymers of acrylamide and acrylic acid are efficient for water up to 75°C at low salt concentrations. Addition of ATBS to these polymers will increase both the temperature and salt tolerance up to 95° C. (Thomas, 2019) The polymer added during the flooding process vary in molecular weight depending on the well's permeability, higher permeabilities require higher molecular weight polymers.

Though polymer flooding is very efficient in oil recovery process, the downside is in the damages created by this polymer like; retention in the porous mediums of the well, incompatibility with the formation fluids and minerals, movement of loose sand particles and high stability of produced water. (Speight, 2013) Polymer flooding is applicable in reservoirs with live oil viscosity up to 10000cP, temperatures up to 140°C, permeabilities greater than 10mD and salinities up to 25g^L-¹TDS. With preferred reservoir conditions like sandstone, water-wet, oil saturations above residual levels, matrix porosity, edge aquifer tolerated reservoirs, low clays and confined-small spacings.(Thomas, 2019)

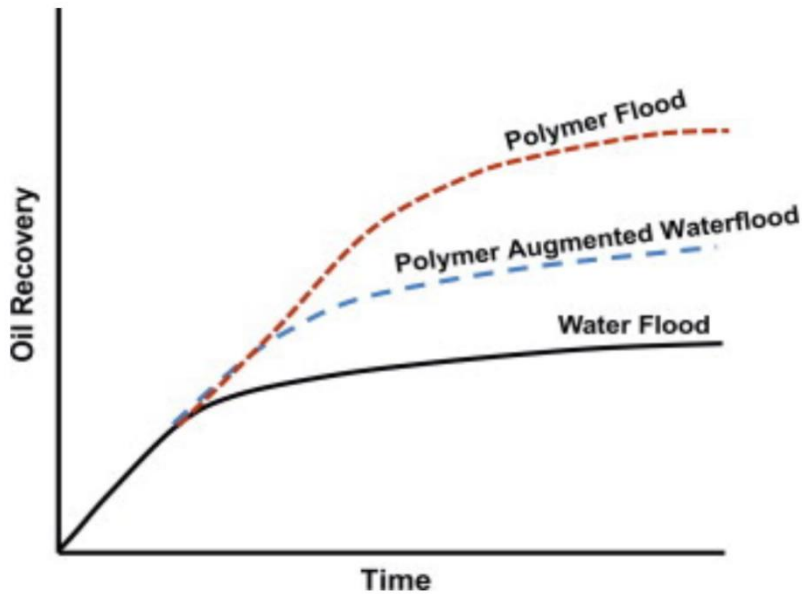


Figure 3.1: Oil recovery by polymer flooding. (Ahmed and Meehan, 2012).

3.2 Polymer flooding produced water (PFPW)

The produced water generated after polymer flooding is known as polymer flooding produced water (PFPW) and usually differ from the produced water from water flooding. Polymer flooding causes increase in the volume of produced water generated during the recovery process due to the ratio of polymer amounts to water volumes needed. The volume of PFPW could be very high in some countries, for instance in Daqing oilfields of china, the annual PFPW is about 6×10^7 m³. (Jing *et al.*, 2010). The produced water from polymer flooding is highly emulsified and stable with very high interfacial tensions. The oil drops present in this water are also very small and the phase stability is high. Besides being harmful to the well, the PFPW could also pose serious problems if discharged to the environment without proper treatment. As a result, Polymer flooding produced water treatment has become an important aspect to consider before using this recovery process.

PFPW is a complex multi-phase emulsion that has solid and liquid impurities, dissolved gases and salt components in addition to Polyacrylamide compounds which are the major concern in the treatment of this water. The added polymer as mentioned earlier increases the viscosity of the water depending on the water salinity. Polymer consumption in polymer flooding increases with increase in salinity. This is due to the salt content being inversely proportional to the viscosity of the water, hence the need for more polymer solutions in water containing high salt concentrations. Since the salinity of produced water vary with location, the content and properties, especially stability also vary for different PFPW and the age of the well. Due to strong Legislations and environmental concern, PFPW needs to be properly treated and reinjected into the production streams rather than disposing them into the ocean or seas as they still contain traces of the polymer which might not be biodegradable. In cases where there is need to dispose the water, strong treatment strategies are used to ensure that the quality meets the standard for disposal.

The water contains about 10 to 1000 mg/L of polymers and 300 mg/L of solids unlike the low amounts in conventional produced water and hence require stronger treatment

strategies. The effects of polymers present in PFPW include acting as flocculants to agglomerate particles, increasing water viscosity which affects separation by gravity, reducing friction and hence suppressing vortices in treatment equipment and finally enhancing droplets coalescence by charge interactions. (Aguiar and Mansur, 2016; Thomas, 2019) Treatment of PFPW might be problematic due to purification effects, facility pollution, running stability, and economic rationality. (Chen *et al.*, 2015)

3.3 Treatment of PFPW

The treatment of PFPW is done in stages where the oil and gas are first separated from the water and the water is then purified in the second stage. These stages are elaborated below.

Oil and gas removal.

The oil and gas separation involve the use of heating and gravity separators to remove dispersed oil in the water while evacuating gases from the system. This process is primary in the treatment of PFPW, it is used to separate the bulk oil and gas present in the water.

Heating separators

Here the water passes through chambers with high- and low-pressure separators where oil is removed by gravity and later through a dehydration chamber where heat is applied to reduce viscosity and more oil separated from the water.

Gravity separators

This system is coupled with separation aids like hydrocyclones, filters and plate planks, gravity, flow speed and fluid properties are used to separate oil and gas from water. In the separators, water, oil and gas separate by density differences and are removed from different channels of the separator.

Polymer degradation or removal

Polymer removal is important in PFPW treatment if the water is not to be reused for further polymer flooding or to obtain water of desirable purity. The process usually involves altering the polymers chemistry and properties to make it easier for removal. The common polymer degradation methods applicable in treatment of polymer flooding produced water include chemical treatments like precipitation with coagulants and addition of oxidizers, electro oxidation, mechanical, thermal, ultrasonic and UV degradations. Polymer removal can be achieved by polymer flocculation with coagulants, electrocoagulation, precipitation with particles like clay. The polymer degradation and removal strategies ensure lowered viscosity of the produced water in addition to demulsification and coagulation of the droplets to enhance their removal. (Thomas, 2019)

Before water treatment with chemicals and equipment separation, it is normally important to degrade and remove polymers from the water to avoid interference with other water treatment strategies. Viscosity increase by polymers pose great problems in PFPW treatment by reducing coalescence and separation efficiency of the different techniques. The presence of polymers in the water also affect other demulsification process and lowers the efficiency of chemicals used in treatment.

3.3.1 Water treatment

After the removal of oil and gas from the PFPW, Chemical treatments and techniques like enhanced gravity separators with coalescers, gas floatation, filtration, hydrocyclone separation and centrifugation are used to further remove oil drops, salt and polymers from the water.

Chemical treatment

The treatment of PFPW requires addition of different chemicals that are capable of both neutralizing the charges and inducing flocculation of the oil droplets till they coalesce. Leaching solution of alkalis, metallic hydroxides, Poly(Aluminium chloride) PAC, cationic polyacrylamide (CPAM), zwitterionic polymer (ZTP), Aluminium sulfate (AS) and Hydrolysed polyacrylamide (HPAM) are some of the available chemicals for treating PFPW. Since the stabilizing mechanism of PFPW includes interfacial tension stability, double-layer stability, interfacial film stability, space and solid particles stability, (Wang et al., 2011) the chemicals required for destabilizing the water should therefore, be able to counter these stabilization mechanisms. Chemical destabilization by demulsification-flocculation seem to be better chemical treatment option for this type of produced water. (Huang *et al.*, 2019) The mechanism of demulsification-flocculation is that molecules adsorbed on the surface of oil droplets, displace the surfactants and polymers on the drop thereby reducing interfacial tension and film strength so that the stability of the oil droplets reduce. The demulsifiers also neutralize charges of the droplets and reduce the electrostatic repulsion between the oil drops allowing them to agglomerate. When the polymers and surfactants are displaced, flocculants add more neutrality to the droplet charges while bridging them into flocs that coalesce with time. This mechanism is illustrated in Figure 3.2.

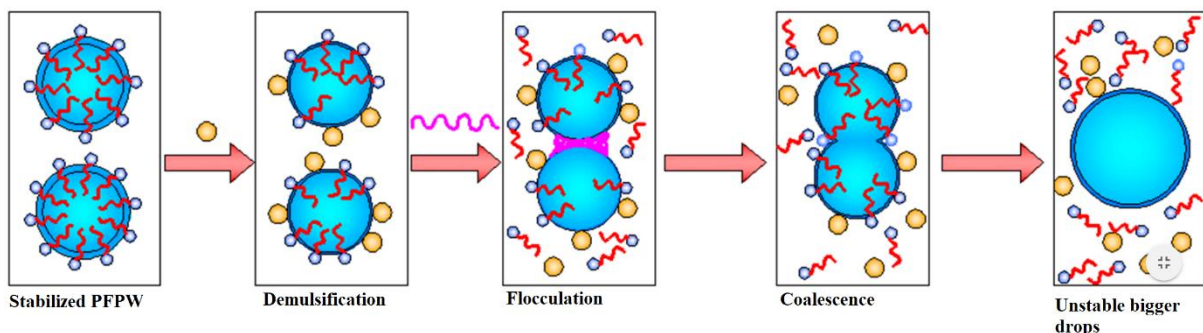


Figure 3.2: Breaking PFPW emulsions. (Huang *et al.*, 2019).

These chemical treatment methods enhance separation of oil from the water and are used with separation equipment to achieve proper water treatment. The aim of the treatment is to cause oil droplets to coalesce and separate to the surface by density from where other techniques help to remove the oil. This treatment does not remove or degrade the polymers in the water, hence the need for polymer degradation and removal process after water treatment.

3.3.2 Water treatment strategies

3.3.2.1 Filtration

Different filtration mechanisms are used in oil and gas industries to remove residual oil and solids from the PFPW. Media filters (walnut-shell and sand filters) and membranes

are the commonly used filtration for PW separation. The former, could be used to remove residual and dispersed oil from the water but are inefficient in removal of polymer flooded produced water. Membrane filtration is more effective in treatment of PFPW as they are capable of removing oil drops, polymers and salts from the water.

Membrane filtration

This process uses microporous films with specific pore ratings to selectively separate a fluid from its components. PFPW is forced through a membrane of varying pore sizes depending on the membrane filtration technique, smaller molecules pass through the pores while larger ones are retained and removed in the process. The major setback in membrane filtration is the fouling from different components of the PW. (Mueller, Cen and Davis, 1997) The common membranes used in oil and gas industries for membrane filtration are ceramic and polymeric membranes, they are usually coupled with the different filtration techniques during treatments of PFPW. Four types of membrane filtration technique used for the purpose are ultrafiltration, reverse osmosis, nanofiltration and Microfiltration.

Ultrafiltration uses pores of size 0.01 and 0.1 μm to remove colour, odour, viruses and colloidal organic matter completely from the water. This is by far the most effective way of treating all forms of produced water. (Igunnu and Chen, 2012) The downside of this technique is the inability to completely remove salt from the water and the decline in permeate flux as a result of membrane fouling downside which is improved by use of additional membranes like the bentonite membrane or hydrophilized PVDF membrane to enhance its efficiency. (Xu *et al.*, 2016). The process runs at low transmembrane pressure between 1 and 30 psi and can serve as pre-treatment to desalination.

Reverse osmosis (RO) separates dissolved and ionic components of the produced water. They are used as added technology for water desalination. Osmotic pressure of the feed solution is suppressed by applying hydraulic pressure which forces clean water to diffuse through a dense, non-porous membrane. (Igunnu and Chen, 2012) This process removes contaminants as small as 0.0001 μm and is applied in PFPW pre-treatment. The downside of this technology is the fouling and scaling on the membranes.

Nanofiltration is used for water softening and removal of metals as they are capable of removing contaminants of size 0.001 μm and total dissolved solids of range 500-25000 ppm. This process is effective with extensive pre-treatment of the PFPW.

Microfiltration uses pores of size 0.1 to 3 μm to remove suspended solids and turbidity. It can operate in cross-flow or dead-end filtration methods. The cross-flow filtration is more effective in removal of the solids than the dead-end filtration as shown in Figures 3.3 (a) and (b).

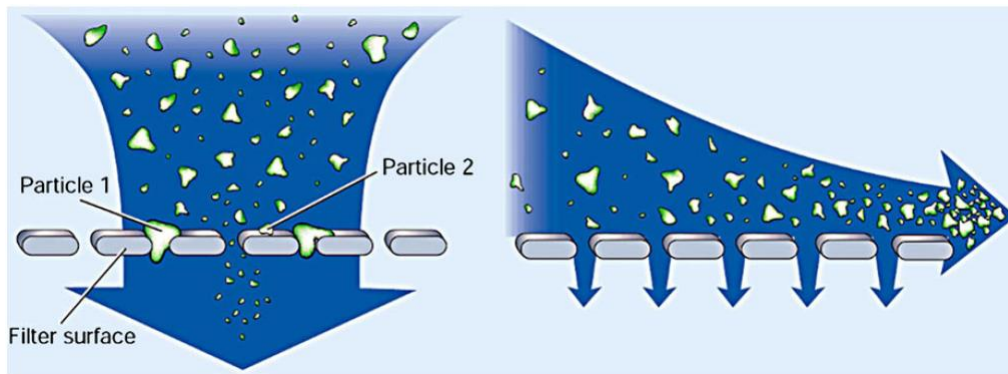


Figure 3.3: Dead-end and cross-flow filtrations (left to right).(Igunnu and Chen, 2012)

Electrodialysis: Due to the content and difficulties in treatment of polymer flooded produced water, most oil industries desalinate and reuse the water for polymer flooding. The major problem encountered in the reuse of PFPW is the high salinity which affects the polymer swelling and efficiency in EOR, thus making desalination a very important task in the treatment of PFPW for reuse in oil wells. The required salt concentration in produced water for reuse in polymer flooding is expected to be minimal and about 500 to 1000ppm. (Sosa-Fernandez *et al.*, 2018) The main goal of using the electrodialysis in PFPW treatment is to desalinate the water to extents that allow for its reuse in the polymer flooding processes. This technique is not enough to treat produced water suitable for disposal into the environment due to residual polymers, organic and inorganic matters, bacteria and solid particles in addition to heavy metals still present in the water.

In this separation technique, series of ion exchange membranes carrying electrically charged functional sites that are arranged in alternating modes between a cathode and anode remove charged substances from the produced water. (Igunnu and Chen, 2012). In other words, the process involves the use of electrochemical potential gradient to selectively move ions from dilute sources to more concentrated sources across an ion-exchange membrane. (Han, Galier and Roux-De Balmann, 2015). Dissolved ions from water moves through the ion exchange membranes and are separated. Positively charged membranes allow only anions to pass through and negatively charged membranes allow only cations. The major drawback of this method is fouling by substances which could change the properties of the membranes and affect the efficiency of the technique. Figure 3.4 illustrates what happens to clean sea water from entry point to disposal or reuse points when electrodialysis is used for the treatment.

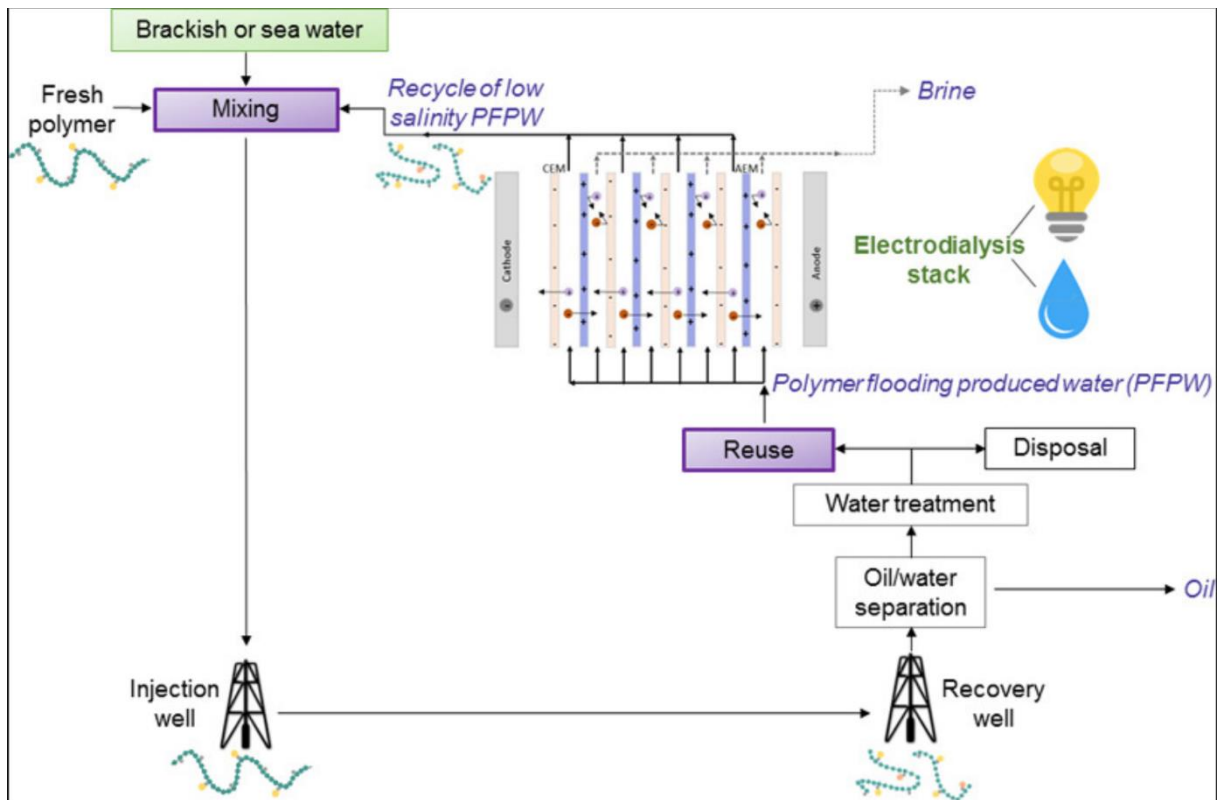


Figure 3.4: PFPW desalination by electro dialysis. (Sosa-Fernandez *et al.*, 2018).

3.3.2.2 Gravity separators

Gravity separators like API, skim piles and tanks and plate coalescers used in addition to deoilers could be used to treat PFPW. Normally gravity separators can effectively separate components of water flooding produced water without deoilers when the polymers present in the water is low and there is low viscosity and high coalescence. High polymer concentration in PFPW however, cause an increase in viscosity and inability of bridged droplets to move together and coalesce. This decreases the coalescence efficiency and rising velocity of the separators thus the need for deoilers. The problem encountered with this treatment strategy is the amount of sludge generated after the addition of deoilers. Estimate shows that water containing 800ppm of polymers treated with conventional deoilers could generate 12kg of sludge (Thomas, 2019).

3.3.2.3 Hydrocyclones

Hydrocyclones are also applicable in the treatment of PFPW where they are used specifically for deoiling. Due to drag-reducing properties caused by the presence of polymers; the process efficiency is greatly reduced. A more effective way of using this process in PFPW treatment is to first degrade or remove the polymers prior to this treatment.

3.3.2.4 Centrifugation.

The application of Disk stack centrifuges in the treatment of PFPW could enhance removal of oily water up to 1000ppm with an efficiency of about 85% irrespective of polymer presence of up to 500ppm (Thomas, 2019). The downside of this method is the limitations in the concentration of polymers present in the water, excess polymer in the water could lead to failure and clogging of the system.

3.3.2.5 Gas flotation

Gas flotation units are used in PFPW treatment for removing oil droplets. Due to increased vertical velocity of the oil, and attachment of these drops to bubbles, they rise to the top and are separated by density. The process is affected greatly by the presence of polymers as they tend to reduce the attachment of the droplets to the bubbles and disrupt coalescence and growth of the droplets. The available solution is degradation of the polymers in the PFPW prior to gas flotation.

In summary, the treatment of polymer flooded produced water is a very difficult task due to the high level of stability of this water caused by very small droplet sizes and polymer activities which tend to increase the Viscosity, surface tension and surface strength. Due to legislations and difficulties in treatment, PFPW is usually treated for reuse in the wells for polymer flooding since they already contain residues of the polymers. Desalination by electrodialysis after chemical treatment with suitable chemical demulsification-flocculation substances is the commonest way of achieving treatment of this water for reuse. In situations where disposal of the water is also required, polymer removal and degradation is first carried out before using treatment technologies like membrane filtrations, gas flotation, centrifugation, hydrocyclones, and gravity separators to remove oil droplets, particles, micro-organisms, suspended inorganics and organics in the water.

4 Emulsions and polymers in solution

4.1 Emulsion theory

An emulsion is a dispersion that contains two immiscible liquids where one of the dispersed liquids is in the dispersed phase and the other in a continuous phase. The two main types of emulsions are oil-in-water (o/w) and water-in-oil (w/o) emulsions. Emulsions can also be double for instance in w/o/w and o/w/o where more than one phase is involved. Most daily use products like paints, glues, cosmetic creams, milk, margarines and mayonnaise are emulsions. Emulsions without amphiphiles or stabilizers will coalesce on collision and cream or sediment over time depending on the size of the droplets, density differences, and viscosity of the continuous phase. The bigger the droplet sizes, the more unstable the system, as such oil drops of size $1\mu\text{m}$ moves 40mm/day and have half-life of 0.77s (Kronberg, 2014), meaning that a shelf life of six months for this type of dispersion will require about 16000000s hence the need for stabilizers to increase the shelf life.

4.1.1 Emulsion stability

Stabilizers used for emulsion stability are known as emulsifiers, they are mostly surfactants that acts by reducing the interfacial tension between the oil/water interface and diffuse into it where they prevent coalescence. Other emulsifiers like high molecular weight polymers, hydrophobic particles, proteins, and liquid crystals are capable of diffusing into the interface to form films, ions, and rheological mechanisms that prevent droplet coalescence and are also useful in the stabilisation of oil/water emulsions.

4.1.2 Breakdown mechanism

There are various processes through which emulsions could be broken, they mostly involve physical processes that tend to reduce the surface forces of the droplets as well as create formations that bring them to fusion and rupture leading to separation into various phases. Some of the breakdown mechanisms include coalescence, creaming and sedimentation, Ostwald ripening and flocculation.

Coalescence

Coalescence is the process where by two or more oil drops fuse into one bigger drop. The process occurs more rapidly in concentrated dispersions. If the droplet pair is exposed to turbulent pressure fluctuations and kinetic energy of oscillations, such that the pair's kinetic energy is larger than their energy of adhesion, the contact between the droplets will be break before fusion. Coalescence is therefore possible only in cases where the energy of adhesion of the coalescing droplets is larger than their kinetic energy. Therefore, the energy of adhesion is critical to coalescence of droplets and reduction in drops kinetic energy enhances coalescence. (Arnold and Stewart, 1999). A simple illustration of the coalescence process is shown in Figure 4.1.

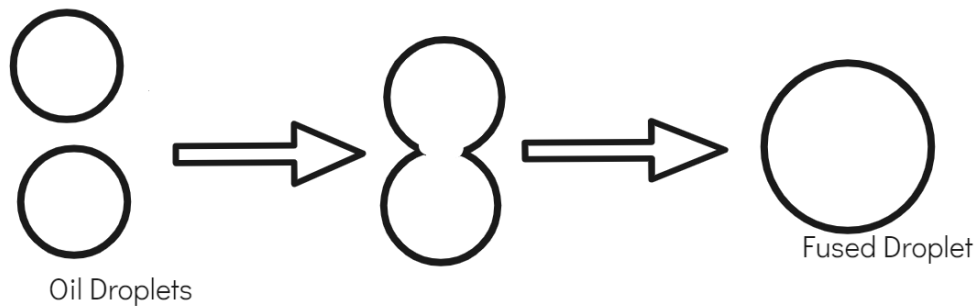


Figure 4.1: Schematic illustration of coalescence process

Creaming and sedimentation

These processes occur when external forces from gravity or centrifuge applied to an emulsion extends their Brownian motion and cause them to separate according to density. Larger droplets move to the surface of the dispersion if they have densities lower than that of the continuous phase, this is called creaming, the reverse is the case for droplets with higher densities than that of the continuous phase, they settle to the bottom by a process known as sedimentation. Smaller drops that are not affected much by the forces tend to remain dispersed in the continuous phase.

Ostwald ripening

Ostwald ripening could be defined as the dissolution of small droplets and redeposition of the drops on the surface of larger droplets by diffusion. The process occurs as a result of varying solubilities of polydispersed emulsions where smaller droplets with larger solubility (due to reducing radius of droplets) tends to diffuse into the bigger droplets or a bulk of fused drops, shifting the droplet size distribution to larger values. This process is due to curvature effects and differences in the concentration gradient which causes the larger molecules to grow at the expense of the smaller ones. (McClements, 2009; Tadros, 2013)

Flocculation

Flocculation is the process whereby oil droplets agglomerate into large units called flocs without a change in the original sizes of each drop. When the repulsive forces acting on the droplets are low, the droplets tend to floc by Van der Waals forces and hydrogen bonding. The chemical substances that cause flocculation are known as flocculants. They are mostly high molecular weight polymers that are either charged or neutral but are capable of neutralizing charges thereby causing displacements of drops and bridging oil droplets into flocs. There are two stages of flocculation, Perikinetic flocculation and orthokinetic flocculation. Perikinetic flocculation occurs from thermal agitations or Brownian movement seconds and after destabilization of emulsions. The driving force is the higher Brownian forces that overcome the potential energy of the droplets causing them to collide and fuse (coalescence) till the floc sizes grow beyond the Brownian force ability. Orthokinetic flocculation occurs by agitation of the emulsion to induce velocity gradients that moves the drops together. (Bratby, John, 2006; Pillai, 1997)

4.1.3 Produced water as an emulsion.

Produced water is an emulsion of oil dispersed or dissolved in a continuous water phase (O/W). Produced water is therefore an oil-in-water emulsion. Depending on the water treatment stage, the oil droplets in produced water could range from 5 to 200 microns

and stabilized by the actions of net attractive and repulsive forces exerted by substances in the water. (Arnold and Stewart, 1999; Dudek, 2018). The presence of polar molecules surrounded by hydration layers in the oil and water interfaces of produced water prevents coalescences of the oil droplets. Also the arrangement of water molecules around a hydrophobic particle surface creates anionic surface potential on particles present at the interfaces causing them to repel other particles of similar charges. (Kelland, 2014).

Produced water stability

Produced water is stabilized by the presence of surface active chemicals and particles. (Deng *et al.*, 2005). The major stabilizing chemicals are mainly resins, asphaltenes, Naphthanic acids and Particles (McLean and Kilpatrick, 1997). While the resins and asphaltenes create thick layers around the droplets and prevent them from coalescing, particles get adsorbed at the oil and water interfaces, preventing them from coming closer to each other due to charge differences and also acting as shields that prevent the drops from coalescing. (Levine, Bowen and Partridge, 1989). Naphthanic acids adsorb at interfaces and due to their surface activeness, they form monolayers, liquid films and negatively charged ions that prevent the drops from coalescing by reducing the interfacial mobility and enhancing resistance to coalesce. (Ese and Kilpatrick, 2004). Oil droplets have negative charges that originate from chemical reactions at the surface from functional groups like -COOH of Naphthanic acids which readily ionize in solutions or by adsorption of ions. The net effect of this charge on the droplets is a repulsion that occurs as they get in contact. Studies show that the mechanism for stability in produced water is also related to the formation of aggregates in produced water by resins and asphaltenes in such a manner that the polar heads remain in the water while the tails remain in the oil phase. This mechanism is deduced from McLean and Yarranton's mechanism for resin and asphaltene stabilized water in oil emulsions. (McLean and Kilpatrick, 1997; Yarranton, Urrutia and Sztukowski, 2007). The formation of this thick, rigid and elastic layer about 2-10nm thick around the drops create distances and cross-links hard enough to prevent coalescence by interfacial rheology and elasticity of the drops. The surface energy of the asphaltene film is so tough that it provides strong forces that restore any deformation in the interface. When the stabilized drops come in contact, they simply bounce back by elasticity and never coalesce together. This mechanism is illustrated in Figure 4.2 as deduced from McLean and Kilpatrick's stabilization of water in oil emulsions.

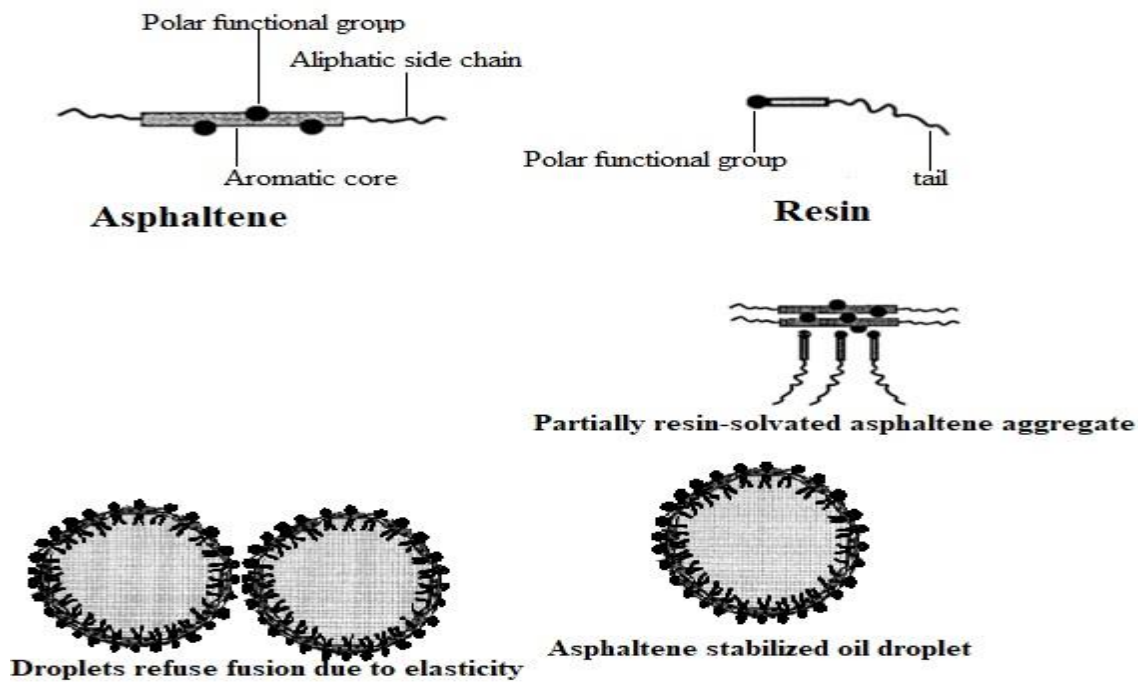


Figure 4.2: PW emulsion stabilization. (McLean and Kilpatrick, 1997).

Destabilization of produced water emulsion.

Breaking produced water into various components of the oil and water require proper understanding of the mechanism and making choice of the appropriate chemical to use. Produced water like some emulsions is thermodynamically unstable and will separate with time, they are however kinetically stable with no spontaneous formation of dispersion resulting to immediate phase separation. The density difference between oil and water causes all oil droplets to move to the water surface where they coalesce with each other and separate into a film of oil. During production of petroleum the forces applied to the produced water causes the oil to disperse into very small droplets that are highly stable and will not phase separate without using demulsifiers and separation techniques. In this case all separation is aimed at causing the coalescence and phase separation of the droplets while avoiding drop breakage. (Ahmadun *et al.*, 2009; Dudek, 2018) Produced water breakdown is achieved in industries through addition of flocculants or polymers to destabilize the droplet charge and get attached to them. These polymer attachments neutralize charges and bridge the drops till they coalesce into larger drops that eventually rupture and cream to the surface by density as other heavier particles sediment.

4.2 Flocculation mechanism

Polymer flocculants contain functional groups that are either charged or uncharged. The charged polymers carry cationic or anionic or amphoteric charges with varying degrees of ionization. Polymer flocculants also have properties that makes them easily absorbable to other surfaces. These properties of the polymer flocculants make them suitable chemicals for breaking produced water emulsions through charge neutralization and adsorption. In general, addition of flocculants in produced water first neutralizes the charge of the produced water and cause the droplets to floc by creating bridges that bind them together. In time the droplets from the flocs coalesce into bigger drops as shown in

Figure 4.1 and eventually ruptures when the force of the oil overcomes the surface pressure. (Wilson and French, 1978)

The mechanism for polymer flocculation could therefore be summarized as bridging and electrostatic patch mechanism. (Bratby, John, 2006)

4.2.1 Polymer bridging

Bridging is an important phenomena in produced water flocculation, it occurs when polymers of long chains are adsorbed by oil droplets at the interfaces, they create bridges that tend to bind to another drop by a free adsorption spot. (Mousa and Hadi, 2016; Tadros, 2013). The stages in polymer bridging are best categorized into dispersion, adsorption, compression and bridging.

Dispersion

This process occurs when polymer flocculants are added to a dispersion, rapid mixing ensures proper dispersion and gives enough room for interactions between the droplets and the polymer. The polymers uncoil into long strands with tails, loops and trains which act as active sites for the adsorption. (Hocking, Klimchuk and Lowen, 1999) This causes the polymer active sites to diffuse to the oil-water interface where adsorption of the polymer takes place. This process is illustrated schematically in Figure 4.3.

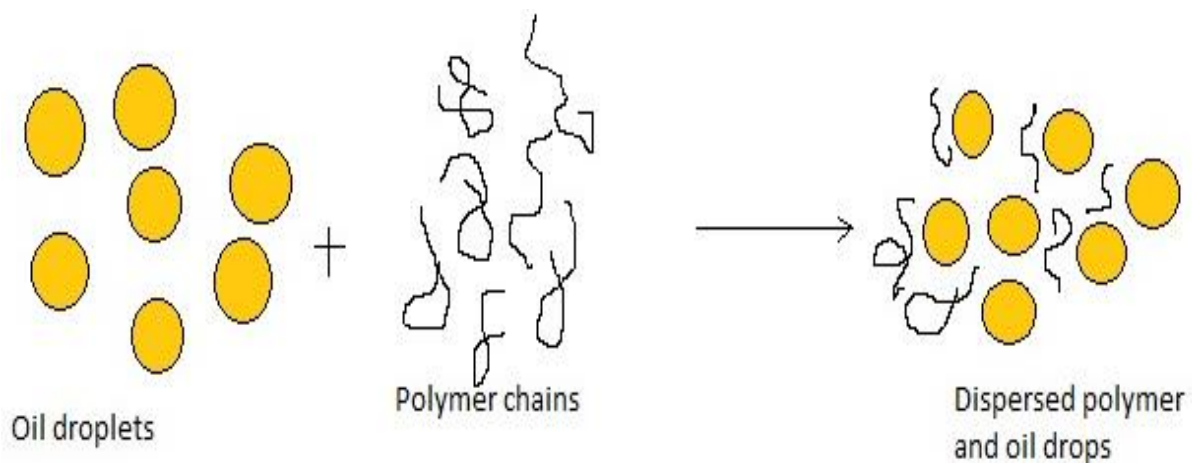


Figure 4.3: Dispersion of polymer around the droplets

Adsorption

Adsorption occurs first at one functional group as the rest of the strand remains freely in the solution, subsequently other points of the polymer adsorb to the droplet along its strand by Brownian movements till all free ends are successfully absorbed as shown in Figure 4.4. The driving forces for this type of adsorption may be due to cationic exchange, electrostatic linkages, Hydrogen or ionic bonding. (Bratby, J., 2006)

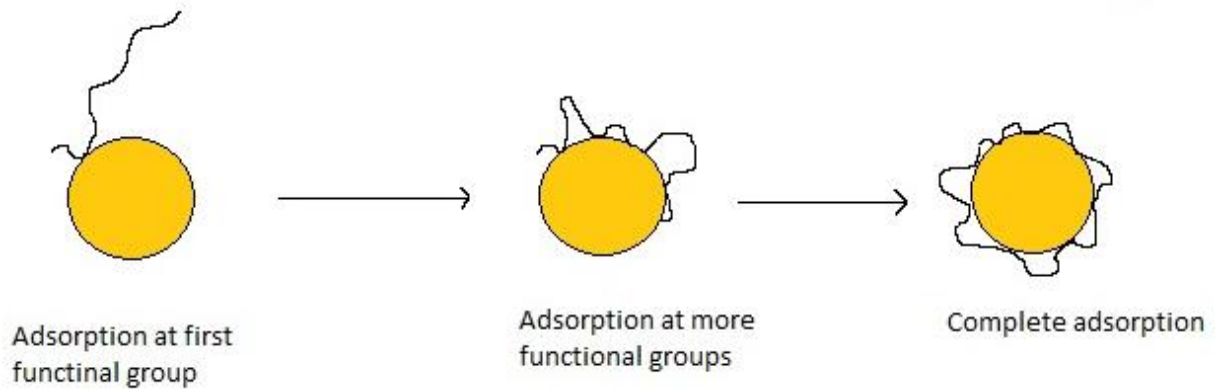


Figure 4.4: Adsorption of polymer chain onto droplet.

Compression

After the polymer adsorption, they compress on the surface of the droplet. The adsorbed loop keeps compressing onto the surface of the drop and become diminished or flattened out till the double layer repulsion becomes greater than the size of the loops. Bridging occurs more when the loops are longer and keeps reducing as the loops flatten. The nature of the adsorbed polymer depends on polymer properties like molecular weight, structure, interaction energy, spacing on the drops, flexibility, charge magnitude and surrounding molecules. Higher molecular weight polymers produce better bridging due to presence of more loops and sites for bridging than the lower molecular weight polymers.

Bridging

Polymer bridging occurs when the extending loops of the polymers in solution adsorb to the surface of another droplet as they continue to flatten out. The result is multiple bridges generated among the polymer strand and the surrounding oil droplets. The strength of the floc formed after polymer bridging depends on the number of loops and bridges formed by the polymer. (Hocking, Klimchuk and Lowen, 1999) This process is illustrated in Figure 4.5

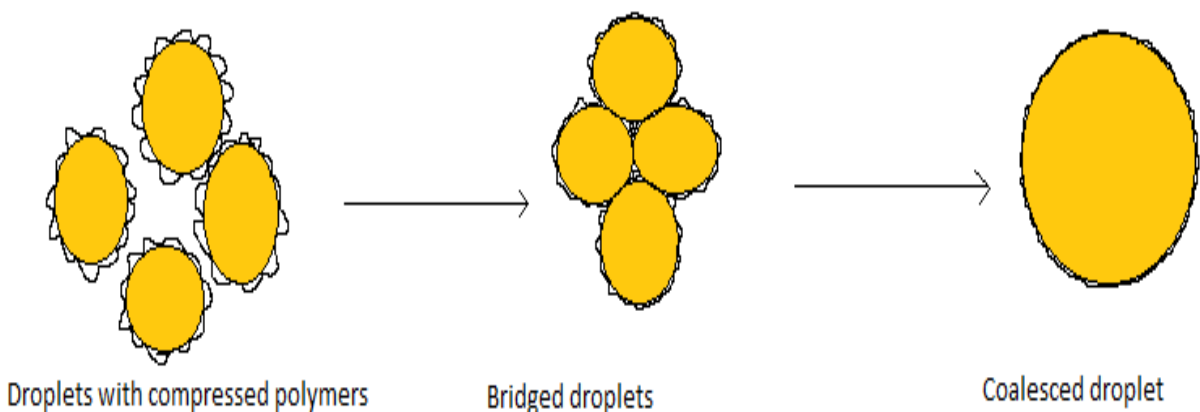


Figure 4.5: Polymer bridging of droplets

4.2.2 Electrostatic patch mechanism

Polymer bridging is more effective with non-ionic and anionic polyelectrolytes due to the presence of no or similar charges between the polyelectrolyte and produced water. In the case of oppositely charged polyelectrolyte and oil droplets where strong electrostatic attractions exist, the mechanism follows an electrostatic patch approach. The adsorption

is such that all parts of the polymer are adsorbed to the droplet surface with no loops extending to the solution as in the case of bridging. The adsorbed polymers then form charged sites with alternating regions of positive and negative charges that tend to attract adjacent droplets containing same type of electrostatic adsorption and produce flocs of charged droplets.

The flocculation process with ionic flocculants could be illustrated schematically as shown in Figure 4.6.

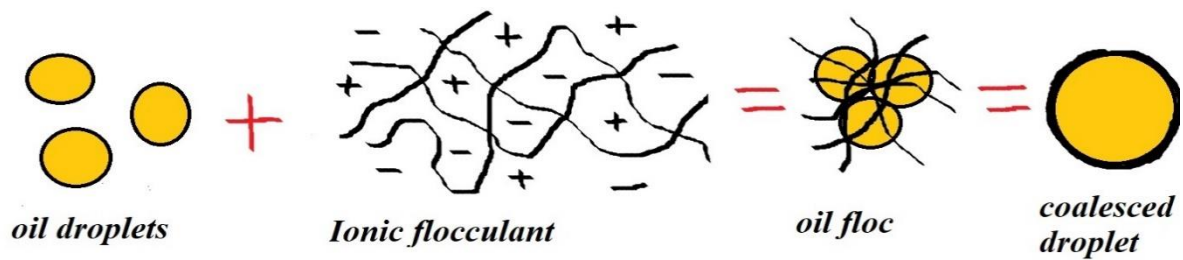


Figure 4.6: Schematic of a flocculation process. Deduced from (Pillai, 1997)

4.3 Flocculants

Most flocculants used for the treatment of produced water are water soluble polymers that display properties capable of interacting with oil droplets and causing them to floc and separate from water. In this section the interaction of these polymers in their aqueous solution is discussed.

4.3.1 Polymers in aqueous solution

Polymers are large molecules containing many repeating units known as monomers. They are grouped into synthetic and natural polymers depending on whether they are polymerised or occur naturally. These polymers could be linear, branched or cross-linked, a classification that is important in understanding their behaviour in water. When a polymer has the same kind of monomers it is known as a homopolymer and those with different kinds of monomers are referred to as copolymers. Copolymers may be arranged in blocks, grafts or randomly depending on the position of each monomer in the chain.

Interaction with water

In solution, water enters the polymer and causes it to swell making it viscous and sticky. The polymer chains then break from their gel and diffuse into the water slowly. Mixing increases the dissolution rate and is affected by pH. Some polymers dissolve faster than others and at varying pH, others like polyvinyl pyridine is insoluble in water at high pH values. It is therefore important to consider the solubility factors of a polymer before choosing it for produced water treatment. Another consideration is the solubility parameter of the polymer, some polymers might not be soluble in water due to a large difference in the interaction energy between the polymer chains and the water molecules when compared to the energy between polymer chains and those between the water molecule.

Polyelectrolytes are more soluble in water than nonionic polymers due to counterions contributing to entropy of the solution. This solubility is affected by salts which tend to lower the entropy of the counterions and cause the polymer to phase separate (*salting*

out). Polyelectrolytes of high polarity are also soluble in the presence of certain amounts of salt irrespective of the entropy changes.

Polymer adsorption

Polymer adsorption occurs in steps, the polymers get dispersed and transported from bulk to the surface, the polymers then attach to the surface and finally arrange themselves on the surface. Polymer adsorption onto surfaces is usually as a result of weak interaction between the polymer and water or from strong interaction between the polymer segments and the surface. Polymers that show poor interaction with water have higher adsorption capability on surfaces than those with strong interactions with water. The poorer the solubility of the polymer in water, the higher the adsorption. This is due to the poor stability of the polymer in water and its ability to seek stability by adsorbing to the solid surface. Addition of salts tends to increase the solubility of polymers in water and decrease its adsorption onto surfaces. Polymer adsorption might be dependent on the polymer's molecular weight if the polymers are attached to the surface by head (common in most polymers in solution) or independent if they adsorb flat to the surface. Higher molecular weight polymers however adsorb more on solid surfaces than lower molecular weight polymers due to the high stability of lower molecular weight polymers when compared to those of higher molecular weights. Initially at lower concentrations all polymers are adsorbed onto a surface due to the availability of enough space to accommodate them. As the concentration of the polymers increases, the higher molecular weight polymers displace the lower molecular weight ones and occupy all available spaces until they reach equilibrium. Figure 4.7 illustrates the adsorption of two polymers of different molecular weights. (Kronberg, 2014)

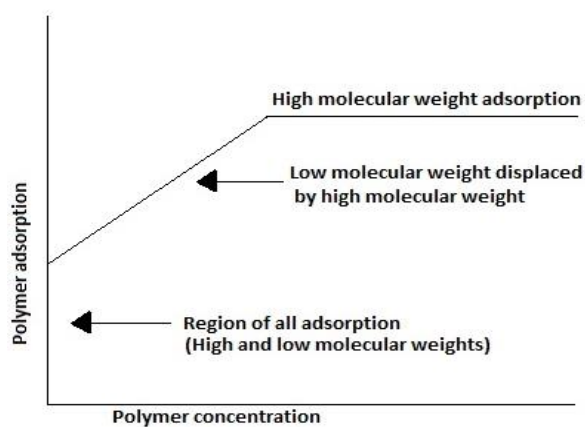


Figure 4.7: Adsorption of different molecular weight polymers. (Kronberg, 2014)

The adsorption of polyelectrolytes in water onto a surface is also affected by the charges of the surface and the polyelectrolyte. When oppositely charged polyelectrolyte adsorb onto a surface, the counter ions of the polymer and surface get released into the surrounding water so that the entropy of the system is increased, and the free energy state lowered. In the case of same charge adsorption, Van der Waals forces and hydrophobic attraction tend to bind the surface and the polymer. The presence of salt could alter these systems and lower adsorption in oppositely charged polymer and surface or cause an increase in adsorption for same charge adsorption between the polymer and surface.

Polymer self-assembly

Amphiphilic block copolymers are known to self-assemble in aqueous interfaces. The hydrophilic ends extend into water and the hydrophobic end into oil to form micelles with core shell structures where the insoluble blocks of the polymer are within the core. (Otsuka, Nagasaki and Kataoka, 2001). The self assembly could also form morphological structures like cylinders, bicontinuous gyroids and lamella. The driving force for this association is the unfavourable enthalpy from mixing. (Mai and Eisenberg, 2012). When two polymers are in solution, they may show segregative phase separation if they have net repulsive interaction or show complete miscibility if they have very weak attraction. They however show associative phase separation if they have strong attraction between the polymers. (Kronberg, 2014).

4.3.2 Types of flocculants typical for produced water treatment

In the petroleum industries, flocculants work together with treatment equipment like hydrocyclones, gas flotation units, gravity separators, centrifugation units and other devices used in produced water treatment by creating flocs unto which oil droplets adsorbed. The flocculants also cause aggregation and fusion of the oil droplets by coalescence and separation through density differences. Though there are many types of water-soluble flocculants that are applicable in produced water treatment, this work is focused on common polymer flocculants used for the treatment. These polymers are either inorganic or organic polymers in aqueous solutions. The inorganic flocculants are in the form of high metal salts added due to their cationic charges to produced water requiring these types of ions or as additives to polymer flocculants. In solution they produce H_3O^+ which destabilizes oil in water emulsions. (Kelland, 2014) Some examples of these flocculants include Lime, Aluminium salts of soda, sulphates, iron, Zinc sulphates, chlorides and metals like iron (III), Aluminium (II) and Zinc (III) salts. The major problem with using these flocculants is their ability to form acids that cause corrosion to the treatment vessels. This problem could be solved by neutralizing with alkalis immediately after the separation process.

Organic flocculants are the most widely used for produced water treatment. The commercially available flocculants for produced water treatment are synthetic water-soluble polymers with average molecular weights of about 1000 to 3×10^7 Dalton. They are mostly acrylamide derivatives and are categorized into polyelectrolytes and non-polyelectrolytes. The polyelectrolytic polymer flocculants carry charged sites in form of ions and are grouped into Anionic flocculants if they carry negative charges or cationic flocculants if they carry positive charges. When polyelectrolytes carry both the negative and positive charges, they are referred to as amphoteric flocculants. The non-ionic flocculants are those that bear no charged ion or at most 1% of charged ions. In most cases these flocculants are copolymers which allows synthesis of flocculants for specific purposes. (Tarleton and Wakeman, 2007).

4.3.2.1 Non-Ionic flocculants

This type of polymer flocculants are polyacrylamides and polyethyleneoxide based polymers that carry no charge and functions mainly by bridging mechanism to cause flocculation of the oil droplets. The polymers are normally very high weight polymers that are capable of stretching sufficiently to the droplet surfaces. The advantage of this type of flocculant is the ability to function over a wide range of pH and ionic strength as they are not affected due to lack of charge.

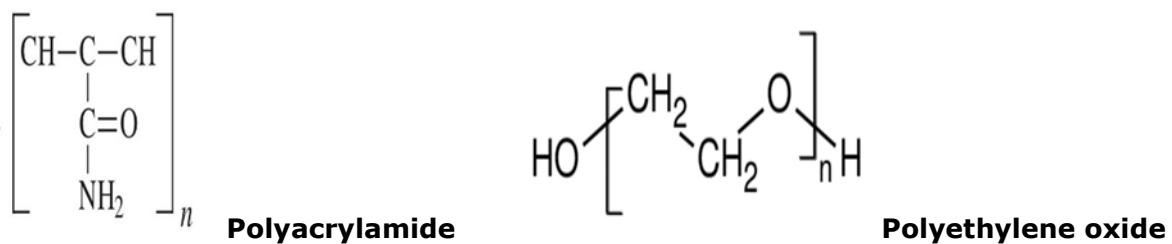


Figure 4.8: Typical structure of a non-ionic polymer flocculants.

4.3.2.2 Anionic flocculants

Anionic polymeric flocculants are only applicable in produced water treatment if the oil droplets are positively charged. These are high molecular weight acrylic polymers that contain carboxyl ions and sulphonic acid groups. They are compounds of acrylic and acrylamide copolymers with hydrophilic surfactants synthesized for treatment of positively charged produced water. Acrylic copolymer with acrylamide neutralized with bases is a common example. Partially hydrolysed polyacrylamide can also be used as anionic polymer flocculant. They are pH dependent and particularly used in less acidic mediums except for flocculants with sulphonic acid groups which are less sensitive to pH variations and maintain their anionic nature at low pH. Examples of this type of flocculants includes compounds of polyacrylates and polymethacrylates like sodium polyacrylate, Poly sodium acrylamino methyl propano sulphonate and polysodium styrene sulphonate.

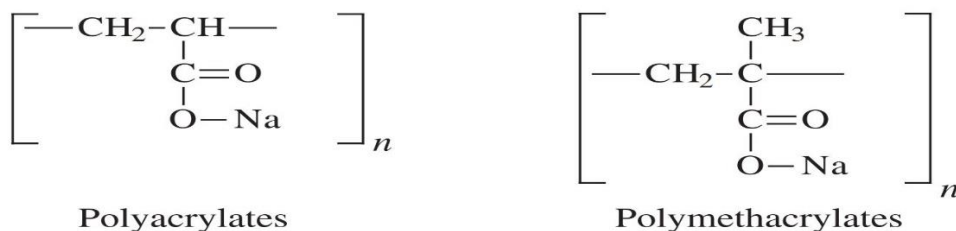


Figure 4.9: Typical examples of anionic polymer flocculants.

4.3.2.3 Cationic flocculants

This is the most widely used type of flocculants for produced water treatment due to the pH and salinity of the water and their ability to tolerate a wide range of these factors. The most commonly used in oil and gas industries nowadays are **Diallyldimethylammonium chloride (DADMAC)** polymers and Acrylamide or acrylate-based polymers. Poly-DADMAC contain five to six rings of cationic groups and the high molecular ones are better options for produced water treatment. In cases where modification is needed, the homopolymer of Poly-DADMAC is copolymerized with Acrylamide and or other nonionic monomeric hydrophilic monomers which help to improve the polymer's charge density. Branching, crosslinking and hydrophobic modifications generally improves the performance of the polymer. (Kelland, 2009) Polyacrylamides are strong hydrophilic polymers that are fairly sensitive to salt and have high affinity to surfaces due to their cationic nature at low pH values. As such they are widely used in treatment of produced water. The polymer is used in forms of Acrylamide

homopolymers or copolymerized with acrylonitrile, methacrylamide or cyclic acids of about 50%. Other cationic polymers like polyalkyleneimines, polyalkanolamines, poly vinylammonium chloride polyallylammonium chloride, branched polyvinyl imidazoline acid salts, cationic polysaccharides and chitosan and condensed tennins are cationic polymers also applicable in the treatment of produced water. They are mostly polymers with quadrivalent nitrogen or more at charge sites along polymer chains with cations derived from protonation of amine groups or quaternary nitrogen groups. Cationic polymers from amines are unaffected by pH except for their polymer chains. Those produced from protonation are severely affected by pH and ionic strengths to extents that make the flocculants unable to function correctly without pH adjustments. For this reason, most cationic flocculants perform better in conjunction with pH modifiers. (Kelland, 2014; Kronberg, 2014)

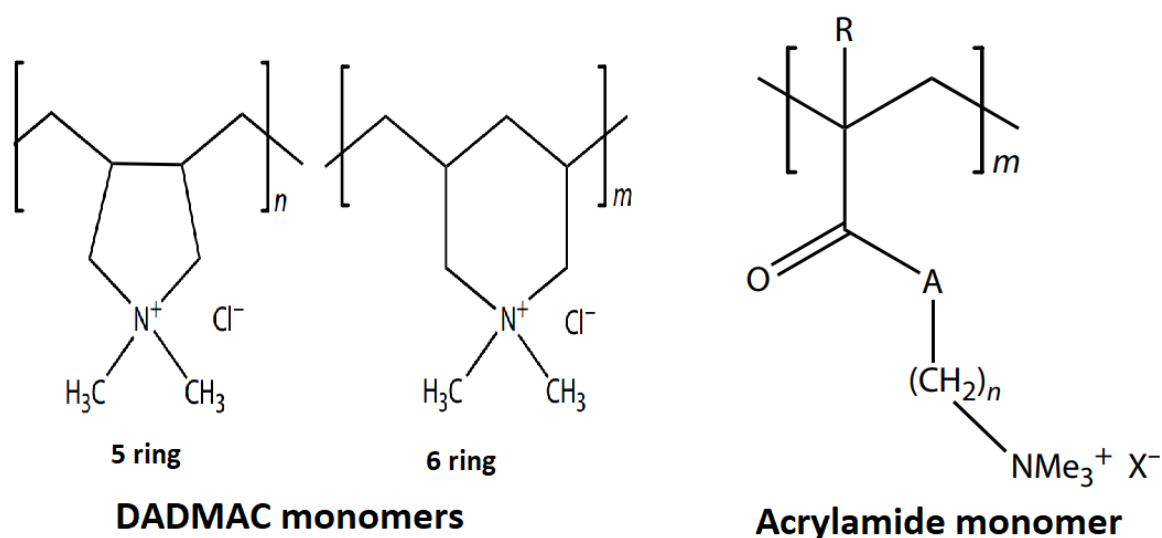


Figure 4.10: Typical examples of cationic polymer flocculants.

4.3.2.4 Amphoteric flocculants

Amphoteric flocculants are polymers with both cationic and anionic charge sites with or without a functional group. They are usually manufactured under controlled conditions and used only in cases where high flocculant dosage levels are necessary and high floc strength is required. (Tarleton and Wakeman, 2007) Copolymerized ones like starch-graft-polyacrylamide (s-g-PAM) produce better results in produced water treatment than the cationic, hydrolytic and amphoteric Polymethyl. (Kelland, 2014).

4.3.3 Effects of different factors on flocculants.

Flocculation in produced water is affected by different factors that tend to inhibit the proper functioning of flocculants. Some of the factors that affect flocculants performance includes, type of flocculant, salinity and ionic strength, water pH, shear forces during flow, size of droplets and particles, concentration and overdosing, molecular weight and process conditions. Though each of these factors play crucial role in the selection of flocculants, only pH, salinity and polymer size in water are focused on in this study.

4.3.3.1 Effects of pH

Different scholars have tried to understand the effect of pH on flocculation using polymers, but no clear or specific mechanism has been established. pH affects the adsorption of polymers unto surfaces. Different polymers are soluble in water at certain

pH values, as such the dispersing and adsorption of these polymers is affected. Strong polyelectrolytes like sulfate-based polymers are generally pH independent whereas weak carboxylate-based polymers depend on pH to function effectively. Polyelectrolytes are very soluble in water due to their counterions contribution to entropy of a system than the nonionic polymers, the net effect of this difference in solubility is the higher tendency of nonionic polymers to adsorb to surfaces than the polyelectrolytes at different pH levels.

When a cationic polymer is adsorbed onto an anionic surface at low pH values, the cationic polymer is fully charged and adsorbs strongly to the surface, unlike in the adsorption of same polymer at higher pH levels where only a fraction of the cationic sites are charged as in Figure 4.6, the adsorption is partial and in a coiled conformation. Studies also show that adsorption of cationic polyacrylamide onto silica surface is strongest at pH 9 where the surface of silica is highly charged and lower at pH 4 where the charge is lower. The adsorbed mass is therefore thicker at low adsorptions as shown in Figure 4.11 due to coiled polymer conformations and flattened when the adsorption is strong.

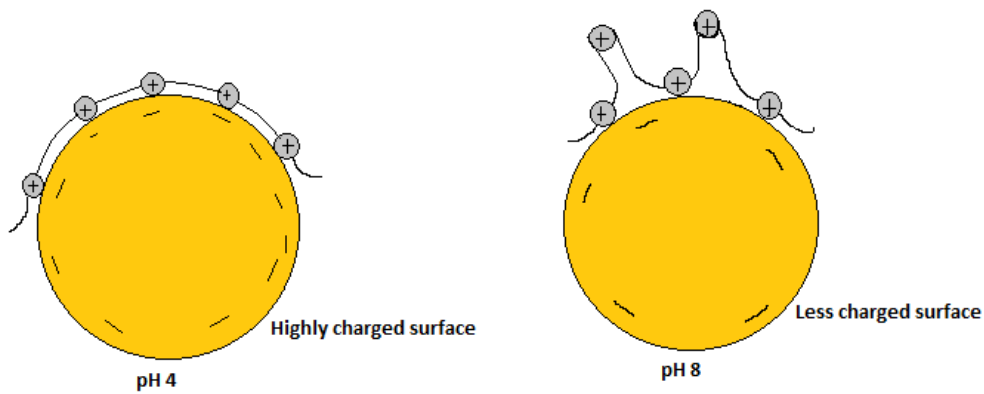


Figure 4.11: Adsorption of cationic polymers at different pH values

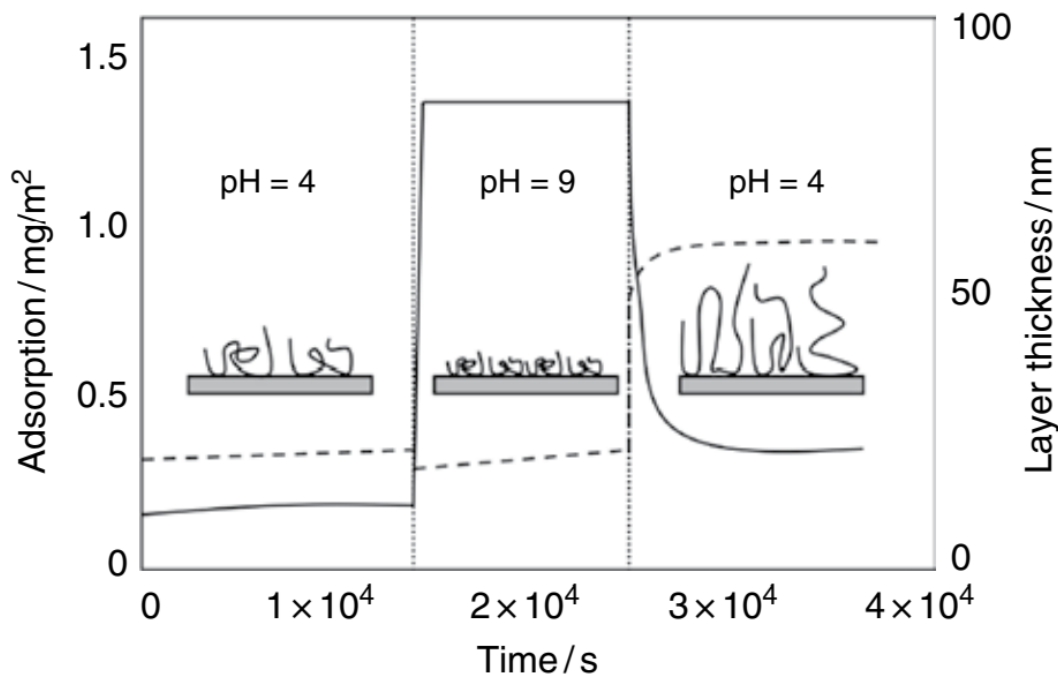


Figure 4.12: Adsorption of polyacrylamide on silica at varying pH.(Kronberg, 2014)

The pH of water plays crucial role in the selection of flocculants for produced water treatment. The flocculants choice increases from non-ionic to highly anionic, as pH increase from 0 to 14. non-ionic flocculants perform better at lower pH below 4 and reduces as the range increases. While the anionic types are best at higher pH values leaving the cationic ones at the mid pH values. The variation in this function of flocculants at different pH levels is due to the presence of carboxylate groups which are inert at lower pH in anionic flocculants and decreases the number of Hydrogen bonding sites, leaving the polymers uncoiled. Non-ionic flocculants however have amide groups that make them perform better at lower pH values. At increasing pH, the carboxylic groups ionize, and the polymers uncoil and become active. The performance of the anionic flocculants are best at pH 9.5 and above where polyacrylamides hydrolyze and reduce its activities making non-ionic flocculants to become inactive. (Pillai, 1997). This is applicable only in situations of coagulation-flocculation process where ions are neutralized before the actual flocculation process. In direct flocculations however medium charge density with high molecular weight cationic polymer is used to bridge the oil drops with loops and tails at all pH ranges. (Lee, Robinson and Chong, 2014)

4.3.3.2 Salinity

In general, salts affect the solubility of polymers in water by lowering or increasing it. Since adsorption of polymers unto a surface is a function of solubility as lower solubility leads to higher adsorption, salts therefore increase the adsorption of polymers unto surfaces if they lower the solubility of the polymer. Salts can also cause an increase in the cloud points of a polymer in solution and decrease in solubility. (Kronberg, 2014). Addition of salts to polyelectrolyte in aqueous solutions lowers the entropy gain from the counterions and make the polymers to phase separate or salt out. Highly polar polyelectrolytes resist salting out in the presence of fair amount of salt. Variation in the salinity of produced water affect the performance of the flocculants as they tend to perform better at certain salinity levels and Ionic strengths. Increase in salinity of produced water mostly results from dissolved metal ions in seas and oceans as explained in the previous chapter. The electrovalent ions present in the water determines the appropriate flocculants type to neutralize and bind oil droplets.

4.3.3.3 Size and shape of polymers in water.

In aqueous solution polymers may form random coils or rods depending on the polymer type. Their interaction with water at increased temperatures can cause them to change conformations by uncoiling and expanding. The degree of this expansion is related to their ionization and increases with increase in ionization. In polyelectrolytes, expansion occurs at certain degree of ionization where the entropy is higher. This behaviour of polymers in water affects their dispersion and adsorption unto a surface. their size.

High molecular weight polymers also adsorb more unto surfaces than the low molecular weight ones. As discussed earlier in this chapter, this is due to the low stability of high molecular weight polymers in water than the lower molecular weight polymers. Polydispersed polymers take longer time to reach equilibrium during adsorption than the monodispersed ones.

The sizes of droplets affect the type of polymer that could be used in the treatment of the produced water. Coalescence is affected by the kinetic energy of the droplets and also the bridging time of polymer flocculants. The smaller the sizes of the droplets, the higher the kinetic energy and less ability to coalesce due to poor adhesion energy. Flocculants of higher molecular weight tend to be better choice for treating produced

water with small drop sizes due to the distance the polymers will need to cover during the bridging process and the ability of higher molecular weight polymers to adsorb better onto surfaces than the lower molecular weight polymers.

5 Experiments

5.1 Techniques

5.1.1 Zeta potential and size Characterization.

The dynamic light scattering (DLS) technique could be used for studying polymer flocculants. The operating principle is such that a sample exposed to monochromatic light of known wavelength, undergoes light scattering in different directions as a function of the size and shape of the molecules in the sample. A detector receives and analyses this data using known principles. The technique can also measure the Brownian motion polymer droplets colliding with each other as a matter of time. This measurement is however affected by the temperature of the system as Brownian motion is affected by temperature changes. Other factors that affects this motion include size of polymers, and solvent viscosity. The more viscous the polymer solution, the slower the molecules diffuse and the bigger the molecules, the slower they will move. (Sandhu *et al.*, 2018)

The Velocity of Brownian motion is related to the translational diffusion coefficient D , which could be converted to particle or drop sizes using the Stokes-Einstein equation as shown in equation (1).

$$dH = \frac{kT}{3\eta\pi D} \quad (1)$$

Where dH = hydrodynamic diameter, k = Boltzmann's constant ($1.38 \times 10^{-23} \text{NmK}^{-1}$), T = absolute temperature, η = solvent viscosity (Nsm^{-2}), D = diffusion coefficient (m^2s^{-1}); T : absolute temperature (K).

The Zeta sizer uses the DLS to measure droplet sizes of a polymer flocculant. In the zeta sizer the Dynamic light scattering measures the diameter of spheres that diffuse at the same speed as particles or drops being measured by measuring their Brownian motion and interpreting it with known theories.

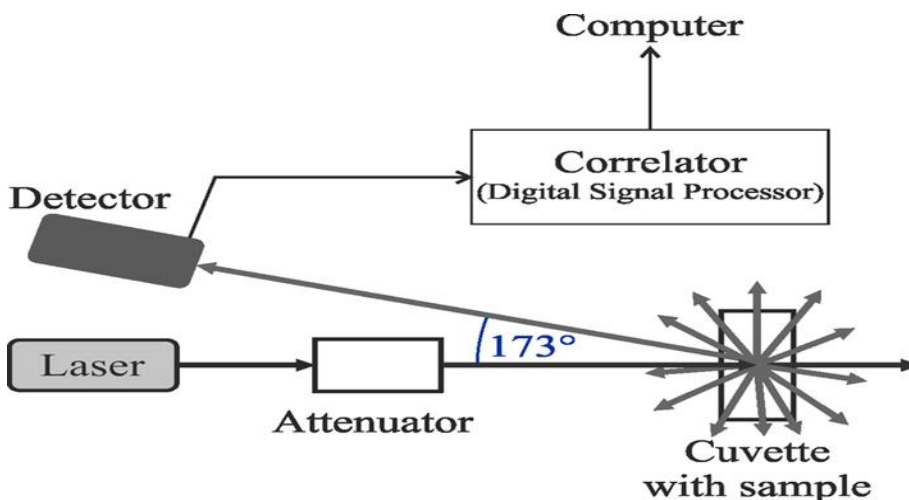


Figure 5.1: Schematic of the DLS working principle. (Eberhard, 2012).

The zeta sizer also measures Zeta potential through a process known as Electrophoretic Light Scattering (ELS) by electrophoretic mobility of charged drops. This is done by measuring how fast a polymer drop moves in a liquid when an electric field is applied to it. In a folded capillary cell containing the sample, electric field is passed through the electrode ends that bear either a Negative or positive charge. The charged drops move towards an oppositely charged electrode and the mobility rate of the drop is used to determine its ZP.

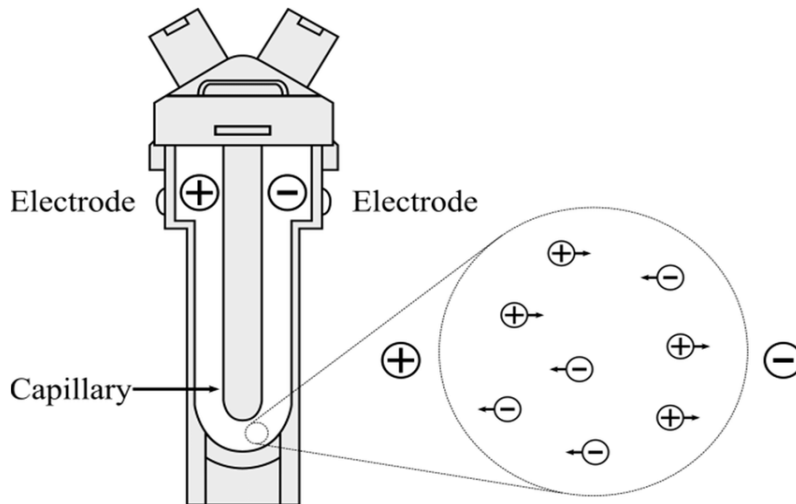


Figure 5.2: Folded capillary cell and Zeta Potential measurement. (Lazaro, 2014)

The knowledge of the velocity and electric field of the drop is used to estimate the zeta potential. The effectiveness of this characterization process is affected by the shape and length of polymers when used for polymer characterization. Some polymers remain uncoiled in solution due to solubility factors depending on their molecular weight.

Flocculant aggregation causes an increase in size a phenomenon that is useful in studying the effects of Mw, pH, and salinity on flocculants assembly. The state of the aggregates formed is also affected by the changes in pH and addition of charged polymer flocculants. Measuring the zeta potential therefore provides information on the charge stability and changes that are related to flocculants ability to aggregate in solution. (Mavern, 2013)

5.1.2 Polydispersity Index determination

Polydispersity index PDI could be defined as the measure of the heterogeneity of a sample in relation to its size. It measures the broadness of molecular weight distribution such that the larger the PDI the broader the molecular weight distribution. From a polymeric point of view, it is the ratio of a polymer's average molecular weight to its number average. Values less than 0.05 are said to be monodispersed while those greater than 0.7 are said to have broad size distributions or polydispersity. PDI is measured with the DLS technique using the zeta sizer, the results are accurate if the PDI is less or equal to 0.7. (Mudalige *et al.*, 2019)

5.1.3 Adsorption to solid surfaces

Polymer adsorption could be studied using the Quartz Crystal Microbalance with dissipation (QCM-D). The instrument operates based on the property of piezoelectricity where the piezoelectric quartz crystal is installed between two known metal electrodes. The passage of voltage through the electrode causes the crystals to vibrate in such a

manner that the frequency of oscillation of the crystal is related to the quantity or mass adsorbed to its surface. This change in frequency could be interpreted using the Sauerbrey equation. (Subramanian *et al.*, 2018)

The Sauerbrey equation is only valid for even and rigid distribution of adsorbed mass on the crystal surface where the mass is less than the mass of the crystal, in other words the energy losses are small. For the experiment carried out with polyDADMAC it was assumed that the polymer is evenly distributed on the silica surface and the adsorption is rigid from the overall shape of the graphs. The ability to maintain constant temperature with cooling systems in the machine and extent of mass adsorbed were also used as criteria to validate Sauerbrey equation for the result analysis in this work.

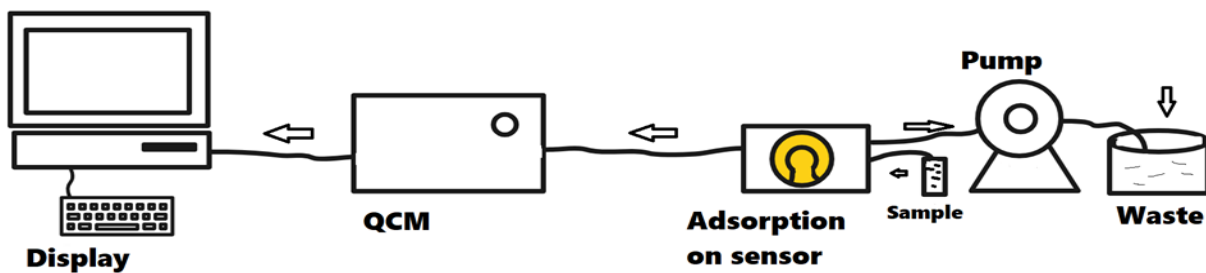


Figure 5.3: Schematic representation of the QCM-D setup.

5.2 Materials

5.2.1 Water solutions.

Salt water was prepared by dissolving analytical grade of pure NaCl (99%) in water collected from Millipore ultrapure water machine. Various concentrations ranging from 1g/L to 35g/L of NaCl were prepared and used for the preparation of the tested samples. The salt crystals were weighed into a volumetric flask (1L) which was already filled halfway with deionized water at room temperature. The flask was filled to the 1L mark and covered with a stopper before inverting 10 times to ensure adequate mixing and left sitting for at least one hour before use. The various pH water used for the experiment were prepared using 0.3M Hydrochloric acid (HCl) and 0.5M Sodium hydroxide (NaOH). 1g/L of the NaCl solution was poured into a beaker and placed on a magnetic stirrer and allowed to mix slowly as NaOH and HCl were added in drops to adjust the solutions pH. pH meter was used to monitor the pH after calibration with electrolytes of known pH. With the pH solution, various samples were also prepared for testing. The ionic strength of the solutions for all the pH values used in these experiments vary from one pH level to another and also with varying salt solutions.

5.2.2 Flocculants

PolyDADMAC is a cationic linear polymer used in produced water treatment. Its synthesis is by radical polymerization through free radically initiated addition polymerization of the monomer diallyldimethylammonium chloride. They have pyrrolidine rings as their repeating unit and are highly resistant to chlorine in addition to being applicable at different pH range. (Wilson, 2008)

Polydiallyldimethylammonium chloride (polyDADMAC) from Sigma aldrich of four types based on molecular weights were studied. The flocculants were denoted as F500k, F350k, F200k and F100k according to their Maximum molecular weights. The choice of the

various flocculants was to ensure same chemical compositions but varying molecular weights and concentrations as a good measure for testing the effects of pH, Salinity and sizes.

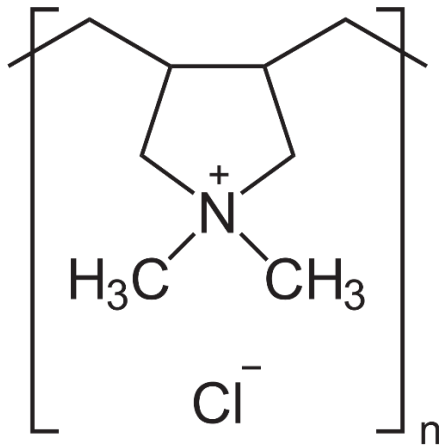


Figure 5.4: Structure of Polydiallyldimethylammonium chloride.

The properties of these flocculants are summarized in table 4.1. It shows the concentrations, molecular weights, refractive indexes, Viscosity and density

	F500k	F350k	F200k	F100k
Molecular weight in thousands	400 to 500	200 to 350	100 to 200	<100
Concentration in water (wt.%)	20	20	20	35
Refractive index (N20/D)	1.37	1.375	1.375	1.417
Viscosity (cP at 25°C)	600 to 900	250-500	60 to 180	100-200
Density (g/L at 25°C)	1.04	1.04	1.04	1.09

Table 5.1: Properties of Polydiallyldimethylammonium chloride.

Different concentrations of these flocculants were tested in water and salt water at different pH values.

5.3 Methods and Procedures

5.3.1 Size measurement in salt water

Different concentrations (100ppm, 200ppm, 300ppm, 500ppm 1000ppm and 5000ppm) of the flocculants were prepared by dissolving each of flocculants F500k, F350k, F200k and F100k in salt water of concentration 1g/L. In total 24 samples were prepared and used for the first size measurements with the Zeta sizer at 25 °C after sonicating for 2 minutes.

To vary the effects of salt concentration on droplet sizes, 100ppm and 1000ppm of each of flocculants F500k, F350k, F200k and F100k were prepared using salt water of

concentrations 0.1 g/L, 0.5 g/L, 5 g/L and 35 g/L of NaCl. In total 32 samples were prepared for the size measurements at varying salt concentrations. Each sample was analysed using the Malvern Zeta sizer Nano series at 25°C after sonicating for 2 minutes.

5.3.2 Zeta potential and size measurements

Salt water containing 1g/L NaCl was adjusted using HCl and NaHO to get salt water of pH 2, 3, 4, 5, 8, 9, and 10. The flocculants F500k, F350k, F200k, F100k were then dissolved in these water to produce samples of concentrations, 100ppm and 1000ppm. In total 48 samples were tested. The mixing of the samples in a sonicator was constant for 2 minutes and the measurements were done at 25°C using the Malvern zeta sizer.

5.3.3 Adsorption on solid surface.

Adsorption of the flocculants in silicodioxide surface was tested using Q-Sense E1 Quartz Crystal Microbalance (QCM). To test for effect of pH the samples were prepared by using salt water of concentration 1g/L NaCl adjusted to pH 3 and 10 using a pH meter. 10000ppm and 1000ppm of the flocculants F500k, F350k, F200k and F100k (16 samples) were tested. First the sensor was placed in a UV machine for 15 minutes and afterwards soaked in a Sodium dodecyl sulfate (SDS) bath for 30 minutes before rinsing with deionized water and drying with Nitrogen and placing again in UV for 10 minutes. This ensures that the surface of the sensor is free of any contaminant. The baseline for the sample was established by first acquiring the frequencies in air and later in water before establishing the base line. The samples were run at 25°C to ensure uniformity with previous experiments. During the process, water was first run through the system, followed by the sample, and followed by the base solvent before finally rinsing with water. The Data points were evaluated from the third fundamental frequency using the Sauerbrey equation, and graphs plotted to show the adsorption with time.

To vary the salt concentration, another set of samples were prepared using salt water of concentrations 35g/L and 1g/L to dissolve Flocculants F500k, F350k, F200k and F100k at 1000ppm and 10000ppm. In total 16 samples were prepared and tested same way as in 1g/L NaCl.

6 Results

This section presents results obtained from experiments with PolyDADMAC of varying molecular weights. As mentioned earlier the flocculants are represented as F500k, F350k, F200k and F100k according to molecular weight range. The results contain data on measured size distributions and adsorption at varying pH ranges and salt concentrations.

Results taken from the zeta sizer were the averages of 3 measurement points while that from the QCM were multiple data points in thousands analysed and plotted. All sizes from the zeta sizer is measured in diameter by nanometer (d.nm) and the zeta potentials in millivolts (mV) while adsorptions unto silica was measured in milligrams per meters square (mgm^{-2}).

6.1 Size distribution

The size distribution for flocculants F500k, F350k, F200k and F100k dispersed in water, salt water, and different pH solutions studied with the Mavern zetasizer reveals the effects of these factors on flocculants aggregation in solution. Increase in sizes of the flocs after dispersion depicts effective aggregation while increase in the Polydispersity Index reveals less dispersion of the flocculants in solution.

6.1.1 Effect of concentration

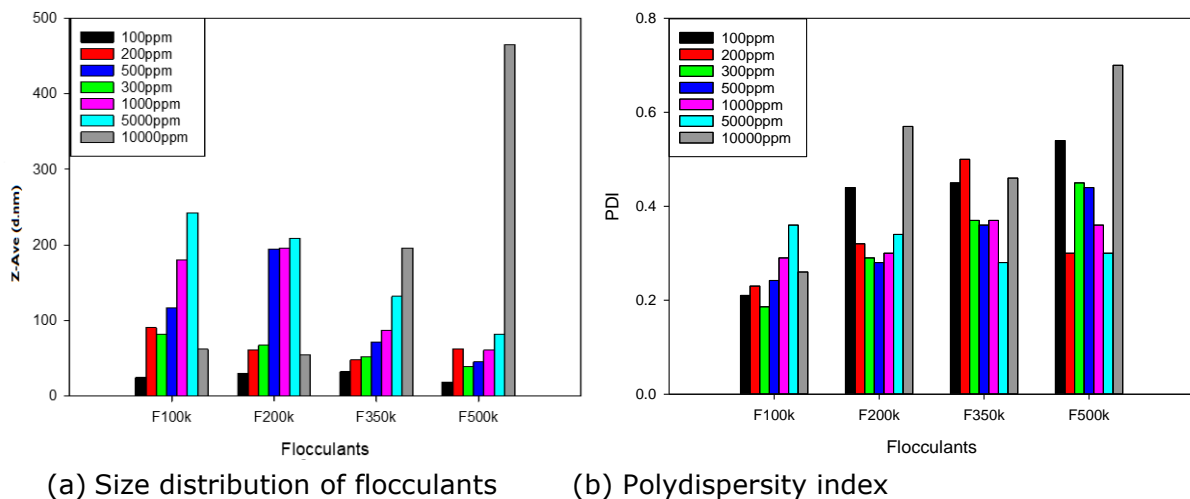


Figure 6.1: Size distribution of the flocculants and their PDI.

Size measurement for solutions prepared with 1g/L of NaCl and different concentrations of the flocculants at 100ppm, 200ppm, 300ppm, 500ppm, 1000ppm, 5000ppm and 10000ppm is shown in Figure 6.1. The presence of different molecular weight polymers of diverse chains and length is known to affect the polydispersity and size distribution of the flocculants in solution. It can therefore be observed that various flocculants of same concentration show different size distributions and PDI. Flocculants F100k, F200k, F350k and F500k tend to show an increase in aggregate sizes as their concentrations increase

from 100ppm to 10000ppm, except for flocculants F100k and F200k at 10000ppm where the aggregate size is lower at high concentrations. This is however due to the presence of high concentrations of lower molecular weight polymers in the solution. Flocculants aggregation is also best at 5000ppm for flocculants F100k and F200k. In flocculants F350k and F500k the aggregation is best at 10000ppm concentration showing that increase in flocculants concentration with increasing molecular weights affects flocculants aggregation positively.

6.1.2 Effect of salinity

At varying salt concentrations, the sizes of flocs in solution also vary. Measurements of two concentrations (100ppm and 1000ppm) of the flocculants at varying salt (NaCl) concentrations; 0ppm, 100ppm, 500ppm, 1000ppm, 5000ppm and 35000ppm was carried out. Figure 6.2 and Figure 6.3 show the size distributions and PDI of the flocculants respectively.

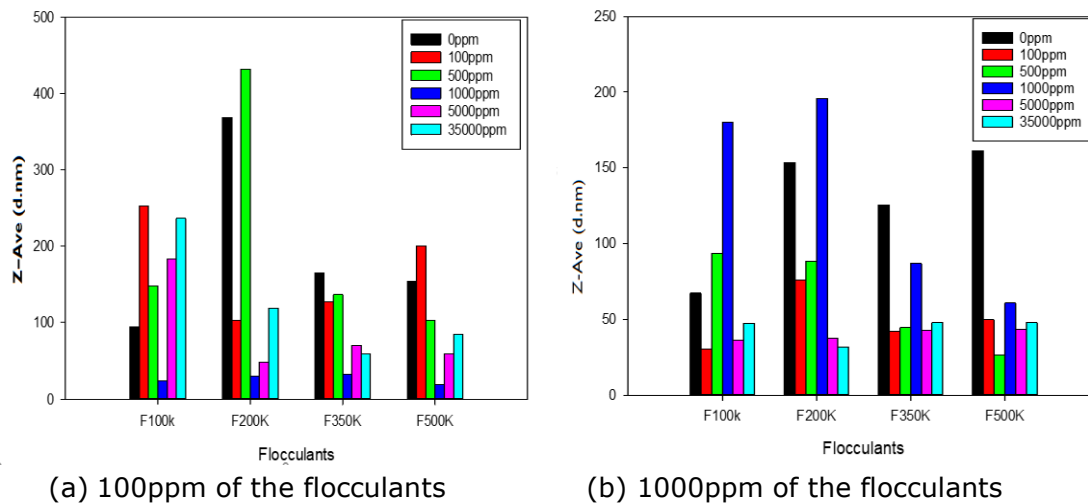


Figure 6.2: Size distributions of the flocculants at varying salt concentrations.

From Figures 6.2 (a) and 6.2 (b) flocculant F200k showed highest floc size at 500ppm of salt and concentration of 100ppm, which is higher than its floc size at 10000ppm. At 100ppm of salt F200k also show highest floc sizes at concentration of 1000ppm. In general, more adsorptions were observed at lower concentrations of the flocculants than at higher ones.

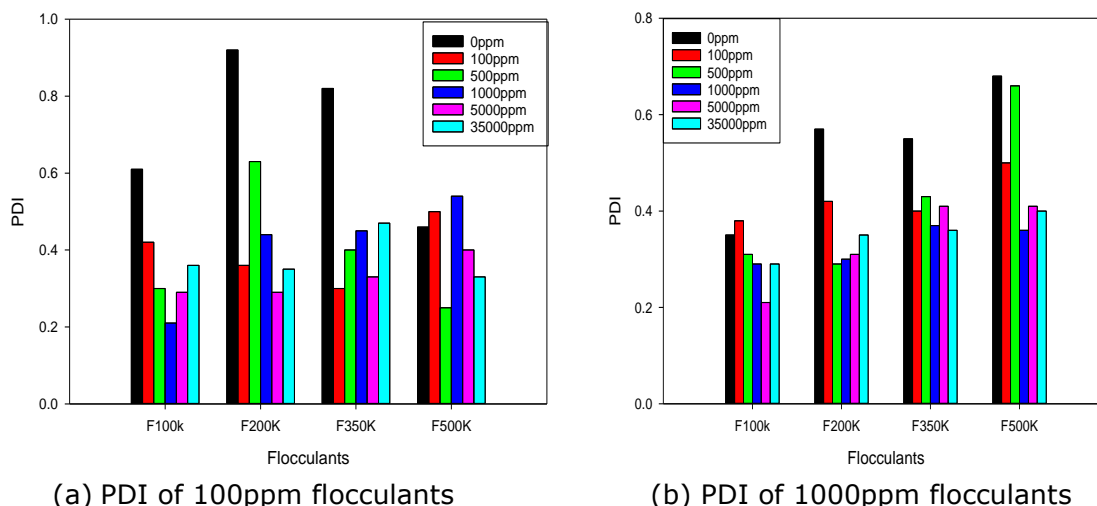


Figure 6.3: PDI of the flocculants at varying salt concentrations.

Figure 6.3 (a) and (b) show the PDI of the different flocculants at 100ppm and 1000ppm concentrations in varying salt concentrations. The flocculants tend to be more dispersed at lower concentrations as shown in (a) than in (b).

6.1.3 Effect of pH

The presence of divalent ions in the solution favours coalescence by minimizing the electrical double layer on the droplet surface. This is mostly observed across the pH by measuring their sizes and zeta potentials, where higher sizes indicate effective flocculants aggregation and lower zeta potentials also favour this assembly. Two concentrations of the flocculants 100ppm and 1000ppm were tested by varying the pH of the solutions from 3 to 9. The results of the size distribution of the flocculants is shown in Figure 6.4 and their zeta potentials in Figure 6.5.

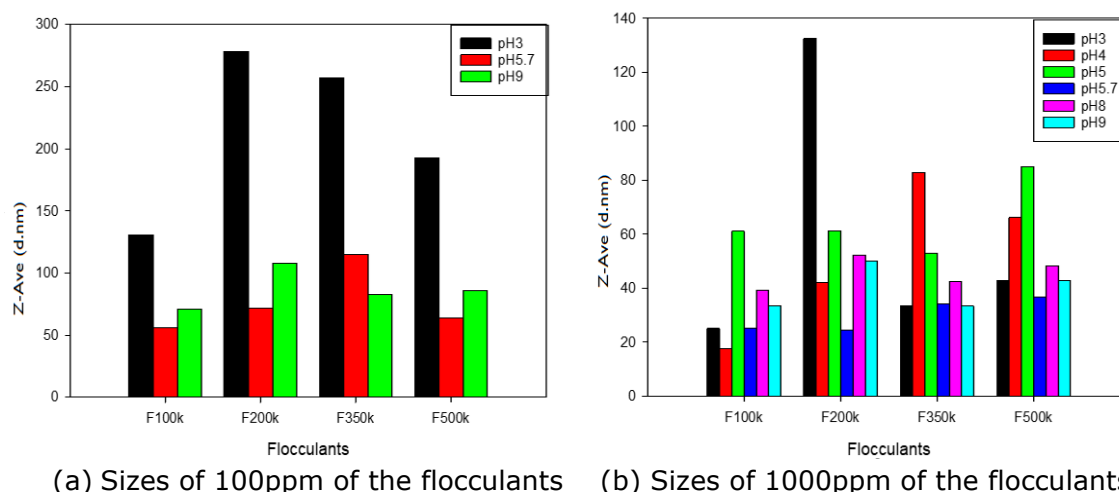
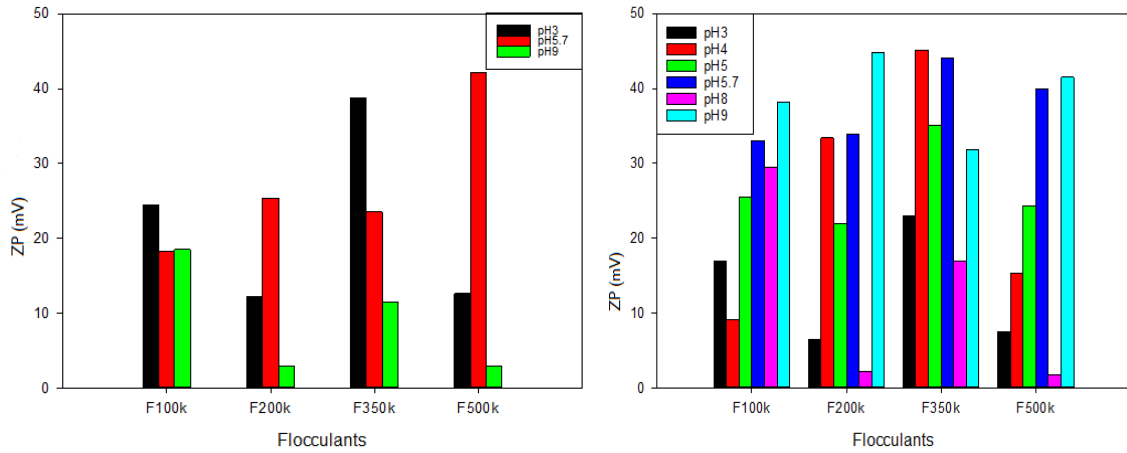


Figure 6.4: Size distributions of the flocculants at varying pH levels.

From Figure 6.4 (a) Typically largest floc sizes were detected at lower pH values as shown in Figure 6.4 (a) for 100ppm of the flocculants. At 1000ppm however, the highest floc sizes lie between pH3 and pH5.



(a) ZP of 100ppm of the flocculants

(b) ZP of 1000ppm of the flocculants

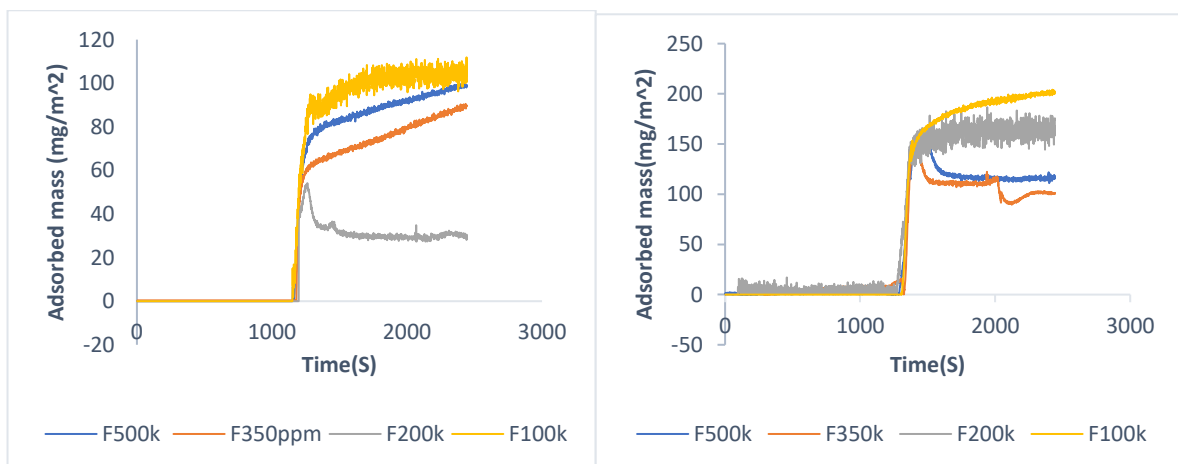
Figure 6.5: Zeta potentials of the flocculants.

Figure 6.5 (a) and (b) shows that all the zeta potential measurements are positive. Some polymers are more charged than others at different molecular weight and concentrations.

6.2 Adsorption on solid surface

The ability of the flocculants to adsorb on solid surface was tested using silica coated sensors for a QCM-D measurement. The expectation is different adsorption at varying salt concentration and pH as means of verifying the effects of these factors on flocculants adsorption unto surfaces. Two different concentrations 1000ppm and 10000ppm of the various flocculants were studied by varying the salt (NaCl) concentrations of the samples from 1g/L to 35g/L and from pH 3 to pH 10. The results were analysed by generally looking at the peaks of each flocculant adsorption at a point in time of the adsorption. This is due the nature of the graphs for adsorbed mass with time for all the flocculants in both salt water and different pH ranges. The solvent and rinsing parts of the graph are not shown in the graphs below, only the first parts of rapid adsorption is represented. 10 units in the time (X) axis corresponds to 3 seconds in real time.

6.2.1 Effects of varying Varying salt concentrations.



(a) 1000ppm of the flocculants

(b) 10000ppm of the flocculants

Figure 6.6: Adsorption of the flocculants at 1000ppm NaCl concentration.

Figure 6.6 (a) shows the adsorbed mass of 1000ppm of the different flocculants F100k, F200k, F350k and F500k in 1g/l NaCl. As measured from point 2440, F100k had the highest mass adsorbed and the adsorption decreased from F100k (103mg/m²) to F500k (98mg/m²), F350k (89mg/m²) with F200k (29mg/m²) having the lowest adsorbed mass. The mass adsorbed ranged from about 29mg/m² to about 103mg/m². At increased concentration of the flocculants as shown in Figure 6.6 (b), the mass adsorbed ranged from 100mg/m² to 200mg/m². F100k had the highest adsorbed mass, which decreased from F100k (200mg/m²) to F200k (162mg/m²), F500k (115mg/m²) and F350k (100mg/m²) had the lowest adsorption at this concentration.

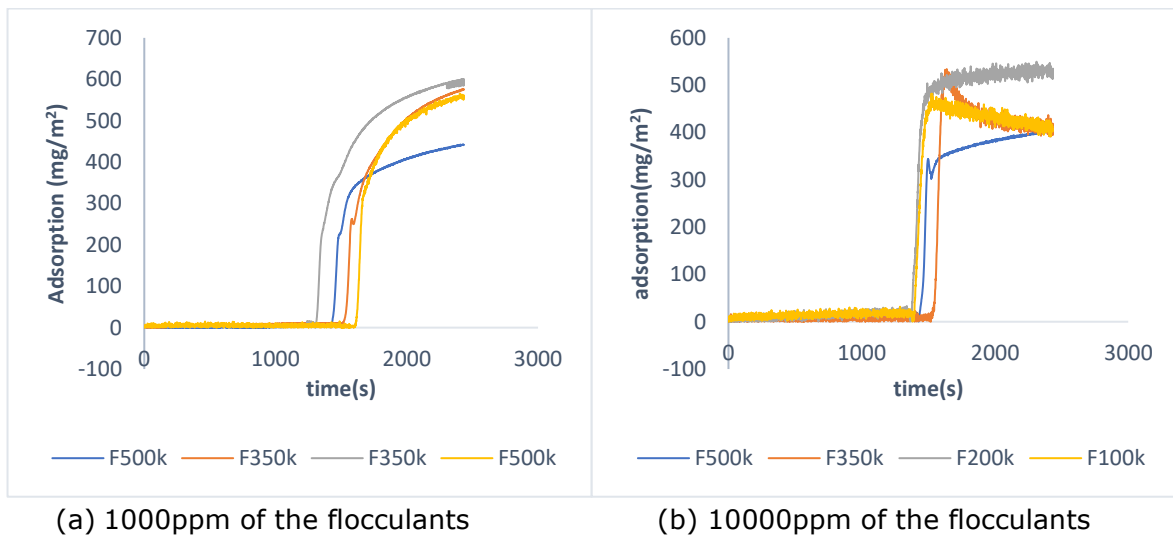


Figure 6.7: Adsorption of the flocculants at 35000ppm NaCl concentration.

Figures 6.7 (a) and (b) shows the adsorptions of the different flocculants F100k, F200k, F350k and F500k at 1000ppm and 10000ppm respectively in 35g/L NaCl. At 1000ppm of the flocculants the highest mass adsorbed was 598mg/m² and the lowest 442mg/m² as measured from point 2423, it also decreased from F350k (598mg/m²) to F200k (572mg/m²), F500k (570mg/m²) and F100k (442mg/m²) had the lowest adsorbed mass. At increased concentration (10000ppm) of the flocculants, the highest mass adsorbed was at 533mg/m² and lowest at 403mg/m² and decreased from F200k (533mg/m²) to F350k (412mg/m²), F100k (412mg/m²) and F500k (403mg/m²) had the least adsorbed mass. Where F500k, F350k and F100k seem to have similar amounts adsorbed at this point.

Comparing the amount of flocculants adsorbed at different salt concentrations reveals higher amounts of the flocculants were adsorbed at higher salt concentrations. This might be due to the nature of PolyDADMAC as a flocculant with high tolerance for salt and pH. When the salt concentration is low, higher concentrations of the flocculants had better adsorption and vice versa, this is due to the difference in solubilities of high molecular weight polymers from the lower molecular weight ones. Decrease in salt concentrations decrease solubility and increase adsorption for higher molecular weight polymers than their lower counterparts.

6.2.2 Effects of pH

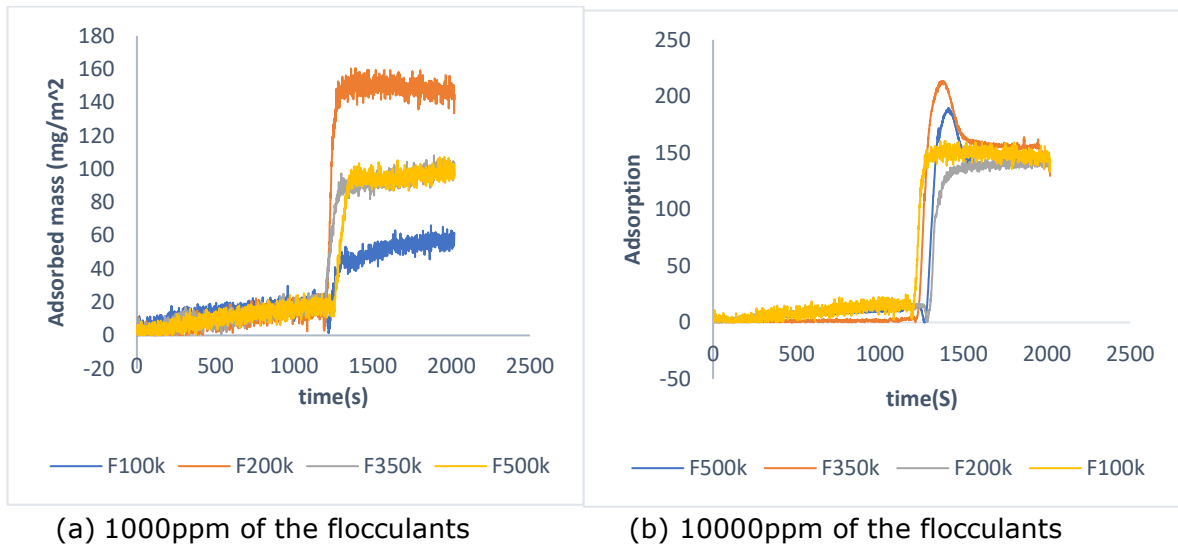


Figure 6.8: Adsorption of the flocculants at pH3.

Figure 6.8 (a) shows the adsorption of 1000ppm of all flocculants at pH3. Values taken from point 1895 showed that F200k had the highest adsorbed mass of 148mg/m², flocculants F500k and F350k had adsorbed mass of 99mg/m² and F100k had the lowest adsorption of 48mg/m². In Figure 6.8 (b), at 10000ppm the adsorbed mass for all flocculant types were almost same with little variations. The highest adsorbed mass was 149mg/m² by F350k and 148mg/m² for F500k and F100k. The lowest adsorption is seen in F200k with 142mg/m². Due to desorption, F500k and F350k may have lost masses to get to their values as shown in the highest peaks of Figure 6.8 (b)

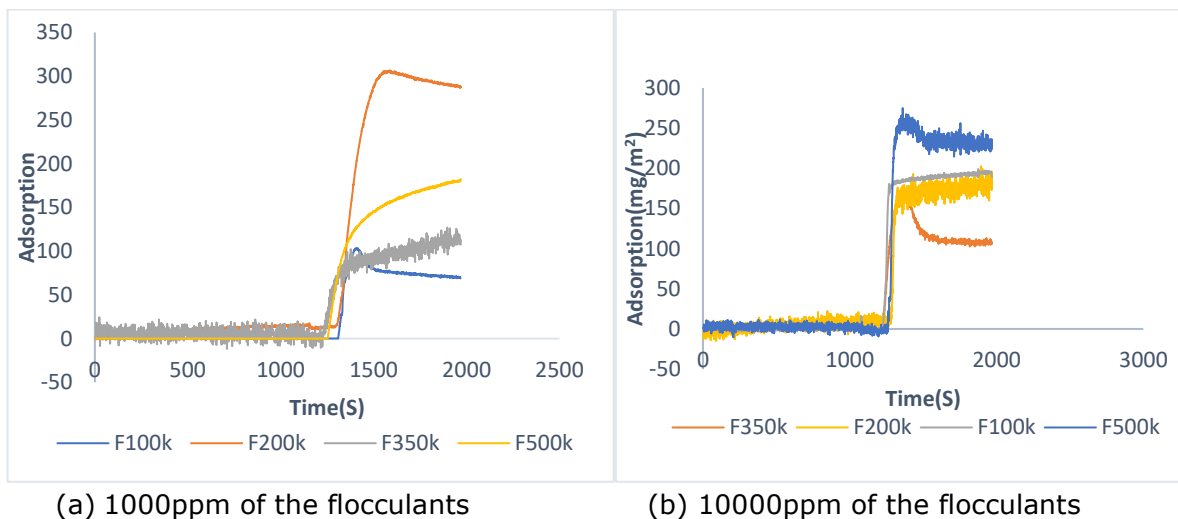


Figure 6.9: Adsorption of the flocculants at pH10

Figure 6.9 (a) and (b) show the adsorbed masses of 1000ppm and 10000ppm respectively of flocculants F500k, F350k, F200k and F100k at pH10. Taking measurements from point 192 revealed that at 1000ppm of the flocculants, the mass

adsorbed varied from 69mg/m² to 288mg/m² with F200k having the highest mass and F100k having the lowest. 181mg/m² and 113 mg/m² of F500k and F350k respectively were also adsorbed at this concentration. At a concentration of 10000ppm, F500k had the highest mass adsorbed at 235mg/m², the adsorbed mass decreases from this number to 194mg/m² in F100k, and to 183mg/m² in F200k and finally to 108mg/m² in F350k. It was obvious from both results that the mass adsorbed by all flocculants increased with increasing concentration of the flocculants except for flocculant F200k. In comparison with pH3, all mass adsorbed at pH10 are higher for all flocculants than those of pH3 irrespective of their concentration.

6.3 Adsorptions of each flocculant type at varying pH and salt.

Studying the effects of varying both salt concentrations and pH levels for each flocculant type is essential in determining the effect of these factors on a particular type and concentration of the flocculant. Specifically, as each of the factors behaved in such a manner that affects the flocculants irrespective of other factors, this section outlines the effect of the different factors on each type and concentration of the flocculants.

1000ppm and 10000ppm of the flocculants were tested for adsorption by varying the salt (NaCl) concentration from 1g/L to 35g/L and varying the pH from pH 3 and pH10. Figures 6.10 to 6.13 show the results of these experiments.

6.3.1 Effects of varying pH and salts on flocculant F500k

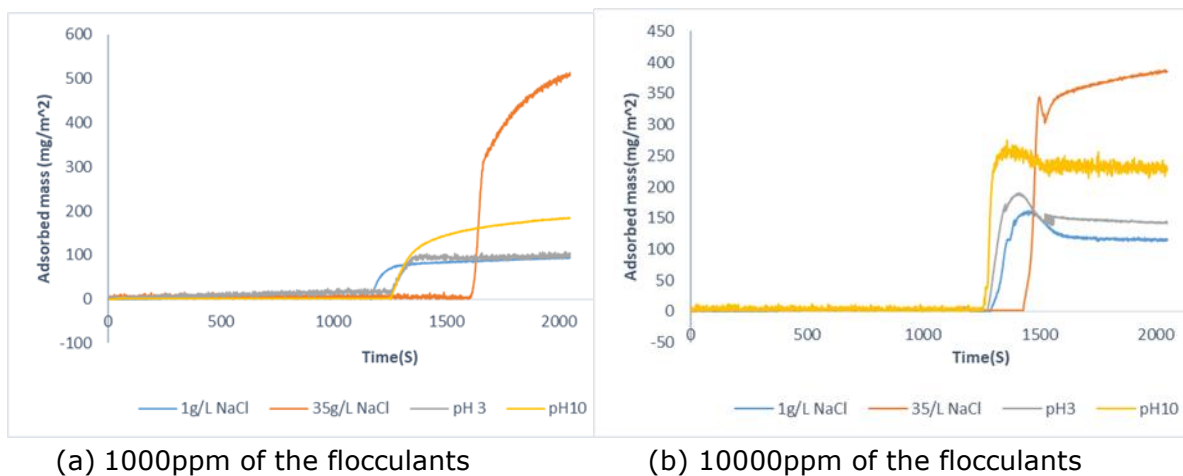


Figure 6.10: Effects of varying pH and NaCl on flocculant F500k.

Figures 6.10 (a) and (b) show the masses adsorbed at 1000ppm and 10000ppm of F500k at varying pH and salt concentration. As measured from point 2049, the highest adsorptions were seen at higher salt concentrations than at lower ones, also more masses were adsorbed at pH 10 than pH 3

6.3.2 Effects of varying pH and salts on flocculant F350k.

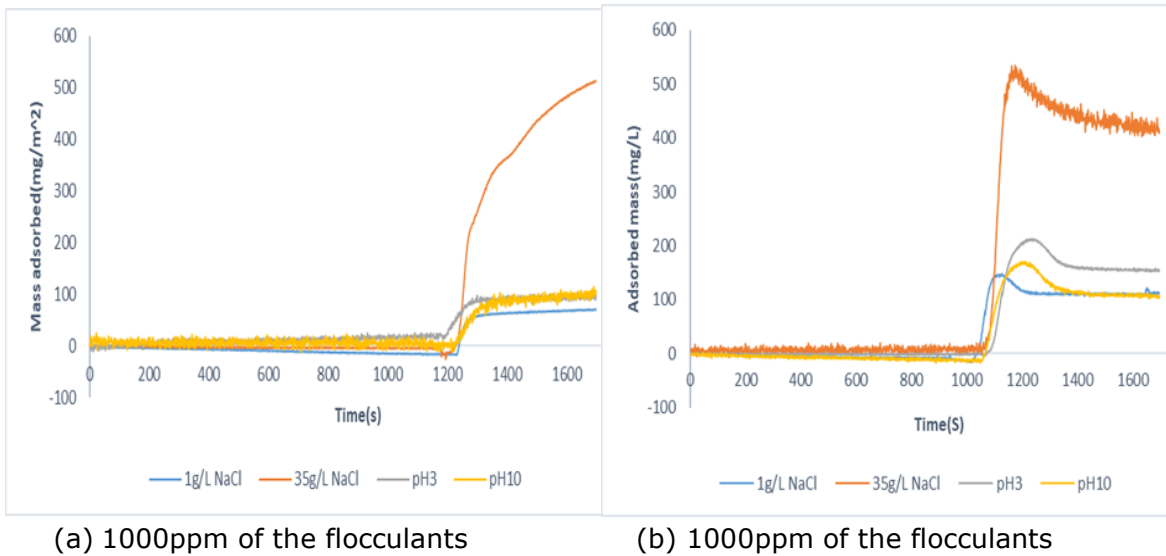


Figure 6.11: Effects of varying pH and NaCl on flocculant F350k.

Figure 6.11(a) and (b) shows the different adsorbed masses for flocculants F350k at varying salinities and pH. From data taken at point 1698, the highest adsorbed masses were also seen at higher salt concentrations than at lower salt concentrations. Though the adsorption shown at higher concentrations for all flocculant types were generally higher than those of lower concentration, more masses seemed to be adsorbed at pH10 than pH3.

6.3.3 Effects of varying pH and salts on flocculant F200k.

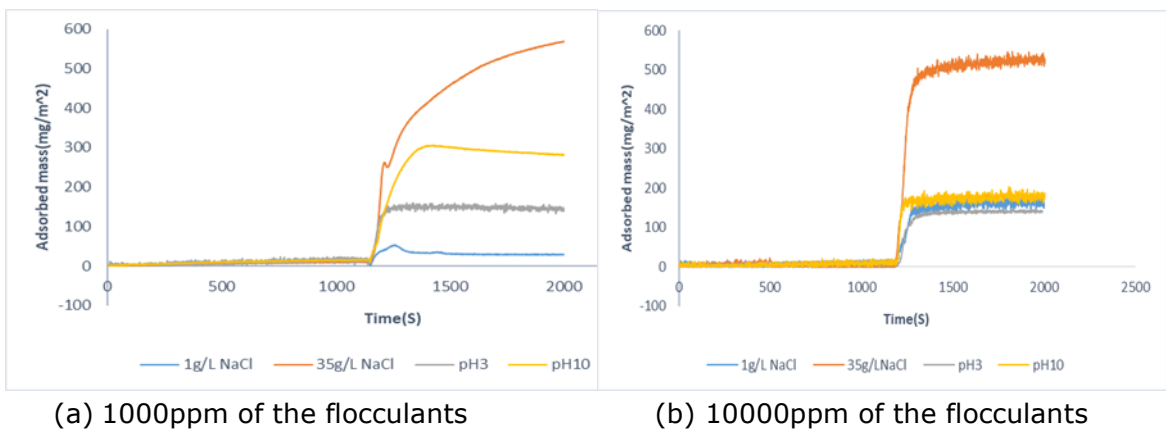


Figure 6.12: Effects of varying pH and NaCl on flocculant F200k.

Figure 6.12 (a) and Figure 6.12 (b) show the masses adsorbed at 1000ppm and 10000ppm of F200k at varying concentrations of pH and NaCl. With data measured from point 1988, Highest masses were adsorbed at 35g/L NaCl than at 1g/L of the salt where the mass increased at increasing concentration of the flocculants. Adsorption seemed to be higher at pH10 than pH 3 and decreased with increasing concentrations of the flocculants.

6.3.4 Effects of varying pH and salts on flocculant F100k.

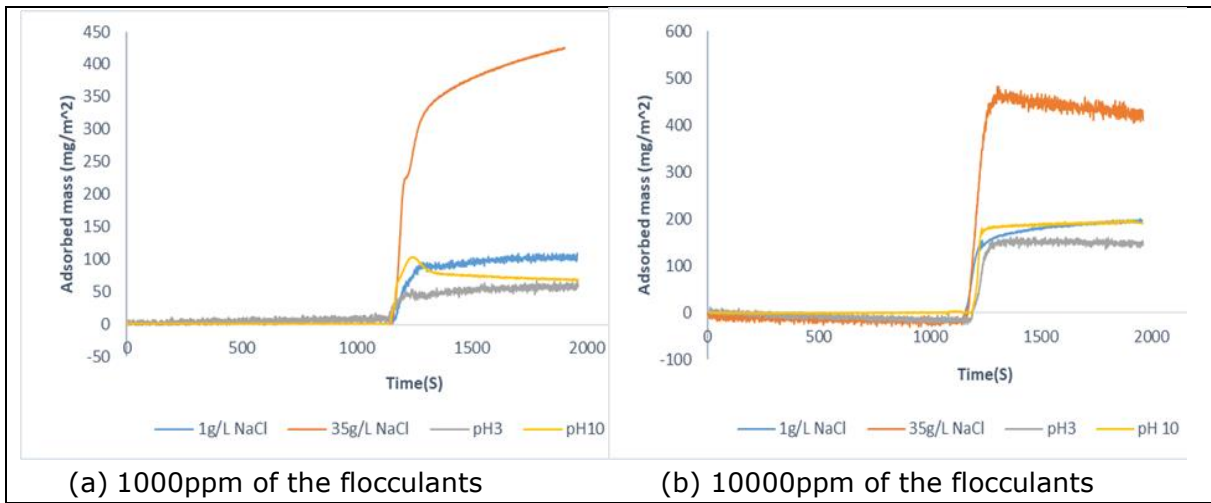


Figure 6.13: Effects of varying pH and NaCl on flocculant F100k.

Figure 6.13 (a) represent the graph of the mass adsorbed at 1000ppm of F100k flocculants at varying pH and salinity. Data measured from point 1946, showed that the highest adsorbed mass was at 35g/L NaCl than at 1g/L NaCl both at high and lower concentrations of the flocculant. The adsorbed masses were also higher at pH 10 than pH 3 for both concentrations of the flocculants.

7 Discussions

7.1 Influence on the size distribution and PDI.

From the results obtained from the zeta sizer experiments, the size of the different flocculants tended to vary with introduction of new parameters like varying salt concentrations and pH. At different concentrations of the flocculants, the aggregate sizes tended to increase with increasing concentration of the flocculants and decreased from F100k to F500k according to the flocculants molecular weight, except for few concentrations where the behaviour is the other way round. PDI is also reasonably low at these concentrations as shown in Figure 6.3 indicating that the flocculants are more dispersed at lower molecular weights than at higher ones. This is due to higher solubility of polymers at lower molecular weight than at higher molecular weight. (Kronberg, Holmberg and Lindman, 2014).

The influence of salinity on aggregate sizes as measured with the zeta sizer followed diverse trends due to the shape and length of the polymers. The sizes of the aggregates seemed to be very high without salts and also had a very high PDI indicating that at this point the flocculants were not polydispersed in water. The sizes of aggregates formed varied individually with variation in salt concentrations.

At varying pH levels and lower concentrations of the flocculants, the aggregate sizes were highest at pH3 than pH9 and lowest at pH 5.7 except in F350k where the mass adsorbed at pH 5.7 is higher than that adsorbed at pH9. At higher concentrations of the flocculant, all flocculants tended to show higher aggregate size distributions at pH3, pH4 and pH5. The lowest sizes were found at pH 5.7 except in flocculant F100k and at pH 4, where the size of the aggregates was lower than that of pH 5.7. At higher pH values (pH8, pH9), the aggregate size distribution was also higher than that of pH5.7. It can be inferred that the aggregate sizes were higher in acid mediums from 4 to 5 and alkaline mediums of 8 and 9 depending on the type of flocculant.

7.2 Influence on mass adsorbed

At varying concentrations of the flocculants, the mass adsorbed to silica surface showed that more mass was adsorbed at higher concentrations than at lower concentrations of the flocculants. The mass adsorbed also depended on the flocculant type and molecular weight. At lower concentrations of the flocculants, adsorbed mass increased from F200k to F350k to F500k and F100k had the highest adsorption, while at higher concentration of the flocculants the adsorbed mass increased from F350k to F500k to F200k and finally to F100k.

At varying salinity, more masses were adsorbed at higher salt concentrations than at lower concentrations of the salt irrespective of the flocculant's concentration. However, the mass adsorbed was also dependent on each flocculant type and generally increased with increase in the concentration of the flocculants.

At varying pH levels, more mass was adsorbed at pH 10 in all flocculants than pH3 as shown in Figures 6.10, 6.11a, 6.12, and 6.13 except in Figure 6.11b, where the mass

adsorbed was more at pH3 than pH 10. This might be due to strong charge interactions between the charged groups of polyDADMAC and the silica surface at this pH.

8 Conclusion

Experiments were carried out to investigate the effect of salinity, pH, and aggregate sizes of different flocculants in addition to reviewing polymer flooded produced water. The experiments were conducted using Dynamic light scattering method and Quartz Crystal Microbalance with Dissipation (QCM-D) to measure the aggregate size distribution and mass adsorbed on Silica surface. The measured sizes helped understand the principles and mechanism of flocculants assembly in water, while the adsorbed mass provided information on conformational changes and adsorptional geometry of polymers at solid/liquid interfaces.

Different concentrations of flocculants of varying molecular weight from 100000 to 500000 were tested by varying their salinity, Mw and pH.

The result revealed that the aggregate size distribution varied greatly at different concentrations when salinity and pH were varied. Results from adsorption showed that more mass were generally adsorbed unto solid surfaces at higher salt concentrations and pH levels than when these factors are less. The aggregate size distribution for different flocculants varied individually with an increase or decrease in the amounts of these factors and the concentrations of the flocculants with no regular trend.

Salinity, and pH affect aggregation of flocculants and depended on the amounts of these factors introduced into the system. Each flocculants type performed best at specific salinities and pH. The choice of polymeric flocculant for use in produced water treatment is dependent on the salinity and pH of the water and the Mw of the flocculant.

A review of PFPW showed that addition of polymers in water during EOR increases the viscosity of the water and enhances recovery of oil up to 50%. The water generated from the process usually contain high amounts of polymers and water volumes when compared to the regular produced water. In Oil and gas industries, the aim of treating the water is mainly for re-use in production except in cases when there is need to discharge the water. Proper treatment of PFPW involves oil and gas removal, water treatment with chemical agents, use of techniques like filtration, hydrocyclones, centrifugation and gas flotation to remove dispersed substances in the water. The polymers present in the water are removed by degradation through altering the polymer chemistry and flocculation with coagulants and electrocoagulants or precipitation with particle like clay before separating it from the fluid bulk. Polymers are usually removed from PFPW before effecting other treatment methods in order to avoid interference.

Bibliography

- Aguiar, J. I. and Mansur, C. (2016) THE INFLUENCE OF POLYMER FLOODING ON PRODUCED OILY WATER: A REVIEW, *Brazilian Journal of Petroleum and Gas*, 10, pp. 49-61. doi: 10.5419/bjpg2016-0005.
- Ahmadun, F. R. *et al.* (2009) Review of technologies for oil and gas produced water treatment, *Journal of Hazardous Materials*, 170(2-3), pp. 530-551. doi: 10.1016/j.jhazmat.2009.05.044.
- Ahmed, T. and Meehan, D. N. (2012) 6.4.2 Surfactant Slug and Micellar Solution Flood *Advanced Reservoir Management and Engineering (2nd Edition)*. Elsevier.
- Ancheyta, J. and Ancheyta, J. (2011) *Modeling and Simulation of Catalytic Reactors for Petroleum Refining*. New York, UNITED STATES: John Wiley & Sons, Incorporated.
- Arnold, K. and Stewart, M. (1999) 9. Produced Water Treating Systems *Surface Production Operations - Design of Oil Handling Systems and Facilities, Volume 1 (3rd Edition)*. Elsevier.
- Arthur, J. *et al.* (2005) Technical Summary of Oil & Gas Produced Water Treatment Technologies.
- Bratby, J. (2006) Coagulation and flocculation in water and wastewater treatment, *Water* 21, (AUG.), pp. 25-27. Available at: <https://www.scopus.com/inward/record.uri?eid=2-s2.0-33747183334&partnerID=40&md5=ae25e50a08731a348f6d715f831cd4f2>.
- Bratby, J. (2006) *Coagulation and Flocculation in Water and Wastewater Treatment - Second Edition*. IWA Publishing.
- Chen, H.-x. *et al.* (2015) Oil-water separation property of polymer-contained wastewater from polymer-flooding oilfields in Bohai Bay, China, *Environmental Technology*, 36(11), pp. 1373-1380. doi: 10.1080/09593330.2014.990522.
- Deng, S. *et al.* (2005) Destabilization of oil droplets in produced water from ASP flooding, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 252(2-3), pp. 113-119. doi: 10.1016/j.colsurfa.2004.09.033.
- Dudek, M. (2018) *Produced Water Quality and Microfluidic Methods for Studying Drop-Drop and Drop-Bubble Interactions in Produced Water*. PhD, NTNU. Available at: <http://hdl.handle.net/11250/2564008> (Accessed: 03.02.2020).
- Ese, M. H. and Kilpatrick, P. K. (2004) Stabilization of Water-in-Oil Emulsions by Naphthenic Acids and Their Salts: Model Compounds, Role of pH, and Soap:Acid Ratio, *Journal of Dispersion Science and Technology*, 25(3), pp. 253-261. doi: 10.1081/DIS-120038634.
- Gass, N. O. (2017) *Facts and development trends*. (Environmental work by the oil and gas industry). Oslo.
- Han, L., Galier, S. and Roux-De Balmann, H. (2015) Ion hydration number and electroosmosis during electrodialysis of mixed salt solution, *Desalination*, 373, pp. 38-46. doi: 10.1016/j.desal.2015.06.023.
- Hocking, M. B., Klimchuk, K. A. and Lowen, S. (1999) Polymeric Flocculants and Flocculation, *Journal of Macromolecular Science, Part C*, 39(2), pp. 177-203. doi: 10.1081/MC-100101419.
- Huang, B. *et al.* (2019) Study on Demulsification-Flocculation Mechanism of Oil-Water Emulsion in Produced Water from Alkali/Surfactant/Polymer Flooding, *Polymers*, 11(3), pp. 13. doi: 10.3390/polym11030395.
- Igunnu, E. T. and Chen, G. Z. (2012) Produced water treatment technologies, *International Journal of Low-Carbon Technologies*, 9(3), pp. 157-177. doi: 10.1093/ijlct/cts049.

- Jing, G. L. *et al.* (2010) Development of a four-grade and four-segment electro dialysis setup for desalination of polymer-flooding produced water, *Desalination*, 264(3), pp. 214-219. doi: 10.1016/j.desal.2010.06.042.
- Kelland, M. (2009) *Production Chemicals for the Oil and Gas Industry*.
- Kelland, M. A. (2014) Production chemicals for the oil and gas industry. Available at: <http://www.crcnetbase.com/isbn/9781439873793>.
- Kronberg, B., Holmberg, K. and Lindman, B. (2014) Surface chemistry of surfactants and polymers. Available at: <http://www.books24x7.com/marc.asp?bookid=72935>.
- Kronberg, B., kirjoittaja (2014) *Surface chemistry of surfactants and polymers*. Wiley.
- Lazaro, A. (2014) *Nano-silica production at low temperatures from the dissolution of olivine - Synthesis, tailoring and modelling*.
- Lee, C. S., Robinson, J. and Chong, M. F. (2014) A review on application of flocculants in wastewater treatment, *Process Safety and Environmental Protection*, 92(6), pp. 489-508. doi: 10.1016/j.psep.2014.04.010.
- Lee, K. (2011) *Produced Water: Environmental Risks and Advances in Mitigation Technologies*.
- Levine, S., Bowen, B. D. and Partridge, S. J. (1989) Stabilization of emulsions by fine particles I. Partitioning of particles between continuous phase and oil/water interface, *Colloids and Surfaces*, 38(2), pp. 325-343. doi: [https://doi.org/10.1016/0166-6622\(89\)80271-9](https://doi.org/10.1016/0166-6622(89)80271-9).
- Mai, Y. and Eisenberg, A. (2012) Self-Assembly of Block Copolymers, *Chemical Society reviews*, 41, pp. 5969-5985. doi: 10.1039/c2cs35115c.
- Mavern (2013) *Zeta sizer nano series. User manual* (Accessed: 02.03 2020).
- McClements, D. J. (2009) CHAPTER 4 - Biopolymers in Food Emulsions, in Kasapis, S., Norton, I. T. and Ubbink, J. B. (ed.) *Modern Biopolymer Science*. San Diego: Academic Press, pp. 129-166.
- McLean, J. D. and Kilpatrick, P. K. (1997) Effects of Asphaltene Solvency on Stability of Water-in-Crude-Oil Emulsions, *Journal of Colloid and Interface Science*, 189(2), pp. 242-253. doi: <https://doi.org/10.1006/jcis.1997.4807>.
- Mousa, K. and Hadi, H. (2016) Coagulation/Flocculation Process for Produced Water Treatment, *International Journal of Current Engineering and Technology*, 6.
- Mudalige, T. *et al.* (2019) Chapter 11 - Characterization of Nanomaterials: Tools and Challenges, in López Rubio, A., *et al.* (ed.) *Nanomaterials for Food Applications*. Elsevier, pp. 313-353.
- Mueller, J., Cen, Y. and Davis, R. H. (1997) Crossflow microfiltration of oily water, *Journal of Membrane Science*, 129(2), pp. 221-235.
- Nabzar, L. (2011) *Water in fuel production Oil production and refining*.
- Neff, J., Boesch, D. and Rabalais, N. (1987) *Offshore oil and gas development activities potentially causing long-term environmental effects*. United States: Elsevier Science Pub. Co. Inc., New York, NY.
- Neff, J. (2002) Bioaccumulation in Marine Organisms: Effect of Contaminants from Oil Well Produced Water, pp. 241-313.
- NRPA (2004) *Natural Radioactivity in Produced Water from the Norwegian Oil and Gas Industry in 2003*. (StrålevernRapport 2005:2. Østerås: Norwegian Radiation Protection Authority Postboks 55). Norway.
- Otsuka, H., Nagasaki, Y. and Kataoka, K. (2001) Self-assembly of block copolymers, *Materials Today*, 4(3), pp. 30-36. doi: [https://doi.org/10.1016/S1369-7021\(01\)80036-5](https://doi.org/10.1016/S1369-7021(01)80036-5).
- Ottaviano, J. G., Cai, J. and Murphy, R. S. (2014) Assessing the decontamination efficiency of a three-component flocculating system in the treatment of oilfield-produced water, *Water research*, 52, pp. 122-130. doi: <http://dx.doi.org/10.1016/j.watres.2014.01.004>.
- Panneer Selvam, A. K. (2018) *Removal of dispersed oil drops by induced gas flotation*. Available at: <http://hdl.handle.net/11250/2574192>.
- Pillai, J. (1997) Flocculants and Coagulants: The Keys to Water and Waste Management in Aggregate Production.

- Presswire (2018) Increasing demand for petroleum products boosts the Global Crude Oil market at a CAGR of 3.18% by 2026, *M2 Presswire*.
- Sandhu, R. *et al.* (2018) Dynamic light scattering (DLS) technique, principle, theoretical considerations and applications. pp. 135-137.
- Shvets, V. F. *et al.* (2016) New ways to increase the depth of crude oil refining, *Russian Journal of Applied Chemistry*, 89(11), pp. 1806-1815. doi: 10.1134/S1070427216110112.
- Sönnichsen, N. (2020) *Daily demand for crude oil worldwide from 2006 to 2020*. Available at: <https://www.statista.com/statistics/271823/daily-global-crude-oil-demand-since-2006/>.
- Sosa-Fernandez, P. A. *et al.* (2018) Electrodialysis-based desalination and reuse of sea and brackish polymer-flooding produced water, *Desalination*, 447, pp. 120-132. doi: 10.1016/j.desal.2018.09.012.
- Speight, G. (2013) Heavy oil recovery process, in Speight, J. G. (ed.) *Heavy Oil Production Processes*. Boston: Gulf Professional Publishing, pp. 1-148.
- Subramanian, S. *et al.* (2018) Influence of Fatty-Alkylamine Amphiphile on the Asphaltene Adsorption/Deposition at the Solid/Liquid Interface under Precipitating Conditions, *Energy & Fuels*, 32(4), pp. 4772-4782. doi: 10.1021/acs.energyfuels.8b00059.
- Tadros, T. (2013) Emulsion Formation, Stability, and Rheology. Emulsion Formation and Stability. 10.1002/9783527647941.ch1.
- Tarleton, E. S. and Wakeman, R. J. (2007) 3 - Pretreatment of suspensions, in Tarleton, E. S. and Wakeman, R. J. (ed.) *Solid/Liquid Separation*. Oxford: Butterworth-Heinemann, pp. 126-151.
- Thomas, A. (2019) Essentials of polymer flooding technique. Available at: <https://search.ebscohost.com/login.aspx?direct=true&scope=site&db=nlebk&db=nlabk&AN=2089003>.
- Veil, J. A. *et al.* (2004) *A white paper describing produced water from production of crude oil, natural gas, and coal bed methane*. United States. Available at: <https://www.osti.gov/servlets/purl/821666>.
- Wilson, D. J. and French, R. H. (1978) Kinetic and Equilibrium Aspects of Flocc Coagulation. II. Slow Mixing Criteria, *Separation Science and Technology*, 13(2), pp. 95-106. doi: 10.1080/01496397808057092.
- Wilson, J. (2008) *Synthesis, Properties and Analysis of polyDADMAC for water purification*. Doctoral thesis, , University of Stellenbosch, S.A.
- Xu, J. *et al.* (2016) Pilot study on hydrophilized PVDF membrane treating produced water from polymer flooding for reuse, *Process Safety and Environmental Protection*, 104, pp. 564-570.
- Yarranton, H. W., Urrutia, P. and Sztukowski, D. M. (2007) Effect of interfacial rheology on model emulsion coalescence II. Emulsion coalescence, *Journal of Colloid and Interface Science*, 310(1), pp. 253-259.
- Zheng, J. *et al.* (2016) Offshore produced water management: A review of current practice and challenges in harsh/Arctic environments, *Marine Pollution Bulletin*, 104(1), pp. 7-19. doi: <https://doi.org/10.1016/j.marpolbul.2016.01.004>.

Appendices

Appendix 1: Zetasizer results for varying salt concentrations.

100ppm of the flocculants at varying salt concentrations

	Oppm	100ppm	500ppm	1000ppm	5000ppm	35000ppm
F100k	94.8	253.3	147.8	24.5	183.3	236.4
F200K	368.7	103.5	432.1	30.15	48.7	118.9
F350K	165.4	127.3	136.8	32.05	70.22	59.53
F500K	153.9	200.7	102.7	18.8	59.21	84.39

1000ppm of the flocculants at varying salt concentrations

	Oppm	100ppm	500ppm	1000ppm	5000ppm	35000ppm
F100k	67.05	30.52	93.64	180	35.94	47.14
F200K	153.3	75.58	88	196	37.38	31.35
F350K	125.4	41.9	44.33	86.69	42.73	47.64
F500K	161.5	49.6	26.32	60.58	43.24	47.84

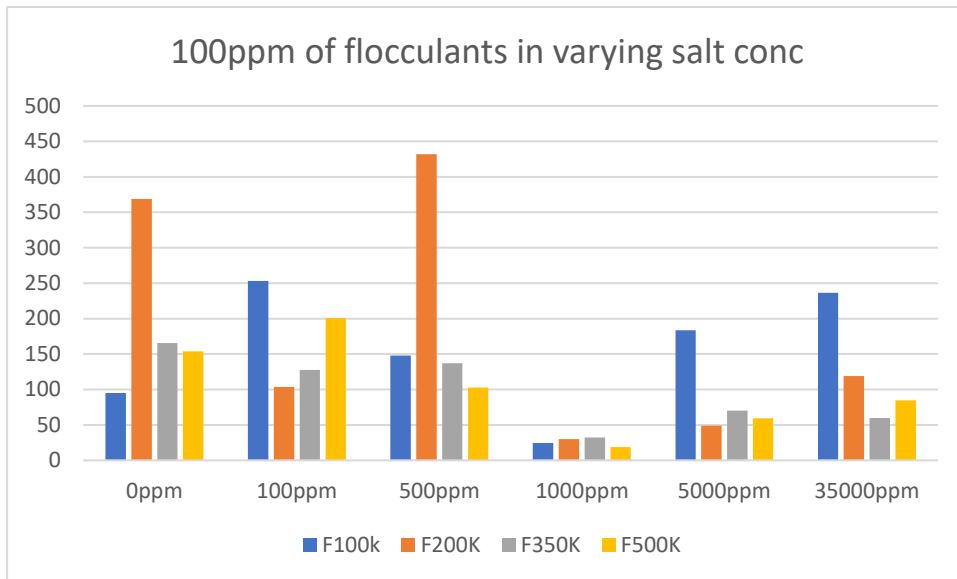
Polydispersity index of **100ppm** flocculants at varying salt concentrations

	Oppm	100ppm	500ppm	1000ppm	5000ppm	35000ppm
F100k	0.61	0.42	0.3	0.21	0.29	0.36
F200K	0.92	0.36	0.63	0.44	0.29	0.35
F350K	0.82	0.3	0.4	0.45	0.33	0.47
F500K	0.46	0.5	0.25	0.54	0.4	0.33

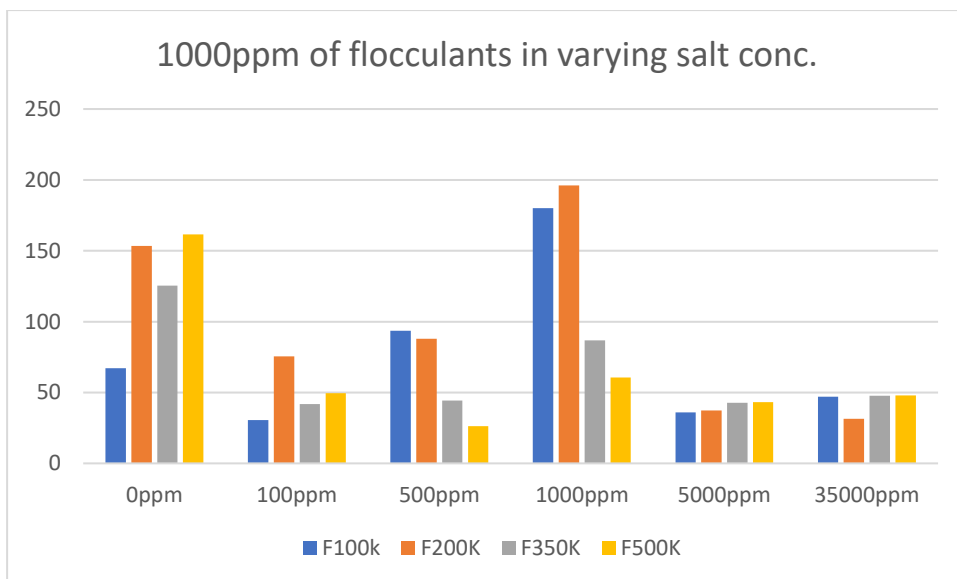
Polydispersity index of **1000ppm** flocculants at varying salt concentrations

	Oppm	100ppm	500ppm	1000ppm	5000ppm	35000ppm
F100k	0.35	0.38	0.31	0.29	0.21	0.29
F200K	0.57	0.42	0.29	0.3	0.31	0.35
F350K	0.55	0.4	0.43	0.37	0.41	0.36
F500K	0.68	0.5	0.66	0.36	0.41	0.4

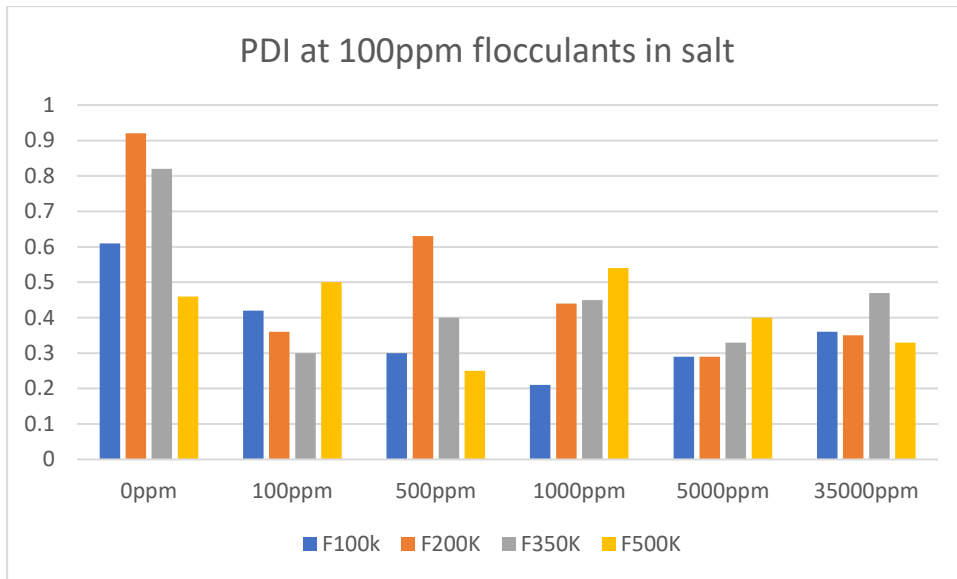
Appendix 2: Graphs of zeta sizer experiments for varying salt concentrations.



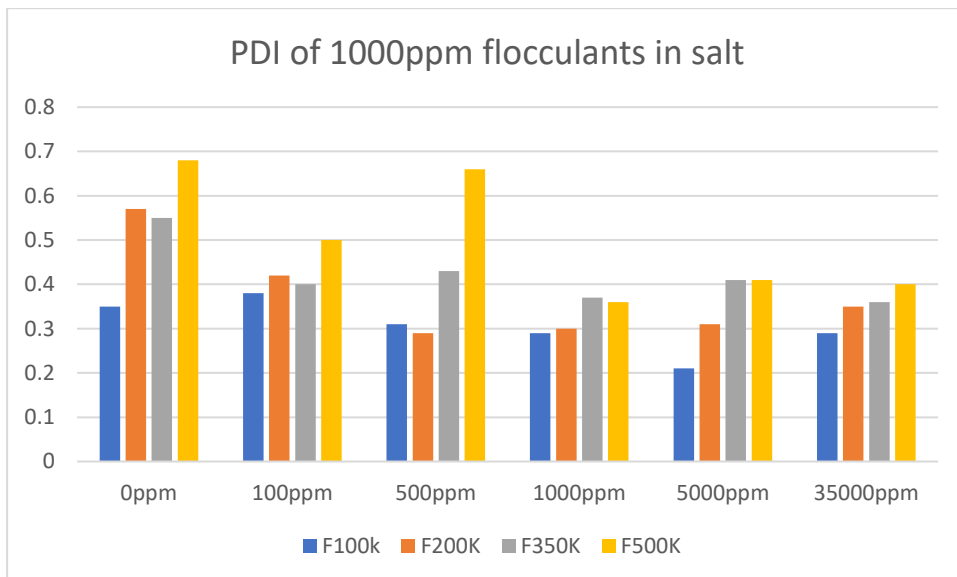
(a)



(b)



(c)



(d)

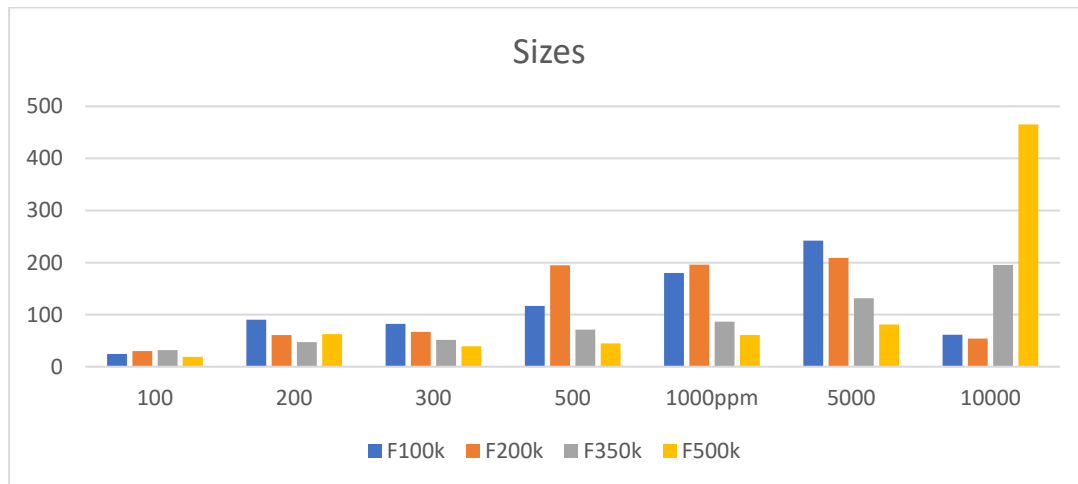
Appendix 3: Zeta sizer results for varying flocculant concentrations.

Sizes of different concentrations of the flocculants in water.

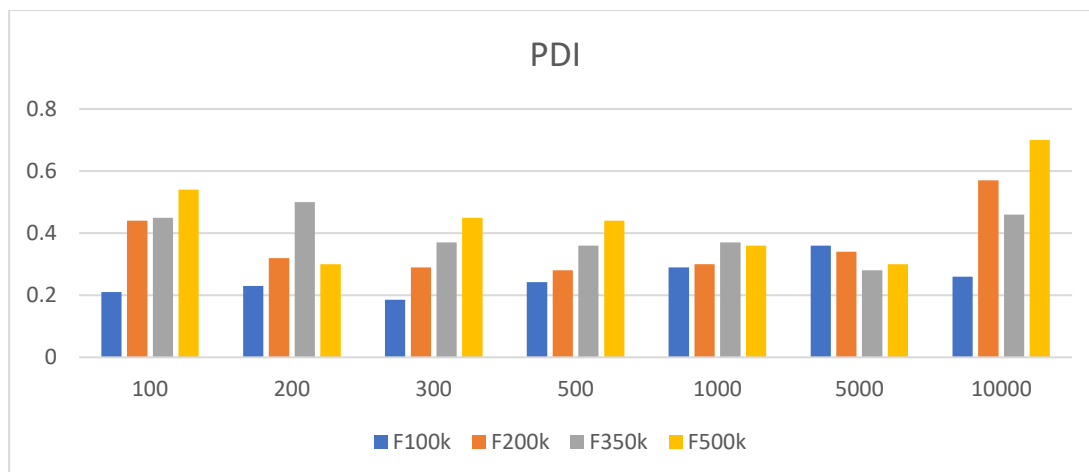
	100ppm	200ppm	300ppm	500ppm	1000ppm	5000ppm	10000ppm
F100k	24.5	90.36	82.15	116.6	180	242.4	61.56
F200k	30.15	60.9	66.9	194.5	196	209	53.79
F350k	32.05	47.5	51.51	71.29	86.69	131.6	195.6
F500k	18.8	62.65	38.96	44.8	60.58	81.28	465.5

Polydispersity Index of varying flocculant concentrations in water

	100ppm	200ppm	300ppm	500ppm	1000ppm	5000ppm	10000ppm
F100k	0.21	0.23	0.186	0.242	0.29	0.36	0.26
F200k	0.44	0.32	0.29	0.28	0.3	0.34	0.57
F350k	0.45	0.5	0.37	0.36	0.37	0.28	0.46
F500k	0.54	0.3	0.45	0.44	0.36	0.3	0.7



Graph of varying flocculant concentrations in water



PDI graph of varying concentrations of the flocculants in water.

Appendix 4: Zeta sizer results for varying flocculants pH.

100ppm of the flocculants

	pH3	pH5.7	pH9
F100k	130.9	56.1	71.01
F200k	278.5	71.72	108.1
F350k	257.1	115	82.58
F500k	192.9	63.4	85.55

1000ppm of the flocculants

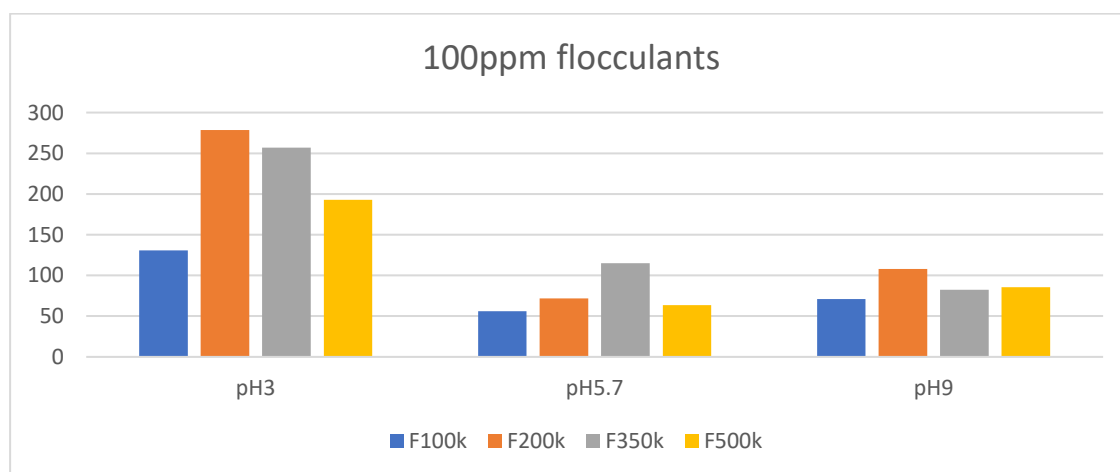
	pH3	pH4	pH5	pH5.7	pH8	pH9
F100k	25.08	17.49	61.12	25.22	39.27	33.46
F200k	132.5	42	61.23	24.58	52.3	49.95
F350k	33.61	82.92	53.04	34.12	42.47	33.34
F500k	42.82	66.2	85.09	36.8	48.36	42.95

PDI of 100ppm of the flocculants at varying pH

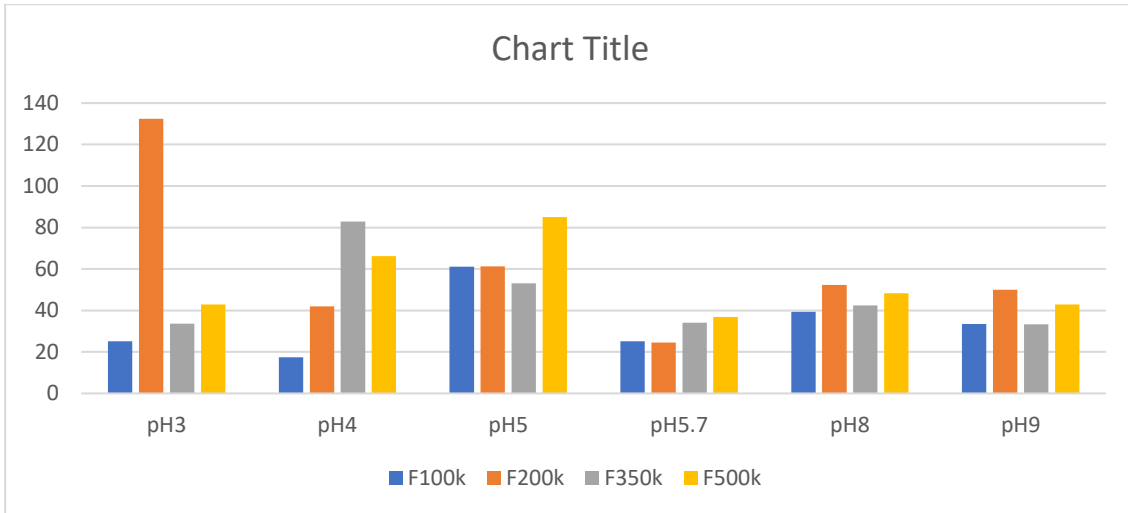
	pH3	pH5.7	pH9
F100k	0.94	0.5	0.65
F200k	0.65	0.61	0.55
F350k	0.72	0.8	0.7
F500k	0.65	0.4	0.68

PDI of 1000ppm of the flocculants at varying pH

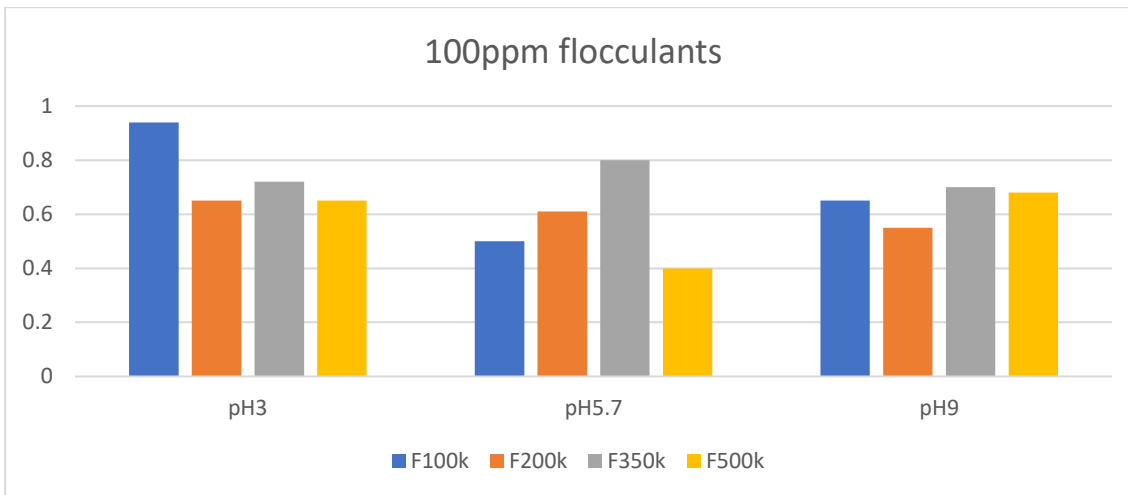
	pH3	pH4	pH5	pH5.7	pH8	pH9
F100k	0.52	0.36	0.2	0.58	0.58	0.43
F200k	0.52	0.59	0.55	0.41	0.55	0.64
F350k	0.71	0.57	0.71	0.7	0.46	0.67
F500k	0.71	0.62	0.66	0.76	0.58	0.7



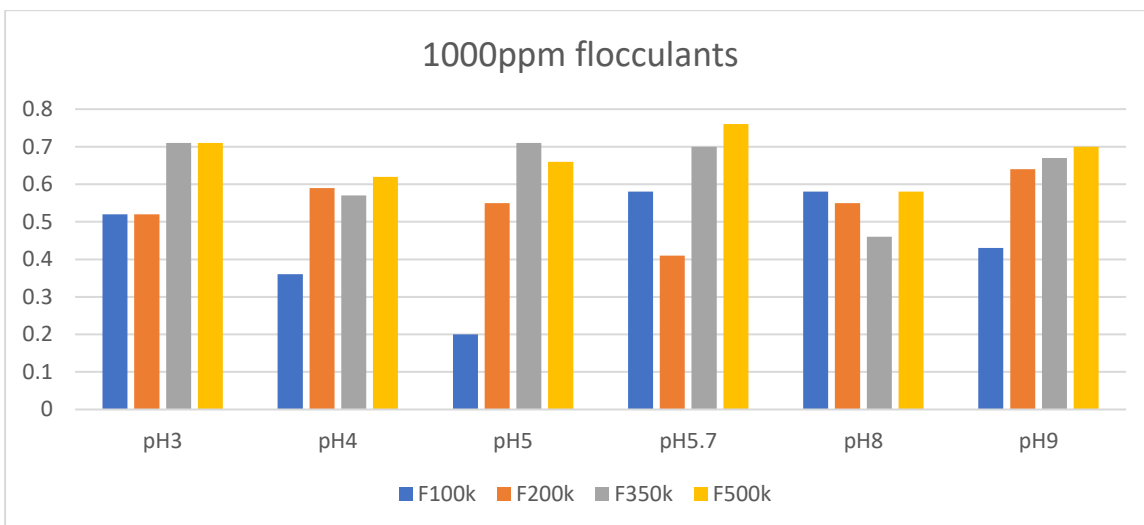
Graph of 100ppm of the flocculants at varying pH levels



Graph of 1000ppm of flocculants at varying pH levels.



PDI graph of 100ppm of the flocculants in water.



PDI graph of 1000ppm of the flocculants in water.

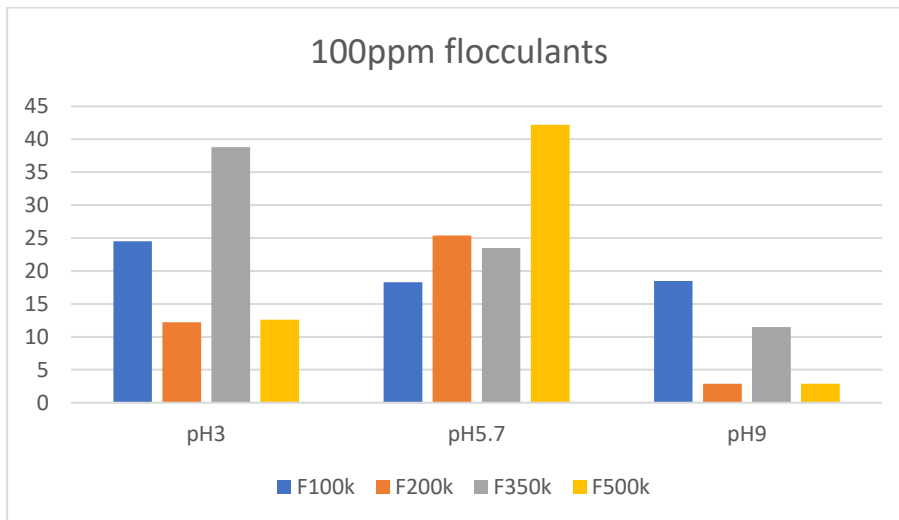
Appendix 5: Zeta potential measurements

ZP of 100ppm of flocculants in water

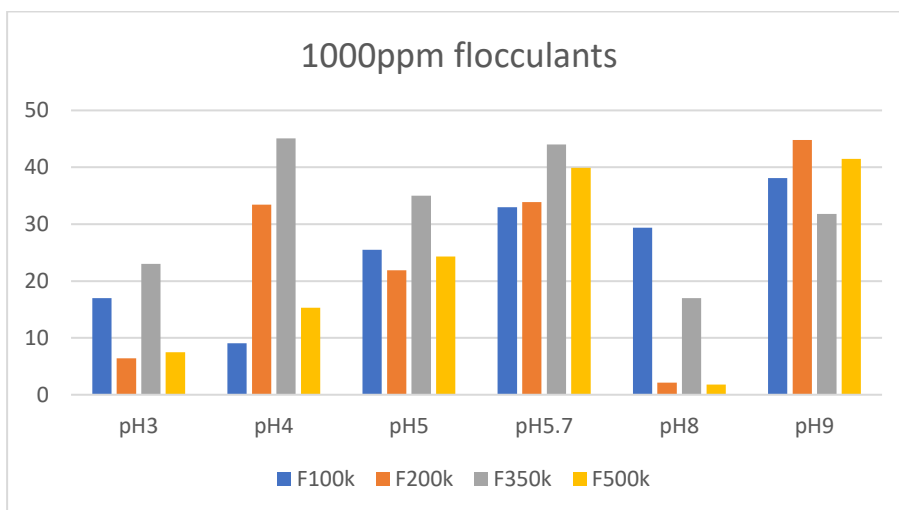
	pH3	pH5.7	pH9
F100k	24.5	18.3	18.5
F200k	12.2	25.4	2.9
F350k	38.8	23.5	11.5
F500k	12.6	42.2	2.9

ZP of 1000ppm of flocculants in water.

	pH3	pH4	pH5	pH5.7	pH8	pH9
F100k	17	9.08	25.5	33	29.4	38.1
F200k	6.4	33.4	21.9	33.9	2.12	44.8
F350k	23	45.1	35	44	17	31.8
F500k	7.5	15.3	24.3	39.9	1.79	41.5

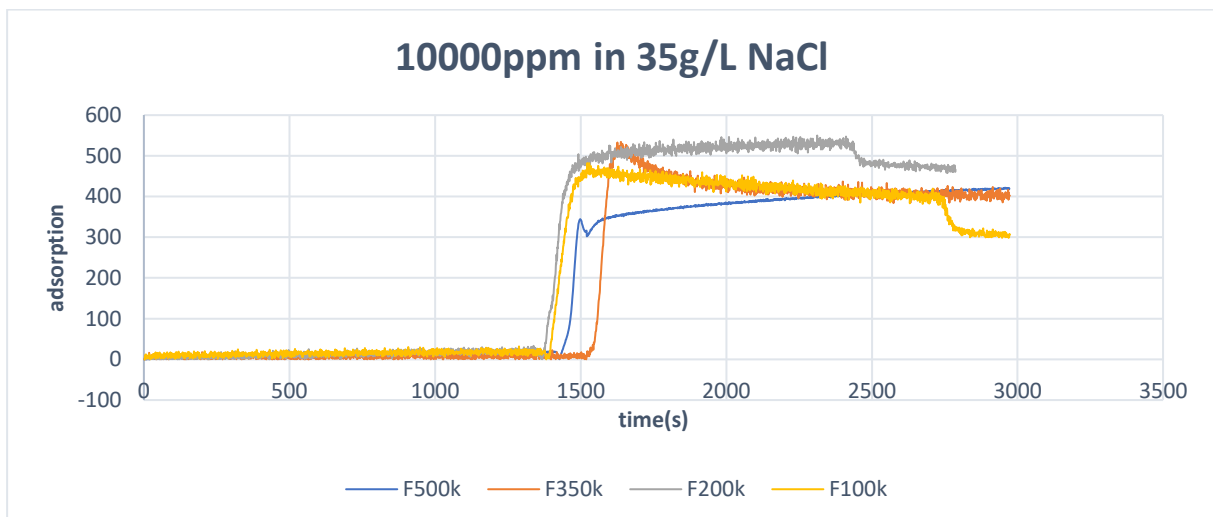
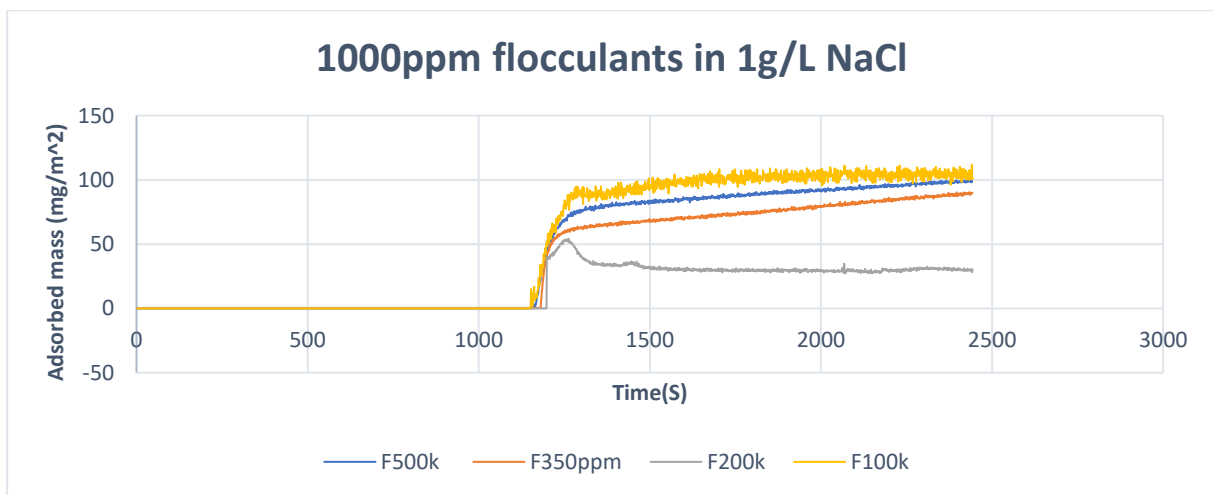
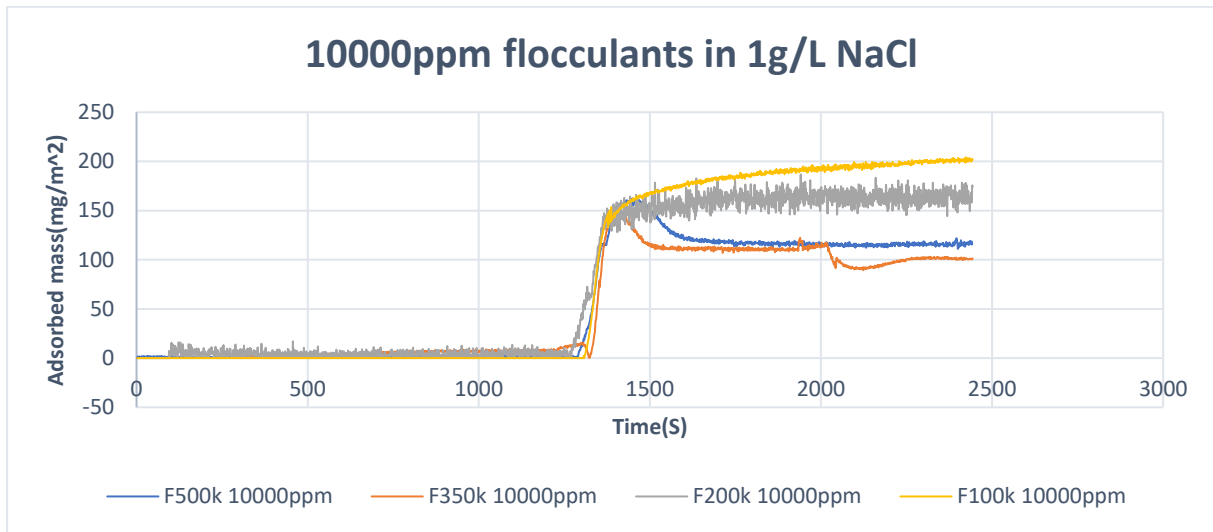


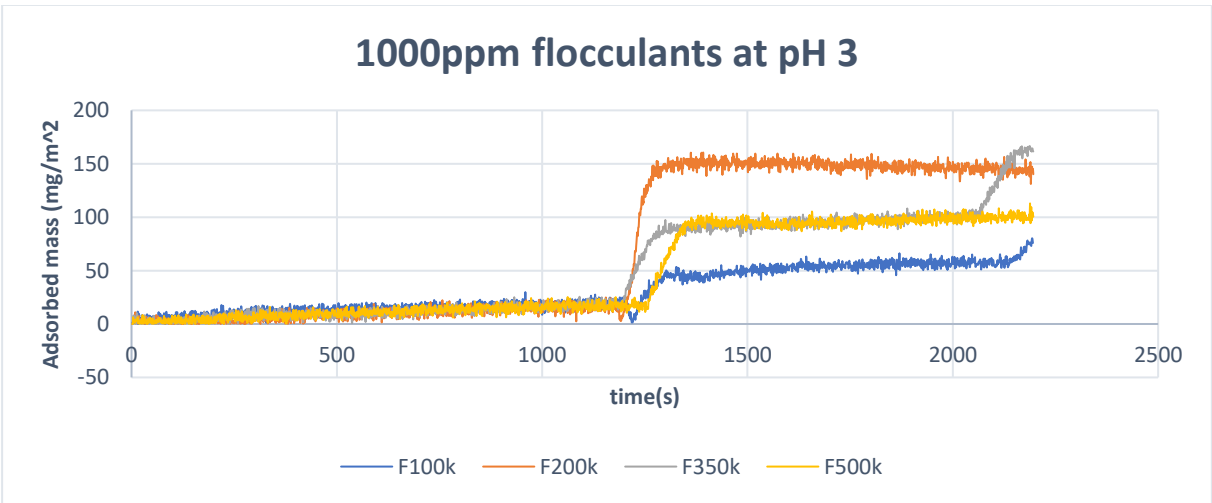
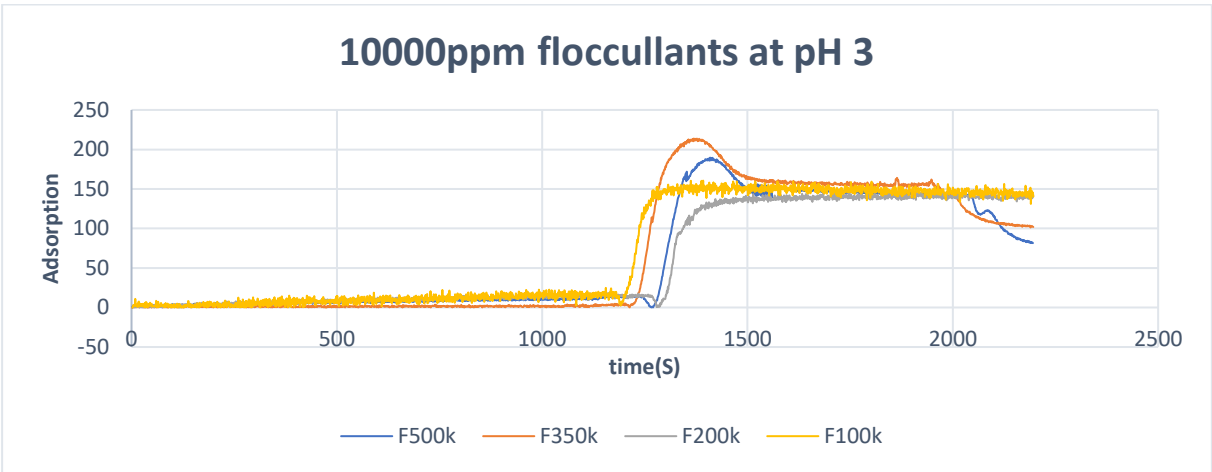
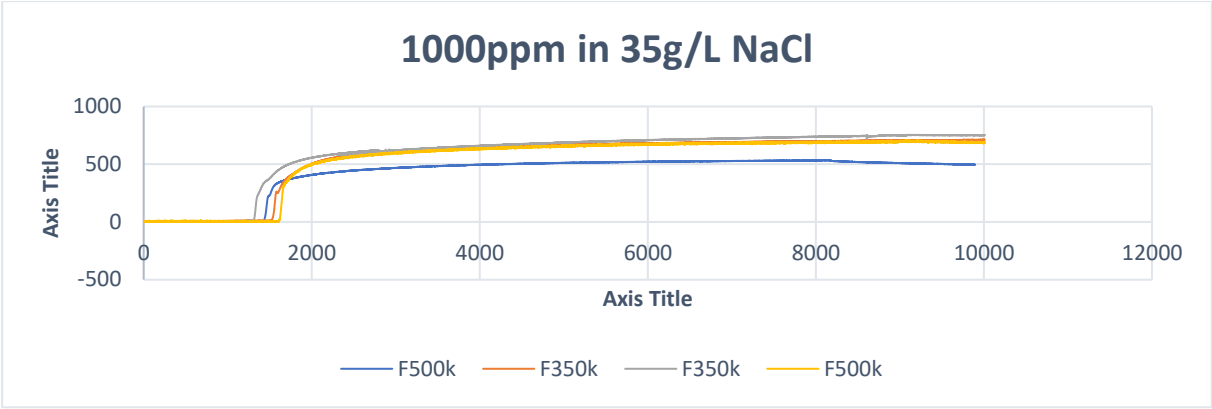
Zeta potential of 100ppm of the flocculants

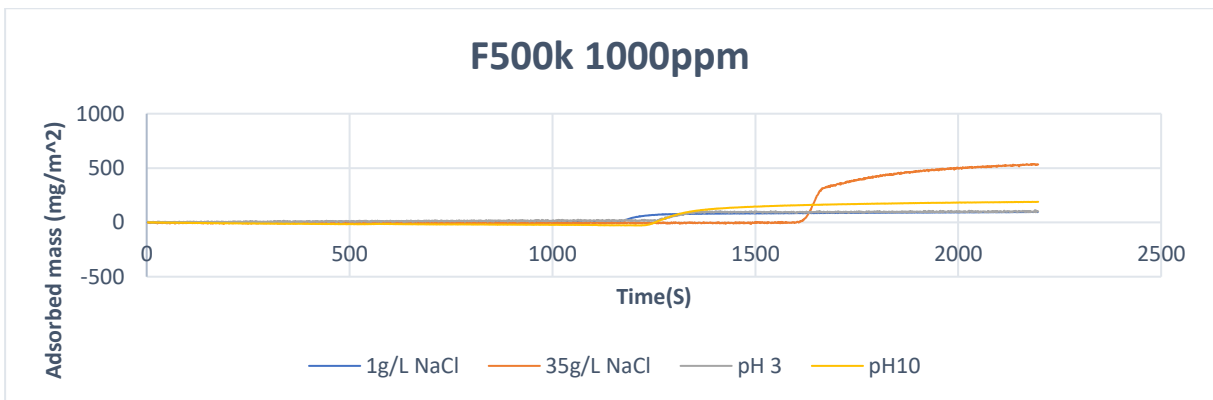
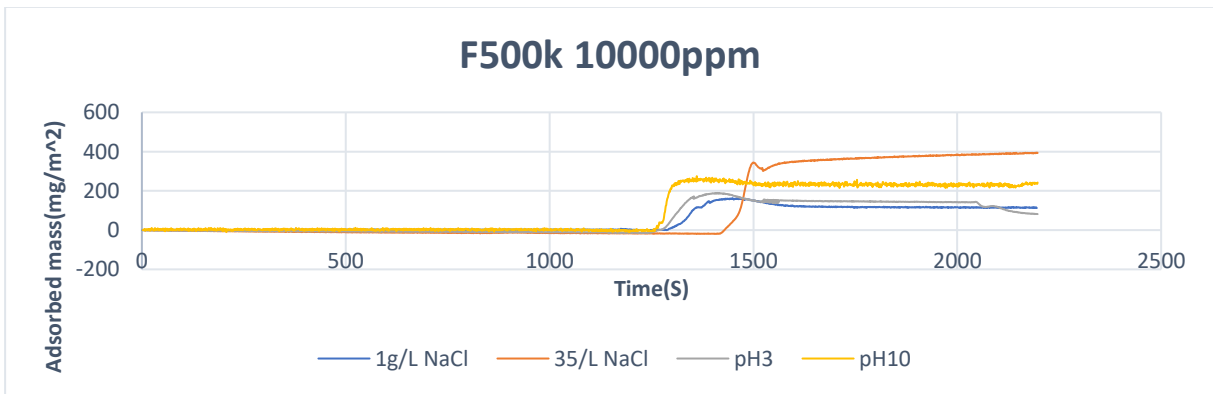
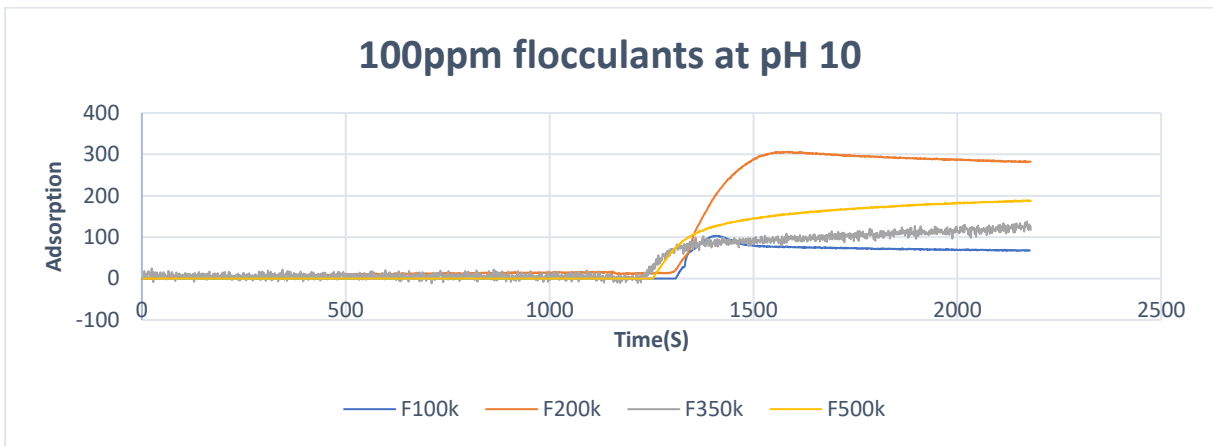
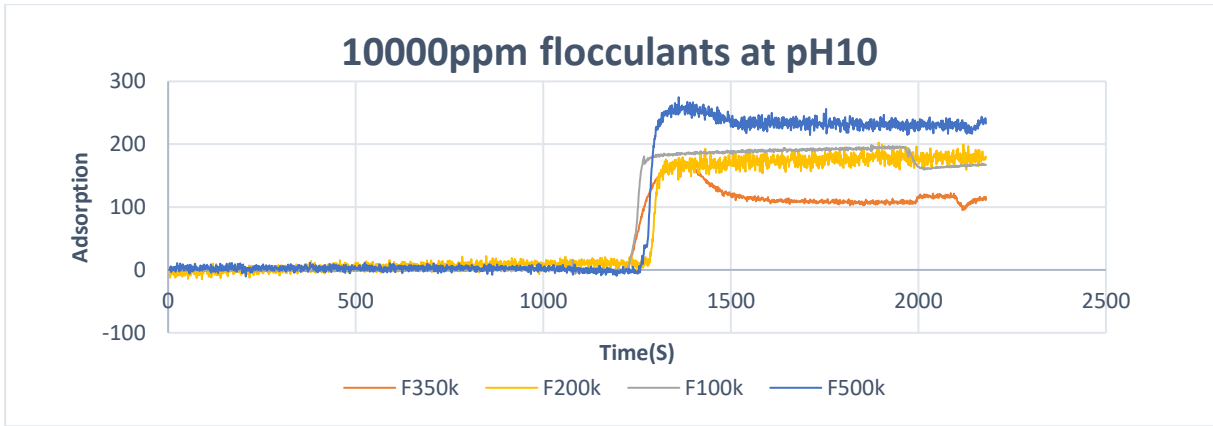


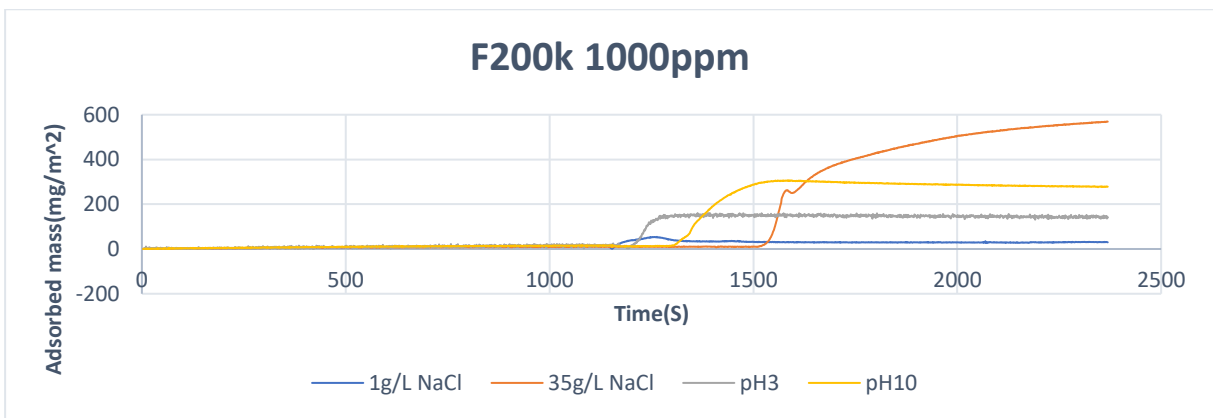
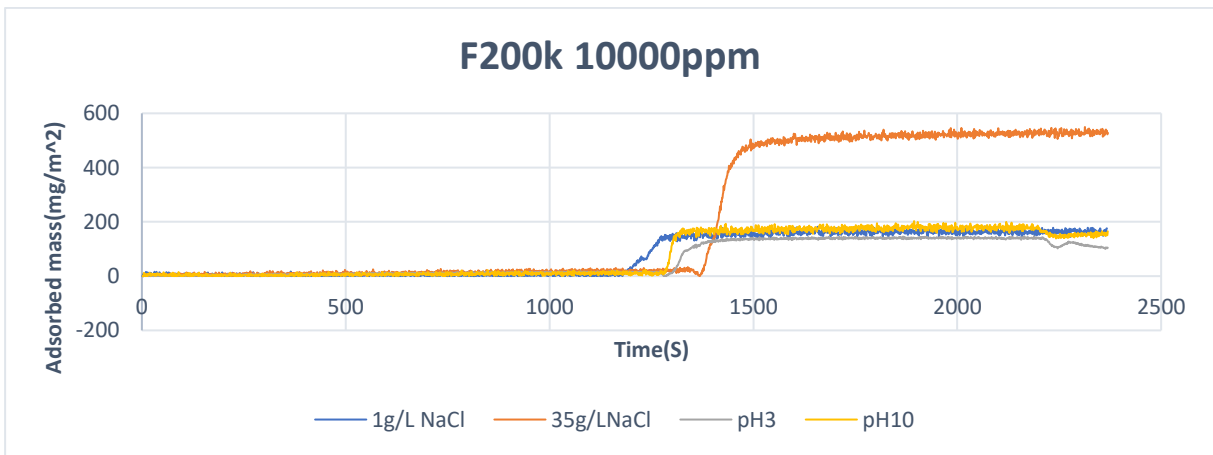
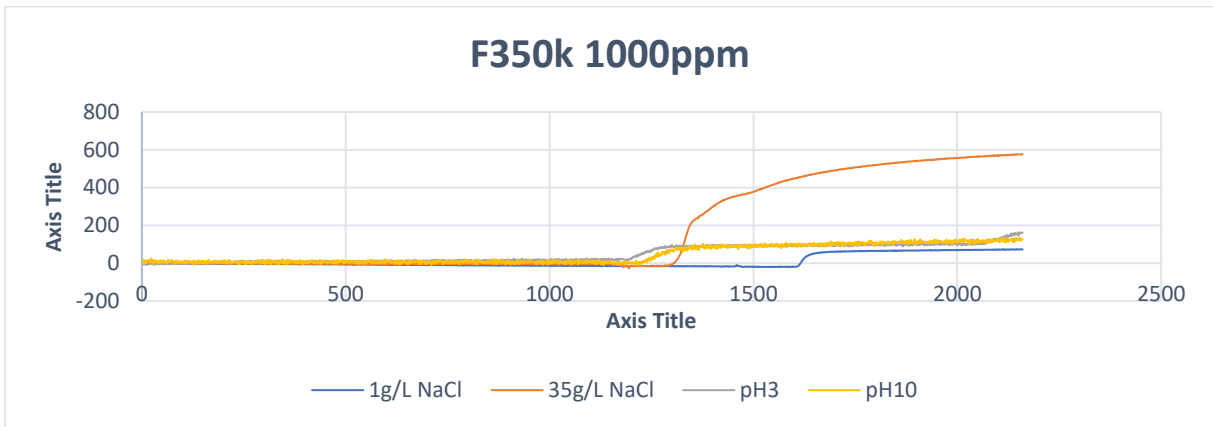
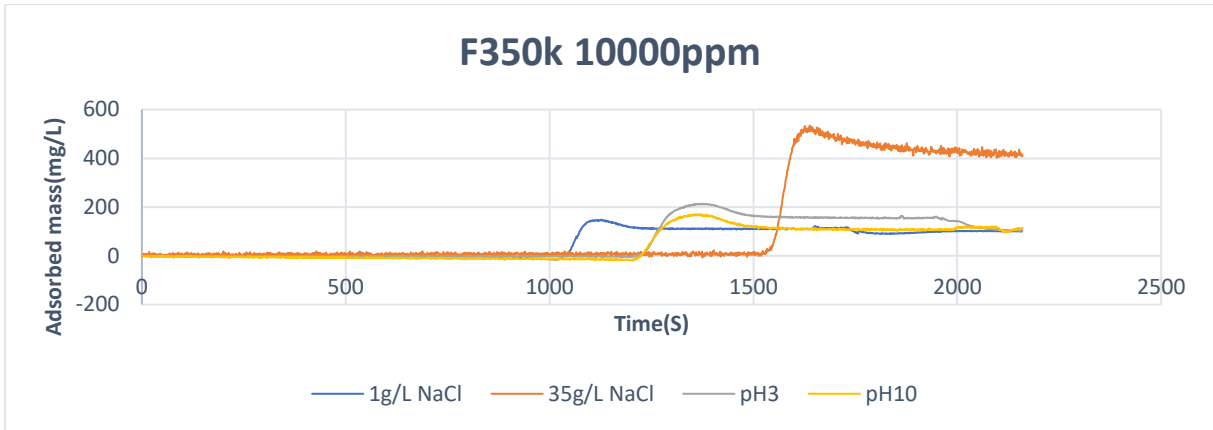
Zeta potential of 1000ppm of the flocculants

Appendix 6: Results of adsorption experiments at varying salts and pH.

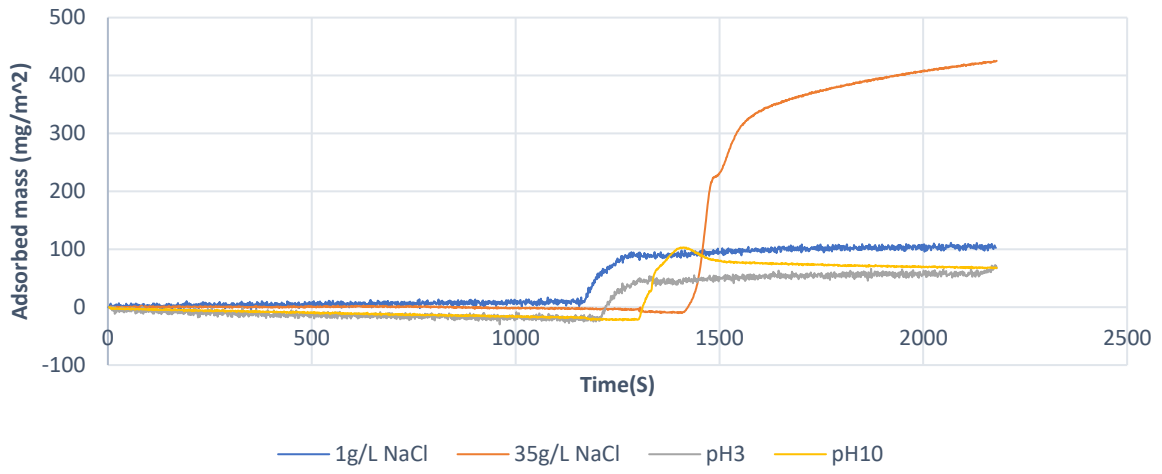








F100k 1000ppm



F100k 10000ppm

